

# Mineral indicators of porphyry Cu fertility

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## Abstract

‘Fertile’ magmas which generate metal-rich porphyry Cu deposits are thought to form by similar processes to normal ‘barren’ arc magmas which are unrelated to mineralisation. However, fertile magmas contain distinctive trace element signatures, which highlight the processes by which they achieved high ore-forming potential. These ‘indicators of fertility’ make potentially useful tools to be used in the exploration of porphyry systems and may be amplified in minerals within these rocks.

Intrusive rocks were collected from the Resolution and Oyu Tolgoi porphyry Cu deposits. A combination of whole rock geochemistry, and trace element analyses of apatite and zircon were carried out, and these data were compared to literature data for barren rocks.

Rocks from both systems indicators of fertility, some of which (especially Sr/Y) were found to be susceptible to feldspar-destructive hydrothermal alteration. The presence of these anomalies (e.g. La/Yb, Eu/Eu\*, V/Sc) is indicative of garnet control on deep crustal fractionation, which may occur due to localised increases in melt H<sub>2</sub>O.

Zircons from Oyu Tolgoi show that Eu/Eu\* and Ce<sup>4+</sup>/Ce<sup>3+</sup> ratios in zircon were strongly controlled by the co-crystallisation of titanite, limiting their utility as measures of redox. Ce/Ce\* may provide a better measure of melt redox in zircon, but is difficult to measure. Eu/Eu\* may still be useful for distinguishing barren and fertile systems.

Igneous apatite has high Sr and Eu/Eu\* compared to barren systems. Hydrothermal apatite from a number of porphyry systems were found to contain uniquely high Fe, Mn, Pb, Sr, and Eu/Eu\*, which possibly relate to their precipitation from metal rich brines. The magnitude of Mn enrichment may also be sensitive to bulk rock Cu content.

These results highlight the potential of apatite and zircon as mineral indicators of porphyry fertility, and recommendations are made for how they may be used in exploration.

**Declaration**

This thesis is my own original work, and the work of other authors is fully referenced.

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# Chapter 1: Introduction

## 1.1 Background

Porphyry Cu deposits are large volumes of hydrothermally altered rock with associated Cu-(Mo-Au) mineralisation, centred on porphyritic stocks and dykes. Metal-bearing hydrothermal fluids released from underlying magmatic systems are channelled through these porphyry intrusions, causing significant chemical alteration to the intrusions and the surrounding rock and the growth of new mineral phases, some of which are of economic importance. Porphyry deposits contain varying abundances of Cu, Mo, and Au, and some rarer examples exist of porphyry Sn  $\pm$  W systems. Base metals are concentrated in the form of metals sulphides (e.g. chalcopyrite, bornite, chalcocite, molybdenite) and indeed porphyry deposits could be thought of as significant crustal sulphur anomalies, as well as metal anomalies. These deposits account for approximately three quarters of the global supply of Cu, one fifth of the total Au, and half the total Mo (Sillitoe, 2010), although porphyry deposits do not constitute such a large fraction of global Sn or W mineralisation (Seedorff et al., 2005).

Porphyry deposits are generally associated with magmas generated at convergent margins, and often form beneath dormant volcanic centres (Sillitoe, 2010). Porphyry deposits are formed at shallow crustal depths (2 – 5 km; e.g. Richards, 2003) which, together with their location in active arcs and areas of uplift and erosion, leads to their low preservation potential. Although porphyry deposits have been forming since the Archaean, the majority of extant deposits are Cenozoic (Singer, 1995). Mineralisation at porphyry systems is typically low grade (median = 0.44 wt. % Cu), and 90% of porphyry systems have Cu grades of < 0.75 wt. % Cu (Singer, 1995).

## **1.2 Deposit characteristics**

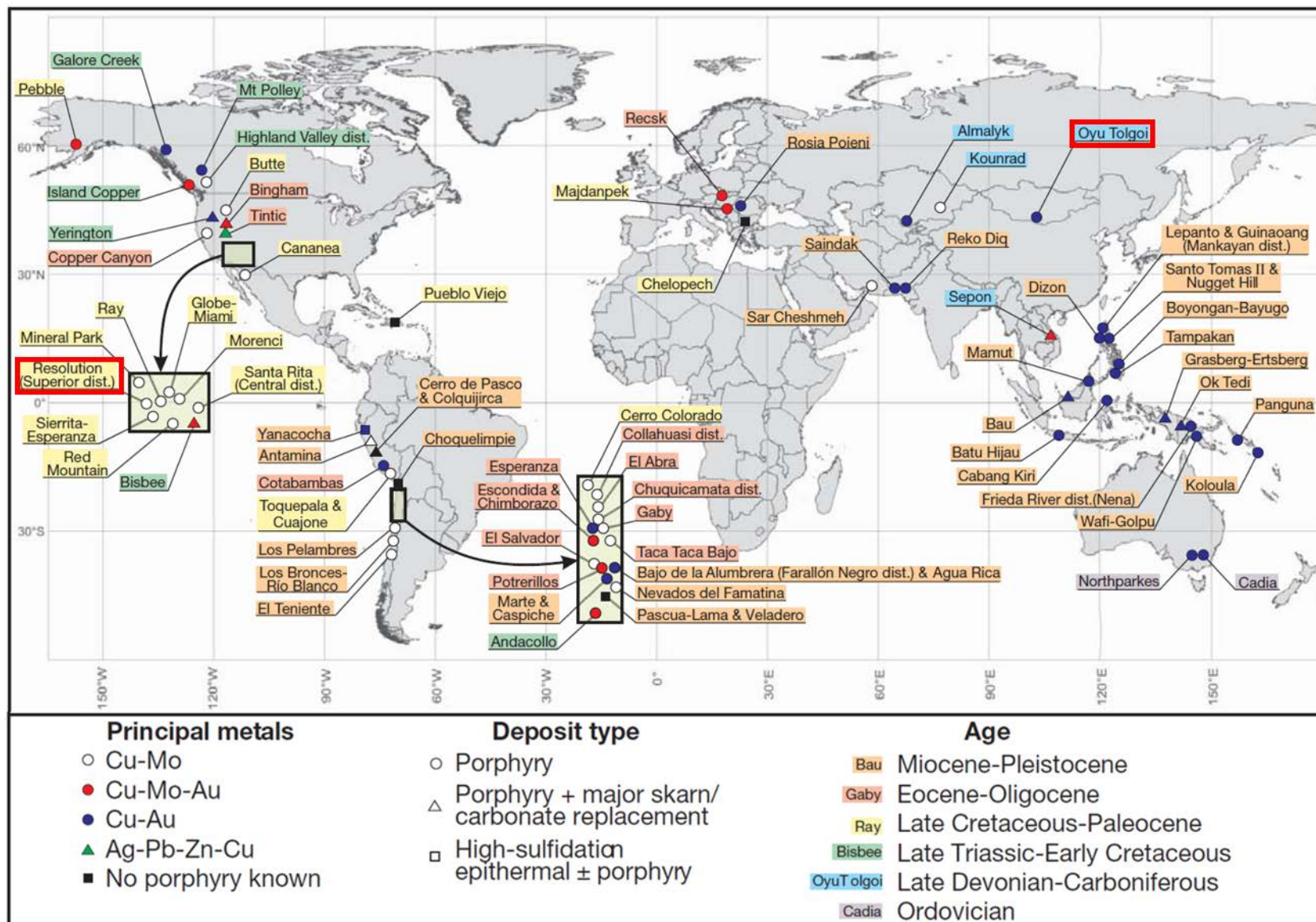
### **1.2.1 Types of porphyry system**

A variety of types of porphyry system exist, with varying sizes and metal concentrations. One characteristic common to all types is the presence of intermediate- to felsic porphyritic intrusions from which they derive their name, and with which they are intimately and ubiquitously associated.

Porphyry systems are defined on the basis of the relative abundance of ore metals. Typically, porphyry Cu systems contain appreciable amount of another base or precious metal, which is usually Mo or Au, and in some cases all three metals are in economic concentrations (e.g. Bingham Canyon porphyry Cu-Mo-Au, Utah; Porter et al., 2012). The size of a porphyry system is also the basis for its classification. Size is measured in megatons (Mt) of metal. Porphyry Cu systems with >2 Mt copper are referred to as ‘giant’, and those with >24 Mt copper are called ‘supergiant’ (Singer, 1995).

### **1.2.2 Spatial-temporal distribution**

Porphyry deposits are spatially and temporally related to magmatic arcs, and often form beneath dormant volcanic centres (Sillitoe, 2010). Some porphyry systems have been identified as forming in post-subduction environments, such as collisional or extensional regimes (Richards, 2009). One compelling characteristic of porphyry Cu deposits is that for the most part, they form in spatially restricted segments of volcanic arcs (<1000 km in length) over relatively brief periods of time (<20 m.y.), with preceding and succeeding magmatism generating no mineralisation.





*Figure 1.1. (above). Distribution of porphyry systems around the world, colour coded by age and style of mineralisation. The two porphyry systems that are the focus of this study (Oyu Tolgoi and Resolution) are highlighted in red. Modified from Sillitoe (2010).*

---

This is thought to be due to the optimisation and convergence of a number of typical arc processes, including the onset of compressive tectonics (Sillitoe, 1998), which trap magmas at the base of the crust, where they become enriched in volatiles (e.g. Richards, 2003; 2013; Rohlach and Loucks, 2005; Loucks, 2014).

### 1.2.3 Deposit architecture and formation

Mineralisation in porphyry systems is centred on the tops of porphyry intrusions, which are themselves the apex of a broader magmatic system which may extent up to 10 km below (e.g. Seedorff et al., 2008; Fig. 1.2). Porphyry intrusions are fed by underlying felsic magma chambers, which are the source of all the components required for deposit formation (e.g. the metals, hydrothermal fluids, sulphur, and heat). These intermediate to felsic magma chambers contain dissolved H<sub>2</sub>O (2 – 5 wt. %; Burnham, 1979, Annen et al., 2006). A combination of cooling, de-pressurisation upon ascent, and continued crystallisation causes the solubility of H<sub>2</sub>O in the melts to decrease, and the concentration to increase, which leads ultimately to the saturation of an aqueous fluid (Burnham, 1979). In porphyry systems, the fluids that are formed are typically S-rich, and contain other ligands which increase the compatibility of metals in the fluids (e.g. Cl; Candela and Holland, 1984). Metals from the melt concentrate in the mobile fluid phase, which ascends into the shallow parts of felsic magma chambers either as a separate volatile phase, or entrained in a bubble-rich magma (e.g. Cloos, 2001). In idealised cases, metal- and sulphur-bearing fluids are channelled through narrow intrusions in the roofs of felsic magma chambers, and collect in the ‘cupolas’

at the top of these intrusions (Fig. 1.2). From here, channelised, fracture-controlled fluid flow into the surrounding country rock (Richards, 2011) is concomitant with a drop in temperature, due to the steep temperature gradients in such environments (Cloos, 2001). These conditions, together with the interactions between hydrothermal fluids and the surrounding country rock, cause Cu sulphides to be precipitated from the fluid. (e.g. Heinrich et al., 1999; Landtwing et al., 2005; Sillitoe, 2010). The size and grade of a resulting deposit depends upon several factors, including the efficiency with which metals are stripped from the magma (Cloos, 2001; Shinohara et al., 1995), and the focussing of sufficient volumes of fluids through narrow packages of rock above porphyry cupolas (e.g. Wilkinson, 2013).

As they are emplaced at depth (5-15 km; Fig. 1.2), special tectonic conditions (such as large extensional faulting) are required to expose the deep roots of porphyry systems (Sillitoe, 1973; Seedorff et al., 2008; Sillitoe, 2010). Only a small number of examples of confirmed porphyry-pluton relationships are known to exist (e.g. Yerignton batholith, Nevada; Dilles et al., 1987). At most deposits, only the porphyry intrusions themselves are observed. These intrusions are typically found as small (< 1km) bodies with a range of dimensions, from plug-like stocks to elongate dykes. Where exposed, the roots of porphyry intrusions contain a similar assemblage to the upper regions, but are progressively coarser and texturally grade into underlying coarse-grained felsic plutons (e.g. Seedorff et al., 2008).

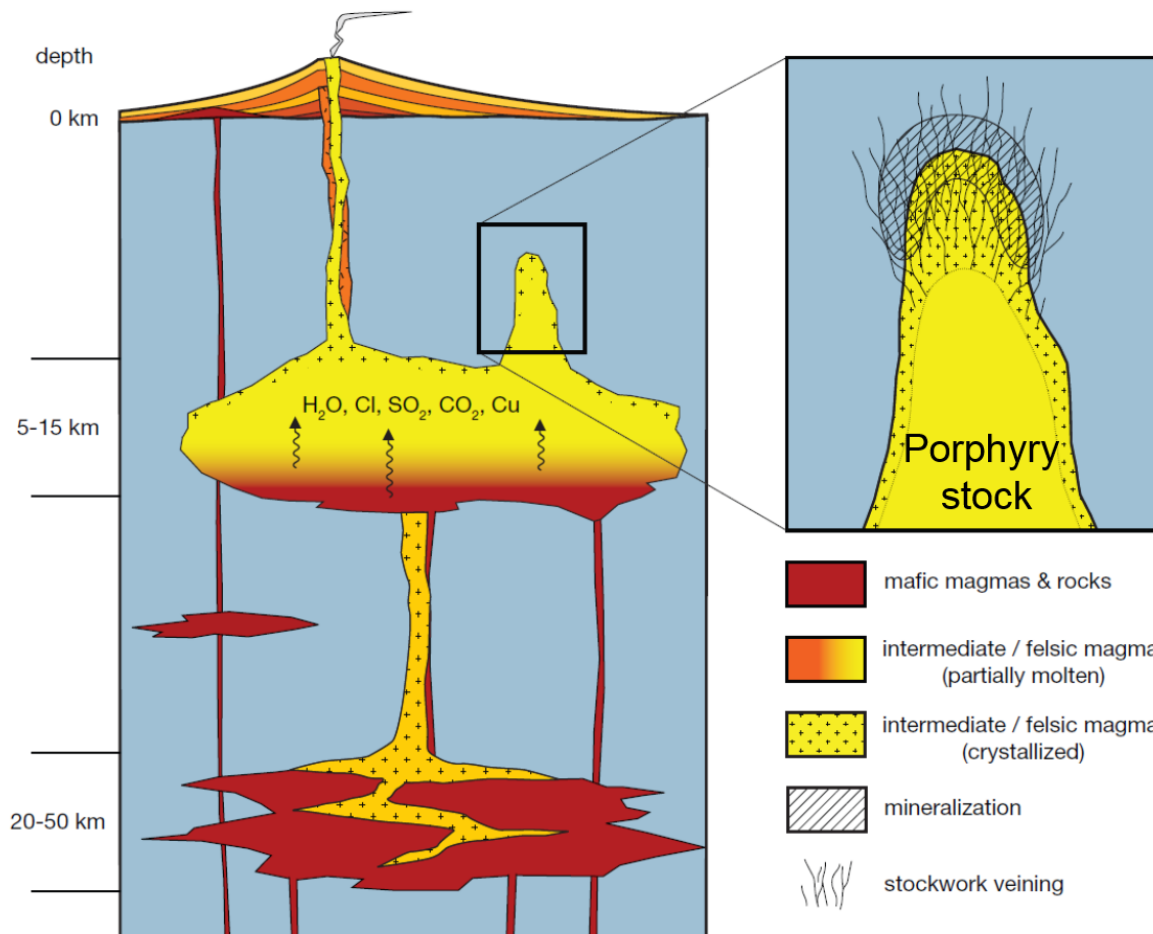


Figure 1.2. The location of a porphyry system (inset) at the apex of a magmatic system which extends to the base of the crust. Porphyry stocks are underlain by felsic magma chambers, which provide necessary components for deposit formation. Metal rich fluids from the chamber ascend into the apex (or cupola) of the porphyry stock, from where they are focussed into the surrounding rock and generate mineralisation. Modified from Audétat and Simon (2012).

#### 1.2.4 Alteration assemblages

Ore mineralisation in porphyry systems is associated with large-volume hydrothermal alteration, and several distinctive styles of wall rock alteration and mineralisation are characteristic of porphyry systems (e.g. Meyer and Hemley, 1967). These alteration styles are radially and vertically zoned around the causative intrusion(s), and are generated by interactions between magmatic-hydrothermal fluids and the surrounding wall rocks.

Alteration can affect several cubic km of rock (e.g. Lowell and Guilbert, 1970), and because the distribution of alteration assemblages is systematic, alteration zoning has been used as a useful guide in porphyry Cu exploration.

Hydrothermal alteration causes changes in mineralogy and geochemistry of these rocks, including the replacement of pre-existing minerals, and the precipitation of new phases. Alteration may be pervasive throughout the rock, may affect selected minerals only, or may be localised to narrow halos (or ‘selvages’) surrounding veins.

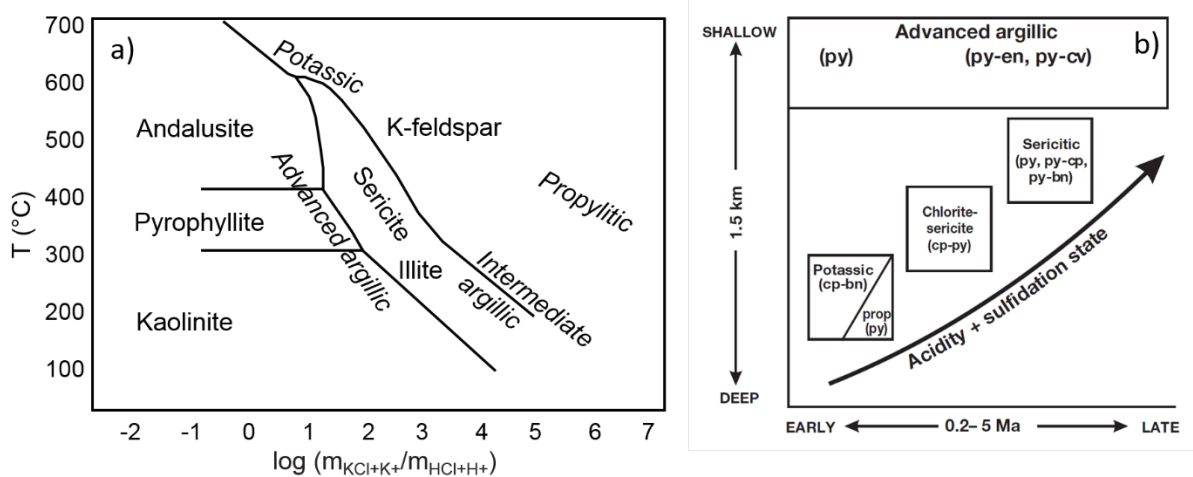


Figure 1.3. (a) Phase diagram for the system  $K_2O-Al_2O_3-SiO_2-H_2O-KCl-HCl$ , defining the effect that hydrothermal fluid temperature and composition have on alteration style. Boundaries of the major porphyry alteration systems are marked on. (b) The evolution of porphyry hydrothermal systems, from deep, high temperature, early potassic alteration, to shallow, late-stage acidic sericitic to advanced argillic. Modified after (a) Seedorff et al. (2005) and (b) Sillitoe (2010).

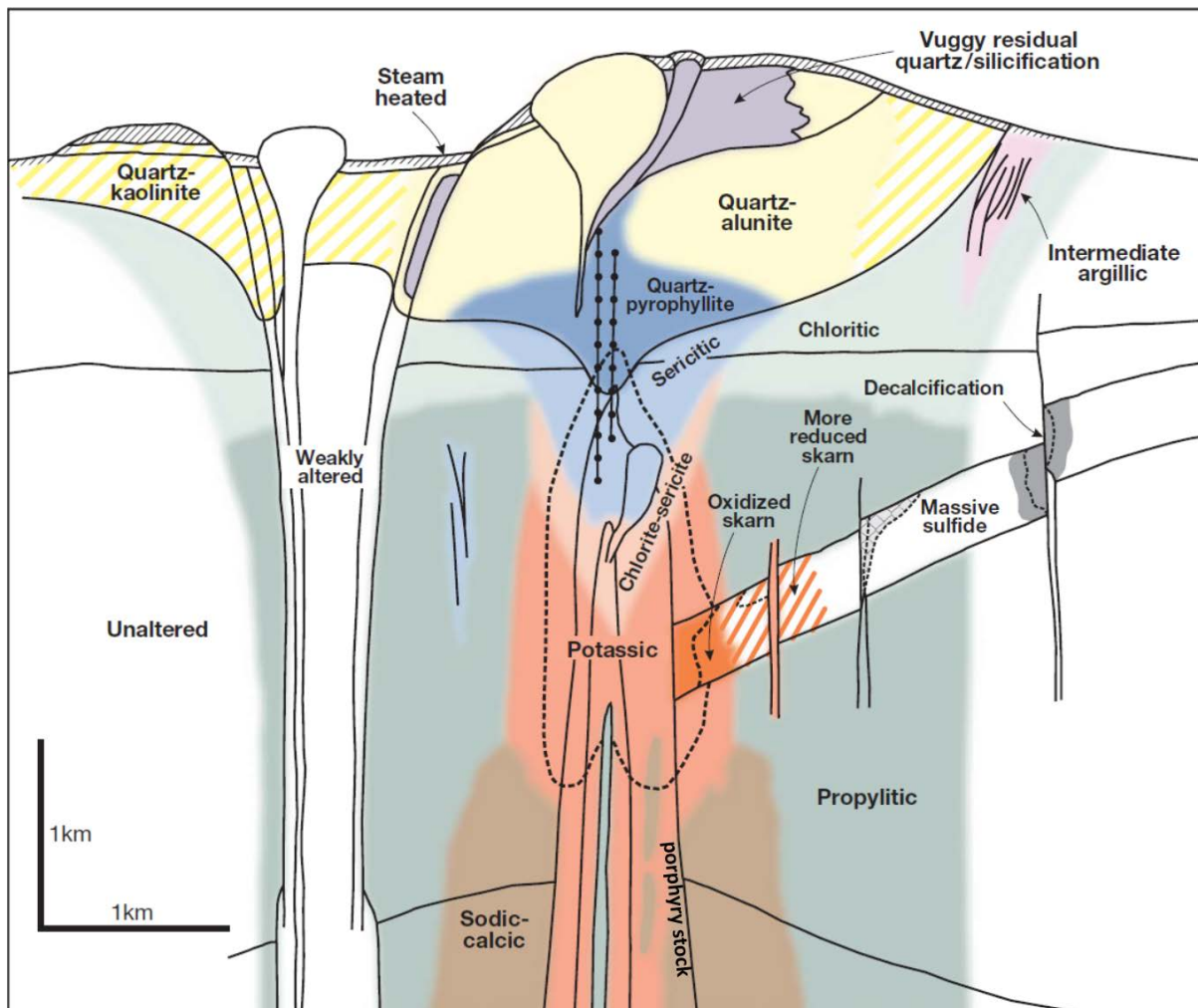


Figure 1.4. Alteration zoning around a porphyry stock. Deep potassic alteration in the core of the system grades outwards to propylitic alteration. More acidic alteration styles (e.g. sericitic, argillic) overprint early potassic alteration from above. Local variations in wall rock chemistry can cause changes in the style of mineralisation (e.g. limestone, which is strongly reactive, may locally be altered to skarns). From Sillitoe (2010).

The style of alteration is dependent upon the chemistry of the wall rock, and the chemistry and temperature of the fluids, in particular the ratio of  $K^+$  to  $H^+$  cations (Fig. 1.3a; Seedorff et al., 2005). Potassic alteration is typically found at the deep core of porphyry systems (Fig. 1.4), and is generated by high temperature fluids in the early stages of alteration (Fig. 1.3b). This alteration style is dominated by the addition of K-feldspar and biotite, with

subordinate magnetite, anhydrite, apatite, and occasionally albite (Lowell and Guilbert, 1970) and is common to most porphyry Cu systems (Seedorff et al., 2005). In mafic wall rocks, biotite is the dominant K-silicate alteration phase, whereas K-feldspar predominates in felsic rocks (e.g. the porphyry intrusions themselves). In most porphyry systems, potassic alteration contributes the greatest volume of metal sulphides, primarily chalcopyrite and subordinate bornite (Einaudi et al., 2003).

The potassic zone grades laterally into a propylitic alteration zone, which is characterised by the presence of chlorite, epidote, and actinolite with accessory albite, calcite (Beane and Titley, 1981; Beane and Bodnar, 1995). This mineral assemblage has led to them being informally referred to as ‘greenrocks’. Propylitic alteration is distal to the deposit, is not commonly associated with Cu mineralisation, and is considered to be generated by the heating of distal meteoric water by (e.g. Meyer and Hemley, 1967). Chlorite is predominant in the shallow parts of the propylitic zone (Fig. 1.4)

Successive periods of alteration by fluids with different chemistry and temperature may overprint earlier alteration events. A common example of this in porphyry systems is the development of sericitic (phyllic) alteration styles. They occur at a later stage than potassic and propylitic alteration, and many porphyry systems show the overprinting of potassic by sericitic alteration (Fig. 1.4). Sericitic alteration is characterised by the replacement of feldspar with sericite mica, with the addition of quartz and pyrite (often replacing mafic phases, e.g. biotite). This leads to the loss of Na, Ca, and Mg from the rock, and potentially other fluid mobile elements that are found in feldspar (e.g. Sr; Beane and Titley, 1981). The fluids that generate sericitic alteration are lower temperature and pH than those that generate potassic alteration (Fig. 1.3). The destruction of mafic phases, and the addition of white micas imparts a white to green/grey colour on rocks affected by this alteration style (Sillitoe, 2010).

Crystal habits of feldspars are frequently intact, and complete sericitisation of feldspar may be recognised in hand specimen due to their ‘whispy’ edges and matt texture. However, strong quartz-sericitic alteration can completely obliterate original igneous textures.

Advanced argillic alteration typically forms in the shallowest ‘lithocap’ portions of porphyry systems, by fluids with low temperature and pH. The acidity of the fluids leads to extensive leaching of alkali cations from the rock, leaving residual quartz and depositing an assemblage of clay minerals (primarily kaolinite, dickite, and pyrophyllite at higher temperatures; Fig 1.3a). F-rich fluids that cause advanced argillic alteration may also precipitate fluorite, and topaz (e.g. Perello et al., 2001; Khashgerel et al., 2008, Sillitoe, 2010). Rocks that are most strongly affected by this alteration are those with low acid buffering ability (i.e. felsic rocks, rather than mafic rocks; Beane and Titley, 1981). Advanced argillic alteration is much less common in porphyry systems associated with alkaline magmas, due to the control of  $K^+/H^+$  on magma type.

#### 1.2.5 Mineralisation assemblages and orebody geometry

The style of Cu mineralisation associated with porphyry systems is dependent primarily on the sulphidation state of fluids, which is controlled by temperature (higher sulphidation at lower-T) and S fugacity of the fluid (e.g. Einaudi et al., 2003). Low sulphidation states typically associated with potassic alteration favour the formation of chalcopyrite + bornite, whereas higher sulphidation state fluids are associated with pyrite ± enargite ± covellite ± chalcocite.

Orebodies are found in a number of shapes, with the most common type being upright cylinders (e.g. Sillitoe and Gappe, 1984), or inverted ‘cups’ or shells (e.g. Hehnke et al., 2012), all of which are centred on the causative intrusion

### 1.2.6 Metal transport in hydrothermal fluids

The chemistry of hydrothermal fluids strongly affects the ability of such fluids to carry metals. For example, it has been demonstrated in experimental studies (Candela and Holland, 1984; Bai and van Groos, 1999) and studies of natural co-existing fluid and melt inclusions (Audétat and Pettlke, 2003; Audétat et al., 2010) that fluids with high Cl contents are able to carry higher concentrations of Cu. Candela and Holland (1984) showed that the compatibility of Cu in aqueous fluids over silicate melts increases by a factor of 9.1 with every +1 increase in the molality of Cl in the fluid. The same relationship has also been demonstrated for Au in aqueous fluids (Ulrich et al., 1999). Sulphur has also been considered by some workers to be an important ligand in the transportation of Cu in aqueous fluids (e.g. Simon et al., 2006; Seo et al., 2009).

Partition coefficients are typically lower for Mo than for Cu between aqueous fluids and silicate melts (Candela and Holland, 1984; Bai and van Groos, 1999). F is thought to play an important role in generation of Mo-rich porphyry deposits, but not due to enhanced fluid partitioning. For example, Candela and Holland (1984) showed that increasing the F or Cl content of the fluid had no effect on the partitioning of Mo between fluids and aqueous liquids. However, NaF-rich magmas can increase the solubility of Mo in melts (Bai and van Groos, 1999), which means that Mo behaves incompatibly during fluid exsolution and fractionation crystallisation, and highly fractionated, F-rich magmas may therefore carry high melt Mo content. This is supported by an empirical link between highly fractionated, F-rich granites, and porphyry Mo systems (e.g. Henderson; Gunow et al., 1980)



### **1.3 Generation of porphyry magmas**

#### **1.3.1 Arc magma genesis**

The generation and evolution of magmas associated with porphyry systems is considered to be broadly similar to typical arc magmas, which occurs as follows. Volatiles are emitted from subducting oceanic crust due to dehydration metamorphic reactions involving hydrous phases (e.g. hornblende; Peacock, 1993; Fig. 1.5a). These slab fluids cause metasomatism in the overlying mantle wedge, which becomes enriched in fluid-mobile LILE (large ion lithophile elements; Ba, Rb, K, Sr; Tatsumi et al., 1986, Davidson, 1996), but relatively depleted in Nb, Ta, and other HFSE (high field strength elements), as these are retained in minerals in the down-going ocean crust (e.g. rutile). Enriched LILE and depleted HFSE are often referred to as the ‘subduction signature’, as they are characteristic of arc magmas. Metasomatising the mantle wedge by fluxing with slab fluids lowers the melting temperature, and basaltic partial melts are permitted to form. This is considered to be the primary mechanism of melt generation at convergent margins (Ringwood, 1977; Wyllie, 1978; Tatsumi, 1989; Davies and Stevenson, 1992; Peacock, 1993), although direct slab melting may rarely occur where young (i.e. hot) oceanic crust is subducted (e.g. adakites; Defant and Drummond, 1990). Basaltic partial melts coalesce and ascend into the lithosphere, and begin to pond at (or close to) the base of the crust, due to the neutral buoyancy of basaltic melts at this location (Hildreth, 1981). Repeated injection of basaltic melts raises the ambient temperature of the lower crust, generating a thermally stable deep crustal hot zone (Annen et al., 2006), also known as a MASH zone (melting, assimilation, storage, hybridisation; Hildreth and Moorbath, 1988). In this environment, basaltic melts begin to cool and crystallise.

Primary basaltic arc melts typically contain on the order of 2-6 wt. % H<sub>2</sub>O; (Anderson, 1979; Murphy et al., 2000; Cervantes & Wallace, 2003; Plank et al., 2013), and the crystallisation of an anhydrous mafic assemblage causes the H<sub>2</sub>O and SiO<sub>2</sub> content of the residual melts to increase, generating sequences of mafic cumulates and residual intermediate to silicic melts that typically contain between 4-6 wt. % H<sub>2</sub>O (Anderson, 1979; Green, 1982; Barclay et al., 1998; Devine et al., 1998; Carmichael, 2002, 2004; Blundy & Cashman, 2005), but may contain dissolved H<sub>2</sub>O contents of up to 10 wt. % due to the high pressure (~1 GPa) at the base of the crust (Annen et al., 2006). These melts may interact with the lower crust which, due to the increase in ambient temperature, is liable to partially melt. Mafic cumulates formed at the base of the crust may become gravitationally unstable, being denser than the surrounding lithosphere, and may delaminate and return to the mantle (Kay & Kay, 1993; Jull & Keleman, 2001), driving the composition of the bulk crust towards andesite (Annen et al., 2006).

Residual hydrous intermediate/silicic melts generated in deep crustal hot zones are less dense, due to their higher dissolved volatile content and silicic composition. As a result, these melts will ascend into the shallow crust, where they stall to form large felsic magma chambers. Stalling may be caused by the exsolution of a volatile phase which will occur at deeper levels in more hydrous magmas (Cashman, 2004). Shallow crustal magma chambers are the source of magmas for volcanic eruptions, and also the source of heat, metals, volatiles, sulphur for the formation of porphyry systems (Richards, 2003).

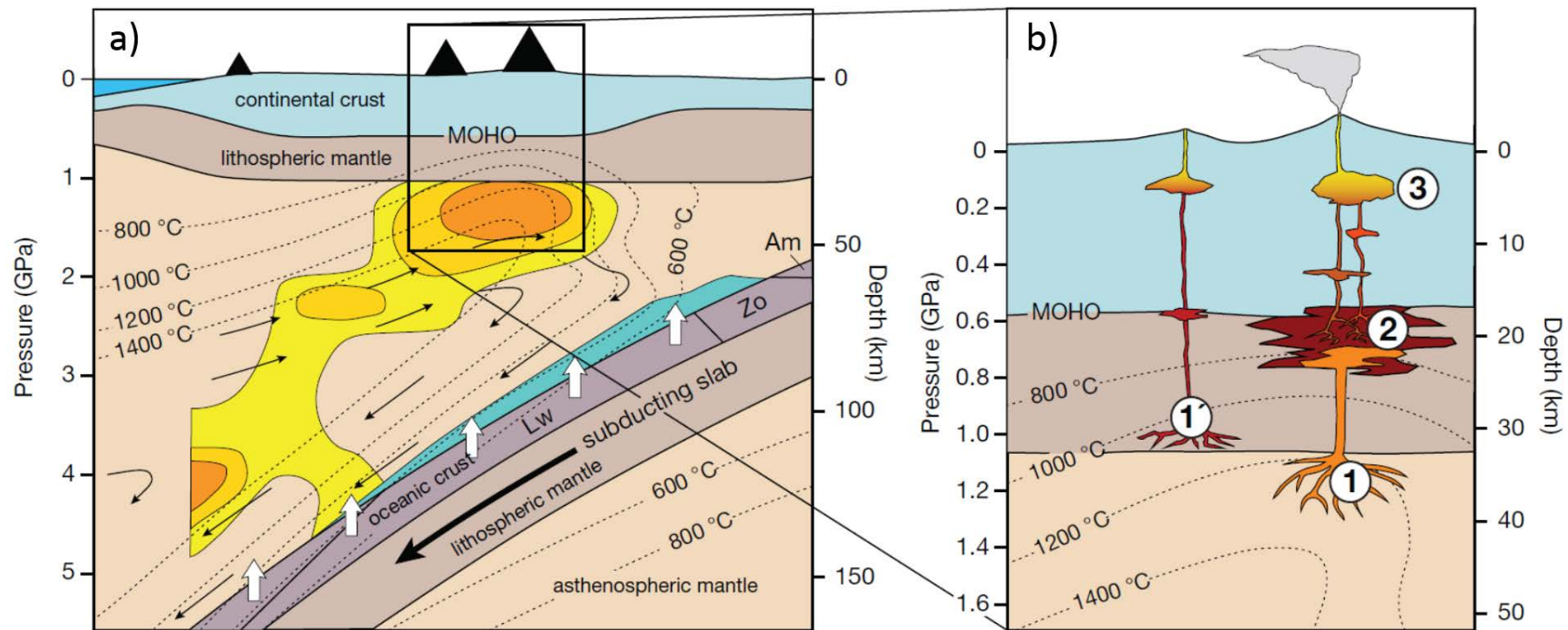


Figure 1.5. A cross section showing the structure of a subduction zone. (a) The relationship between the subducting slab and the mantle wedge. White arrows indicate the dehydration of the down-going slab, which fluxes the mantle wedge above with metasomatic fluids, generating partial melting. Shaded yellow/orange regions are areas of seismic low velocity, which are inferred to contain partial mantle melts. (b) Mantle melts generated at location [1] ascend to the Moho [2], and pond to form deep crustal hot zones (or 'MASH' zones). Felsic magmas are generated in hot zones, and ascend into the shallow crust to form large felsic magma chambers [3], above which porphyry deposits may form. See text for full discussion. From Audétat and Simon (2012).

### 1.3.2 Fertile and barren magmas

The terms ‘fertile’ and ‘barren’ are used to distinguish rocks with geochemical signatures which are indicative of high ore-forming potential. Fertile magmas are H<sub>2</sub>O, sulphur rich, and oxidised. These magmas must also contain ore metals, but it is not necessarily a requirement for porphyry magmas to be anomalously metal-rich in order to form a porphyry deposit, as most H<sub>2</sub>O bearing calcalkaline rocks have the potential to form a porphyry deposit (e.g. Cline and Bodnar, 1991; Cline, 1995).

To compare the chemistry of fertile and barren arc magmas, data for barren and fertile arcs were collated. For fertile arcs, data from ostensibly unaltered igneous rocks associated with porphyry intrusions (n=253) were drawn from a variety of literature sources for the following porphyry systems: several deposits from the Laramide province (Lang and Titley, 1998), Chuquicamata (Ballard et al., 2012), El Teniente (Kay et al., 2005; Stern et al., 2011), Rio Blanco-Los Bronces (Stern and Skewes, 1995), Escondida (Richards et al., 2001), El Salvador (Lee, 2008), Los Pelambres (Reich et al., 2003). The Aleutians arc was selected to be representative of barren arc. This is because it is a hydrous arc which produces tholeiitic to calc-alkaline magmatism (Zimmer et al., 2010), but has no known association with porphyry Cu mineralisation (e.g. Loucks, 2014). Data from the Aleutians arc are drawn from the GEOROC whole rock database ([georoc.mpch-mainz.gwdg.de](http://georoc.mpch-mainz.gwdg.de)), which comprises 2396 whole rock analyses at the time of writing. Not every whole rock analysis in the GEOROC database has a complete geochemical suite, so for some elements the number of analyses is lower than 2396.

Fertile magmas associated with porphyry deposits share many characteristics with typical arc magmas, with some subtle and critical differences. They span nearly the entire range of compositions of volcanic rocks, from calcalkaline to alkalic, intermediate to felsic (Fig. 1.6), and metaluminous to weakly peraluminous. The majority of intrusions most closely associated

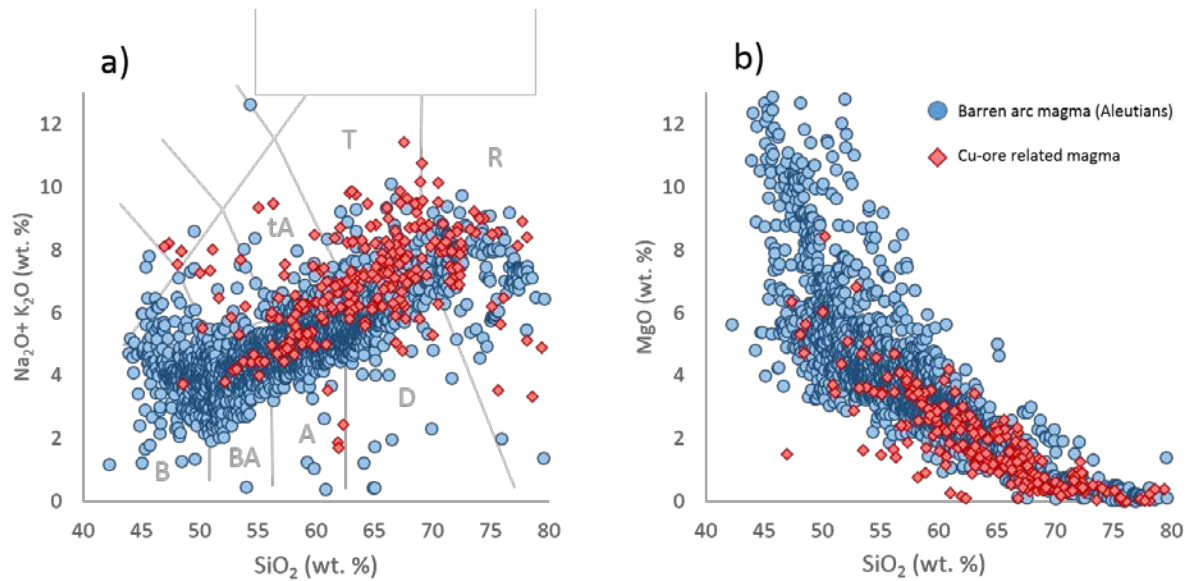


Figure 1.6. A comparison between barren arc magmas and those associated with Cu mineralisation in terms of: (a) total alkalis vs SiO<sub>2</sub>, and (b) MgO vs SiO<sub>2</sub>. Broad overlap exists between these two datasets, indicating that magmas at porphyry systems are members of a broader family of arc magmas, and fertile and barren magmas form by similar processes. See text for sources of data.

With mineralisation comprise intermediate, metalumious, calcalkaline magmatic rocks (Seedorff et al., 2005). In general, igneous rocks associated with porphyry Cu-Au deposits tend to be more alkaline (Mueller and Groves, 1993; Sillitoe, 1997, Mueller et al., 2001), and intrusions related to porphyry Mo deposits are typically more highly fractionated (Seedorff et al., 2005). As a result of these geochemical similarities, it is widely held that magmas associated with porphyry deposits do not form by entirely unique processes, but by some combination of more typical arc processes which are optimised in the case of porphyry formation. The nature and relative importance of these processes is the subject of some debate (e.g. Richards, 2013; Wilkinson, 2013) but some processes, such as high magmatic H<sub>2</sub>O, are widely held to be important.

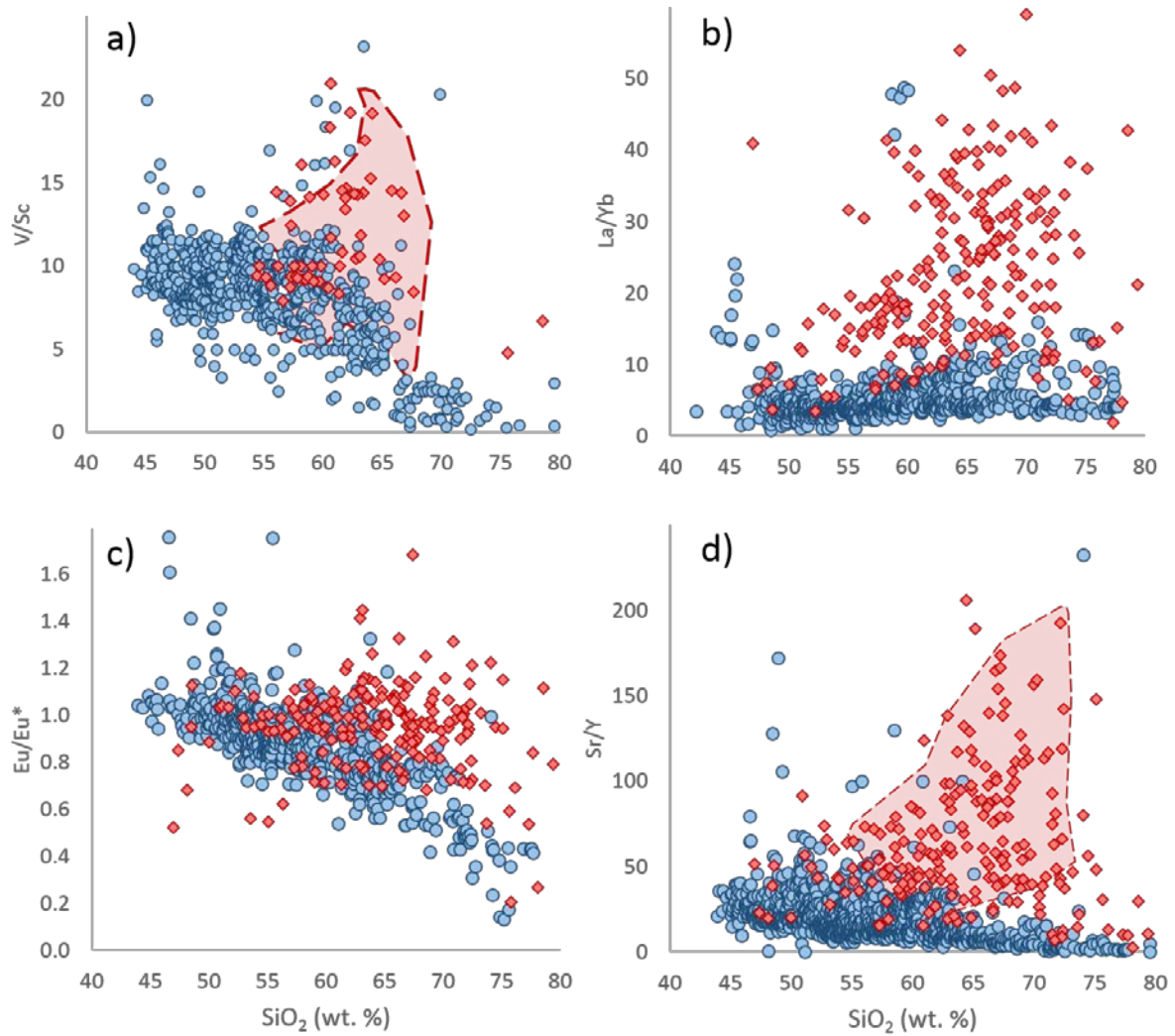


Figure 1.7. The divergence of fertile magmas from typical barren fractionation trends for trace element fertility signatures. (a-d) Fertile magmas evolve to higher  $\text{V/Sc}$ ,  $\text{La/Yb}$ ,  $\text{Eu/Eu}^*$  and  $\text{Sr/Y}$ , whereas typical barren arc magmas show decreases in  $\text{V/Sc}$ ,  $\text{Sr/Y}$ , and  $\text{Eu/Eu}^*$  with fractionation.  $\text{La/Yb}$  of barren arc magmas increases with increased fractionation, but not to the same extent as in fertile magmas. Red shaded field in (a) and (d) is the field of fertile rocks from Loucks (2014). Data sources as in Figure 1.6. See text for discussion.

In terms of trace elements, magmas associated with porphyry systems may begin to be distinguished from typical arc magmas. In particular, porphyry magmas are elevated in  $\text{Sr/Y}$ , high  $\text{La/Yb}$ ,  $\text{V/Sc}$ , and  $\text{Eu/Eu}^*$  with respect to typical barren rocks (e.g. Rohrlach and Loucks, 2005; Richards, 2012; Chiaradia et al., 2012; Loucks, 2014; Fig 1.7).  $\text{Eu/Eu}^*$  is a

measure of the abundance of Eu with respect to its neighbouring elements, Sm and Gd ( $\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N}/(\text{Sm}_\text{N} \times \text{Gd}_\text{N})^{0.5}$ , where subscript N denotes chondrite normalised values (from Sun and McDonough, 1989). A compilation of analyses from porphyry systems generated by Loucks (2014) shows that these characteristics are common to porphyry Cu systems irrespective of location deposit type (Cu, Cu-Au, Cu-Mo) and collectively, these signatures are referred to as ‘fertility signatures’.

### 1.3.3 Partitioning behaviour

Much of the discussion involving the generation and evolution of fertility signatures involves the distribution of elements between various mineral, melt, and fluid phases during melting, crystallisation, and volatile exsolution. Partitioning of elements between different phases during these processes is expressed in terms of a partition coefficient (or distribution coefficient)  $D$ , which is calculated as the quotient of the concentration of an element in one phase over another. For example, the partition coefficient for Sr between plagioclase and silicate melt may be expressed thus:

$$D_{\text{Sr}}^{\text{Pl/l}} = \frac{C_{\text{Sr}}^{\text{Pl}}}{C_{\text{Sr}}^{\text{l}}} \quad (1.1)$$

where  $C_{\text{Sr}}^{\text{Pl}}$  and  $C_{\text{Sr}}^{\text{l}}$  are the concentrations of Sr in plagioclase and the liquid, respectively. At equilibrium, a partition coefficient  $> 1$  indicates that the element in question is more stable in the phase on the numerator (in this case, plagioclase) than the denominator (i.e. the melt). In such a case, Sr is said to be compatible in plagioclase. Conversely, an element which prefers to remain in melt during crystallisation is said to be incompatible. Incompatible elements increase in concentration in residual melts during fractionation.

| Mineral        | Apatite | Titanite | Hornblende | Plagioclase       | Clinopyroxene | Olivine | Zircon  | Garnet              |
|----------------|---------|----------|------------|-------------------|---------------|---------|---------|---------------------|
| Ref.           | [1]     | [2]      | [3]        | [4]               | [5]           | [6]     | [1]     | [7]                 |
|                | Dacite  | Rhyolite | Andesite   | Basaltic Andesite | Andesite      | Basalt  | Dacite  | High-alumina basalt |
| La             | 36      | 113      | 0.37       | 0.18              | 0.05          | 0.012   | 0.00046 | <0.01               |
| Ce             | 48      | 223      | 0.73       | 0.14              | 0.08          | 0.009   | 0.36    | 0.01                |
| Pr             | 64      | 431      | 0.73       | 0.13              | 0.13          | 0.005   | 0.0172  | 0.03                |
| Nd             | 77      | 639      | 0.73       | 0.12              | 0.18          | 0.004   | 0.077   | 0.05                |
| Pm             | 85      | 785      | 1.37       | 0.1               | 0.28          | 0.004   | 0.2     | 0.2                 |
| Sm             | 93      | 930      | 2.01       | 0.08              | 0.38          | 0.003   | 0.8     | 0.3                 |
| Eu             | 55      | 661      | 1.33       | 0.79              | 0.48          | 0.003   | 1.22    | 0.4                 |
| Gd             | 127     | 855      | 2.3        | 0.07              | 0.58          | 0.004   | 8       | 1.3                 |
| Tb             | 102     | 895      | 2.49       | 0.06              | 0.68          | 0.004   | 20.7    | 1.7                 |
| Dy             | 76      | 935      | 2.68       | 0.03              | 0.77          | 0.005   | 45.9    | 2.2                 |
| Ho             | 62      | 786      | 2.58       | 0.03              | 0.74          | 0.007   | 80      | 2.9                 |
| Er             | 57      | 636      | 2.47       | 0.02              | 0.71          | 0.008   | 136     | 3.6                 |
| Tm             | 53      | 515      | 2.29       | 0.02              | 0.67          | 0.009   | 197     | 5.1                 |
| Yb             | 48      | 393      | 2.1        | 0.01              | 0.63          | 0.013   | 277     | 6.6                 |
| Lu             | 33      | 300      | 1.7        | 0.01              | 0.6           | 0.019   | 325     | 7.1                 |
| Sr             |         |          | 0.51       | 1.16              |               |         |         | 0.003               |
| Y              |         |          | 1.47       | 0.04              |               |         |         | 3.1                 |
| Pressure (MPa) | ?       | ~200     | 1000       | 0.1               | ?             | ?       | ?       | 2000                |
| Temp. (°C)     | ?       | 700-760  | 800        | 1100              | ?             | ?       | ?       | 1300                |

*Table 1.1. Partition coefficients for selected trace element, which were used in fractionation models in this study. References are: 1 = Sano et al. (2002); 2 = Bachmann et al. (2005); 3 = Klein et al. (1997); 4 = Dunn and Sen (1994); 5 = Fujimaki et al. (1986); 6 = Frey (1969); 7 = Johnson et al., (1994). Values in italics are interpolated between neighbouring partition coefficients. “?” indicates intensive parameters are not reported/unknown in original study.*

Elemental compatibility must be considered in terms of all the phases present in the system. For example, during fractional crystallisation, a given element will be incompatible in some phases, and compatible in others. The overall compatibility (bulk partition coefficient) of this element may be expressed as the sum of individual  $D^{\text{mineral/melt}}$  values multiplied by the fraction of that in the crystallisation assemblage:



$$\bar{D}_i = \sum X_A D_i^A \quad (1.2)$$

where  $\bar{D}_i$  is the bulk partition coefficient for element  $i$ ,  $X_A$  is the fraction of mineral A in the crystallising assemblage, and  $D_i^A$  is the partition coefficient for element  $i$  in mineral A. The bulk compatibility of a certain element can be greatly enhanced by the onset of crystallisation of a phase into which it is especially compatible. Continued fractionation would concentrate the element in this phase, thus depleting the residual melt concentration of this element. For example, Sr is strongly compatible in plagioclase ( $D_{\text{Sr}} = 15.6$  in albite at 900°C; Blundy and Wood, 1991), so the onset of plagioclase crystallisation may strongly deplete residual melts in Sr. Conversely, the suppression of plagioclase crystallisation, and the promotion of other phases into which Sr is incompatible will generate residual melt enrichments in Sr.

In this study, several attempts have been made to model the effects of mineral/melt partitioning during the magmatic crystallisation REE, Y, and Sr. The particular focus has been the impact that the crystallisation of certain phases has on the composition of residual melts, and on co-precipitating minerals. Unless otherwise stated, the partition coefficients used for these models are listed in Table 1.1. Partition coefficients were selected to most closely represent the conditions relevant to the model (pressure, temperature, oxygen fugacity, starting melt composition)

#### 1.3.4 Generating signatures of magmatic fertility

The geochemical characteristics of fertile magmas have been suggested to form in a number of ways, including direct melting of the slab or lower crust, and the hydrous fractionation of a deep crustal assemblage.

High Sr/Y and La/Yb signatures in porphyry magmas are similar to those of adakites, which form due to the partial melting of subducting oceanic lithosphere. The presence of

garnet in the eclogitised down-going slab controls the budget of Y and Yb during slab melting, as both are strongly compatible in garnet ( $D_Y = 3.1$ ;  $D_{Yb} = 6.6$ ), whereas Sr and LREE are incompatible ( $D_{Sr} = 0.003$ ;  $D_{La} = 0.0016$ ; Johnson et al., 1994). During partial slab melting, garnet is often a residual phase (e.g. Kay, 1978), meaning that slab melts are deficient in Y and Yb and relatively enriched in La and Sr, leading to elevated Sr/Y and La/Yb. These geochemical similarities have lead some authors to draw a genetic link between slab melts and the formation of porphyry Cu deposits (Thiéblemont et al., 1997; Sajona and Maury, 1998; Oyarzun et al., 2001). However, several lines of evidence suggest that such a genetic link is not necessary and in the case of most porphyry systems, is unlikely. First, geophysical models predict that slab temperatures are not typically high enough for significant slab melting to occur (e.g. Arcay et al., 2007). Where slab melts do occur, their geochemical signatures may be masked by subsequent and extensive open system processes (e.g. fractionation crystallisation, magma mixing, assimilation of pre-existing arc crust). Porphyry deposits are very rare in the Archean, whereas adakitic rocks related to slab melting are more common due to higher slab temperatures, which contradicts the suggested link between porphyry deposit genesis and slab melting. Furthermore, it is possible to generate ‘adakite-like’ signatures by more typical arc processes, without invoking the partial melting of the down-going slab (for review, see Richards and Kerrich, 2007).

In thickened mature arc crust, garnet- and amphibole-bearing mafic rocks commonly comprise the deep crust. Primary melts ascending from the mantle and stalling in the deep crust may interact with these rocks, which may partially melt if the ambient temperature is high enough (Hildreth and Moorbath, 1988). Equilibration with deep crustal garnet-bearing rocks can cause melt depletion in HREE and Y, generating high La/Yb and Sr/Y. A magmatic contribution from lower crustal rocks has been invoked to explain geochemical signatures of porphyry magmas from Central Chile (e.g. Kay et al., 2005).

Fertility signatures may be also explained without reference to partially melted rocks with garnet in the residue. A major control on the distribution of Sr and Eu in silicate magmas is the crystallisation of plagioclase, which has high partition coefficients for both Sr and  $\text{Eu}^{2+}$  (e.g. Blundy and Wood, 1991). Experimental studies of water-saturated crystallisation of basaltic magmas in the shallow crust demonstrate that plagioclase is a common phase in the crystallisation assemblage (e.g. Sisson and Grove, 1992; 1993), but the temperature of plagioclase saturation in the shallow crust (and thus, the timing of its crystallisation with respect to other phases) is reduced at higher melt  $\text{H}_2\text{O}$  (Arculus and Wills, 1980; Blatter and Carmichael, 1998). At high magmatic  $\text{H}_2\text{O}$  contents (up to 10 wt. %), and high pressures found at the base of the arc crust (0.8 to 1.2 GPa), plagioclase is less stable, and becomes a subordinate phase during fractional crystallisation (Muentener et al., 2001; Alonso-Perez et al., 2009). High  $\text{H}_2\text{O}$  contents stabilise hornblende and garnet as liquidus phases, so the extensive fractional crystallisation of hydrous magmas at high pressure cause residual melts to become enriched in Sr, and depleted in Y and Yb. High magmatic  $\text{H}_2\text{O}$  also suppresses the anorthite (Ca-rich) end member of plagioclase to a greater extent than albite (see Arculus and Wills, 1980). The resultant distortion of the plagioclase phase loop means that plagioclase has a higher anorthite component upon crystallisation in hydrous melts. The partitioning of Sr into plagioclase is less strong in anorthite than albite (Blundy and Wood, 1991), which reduces the uptake of Sr into plagioclase when it does crystallise.

The suppression of plagioclase crystallisation also leads to the accumulation of Eu in residual melts with respect to other REE. Eu is compatible in hornblende, and is weakly

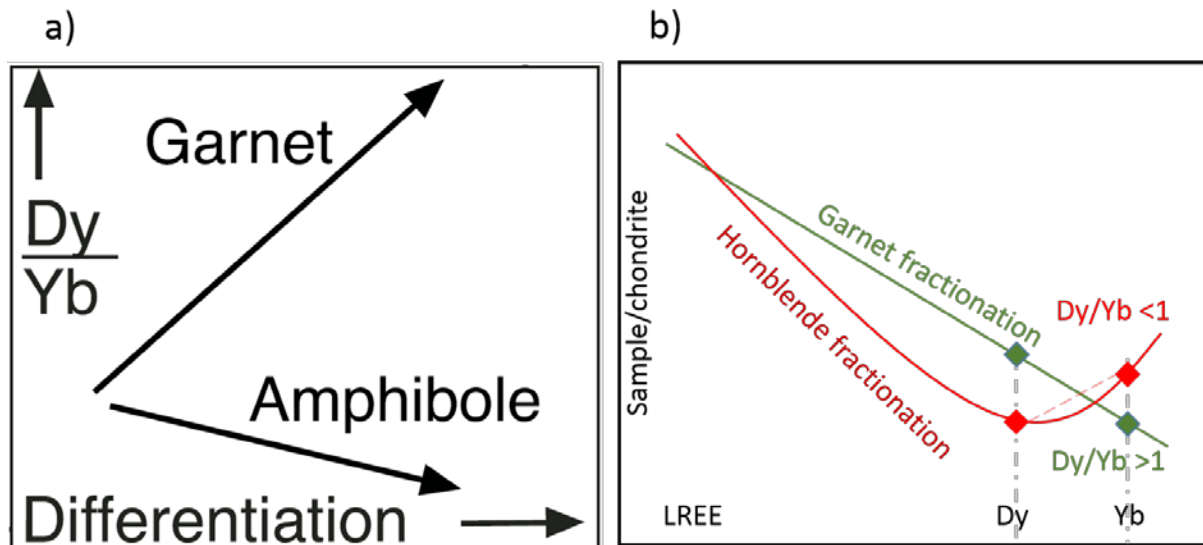


Figure 1.8. (a) The geochemical criteria by which the fractionation of garnet and amphibole (e.g. hornblende) may be distinguished from whole rock geochemistry.  $SiO_2$  is the most commonly used index of fractionation. From Davidson et al. (2007). (b) A schematic diagram showing the relative effects of garnet vs hornblende fractionation on whole rock REE patterns.

incompatible in garnet (Johnson et al., 1994; Table 1.1), but in both phases, Eu it is less compatible than its neighbouring REE (Sm and Gd), so extensive hornblende  $\pm$  garnet fractionation, or the interaction between mantle melts and garnetiferous lower crust, leads to elevated Eu with respect to Sm and Gd (i.e. higher  $Eu/Eu^*$ ). Melt redox conditions may also have an effect on Eu partitioning, due to the preference of plagioclase for  $Eu^{2+}$  over  $Eu^{3+}$ . Oxidised melts (high  $Eu^{3+}/Eu^{2+}$ ) will become less depleted in Eu during plagioclase fractionation than reduced melts. The relative effects of garnet and hornblende fractionation in the petrogenesis of arc rocks may be distinguished on the basis of the relative abundance of MREE and HREE in the whole rock. Hornblende has higher partition coefficients for MREE relative to HREE ( $D_{Dy}/D_{Yb} = 1.27$ ) meaning that fractionation of an assemblage dominated by hornblende leads to progressive MREE depletion in residual melts, and relative enrichment of HREE with respect to MREE (Fig. 1.8 b). Conversely, garnet preferentially

partitions HREE ( $D_{Dy}/D_{Yb} = 0.33$ ), leading to significant depletions in HREE in residual melts with increased fractionation, and the formation REE patterns with greater HREE depletion than MREE (Fig. 1.8b). These effects may be demonstrated in on plots of  $D_{Yn}/Yb_N$  vs  $SiO_2$  (e.g. Davidson et al., 2007; Fig 1.8), as  $D_{Yn}/Yb_N$  increases with garnet fractionation, and decreases with hornblende fractionation (Fig 1.8a). As well as garnet and hornblende, other phases preferentially partition M- or HREE. For example, titanite (sphene) strongly partitions all REE, and especially MREE ( $D_{Dy}/D_{Yb} = 2.38$ ; Bachmann et al., 2005). The presence of titanite solely in oxidised magmas (Wones, 1989) mean its effects may be significant in the crystallisation of felsic porphyry magmas, which are themselves oxidised (Ballard et al., 2002. Zircon fractionates HREE with respect to LREE ( $D_{La} = 0.00046$ ;  $D_{Yb} = 277$ ; Burnham and Berry, 2012), although does not crystallise in significant enough volumes to exercise a significant control on melt REE chemistry.

These processes cause fertile arc magmas to diverge from typical arc fractionation trends. Typical arcs show decreasing  $Sr/Y$  and  $Eu/Eu^*$  with increasing  $SiO_2$ . Plotting unaltered rocks from fertile porphyry systems on these Harker diagrams shows that as the  $Sr/Y$  of typical arcs rocks decreases with increasing  $SiO_2$ , fertile porphyry rocks increase in  $Sr/Y$  with increasing fractionation, reaching peak values in intermediate to felsic rocks. (Fig. 1.7 d). Similarly,  $Eu/Eu^*$  decreases with increasing fractionation in typical rocks, but in fertile rocks,  $Eu/Eu^*$  stays close to 1 and in some cases extending above unity (Fig. 1.7 c)

Another feature of the crystallisation of magmas at high- $H_2O$  and pressure is the promotion of hornblende ahead of titanomagnetite in the fractionation assemblage (Loucks, 2014; Fig. 1.9). This is because early hornblende crystallisation depletes residual melts in Fe. Early hornblende Another feature of the crystallisation of magmas at high- $H_2O$  and pressure is the promotion of hornblende ahead of titanomagnetite in the fractionation assemblage (Loucks,

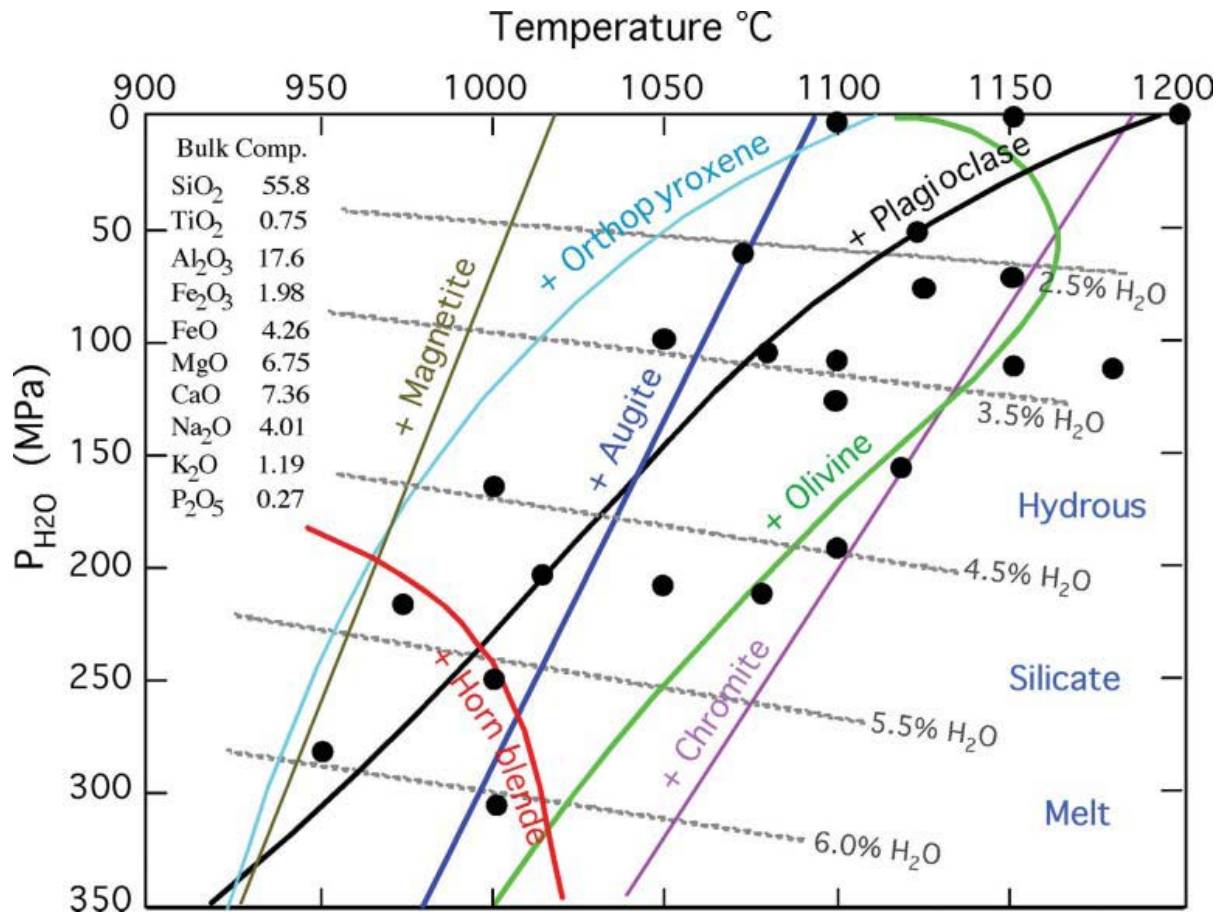


Figure 1.9. Experimentally determined H<sub>2</sub>O-saturated stability of various common igneous phases as a function of H<sub>2</sub>O ( $P_{H_2O}$  in MPa) in the melt. High H<sub>2</sub>O causes the suppression of plagioclase and (titano-) magnetite to lower temperatures, and the promotion of hornblende in the fractionation sequence. Fractionation of such an assemblage causes residual melt depletions in trace elements which partition into hornblende (e.g. Sc, Y) and enrichment in trace elements that ordinarily partition into plagioclase or titanomagnetite (e.g. Sr, V), thus causing enrichments in Sr/Y and V/Sc. From Loucks (2014).

2014; Fig. 1.9). This is because early hornblende crystallisation depletes residual melts in Fe. Early hornblende fractionation also causes melts to become depleted in Sc, which partitions more strongly into hornblende (and augite) than titanomagnetite. The suppression of titanomagnetite means that V content of such melts increases, because titanomagnetite is typically the largest sink of V in arc magmas (Shervais, 1982). This is the case for oxidised melts where V is predominantly present as V<sup>4+</sup> (instead of V<sup>3+</sup> or V<sup>5+</sup>; Canil, 1999) which

substitutes readily for  $\text{Ti}^{4+}$ . Increases in V/Sc in the residual melts of fertile magmas (Fig. 1.7a) are therefore likely to be due to the promotion of hornblende, and the suppression of titanomagnetite in the fractionation sequence, which is achieved at high pressure and magmatic  $\text{H}_2\text{O}$  content.

### 1.3.5 The importance of high magmatic $\text{H}_2\text{O}$ and $f\text{O}_2$ on fertility

The crystallisation of hornblende and suppression of plagioclase do not have a direct effect on the fertility of the magmas. Rather, they occur in response to other processes which are important for ore formation, such as the increase in melt  $\text{H}_2\text{O}$  content.  $\text{H}_2\text{O}$  in magmas is a pre-requisite for ore formation (Richards, 2011), because magmatically-derived hydrothermal fluids are responsible for the concentration, transport, and deposition of metals from magmas to wall rocks.

The oxidation state of magmas also plays a critical role in preserving the fertility of a system. It is largely to do with the speciation of sulphur between sulphate ( $\text{SO}_4^{2-}$ ) and sulphide ( $\text{S}^{2-}$ ). Magmas associated with porphyry systems are interpreted to be highly oxidised, based on estimates from mineral chemistry (e.g. Ballard et al., 2002; Dilles et al., 2015). Under oxidising conditions (FMQ +1 to +3), the dominant sulphur species is sulphate. Relatively small decreases in  $f\text{O}_2$  can drastically increase the proportion of sulphide, and under relatively reducing conditions (FMQ -1 to 0), sulphide predominates in the melt (Fig 1.10a). The presence of sulphide species in the melt has two important consequences. Firstly, sulphide is less soluble in melts than sulphate (Fig 1.10b). When a sulphide melt is exsolved, the partition coefficients for Cu into the sulphide melt are so high ( $D_{\text{Cu}}$  up to 1000; Li and Audétat, 2012) that Cu is

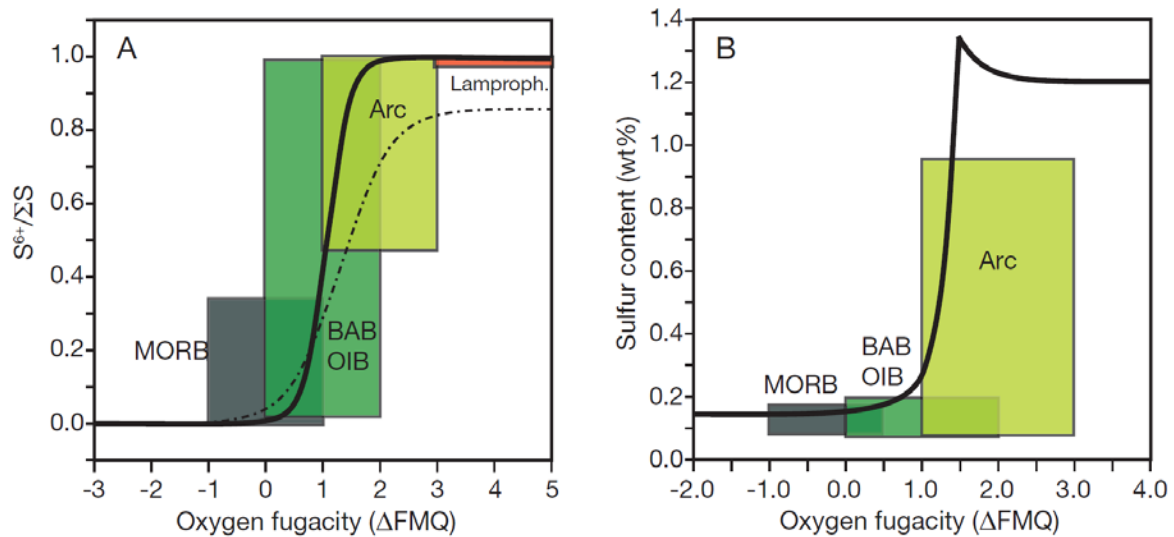


Figure 1.10. (a) The ratio of oxidised sulphur species ( $S^{6+}$ ) to total sulphur in the melt, as a function of oxygen fugacity. Small changes in redox (from  $\sim$ FMQ 0 to FMQ +2, where 'FMQ' is the fayalite-quartz-magnetite redox buffer) cause drastic increases in the abundance of oxidised sulphur species in the melt. (b) The sulphur solubility in the melt, as a function of redox conditions.  $S^{6+}$  is more soluble in melts than reduced sulphur species, so melts may attain higher S at more oxidised conditions. Arc magmas typically form at the upper limit of this transition, so are susceptible to changes in  $fO_2$ . From Audétat and Simon (2012).

effectively stripped from the silicate melt, which significantly hampers its ore-forming potential if those sulphides are lost from the melt (i.e. in a cumulate). Cu does not have the same affinity with sulphate, and so will not be stripped from oxidised melts in the same way. Also, the enhanced sulphate solubility means silicate melts may be enriched in sulphur, which is an important component for generating an ore deposit.

However, Cu in arc lavas shows systematic decreases with increased fractionation. Cu is incompatible in major silicate phases (Stanton, 1994), so it is likely that Cu is fractionated from the silicate melt by sulphide melts. The loss of sulphides from the melt is potentially triggered by the crystallisation of magnetite (Jenner et al., 2010), or the assimilation of reduced country rock (Cloos, 2010). Given the fact that most arc magmas sit on the boundary



between oxidised and reduced sulphur species, the presence of Cu in melts is highly sensitive to small changes in redox.

The effect of sulphide saturation on the fertility of magmatic systems remains controversial. On the one hand, the loss of Cu from a silicate melt will drastically reduce its fertility. However, this process would generate zones in magmatic systems that are enriched in Cu-bearing sulphides. If a subsequent melt or fluid is able to digest these accumulations of sulphides, it will become enriched in Cu and S, and have an enhanced ore-forming potential as a result (Wilkinson, 2013).

#### 1.3.6 The role of tectonics in the generation of fertile melts

Although the processes mentioned above may be common to many types of arc magmas which fractionate in the deep crust, hydrous fraction is more extensive in the case of porphyry magmas. This is partly due to tectonic controls on magma ascent. Magmas trapped at the base of the crust can become highly fertile, as they can become enriched in volatiles, metals, and sulphur by repeated influx of new mafic material, without extensive loss of material to the shallow crust, or the surface through eruption. Rohrlach and Loucks (2005) showed that magmas associated with ore formation at the Tampakan porphyry Cu (-Au) deposit (Philippines) underwent repeated cycles of fractionation in the deep crust, and replenishment by hydrous mafic melts, causes a ‘ramping up’ of volatile contents up to 8 wt. % H<sub>2</sub>O. In order to trap magmas at the base of the crust, a switch to compressive tectonic conditions is required, and may be induced by variations in steady-state subduction, such as ‘flat slab’ subduction (e.g. Laramide orogeny; English et al., 2003), or the subduction of seafloor anomalies (such as aseismic ridges or seamounts; Dominguez et al., 1998). For example, the subduction of the Juan Fernandez ridge underneath the South American plate has been linked to the formation of three large porphyry systems in the Chilean Andes

(Hollings et al., 2005). The observation that porphyry formation occurs only in restricted arc segments for brief periods of time may be explained by the transient nature of and limited spatial extent of such tectonic processes.

Porphyry systems usually form at the end of magmatic cycles, where they represent the final intrusive event (e.g. Richards et al., 2001). This suggests that extensive fractionation must take place for magmas to become sufficiently fertile for ore formation (Richards, 2003). When tectonic conditions are relaxed, fertile magmas may ascend into the shallow crust, from where mineralisation may occur. Transpressive tectonic regimes, such as fault jogs in orogen-parallel strike-slip faults, provide a passive mechanism by which magmas may be drawn towards the surface due to localised extension in an environment where oblique compression may predominate (Richards, 2003).

#### 1.3.7 What is the cause of high Cu grades in some deposits?

If oxidised, water- and sulphur-rich magmas are capable of producing a large tonnage ore bodies, how then do ore bodies with high grade form? One important factor controlling the grade of a deposit is the chemistry and physical structure of the wall rocks into which porphyry intrusions and fluids are emplaced. For example, mafic host rocks are capable of efficiently precipitating Cu from oxidised ore fluids due to their ferrous Fe content (Sillitoe, 2010). Several large, high grade porphyry systems are hosted in thick sequences of mafic rocks, including as Resolution (Hehnke et al., 2012), Hugo Dummett (Oyu Tolgoi; Crane and Kavalieris, 2012), and El Teniente (Skewes et al., 2002). Carbonate host rocks are particularly reactive chemical ‘traps’, generate high-grade skarn-type mineralisation (Meinert et al., 1997). Carbonate rocks are also relatively impermeable, especially where they have undergone contact metamorphism close to intrusive contacts. This restricts fluid flow, and leads to the generation of high grade ore bodies (Sillitoe, 1997). Highly focussed fluid flow

along narrow structural corridors can also generate high-grade deposits, especially when mineralisation from repeated pulses of fluid are superimposed one upon another (e.g. Richards, 2013).

However, the presence of receptive host rocks and fluid focussing alone are unlikely to control grade, because deposits close by one another which are hosted in the same rocks can have very different grades. For example, the low-grade Heruga and high-grade Hugo Dummett deposits at Oyu Tolgoi are hosted in the same augite basalt host rocks, and yet have very different grade (Crane and Kavalieris, 2012; see Chapter 3 of this study). Similarly, the high grade Resolution deposit is hosted in the same Proterozoic diabase as the nearby Superior East (Sell, 1995) and Ray (Phillips et al., 1974), both of which are lower grade. Fluid chemistry may play an important role in controlling the grade of a system. Fluid inclusions from fertile intrusions can contain between one and three orders of magnitude higher metal content than similar fluids from barren systems (Audétat et al., 2008; see Wilkinson, 2013 for discussion) and may provide a simple explanation for the high Cu contents of some deposits, although the origins of such fluid and their importance in ore formation are poorly understood.

#### **1.4 Indicator minerals in exploration**

In the early years of porphyry exploration, most deposits were identified due to their location close to (or at) the surface, and could be distinguished by their large alteration halos, or supergene mineralisation blankets (e.g. Bajo de la Alumbrera) which could be identified by a combination of field mapping and aerial photographs. However, most systems that are exposed at the surface have been discovered (e.g. Richards, 2003), and modern exploration for porphyry deposits is focussing increasingly on those that are located under the cover of sedimentary rocks (as is the case at Resolution), or located in the footwall of thrust fault

which emplace allochthonous crust above the deposit (e.g. Oyu Tolgoi; Northparkes, Australia). These are known as ‘blind’ deposits, as there is no clear surface expression of their presence. The recent location of large, high-grade blind deposits in previously well-explored porphyry districts (e.g. Resolution, in the Laramide province) highlights the importance of blind deposits in the future of base metal mining.

One of the largest costs for exploration companies is diamond drilling, where rock core is extracted from the ground for geochemical and petrographic assessment. The identification of rocks or minerals which indicate the fertility of a system during regional exploration, or early in a drilling program, has the potential to greatly reduce the cost of exploration projects.

Minerals which carry signatures that indicate fertility are of particular importance, as they may survive weathering and erosion, and become concentrated in stream sediments. For a particular mineral to be successful as an indicator of the fertility of an orebody, it must possess a number of physical and chemical characteristics. Good mineral indicators are:

- **Robust.** Mineral indicators must be resistant to chemical alteration and physical abrasion. Any geochemical or textural characteristic that is indicative of fertility must, once formed, be retained by the mineral and must remain unchanged by post-crystallisation processes. Such minerals may be found in the context of the bedrock in which they formed, but also may survive chemical and physical weathering and be present in sediments close to (or overlying) the deposit. For example, glacial till overlying the giant Pebble Porphyry Cu-Au-Mo (Alaska, USA) contains a greater abundance of pristine gold grains closer to the deposit (Kelley et al., 2011).
- **Abundant and widespread.** Minerals which are extremely rare, or only located only in specific rock types or alteration styles which may or may not be present in a

porphyry system, have a smaller chance of being observed. Consequently, these minerals are less useful as indicator minerals. A mineral which is common and is found in a variety of environments is a better prospective indicator mineral.

- **Easy to identify/isolate.**
- **Contain unequivocal signatures.** A geochemical signature which may indicate the presence of a fertile system, but may also indicate another process which is unrelated to mineralisation, is of less value than a signature which is unequivocally related to the proximity to a large orebody.
- **Easy to analyse.** A geochemical signature which is only analysable by expensive or unavailable techniques (e.g. synchrotron) is economically unviable as a mineral indicator. Ideally, a chemical signature could be analysed by SEM (scanning electron microscope) or EMPA (electron microprobe analysis), although the increasing availability of other in situ analytical techniques (e.g. LA-ICP-MS), and the higher sensitivity of such techniques (meaning more elements are within the limit of detection) makes such techniques more viable.

## **1.5 Field studies: two examples of high-grade porphyry systems**

To investigate the potential geochemical differences between deposits of different size and grade, two large porphyry systems were selected for this study; the late-Cretaceous Resolution porphyry Cu-Mo deposit (Arizona), and the late-Devonian Oyu Tolgoi porphyry Cu-Au deposit (Mongolia). These deposits were selected as they represent the diversity of porphyry mineralisation style (Cu-Mo vs Cu-Au), tectonic setting (continental vs. oceanic arc), and age (early Cenozoic to Palaeozoic respectively). As such, conclusions which are common to both systems stand a better chance of being common to all porphyry Cu systems.

Two questions are important here, and shall be considered throughout. First, what are the geochemical differences between mineralised (fertile) and barren systems? To assess this question, comparisons are drawn between the geochemistry of rocks and minerals from both Resolution and Oyu Tolgoi, and data from ostensibly barren systems (volcanic arcs) drawn from the literature.

The second question is; what are the differences between low- and high-grade mineralised systems? Oyu Tolgoi is a useful system to undertake such a comparison, as it comprises several porphyry systems, some of which are much higher grade and tonnage than others in spite of their apparent spatial, temporal, and geochemical relationships. In this study, the high-grade, high-tonnage Hugo Dummett Cu-Au system will be compared to the low-grade, low-tonnage Cu-Mo Heruga deposit.

Chapters 3 and 4 of this study contain a description of the background geology of both study areas, a description of the texture and mineralogy of the rocks collected at these deposits. Both chapters go on to describe the bulk rock geochemistry of rocks collected, and compare them to average arcs, and magmatic rocks from other porphyry systems.

Chapter 5 focuses on zircon, describing the texture, geochemistry, and U-Pb geochronology of zircons from both Oyu Tolgoi and Resolution.

In Chapter 6, the texture and geochemistry of igneous and hydrothermal apatite from both deposits is described.

Chapter 7 comprises a discussion of the key findings of this study, and a development of how these findings may be implemented during exploration for major porphyry systems.

## Chapter 2: Analytical Methods

### 2.1 Introduction

Laboratory work conducted for this study consists of whole rock geochemistry, scanning electron microscope imaging of selected rocks samples, electron probe microanalysis (EPMA) and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) of apatite and zircons from both Resolution and Oyu Tolgoi. In addition, U-Pb dating of zircons was also conducted by LA-ICP-MS. The methods used for each of these techniques are described in this chapter.

#### 2.1.1 Accuracy and precision of geochemical data

The accuracy and precision of chemical analyses for each method were assessed with reference to analysed standard materials. A summary of the methods used to quantify the accuracy and precision of data in this study is presented here. The accuracy of a particular analytical method was quantified by calculating the percentage bias with reference to measured standards, using the following formula:

$$Bias (\%) = \left[ \frac{\frac{1}{n} \sum (X_{measured}^i - X_{reference}^i)}{X_{reference}^i} \right] \times 100 \quad (2.1)$$

where  $X_{measured}^i$  is the mean concentration of element  $i$  measured in the standard,  $X_{reference}^i$  is the known concentration of element  $i$  in the standard, and  $n$  is the number of analyses. Positive values of percentage bias indicate an overestimate in the measured value with respect to the reference value, and negative values represent an underestimate.

The precision of each method was assessed by calculating the relative standard deviation (RSD) of all standard analyses:

$$RSD (\%) = \left[ \frac{\sigma}{\bar{X}_{measured}^i} \right] \times 100 \quad (2.2)$$

where  $\bar{X}_{measured}^i$  and  $\sigma$  are the mean concentration of element  $i$  and the standard deviation respectively. RSD is an appropriate measure of standard deviation because it allows the precision of elements of vastly differing concentrations to be directly compared.

## 2.2 Whole Rock Geochemistry

### 2.2.1 Sample preparation

73 samples from Resolution and 70 samples from Oyu Tolgoi were prepared and analysed at ALS Minerals Vancouver and Ulaanbaatar respectively (quality certificates found at <http://www.alsglobal.com/en/Our-Services/Minerals/Geochemistry/Downloads>), using the same sample methods. All samples selected for whole rock geochemistry are fragments of larger samples, the remainder of which was retained for petrographic analysis.

Whole rock samples were first heated to 120°C and their dry weight was recorded. Fine crushing (with 70% passing 2 mm sieve) was conducted by roll crusher, and a 25% coarse fraction was riffle split and returned to Rio Tinto. Finally, the remaining sample was pulverised to 85% passing through a 75 µm sieve. Clean, barren material was processed through the crushers between each sample. After homogenisation of the pulp, each sample was split into two portions; 0.2 g being used to analyse for major and trace elements, base metals, volatiles, C and S, and a further 10-50 g was used to determine Au, Pt and Pd.



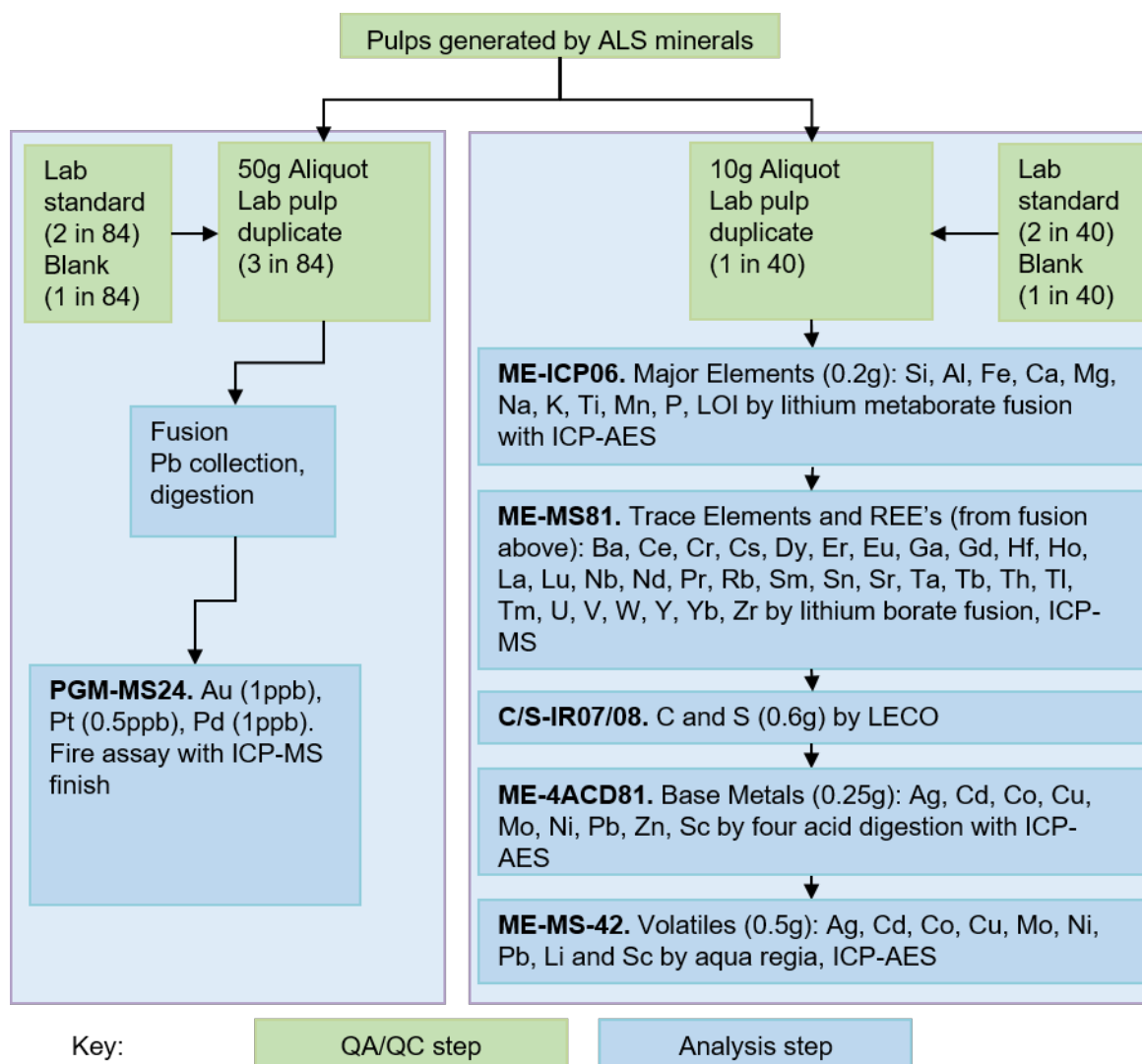


Figure 2.1. Work flowsheet showing the steps followed by ALS minerals during whole rock analysis. “QA/QC” = quality assessment and quality control.

The chemistry of various groups of elements was determined using different analytical methods, which have been given their own name by ALS Minerals. A brief description of the relevant methods is described herein (Fig. 2.1).

### 2.2.2 Major Elements

Major elements ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SrO}$ , and  $\text{BaO}$ ) were analysed using method ME-ICP06. 0.2 g of sample was mixed lithium metaborate (0.9 g), fused at  $1000^\circ\text{C}$ , and subsequently dissolved in 100 mL of 4% nitric/2% hydrochloric acid. The resultant solution was analysed by ICP-AES.

### 2.2.3 Trace elements (inc. REE)

Trace elements (Ba, Ce, Cr, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Nb, Nd, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tl, Tm, U, V, W, Y, Yb, Zr) were measured by method ME-MS81, which utilised the same fusion and dissolution as ME-ICP06, but finished with ICP-MS analysis.

### 2.2.4 Base and platinum group metals (including Au)

Sample were also analysed for base metals (Ag, Cd, Co, Cu, Mo, Ni, Pb, Zn) by lithium metaborate fusion, but underwent four acid digestion before being analysed by ICP-AES (method code ME-4ACD81). This is because a four acid digest is required to fully decompose certain sulphides and metal oxides. Given that the upper detection limit of Cu for method ME-4ACD81 is 1 wt. %, samples with higher Cu content were additionally analysed by method Cu-0G62. In this case, the sample is digested in nitric, perchloric, hydrofluoric, and hydrochloric acid, before being dried, heated and further digested in a solution of hydrochloric acid and deionized water. This solution is then further diluted with deionized water, and analysed by ICP-AES. Pt, Pd, and Au are analysed by method PGM-MS24, where they are fused by fire assay, and analysed by ICP-MS.

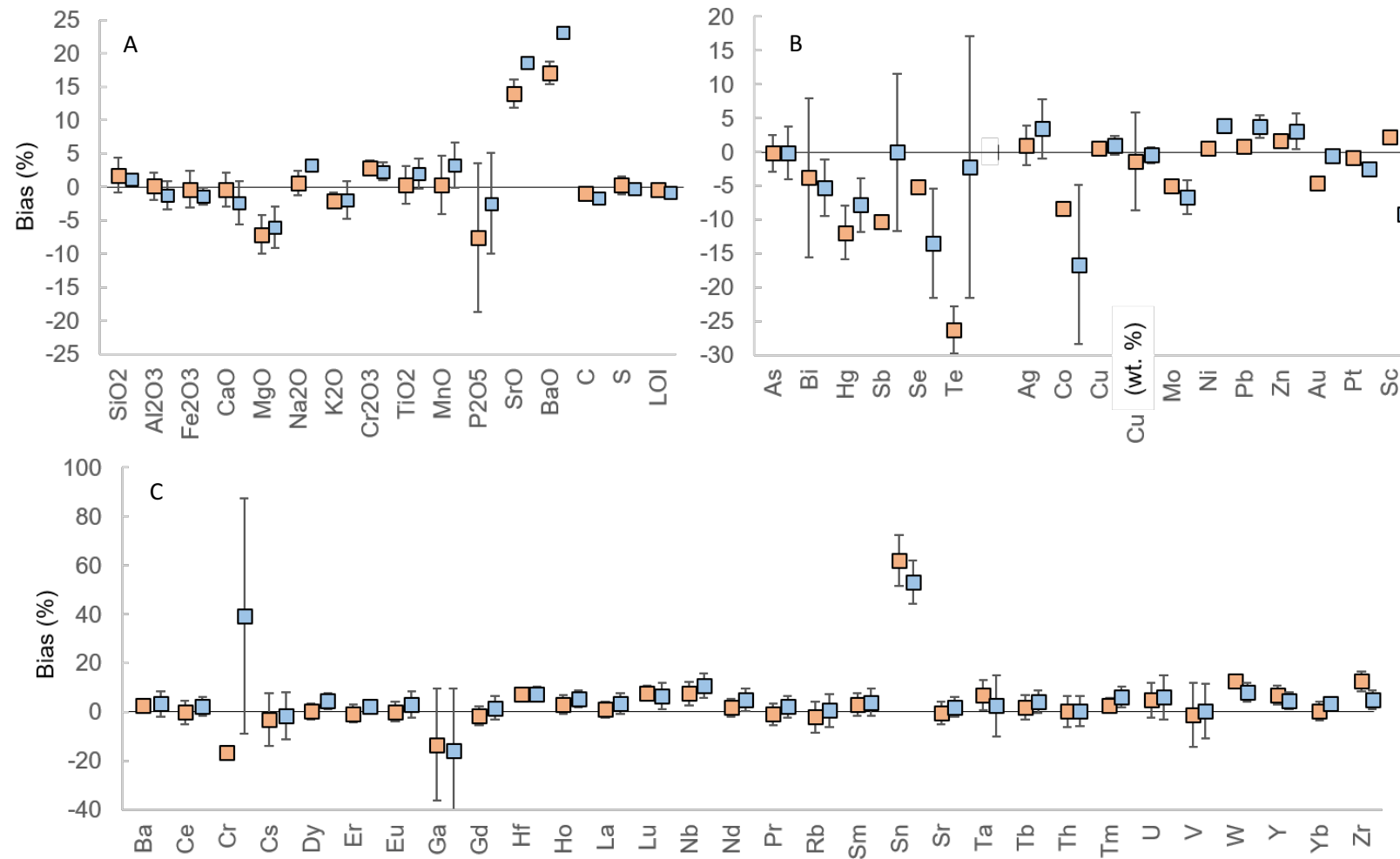


Figure 2.2. Mean bias values for whole rock data. Orange squares are values calculated from standards analysed with Resolution rocks; blue squares are standards from Oyu Tolgoi analyses. a) Major elements, b) volatile and base metals, and c) trace elements. Error bars are  $1\sigma$ .

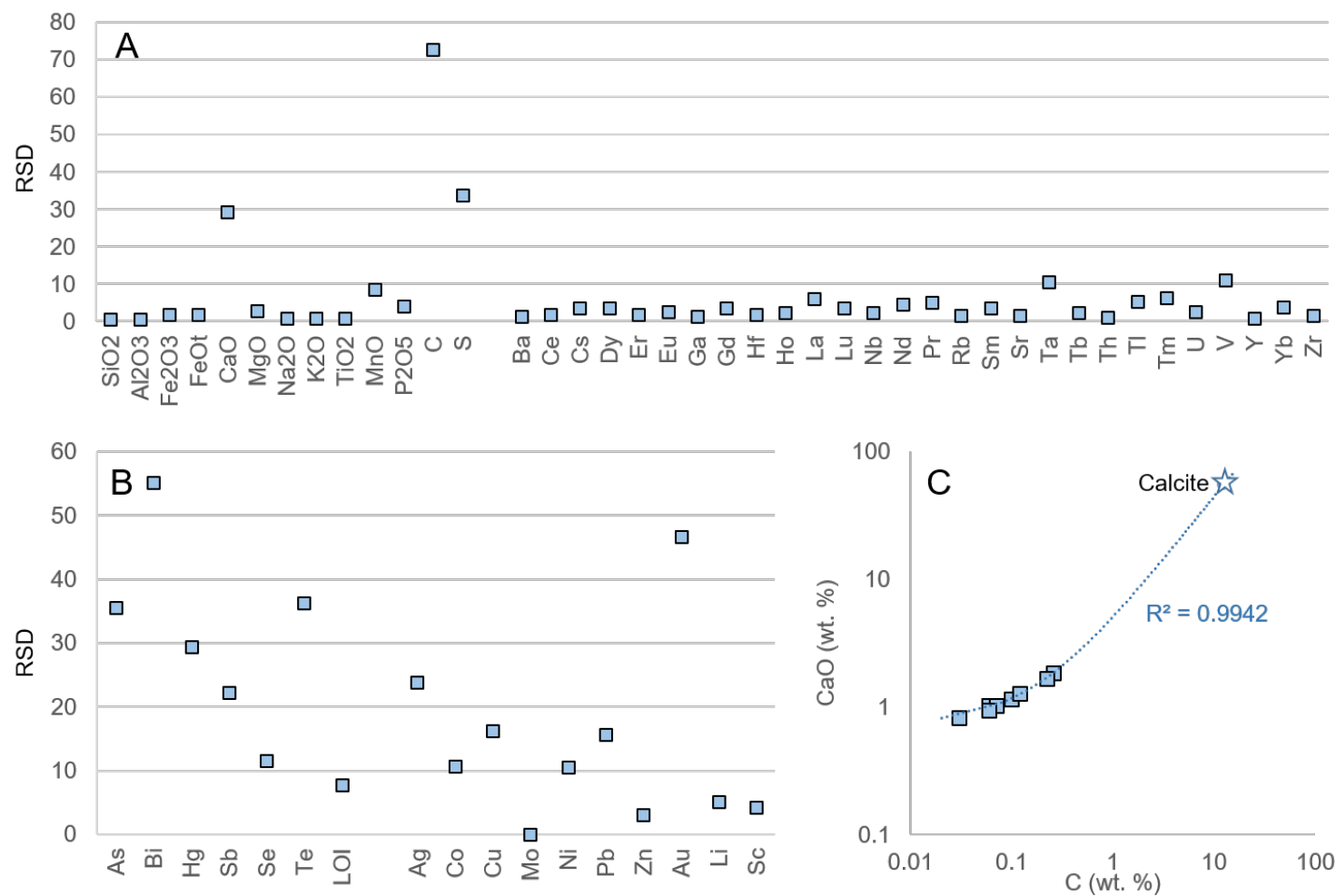


Figure 2.3. Relative standard deviation (RSD) of multiple analyses of the same rock sample (n=9). a) Major and trace elements, b) volatile and base metals. The correlation between CaO and C trends towards the composition of pure calcite (c), implying that heterogeneity between samples may account for high RSD values for CaO and C.

## 2.2.5 Loss on ignition, Carbon, Sulphur, and Volatile elements (also Li and Sc)

Loss on ignition (method code 0A-GRA05) was calculated by heating 1 g of sample to 1000°C for an hour, and measuring the difference in weight. Carbon and Sulphur were analysed using method C-IR07 and S-IR08 respectively. 0.6 g of sample was heated to 1350°C in the presence of an oxygen stream, and the resultant sulphur dioxide and carbon dioxide was measured by infrared detection (Leco) to determine total sulphur and carbon. Volatile elements (As, Bi, Hg, Sb, Se, and Te, with the addition of Li and Sc) were analysed using method ME-MS42. A fraction of the sample was heated and digested with aqua regia, before being cooled and diluted by 12.5 mL of deionised water. The resultant solution was analysed by ICP-AES.

## 2.2.6 Quality control (accuracy and precision)

Standards were analysed twice every 40 samples, and duplicate analyses of selected samples were analysed once every 40 samples. Blanks were also analysed once every 40 samples. Several standards were analysed for the following groups of elements: Major (AMIS0085, AMIS0167, SY-4, OREAS-146, OREAS-104) and trace elements (SY-4, OREAS-146, OREAS-104), base metals (MRGeo08, OREAS-45b, GBM908-5), volatile elements (MRGeo08, GEOMS-03), LOI (LKSD-2), and C and S (MA-1b). GBM903-13 was used as a standard for samples where Cu values are >1 wt. %. GPP-01/02 were measured for Au, Pt, and Pd. RSD of the standards was used as a measure of analytical uncertainty.

Major elements, including C, S, and LOI, have mean percentage bias values within  $\pm 10\%$  of reference values (Fig. 2.2 a), with two notable exceptions. SrO and BaO measured by major element method ME-ICP06 show a bias of between +15 and +25 %, whereas Sr and Ba measured by method ME-MS81 shows much smaller bias (+4 to 0 %; Fig. 2.2 c). Consequently, only Sr and Ba measured by the latter method shall be discussed in this study.

Most trace elements showed a mean bias of between  $\pm 10\%$ , with the exception of Ga, Sn, and Cr (Fig. 2.2 c), because the concentrations of the standards are close to the limit of detection. These elements will not be considered further.

Base metals mostly have mean percentage bias values between  $\pm 5\%$  (Fig. 2.2 b). Co has a negative bias of  $-16\%$  in the Oyu Tolgoi experiments, and  $-8\%$  in the Resolution experiments. Volatile elements Hg, Sb, and Te are all greater than  $-10\%$  in the Resolution experiments, and will also not be discussed further.

The most homogeneous of the felsic Apache Leap porphyry samples (R-RF-G; see Chapter 3 for rock description) was split into 9 pieces and each was analysed individually. There was very little variation between samples, with RSD for nearly all elements being less than  $\pm 5\%$  (Fig. 2.3 a,b). The RSD of these samples will be used to approximate analytical error of the whole rock method, and are presented (along with LOD) in (Fig. 2.1). CaO, S, and C show high values for RSD due to the variable abundance of calcite and anhydrite veinlets in the splits. CaO and C show a positive correlation trending towards the pure calcite composition (Fig. 2.3 c).

### **2.3 Scanning electron microscopy (SEM)**

Scanning electron microscopy was used for mineral identification and for the acquisition of backscatter electron (BSE) and cathodoluminescence (CL) images. The Zeiss EVO SEM in the Imaging and Analysis Centre at the Natural History Museum was used for all SEM work, with a beam current and accelerating voltage of  $3 \pm 0.3$  nA and 20 kV respectively. SEM work was conducted on thin sections, and also polished blocks of mounted apatite and zircon.

|         |                           |                                         |                                         |              |              |                            |                           |                           |              |                                        |            |            |           |           |
|---------|---------------------------|-----------------------------------------|-----------------------------------------|--------------|--------------|----------------------------|---------------------------|---------------------------|--------------|----------------------------------------|------------|------------|-----------|-----------|
|         | SiO <sub>2</sub><br>wt. % | Al <sub>2</sub> O <sub>3</sub><br>wt. % | Fe <sub>2</sub> O <sub>3</sub><br>wt. % | CaO<br>wt. % | MgO<br>wt. % | Na <sub>2</sub> O<br>wt. % | K <sub>2</sub> O<br>wt. % | TiO <sub>2</sub><br>wt. % | MnO<br>wt. % | P <sub>2</sub> O <sub>5</sub><br>wt. % | C<br>wt. % | S<br>wt. % | Ba<br>ppm | Ce<br>ppm |
| RSD (%) | 0.70                      | 0.60                                    | 1.76                                    | 29.08*       | 2.97         | 0.77                       | 0.94                      | 0.99                      | 8.57         | 4.09                                   | 72.81*     | 33.88      | 1.31      | 1.84      |
| LOD     | 0.01                      | 0.01                                    | 0.01                                    | 0.01         | 0.01         | 0.01                       | 0.01                      | 0.01                      | 0.01         | 0.01                                   | 0.01       | 0.01       | 0.5       | 0.5       |
|         | Cs<br>ppm                 | Dy<br>ppm                               | Er<br>ppm                               | Eu<br>ppm    | Ga<br>ppm    | Gd<br>ppm                  | Hf<br>ppm                 | Ho<br>ppm                 | La<br>ppm    | Lu<br>ppm                              | Nb<br>ppm  | Nd<br>ppm  | Pr<br>ppm | Rb<br>ppm |
| RSD (%) | 3.49                      | 3.53                                    | 1.98                                    | 2.62         | 1.26         | 3.52                       | 1.89                      | 2.40                      | 6.07         | 3.61                                   | 2.31       | 4.59       | 5.18      | 1.64      |
| LOD     | 0.01                      | 0.05                                    | 0.03                                    | 0.03         | 0.1          | 0.05                       | 0.2                       | 0.01                      | 0.5          | 0.01                                   | 0.2        | 0.1        | 0.03      | 0.2       |
|         | Sm<br>ppm                 | Sr<br>ppm                               | Ta<br>ppm                               | Tb<br>ppm    | Th<br>ppm    | Tl<br>ppm                  | Tm<br>ppm                 | U<br>ppm                  | V<br>ppm     | Y<br>ppm                               | Yb<br>ppm  | Zr<br>ppm  | As<br>ppm | Bi<br>ppm |
| RSD (%) | 3.64                      | 1.66                                    | 10.71                                   | 2.26         | 1.21         | 5.45                       | 6.30                      | 2.56                      | 10.99        | 0.97                                   | 3.93       | 1.74       | 35.63     | 55.21     |
| LOD     | 0.03                      | 0.1                                     | 0.1                                     | 0.01         | 0.05         | 0.5                        | 0.01                      | 0.05                      | 5            | 0.5                                    | 0.03       | 2          | 0.1       | 0.01      |
|         | Hg<br>ppm                 | Sb<br>ppm                               | Se<br>ppm                               | Te<br>ppm    |              | Ag<br>ppm                  | Co<br>ppm                 | Cu<br>ppm                 | Ni<br>ppm    | Pb<br>ppm                              | Zn<br>ppm  | Au<br>ppm  | Li<br>ppm | Sc<br>ppm |
| RSD (%) | 29.43                     | 22.26                                   | 11.54                                   | 36.36        |              | 23.83                      | 10.71                     | 16.31                     | 10.61        | 15.73                                  | 3.07       | 46.70      | 5.11      | 4.18      |
| LOD     | 0.005                     | 0.05                                    | 0.2                                     | 0.01         |              | 0.5                        | 1                         | 1                         | 1            | 2                                      | 2          | 0.001      | 10        | 1         |

Table 2.1. Table of relative standard deviation (RSD) and limit of detection (LOD) for whole rock analyses in this study. RSD was calculated from 9 analyses of the same sample (R-RF-G). The extremely high RSD for CaO and C relates to heterogeneous volumes of calcite in the sample. Where required, a value of 3% will be used as the error for

CaO.

## 2.4 Electron probe microanalysis (EPMA)

EPMA data for apatite and zircon are presented in this study. In both cases, the instrument used was the Cameca SX100 in the Imaging and Analysis Centre at the Natural History Museum.

### 2.4.1 Limits of detection and analytical error

LODs and analytical error were calculated automatically by the Cameca software, as  $3\sigma$  of the background counts. The error of each analysis is calculated as  $2\sigma$  of the number of counts in an analysis peak. LODs and analytical errors are presented in (Table 2.2).

| Apatite EPMA |           |             | Zircon EPMA |           |             |
|--------------|-----------|-------------|-------------|-----------|-------------|
|              | LOD (ppm) | Error (ppm) |             | LOD (ppm) | Error (ppm) |
| F            | 1231      | 2200        | Si          | 284       | 2720        |
| Na           | 517       | 575         | Ca          | 211       | 200         |
| Si           | 272       | 269         | Ti          | 171       | 100         |
| P            | 443       | 3997        | Fe          | 195       | 200         |
| S            | 549       | 619         | Y           | 174       | 100         |
| Cl           | 600       | 1350        | Zr          | 997       | 5620        |
| K            | 389       | 322         | Hf          | 298       | 500         |
| Ca           | 536       | 5978        | Th          | 434       | 400         |
| Mn           | 570       | 481         | U           | 591       | 500         |
| Fe           | 551       | 475         |             |           |             |
| Sr           | 814       | 859         |             |           |             |
| Ce           | 899       | 825         |             |           |             |
| Mg           | 237       | 233         |             |           |             |
| La           | 419       | 400         |             |           |             |
| Al           | 196       | 200         |             |           |             |

Table 2.2. Limit of detection (LOD) and errors for apatite and zircon by EPMA. See text for a description of the calculation of these values.



## 2.4.2 Apatite

Electron microprobe analyses of apatite were carried out with an accelerating voltage of 20 kV, a beam current of 20 nA, and a spot size of 10  $\mu\text{m}$ . Apatites were analysed for F, Cl, S, Na, Mg, P, Ca, Mn, Fe, and Sr. Two natural apatite standards were also analysed; an F-rich apatite (Durango, Mexico), and a Cl-rich apatite (Epiwala, Sri Lanka). The measurement of F in apatite by EPMA is potentially problematic, due to the anisotropic mobility of F (Stormer et al., 1993; Pyle et al., 2002; Henderson, 2011). The defocused spot size of 10  $\mu\text{m}$  was used in an attempt to mitigate against this problem. F was the first element to be measured during each analysis, as continued application of an electron beam can cause heating of the sample, and F is more mobile in apatite at higher temperatures (Henderson, 2011). In spite of this, the accuracy of F values in both Durango and Epiwala apatites is poor, with mean bias values of -10.3 % and -17.1 % respectively (Fig. 2.4). The origin of this underestimate is uncertain, and is possibly due to an incorrect reference value for F in the standard. In any case, F values in this study are presented, but will only be discussed qualitatively.

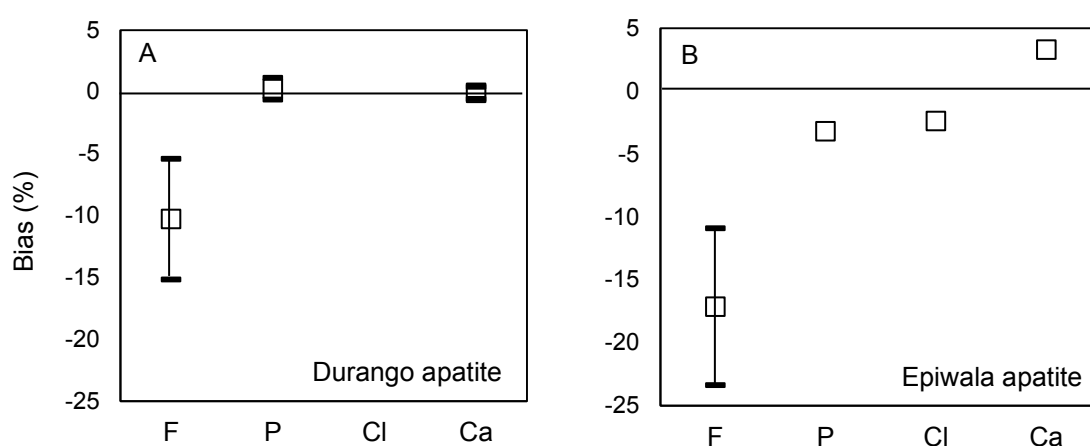


Figure 2.4. Mean percentage bias of two apatite standards measured by EPMA: a) Durango apatite, and b) Epiwala apatite. Error bars are  $1\sigma$ . Cl was below detection limit in Durango apatite. Errors for P, Cl, and Ca in Epiwala apatite are smaller than the symbol size for mean bias.

S, Si, K, Mn, Fe, Na, Mg, and Sr values in both standards are too close to the LOD to determine the accuracy or precision of their measurement. Other elements (Ca, P, Cl) have a mean bias between  $\pm 5\%$ . Cl values are typically below detection limit in Durango apatite, but show a mean bias of -2.4 % in the Epiwala apatite (Fig. 2.4 b)

Ca was used as the calibration element LA-ICP-MS analysis of apatite. Concentrations determined by EMPA for all apatite samples ( $n = 918$ ) were found to have a mean value of  $39.15 \pm 0.44$  wt. % ( $1\sigma$ ,  $n = 918$ ). Due to this small variability, the mean value for Ca was used to calibrate LA-ICP-MS data.

### 2.4.3 Zircon

A small number of zircon major element analyses ( $n = 230$ ) were conducted by EMPA. A beam current of 40 nA, an accelerating voltage of 20 kV, and spot size of 10  $\mu\text{m}$  were used. Nine elements were analysed by EPMA: Si, Ca, Ti, Fe, Y, Zr, Hf, Th, and U, and a zircon standard (STD100) was also analysed. Measured values for this standard closely match reference values, with a mean bias of 0.36%, -0.09%, and 1.12%, and a RSD of  $\pm 1.2\%$ ,  $\pm 0.3\%$ , and  $\pm 0.8\%$  for Si, Zr, and Hf respectively ( $n = 5$ ; Table 2.3). Ca, Ti, Fe, Y, Th, and U were close to (or below) the LOD for this technique.

|       | Reference value | #1    | #2    | #3     | #4     | #5    | mean bias | RSD  |
|-------|-----------------|-------|-------|--------|--------|-------|-----------|------|
| Si    | 15.15           | 15.12 | 15.16 | 15.37  | 15.39  | 14.98 | 0.36      | 1.15 |
| Zr    | 49.1            | 48.87 | 48.96 | 49.11  | 49.24  | 49.11 | -0.09     | 0.29 |
| Hf    | 0.89            | 0.89  | 0.9   | 0.9    | 0.9    | 0.91  | 1.12      | 0.79 |
| O     |                 | 34.51 | 34.6  | 34.91  | 34.96  | 34.44 |           |      |
| Total |                 | 99.39 | 99.62 | 100.29 | 100.49 | 99.44 |           |      |

Table 2.3. EPMA analyses of zircon standard STD100, with mean bias and RSD values for Si, Zr, and Hf.

EPMA analysis of zircon was primarily undertaken to ascertain the Si content of zircon grains, to be used to calibrate subsequent LA-ICP-MS data. However, there is a very narrow range of Si values in all analysed zircons, irrespective of their origin (mean = 15.27 wt. % Si,  $2\sigma = 0.22$  wt. %). Such variations in the calibration element are not sufficiently great to cause large variability in the analysed samples. As a result, EPMA analysis of zircon grains was discontinued and the mean Si value was used to calibrate zircon LA-ICP-MS data.

## **2.5 Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)**

Two laser ablation instruments were used in this study, both at the Image Analysis Centre of the Natural History Museum. An Agilent 7700x quadrupole ICP-MS coupled to an ESI NWR193 excimer laser was used for apatite trace element work, and an Agilent 7500cs ICP-MS coupled to an ESI New Wave UP193FX laser ablation system for zircon work.

### **2.5.1 Limits of detection and analytical error**

The RSD of multiple analyses of the secondary standard (calibrated using the primary standard) was selected to represent analytical error in both apatite and zircon experiments. This method is legitimate, because the RSD of each element in the standard is independent of the absolute concentration. LOD for each individual analysis is calculated as  $3\sigma$  of the background value, and the mean of these values is quoted as the LOD for that element. RSD and LODs are presented in Table 2.4.

|       | Apatite LA-ICP-MS |           |  |       | Zircon LA-ICP-MS |           |
|-------|-------------------|-----------|--|-------|------------------|-----------|
|       | RSD (%)           | LOD (ppm) |  |       | RSD (%)          | LOD (ppm) |
| 23Na  | 2.18              | 11.65     |  | 24Mg  | 1.91             | 0.22      |
| 24Mg  | 3.92              | 0.4       |  | 29Si  | 0.13             | 198       |
| 27Al  | 2.25              | 0.77      |  | 43Ca  | 2.02             | 94        |
| 29Si  | 2.84              | 455.96    |  | 45Sc  | 2.14             | 0.2       |
| 39K   | 5.41              | 6.57      |  | 49Ti  | 2.88             | 1.39      |
| 45Sc  | 1.74              | 0.3       |  | 51V   | 2.4              | 0.06      |
| 51V   | 1.78              | 0.05      |  | 52Cr  | -                | 2.04      |
| 55Mn  | 2.11              | 4.49      |  | 55Mn  | 2.1              | 0.24      |
| 57Fe  | 36.03*            | 13.35     |  | 57Fe  | 14.93*           | 8.03      |
| 88Sr  | 1.89              | 0.65      |  | 59Co  | 2.67             | 0.06      |
| 89Y   | 3.04              | 1.57      |  | 60Ni  | 2.81             | 0.28      |
| 90Zr  | 3.35              | 0.03      |  | 65Cu  | 3.47             | 0.32      |
| 137Ba | 2.42              | 0.08      |  | 66Zn  | 4.11             | 0.39      |
| 139La | 2.39              | 0.29      |  | 85Rb  | 2.54             | 0.04      |
| 140Ce | 1.9               | 1.44      |  | 88Sr  | 2.18             | 0.02      |
| 141Pr | 2.05              | 0.18      |  | 89Y   | 2.42             | 0.15      |
| 145Nd | 2.9               | 0.97      |  | 93Nb  | 2.56             | 0.03      |
| 147Sm | 2.86              | 0.32      |  | 95Mo  | 2.44             | 0.15      |
| 151Eu | 2.13              | 0.06      |  | 133Cs | -                | 0.02      |
| 157Gd | 3.06              | 0.38      |  | 137Ba | 2.72             | 0.15      |
| 159Tb | 3.02              | 0.05      |  | 139La | 2.09             | 0.02      |
| 163Dy | 3.05              | 0.35      |  | 140Ce | 2.25             | 0.02      |
| 165Ho | 3.14              | 0.07      |  | 141Pr | 2.45             | 0.02      |
| 167Er | 3.17              | 0.2       |  | 145Nd | 2.18             | 0.19      |
| 169Tm | 3.13              | 0.03      |  | 147Sm | 3.13             | 0.11      |
| 173Yb | 3.04              | 0.15      |  | 151Eu | 3.23             | 0.03      |
| 175Lu | 3.34              | 0.02      |  | 157Gd | 1.78             | 0.12      |
| 208Pb | 2.7               | 0.14      |  | 159Tb | 2.97             | 0.02      |
| 232Th | 3.87              | 0.02      |  | 163Dy | 2.31             | 0.09      |
| 238U  | 2.46              | 0.03      |  | 165Ho | 3.59             | 0.03      |
|       |                   |           |  | 167Er | 3.13             | 0.12      |
|       |                   |           |  | 169Tm | 3.36             | 0.03      |
|       |                   |           |  | 173Yb | 3.66             | 0.21      |
|       |                   |           |  | 175Lu | 4.57             | 0.03      |
|       |                   |           |  | 177Hf | 4.72             | 1.98      |
|       |                   |           |  | 181Ta | 3.05             | 0.02      |
|       |                   |           |  | 182W  | 9.26             | 0.07      |
|       |                   |           |  | 208Pb | 3.3              | 0.06      |
|       |                   |           |  | 232Th | 2.28             | 0.06      |
|       |                   |           |  | 238U  | 2.55             | 0.09      |

Table 2.4. Relative standard deviation (RSD) and limits of detection (LOD) for LA-ICP-MS analyses of apatite and zircon. Note the high RSD for Fe – see text for discussion.

## 2.5.2 Apatite

Apatites were analysed for  $^{23}\text{Na}$ ,  $^{24}\text{Mg}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{45}\text{Sc}$ ,  $^{51}\text{V}$ ,  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$ ,  $^{90}\text{Zr}$ ,  $^{137}\text{Ba}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{145}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{151}\text{Eu}$ ,  $^{157}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{167}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{173}\text{Yb}$ ,  $^{175}\text{Lu}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$ . Other elements were also analysed to check for contamination during ablation ( $^7\text{Li}$ ,  $^{11}\text{B}$ ,  $^{39}\text{K}$ ,  $^{52}\text{Cr}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{63}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{75}\text{As}$ ,  $^{85}\text{Rb}$ ,  $^{93}\text{Nb}$ ,  $^{95}\text{Mo}$ ,  $^{107}\text{Ag}$ ,  $^{111}\text{Cd}$ ,  $^{118}\text{Sn}$ ,  $^{121}\text{Sb}$ ,  $^{177}\text{Hf}$ ,  $^{181}\text{Ta}$ ,  $^{195}\text{Pt}$ ,  $^{197}\text{Au}$ , and  $^{209}\text{Bi}$ ), which were nearly always below detection limit. A spot size of 35  $\mu\text{m}$  and a fluence of  $\sim 2.5 \text{ J cm}^2$  were used for apatite, and a spot size of 50  $\mu\text{m}$  and fluence of  $3.5 \text{ J cm}^2$  were used for the standards. GSD-1g was used as calibration standard, and NIST-612 as the secondary standard.  $^{43}\text{Ca}$  was used to calibrate apatite data (see 2.4.2), which were processed using ExLAM (Zacharias and Wilkinson, 2007).

Measured values for the secondary standard (NIST-612) calibrated with GSD-1g show a percentage bias between  $\pm 10 \%$  for most elements (Fig. 2.5). The Fe content for the secondary standard is overestimated by an average of approximately  $+38 \%$  from published values, partly a result of the 5 orders of magnitude difference between the Fe content of the calibration

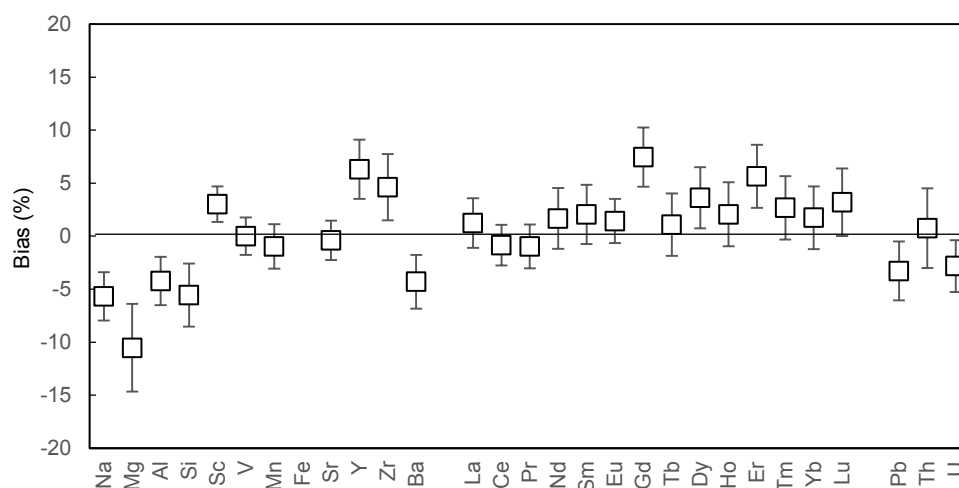


Figure 2.5. Percentage bias calculated from the calibration of secondary standard (NIST-610) using primary standard GSD-1g for apatite experiments. Note that Fe values are high and have been omitted; see text for discussion. Error bars are  $1\sigma$ .

standard (103382 ppm) and secondary standard (51 ppm). This problem is reduced when determining Fe in apatite, which contains on the order of 100s and 1000s of ppm Fe. RSD values for all elements are <5 %, with the exception of Fe, which has large values ( $\pm 36$  %; Table 2.4).

Mn concentrations determined by EMPA closely correlate with those obtained by LA-ICP-MS ( $r^2 = 0.876$ , with the intercept set at the origin; (Fig. 2.6 a). Fe shows more significant deviations from the 1:1 line, although most analyses are within error of this line (Fig. 2.6 b). A small number of analyses deviate significantly from the 1:1 line in both graphs. This is likely due to fine scale heterogeneity in the sample, and the difference between the spot size for EPMA and LA-ICP-MS.

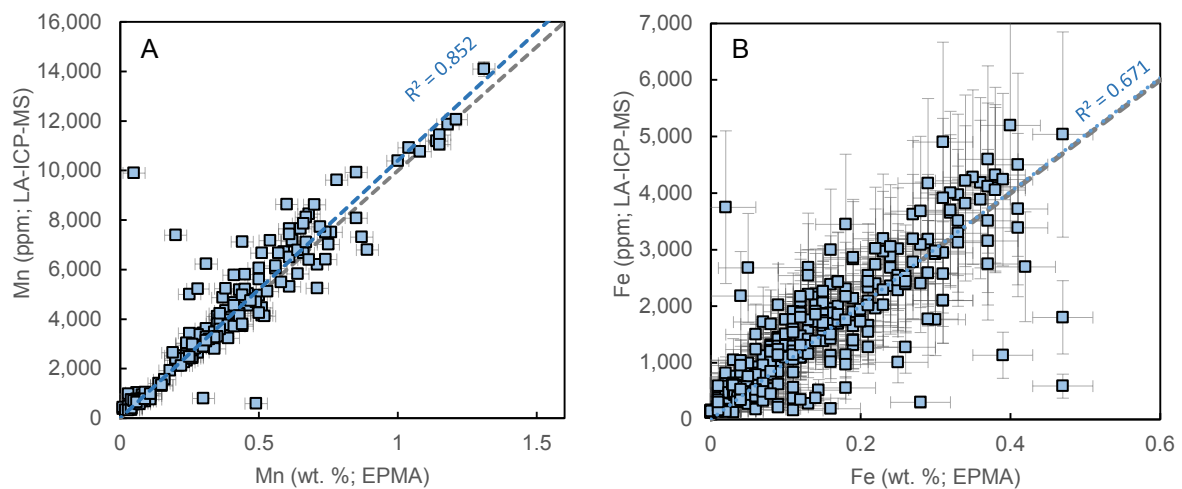


Figure 2.6. Comparison between LA-ICP-MS and EPMA data for a) Mn, and b) Fe in apatite. Error values are found in Table 2.4.

### 2.5.3 Zircon

Zircons were analysed for the following isotope masses:  $^{24}\text{Mg}$ ,  $^{29}\text{Si}$ ,  $^{43}\text{Ca}$ ,  $^{45}\text{Sc}$ ,  $^{49}\text{Ti}$ ,  $^{51}\text{V}$ ,  $^{55}\text{Mn}$ ,  $^{57}\text{Fe}$ ,  $^{59}\text{Co}$ ,  $^{60}\text{Ni}$ ,  $^{65}\text{Cu}$ ,  $^{66}\text{Zn}$ ,  $^{85}\text{Rb}$ ,  $^{88}\text{Sr}$ ,  $^{89}\text{Y}$ ,  $^{93}\text{Nb}$ ,  $^{95}\text{Mo}$ ,  $^{137}\text{Ba}$ ,  $^{139}\text{La}$ ,  $^{140}\text{Ce}$ ,  $^{141}\text{Pr}$ ,  $^{145}\text{Nd}$ ,  $^{147}\text{Sm}$ ,  $^{151}\text{Eu}$ ,  $^{157}\text{Gd}$ ,  $^{159}\text{Tb}$ ,  $^{163}\text{Dy}$ ,  $^{165}\text{Ho}$ ,  $^{167}\text{Er}$ ,  $^{169}\text{Tm}$ ,  $^{173}\text{Yb}$ ,  $^{175}\text{Lu}$ ,  $^{177}\text{Hf}$ ,  $^{181}\text{Ta}$ ,  $^{182}\text{W}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$ , and  $^{238}\text{U}$ . NIST-612 and BCR were used as the primary and secondary standards respectively. A fluence of 2.5 to 3.0 J cm<sup>2</sup> and a spot size of 30 µm were used. ExLAM (Zacharias and Wilkinson, 2007) was also used to process trace element data. Measured values of the BCR calibrated with NIST-612 show a percentage bias of  $\pm 10\%$  for most elements (Fig. 2.7). Percentage bias is greater for Cu and Y than for other elements. Fe, Ni, and Zn have been omitted from Figure 2.7, because calculated values for these elements deviated more than 25% from published values. The reason for the poor accuracy of Fe is discussed above (2.5.2). The reason for the inaccuracy of Ni and Zn is unclear, and may be due to the difference in the matrix (and, thus, in ablation characteristics) of the two standards. These elements are not discussed in Chapter 5 (Zircon).

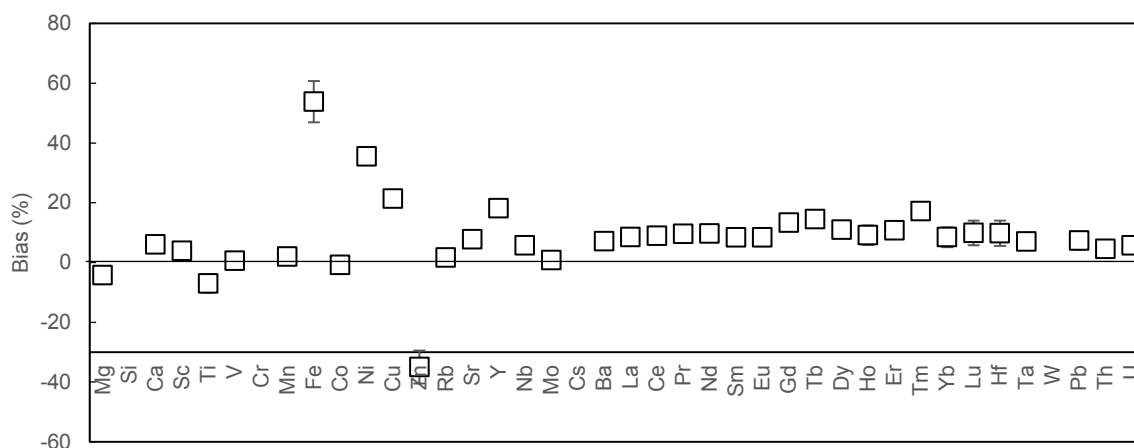


Figure 2.7. Percentage bias calculated from the calibration of secondary standard (BCR) using primary standard NIST-612 for zircon experiments. Note that Fe values are high and have been omitted, see text for discussion. Error bars are  $1\sigma$ , and are mostly smaller than symbol size.

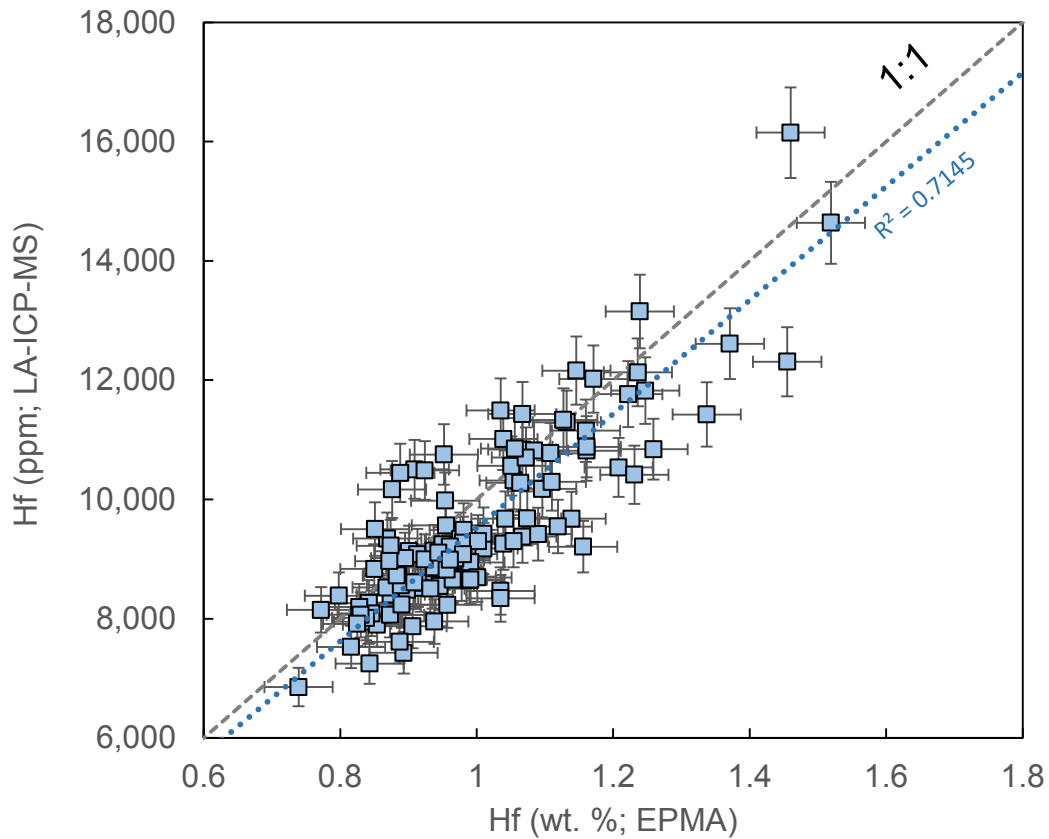


Figure 2.8. Comparison between LA-ICP-MS and EPMA data for Hf in zircon. Error values are found in Table 2.4.

Hf contents calculated by EPMA and LA-ICP-MS for the same zircon spots show a reasonable correlation with one another ( $R^2 = 0.72$ ; intercept set at the origin; Fig. 2.8).

## 2.6 U-Pb zircon dating

### 2.6.1 Background

The applicability of U-Pb series geochemistry in dating geological materials has been known for over a century (Holmes, 1911) and is now the most widely used radiometric dating technique in Earth Sciences (Schoene, 2014). The popularity of U-Pb dating is in part due to the long half-life of U isotopes, which allow for dating of material from nearly all geological



time periods. Furthermore, U-Pb series geochronology consists of two parallel isotopic systems, the combination of which may provide a robust measure of ages where deviation from model ages may be more easily recognised. Modern advances in analytical techniques, particularly the advent of LA-ICP-MS, allow smaller amounts of material to be analysed *in-situ*, thus placing geological ages in the textural context of the rock. In-situ mineral geochronology may also be combined with mineral chemistry, so that geochemical processes may be time-integrated.

Although U-Pb dating has been used in a number of U-bearing minerals (e.g. monazite, baddeleyite, apatite), zircon is the most popular mineral for such techniques. This is in part due to the abundance of zircon in metamorphic and felsic igneous rocks, high U contents ( $\sim 10^2$  to  $10^3$  ppm), and a resistance to high temperature diffusive re-equilibration (e.g. Cherniak et al., 1997; Watson & Cherniak, 1997). The effective exclusion of ‘common’ Pb during crystallisation means that common Pb is normally such a small fraction of total Pb that it has a negligible effect on radiometric dating, and corrections for common Pb in zircon are normally not required (Schoene, 2014).

U-Pb dating relies on the decay to stable Pb of two radioactive U isotopes ( $^{235}\text{U}$  to  $^{207}\text{Pb}$ , and  $^{238}\text{U}$  to  $^{206}\text{Pb}$ ) via alpha and beta decay through several relatively short-lived intermediate isotopes (Fig. 2.9). Both U isotopes are long-lived, with half-lives of 0.7 and 4.5 Gy for  $^{235}\text{U}$  and  $^{238}\text{U}$  respectively. Their decay is commonly expressed in terms of the ratio of both parent

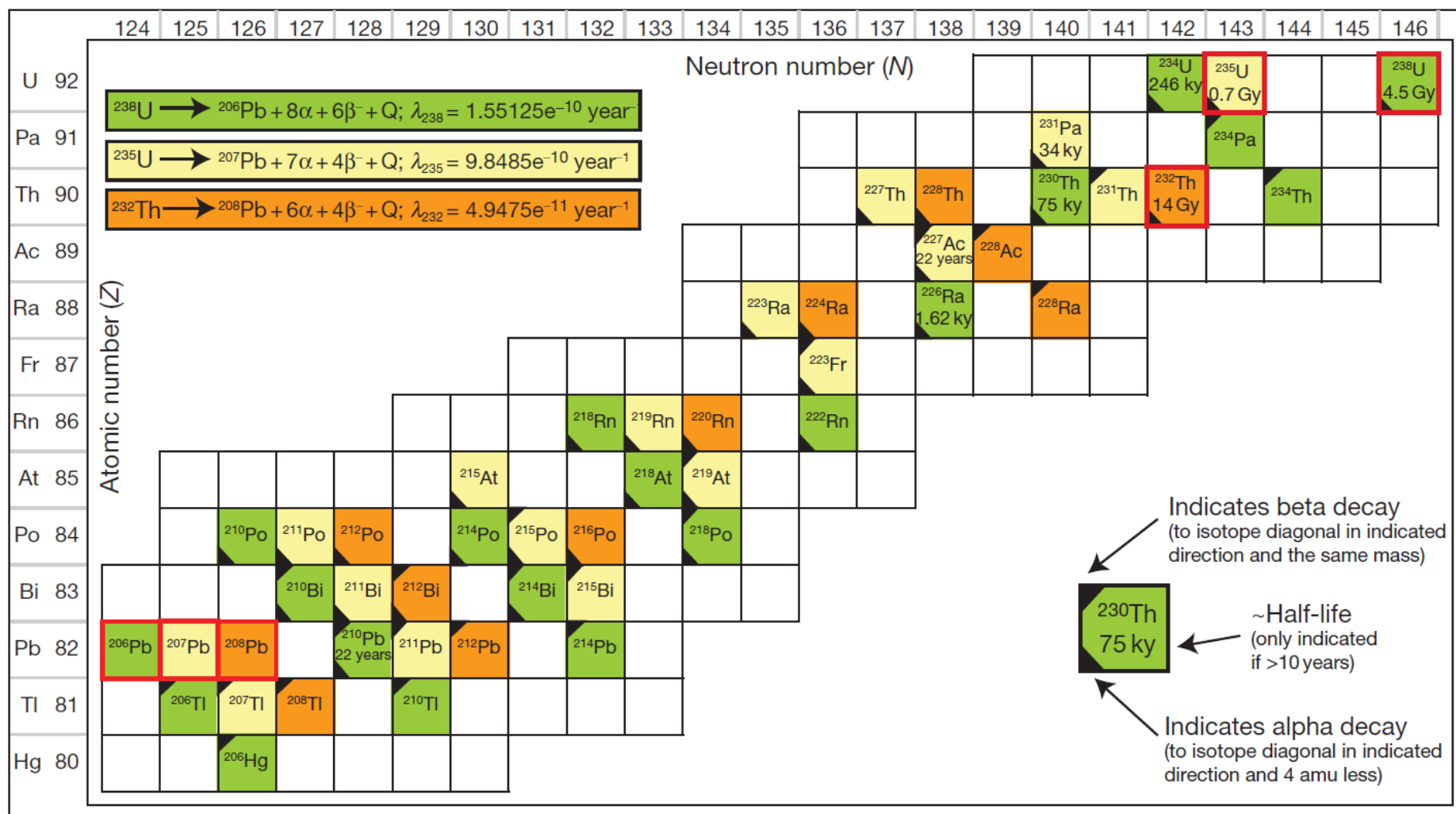


Figure 2.9. A summary of the decay chains of U-series isotopes. From Schoene (2014)

and daughter isotopes to nonradiogenic  $^{204}\text{Pb}$ , which means the absolute abundances of individual isotopes do not need to be determined. These decay systems may be written thus:

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right) = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \left(\frac{^{238}\text{U}}{^{204}\text{Pb}}\right) (e^{\lambda_{238}t} - 1) \quad (2.3)$$

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right) = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0 + \left(\frac{^{235}\text{U}}{^{204}\text{Pb}}\right) (e^{\lambda_{235}t} - 1) \quad (2.4)$$

where  $\lambda_{238}$  and  $\lambda_{235}$  are the decay constant for  $^{238}\text{U} \rightarrow ^{206}\text{Pb}$  and  $^{235}\text{U} \rightarrow ^{207}\text{Pb}$ ,  $t$  is time since the closure of the system (Myr), and the Pb isotope ratio with the subscript '0' is the value at the time of the closure of the system ( $t = 0$ ), i.e. a measure of the presence of common Pb. As zircon effectively excludes Pb partitioning during crystallisation (i.e.  $\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0 = 0$ ), equations

(3) and (4) may be re-written:

$$\left(\frac{^{206}\text{Pb}}{^{238}\text{U}}\right) = (e^{\lambda_{238}t} - 1) \quad (2.5)$$

$$\left(\frac{^{207}\text{Pb}}{^{235}\text{U}}\right) = (e^{\lambda_{235}t} - 1) \quad (2.6)$$

When solved for  $t$ , equations (5) and (6) express as a curved line in  $^{207}\text{Pb}/^{235}\text{U}$  vs.  $^{206}\text{Pb}/^{238}\text{U}$  space. This is called the 'line of concordia', and it represents model  $^{207}\text{Pb}/^{235}\text{U}$  and  $^{206}\text{Pb}/^{238}\text{U}$  ratios at different ages. The fact that the concordia line is curved is due to the different decay constants for  $^{235}\text{U}$  and  $^{238}\text{U}$ . Measured  $^{207}\text{Pb}/^{235}\text{U}$  and  $^{206}\text{Pb}/^{238}\text{U}$  ratios for individual zircon grains (or zones within grains) may be plotted on these diagrams, known as Wetherill concordia plots. Deviation of measured isotope ratios from the line of concordia (or,

‘discordance’) represents open system behaviour, and thus Wetherill plots are useful for assessing the reliability of a calculated zircon ages. Discordance most commonly results from Pb loss, and from the mixing of different aged material, both of which cause systematic deviation from the concordia line.

## 2.6.2 U/Pb analytical method

An ESI New Wave UP193FX Laser Ablation System coupled to an Agilent 7500cs ICP-MS was used for U-Pb isotope analysis. A fluence of  $\sim 2.8 \text{ J cm}^2$  and a rastering beam with rectangular dimensions ( $30 \times 50 \text{ }\mu\text{m}$ ) were used. A total of 23 experiments were run over 4 days. Each experiment consisted of approximately 13 natural zircon analyses between 2 sets of 4 analyses of zircon standard 91500. Each analysis consisted of a 40 s measurement of background values, followed by a 95 s measurement of ablated sample. All zircons were analysed from polished blocks, and an effort was made to match trace element and U-Pb laser spots to the same zones, as observed in SEM-CL images. Blocks were re-polished between U-Pb and trace element analysis.

The following isotopes were measured during analysis:  $^{201}\text{Hg}$ ,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ . Each isotope was measured for a dwell time of 10 ms, with the exception of  $^{235}\text{U}$  and  $^{207}\text{Pb}$  which were measure for 30 ms due to low abundance of these isotopes. 4 isotope ratios were then calculated from the isotope counts per second values:  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{206}\text{Pb}/^{238}\text{U}$ ,  $^{207}\text{Pb}/^{235}\text{U}$ , and  $^{207}\text{Pb}/^{206}\text{Pb}$ .  $^{201}\text{Hg}$  was analysed to monitor the presence of common Pb. This is because there exists an isobaric interference between non-radiogenic  $^{204}\text{Pb}$  and  $^{204}\text{Hg}$ . An increase in  $^{204}\text{Pb}$  during analysis without a concomitant increase in  $^{201}\text{Hg}$  suggests a source for  $^{204}\text{Pb}$  which is not due to isobaric interference of  $^{204}\text{Hg}$ , and thus the presence of common Pb in the sample. Samples that showed systematic variation in  $^{204}\text{Hg}/^{204}\text{Pb}$  between the background and sample were rejected.

## **Chapter 3: The petrography and whole rock geochemistry of magmatic rocks associated with Resolution Porphyry Cu – Mo deposit, Arizona**

### **3.1 Introduction**

The Resolution porphyry Cu (+ Mo) deposit is a large, high grade porphyry system of late-Cretaceous age situated near the town of Superior, 90 km east of Phoenix (Fig. 3.1). With an Inferred Resource of 1,624 Mt of ore, and a grade of 1.47% Cu and 0.037% Mo (Rio Tinto, 2010), Resolution is one of the largest undeveloped copper resources in the world (Leveille and Stegen, 2012). The deposit is located within the well-explored Laramide porphyry Cu province, and is within 30 km of several other Laramide porphyry systems, including Ray, Copper Cities, Pinto Valley, and Miami-Inspiration. Mining in the Superior (Pioneer) district began in 1875, with the discovery of supergene silver and copper mineralisation along the Magma vein. Mining the Magma Vein and associated manto deposits continued until the mid-1990s, when an exploration program was instigated to expand the rapidly depleting reserves. The Resolution deposit (originally known as ‘Magma porphyry’) was discovered in 1994 during drilling from the deep levels of the Magma Mine (Manske and Paul, 2002). Mineralisation at Resolution is hosted in Proterozoic and Palaeozoic sediments and diabase sills, Mesozoic carbonates and volcanoclastic units, and is situated in the centre of a graben. The deposit is completely hidden by >1 km of Cenozoic post-mineral cover, consisting of conglomerates and tuffs. This cover has led to the excellent preservation of the system and contributed to its relatively recent discovery. Based on the dome-shaped orebody and the radial foliation of secondary biotite, mineralisation is inferred to be associated with a large, as-yet undiscovered central stock below the current level of drilling (Hehnke et al., 2012).

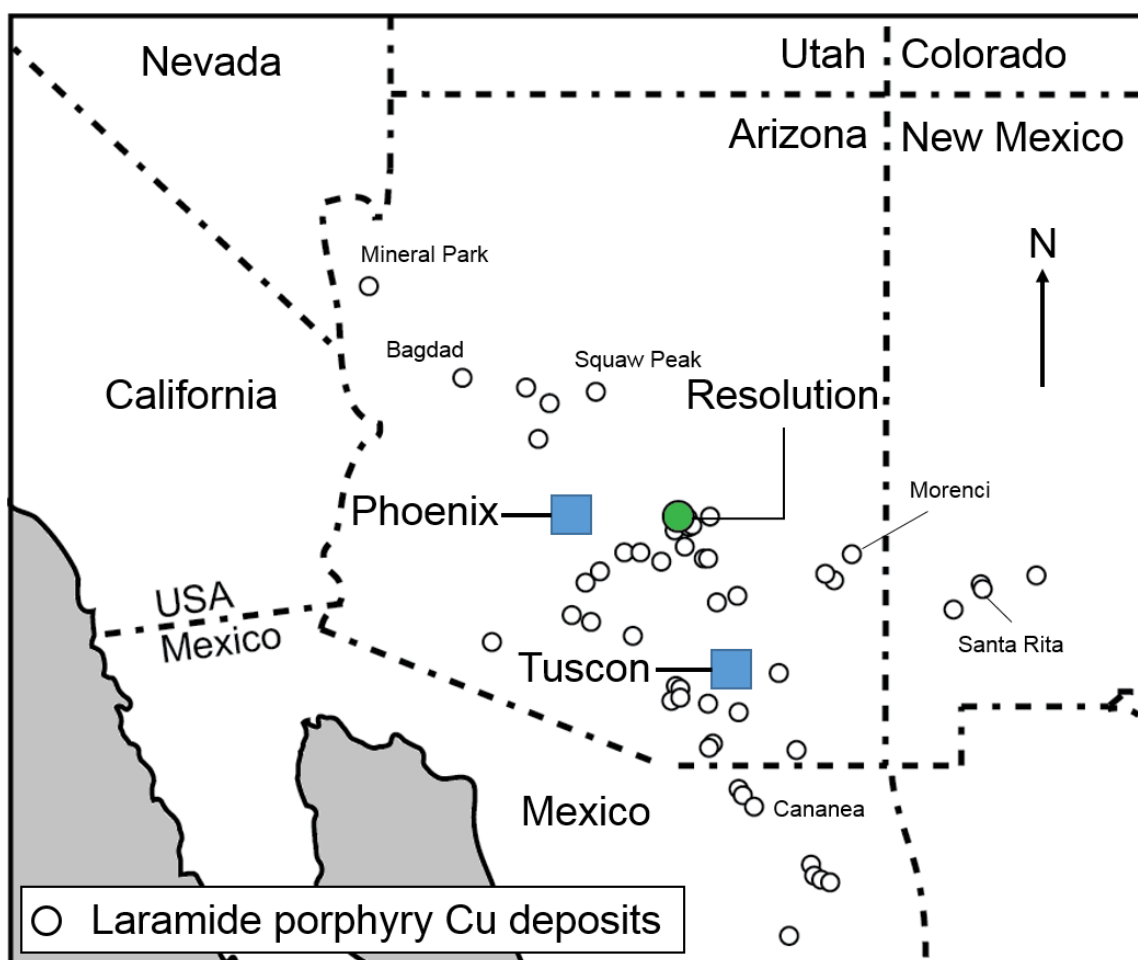


Figure 3.1. Location of Resolution and other porphyry Cu systems in the Laramide province, selected examples of which are labelled.

Resolution carries a uniquely high hypogene Cu grade compared to typical Arizonan porphyry systems (<0.4 wt. % Cu; Lowell and Guilbert, 1970), which is thought to be partly due to the especially reactive mafic and carbonate host rocks (Sillitoe et al., 2010; Ballantyne et al., 2003), as well as the lack of grade-diluting post-mineral intrusions or the significant structural dismemberment seen in other Laramide porphyry systems (e.g. Yerington; Pinto Valley). Several focussed pulses of mineralisation had a significant additive effect on Cu grade. In particular, a late, high-sulphidation episode of mineralisation associated with hydrolytic alteration boosted Cu grades by precipitating an assemblage of bornite, chalcocite, digenite and pyrite.

## 3.2 Regional Geology

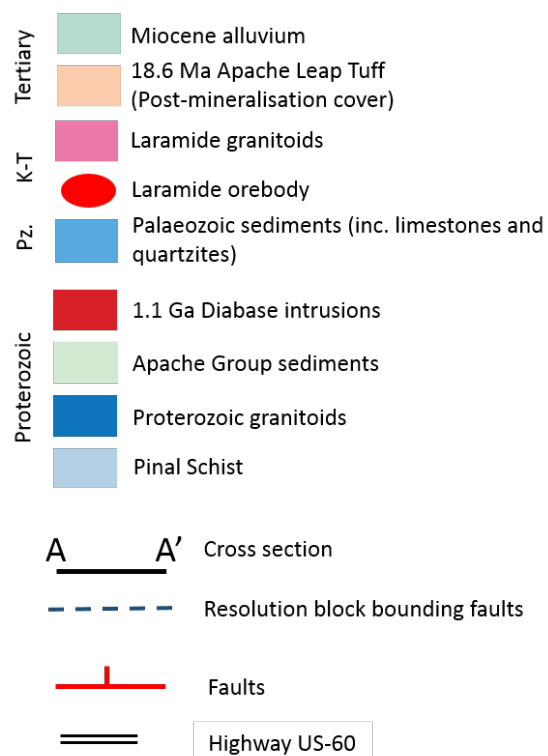
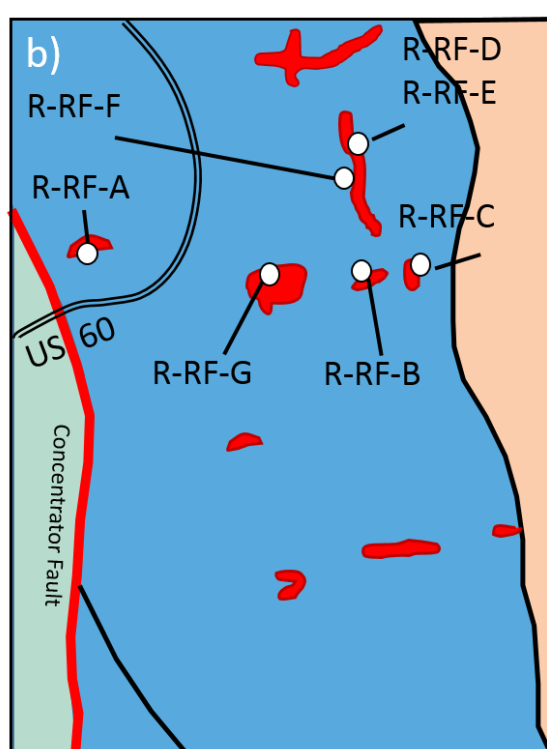
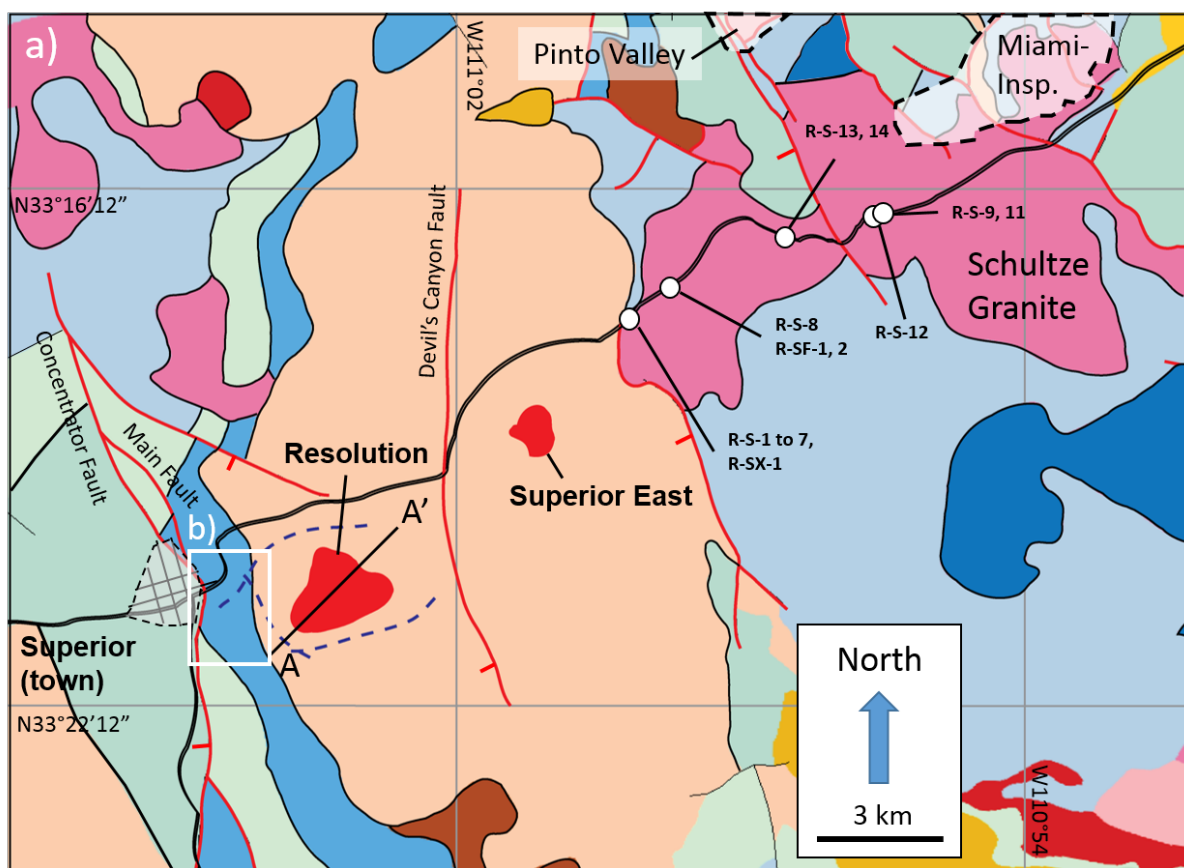
### 3.2.1 Proterozoic basement

The basement in Arizona comprises a patchwork of Palaeoproterozoic metamorphic rocks intruded by Mesoproterozoic granitoids. It can be divided into broad ENE-trending units that relate to accretion and subduction-related metamorphism and magmatism on the southern margin of Laurentia (Whitmeyer and Karlstrom, 2007). In the Resolution district, the oldest unit is the Pinal Schist. Originally quartz wackes deposited as turbidites in an inundated continental rift (Condie and De Malas, 1985), they were metamorphosed to greenschist facies during the Mazatzal orogeny  $\sim 1.7$  Ga (Keep, 1996). Although the Pinal Schist lies beneath the  $>1\%$  Cu shell at Resolution, and is only intersected in the deepest drill holes (Hehnke et al., 2012), it hosts mineralisation at the nearby Superior East and Ray porphyry deposits (Phillips et al., 1974; Sell, 1995).

The Pinal Schist was intruded by numerous large granitoids during the Proterozoic. These granitoids are broadly bimodal in age, and are also related to the Mazatzal orogeny (1.65 – 1.60 Ga), or a later stage of A-type granite formation (1.45 to 1.35 Ga; Whitmeyer and Karlstrom, 2007) on the boundary of Laurentia. In the Resolution area, Proterozoic granites include the Madera Granodiorite ( $\sim 1.63$  Ga; Banks et al, 1976; Livingston and Damon, 1969), the Ruin Granite (1.42 Ga; Creasey 1980) and the Willow Spring Granodiorite (1.44 Ga; Isachsen et al., 1999). Proterozoic granites outcrop in multiple locations in close proximity to

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*Figure 3.2. (next page) (a) Simplified geology of the Resolution district. The surface project of the orebodies at Resolution and the nearby Superior East are shown. Miami-Inspiration and Pinto Valley mines are also highlighted, on the margins of the Schultze Granite. The location of samples of the Schultze Granite discussed in this study have been highlighted (b) Inset. The location of Apache Leap intrusions. R-RF-A is the mafic Apache Leap intrusion, and R-RF-G is the felsic intrusion studied herein. Modified after USGS Arizona sheet (1:1,000,000)*





Resolution, especially in the Globe-Miami district (Fig. 3.2), but are not observed in drill core in the Resolution deposit.

Unconformably overlying the crystalline basement is the >500m thick Apache Group, consisting of shale, quartzite, limestone, and small basaltic lava flows that formed in an intracratonic basement (Wrucke, 1989). In the late Mesoproterozoic (1.1 Ga), the Apache Group and basement were intruded by large diabase sills, which dilate the Apache Group to up to 100% its original thickness (Fig. 3.3; Wrucke, 1989).

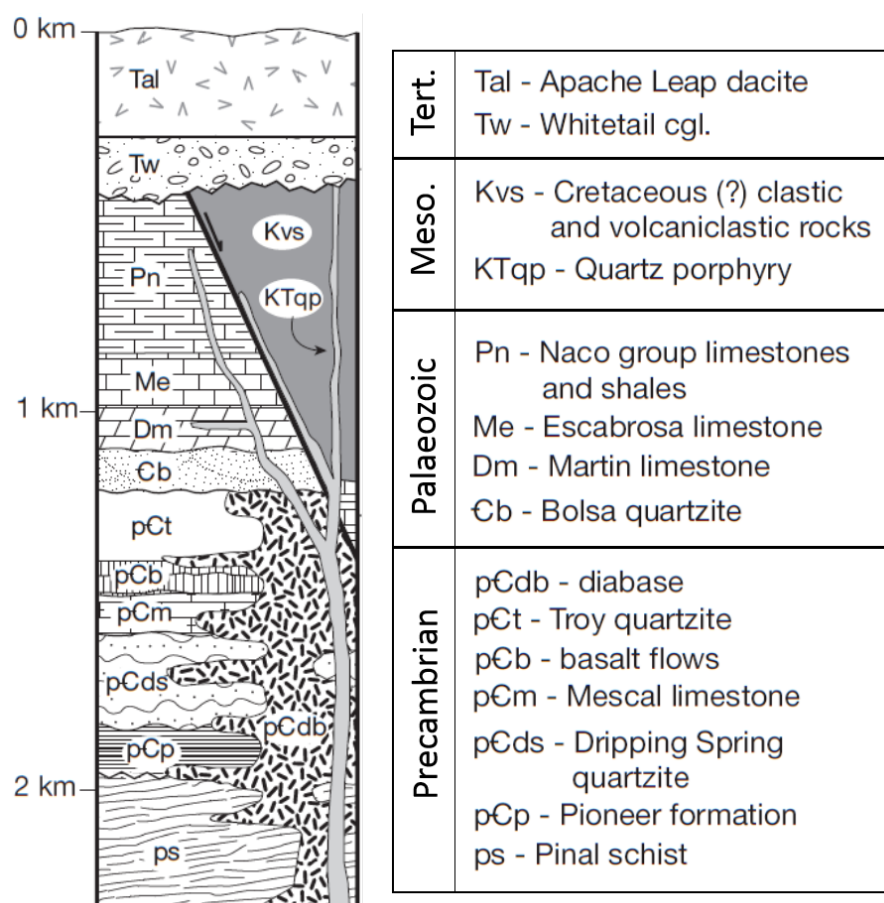


Figure 3.3. Generalised stratigraphy of the Resolution deposit. The Kvs are only found within the covered Resolution block and does not outcrop elsewhere. From Manske and Paul (2002).

### 3.2.2 Palaeozoic

The Palaeozoic is marked by a period of carbonate deposition. The shallow angular unconformity between Palaeozoic carbonates and the Precambrian Apache Group indicates little tilting in the intervening time, and the development of a passive margin (Dickinson, 1989). Palaeozoic carbonate sediments are subdivided into the Cambrian Bolsa, Devonian Martin, Mississippian Escabrosa, and Pennsylvanian Naco Limestones (Fig. 3.3). The paucity of Ordovician, Silurian and some Devonian strata suggest minimal deposition during these times, and along with the presence of some intercalated aeolian deposits, indicate repeated marine regression-transgression events (Dickinson 1989).

### 3.2.3 Mesozoic

The onset of subduction in the Mesozoic heralded a shift in the tectonics and depositional environments of the region. Three orogenic events, the Nevadan, the Sevier and the Laramide, caused tilting of the Proterozoic and Palaeozoic strata and generated substantial arc magmatism from the Jurassic through to the Eocene. Migration of the arc occurred over this period from present day California into Nevada, and eventually Arizona, and has been attributed to the flattening of the subducting slab (e.g. Leveille and Stegen, 2012). Porphyry Cu deposits of southern Arizona are most commonly associated with the Laramide orogeny, although some Cu-Mo mineralisation is known from the Jurassic and Cretaceous (Barton, 1996). Intrusion of several large dioritic to felsic plutons, such as the Schultze Granite, Tea Cup Granite and the Silver King Diorite, are associated with porphyry stocks, alteration and mineralisation (Fig. 3.2 a). During the Cretaceous, volcanoclastic and sedimentary rocks formed in back-arc and foreland basin environments across southern Arizona (Titley, 1972), and in the Superior region, they are only found within the Resolution block (Kvs; Fig. 3.3).

### 3.2.4 Cenozoic

Overlain unconformably onto the district is the Whitetail Conglomerate, a terrigenous unit with locally derived clasts deposited in erosional depressions formed during Basin and Range tectonism (Peterson et al., 1960). This unit is thinnest near the town of Superior and not continuously exposed, but thickens to 1 km towards the east (Ballantyne et al., 2003; Fig. 3.4). A thick unit of dacitic welded ashfall deposits known as the Apache Leap Tuff was superposed onto the Whitetail Conglomerate at 18.6 Ma. Erupted in rapid succession, these repeated ash flows cooled as one body forming columnar joints.

## 3.3 Deposit Geology

The focus of this study is the intrusive igneous rocks and hydrothermal breccias at Resolution, which are discussed in detail in Section 3.4. The following section comprises a brief description of other aspects of the deposit geology derived from literature sources.

### 3.3.1 Structure

Resolution is hosted within a ~3 x 3 km fault-bound, basement-cored graben (Manske and Paul, 2002). Boundary faults are found to the north, south and west (Fig. 3.2 a). Movement along the western boundary fault is thought to have occurred during the deposition of the sediments and volcanoclastic material which infills the block (i.e. Kvs), with the northern and southern boundary faults acting as ‘scissor faults’, i.e., greater displacement in the west (Hehnke et al., 2012). Bedding within the Resolution graben gently dips to the northwest (Fig. 3.4). A pervasive ENE-trending structural fabric, formed during the development of the basement in the Proterozoic, is observed throughout south-central Arizona. Several geological features follow this trend, including the dominant foliation of the Pinal Schist, the distribution of porphyry deposits and the orientation of faults and mineralised veins in the Superior area (Hehnke et al., 2012). The locations of Resolution,

Superior East, and Pinto Valley and Miami Inspiration deposits also follow an ENE trend (Fig. 3.2 a).

A series of N-trending normal faults, developed during Cenozoic Basin and Range extension, show downward displacement to the west in all units, and expose Palaeozoic and Proterozoic rocks at the base of Apache Leap near Superior (Fig. 3.2 a). The Resolution block sits between the Devil's Canyon Fault to the east, and the Main and Concentrator Faults to the west. The minor displacement of the Apache Leap tuff, which overlies the deposit, suggests that this unit formed syn-tectonically with Basin and Range deformation (Richard and Spencer, 1998).

### 3.3.2 Wall Rocks

#### *3.3.2.1 Precambrian diabase (1.1 Ga)*

The Mesoproterozoic 'diabase' sills intrude the Apache Group sediments, and are intersected in the deepest portions of the deposit. Unaltered, unmineralised 1.1 Ga diabase intrusions, such as those which outcrop in the Apache Group to the north of Superior, contain a holocrystalline assemblage of plagioclase and clinopyroxene (Schwarz, 2010). However, the diabase is ubiquitously altered in the Resolution deposit, where it hosts a significant fraction of the high grade mineralisation (36 vol. % of the 1% Cu ore shell; Hehnke et al., 2012). Biotite-rich potassic alteration is the most common alteration style, although sericitic, advanced argillic, and distal propylitic alteration are also observed (Schwarz, 2010; Hehnke et al., 2012).

#### *3.3.2.2 Palaeozoic sediments*

The Palaeozoic sedimentary sequence is significantly thinner within the Resolution block than outside it. For example, the Palaeozoic carbonate sequence (the Martin, Escabrosa, and Naco Formations), which attains a thickness of some 700 m elsewhere within in the

Superior district, is significantly thinner within the Resolution block (~200 m; Winant, 2010; Fig. 3.4). In the west of the deposit, the Palaeozoic sequence has been entirely eroded away, meaning the Cretaceous sedimentary and volcanoclastic units lie unconformably on top of the Proterozoic sequence (Fig. 3.7). These observations have lead mine geologists to suppose that the graben in which the deposit is hosted initially developed as a horst before the Cretaceous. (Hehnke et al., 2012).

Where present, Palaeozoic limestones are altered to magnesian and calcic skarns, which hosts 10 % of the mineralisation in the 1 % Cu shell (Hehnke et al., 2012).

#### *3.3.2.3 Cretaceous basinal sediments and volcanoclastic rocks*

A sequence of Cretaceous sandstones and volcanoclastic rock (Kqs and Kvs respectively) up to 1 km thick, which do not outcrop in the Superior area, are preserved within the Resolution block. These directly overlie the Proterozoic basement, and the Palaeozoic sequence where the latter exists (Fig. 3.4). The basal Cretaceous unit (Kqs) occurs only in the northwest of the graben. U-Pb dating of detrital zircons in the Kqs gives a maximum age of  $96.8 \pm 2.2$  Ma (Zulliger, 2007).

The Kvs consists of andesitic and dacitic volcanoclastic rocks. The andesitic units are 74 to 75 Ma (Hehnke et al., 2012) and are lithologically similar to the temporally-equivalent Williamson Canyon volcanics of the Christmas region (75 and 80 Ma; Manske and Paul, 2002). The dacitic sequence, which unconformably overlies Proterozoic rocks in the south east of the graben, is younger than the andesitic units (67 to 66 Ma, Hehnke et al., 2012). The Kvs and Kqs host ~17% of the >1% Cu mineralisation (Hehnke et al., 2012).

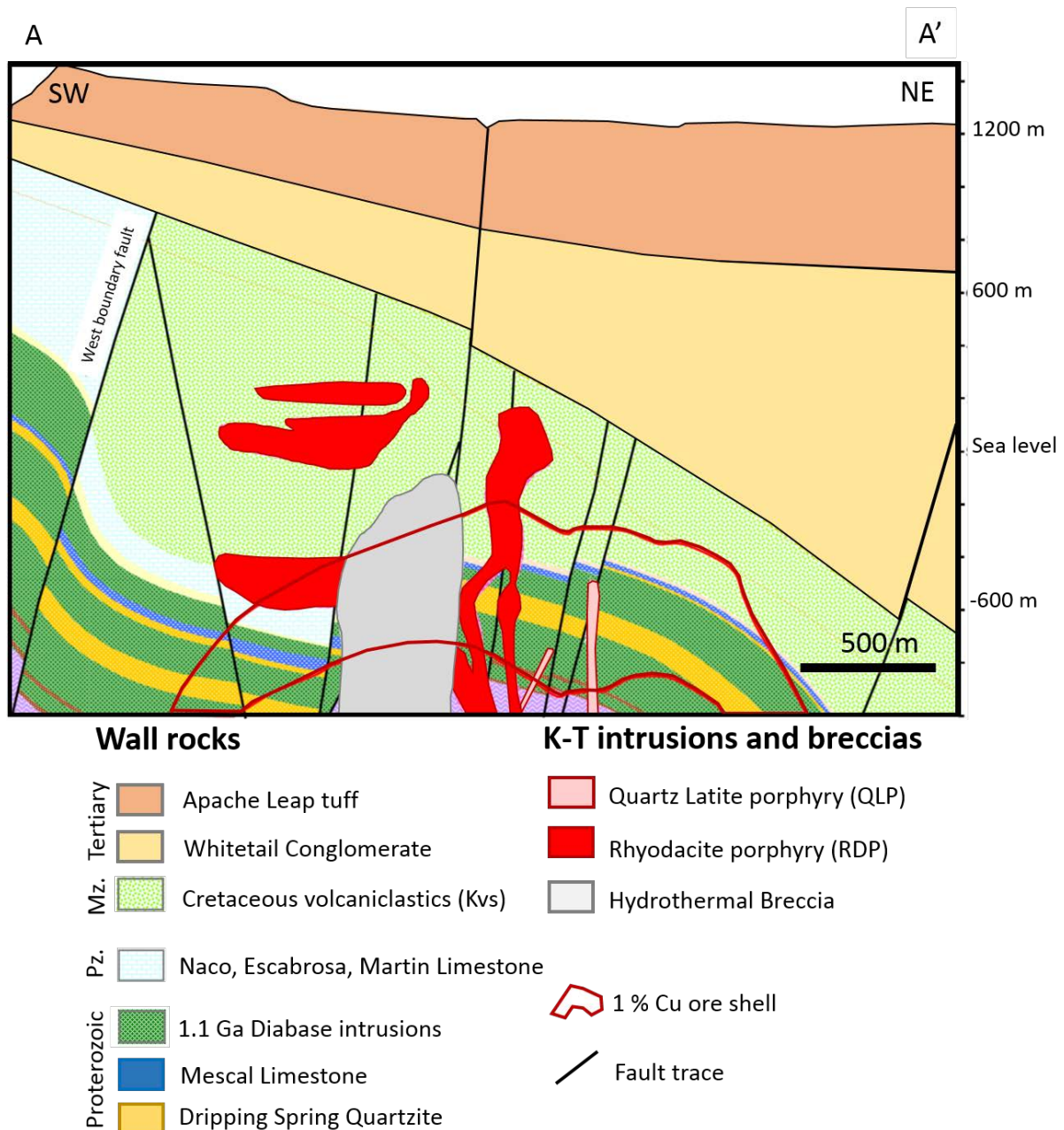


Figure 3.4. Cross section through the Resolution graben, oriented NE-SW, corresponding to line A-A' on Figure 2.2. QLP and RDP intrusions are found in the centre of the Resolution block. Line A-A' crosses the West boundary fault of the graben at its south western margin. Several small post mineral faults cross the deposit, most of which terminate at the contact between the Kvs and the Whitetail conglomerate. Note the near absence of Palaeozoic sediments within the Resolution block, i.e. NE of the boundary fault. Modified from the Resolution Copper mining resource model (2009).

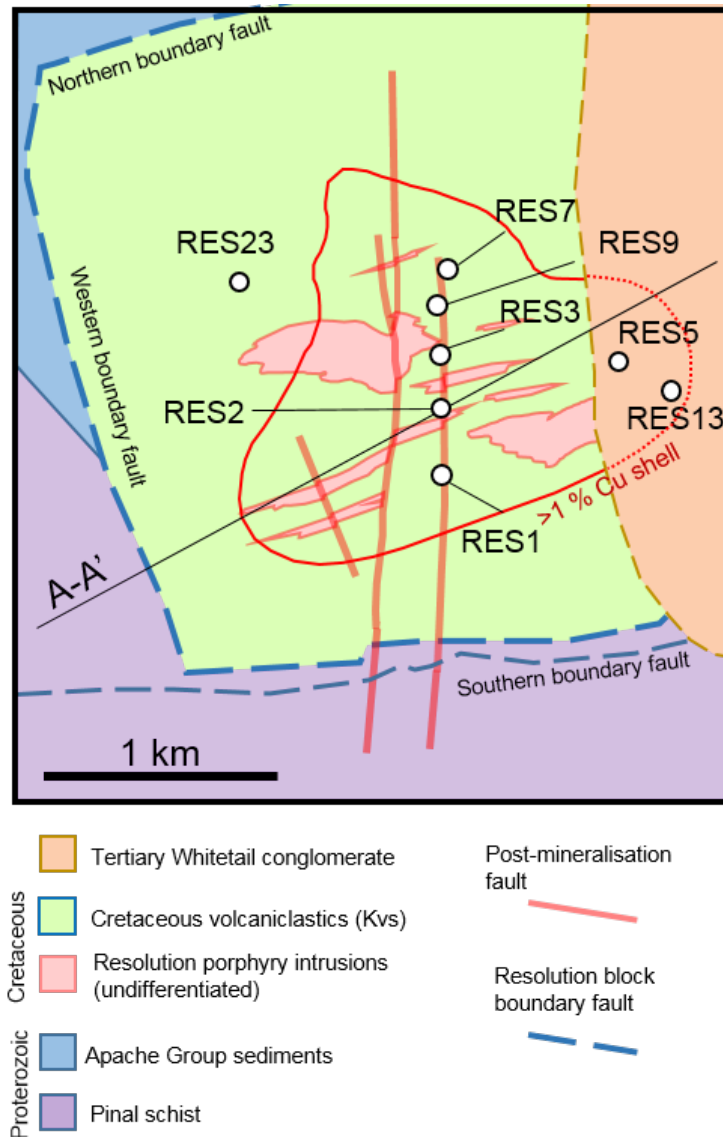


Figure 3.5. Deposit underground map of the Resolution block at sea level. Surface locations of drill holes logged are marked on. Outline of orebody as in Figure 3.2. Modified from Manske and Paul (2002).

### 3.3.3 Mineralisation

The >1% Cu zone at Resolution is found in the shape of an inverted shell in the centre of the graben (Fig. 3.4). The ore body has approximately equal dimensions in plan view (Fig. 3.5), and the edges of the >1 % shell are not well defined as they extend beyond the level of deepest drilling (Hehnke et al., 2012).

Chalcopyrite is the primary Cu mineral at Resolution, although bornite, chalcocite and digenite are also present in decreasing order of abundance (Hehnke et al., 2012). Chalcopyrite is associated with rocks that contain solely potassic alteration and it predominates in biotite-altered diabase (e.g. Schwarz, 2010). Rocks with sericitic alteration display a higher Cu grade assemblage of chalcopyrite + bornite (+ pyrite). Advanced argillic alteration is associated with the addition of a high sulphidation assemblage of bornite + chalcocite, at the expense of chalcopyrite. Thus, the later hydrolytic stages of alteration have a significant additive effect on Cu grade. This is unusual for porphyry deposits, where potassic alteration is considered the main contributor to mineralisation, and hydrolytic alteration stages may be low grade or barren (Sillitoe, 2010).

### **3.4 Lithological description of studied rocks**

Fieldwork for this project was conducted on site at Resolution between November and December 2011. The majority of the fieldwork involved logging diamond drill core, with an emphasis on the Late Cretaceous igneous intrusions and associated igneous and hydrothermal breccias. Logged intervals were chosen to represent the range of igneous texture, alteration style, ore grade, and depth within the deposit. In addition to diamond drilling, 2 days of fieldwork were conducted in the area around Resolution, in order to collect samples of the Schultze Granite, and the Cretaceous unmineralised porphyry intrusions which outcrop at the base of Apache Leap, (the ‘Apache Leap intrusions’).

#### **3.4.1 Resolution Porphyry Intrusions**

Previous workers have identified 4 porphyritic intrusion types which, although they have the same phenocryst and groundmass assemblage, are distinguished based on the varying proportions and volumetric abundance of phenocrysts (Hehnke et al., 2012). All intrusions are felsic, and contain quartz and feldspar as the dominant phenocrysts, with subordinate biotite



phenocrysts. The most striking feature of these rocks is the complete absence of plagioclase feldspar. All feldspars, both as phenocrysts and in the groundmass, are K-feldspar.

#### 3.4.1.1 Classifying the Resolution intrusions

These intrusions are referred to by Resolution mine geologists as, in decreasing order of abundance, rhyodacite porphyry (RDP), quartz latite porphyry (QLP), latite porphyry (LP), and aplite intrusion (AP). However, these names are not realistic descriptions of these rocks. Given that plagioclase is entirely absent of all of the Resolution intrusions studied herein, these rocks all classify as *alkali feldspar granites* (or alkali feldspar rhyolite, when using the volcanic QAPF classification), because they contain approximately equal proportions of quartz and K-feldspar when both phenocrysts and groundmass are taken into consideration (Fig. 3.6).

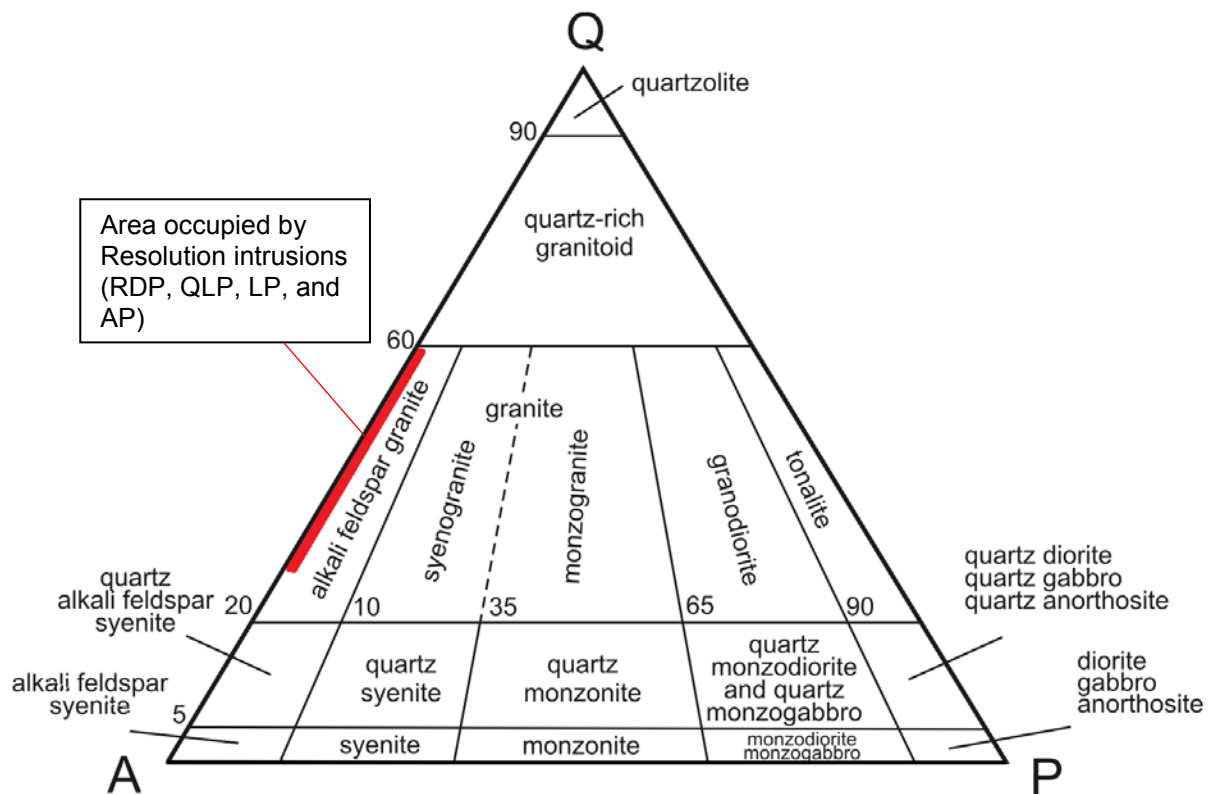


Figure 3.6. Quartz-Alkali-Plagioclase-(Foid) (QAPF) classification diagram. Resolution intrusions contain no plagioclase, and plot as alkali feldspar granites on the basis of their approximately equal proportions of quartz and K-feldspar. However, mining terminology (rhyodacite, quartz latite, and latite) are retained herein. See text for discussion and justification. Diagram after Streckeisen (1974). Q = quartz, A = alkali, P = plagioclase.

In spite of this, the mining terminology (RDP, QLP, LP) is retained, and used herein. This is because the mining terminology is a more realistic description of the protolith of these rocks, before the intense hydrothermal alteration. The absence of plagioclase in these rocks (and thus, their classification as alkali feldspar granites) is a consequence of hydrothermal alteration. Also, using the mining terminology (which relies on the proportion of different phenocrysts, and not on the total volume of individual minerals) takes into consideration differences in texture. Using the mining terminology also allows this study to be compared to previously published literature.

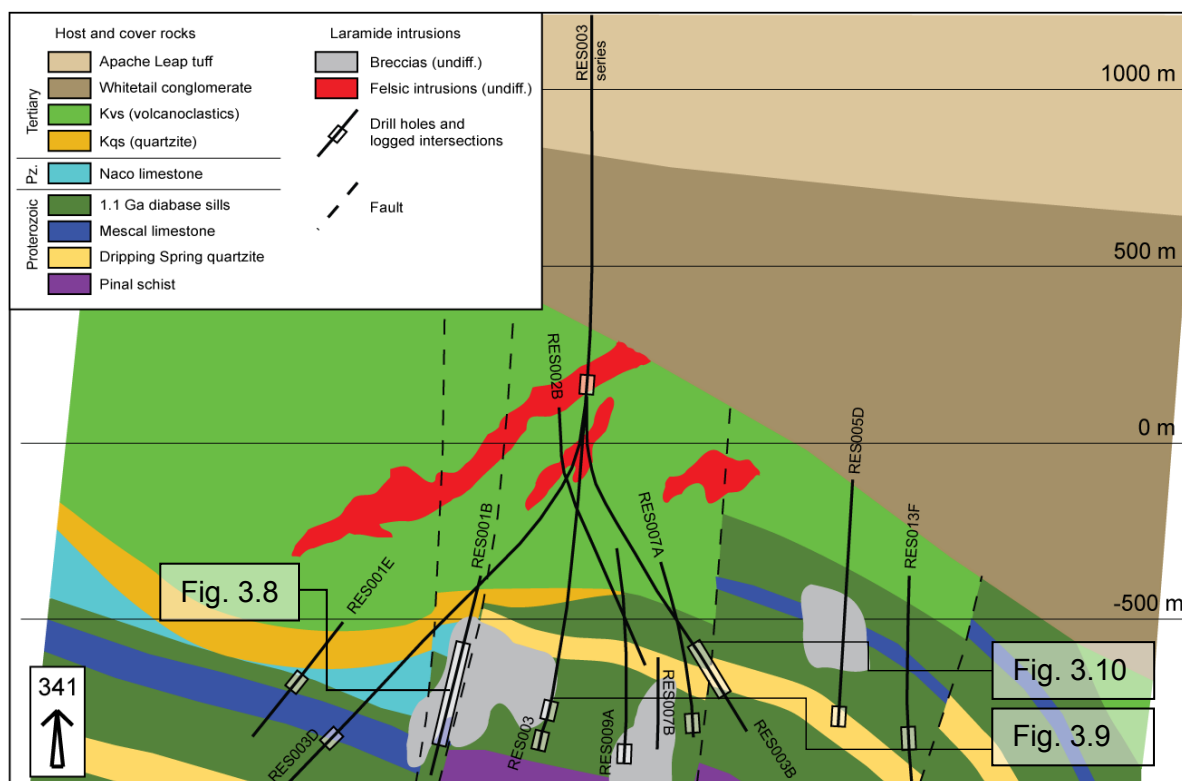


Figure 3.7. A representative section through the centre of the Resolution deposit, showing the main host rocks and the distribution of Laramide intrusions and breccias. Drill traces and logged intersections are shown. Not that several intrusions smaller than the scale of this section were logged in each selected intersection. Taken from the RCC deposit model.

#### *3.4.1.2 Distribution of intrusions*

The rhyodacite porphyry is the most volumetrically abundant intrusion type within the deposit. It forms one major stock to the east of the deposit (known by mine geologists as the “RES5 Stock”, after the drill hole which intersects it), and several smaller stocks and dykes in the centre of the deposit. Quartz latite porphyry dykes are common in the deposit, and occurs primarily as isolated narrow dykes (e.g. Fig. 3.10). The latite porphyry is the second most volumetrically minor of the Resolution intrusions, and occurs only as isolated, minor dykes. Aplitic dykes are present only as narrow dykes in the deepest portions of the centre of the system (Fig. 3.8). In this study, AP was observed in drill holes RES2A and RES3 below the 1980m level, although one shallower intrusion was identified in RES2B at ~1730m from which the two AP samples collected in this study were taken (R-2B-3 and R-2B-15).

#### *3.4.1.3 Textural distinction between intrusions*

The three main intrusions at Resolution are distinguished in drill core on the abundance of phenocrysts. RDP intrusions have a ‘crowded’ texture (phenocrysts > 50 vol. %), and contain quartz ‘eyes’ (large ‘rounded’ subhedral quartz phenocrysts) in excess of 20% of the total rock volume. QLP intrusions have an ‘uncrowded’ texture (phenocrysts <50 vol. %), and contain a smaller volume fraction of quartz eyes (5 – 20 vol. %). LP intrusions have a similar ‘crowded’ texture to RDP intrusions, but contain significantly fewer quartz eye phenocrysts (<5 vol. %).

In spite of the difference in phenocryst abundances, all Resolution intrusions contain similar proportions of feldspar and quartz when the groundmass is taken into consideration. Also, some drill hole intersections which were examined during this study are difficult to classify based on the classification presented in Table 3.1, e.g. having abundant quartz eyes (>20 vol. %), but an ‘uncrowded’ texture. Thus, it is likely that the different intrusions are textural variations of a common magma type.

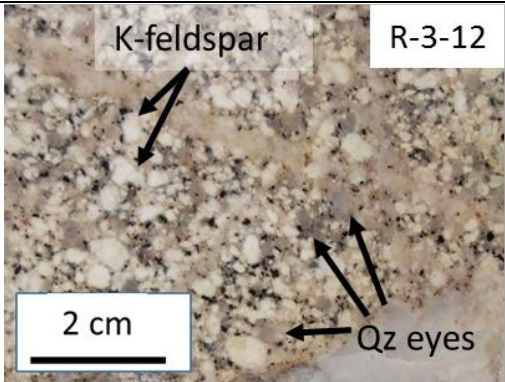
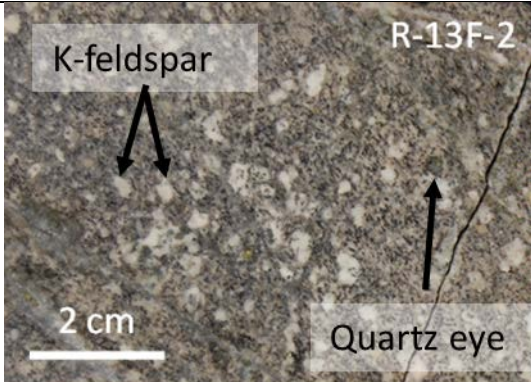
|                       | Rhyodacite Porphyry (RDP)                                                                                                                                                                                                                                                                                                                                              | Quartz Latite Porphyry (QLP)                                                                                                                                                                                                                         | Latite Porphyry (LP)                                                                                                                                |
|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|
|                       |                                                                                                                                                                                                                                                                                       |                                                                                                                                                                    |                                                                  |
| Distribution          | Dominant felsic porphyry. Two large stocks in the east and west of the graben                                                                                                                                                                                                                                                                                          | Occasional narrow ENE-trending dykes in the central portion of the deposit                                                                                                                                                                           | Rare intrusions, mostly found in the deeper portions of the graben.                                                                                 |
| Timing                | Pre mineralisation – cut by all barren quartz veins                                                                                                                                                                                                                                                                                                                    | Pre-to early syn-mineralisation – Some intersections show QLP cross cutting RDP, and truncating barren quartz veins.                                                                                                                                 | Uncertain – contacts between LP and other Laramide intrusions are rare.                                                                             |
| Phenocryst assemblage | Crowded phenocryst assemblage of quartz eyes, K-feldspar (2-3 mm in size), and subordinate biotite, accounting for up to 50% of the rock by volume. Some samples show K-feldspar megacrysts, up to 3 cm in size. Quartz eyes > 20%                                                                                                                                     | Uncrowded texture, containing sparse K-feldspar phenocrysts (up to 3 mm), quartz eyes, and biotite phenocrysts. Total phenocrysts constitute <25 vol. % of the rock. Quartz eyes between 5 and 20%                                                   | Crowded feldspar porphyry (up to 50% phenocrysts). Notable absence of quartz eye phenocrysts (<5 vol. %) distinguishes this rock type from the RDP. |
| Groundmass assemblage | K-feldspar + quartz, <100 µm. Anhydrite in deeper portions of the system, secondary biotite in potassic alteration                                                                                                                                                                                                                                                     | Similar to RDP. Secondary biotite in the matrix is common to these rocks. Some secondary biotite is foliated into lenticular aggregates, imparting a weak foliation on rock fabric.                                                                  | Similar to other two rock types.                                                                                                                    |
| Accessory minerals    | Apatite common in potassic-sericitic alteration, but destroyed in strong sericitic. Rutile a common replacement mineral after biotite. Zircon rare, but typically present. Fluorite and topaz present in some samples. Minor barite and monazite                                                                                                                       |                                                                                                                                                                                                                                                      |                                                                                                                                                     |
| Alteration styles     | <p>Potassic-sericitic to sericitic. K-feldspar phenocrysts and occasional megacrysts commonly altered to sericite. In strong phyllic alteration, groundmass K-feldspar is also altered to sericite.</p> <p>Minor advanced argillic alteration most easily distinguished due to the presence of dickite veins, and matt, 'waxy' feldspars which are easy to scratch</p> | <p>Potassic-phyllic to phyllic, minor advanced argillic.</p> <p>K-feldspars commonly altered to sericite or clay, including groundmass K-feldspars in strong sericitic alteration. Secondary biotite found in rocks with no biotite phenocrysts.</p> | Potassic-sericitic to sericitic.                                                                                                                    |

Table 3.1. Summary of the textural characteristics and distribution of the main Laramide intrusion types in the Resolution deposit.

| Hole ID: RES001B       |          |                           | Deposit: Resolution |           |                          |                                                                                                 | Depth: 2090 to 2182                                                                                                                                                                                                 |                                                                                          |
|------------------------|----------|---------------------------|---------------------|-----------|--------------------------|-------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Hole depth<br>(metres) | Sample # | Lithology<br>(base depth) | Grade               |           | Alteration<br>assemblage |                                                                                                 | Comments<br>(Igneous and hydrothermal texture)                                                                                                                                                                      | <br># |
|                        |          |                           | Mo<br>ppm           | Cu<br>wt% | K-sil                    | Sericite                                                                                        |                                                                                                                                                                                                                     |                                                                                          |
| 2092                   |          | Bx1                       |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     | 164                                                                                      |
| 2094                   |          | KTqlp                     |                     |           |                          |                                                                                                 | Py + qz veins                                                                                                                                                                                                       |                                                                                          |
| 2096                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2098                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2100                   | R-1B-9   |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2102                   |          | Diab                      | 2101.50             |           |                          |                                                                                                 | Igneous textures:<br>Fsp (2-3mm, ~30%, sub- euhedral)<br>Qz eyes - (2 - 5mm, 5-10 % some agglomerate grains)<br>Bt - Some phenocrysts (<5%), large amount of biotisation in<br>gmass, with a preferred orientation) | 165                                                                                      |
| 2104                   |          |                           | 2103.63             |           |                          |                                                                                                 |                                                                                                                                                                                                                     | 166                                                                                      |
| 2106                   |          | KTqlp                     |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2108                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2110                   |          |                           |                     |           |                          |                                                                                                 | Short intersection of diabase (1m)                                                                                                                                                                                  |                                                                                          |
| 2112                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2114                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2116                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
|                        |          |                           |                     |           |                          |                                                                                                 | Clasts of diabase (2-5 mm), distinguishable by the presence<br>of leucoxene (10%,1mm) surrounded by shreddy biotite                                                                                                 | 169                                                                                      |
| 2138                   | R-1B-15  | KTqlp                     |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     | 170                                                                                      |
| 2140                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2142                   | R-1B-1   |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2144                   | R-1B-16  |                           |                     |           |                          |                                                                                                 | Diabase clasts up to 20cm of core. Cross-cut by QSP veins                                                                                                                                                           | 168                                                                                      |
| 2146                   |          |                           | 2147.50             |           |                          |                                                                                                 |                                                                                                                                                                                                                     | 172                                                                                      |
| 2148                   |          |                           |                     |           |                          |                                                                                                 | Boundary not clear (approximate location)                                                                                                                                                                           | 173                                                                                      |
| 2150                   | R-1B-7   | Bx4                       |                     |           |                          |                                                                                                 | Breccia matrix (Igneous textures)<br>Fsp (1-3mm, ~40-50%, "crowded" texture, sub- euhedral)<br>Qz eyes - (up to 6mm, 35 % several agglomerate grains)<br>Bt - Some phenocrysts (1-2mm, 5-10%),                      | 174                                                                                      |
| 2152                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2154                   |          |                           |                     |           |                          |                                                                                                 | Polymict breccia clasts                                                                                                                                                                                             | 175                                                                                      |
| 2156                   |          |                           |                     |           |                          |                                                                                                 | - Diabase (up to 5 cm)                                                                                                                                                                                              |                                                                                          |
| 2158                   |          |                           |                     |           |                          | - Quartz vein clasts (unmineralised, ~2cm)                                                      | 176                                                                                                                                                                                                                 |                                                                                          |
| 2160                   | R-1B-17  |                           | 2160.00             |           |                          | - Sedimentary rocks (layered rocks, 2-3 mm, unknown prov.)<br>All cut by Qz veins and QSP veins | 177                                                                                                                                                                                                                 |                                                                                          |
| 2162                   |          | Bx1                       |                     |           |                          | Concentration of mafic clasts beomes more dense at ~2160m<br>Contains clasts of felsic porphyry |                                                                                                                                                                                                                     |                                                                                          |
| 2164                   | R-1B-18  |                           |                     | 2166.40   |                          |                                                                                                 | Small clasts of "crowded" felsic porphyry (1-2 cm)<br>- Fsp phenos liberated into the groundmass                                                                                                                    | 178                                                                                      |
| 2166                   |          | Bx4                       |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2168                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2170                   | R-1B-20  |                           |                     | 2173.10   |                          |                                                                                                 | Quartz and country rock clasts (rounded, 2-5 cm) in matrix of<br>felsic porphyry<br>- Fsp (2-3 mm, 50-60%, equant to sub-elongate)<br>- Qz eyes (20%, 4-5mm, subhedral (rounded))<br>Biotite (~1mm, <5%)            | 177b<br>178b<br>179                                                                      |
| 2172                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2174                   |          | Bx1                       |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2176                   |          |                           |                     |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |
| 2178                   |          |                           |                     |           |                          |                                                                                                 | Hydrothermal breccia matrix is strongly biotised, and contains<br>clasts of sericitised felsic porphyry                                                                                                             | 180                                                                                      |
| 2180                   |          | pCp                       | 2180.89             |           |                          |                                                                                                 |                                                                                                                                                                                                                     |                                                                                          |

Figure 3.8. Petrological log for drill hole RES001B from Resolution, between 2090 and 2182 m depth.

| Hole ID: RES003        |          |                           | Deposit: Resolution |           |                          |          | Depth: 2026 to 2102                                            |                                                                                          |
|------------------------|----------|---------------------------|---------------------|-----------|--------------------------|----------|----------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Hole depth<br>(metres) | Sample # | Lithology<br>(base depth) | Grade               |           | Alteration<br>assemblage |          | Comments<br>(Igneous and hydrothermal texture)                 | <br># |
|                        |          |                           | Mo<br>ppm           | Cu<br>wt% | K-sil                    | Sericite |                                                                |                                                                                          |
| 2028                   |          | Diab.                     |                     |           |                          |          | Ptygmatic qz + anh + cpy veins in diabase. Anastomosing and    | 17                                                                                       |
| 2030                   |          | 2031.60                   |                     |           |                          |          | Boundary is marked by ptygmatic qz vein                        |                                                                                          |
| 2032                   |          | KTrdp                     |                     |           |                          |          | Diabase is strongly biotised, with interstitial leucoxene and  | 18                                                                                       |
| 2034                   |          | 2034.49                   |                     |           |                          |          | pale blue sericite                                             |                                                                                          |
| 2036                   | R-3-9 →  |                           |                     |           |                          |          | Large amounts of disseminated cpy                              | 18                                                                                       |
| 2038                   |          |                           |                     |           |                          |          | Intense sericitisation                                         |                                                                                          |
| 2040                   |          |                           |                     |           |                          |          | RDP contains K feldspar megacrysts (up to 2 cm)                | 19                                                                                       |
| 2042                   | R-3-11 → |                           |                     |           |                          |          | Igneous textures:                                              |                                                                                          |
| 2044                   |          |                           |                     |           |                          |          | Crowded porphyry (phenos ~60-70%)                              | 20                                                                                       |
| 2046                   |          |                           |                     |           |                          |          | - Fsp - 40-50%, equant to semi-elongate (ser. to clay altered) |                                                                                          |
| 2048                   |          |                           |                     |           |                          |          | <1-2 mm,                                                       | 21                                                                                       |
| 2050                   |          |                           |                     |           |                          |          | - Qz - (20%, mostly quartz eyes 4-5mm)                         |                                                                                          |
| 2052                   |          |                           |                     |           |                          |          | - Bt largely altered to py (<5%)                               | 21                                                                                       |
| 2054                   |          |                           |                     |           |                          |          | Silicification in the gmass. Many barren qz veins.             |                                                                                          |
| 2056                   | R-3-5 →  |                           |                     |           |                          |          | Strong ser. alteration                                         | 21                                                                                       |
| 2058                   |          |                           |                     |           |                          |          | Intense qz + py + cpy vein                                     |                                                                                          |
| 2060                   |          |                           |                     |           |                          |          | Stronger potassic alteration - Bt phenos 20%, 1mm.             | 22                                                                                       |
| 2062                   | R-3-12 → |                           |                     |           |                          |          | Finegrained bt in gmass, <<1mm                                 |                                                                                          |
|                        |          |                           |                     |           |                          |          | - Anhydrite veins                                              | 22                                                                                       |
| 2086                   |          | KTrdp                     |                     |           |                          |          | Aplite igneous textures:                                       |                                                                                          |
| 2088                   |          | 2089.00                   |                     |           |                          |          | - Extremely finegrained (<1mm). Approximately equal props.     | 20                                                                                       |
| 2090                   | R-3-7 →  | ap                        |                     |           |                          |          | of qz and fsp. Equigranular.                                   |                                                                                          |
| 2092                   |          | 2091.56                   |                     |           |                          |          | Occasional qz. eyes (3mm)                                      | 21                                                                                       |
| 2094                   |          |                           |                     |           |                          |          | - Biotite <1%.                                                 |                                                                                          |
| 2096                   | R-3-3 →  | KTrdp                     |                     |           |                          |          | Strong ser alteration in aplite                                | 22                                                                                       |
| 2098                   |          | 2097.30                   |                     |           |                          |          | RDP contains K feldspar megacrysts (up to 2 cm)                |                                                                                          |
| 2100                   |          | ap                        |                     |           |                          |          |                                                                |                                                                                          |
|                        |          | KTrdp                     |                     |           |                          |          |                                                                |                                                                                          |
|                        |          | ap                        |                     |           |                          |          |                                                                |                                                                                          |
|                        |          | KTrdp                     |                     |           |                          |          |                                                                |                                                                                          |

Figure 3.9. Petrological log for drill hole RES003 from Resolution, between 2026 and 2102 m depth.



| Hole ID: RES003B       |                      |                           | Deposit: Resolution |           |                          |          | Depth: 1910 to 1982                                                                                                                                             |                                                                                          |
|------------------------|----------------------|---------------------------|---------------------|-----------|--------------------------|----------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Hole depth<br>(metres) | Sample #             | Lithology<br>(base depth) | Grade               |           | Alteration<br>assemblage |          | Comments<br>(Igneous and hydrothermal texture)                                                                                                                  | <br># |
|                        |                      |                           | Mo<br>ppm           | Cu<br>wt% | K-sil                    | Sericite |                                                                                                                                                                 |                                                                                          |
| 1912                   |                      | Diabase                   |                     |           |                          |          | Veins in diabase:<br>- Qz + cpy (+ py)<br>- Barren qz veins (folded and faulted on a small scale)<br>- early qz (+ minor cpy) veins with biotite halos          | 31<br>32                                                                                 |
| 1914                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1916                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1918                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1920                   |                      | KTqlp                     | 1920.00             |           |                          |          | Large (5cm) Qz + mo veins and disseminated cpy at contact.                                                                                                      | 33                                                                                       |
| 1922                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1924                   |                      | Diabase                   |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1926                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1928                   |                      | Diabase                   | 1929.02             |           |                          |          | Intense cpy (+ py) veining between @ 1921.5, and<br>between 1923 and 1924m<br>- accompanied by more intense ser. alteration.                                    |                                                                                          |
| 1930                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1932                   |                      | KTqlp                     |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1934                   |                      |                           | 1934.2              |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1936                   |                      | Diab.                     | 1937.46             |           |                          |          | Igneous textures largely obscured by alteration.<br>- "uncrowded" texture (i.e. phenos <50%)<br>- Sparse quartz eye p[henocrysts (<10 %)                        |                                                                                          |
| 1938                   |                      | Diab.                     |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1940                   |                      | KTqlp                     |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1942                   |                      | Diab.                     | 1943.00             |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1944                   |                      | KTrdp                     |                     |           |                          |          | Contact marked by large py vein                                                                                                                                 | 34<br>35<br>36                                                                           |
| 1946                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1948                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1950                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1952                   |                      |                           |                     |           |                          |          | Igneous textures:<br>- Fsp (up to 6mm, av. = 2mm, 40%) Mostly altered to ser.<br>- Qz eyes (1-2mm, some up to 6mm, 20%)<br>- Bt completely altered to py. (<5%) | 37                                                                                       |
| 1954                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1956                   |                      |                           | 1955.70             |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1958                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1960                   | R-1B-11 →            | Bx2                       |                     |           |                          |          | Qz veins (~5cm thick) with vugs - anh lost? These veins are<br>assoc. with strong ser. alt.                                                                     | 38<br>39<br>40<br>41                                                                     |
| 1962                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1964                   |                      |                           | 1963.5              |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1966                   | R-1B-18<br>R-1B-17 ↔ | KTrdp                     | 1967.4              |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1968                   |                      | Bx2                       |                     |           |                          |          | Lower contact difficult to define due to alteration and<br>intense veining.                                                                                     | 43                                                                                       |
| 1970                   | R-1B-13 →            |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1972                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1974                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1976                   |                      |                           |                     |           |                          |          | Extremely large clasts of diabase (up to 20 cm) along length<br>of core<br>- Clasts cut by mineralised veins                                                    | 44<br>45<br>42                                                                           |
| 1978                   |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
| 1980                   | R-1B-19 →            |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |
|                        |                      |                           |                     |           |                          |          |                                                                                                                                                                 |                                                                                          |

Figure 3.10. Petrological log for drill hole RES003B from Resolution, between 1910 and 1982 m depth.

#### *3.4.1.1 Mineralogy*

Quartz is ubiquitously present in the groundmass of all porphyry intrusions and as larger quartz “eye” phenocrysts in some rocks (Fig. 3.11 a,b). Sub- to anhedral, fine-grained quartz (mostly <50 µm, some up to ~200 µm) typically comprises 30-40% of the groundmass and is inter-grown with small K-feldspar crystals (Fig. 3.11 b,c). Cathodoluminescence (CL) reveals a typical bimodal zoning in this quartz, with light cores and relatively darker rims. Most quartz eye phenocrysts are large (up to 2 mm), sub- to euhedral, and have prismatic habits which are occasionally rounded at the edges. Some quartz phenocrysts are more angular. CL images of quartz phenocrysts show a complex pattern of concentric zones and thin, CL-dark crosscutting fractures (Fig. 3.11 b). They occasionally contain significant embayments, which cut through the growth zones and are infilled with the same mineral assemblage and texture as the groundmass (Fig. 3.11 b). Quartz eyes are cut by early barren quartz veins, indicating that they predate the early hydrothermal history of the host rocks.

All feldspars in the Resolution porphyry intrusions are K-feldspars; there is a notable paucity of plagioclase. K-feldspar is found as phenocrysts (up to 3 mm) and as microcrysts in the groundmass. Phenocrysts are tabular to equant, are mostly euhedral, and constitute up to 40% of a rock (where the texture is crowded). The phenocrysts are commonly altered to sericite and/or clay minerals, often completely so (Fig. 3.11 c). In samples where K-feldspar phenocrysts are completely altered to sericite, the groundmass K-feldspar may be intact, unless phyllic alteration is very strong in which case the groundmass is also altered to sericite. Large (1-2 cm) K-feldspar megacrysts are occasionally found in the RDP. These megacrysts are euhedral, and have concentric zoning patterns. Megacrysts are variably altered to sericite, and may display minor hydrothermal overprinting along veins and cracks as seen in SEM backscatter images.



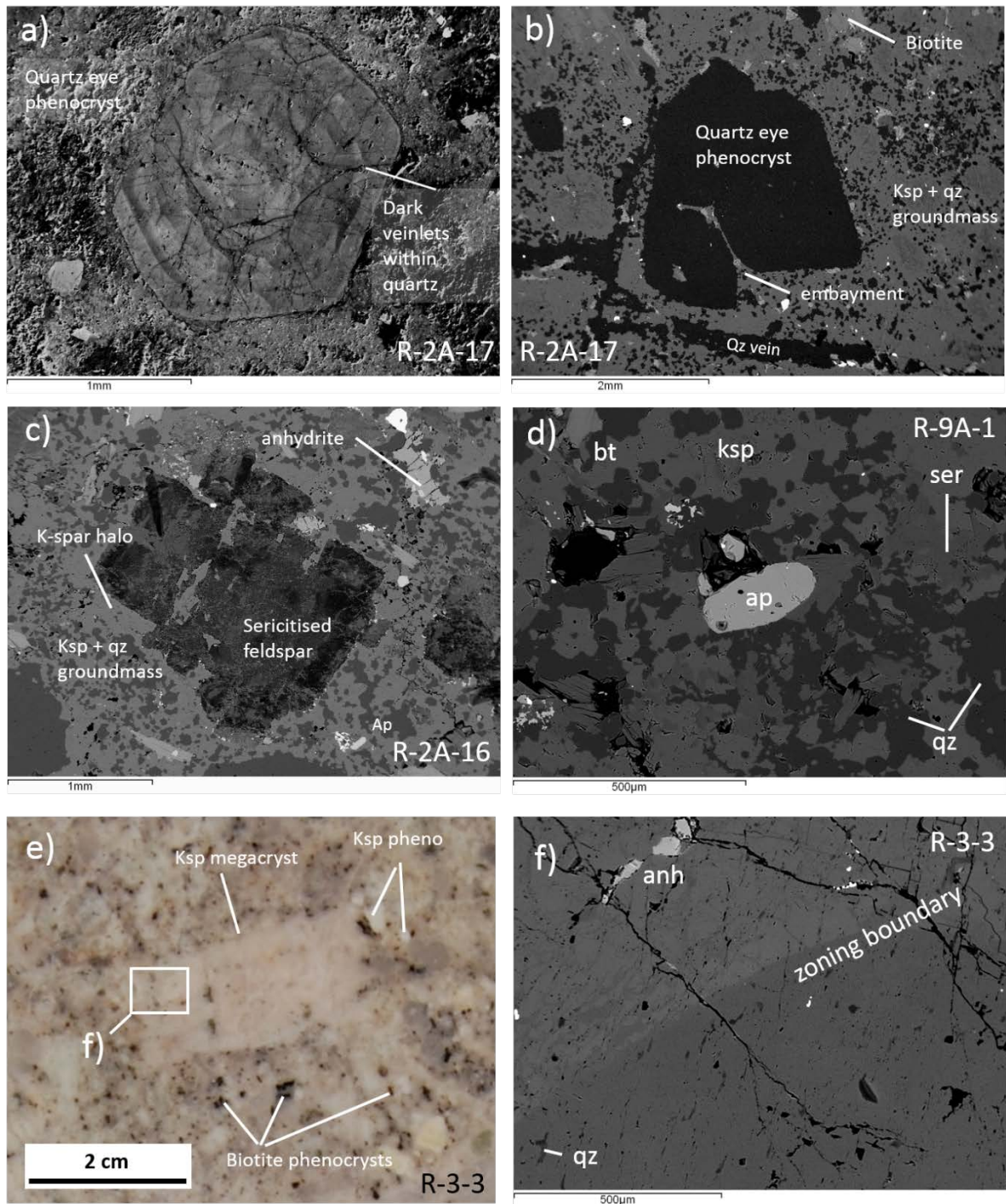


Figure 3.11. (a) Zoned quartz eye phenocryst. (b) Quartz eye phenocryst with embayments. (c) Sericitised K-feldspar in a matrix of K-feldspar, quartz and anhydrite. (d) Typical groundmass of porphyry intrusions with apatite crystal and minor sericitisation. (e) K-feldspar megacryst in RDP. (f) Detail of megacryst, showing zoning and the absence of plagioclase inclusions. All figures are SEM backscatter images except for (e), which is a field photograph. Ap - apatite, anh - anhydrite, ksp - K-feldspar, qz - quartz.

Unlike the megacrysts in the Schultze Granite, they do not contain any inclusions of plagioclase (Fig. 3.11 f). Biotite is found both as large (~500 µm, <1 mm) primary magmatic phenocrysts, and as much smaller, secondary (hydrothermal) crystals, which often occur together in clots. Rutile, sericite and Mg-rich biotite is a common alteration assemblage found after primary biotite phenocrysts. Secondary biotite is especially common in the groundmass of QLP intrusions (Table. 3.1). In rocks that are strongly sericitised, biotite is completely replaced by sulphides. Apatite is the most abundant accessory phase, and is typically found in the groundmass as subhedral to euhedral crystals up to 300 µm in diameter. Apatite is much less common in rocks affected by strong sericitic alteration. Anhydrite is found in many intrusions in veins, and as patches in the groundmass, often associated with apatite. Zircon is present in the groundmass, and grains are mostly <100 µm.

### 3.4.2 Breccias

Two main breccia types are observed at Resolution, and have been referred to by previous authors as the hydrothermal and the igneous ‘intrusion’ breccia (c.f. Hehnke et al., 2012). Both breccias contain a variety of clasts of the country rock. The primary difference between them is the composition and texture of the matrix. Breccias host approximately 10 vol. % of the mineralisation within the 1 % Cu shell (Hehnke et al., 2012), the majority of which is hosted in the hydrothermal breccia. Breccias are spatially associated with porphyry intrusions, and both are emplaced in the same ENE-trending structural corridor (Zulliger et al, 2007; Fig. 3.4).

#### *3.4.2.1 Intrusion breccia*

The matrix of the intrusion breccia is very similar in texture and mineral assemblage to the RDP. Indeed, the intrusion breccia is commonly observed at the margins of RDP intrusions



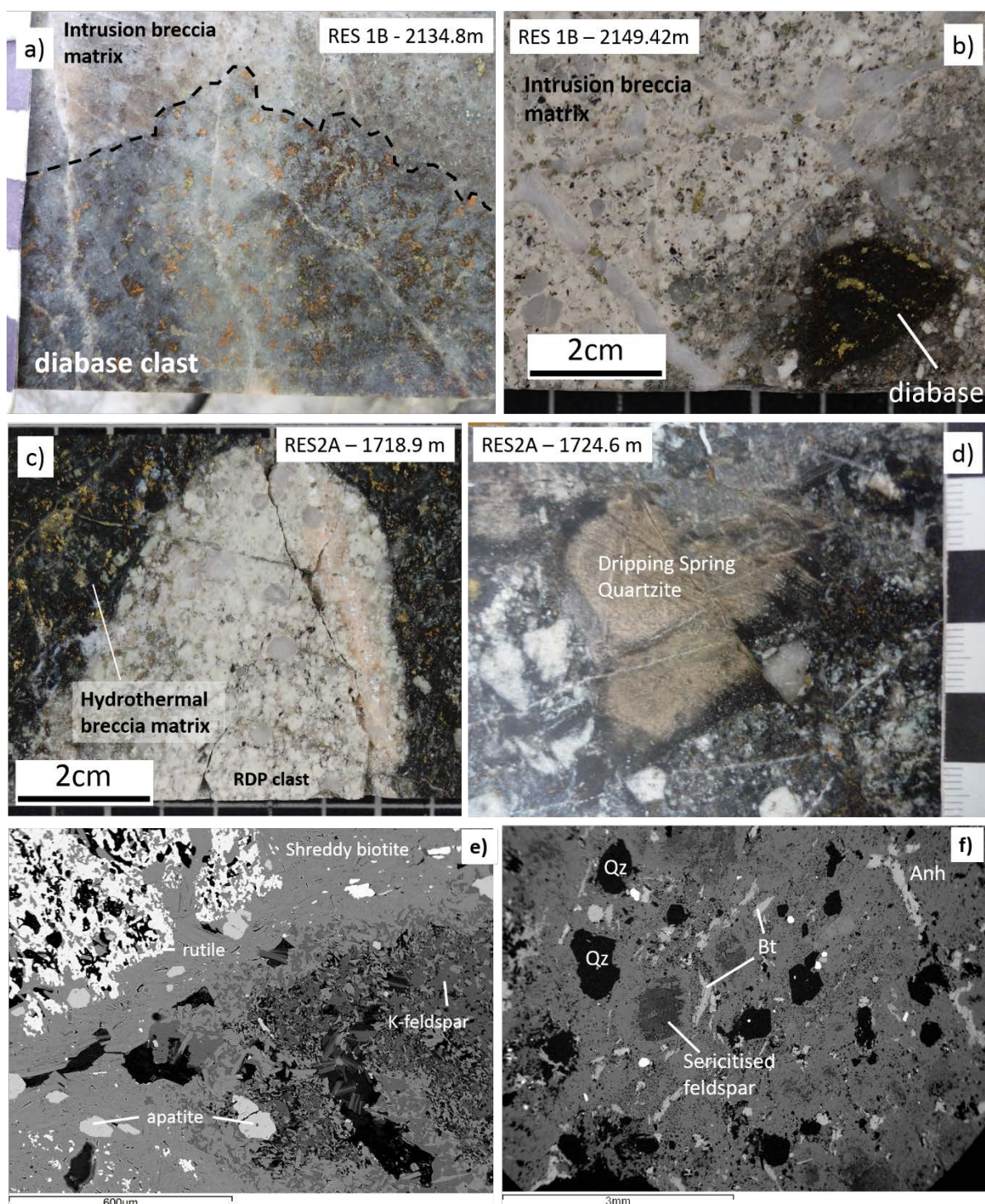


Figure 3.12. Representative images of breccias. (a) Diabase clast in intrusion breccia matrix. Clast and matrix cut by anhydrite veins. (b) Intrusion breccia with mineralised clast of diabase. (c) RDP clast in hydrothermal breccia. (d) Clasts of quartzite in heterolithic hydrothermal breccia. (e) SEM backscatter image of hydrothermal breccia matrix (R-2A-10m). (f) SEM backscatter image of intrusion breccia matrix (R-1B-7). Qz – quartz, Bt – biotite.

(Hehnke et al., 2012), and the boundary between the two is often transitional. The intrusion breccia is predominantly matrix supported, with angular to sub-rounded clasts comprising 5 to 25 vol. % of the rock. Clasts comprise all wall rock lithologies, especially the diabase. Some diabase clasts are strongly mineralised, with disseminated chalcopyrite in a biotite-rich matrix. Both the matrix and clasts are cut by all generations of veins, indicating that this breccia predates mineralisation (Fig. 3.12 a) The intrusion breccia matrix contains a crowded phenocryst assemblage of rounded quartz eyes (10-20%; up to 7mm in size; subhedral to euhedral, some angular broken clasts), K-feldspar (40%; euhedral, 1-2 mm, mostly completely sericitised), and biotite (<10%, <1 – 2mm, euhedral to subhedral). Groundmass (30-40%, quartz and sericite) comprises a fine-grained assemblage (~20 µm) of quartz and K-feldspar (most of which is sericitised), with subordinate anhydrite and secondary biotite.

#### *3.4.2.2 Hydrothermal Breccia*

The largest hydrothermal breccia body is an elongate (500 m length) body associated with the northern margin of the eastern RDP stock (Hehnke et al., 2012), but other bodies occur throughout the deposit. The breccia is mostly hosted in the diabase. Intervals of up to 100m of hydrothermal breccia are observed in some drill cores. For example, a narrow interval of diabase-hosted hydrothermal breccia in drill hole RES3 contains clasts that are almost solely diabase.

Clasts in the hydrothermal breccia usually consist of fragments of the country rock immediately adjacent to the breccia body. The breccia is dominantly matrix supported, and clasts are sub-rounded to sub-angular, and range in size from 5 mm to 10 cm. Clasts of RDP are very common (Fig. 3.12 c). They have a crowded texture (~50% phenocrysts), with a phenocryst assemblage of feldspars (25 %; completely altered to sericite; euhedral relict grains up to 5 mm), biotite (5 %, euhedral; up to 2mm) and quartz (20%; quartz eye phenocrysts

between up to 8mm, euhedral to subhedral). Crystals from the RDP clasts are occasionally disaggregated, with feldspar phenocrysts liberated into the surrounding matrix. As well as clasts of RDP, fragments of the Apache Group sediments, such as the Dripping Spring quartzite, are also observed in this rock (Fig. 3.12 d).

The matrix of the hydrothermal breccia is dark in colour and has a speckled appearance. It is characterised by clots of rutile, chalcopyrite, and subordinate pyrite, surrounded by halos of shreddy secondary biotite grains <30 µm in size (Fig. 3.12 e). Between these biotitised patches are areas of fine-grained, anhedral K-feldspar (<30 µm). Large apatite phenocrysts are also present in these rocks, with many euhedral grains up to 1 mm in length that contain small inclusions of K-feldspar. Biotite in the matrix of the hydrothermal breccia occasionally shows a strong foliation.

### 3.4.3 Schultze Granite and associated lithologies

Several Laramide intrusions are found outside the Resolution block close to the deposit. The largest of these, the Schultze Granite, is a large, felsic batholith of Laramide age (67 to 61 Ma; Seedorff et al., 2005b; Stavast, 2006). The granite outcrops ~7 km ENE of Resolution, between the towns of Superior and Globe (Fig. 3.2 a), and has approximate minimum dimensions of 8.5 x 3 km elongated in an ENE direction. It was primarily intruded into the Pinal Schist, but cuts Proterozoic granitoids along part of its northern margin (Fig. 3.2 a). The western extent of the granite is uncertain as it is nonconformably overlain by the Apache Leap tuff; it possibly extends beneath the Resolution deposit, although at a greater depth than the current level of drilling. The granite is thought to have been emplaced at a palaeodepth of >10 km (Stavast, 2006), and has been exhumed by Basin and Range extension across large, district scale normal faults that trend approximately NNW (Seedorff et al., 2008). The granite is composed of multiple phases (e.g. Creasey, 1984; Stavast, 2006) some of which contain large



(up to 4 cm) K-feldspar megacrysts, some host mafic enclaves, and some are cross-cut by later aplite dykes. Porphyritic phases on the margins of the granite are intimately associated with mineralisation, forming a number of economic deposits, including Miami-Inspiration and Pinto Valley (Fig. 3.2). The close spatial and temporal relationship between the Schultze Granite and the Resolution deposit have led some workers to consider it to be the parent pluton to the Resolution stocks and dykes (Stavast, 2006; Seedorff et al., 2006). The mineralogical similarity, especially the presence of K-feldspar megacrysts in both Resolution intrusions and the Schultze granite, suggests a petrogenetic link between them (Zulliger, 2007).

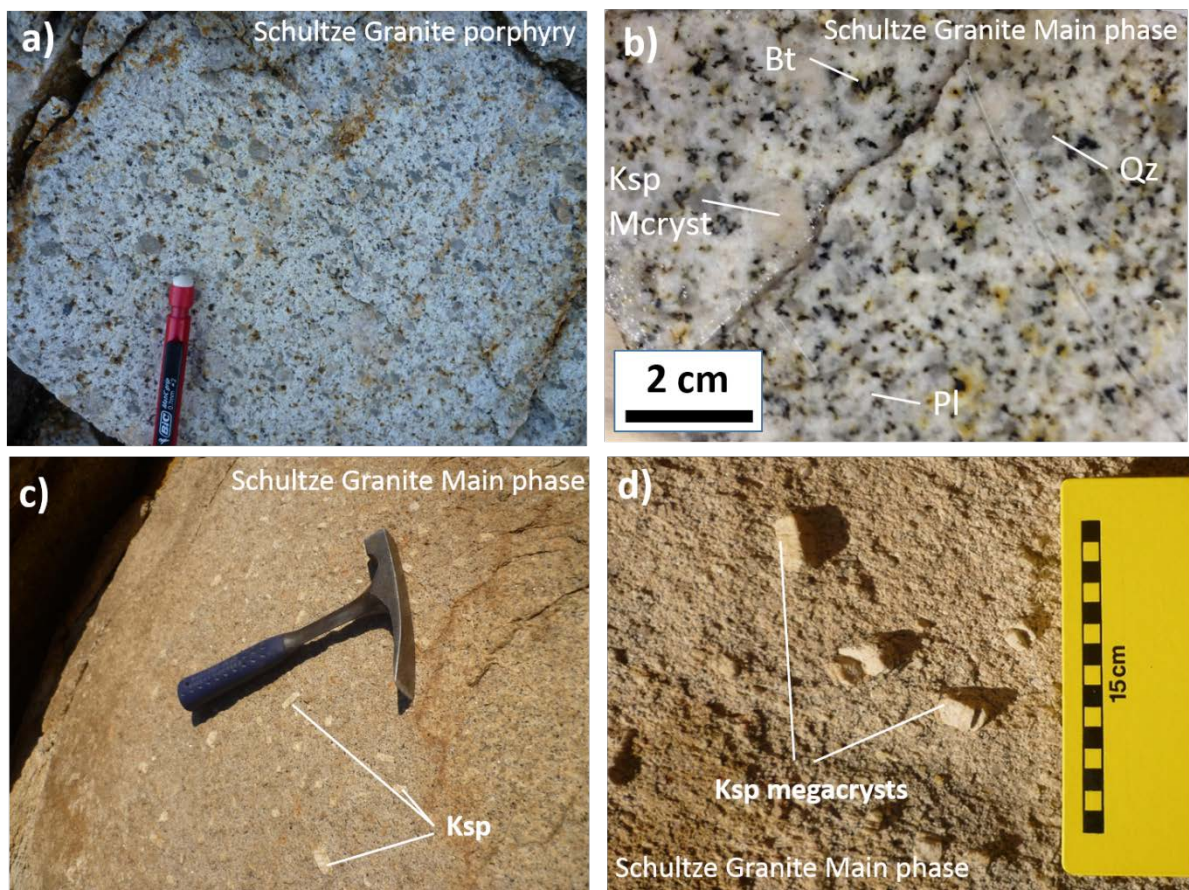


Figure 3.13. Field photographs of the Schultze Granite. (a) Porphyry phase, with rounded quartz eye phenocrysts. (b) Main phase (Sample R-S-11). (c-d) Main phase with K-feldspar phenocrysts.

A brief survey of the Schultze Granite was taken over the course of 1 field day. 12 samples were collected from the Schultze Granite and associated lithologies, of which 10 were studied in detail. Samples were collected from road cuttings at 5 locations along highway US-60 between Superior and Globe (Appendix 1; Fig. 3.2 a). Samples collected are 6 from the Schultze Granite main phase, 1 sample of Schultze Granite porphyry, 2 samples of aplite dykes, 2 samples of a biotite-rich enclave, and several samples of K-feldspar megacrysts, of which 2 megacrysts were studied in detail (R-SF-1 and R-SF-2).

#### *3.4.3.1 Schultze Granite (main phase)*

The main phase of the Schultze Granite is the most volumetrically significant phase, accounting for the vast majority of the body of the granite. It consists of a coarse grained assemblage of quartz, K-feldspar, plagioclase, and biotite, with accessory monazite, apatite, and zircon (Fig. 3.13 b).

Plagioclase crystals are mostly 0.5 to 2 mm in size, are euhedral to subhedral, and account for approximately 30 – 40 vol. % of the granite. Fine oscillatory zoning ( $<1\ \mu\text{m}$ ) is common in plagioclase crystals. Cores of plagioclase crystals frequently show signs of disequilibrium, such as sieve textures and minor alteration to sericite. Quartz (~25 to 30 vol. %) is present primarily as subhedral to anhedral grains up to 3 mm in size, although most quartz grains are  $<500\ \mu\text{m}$ . Quartz is found in the interstitial spaces between plagioclase crystals, and occasionally as inclusion within them. Biotite is a sparse phenocryst within the Schultze Granite, accounting for 5 to 10 vol. %. Biotite is frequently inter-grown with magnetite. K feldspar is found in two varieties. It occurs as anhedral grains  $<1\text{mm}$  in size between euhedral plagioclase crystals (Fig. 3.14 b). K-feldspar is also present as large megacrysts up to 5 cm in size (Fig. 3.14 b). The abundance of K-feldspar megacrysts in a rock varies between localities, from ~10 vol. %, to nearly entirely absent in some samples.

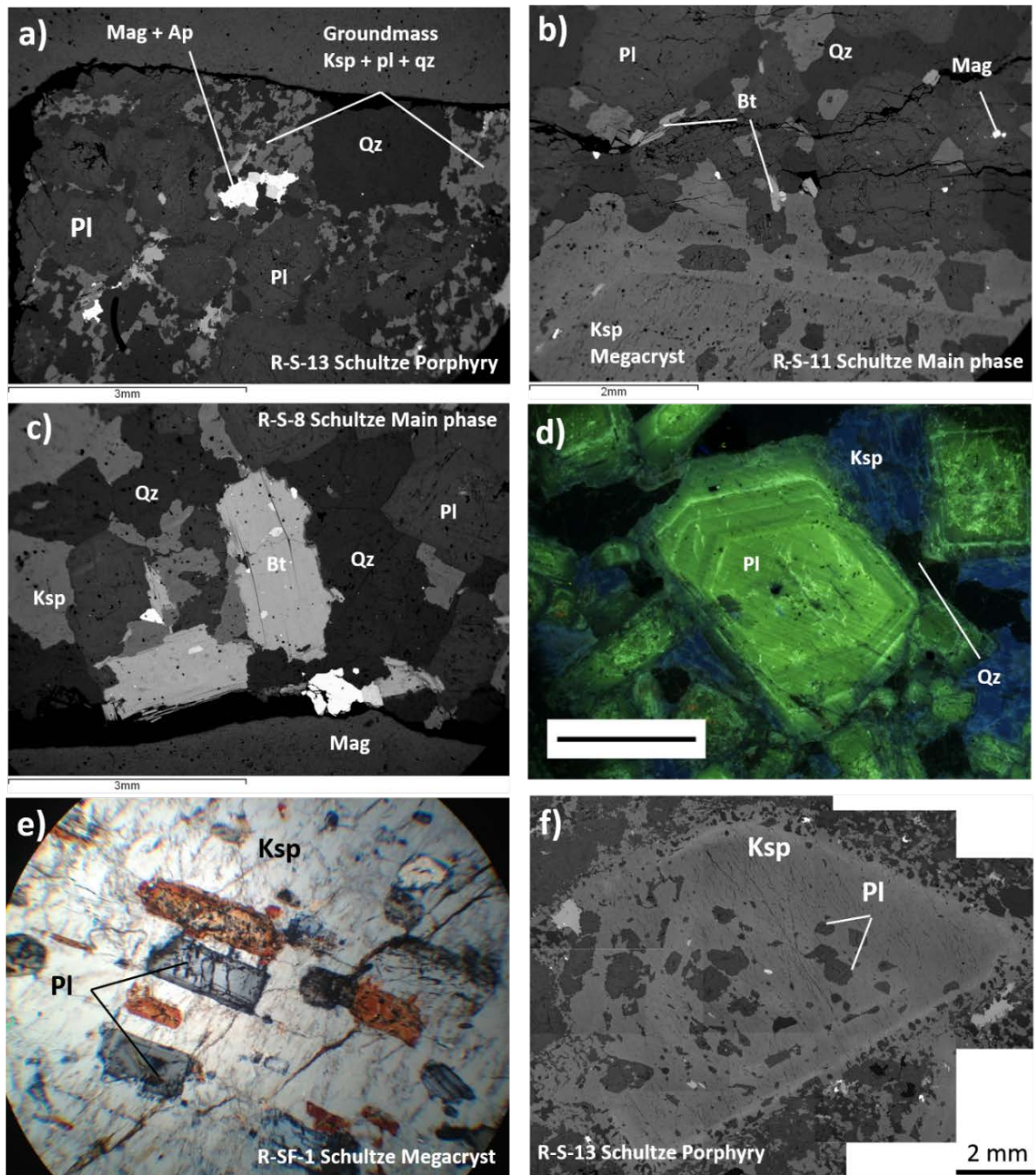


Figure 3.14. The petrography of the Schultz Granite and associated lithologies. (a) Schultz Granite porphyry phase, with fine grained groundmass. (b) Margin of K-feldspar megacryst in the Schultz Granite main phase. (c) Biotite and magnetite in the Granite (d) zoned plagioclase crystals in the Schultz Granite (sample R-S-8). (e) Aligned plagioclase phenocrysts in K-feldspar megacrysts. (f) K-feldspar megacryst in the Schultz Granite porphyry. 'Tendrils' of the megacryst extend into the groundmass of the intrusion. (a-c), and (f) are SEM backscatter images, (d) was taken with a CL microscope, (e) is a transmitted light image.



#### 3.4.3.2 *Schultze Granite porphyry*

The use of the term ‘porphyry’ in the case of the Schultze Granite porphyry refers only to phenocrysts of K-feldspar, quartz, and biotite in a fine grained groundmass (<1 mm K-feldspar) of the same assemblage, as opposed to the porphyritic texture present in the coarse grained K-feldspar megacryst bearing phases. Porphyry phases have been noted by previous authors (Stavast, 2006), and are infrequent throughout the granite. Several porphyry intrusions occur at the margins of the Schultze Granite, and are exposed in the mining pits of Miami-Inspiration and Copper Cities deposits (Seedorff et al., 2008). A sample of Schultze Granite porphyry (R-S-13) was collected from an outcrop on the south side of US-60, immediately before the bridge over Pinto Creek (Fig. 3.2 a) The porphyry phase has a boundary which is gradational with the main phase of the granite, and is on the order of 10s of metres in width. The exact dimensions are unclear due to the subtlety of the textural variation between it and the main phase of the granite. In hand specimen, the porphyry phase may be distinguished by the presence of rounded quartz eye phenocrysts, and a fine grained, aplitic matrix. Phenocrysts of plagioclase are <3mm in size, euhedral, and contain inclusions of apatite and biotite (Fig. 3.14 a). The aplitic groundmass is primarily composed of K-feldspar and quartz, with some subordinate plagioclase. Grains in the groundmass are anhedral and are typically 250 µm or less in size. Some K-feldspar megacrysts are also observed in this rock (Fig. 3.14 f).

#### 3.4.3.3 *K-feldspar megacrysts*

The main phase of the Schultze Granite shows some textural heterogeneity, primary due to the relative abundance of K-feldspar megacrysts. Several samples of large K-feldspar megacrysts (up to 3 cm) were collected, and thin sections were made of 2 of these samples. These megacrysts had been weathered out of the host rock, and were concentrated in a stream bed on the south side of US-60. Megacrysts were also studied in situ in the granites.

Megacrysts are typically zoned, and the zoning patterns are frequently irregular. They contain abundant

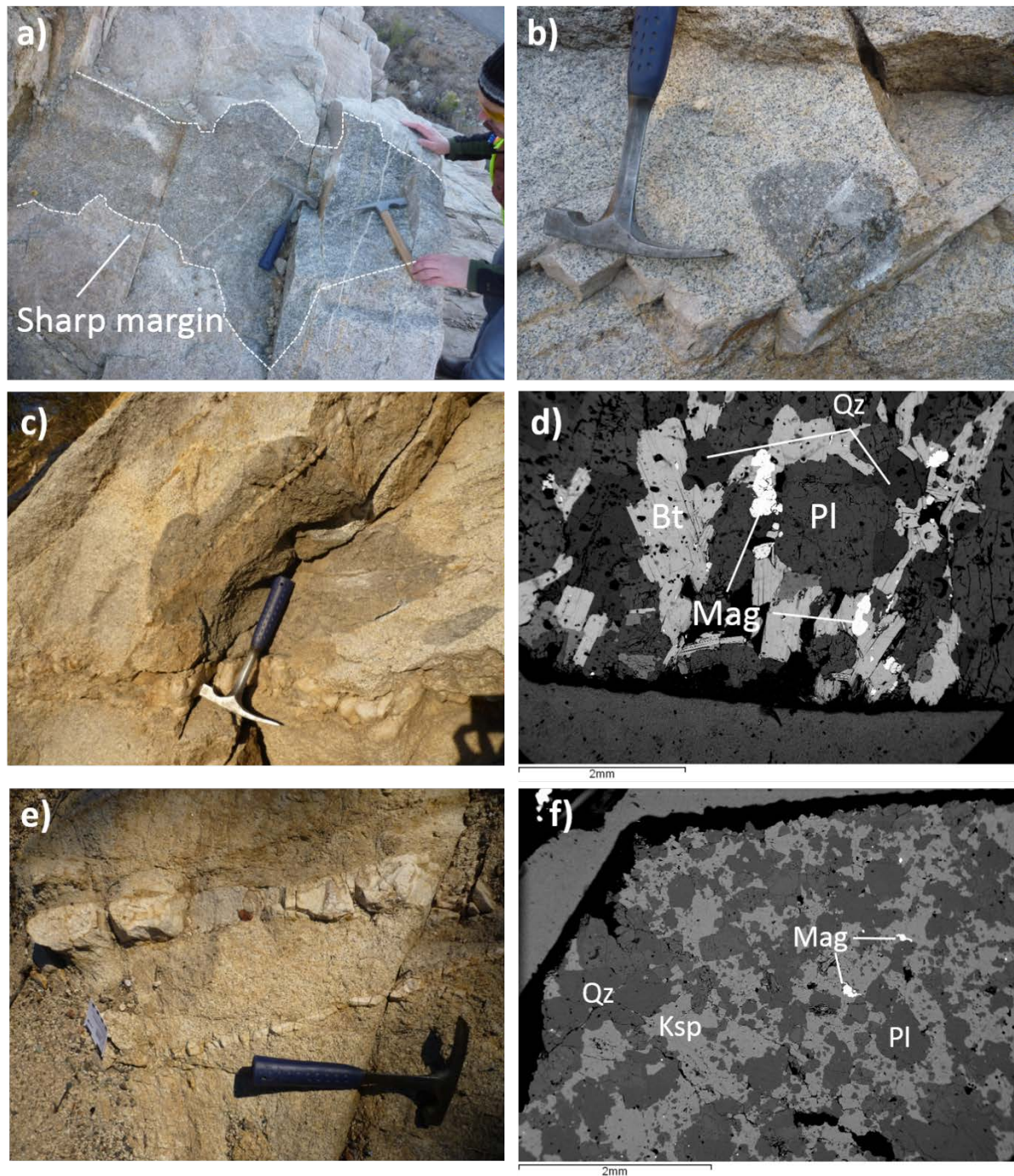


Figure 3.15. (a-c) Biotite rich enclaves in the Schultze Granite. (d) SEM backscatter image of sample R-S-13, the enclave pictures in (a). (e) Aplite dykes in the Schultze Granite. (f) SEM backscatter image of a sample (R-S-1) of Schultze aplite dykes.

inclusions of plagioclase, and subordinate quartz and biotite. Magnetite and apatite inclusions are found in some samples. Phenocrysts are aligned with their long axes parallel to zones (Fig. 3.14 e). Megacrysts commonly show perthite exsolution lamellae, which are darker than plagioclase inclusions in backscatter SEM images. When observed in the context of the rock, the margins of the megacryst may be seen extending out as ‘tendrils’ in between the grains of the surrounding matrix (Fig. 3.14)

#### *3.4.3.4 Biotite-rich enclaves*

The Schultze Granite contains enclaves of biotite-rich material. These enclaves are sparsely distributed throughout the granite, and vary in size from 0.5 to 3 m in size (Fig. 3.15 a-d). One such example, from which sample R-S-12 was collected, is located in the central section of the granite. This enclave is approximately equidimensional in outcrop, with dimensions of 2x3 m. The margins of this enclave are irregular and sharp, with no chilled or baked margins present in the enclave or the host granite (Fig. 3.15 a). Both the host granite and the enclave are cut by minor quartz veins. The rock is darker in colour than the surrounding main phase granite, and contains approximately equal proportions of biotite (1 mm or less, subhedral), plagioclase (1-2 mm, subhedral to euhedral), K-feldspar (< 1mm, anhedral), with subordinate and anhedral quartz (<10 %, < 1mm). Sample R-SX-1 is a sample from a smaller biotite-rich enclave, which has a similar texture. Large apatite (up to 500 µm) is a common accessory mineral in these enclaves, along with subordinate monazite, usually found as inclusions in apatite.

#### *3.4.3.5 Aplite dykes*

Narrow aplite dykes are (<20 cm wide) are observed cross-cutting the granite in the western margin near the contact with the Apache Leap tuff. These dykes are upright and bifurcating, and strike in a NNE direction. They comprise a fine-grained assemblage (< 1mm) of subhedral plagioclase, quartz and K-feldspar (~40 %). Very few ferromagnesian minerals

are present in these rocks. Small (20  $\mu\text{m}$ ) grains of magnetite are occasionally observed (Fig. 3.15 f)

#### *3.4.3.6 Apache Leap intrusions*

Several small Laramide dykes and sills outcrop in the Apache Leap hills above the town of Superior, close to the Resolution deposit. They are intruded into the Palaeozoic rocks, primarily of the Naco Formation. Most of these intrusions are felsic, and one is mafic. Felsic Apache Leap intrusions are narrow (<10 m wide) dykes and sills that generally strike in the direction of the deposit, subparallel to the Magma Vein and the North and South Boundary Faults (059°; Fig. 3.2 b).

One intrusion is larger than the others (~20 m wide) with an equidimensional outcrop pattern (R-RF-G; Fig. 3.2 b). The contact between these intrusions and the Naco Fm is only clearly exposed in a few places (Fig. 3.16 a). Samples were collected from 3 intrusions on either side of a small valley south of US-60, although other intrusions have previously been mapped further along the Apache Leap escarpment (H. Martin, pers. comm., 2011). Felsic Apache Leap intrusions are typically sparsely porphyritic (Fig. 3.16 b), with a phenocryst assemblage of plagioclase (15 %), quartz eyes (5 %), and subordinate chloritised hornblende (<5 %), in a light brown to green groundmass (70 %). Euhedral phenocrysts of albitic plagioclase are up to 5 mm in size, and are partly altered to sericite and calcite. Quartz eyes up to 3 mm in size are occasional phenocrysts. These grains have rounded edges and in some cases have an irregular shape. Relict hornblende phenocrysts are small (<1 mm), and are completely altered to a fine-grained assemblage of chlorite with subordinate titanite and rutile. The groundmass comprises a fine-grained assemblage (< 10  $\mu\text{m}$ ) of subhedral albite, K-feldspar, quartz, and calcite, with accessory magnetite (<50  $\mu\text{m}$ ) and titanite (<1  $\mu\text{m}$ ; Fig. 3.16 c). Euhedral apatite grains (up to 400  $\mu\text{m}$ ) are a common accessory phase in the groundmass. Large patches of inter-grown calcite and quartz are common in the groundmass.



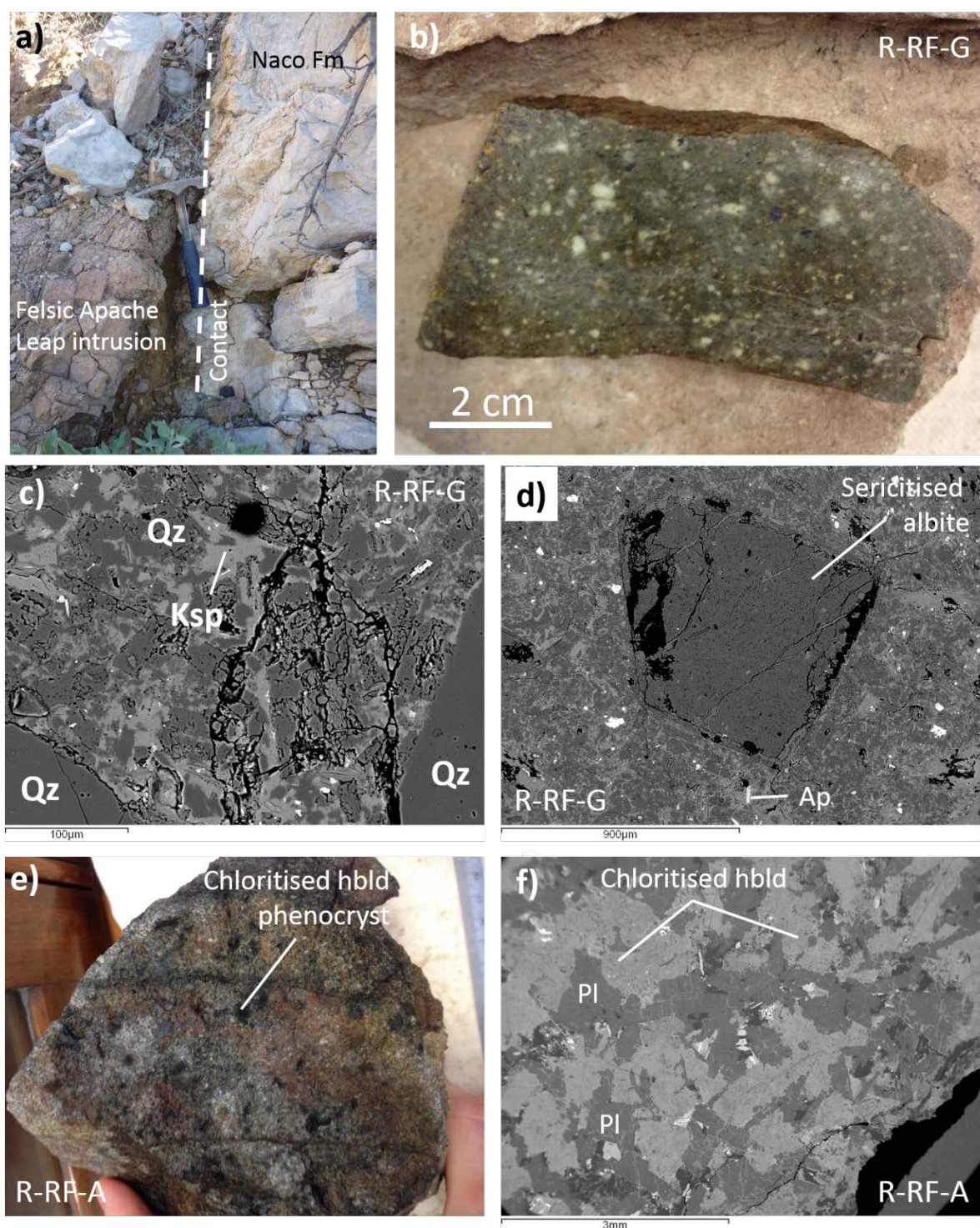


Figure 3.16. Representative images of the Apache Leap intrusions. (a) The contact between an intrusion and the Naco Fm, facing 059°. (b) Sample R-RF-G. (c) SEM backscatter image of the groundmass of R-RF-G. (d) Sericitised feldspar phenocryst of sample R-RF-G. (e) Sample R-RF-A (mafic Apache Leap intrusion). (f) SEM backscatter image of the matrix of R-RF-A.

The mafic Apache Leap intrusion outcrops behind the Magma Club at the eastern edge of Superior. It is a small intrusion with a poor exposure, and is has approximate dimensions of 10 x 10 m. It is hosted in Cambrian Troy quartzite, although the contact is not directly observable. Sample R-RF-A was collected from this locality. This rock is dark green in colour, with red oxidised patches located along cracks (Fig. 3.16 e). The rock is holocrystalline, and contains a medium-grained mineral assemblage, with some larger hornblende phenocrysts. The groundmass assemblage of plagioclase and altered hornblende. Plagioclase laths are sub-euhedral, and are up to 1mm in size. In backscatter images, simple zoning is observed, with darker rims and lighter cores. The mafic component, which is considered to be hornblende due to the habit of relict crystals, has been completely altered to chlorite and calcite, and has a modal abundance of approximately 45% of the rock. Relict hornblende phenocrysts are elongate euhedral laths, up to 1 cm in length. Apatite is the most common accessory phase, occurring as elongate laths up to 200  $\mu\text{m}$  in length.

*Table 3.2. (next page). Summary of the geochemical characteristics of Resolution intrusions. Coloured boxes indicate % difference from median felsic arc value. Dark green cells = >200% difference (i.e. > median felsic arc  $\times$  2), light green = >150%, pale red = <50%, dark red = <25%. LOD = limit of detection. “1st Q” and “3<sup>rd</sup> Q” are the 1st and 3rd quartile respectively, and min and max are the minimum and maximum value determined for each group during this study.*

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|                                |       | Potassic |         |       |         |       | Sericitic |        |        |        |       | Aplite  |        | LOD   | Median felsic arc |
|--------------------------------|-------|----------|---------|-------|---------|-------|-----------|--------|--------|--------|-------|---------|--------|-------|-------------------|
|                                |       | min.     | 1st     | med.  | 3rd     | max.  | min.      | 1st    | med.   | 3rd    | max.  | R-2B-14 | R-2B-2 |       |                   |
| SiO <sub>2</sub>               | wt. % | 61       | 67.325  | 68.9  | 70.025  | 74.2  | 60.6      | 68.275 | 72.1   | 74.15  | 77.7  | 68.4    | 65     | 0.01  | 68.6              |
| Al <sub>2</sub> O <sub>3</sub> | wt. % | 9.82     | 13.225  | 14.1  | 15.1875 | 15.9  | 9.93      | 11.6   | 13.5   | 14.375 | 15.7  | 15.9    | 13.85  | 0.01  | 15.2              |
| FeOt                           | wt. % | 0.95     | 1.64    | 2.16  | 2.84    | 3.58  | 0.45      | 2.70   | 3.04   | 3.93   | 6.33  | 3.58    | 6.6    | 0.01  | 3.29              |
| CaO                            | wt. % | 0.05     | 0.25    | 0.595 | 2.255   | 3.89  | 0.03      | 0.0975 | 0.24   | 1.0425 | 3.09  | 0.07    | 0.12   | 0.01  | 2.43              |
| MgO                            | wt. % | 0.41     | 0.65    | 1.025 | 1.1675  | 2.12  | 0.09      | 0.4175 | 0.57   | 0.9725 | 2     | 0.55    | 0.69   | 0.01  | 0.92              |
| Na <sub>2</sub> O              | wt. % | 0.04     | 0.14    | 0.19  | 0.2375  | 0.36  | 0.02      | 0.04   | 0.06   | 0.0725 | 0.26  | 0.04    | 0.03   | 0.01  | 4.37              |
| K <sub>2</sub> O               | wt. % | 4.23     | 7.2325  | 8.03  | 8.505   | 9.77  | 1.15      | 3.5175 | 4.135  | 4.6125 | 9     | 3.72    | 3.83   | 0.01  | 2.61              |
| TiO <sub>2</sub>               | wt. % | 0.23     | 0.2975  | 0.425 | 0.465   | 0.61  | 0.06      | 0.2675 | 0.33   | 0.3875 | 0.63  | 0.86    | 0.56   | 0.01  | 0.52              |
| MnO                            | wt. % | 0.01     | 0.01    | 0.01  | 0.02    | 0.1   | 0.01      | 0.01   | 0.01   | 0.01   | 0.03  | bdl     | bdl    | 0.01  | 0.10              |
| P <sub>2</sub> O <sub>5</sub>  | wt. % | 0.05     | 0.0925  | 0.11  | 0.16    | 0.37  | 0.04      | 0.08   | 0.1    | 0.13   | 0.24  | 0.1     | 0.13   | 0.01  | 0.14              |
| C                              | wt. % | 0.01     | 0.02    | 0.03  | 0.0475  | 0.35  | 0.01      | 0.02   | 0.02   | 0.03   | 0.06  | 0.01    | 0.02   | 0.01  | 0.02              |
| S                              | wt. % | 0.77     | 1.18    | 1.775 | 2.04    | 2.52  | 0.41      | 1.7825 | 2.595  | 3.5225 | 5.15  | 2.87    | 5.31   | 0.01  | 0.01              |
| Ba                             | ppm   | 206      | 696.25  | 755   | 830     | 949   | 136       | 327    | 649.5  | 875.25 | 1175  | 183     | 346    | 0.5   | 800               |
| Hf                             | ppm   | 2.8      | 3.125   | 3.45  | 3.925   | 4.7   | 1.3       | 2.775  | 3.35   | 3.525  | 5     | 6       | 4.7    | 0.2   | 5.7               |
| Nb                             | ppm   | 4.2      | 5.65    | 6.6   | 6.975   | 7.4   | 3.3       | 5.575  | 6.3    | 6.925  | 10.4  | 10.5    | 10.1   | 0.2   | 7.7               |
| Rb                             | ppm   | 155      | 189.375 | 205.5 | 220.5   | 256   | 34.7      | 121    | 161    | 177.5  | 210   | 127.5   | 153    | 0.2   | 62.4              |
| Sr                             | ppm   | 37.8     | 123.125 | 260   | 325.25  | 378   | 22.6      | 74.85  | 148    | 247.25 | 587   | 239     | 196.5  | 0.1   | 221               |
| Ta                             | ppm   | 0.3      | 0.425   | 0.5   | 0.5     | 0.7   | 0.3       | 0.4    | 0.5    | 0.525  | 1.5   | 0.8     | 0.8    | 0.1   | 0.58              |
| Th                             | ppm   | 3.36     | 3.9175  | 4.28  | 4.9325  | 6.11  | 2.53      | 3.15   | 3.96   | 4.6725 | 6.84  | 7.62    | 7.12   | 0.05  | 5.53              |
| U                              | ppm   | 1.04     | 1.4625  | 1.775 | 1.92    | 3.97  | 0.8       | 1.1475 | 1.49   | 1.8375 | 6.23  | 10.15   | 10.05  | 0.05  | 2.48              |
| V                              | ppm   | 34       | 48.75   | 74    | 92.75   | 203   | 5         | 55.5   | 71.5   | 97.25  | 130   | 200     | 148    | 5     | 27.5              |
| Y                              | ppm   | 8.3      | 11.025  | 12.4  | 16.675  | 44.7  | 3.5       | 7.7    | 9.7    | 13.8   | 26.7  | 10.5    | 11.8   | 0.5   | 37.7              |
| Zr                             | ppm   | 88       | 105.25  | 113   | 138.25  | 158   | 24        | 92.5   | 108    | 118.75 | 191   | 222     | 160    | 2     | 178               |
| Ag                             | ppm   | 0.25     | 0.25    | 0.85  | 1.2     | 4.5   | 0.25      | 0.4375 | 0.7    | 1.225  | 6.5   | 4.6     | 0.7    | 0.5   | 2.1               |
| Co                             | ppm   | 0.5      | 2.25    | 4     | 9.25    | 21    | 0.5       | 2      | 6      | 18.25  | 28    | 20      | 34     | 1     | 9.71              |
| Cu                             | ppm   | 225      | 1630    | 4545  | 9372.5  | 16250 | 63        | 1512.5 | 5230   | 7977.5 | 33700 | 2600    | 4120   | 1     | 19                |
| Mo                             | ppm   | 2        | 31      | 73    | 131     | 477   | 5         | 55.75  | 106    | 184.5  | 1615  | 266     | 828    | 1     | 3.9               |
| Ni                             | ppm   | 5        | 7.25    | 9     | 12.75   | 23    | 1         | 5.75   | 8.5    | 14.25  | 57    | 14      | 12     | 1     | 6.3               |
| Pb                             | ppm   | 2        | 6       | 8.5   | 16.25   | 20    | 2         | 6      | 10.5   | 50.75  | 255   | 404     | 11     | 2     | 12.1              |
| Zn                             | ppm   | 10       | 23.25   | 37.5  | 69      | 581   | 2         | 6.75   | 14.5   | 35     | 272   | 9       | 11     | 2     | 80                |
| Au                             | ppm   | 0.001    | 0.0035  | 0.011 | 0.018   | 0.057 | 0.001     | 0.0048 | 0.0095 | 0.0205 | 0.074 | 0.023   | 0.011  | 0.001 | 0.002             |
| Sc                             | ppm   | 0.5      | 1.75    | 2.4   | 3.025   | 4.6   | 0.3       | 0.5    | 0.7    | 1.125  | 2.5   | 1.2     | 0.9    | 0.1   | 12                |

|                                  |       | Potassic |        |       |        |       | Sericitic |        |       |        |       | Aplite  |        | LOD  | Median felsic arc |
|----------------------------------|-------|----------|--------|-------|--------|-------|-----------|--------|-------|--------|-------|---------|--------|------|-------------------|
|                                  |       | min.     | 1st    | med.  | 3rd    | max.  | min.      | 1st    | med.  | 3rd    | max.  | R-2B-14 | R-2B-2 |      |                   |
| La                               | ppm   | 16       | 18.2   | 23.85 | 26.5   | 43.7  | 8.1       | 13.5   | 19.45 | 24.4   | 40    | 23.1    | 21.3   | 0.5  | 18.81             |
| Ce                               | ppm   | 33.5     | 37.925 | 47.3  | 53.9   | 91.1  | 16.3      | 29.35  | 39.55 | 49.075 | 80.2  | 46.4    | 42.3   | 0.5  | 38.47             |
| Pr                               | ppm   | 4.03     | 4.4125 | 5.46  | 6.3225 | 10.75 | 1.86      | 3.43   | 4.42  | 5.66   | 9.2   | 5.51    | 5.05   | 0.03 | 5.19              |
| Nd                               | ppm   | 16.2     | 17.025 | 20.15 | 23.7   | 39.8  | 6.9       | 12.975 | 17.4  | 22     | 36.7  | 21.4    | 19.2   | 0.1  | 20.93             |
| Sm                               | ppm   | 2.7      | 3.255  | 3.755 | 4.5725 | 6.67  | 1.44      | 2.3175 | 3.225 | 4.0175 | 10.95 | 4       | 3.47   | 0.03 | 5.35              |
| Eu                               | ppm   | 0.75     | 0.885  | 1.005 | 1.3375 | 2.07  | 0.38      | 0.6675 | 0.825 | 1.0425 | 2.46  | 0.85    | 0.75   | 0.03 | 1.14              |
| Gd                               | ppm   | 1.88     | 2.4675 | 2.78  | 3.73   | 8.13  | 1.11      | 1.8475 | 2.405 | 3.23   | 7.87  | 2.43    | 2.31   | 0.05 | 6.18              |
| Tb                               | ppm   | 0.26     | 0.35   | 0.4   | 0.505  | 1.32  | 0.14      | 0.25   | 0.335 | 0.455  | 1.03  | 0.27    | 0.34   | 0.01 | 1.03              |
| Dy                               | ppm   | 1.43     | 1.8675 | 2.225 | 2.7975 | 7.54  | 0.63      | 1.345  | 1.805 | 2.4325 | 4.93  | 1.51    | 1.83   | 0.05 | 6.91              |
| Ho                               | ppm   | 0.29     | 0.39   | 0.44  | 0.585  | 1.44  | 0.12      | 0.2775 | 0.35  | 0.5025 | 0.99  | 0.34    | 0.4    | 0.01 | 1.46              |
| Er                               | ppm   | 0.76     | 0.9775 | 1.16  | 1.5225 | 3.58  | 0.34      | 0.735  | 0.92  | 1.2325 | 2.43  | 1.1     | 1.21   | 0.03 | 4.19              |
| Tm                               | ppm   | 0.11     | 0.15   | 0.165 | 0.2225 | 0.49  | 0.06      | 0.1175 | 0.135 | 0.185  | 0.38  | 0.21    | 0.2    | 0.01 | 0.65              |
| Yb                               | ppm   | 0.73     | 0.9075 | 1.075 | 1.41   | 2.56  | 0.43      | 0.725  | 0.85  | 1.15   | 2.19  | 1.43    | 1.44   | 0.03 | 3.89              |
| Lu                               | ppm   | 0.12     | 0.1425 | 0.17  | 0.205  | 0.38  | 0.07      | 0.12   | 0.135 | 0.18   | 0.34  | 0.28    | 0.25   | 0.01 | 0.616             |
| LOI                              | wt. % | 1.87     | 2.66   | 3.37  | 4.03   | 5.75  | 1.47      | 3.56   | 4.18  | 4.97   | 6.80  | 5.43    | 6.26   |      | 1.09              |
| Sr/Y                             |       | 1.54     | 10.08  | 14.79 | 27.27  | 34.68 | 1.62      | 6.32   | 15.63 | 28.13  | 68.86 | 22.76   | 16.65  |      | 5.6               |
| V/Sc                             |       | 10.6     | 23.5   | 29.5  | 39.6   | 154.0 | 10.0      | 63.8   | 95.4  | 119.2  | 244.0 | 166.7   | 164.4  |      | 2.5               |
| Eu/Eu*                           |       | 0.83     | 0.87   | 0.94  | 0.99   | 1.08  | 0.77      | 0.89   | 0.93  | 0.98   | 1.20  | 0.83    | 0.81   |      | 0.71              |
| Dy <sub>N</sub> /Yb <sub>N</sub> |       | 1.14     | 1.31   | 1.40  | 1.52   | 1.97  | 0.97      | 1.24   | 1.37  | 1.50   | 1.67  | 0.71    | 0.85   |      | 1.12              |
| La <sub>N</sub> /Yb <sub>N</sub> |       | 7.57     | 11.97  | 15.18 | 17.74  | 28.24 | 6.68      | 10.70  | 16.01 | 20.90  | 31.73 | 11.59   | 10.61  |      | 3.3               |
| La <sub>N</sub> /Sm <sub>N</sub> |       | 4.51     | 5.34   | 5.93  | 6.41   | 6.97  | 2.83      | 5.28   | 5.68  | 6.38   | 8.78  | 5.78    | 6.14   |      | 2.09              |
| ΣREE                             | ppm   | 81.3     | 88.4   | 110.9 | 128.1  | 203.5 | 39.9      | 70.5   | 88.6  | 115.5  | 197.1 | 108.8   | 100.1  |      | 106.4             |
| CCPI                             | %     | 13.3     | 22.2   | 26.6  | 36.4   | 51.3  | 5.5       | 44.4   | 48.8  | 54.4   | 68.1  | 52.4    | 65.4   |      | 32.0              |
| A.I.                             | %     | 68.5     | 79.6   | 91.9  | 95.1   | 98.4  | 61.5      | 85.1   | 93.3  | 96.4   | 98.0  | 97.5    | 96.8   |      | 34.1              |
| ASI                              |       | 0.60     | 0.81   | 0.92  | 1.19   | 1.87  | 0.72      | 1.31   | 1.87  | 1.95   | 7.82  | 2.66    | 2.23   |      | 1.05              |

Table 3.2. (contd).



|                                |       | Apache Leap |        |        |        |        |        | Schultze Aplite |       | Enclave | Schultze Granite main phase |         |         |        |       |        |        | LOD   | Median felsic arc |
|--------------------------------|-------|-------------|--------|--------|--------|--------|--------|-----------------|-------|---------|-----------------------------|---------|---------|--------|-------|--------|--------|-------|-------------------|
|                                |       | R-RF-A      | R-RF-B | R-RF-C | R-RF-D | R-RF-E | R-RF-F | R-S-2           | R-S-7 | R-S-12b | R-S-11b                     | R-S-13b | R-S-14b | R-S-3b | R-S-4 | R-S-8b | R-S-9b |       |                   |
| SiO <sub>2</sub>               | wt. % | 51.3        | 64.1   | 61.2   | 61     | 63.3   | 64.9   | 78.1            | 77.8  | 67.1    | 71                          | 73.4    | 72.2    | 70.9   | 71.1  | 70.9   | 71.4   | 0.01  | 68.6              |
| Al <sub>2</sub> O <sub>3</sub> | wt. % | 14.25       | 15.75  | 15     | 15.25  | 14.85  | 15.45  | 12.75           | 11.8  | 14.8    | 15.4                        | 14.55   | 13.6    | 14.8   | 14.7  | 14.8   | 14.7   | 0.01  | 15.2              |
| FeOt                           | wt. % | 9.4         | 3.9    | 3.5    | 2.9    | 2.8    | 2.9    | 0.3             | 0.5   | 5.0     | 1.8                         | 1.5     | 0.9     | 1.7    | 1.7   | 1.8    | 1.5    | 0.01  | 3.29              |
| CaO                            | wt. % | 10.2        | 2.28   | 6.08   | 6.09   | 4.53   | 3.47   | 0.36            | 0.46  | 2.33    | 1.98                        | 1.42    | 1.06    | 2.04   | 1.71  | 2.13   | 1.63   | 0.01  | 2.43              |
| MgO                            | wt. % | 6.22        | 2.07   | 2.05   | 1.74   | 1.79   | 1.78   | 0.02            | 0.05  | 1.6     | 0.43                        | 0.41    | 0.24    | 0.48   | 0.51  | 0.42   | 0.37   | 0.01  | 0.92              |
| Na <sub>2</sub> O              | wt. % | 1.88        | 2.42   | 0.03   | 0.03   | 0.08   | 1.92   | 2.89            | 3.57  | 4       | 4.55                        | 4.14    | 3.69    | 4.12   | 3.96  | 4.5    | 4.51   | 0.01  | 4.37              |
| K <sub>2</sub> O               | wt. % | 1.47        | 5.52   | 3.23   | 3.04   | 3.97   | 3.53   | 6.52            | 4.59  | 3.13    | 3.26                        | 4.14    | 4.08    | 3.49   | 4.01  | 3.33   | 3.19   | 0.01  | 2.61              |
| TiO <sub>2</sub>               | wt. % | 0.88        | 0.7    | 0.66   | 0.67   | 0.39   | 0.41   | 0.05            | 0.05  | 0.76    | 0.27                        | 0.24    | 0.13    | 0.27   | 0.29  | 0.24   | 0.2    | 0.01  | 0.52              |
| MnO                            | wt. % | 0.17        | 0.05   | 0.08   | 0.12   | 0.05   | 0.06   | bdl             | 0.01  | 0.11    | 0.04                        | 0.03    | 0.02    | 0.03   | 0.03  | 0.04   | 0.04   | 0.01  | 0.10              |
| P <sub>2</sub> O <sub>5</sub>  | wt. % | 0.14        | 0.22   | 0.21   | 0.23   | 0.16   | 0.15   | 0.01            | 0.02  | 0.35    | 0.08                        | 0.09    | 0.11    | 0.1    | 0.09  | 0.09   | 0.09   | 0.01  | 0.14              |
| C                              | wt. % | 0.14        | 0.38   | 1.23   | 1.24   | 0.97   | 0.77   | 0.03            | 0.01  | 0.05    | 0.005                       | 0.01    | 0.01    | 0.01   | 0.02  | 0.02   | 0.01   | 0.01  | 0.02              |
| S                              | wt. % | 0.01        | 0.01   | 0.01   | 0.01   | 0.01   | 0.01   | 0.005           | 0.01  | 0.01    | 0.005                       | 0.005   | 0.005   | 0.005  | 0.01  | 0.005  | 0.005  | 0.01  | 0.01              |
| Ba                             | ppm   | 248         | 1190   | 442    | 363    | 640    | 800    | 221             | 293   | 844     | 1115                        | 1060    | 481     | 1225   | 1110  | 933    | 985    | 0.5   | 800               |
| Hf                             | ppm   | 3.2         | 4.1    | 4.1    | 4.2    | 3.4    | 3.7    | 2.6             | 2.5   | 8.3     | 4.7                         | 4.5     | 2.8     | 4.3    | 4.1   | 3.9    | 3.8    | 0.2   | 5.7               |
| Nb                             | ppm   | 5           | 7      | 6.9    | 7      | 5      | 5.3    | 22              | 7.8   | 18.7    | 8.1                         | 9.1     | 9       | 7.3    | 8.1   | 10.1   | 9.5    | 0.2   | 7.7               |
| Rb                             | ppm   | 78.1        | 205    | 153    | 150.5  | 155    | 160.5  | 291             | 209   | 152.5   | 106.5                       | 128.5   | 150.5   | 90.5   | 148   | 114    | 99.8   | 0.2   | 62.4              |
| Sr                             | ppm   | 160.5       | 368    | 85.1   | 75.4   | 88.9   | 329    | 217             | 251   | 606     | 737                         | 597     | 365     | 671    | 625   | 633    | 608    | 0.1   | 221               |
| Ta                             | ppm   | 0.3         | 0.4    | 0.4    | 0.4    | 0.3    | 0.3    | 4.2             | 1.6   | 1.1     | 0.7                         | 0.7     | 0.8     | 0.7    | 0.7   | 1      | 1.1    | 0.1   | 0.58              |
| Th                             | ppm   | 3.09        | 4.54   | 4.35   | 4.56   | 3.49   | 3.69   | 9.32            | 7.86  | 18.6    | 5.92                        | 5.48    | 4.64    | 5.93   | 6.2   | 5.88   | 4.35   | 0.05  | 5.53              |
| U                              | ppm   | 0.75        | 1.02   | 1.11   | 1.44   | 0.99   | 0.85   | 3.21            | 2.52  | 2.76    | 1.22                        | 1.17    | 1.08    | 0.77   | 0.9   | 1.06   | 0.92   | 0.05  | 2.48              |
| V                              | ppm   | 284         | 116    | 114    | 115    | 66     | 66     | 7               | 8     | 89      | 30                          | 27      | 13      | 35     | 37    | 29     | 27     | 5     | 27.5              |
| Y                              | ppm   | 30.5        | 9.8    | 9.5    | 9.6    | 13.6   | 14.6   | 34.5            | 32.6  | 35.1    | 12.6                        | 12.9    | 13.3    | 11     | 12    | 13.8   | 11.3   | 0.5   | 37.7              |
| Zr                             | ppm   | 122         | 156    | 153    | 155    | 127    | 132    | 30              | 35    | 311     | 178                         | 167     | 88      | 158    | 149   | 146    | 132    | 2     | 178               |
| Ag                             | ppm   | 3           | 1.2    | 1.6    | 2.6    | 0.9    | 0.6    | bdl             | bdl   | bdl     | bdl                         | bdl     | bdl     | bdl    | bdl   | bdl    | bdl    | 0.5   | 2.1               |
| Co                             | ppm   | 39          | 9      | 8      | 11     | 5      | 5      | bdl             | bdl   | 9       | 3                           | bdl     | 0.5     | 2      | 3     | 2      | 2      | 1     | 9.71              |
| Cu                             | ppm   | 136         | 31     | 32     | 45     | 23     | 28     | 4               | 3     | 68      | bdl                         | 4       | 42      | bdl    | 3     | bdl    | 2      | 1     | 19                |
| Mo                             | ppm   | bdl         | bdl    | bdl    | 2      | bdl    | bdl    | bdl             | bdl   | bdl     | bdl                         | bdl     | bdl     | bdl    | bdl   | bdl    | bdl    | 1     | 3.9               |
| Ni                             | ppm   | 55          | 14     | 15     | 16     | 3      | 4      | bdl             | bdl   | 4       | bdl                         | bdl     | bdl     | 2      | 2     | bdl    | bdl    | 1     | 6.3               |
| Pb                             | ppm   | 8           | 10     | 11     | 10     | 2      | 15     | 25              | 23    | 13      | 16                          | 14      | 15      | 19     | 26    | 17     | 18     | 2     | 12.1              |
| Zn                             | ppm   | 136         | 59     | 114    | 530    | 59     | 59     | 4               | 6     | 96      | 32                          | 21      | 14      | 33     | 33    | 28     | 26     | 2     | 80                |
| Au                             | ppm   | 0.005       | 0.001  | 0.003  | 0.001  | 0.001  | 0.001  | bdl             | bdl   | bdl     | bdl                         | bdl     | bdl     | bdl    | bdl   | bdl    | 0.003  | 0.001 | 0.002             |
| Sc                             | ppm   | 6.7         | 2.1    | 2.5    | 2.9    | 1.5    | 1.4    | 0.4             | 0.4   | 7.5     | 2.5                         | 2.2     | 1.7     | 2.4    | 2.6   | 2.4    | 2.3    | 0.1   | 12                |

Table 3.2. (contd).

|                                  |       | Apache Leap |        |        |        |        |        | Schultze Aplite |       | Enclave | Schultze Granite main phase |         |         |        |       |        |        |      | LOD   | Median felsic arc |
|----------------------------------|-------|-------------|--------|--------|--------|--------|--------|-----------------|-------|---------|-----------------------------|---------|---------|--------|-------|--------|--------|------|-------|-------------------|
|                                  |       | R-RF-A      | R-RF-B | R-RF-C | R-RF-D | R-RF-E | R-RF-F | R-S-2           | R-S-7 | R-S-12b | R-S-11b                     | R-S-13b | R-S-14b | R-S-3b | R-S-4 | R-S-8b | R-S-9b |      |       |                   |
| La                               | ppm   | 12.9        | 30.4   | 31.5   | 31.6   | 18.7   | 19.9   | 7.9             | 7.5   | 103     | 31.7                        | 30.2    | 16.4    | 31.6   | 31.5  | 27.9   | 22.4   | 0.5  | 18.81 |                   |
| Ce                               | ppm   | 28.4        | 57.3   | 58.7   | 58.4   | 37.5   | 40     | 19.9            | 16.2  | 207     | 61.9                        | 59.1    | 33.3    | 61.3   | 59.8  | 54.9   | 44.3   | 0.5  | 38.47 |                   |
| Pr                               | ppm   | 3.64        | 6.95   | 6.99   | 7.04   | 4.42   | 4.76   | 2.78            | 2.17  | 23.7    | 7.01                        | 6.57    | 3.85    | 7.05   | 6.93  | 6.39   | 5.12   | 0.03 | 5.19  |                   |
| Nd                               | ppm   | 16.4        | 27.1   | 27.6   | 27.2   | 17.9   | 18.9   | 11.5            | 8.5   | 89.4    | 26.3                        | 24.2    | 14.5    | 25.1   | 25.3  | 22.9   | 18.5   | 0.1  | 20.93 |                   |
| Sm                               | ppm   | 4.14        | 4.59   | 4.76   | 4.62   | 3.46   | 3.63   | 3.76            | 2.44  | 15.5    | 4.45                        | 4.13    | 2.94    | 4.13   | 4.26  | 3.95   | 3.28   | 0.03 | 5.35  |                   |
| Eu                               | ppm   | 1.18        | 1.27   | 1.35   | 1.26   | 0.87   | 0.98   | 0.3             | 0.38  | 1.55    | 0.98                        | 0.94    | 0.5     | 1.02   | 1.02  | 0.91   | 0.76   | 0.03 | 1.14  |                   |
| Gd                               | ppm   | 5.06        | 3.29   | 3.29   | 3.27   | 2.86   | 3.09   | 3.76            | 2.75  | 10.35   | 3.1                         | 3.04    | 2.27    | 2.69   | 2.81  | 2.57   | 2.26   | 0.05 | 6.18  |                   |
| Tb                               | ppm   | 0.82        | 0.4    | 0.37   | 0.38   | 0.41   | 0.42   | 0.71            | 0.61  | 1.35    | 0.41                        | 0.4     | 0.37    | 0.38   | 0.39  | 0.39   | 0.32   | 0.01 | 1.03  |                   |
| Dy                               | ppm   | 4.77        | 1.92   | 1.76   | 1.85   | 2.14   | 2.36   | 4.58            | 4.29  | 6.51    | 2.14                        | 2.08    | 2.02    | 1.95   | 1.96  | 2.3    | 1.93   | 0.05 | 6.91  |                   |
| Ho                               | ppm   | 1.08        | 0.34   | 0.33   | 0.34   | 0.5    | 0.49   | 0.98            | 0.95  | 1.22    | 0.44                        | 0.43    | 0.43    | 0.36   | 0.38  | 0.43   | 0.37   | 0.01 | 1.46  |                   |
| Er                               | ppm   | 2.87        | 0.77   | 0.77   | 0.74   | 1.29   | 1.33   | 2.95            | 3.28  | 2.79    | 1.15                        | 1.12    | 1.11    | 1.07   | 1.08  | 1.27   | 1.05   | 0.03 | 4.19  |                   |
| Tm                               | ppm   | 0.47        | 0.12   | 0.12   | 0.12   | 0.22   | 0.23   | 0.6             | 0.57  | 0.44    | 0.18                        | 0.18    | 0.2     | 0.14   | 0.16  | 0.19   | 0.16   | 0.01 | 0.65  |                   |
| Yb                               | ppm   | 2.77        | 0.69   | 0.66   | 0.66   | 1.23   | 1.33   | 3.89            | 4.29  | 2.3     | 1.1                         | 1.08    | 1.28    | 0.96   | 1.02  | 1.26   | 1.11   | 0.03 | 3.89  |                   |
| Lu                               | ppm   | 0.49        | 0.12   | 0.1    | 0.11   | 0.21   | 0.23   | 0.67            | 0.64  | 0.36    | 0.18                        | 0.18    | 0.2     | 0.15   | 0.16  | 0.2    | 0.16   | 0.01 | 0.616 |                   |
| LOI                              | wt. % | 2.06        | 4.48   | 9.10   | 9.49   | 6.85   | 5.60   | 0.37            | 0.38  | 1.13    | 0.66                        | 0.79    | 0.82    | 0.87   | 0.92  | 0.47   | 0.89   |      | 1.09  |                   |
| Sr/Y                             |       | 5.3         | 37.6   | 9.0    | 7.9    | 6.5    | 22.5   | 6.3             | 7.7   | 17.3    | 58.5                        | 46.3    | 27.4    | 61.0   | 52.1  | 45.9   | 53.8   |      | 5.6   |                   |
| V/Sc                             |       | 42.4        | 55.2   | 45.6   | 39.7   | 44.0   | 47.1   | 17.5            | 20.0  | 11.9    | 12.0                        | 12.3    | 7.6     | 14.6   | 14.2  | 12.1   | 11.7   |      | 2.5   |                   |
| Eu/Eu*                           |       | 0.79        | 1.00   | 1.04   | 0.99   | 0.85   | 0.89   | 0.24            | 0.45  | 0.37    | 0.81                        | 0.81    | 0.59    | 0.94   | 0.90  | 0.87   | 0.85   |      | 0.71  |                   |
| Dy <sub>N</sub> /Yb <sub>N</sub> |       | 1.15        | 1.86   | 1.78   | 1.88   | 1.16   | 1.19   | 0.79            | 0.67  | 1.89    | 1.30                        | 1.29    | 1.06    | 1.36   | 1.29  | 1.22   | 1.16   |      | 1.12  |                   |
| La <sub>N</sub> /Yb <sub>N</sub> |       | 3.34        | 31.60  | 34.23  | 34.34  | 10.91  | 10.73  | 1.46            | 1.25  | 32.12   | 20.67                       | 20.06   | 9.19    | 23.61  | 22.15 | 15.88  | 14.48  |      | 3.3   |                   |
| La <sub>N</sub> /Sm <sub>N</sub> |       | 3.12        | 6.62   | 6.62   | 6.84   | 5.40   | 5.48   | 2.10            | 3.07  | 6.65    | 7.12                        | 7.31    | 5.58    | 7.65   | 7.39  | 7.06   | 6.83   |      | 2.09  |                   |
| ΣREE                             | ppm   | 85          | 135    | 138    | 138    | 92     | 98     | 64              | 55    | 465     | 141                         | 134     | 79      | 138    | 137   | 126    | 102    |      | 106.4 |                   |
| CCPI                             | %     | 82.39       | 42.04  | 62.46  | 60.21  | 52.97  | 46.28  | 3.44            | 6.26  | 48.22   | 22.28                       | 18.55   | 12.44   | 22.34  | 21.51 | 21.67  | 19.56  |      | 32.0  |                   |
| A.I.                             | %     | 38.9        | 61.8   | 46.4   | 43.9   | 55.5   | 49.6   | 66.8            | 53.5  | 42.8    | 36.1                        | 45.0    | 47.6    | 39.2   | 44.4  | 36.1   | 36.7   |      | 34.1  |                   |
| ASI                              |       | 0.8         | 1.0    | 1.1    | 1.2    | 1.2    | 1.2    | 0.9             | 0.9   | 1.1     | 1.1                         | 1.0     | 1.0     | 1.1    | 1.0   | 1.0    | 1.1    | 1.05 |       |                   |

Table 3.2. (contd).

### 3.5 Whole Rock Geochemistry

In all cases, samples for whole rock geochemical analysis were taken from a larger rock sample, the remainder of which was retained for petrological work. Samples were selected to represent a wide variety of rock textures and alteration types. Where possible, large quartz veins were removed from the samples before whole rock analysis. All whole rock geochemistry samples were between 120 g and 740 g, with an average of approximately 260 g.

The whole rock geochemical database (Appendix 2) consists of 70 samples from Resolution. Of these, 48 samples were from drill core, comprising: 3 samples from the matrix of the igneous breccia, 19 samples of RDP, 19 samples of QLP, 5 samples of LP and 2 samples of aplite. Ten samples were collected from the Schultze Granite: 6 samples from the host granite, 1 from coarse-grained granitic porphyry, 1 biotite-rich enclave, and 2 aplite intrusions. Seven samples of unmineralised porphyry intrusions from the Apache Leap range were analysed, including 1 mafic porphyry (R-RF-A).

#### 3.5.1 Focussing questions

The following questions are considered in the presentation and discussion of the whole rock data.

- How does the chemistry of the Resolution rocks compare to typical (barren) arc rocks of similar SiO<sub>2</sub> content?
- How geochemically similar are the Resolution rocks to other Laramide intrusions?
- Do the Resolution rocks contain indicators of fertility (e.g. high Sr/Y, La/Yb, Eu/Eu\*)?
- To what extent does hydrothermal alteration affect whole rock indicators of fertility?

In order to assess these questions, median values for typical arc rocks and typical Laramide rocks were generated. Laramide rock data was drawn from Lang and Titley (1998), who presented 94 whole rock geochemical analyses for fertile porphyry intrusions from across

Arizona. The Aleutian arc was selected as the ‘barren’ arc for these comparative purposes. Median values for the Aleutians arc rocks were generated for rocks with a silica content between 65 and 73 wt. % SiO<sub>2</sub>. These values were calculated to afford a direct comparison between typical arcs and the Resolution dataset of the same degree of fractionation.

These two sets of median values are presented along with median values for the different rock types at Resolution in Table 2.2. In cases where only one value for a particular Resolution rock group is available (e.g. the biotite-rich enclave of the Schultze Granite), these values are presented alongside the medians. In the description and discussion of these data, where the ‘Resolution data’ are discussed, this refers to all the whole rock data from this chapter, including Apache Leap intrusion and Schultze Granite data. ‘Resolution porphyry intrusions’ specifically refers to RDP, QLP, LP, AP and intrusion breccia matrix samples.

### 3.5.2 Major elements

Silica contents for Resolution rocks range from 60.6 to 78.1, with the exception of the mafic Apache Leap intrusion, which has a low silica value (51.3 wt. % SiO<sub>2</sub>). Schultze Granite aplites have the highest silica content (77.8 and 78.1 wt. % SiO<sub>2</sub>). Samples from the main phase of the Schultze Granite samples have SiO<sub>2</sub> values between 71 and 73.4 wt. % SiO<sub>2</sub>. Felsic Apache Leap intrusions have lower silica contents (between 61 and 69.3 wt. % SiO<sub>2</sub>) than the Resolution porphyry intrusions (60.6 to 77.7 wt. % SiO<sub>2</sub>). There is no clear distinction in silica contents between any of the Resolution intrusion types, including the intrusion breccia matrix samples.

The major element chemistry of the Resolution porphyry intrusions has been strongly affected by hydrothermal alteration. For example, Na<sub>2</sub>O concentrations are extremely low

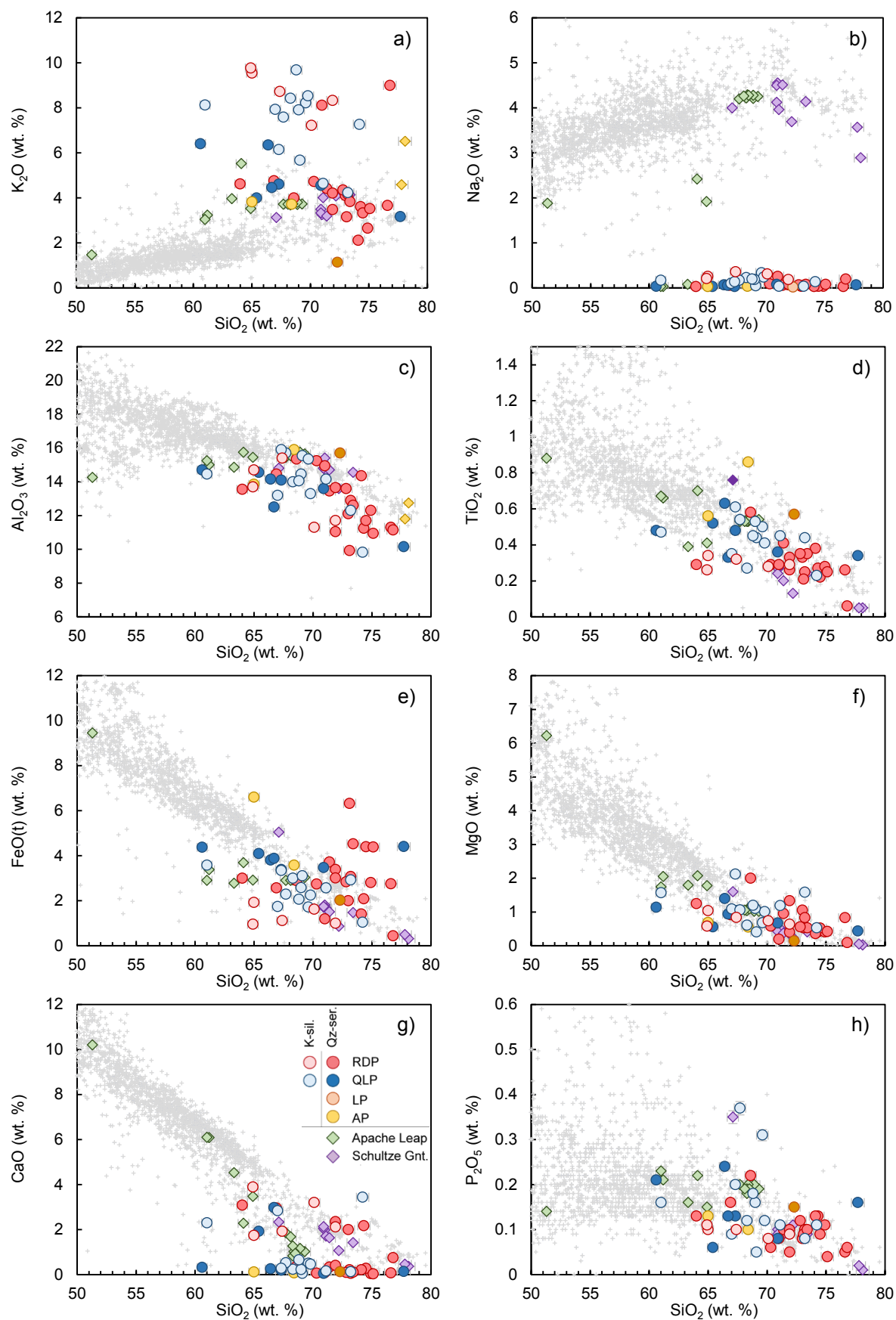


Figure 3.17. (previous page) Harker diagram for major elements: a)  $K_2O$ , b)  $Na_2O$ , c)  $Al_2O_3$ , d)  $TiO_2$ , e)  $FeO$ , f)  $MgO$ , g)  $CaO$ , h)  $P_2O_5$ . Light gray crosses are the barren sample suite from the Aleutians arc. Error bars are smaller than the symbol size for most elements.

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(<0.4 wt. %) compared to rocks from the Schultze Granite, although some felsic Apache Leap intrusions show the same depletions in  $Na_2O$  (Fig. 3.17 b). Potassically altered rocks have elevated  $K_2O$ , with values approaching 10 wt. % (Fig. 3.17 a).  $CaO$  values vary, with some extremely low values (<0.1 wt. %), especially in sericitically altered rocks. Other elements follow liquid lines of descent which are typical of arc rocks, such as  $MgO$ ,  $TiO_2$ , and  $Al_2O_3$ , (Fig. 3.17 c, d, f).

### 3.5.3 Trace elements

Resolution intrusions have multi-element variation plots which are similar to median felsic arc values, with some characteristic differences (Fig. 3.18 a-d). They show strong depletions in Y and Yb, weaker depletions in Zr, Hf, and Sm, and range from depleted to enriched in HFSE (especially Sr and Ba), all with respect to median arc values. There is little systematic difference between potassic and sericitic alteration in terms of these trace elements.

Felsic Apache Leap rocks have trace element patterns which are broadly similar to the Resolution intrusions, with some subtle differences. For example, Y and Yb values are similarly depleted, although Ta is depleted with respect to Nb (Fig. 3.18 f). The Schultze Granite (main phase) trace element patterns are mostly similar to median arc values. Y and Yb are also depleted, and weak depletions are also seen in Zr, Hf, and Sm. The highly fractionated Schultze Granite aplites are strongly depleted in some trace elements, such as Ba,  $P_2O_5$ , Zr, Hf, and Ti (Fig. 3.18 e). By contrast, the more primitive Schultze Granite enclave is enriched in these trace elements with respect to typical arc values, and with respect to the host granite.

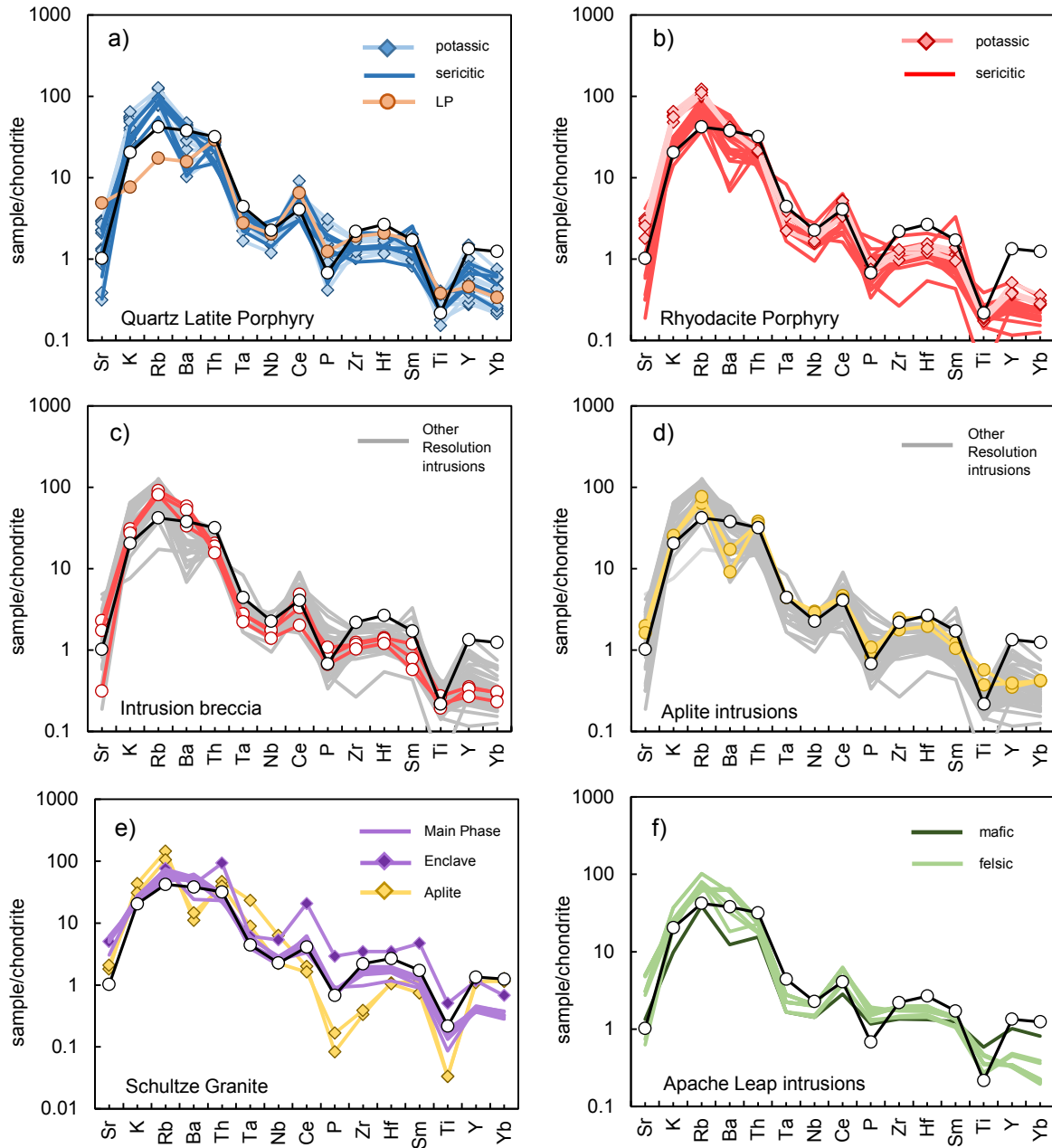


Figure 3.18. MORB-normalised trace element variation diagrams for Resolution rocks. a) quartz latite and latite porphyry, b) rhyodacite porphyry, c) intrusion breccia, d) Resolution aplite intrusions, e) Schultze Granite and associated lithologies, f) Apache Leap intrusions. Black line with open symbols is the median felsic arc value. Normalising values from Rollinson (1993).

### 3.5.4 Rare earth elements

Chondrite normalised REE patterns for the Resolution porphyry intrusions are LREE-enriched, and depleted in M- and HREE, with a greater depletion in HREE (median  $Dy_N/Yb_N$  between 1.17 to 1.45; Fig. 3.19 a-d). REE patterns for Resolution aplite (AP) are slightly different, in that they show a mild enrichment in HREE with respect to MREE (median  $Dy_N/Yb_N = 0.78$ ; Fig. 3.19 c). All Resolution porphyry intrusions lack significant Eu anomalies (median  $Eu/Eu^* = 0.82$  to 1.06).

The Schultze Granite (main phase) samples have similar REE patterns to the Resolution porphyry intrusions (median  $Dy_N/Yb_N = 1.25$  to 1.29; Fig. 3.19 d). However, the Schultze Granite aplite has different REE chemistry. Chondrite normalised values for LREE are broadly equal to HREE, and there is a mild depletion in HREE. Strong negative Eu anomalies also occur (median  $Eu/Eu^* = 0.35$ ). The biotite-rich enclave sample has similar patterns to the main phase granite, albeit with very high  $\Sigma REE$  (466 ppm), and a strong negative Eu anomaly (0.37).

Apache Leap rocks also show similar patterns to Resolution intrusions (Fig. 3.19 f), and show systematic depletions in HREE concentrations with increased  $SiO_2$  content, from the mafic Apache Leap sample, which is the most HREE-enriched ( $La_N/Yb_N = 3.3$ ), to the most  $SiO_2$ -rich felsic sample (max.  $La_N/Yb_N = 30$ ).

The REE patterns of the Resolution porphyry intrusions, felsic Apache Leap intrusion, and Schultze Granite (porphyry and main phases) are strongly similar to those from other Laramide intrusions (Fig. 3.20).



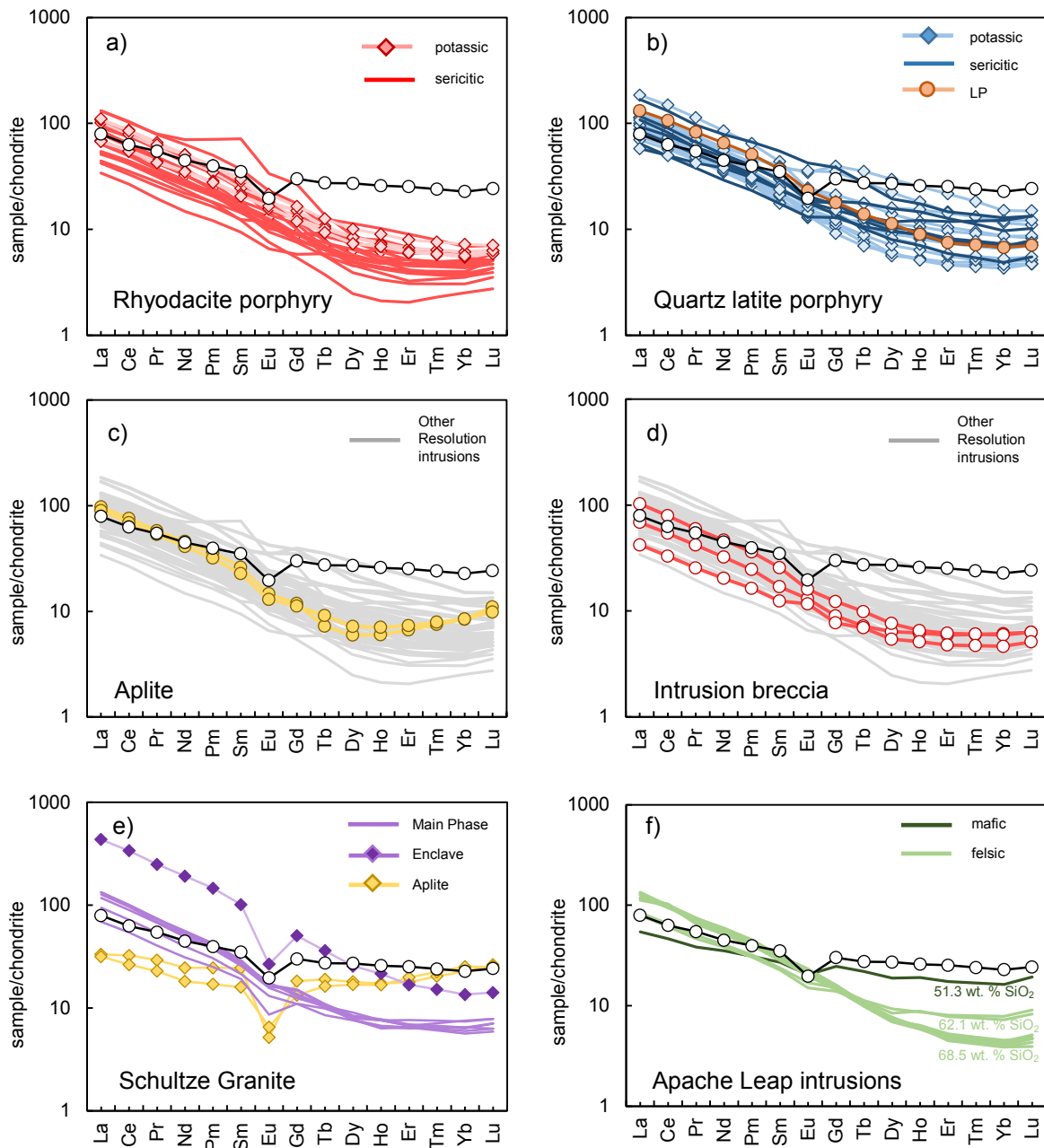


Figure 3.19. Chondrite-normalised trace element variation diagrams for Resolution rocks. a). quartz latite and latite porphyry, b) rhyodacite porphyry, c) intrusion breccia, d) Resolution aplite intrusions, e) Schultze Granite and associated lithologies, f) Apache Leap intrusion. Black line with open symbols is the median felsic arc value. Normalising values from Sun and McDonough (1989).

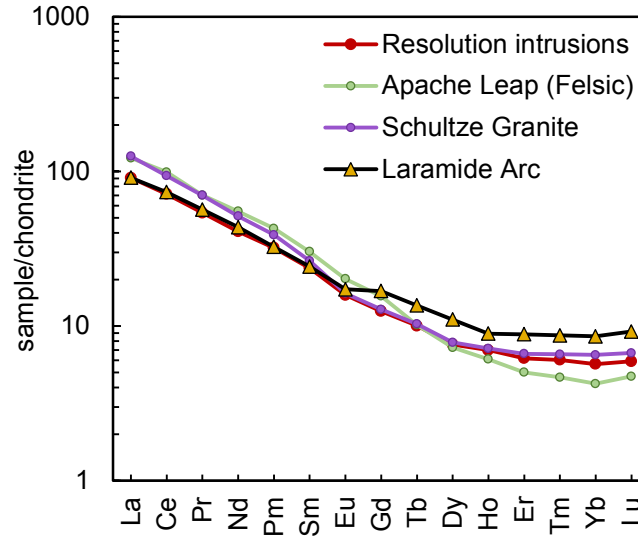


Figure 3.20. Chondrite-normalised REE patterns for median Resolution, felsic Apache Leap, and Schultze Granite (main phase) intrusions. The median value for other porphyry intrusions from the Laramide arc (data from Lang and Titley, 1998) is also shown, to highlight the strong similarity.

### 3.5.5 Fertility indicators

Sr/Y values of Resolution rocks range between the fields of fertile and barren intrusions. Rocks from the Schultze Granite, RDP, and some Apache Leap intrusions in particular have Sr/Y values in the field of ‘adakite-like’ rocks (Fig. 3.21 b). Similarly, La/Yb ratios are high in most rocks, and values in excess of 20 (the lower limit of the ‘adakite-like’ field) not uncommon (Fig. 3.21 c-d).

Eu/Eu\* values of Resolution rocks are consistently between 0.8 and 1.2, even to high silica contents (Fig. 3.21 f). The exception is the Schultze Granite rocks, which frequently show more strong negative Eu anomalies ( $<0.8$ ; Fig. 3.21 f).

V/Sc values for all intrusions are exceptionally higher than both barren and fertile datasets, with values up to 250 (Fig. 3.21 e). This is due to these rocks containing higher V and lower Sc than is typical of arc rocks (Fig. 3.22).

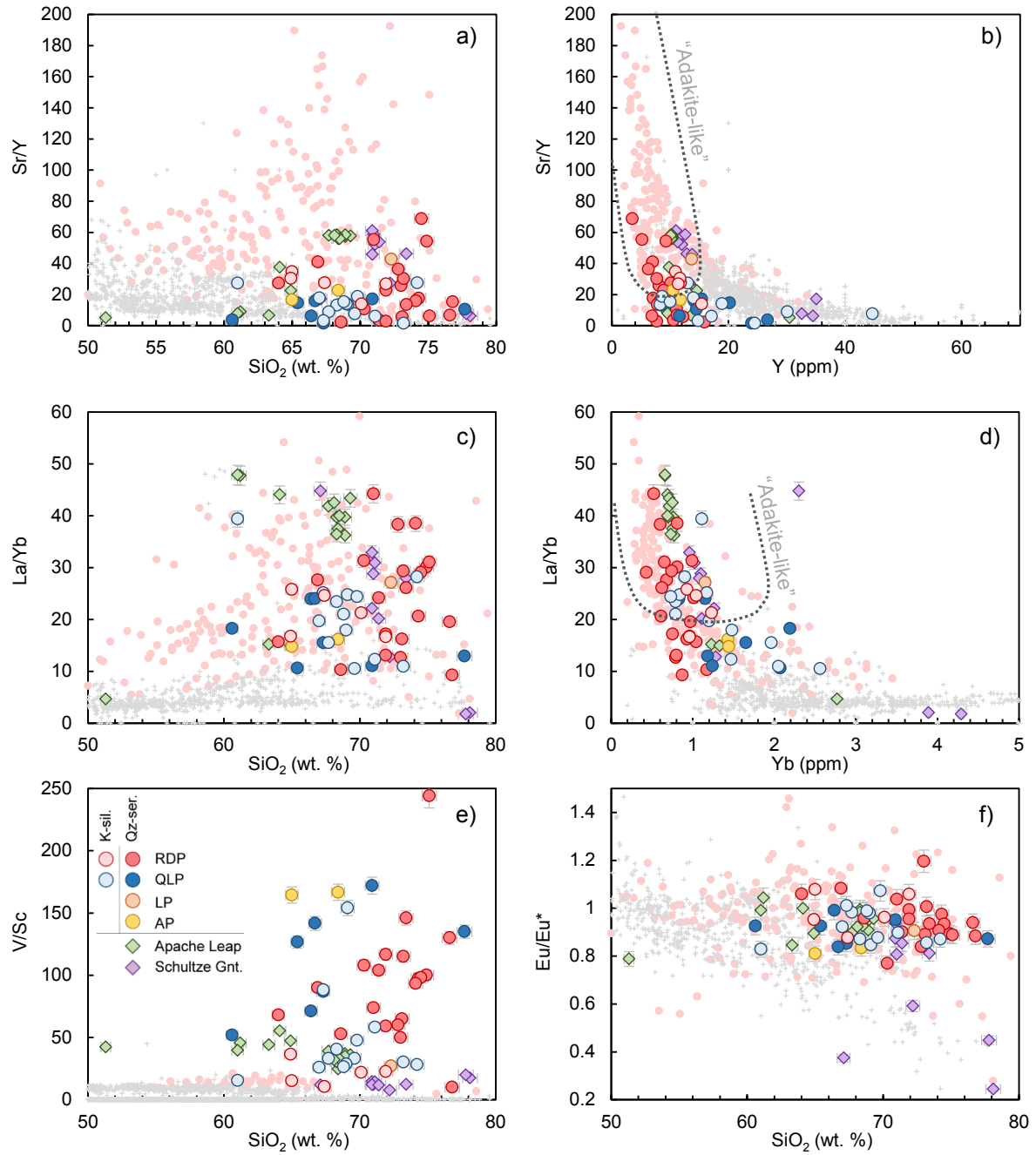


Figure 3.21. Variation of Resolution whole rock geochemistry in terms of certain indicators of magmatic fertility: a,b)  $\text{Sr/Y}$ , c,d)  $\text{La/Yb}$ , e)  $\text{V/Sc}$  and f)  $\text{Eu/Eu}^*$ . Pink symbols are from the 'fertile' dataset of rocks from other porphyry systems. Fields of 'adakite-like' rocks taken from Richards and Kerrich (2007).

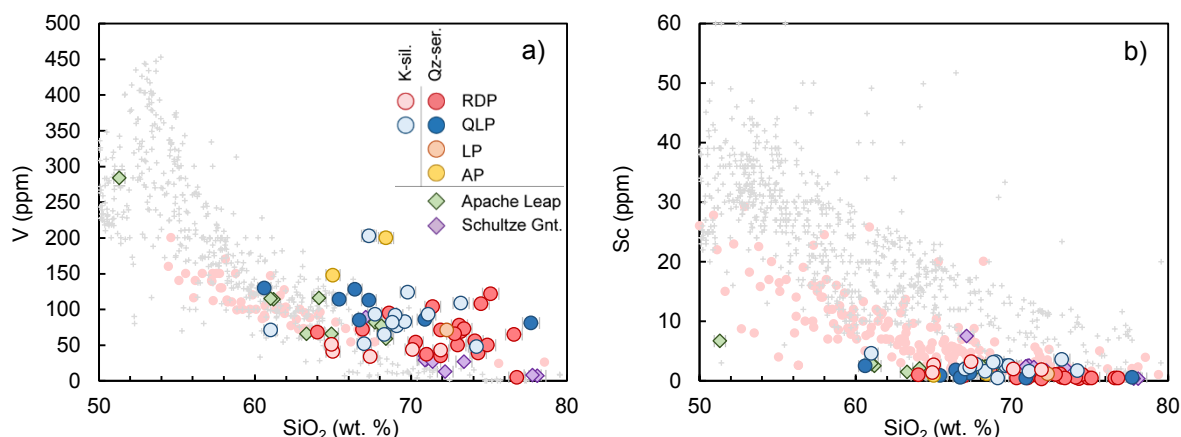


Figure 3.22. Variation of a)  $V$  and b)  $Sc$  with respect to  $SiO_2$  for Resolution rocks, and 'barren' and 'fertile' datasets. Resolution rocks typically have higher  $V$ , and lower  $Sc$  than typical arc magmas.

### 3.5.6 Alteration geochemistry

Several techniques are presented here to assess the effects of different styles of hydrothermal alteration on whole rock geochemistry.

#### 3.5.6.1 Isocon method

The isocon method of Grant (1986; 2005) was applied to whole rock analyses of Resolution intrusions to assess the mass change and mobility of major and selected trace elements during hydrothermal alteration. As all of the Resolution intrusions in this study are strongly affected by hydrothermal alteration, the least altered of the felsic Apache Leap samples (R-RF-F) was selected as the unaltered sample. Two of the Resolution intrusion samples were selected as representative of the two main alteration styles: R-23D-2 (sericitic) and R-13F-2 (potassic). To calculate the isocon, a line passing through the origin, and Zr and  $Al_2O_3$  (the conserved elements) was used, the slope of which is hereafter called ' $s$ '. The concentration change for a given element ( $\Delta C$ ) was calculated with respect to the isocon, using the following formula from Grant (1986):

$$\Delta C = \left[ \left( \frac{1}{s} \right) \times \left( \frac{C_i^A}{C_i^O} \right) - 1 \right] \times C_i^O \quad (3.1)$$

where  $C_i^O$  and  $C_i^A$  are the concentration of element  $i$  in the unaltered and altered rock respectively. Net mass loss was calculated using the following equation:

$$\Delta M = \left[ \left( \frac{1}{s} \right) - 1 \right] \times 100 \quad (3.2)$$

In both potassic and sericitic rocks, the slope of the isocon is  $<1$ , indicating bulk mass gain (Fig. 3.23). Calculated values for  $\Delta M$  are +8.6% (potassic) and +6.2% (sericitic).

Potassic alteration is associated with strong increases  $K_2O$ , and decreases other major elements, especially  $CaO$  and  $Na_2O$  (Fig. 3.24 a). Enrichment occurs in the LREE (La, Ce, and Nd), with M- and HREE largely conserved. Notable depletions occur in V (~25 ppm) and enrichment of Sr (53 ppm) also occurs (Fig. 3.24 c). Sericitic alteration is accompanied by silicification (+3.9 wt. %  $SiO_2$ ), and the loss of  $Na_2O$  and  $CaO$  (Fig. 3.24 b). In the trace elements, there are mild depletions in La and Ce, and mild enrichments in Y M- and HREE are largely conserved. Unlike potassic alteration, there is a very large loss of Sr (~300 ppm) and an increase in V (~30 ppm).

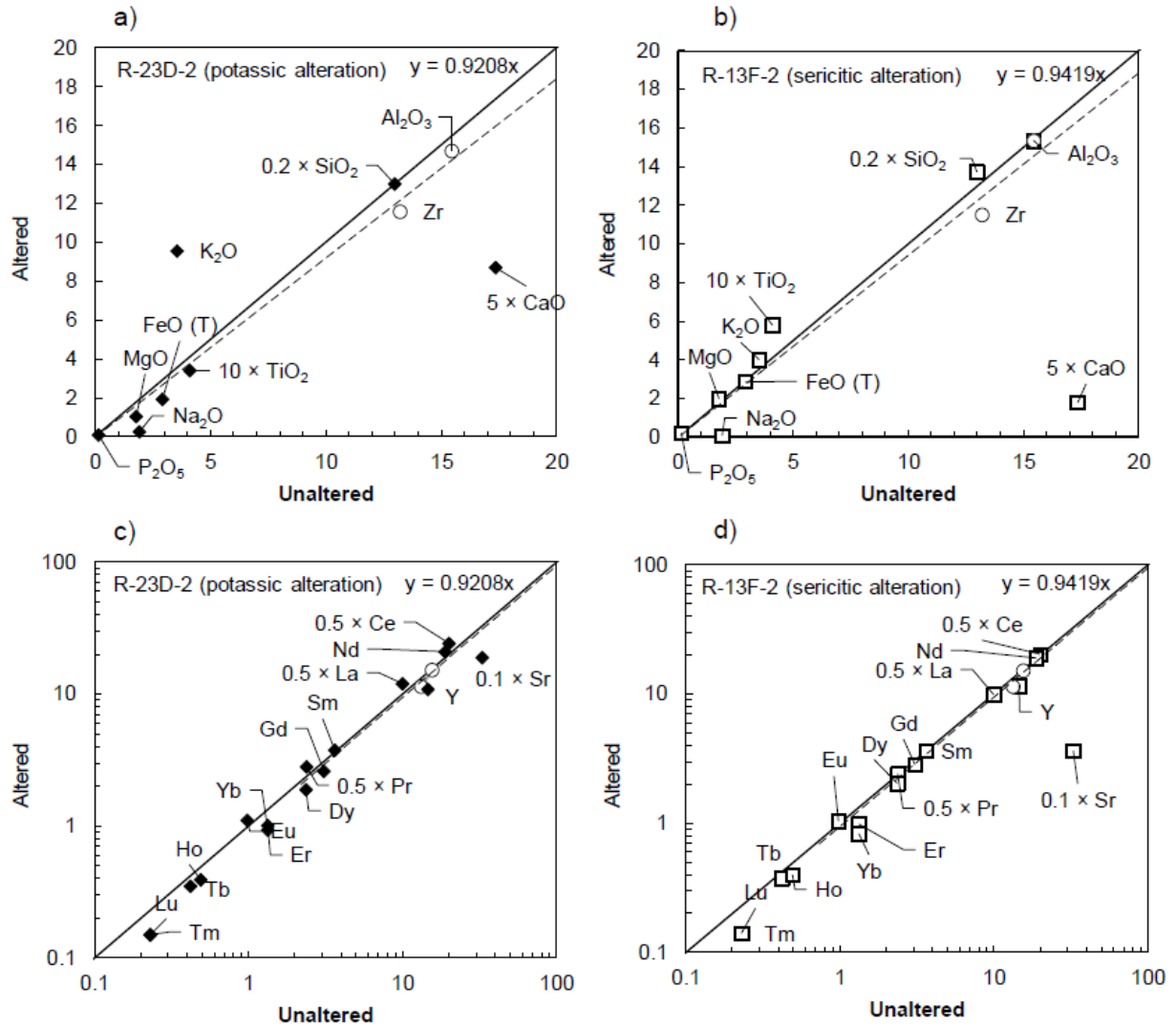


Figure 3.23. Isocon diagrams (after Grant, 1986) for Resolution rocks; potassic alteration, major elements (a) and trace elements (c), and sericitic alteration, major elements (b) and trace elements (d). “Unaltered” is felsic Apache Leap intrusion (R-RF-F) is used as least altered sample.

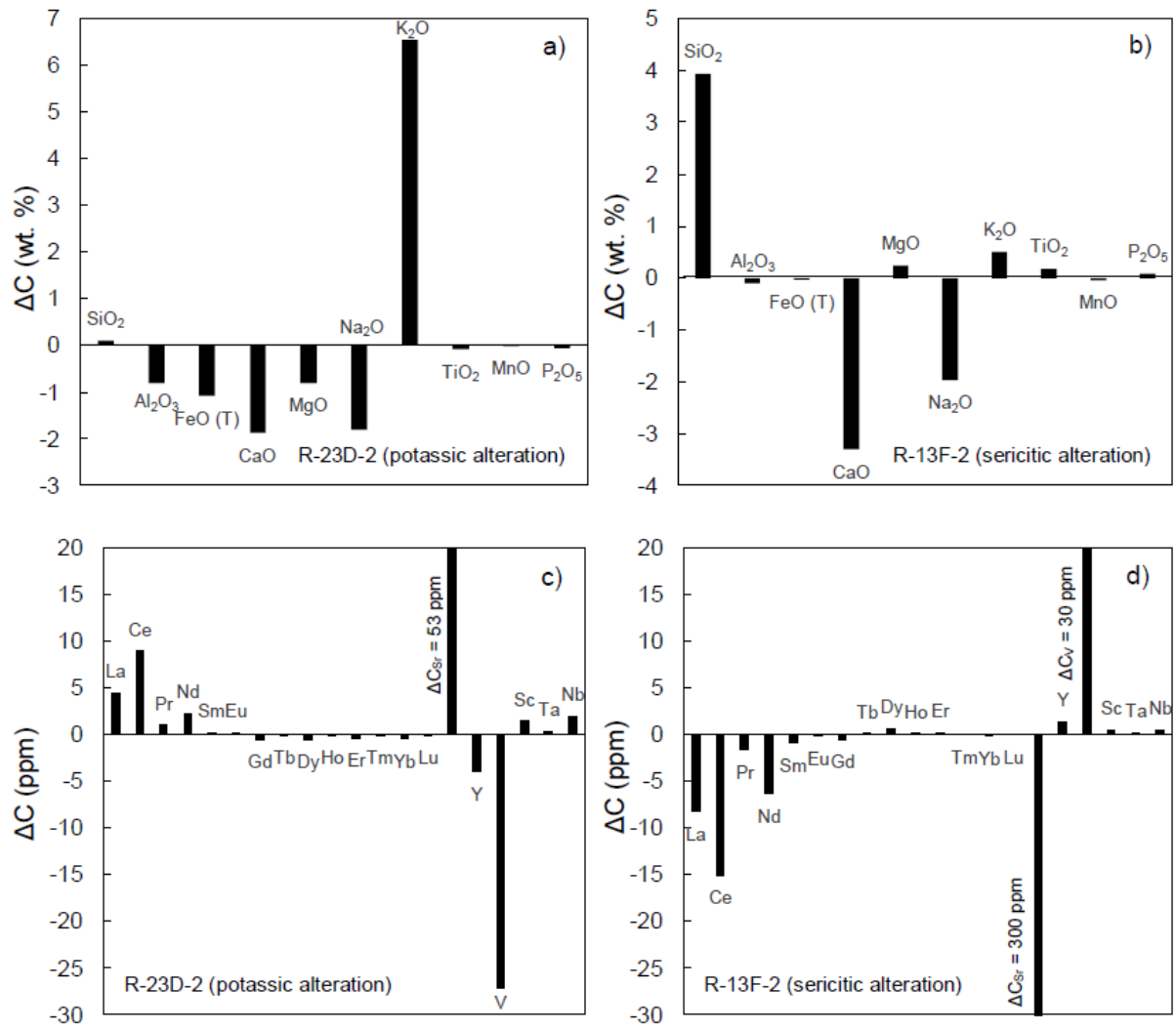


Figure 3.24. Bar charts showing relative losses and gains of (a,b) major elements and (c,d) trace elements) in two rocks which are potassically altered (a,c) and sericitically altered (b,d). Values calculated using the isocon method of Grant (1986).

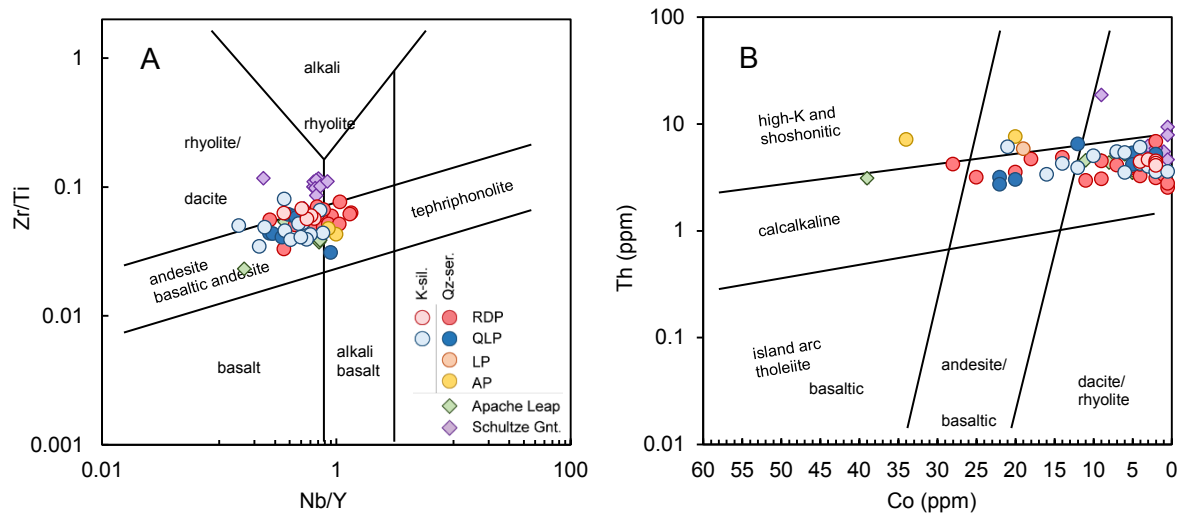


Figure 3.25. Immobility element discriminant diagrams, from a) Pearce (1986), and b) Hastie et al. (2007)

### 3.5.6.1 Immobility element plots

Extensive hydrothermal alteration, especially effecting the  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  concentrations, means that conventional tools for classifying igneous rocks (e.g. total alkali silica) may not be used on Resolution intrusions. The immobile elements discriminant diagrams of Hastie et al. (2007) and Pearce (1986) are used here instead. In both cases, the Resolution intrusions plot on the boundary between andesitic and dacitic/rhyolitic compositions (Fig. 3.25). The Schultze Granite plots in the rhyolitic field (Fig. 3.25 a). Resolution and Schultze Granite classify as calcalkaline rocks, close to the boundary with high-K/shoshonitic rocks.

### 3.5.6.2 Alteration Index and the alteration boxplot

The effects of hydrothermal alteration on bulk rock geochemistry may be assessed by multi-element variation diagrams, such as the 'alteration box plot' (Large et al., 2001). The axes of this diagram are the alteration index (A.I.; Ishikawa et al., 1976) and the chlorite-carbonate-pyrite index (CCPI):



$$A.I. = \frac{100 \times (K_2O + MgO)}{K_2O + MgO + Na_2O + FeO} \quad (3.3)$$

$$CCPI = \frac{100 \times (MgO + FeO)}{K_2O + MgO + Na_2O + CaO} \quad (3.4)$$

Unaltered rocks plot in the central part of the box plot, so the relative abundance of key alteration minerals, which plot around the edge of the box (e.g. K-feldspar, sericite, chlorite-pyrite), may be determined.

Schultze Granite and Apache Leap porphyry intrusions plot in the least-altered field of the box plot, whereas the Resolution porphyry intrusions plot almost exclusively outside it (Fig. 3.26).

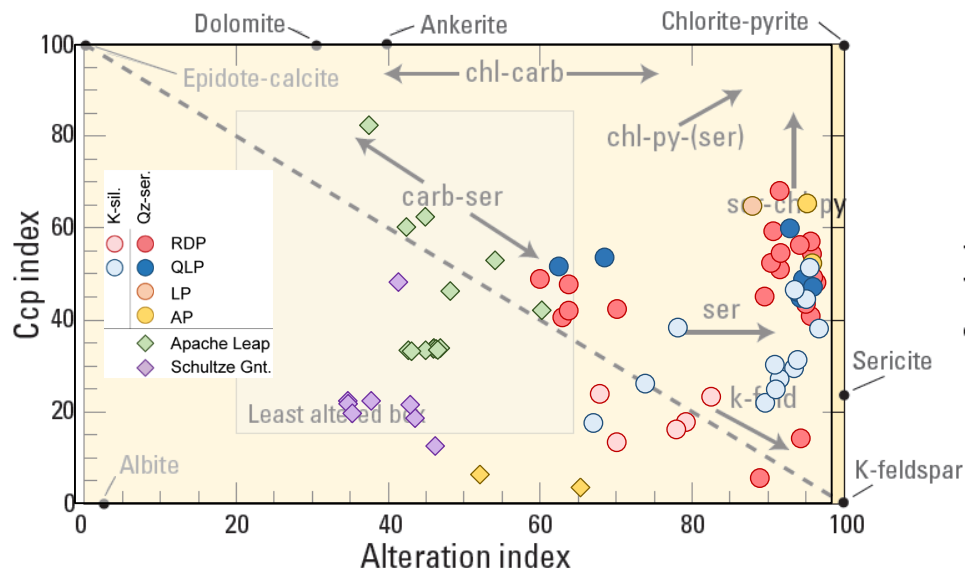


Figure 3.26. Alteration box plot (after Large et al., 2001; Shanks 2012). The majority of Resolution intrusions have very high A.I. (>90), whereas the Schultze Granite and felsic Apache Leap intrusions plot in the least altered field.

Two populations of Resolution porphyry intrusions appear on the box plot (Fig. 3.26). One group shows weak alteration which trends towards the K-feldspar-sericite join, i.e. towards high AI and low CCPI. This group represents mixed potassic-sericitic alteration, which is manifested by a K-feldspar-rich groundmass, and sericitised feldspar phenocrysts (e.g. R-23D-2; Fig. 3.27). The other group has very high AI (> 90%) and moderate CCPI (<70 %), which is associated with strong sericite-pyrite alteration and the replacement of K-feldspar in the groundmass by sericite (e.g. R-13F-2).

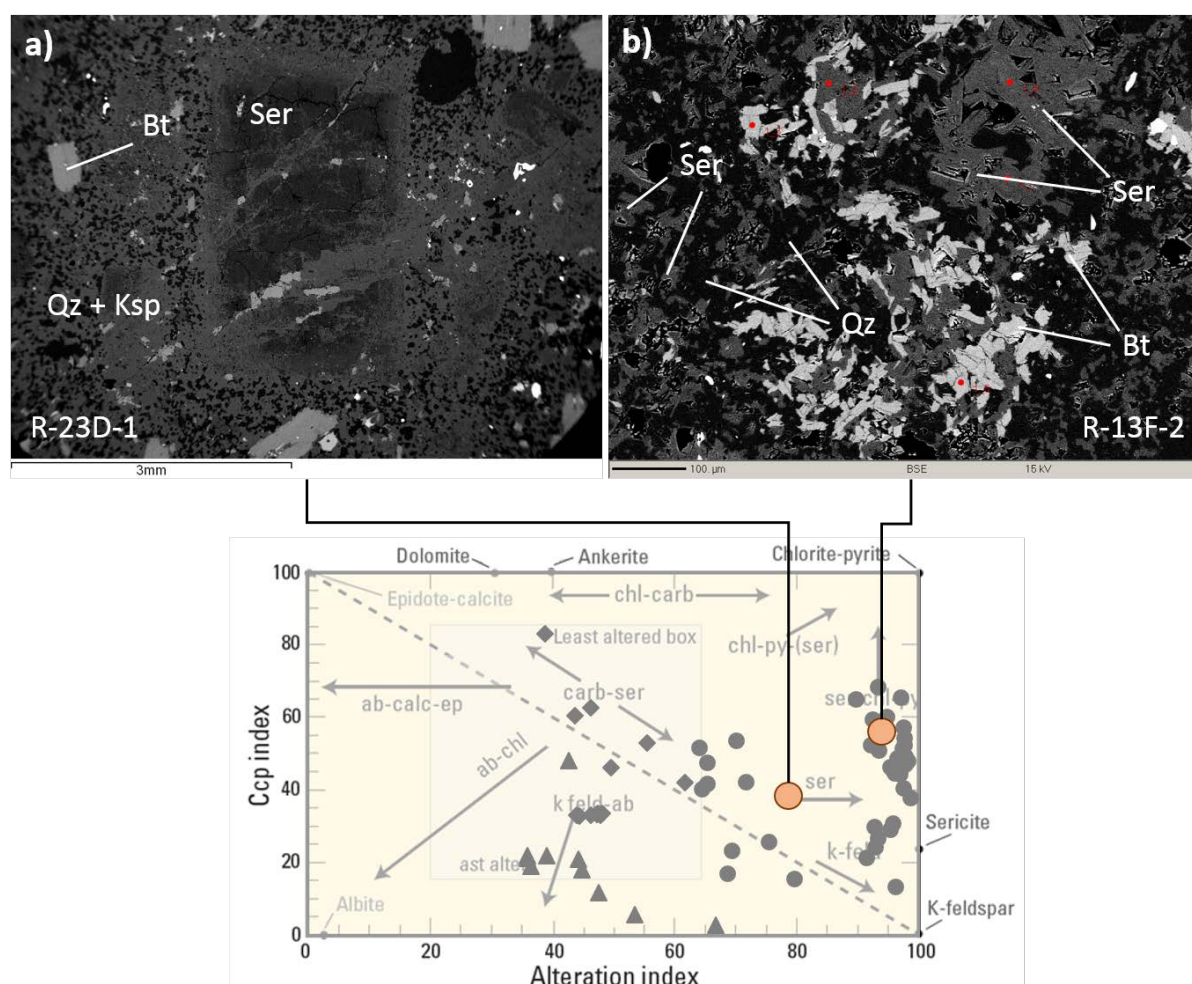


Figure 3.27. Rocks that are least strongly sericite altered (i.e. contain unaltered K-feldspar in the groundmass; e.g. R-23D-1) have lower A.I. than samples with strong sericitic alteration (R-13F-2).

### 3.6 Discussion

#### 3.6.1 The effect of alteration on whole rock indicators of porphyry fertility

To assess the affects of alteration on fertility indicators, a suitable geochemical proxy for alteration must be selected. The alteration index, calculated using Equation 3.3, appears to be a suitable measure of feldspar-destructive hydrothermal alteration, because the highest values are associated with rocks where groundmass K-feldspar has been altered to sericite.

The majority of whole rock analyses with A.I. values  $>80\%$  also have low Sr/Y values ( $<20$ ; Fig. 3.28 a) with only a small number of high Sr/Y, high A.I. values. This likely reflects the loss of Sr from the rock due to a) feldspar destruction, and b) the mobility of Sr in saline hydrothermal fluids. As such, the utility of Sr/Y ratios may be compromised by strongly feldspar-destructive alteration styles (e.g. sericitic).

Neither La/Yb, nor Eu/Eu\* show any change with increasing alteration index. This likely reflects the fact that the REE are not predominantly hosted in feldspars, so would not necessarily be mobilised by strong feldspar-destructive alteration. Isocon analysis indicates LREE mass gain in potassic and mass loss in sericitic alteration, with little change in the concentration of HREE (Fig. 3.24). However, this does not appear to be accompanied by a significant change in La/Yb ratios between sericitic and potassically altered rocks. The presence of LREE-rich accessory phases, (e.g. apatite; Fig. 3.11 d) suggests that the concentration of REE in these rocks (and thus, La/Yb and Eu/Eu\* ratios) is not strongly affected by feldspar destruction.

There is no apparent change in V/Sc with increasing alteration index. Instead, for a given value of A.I., the sericitically altered rocks have considerably higher V/Sc than potassically altered rocks (Fig. 3.24 c). This suggests that, as would be expected, feldspar destruction may not control V/Sc ratios, but they may still vary as a function of alteration.

Indeed, isocon analysis shows mass loss for V in potassically altered rocks, and mass gain in sericitically altered rocks, and little change in Sc for either alteration type. It is unclear what causes this disparity at Resolution, as the sources of V in the Resolution rocks remain poorly constrained. Magnetite is a rare phenocryst in all Resolution rocks, and the presence of V in other mafic phases (e.g. biotite) may not account for the isocon results, as higher V are observed in seritic rocks which commonly lack a mafic phase due to alteration. In any case, the utility of V/Sc ratios as an indicator of fertility may be compromised by its apparent mobility during hydrothermal alteration.

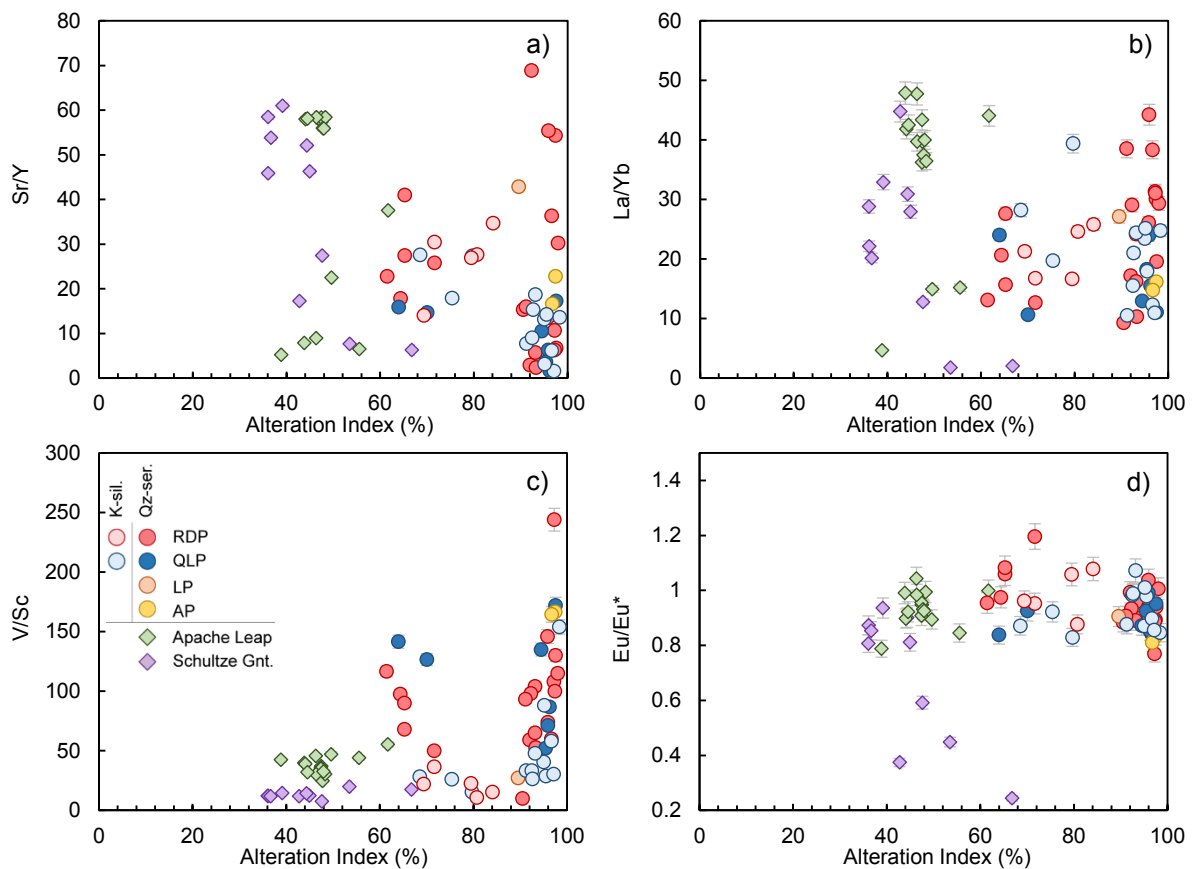


Figure 3.28. Variation of alteration index with a) Sr/Y, b) La/Yb, c) V/Sc, and d) Eu/Eu\* for Resolution rocks.

### 3.6.2 The evolution of the Laramide Schultze-Resolution system

A genetic link between the Schultze Granite and the Resolution intrusions has been previously suggested based on textural, temporal, and spatial considerations. U-Pb zircon dating of the Schultze Granite has yielded ages which overlap within error of the ages derived from the Resolution intrusions (e.g. Stavast, 2006). In terms of texture, the presence of K-feldspar megacrysts in both is considered particularly diagnostic of a co-magmatic link (Zulliger, 2007). However, there are systematic differences between the megacrysts at both systems. Resolution megacrysts are typically smaller and, more significantly, they contain no plagioclase inclusions (Fig. 3.11 f), whereas the Schultze Granite megacrysts are contain abundant plagioclase inclusions (Fig. 3.14 f).

In terms of their geochemistry, the Resolution intrusions lie on common fractionation trends to the Schultze Granite in terms of nominally immobile elements (Fig. 3.17 c,d) and the REE patterns (Fig. 3.20) and MORB-normalised spider patterns of median Resolution intrusions (Fig. 3.18) are strongly similar to the Schultze Granite. However, these geochemical signatures are not unique to Resolution and the Schultze Granite, as they both also resemble the median value for Laramide rocks from around Arizona. As a result, the whole rock geochemistry does not preclude a link between the Resolution intrusions and the Schultze Granite, and the preponderance of other evidence (e.g. spatial coincidence, U-Pb dating) may be sufficient establish the link between them.

Based on the similarities between the whole rock geochemistry of regional Laramide rocks and of the Resolution–Schultze Granite system, it is likely that Laramide magmas of the Resolution deposit were generated and evolved by broadly the same processes. Previous models for the generation and evolution of Laramide magmas commonly involve the addition of a significant crustal component to the magmas. This is based on the overlapping isotopic characteristics of the Laramide rocks, exposed Proterozoic basement, and the lower crustal

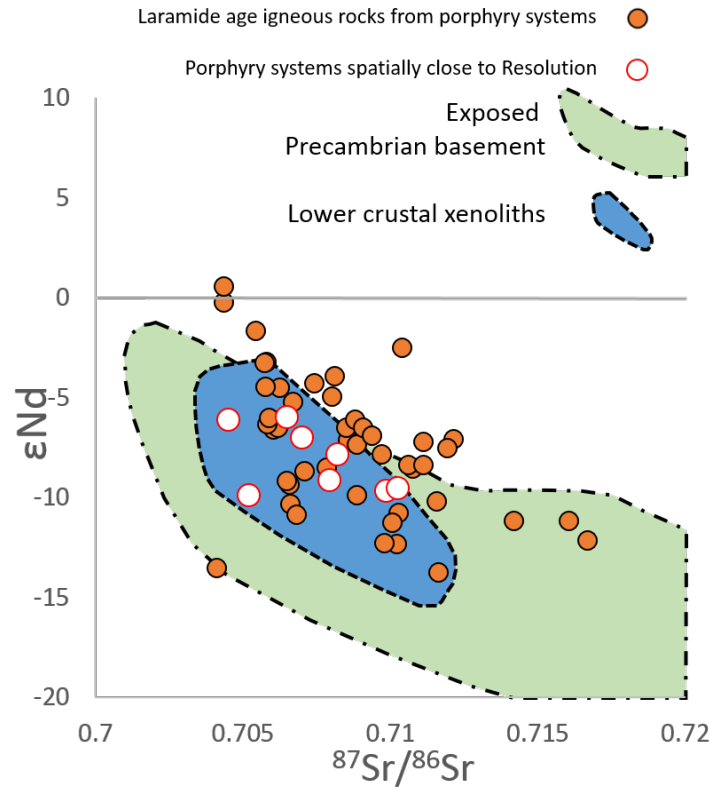


Figure 3.29.  $\epsilon\text{Nd}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  for Laramide porphyry rocks, showing strong overlap with the data for basement and lower crustal xenoliths from the same region. All data from Lang and Titley

xenoliths (Fig. 3.29). Lang and Titley (1998) suggested that the range of wide range of Sr and Nd isotopes in Laramide rocks suggests the assimilation (or direct crustal anatexis) of varying amounts of heterogeneous lower crust. Further isotopic work would be required to establish the nature of any crustal component in the Resolution rocks.

The trace element geochemical characteristics of Resolution rocks suggest modification by fractional crystallisation of hornblende, to generate the MREE-depleted trace element signature. However, partition coefficients for hornblende typically have maximum values at Dy-Ho (e.g. Table 1.1). Fractionating hornblende thus generates the greatest depletion in Dy and Ho on chondrite normalised REE plots. This differs from the REE patterns of Laramide magmas, including the Resolution, Apache Leap intrusion and Schultze Granite samples, which show the most Tm-Yb to have the lowest chondrite normalised values (Fig. 3.19). This

suggests the modest involvement of a HREE-bearing phase during petrogenesis of these rocks. Given the lower crustal depths at which the Laramide rocks are thought to have acquired their crustal signature (Lang and Titley, 1988), it is plausible that garnet had some control over the HREE during magmatic evolution.

### **3.7 Concluding remarks**

Intrusions at Resolution show both strong hydrothermal alteration of varying styles, and some signatures which may indicate magmatic fertility. This means an assessment of the effects of hydrothermal alteration on fertility indicators is possible.

- Sr/Y is particularly susceptible to hydrothermal alteration. Strong sericitic (feldspar-destructive) alteration is accompanied by low Sr/Y ratios. There is a general relationship between the intensity of feldspar-destructive alteration (as quantified by the alteration index, A.I.), and the magnitude of the Sr/Y ratio. Thus, the utility of this ratio as an indicator of fertility is compromised.
- La/Yb and Eu/Eu\* appear to be more robust, and do not vary as a function of alteration index.
- V/Sc is higher in sericitically altered rocks than in potassically altered rocks, suggesting some control of alteration on this parameter, although the nature of this control remains uncertain.

The Resolution deposit is thought to be genetically related to several nearby intrusions, including the large Schultze Granite batholith. This association is based on textural, temporal, and spatial considerations. Whole rock geochemistry from both Resolution and the Schultze Granite affords a geochemical comparison.

- There is a strong similarity between median whole rock REE and trace element concentrations at Resolution and Schultze Granite. These rocks also fall on the same fractionation trends in terms of nominally immobile elements. Thus, the geochemistry of these intrusions does not preclude a magmatic co-genesis.

Both the Resolution and Schultze Granite rocks are geochemically similar to intrusions from other Laramide porphyry systems, suggesting the processes which generated these magmas are common to the other Laramide magmas.

- These include strong interaction and anatexis with the lower crust during magmatic evolution, and subsequent evolution through amphibole fractionation, to generate MREE-depleted REE signatures,
- HREE depletion at both Resolution and other Laramide magmas suggests the involvement of garnet in the evolution of these magmas. This indicates equilibration with lower crustal rock at moderate- to high pressures.



## **Chapter 4: The petrography and whole rock geochemistry of magmatic rocks associated with the Oyu Tolgoi Cu – Au deposits, South Gobi, Mongolia**

### **4.1 Introduction**

The Oyu Tolgoi porphyry system is a cluster of late Devonian porphyry deposits in the Gobi Desert of southern Mongolia, ~650 km south of Ulaanbaatar and 80 km north of the Mongolian-Chinese border (Fig. 4.1). With 41.7 million tonnes of copper and 1,549 tonnes of gold, Oyu Tolgoi is the largest group of high grade Palaeozoic porphyry deposits in the world (Crane and Kavalieris, 2012). The deposits are distributed along a 22 km long, NNE-trending lineament within the Gurvansayhan volcanic arc terrane of the Central Asian Orogenic Belt. Some smaller occurrences of late Devonian porphyry mineralisation are found in the Gurvansayhan terrane, including the Tsagaan Suvarga porphyry Cu-Mo deposit ( $370.4 \pm 0.8$  Ma; Watanabe and Stein, 2000), but Oyu Tolgoi is the largest mineralised centre yet to be discovered. Although copper mineralisation has been known about and exploited at Oyu Tolgoi since the Bronze Age, modern exploration did not begin until the 1980s, and the extent of the Central and South deposits were not fully delineated until the late 1990s. This was followed by a more extensive drilling program which led to the discovery of Hugo Dummett in 2002, and Heruga in 2007. Individual ore bodies at Oyu Tolgoi are named Heruga, Central Oyu, Southwest Oyu, Southwest Oyu and Hugo Dummett. These ore bodies each have a distinctive metal tenor, grade and alteration style, from lower grade Cu-Mo (-Au) at Heruga, to very high grade Cu-Au mineralisation at Hugo Dummett. Mineralisation is hosted primarily in a Devonian age pyroxene-phyric basalt (known as the Augite Basalt), although late Devonian quartz monzonite intrusions also host considerable mineralisation at Hugo Dummett. The quartz monzodiorite and the pyroxene-phyric 'Augite Basalt' wall rocks are unconformably

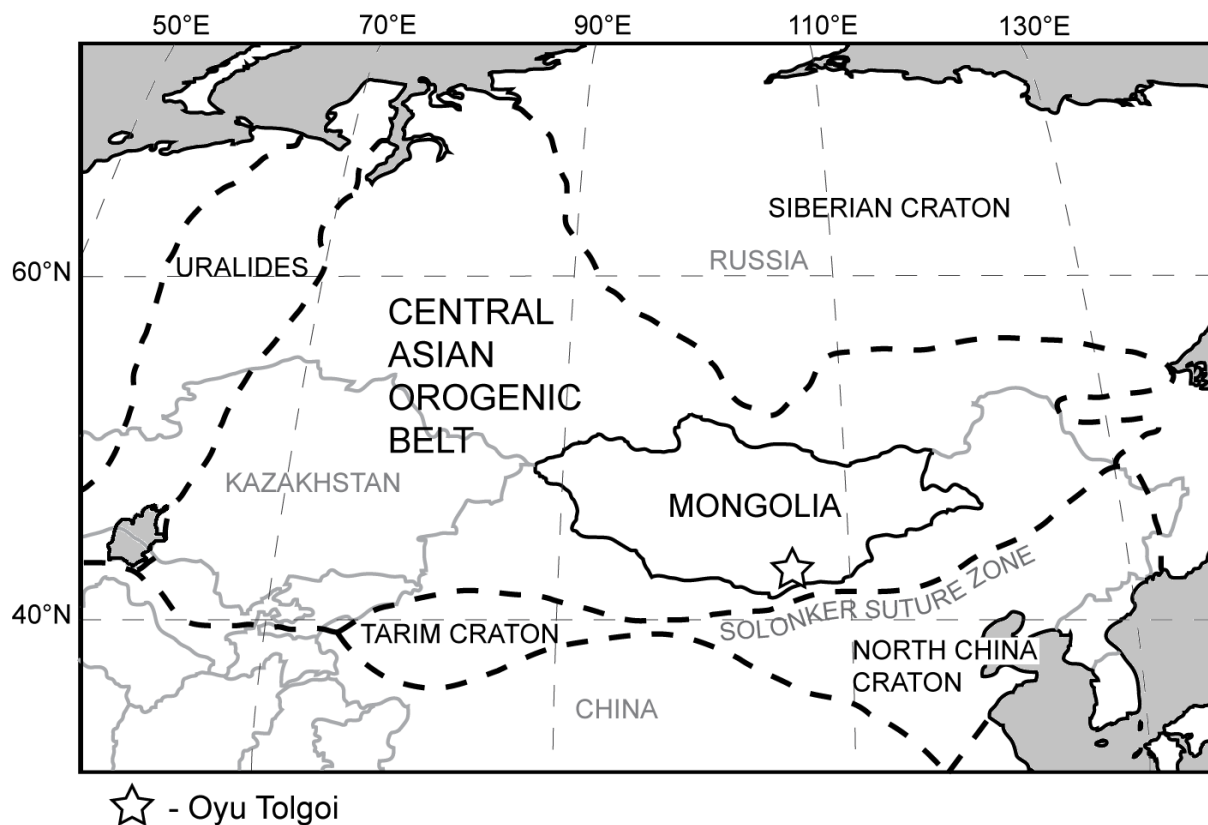


Figure 4.1. Mongolia and Oyu Tolgoi in the context of the Central Asian Orogenic Belt.

overlain by an unmineralised volcanic sequence, thought to be the remains of the coeval volcanic system under which the deposit formed, and late Devonian laminated siltstones. These units lie in the footwall of a district-scale thrust fault (the Contact Fault) with an unmineralised allochthonous assemblage of uncertain age in the hanging wall, which in turn is unconformably overlain by Carboniferous volcanic and sedimentary rocks. Carboniferous to Permian normal faults have exhumed the ore bodies to different structural levels, meaning some deposits are at the surface (Central, South, and Southwest), and some are deeply buried (Heruga North and Hugo Dummett North). Unmineralised biotite granodiorite intrusions immediately postdate mineralisation, and cut both the mineralisation and the overlying Contact fault.

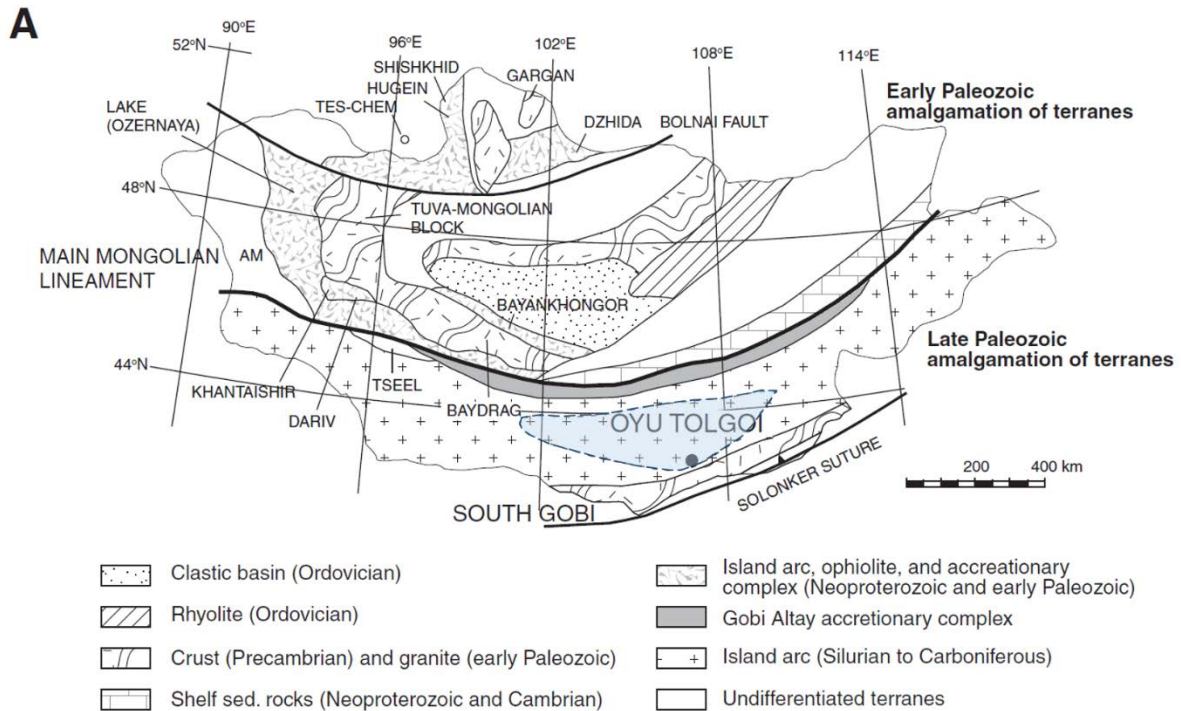


Figure 4.2. Simplified map of the geology of Mongolia. The Gurvansayhan terrane is highlighted in blue. Modified from Wainwright et al., 2011a.

Bornite and chalcopyrite are the dominant Cu minerals, and the relative abundance of each varies between deposits. High Cu grades at Hugo Dummett are attributed to reactive basaltic host rocks (Sillitoe, 2010), strong fluid focussing (Richards, 2013), and high-sulphidation mineralisation associated with late-stage advanced argillic alteration (Khashgerel et al., 2006; 2009). Heruga and Hugo Dummett are the particular focus of this chapter, as they afford a comparison between high grade and low grade mineralisation.

## 4.2 Regional Geology

Oyu Tolgoi is located within a large accretionary orogen, the Central Asian orogenic belt (also known as the Altaids), which extends over all of Mongolia and large parts of Kazakhstan, central Russia and northern China (Fig. 4.1). This orogenic belt developed over 750 Myr from the Neoproterozoic to the Permian (Windley et al., 2007) and involved the accretion of passive margin and deep marine sediments, accretionary wedge sequences, ophiolites and island arc complexes onto two cratons, Siberia and Baltica. The termination of this orogenic event occurred with the eventual closure of the Palaeo-Asian ocean in the late Palaeozoic, when the North China and Tarim cratons collided with the southern margin of the accretionary zone. The boundary of this collision is located along the Solonker Suture Zone, which in part runs parallel to the Chinese-Mongolian border <100 km south of Oyu Tolgoi (Fig. 4.1)

The geology of Mongolia can be broadly divided into northern and southern domains, separated by the Main Mongolian Lineament which runs E to NE through the centre of the country (Fig. 4.2; Badarch et al., 2002). The northern domain contains accreted Precambrian blocks, island arc and ophiolite terranes which formed a stable continental block by the Ordovician. The southern domain consists of several Palaeozoic accretionary terranes, including island arc fragments and accretionary wedge sediments, which were amalgamated onto this stable continental block (Badarch et al., 2002). Oyu Tolgoi is located in the Gurvansayhan Terrane, one of at least four island arc terranes in southern Mongolia (Fig. 4.2; Lamb and Badarch, 2001). This terrane contains a number of imbricate thrust sheets, composed of volcanic arc and sedimentary assemblages, some of which are highly deformed. The terrane was most likely assembled during the Carboniferous because it is intruded by Carboniferous and Permian granites (Lamb and Badarch, 1997; Badarch et al., 2002).

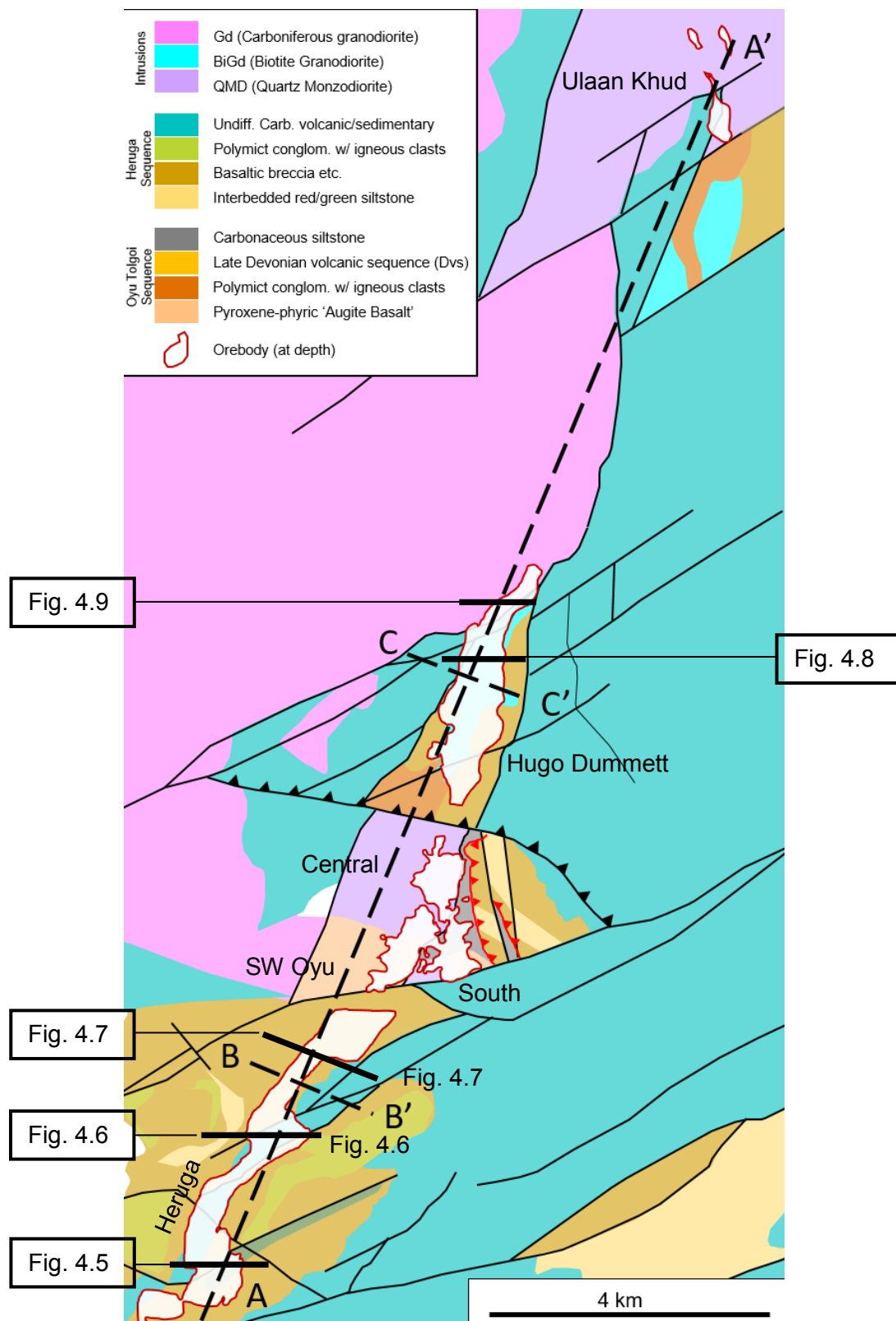


Figure 4.3. Simplified regional geology of the Oyu Tolgoi district. Lines of section labelled A-A', B-B', and C-C' refer to Figure 4.4. Other lines of section related to figures 4.5 to 4.8. Modified after Crane and Kavalieris (2012).

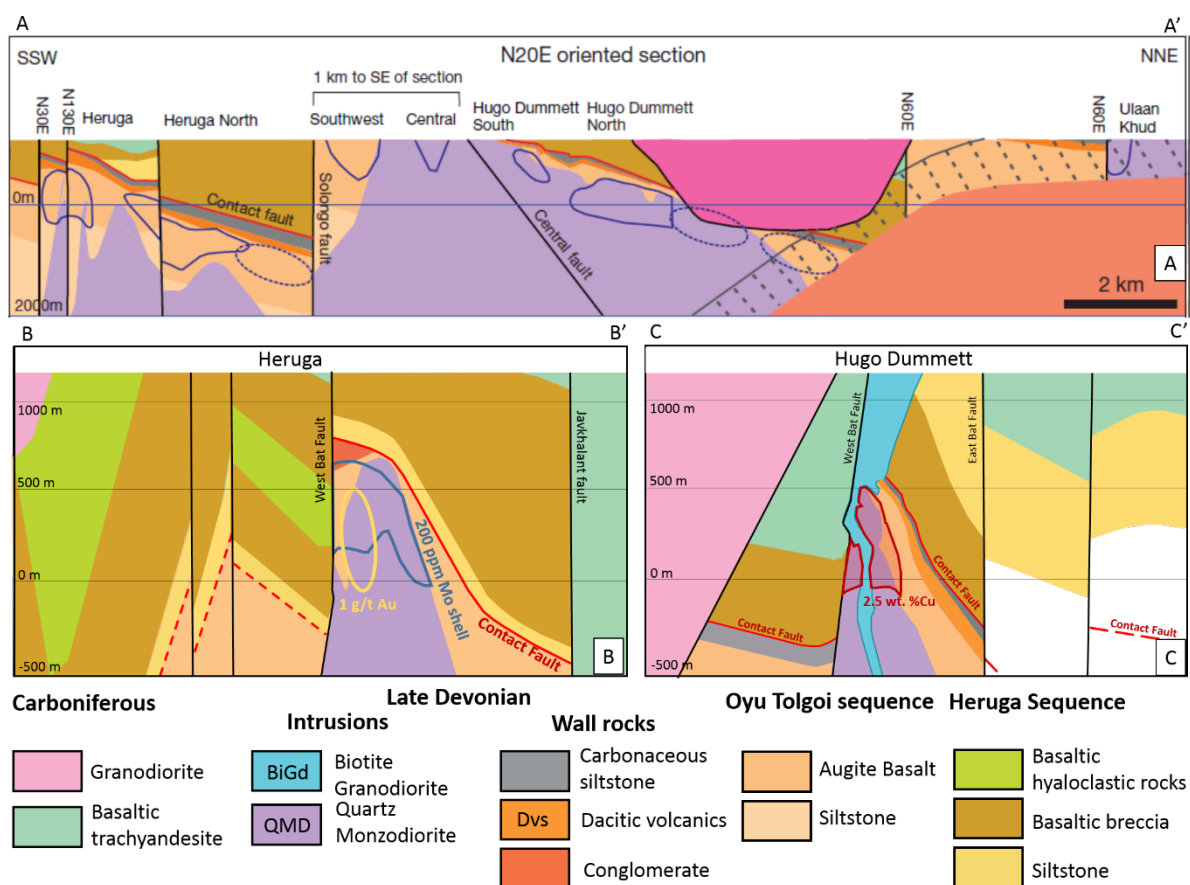


Figure 4.4. Cross sections showing the distribution of lithologies at Oyu Tolgoi (a) NNE cross section along the Oyu Tolgoi trend, showing the displacement of different ore bodies to different depths along major faults. Large intrusion in the far north is the Permian Khanbogd Granite, shaded region is the associated aureole. (b) Cross section through Heruga, looking NNE. (c) Cross section through Hugo Dummett, looking NNE. All sections after Crane and Kavalieris (2012).

### 4.3 Deposit Geology

The focus of this study is the Late Devonian intrusive and volcanic igneous rocks, which are discussed in detail in Section 4.4. The following section comprises a brief description of other aspects of the deposit geology derived from literature sources.

#### 4.3.1 Structure

Oyu Tolgoi comprises several centres of porphyry mineralisation with a diverse range of ore grade, metal tenor, alteration, mineralisation style and geometry. These ore bodies are distributed along a 22 km, NNE-trending structural corridor (Fig. 4.3). Heruga is the most southerly ore body and contains an inferred resource of 970 Mt at 0.48% Cu and 0.48 g/t Au (at 0.6% Cu equiv. cut-off; Rio Tinto Annual Report, 2011). Mineralisation at Heruga becomes progressively deeper further to the north in a zone called Heruga North (Fig. 4.4). The next cluster of deposits to the north are known as Central Oyu, South Oyu, and Southwest Oyu. Here, mineralisation is located close to the surface and consequently these were the first ore bodies to be discovered. The Hugo Dummett deposits are 2-3 km further north east. Like Heruga, mineralisation becomes deeper towards the north and is loosely divided into Hugo Dummett North and South. Unlike Heruga, the Cu grade at Hugo Dummett is exceptionally high, with 1,016 Mt of ore at 1.18% Cu and 0.32 g/t Au (at 0.6% Cu equiv. cut-off; Rio Tinto Annual Report, 2011). Hugo Dummett is also host to significant advanced argillic alteration not evident at Heruga. Two small prospects, Javkhlant and Ulaan Khud, are found on the lineament to the extreme south and north of the other ore bodies respectively. Mineralisation in these two prospects is thought to be lower grade and lower tonnage than in the other systems (Crane and Kavalieris, 2012).

Due to the scarcity of outcrop and the thick post mineral cover, most of the geology of the Oyu Tolgoi deposit and the relationship between different units has been determined by diamond drilling. Two major lithostratigraphic groups have been distinguished, separated by the Contact Fault. The foot wall, which contains the wall rocks, and the intrusions related to mineralisation, is known as the 'Oyu Tolgoi sequence'. The Devonian rocks of the hanging wall are known as the 'Heruga sequence' (Fig. 4.3). These are unconformably overlain by

Carboniferous volcanic and sedimentary rocks, which are not the focus of this study. In most cases, units dip steeply towards the east (Fig. 4.4).

Both the Heruga and Oyu Tolgoi Sequences are cut by the major, steeply dipping West Bat fault, of Carboniferous age (Crane and Kavalieris, 2012), which trends in a NNE direction from Heruga to Hugo Dummett, and cross-cuts mineralised rocks in both deposits (Fig. 4.4). The West Bat fault is cut by ENE-trending faults, of which the Solongo Fault is a major example (Fig. 4.4).

#### 4.3.2 Wall Rocks

##### *4.3.2.1 Oyu Tolgoi Sequence*

Mineralisation at Oyu Tolgoi is primarily hosted in a ~1 km thick sequence of pyroxene-phyric basalt (Augite Basalt), characterised by the presence of large augite phenocrysts up to 10 mm in size, accounting for approximately 35 vol. % of the rock. This basalt is tholeiitic and is massive, showing no internal structures. Volcaniclastic rocks (e.g. peperite) are found at the base of the unit in contact with the underlying laminated siltstones indicating magmatic interaction with wet sediment (Crane and Kavalieris, 2012). The age of the unit is poorly constrained but must be older than 378 Ma, which is the age of the oldest dated zircons from the quartz monzodiorite intrusions (QMD) (Wainwright et al., 2011a). Unconformably overlying these units are a sequence of polymict conglomerates, containing some igneous clasts, and volcanic rocks of Late Devonian age ( $369 \pm 1$  Ma); the latter are fully described in Section 4.4.3.

##### *4.3.2.2 Heruga Sequence*

The allochthonous Heruga sequence makes up the hanging wall that covers mineralisation. It is considered to be overturned based on sedimentary structures (Lewis et al., 2005; Ayush et al., 2006). The base of the sequence consists of late Devonian basaltic to



trachyandesitic basalts, basaltic breccias and volcanoclastic rocks interbedded with thinly laminated siltstones (Crane and Kavalieris, 2012)

The relationship between these late Devonian rocks and the Oyu Tolgoi sequences is uncertain because they do not correlate with any sequences in the footwall, although they are thought to belong to the same formation as the augite basalt based on textural similarities (see Minjin et al., 2004). The late Devonian rocks are unconformably overlain by the Carboniferous Sainshandhudag Formation. The basal unit of this formation is a polymict conglomerate, which is succeeded by sandstones and siltstones, and a lower and upper volcanic sequence which have been dated to between 354 and 339 Ma (Wainwright et al., 2011a).

#### *4.3.2.3 Carboniferous hypabyssal and plutonic intrusions*

Minor intrusions (<20m) which have been dated to be of Carboniferous age are commonly observed in the deposit (all ages in this section from Wainwright, 2008). The most common of these intrusions are porphyritic hornblende biotite andesite ( $345 \pm 2$  Ma), aphanitic rhyolite ( $340 \pm 2$  Ma), and mafic dykes, both as dolerite and basalt. In addition to these hypabyssal intrusions, a medium grained, equigranular granodiorite intrusion ( $350 \pm 4$  Ma) outcrops extensively to the north and west of Hugo Dummett and the Central Oyu deposits (Fig. 4.3) and is likely to be co-magmatic with hornblende biotite andesites (Crane and Kavalieris, 2012). These units were not studied because they are >20 Ma younger than the period of mineralisation.

## **4.4 Lithological description of studied rocks**

Fieldwork for this project was conducted at Oyu Tolgoi in on visit from August to September 2012. All fieldwork involved logging drill core, and focused on intervals of drill core containing Late Devonian igneous rocks (i.e. the QMD, BiGd, and Dvs). Logged intervals were selected to represent the range of alteration style, Cu and Au grade, and depth within the

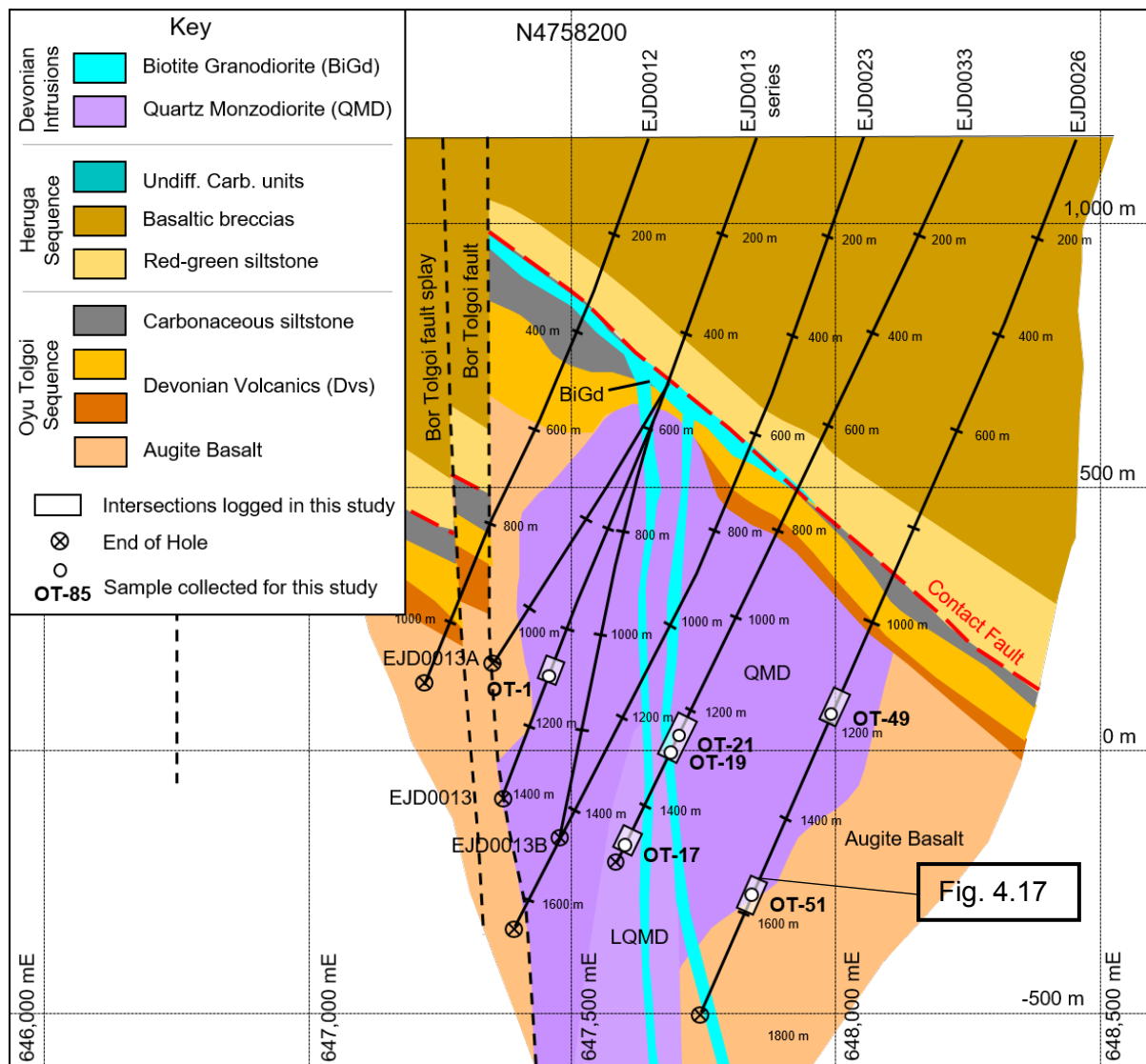


Figure 4.5. E-W section of the Heruga deposit, named N4758200. After Ivanhoe resource model (unpublished).  
Log for hole EJD0026 is found in Figure 4.17.

deposit. Logging focussed especially on alteration style, igneous textures, and the cross-cutting relationships between different igneous units. Due to the eastward dip of the host rocks (Fig. 4.4), drill holes at Oyu Tolgoi mostly plunge down to the west. Two E-W cross sections and one ENE-WSW cross section at Heruga (Figs. 4.5; 4.7; 4.6), and two E-W cross sections at Hugo Dummett (Figs. 4.8 and 4.9) contain most of the logged core intervals.

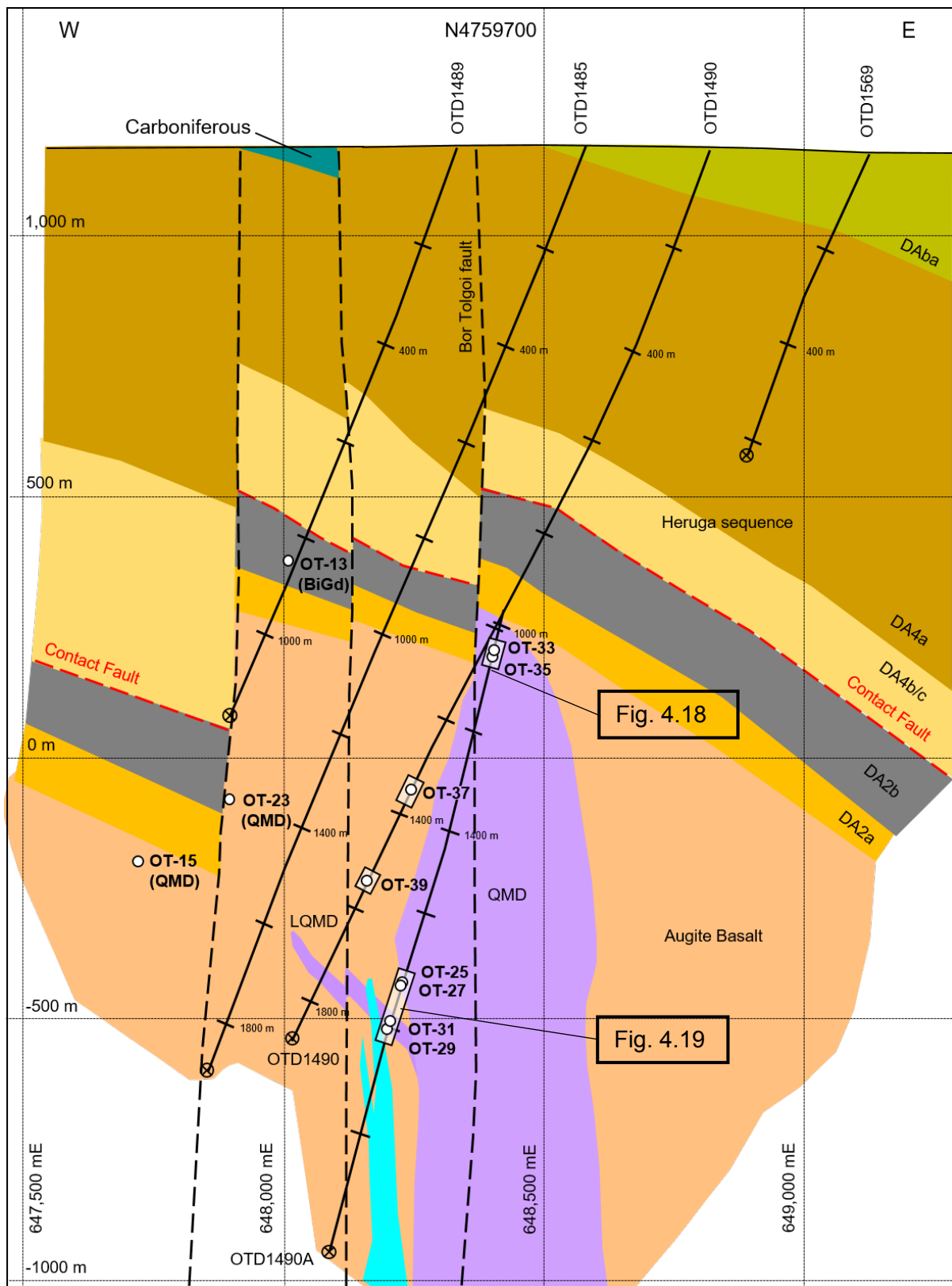


Figure 4.6. E-W section of the Heruga deposit, named N4759700. After Ivanhoe resource model (unpublished).

Same unit colours as in Figure 4.5. Two logs for hole OTD1490A are found in Figures 4.18 and 4.19.

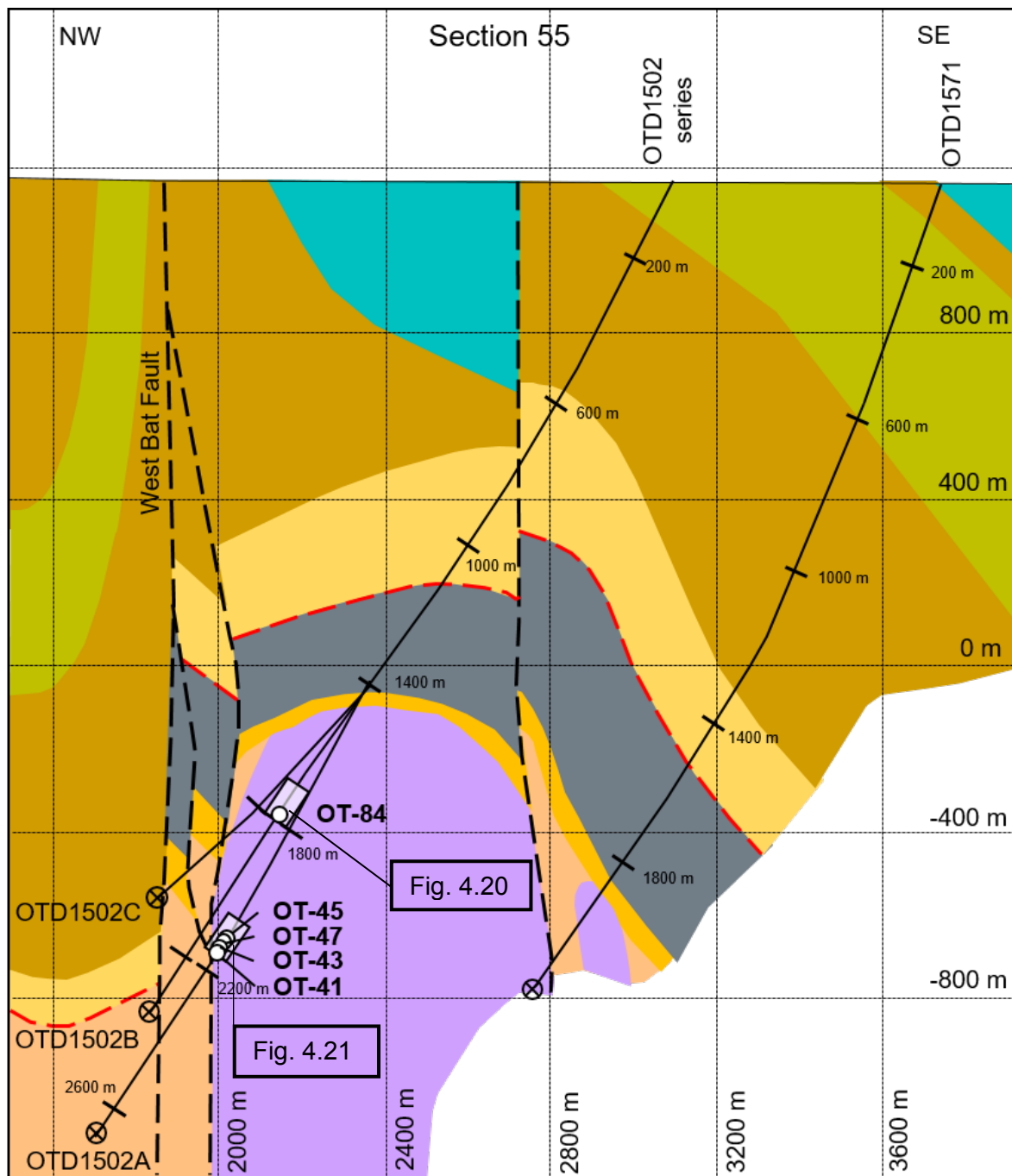


Figure 4.7. ENE-WSW section of the Heruga deposit, named "Section 55". After Ivanhoe resource model (unpublished). Same unit colours as in Figure 4.5. Two logs for hole OTD1502A and OTD1502B are found in Figures 4.20 and 4.21.

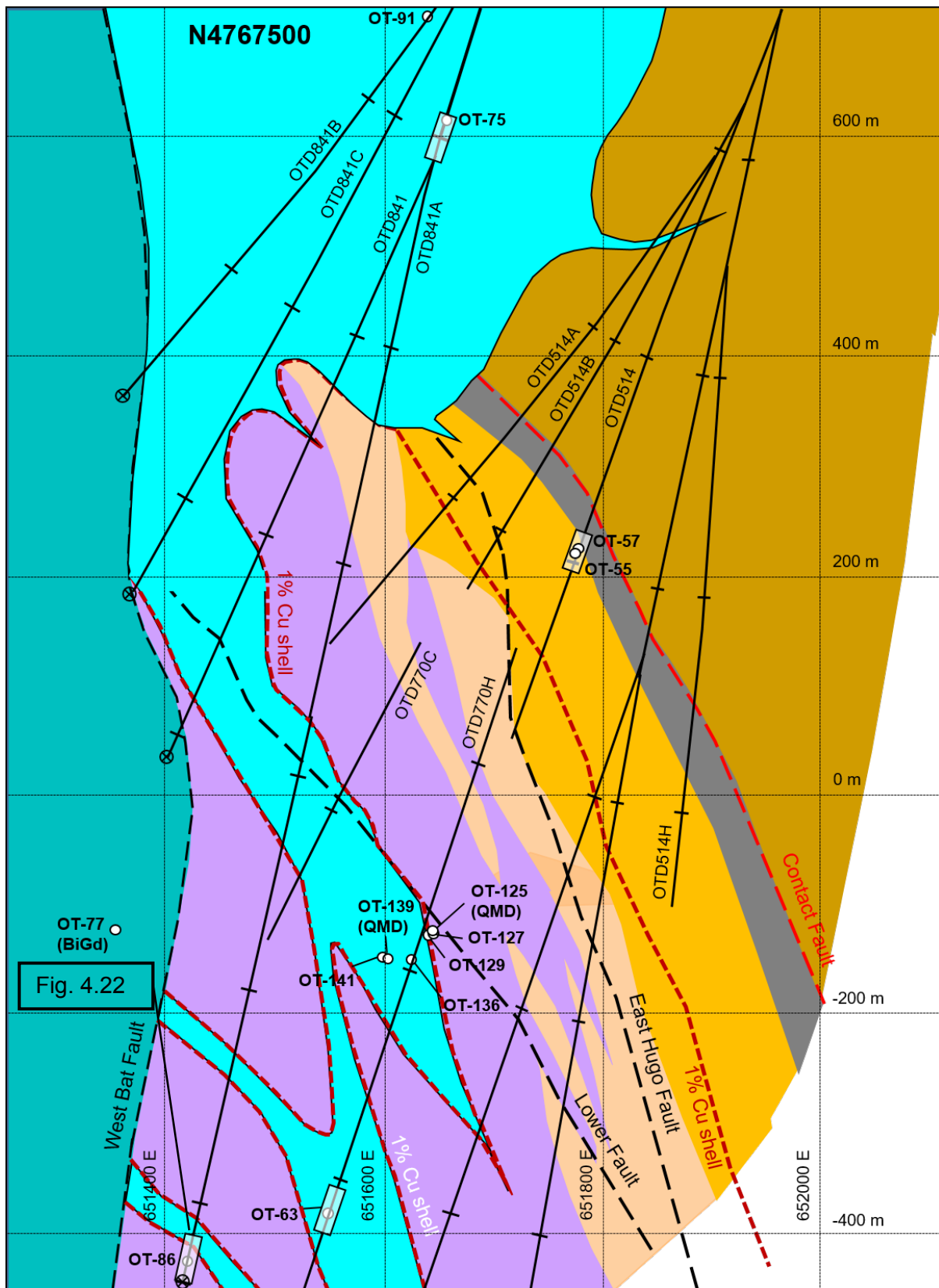


Figure 4.8. E-W section of the Hugo Dummett deposit, named N4767500. After Ivanhoe resource model (unpublished). Same unit colours as in Figure 4.5. Log for hole OTD841A is found in Figure 4.22.

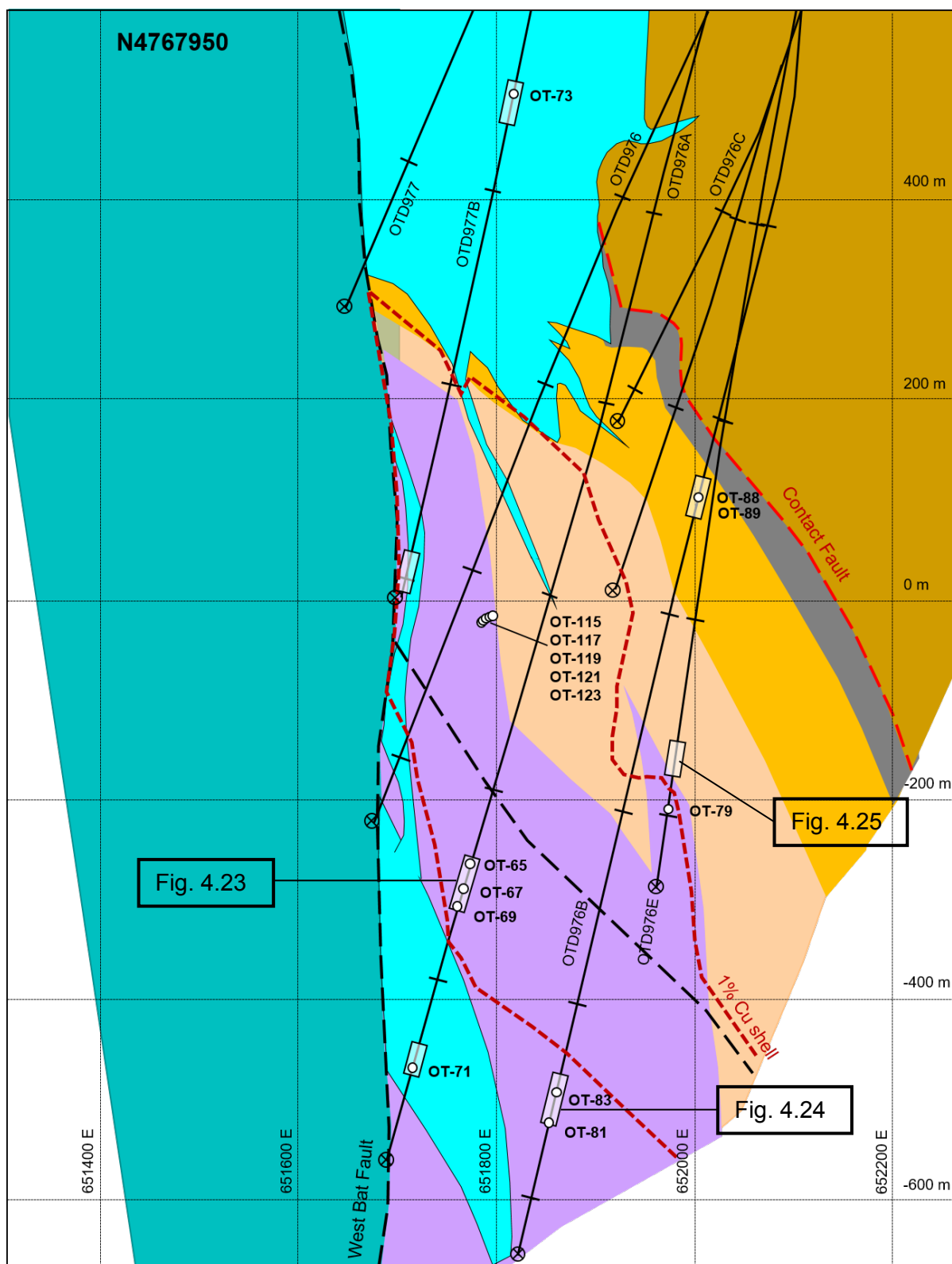


Figure 4.9. E-W section of the Hugo Dummett deposit, named N4767950. After Ivanhoe resource model (unpublished). Same unit colours as in Figure 4.5. Three logs for hole OTD976A, OTD976B, and OTD976E are found in Figures 4.23, 4.24, and 4.25.

#### 4.4.1 Quartz Monzodiorite (QMD)

The most volumetrically significant late Devonian intrusion is a feldspar porphyry, which comprises abundant phenocrysts of plagioclase, subordinate quartz and, in unaltered or weakly altered samples, hornblende. The pervasive hydrothermal alteration makes ascribing a lithologically realistic name to this rock challenging. In the mine literature, this unit is referred to as ‘quartz monzodiorite’ (QMD). This name is an appropriate description of the unaltered protolith based on the QAPF classification (Streckeisen, 1974). However, the unaltered protolith is rarely observed, and strong potassic and quartz-sericitic alteration change the bulk assemblage (Figs. 4.10 and 4.11).

The QMD outcrops in small areas above the Central Oyu deposit (Fig. 4.3), but its nature and distributions is mostly known from drill core. In the Heruga deposit, the QMD occurs as narrow finger- or sheet-like projections (~0.25 km wide, at least 1.5 km high; Fig. 4.6) or broader stocks (0.5 to 1 km wide; Figs. 4.5 and 4.7) which intrude the Oyu Tolgoi sequence rocks, but have not been observed crossing the Contact Fault. In the Hugo Dummett deposits, the QMD comprises ~0.5 km wide stocks which run the length of the deposit. The eastern extent of these stocks is frequently truncated by the West Bat fault (Figs. 4.8 and 4.9).

A porphyritic and an equigranular variety of QMD have been distinguished in this study, which is in agreement with textural analysis of the QMD from other workers (e.g. Wainwright, 2008). Of these two types, the porphyritic variety is by far the most abundant. It contains abundant feldspar (40 – 60%), relict mafic phenocryst (~5%), and occasional quartz phenocrysts (<5%) in a fine grained matrix. All of the phenocryst phases (except quartz) are ubiquitously hydrothermally altered. Relict feldspar phenocrysts are euhedral to subhedral tabular laths, which range in size from 1 – 10 mm, with a mean size of ~2-3mm (Fig. 4.10 c,d). These phenocrysts are frequently aligned, where they show a preferred orientation which is sub-parallel to the length of the core (Fig. 4.10 d,e). As most drill core in this study is vertical



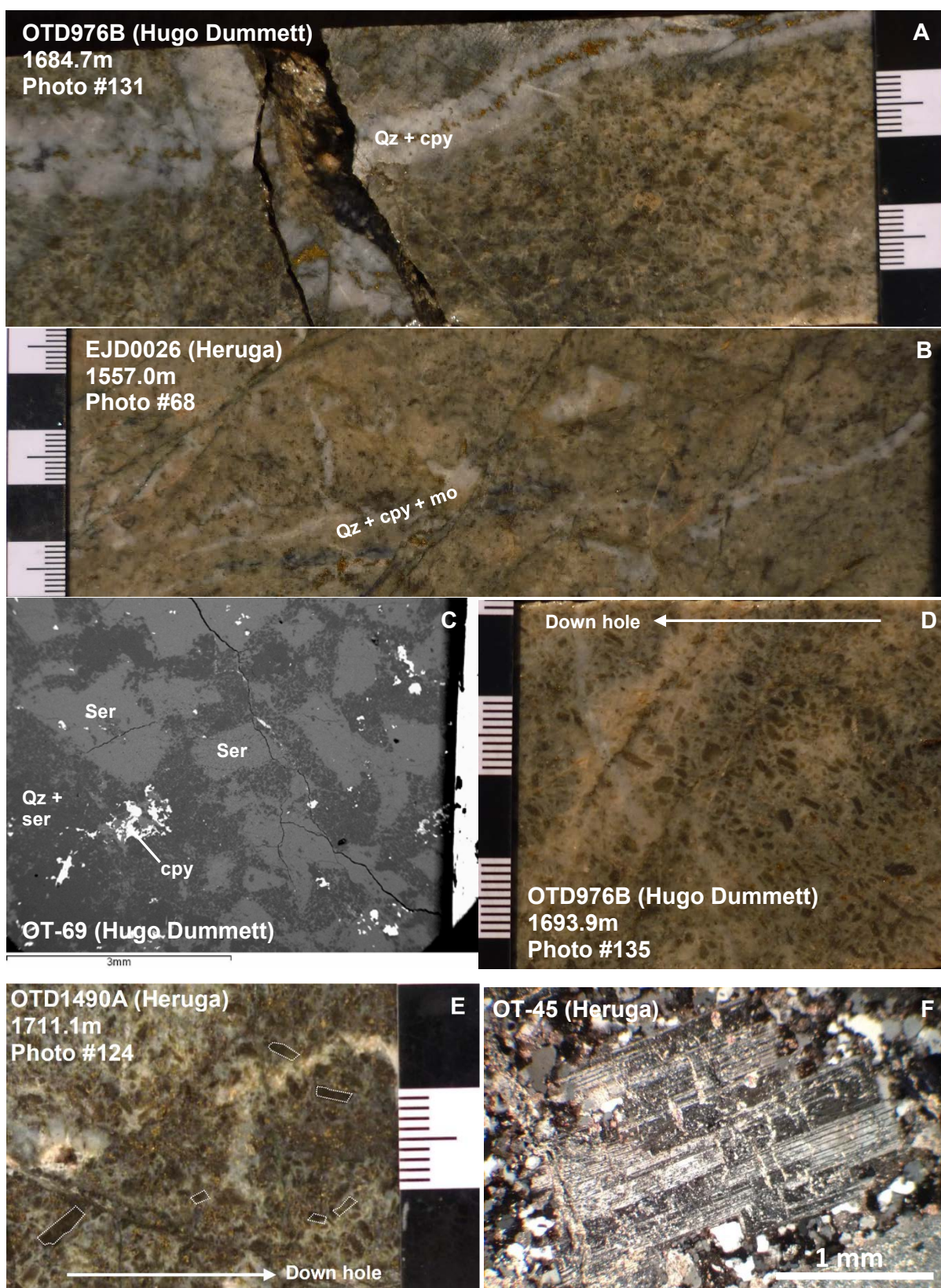


Figure 4.10. Representative images of quartz-sericite altered porphyritic QMD. All images are core photographs, except c) (backscatter SEM) and f) (photomicrograph). f) shows very weak sericite alteration. Note the alignment of feldspar phenocrysts in d) and e). Ser = sericite, qz = quartz, cpy = chalcopyrite, mo = molybdenite.



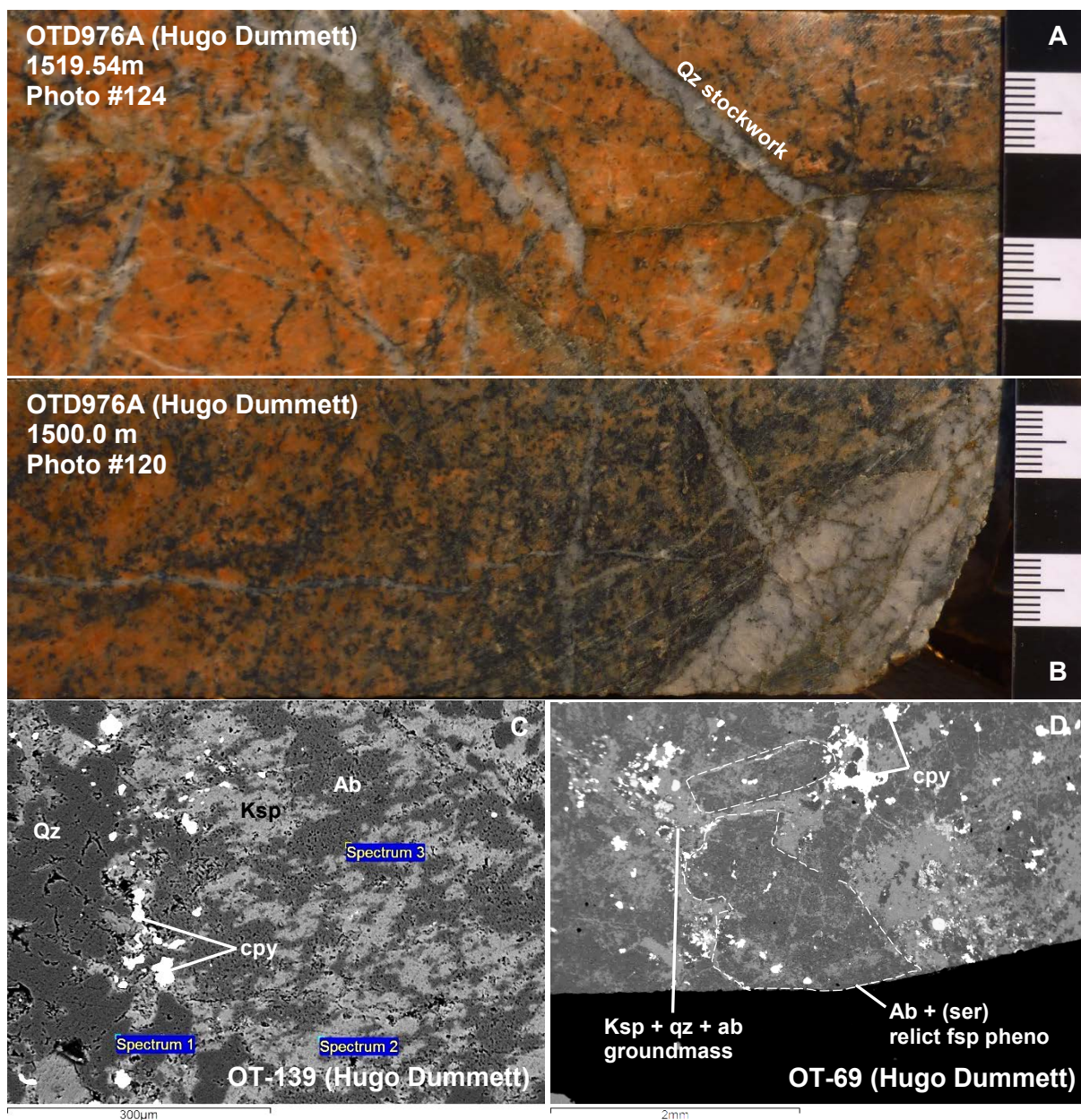


Figure 4.11. Representative images of potassically altered porphyritic QMD. a) Typical strong potassic alteration, showing the characteristic brick red alteration, abundant quartz stockwork veining, with dark bornite. b) Sericitic alteration halo around quartz + pyrite vein, overprinting earlier potassic. c) typical groundmass texture, and d) a zoomed out version of image c) showing the relationships between the groundmass and phenocrysts. a) and b) are core photographs, c) and d) are backscatter electron SEM images. Qz = quartz, ksp = K-feldspar, cpy = chalcopyrite, Ab = albite.

or sub-vertical (Figs. 4.5 to 4.9), this means the orientation of feldspar phenocrysts is also approximately vertical. The abundance of feldspar phenocrysts leads to a ‘crowded’ texture (i.e. % phenocrysts > % groundmass). Quartz does not comprise a significant fraction of the phenocryst assemblage and, where present, are typically small and sub- to anhedral (< 1mm). The nature of the mafic phenocrysts is enigmatic, as they are almost ubiquitously obscured by hydrothermal alteration in the porphyritic QMD. Occasional patches of sulphides may represent an altered mafic phenocryst (e.g. Fig. 4.10 c; Fig. 4.11 d), but the nature of the relict phase is uncertain. Relict mafic phases in the equigranular QMD are hornblende.

One sample of equigranular QMD from SW Oyu (OT-143) was selected for petrographic study. This rock consists of an equigranular assemblage of euhedral to subhedral plagioclase grains (30 vol. %, up to 5mm), inter-grown with subhedral K-feldspar (~30 vol. %, <3 mm). Subordinate anhedral to subhedral quartz grains (<1mm, 10 – 20- vol. %) are found in the interstitial spaces between feldspars (Fig. 4.12). Euhedral, elongate relict hornblende crystals account for 10 – 15 vol. % of this rock, and have been altered to actinolite (analyses of actinolite from this sample are found in Appendix 6). Titanite and apatite are common accessory minerals, and are associated with magnetite (~5 vol. %).

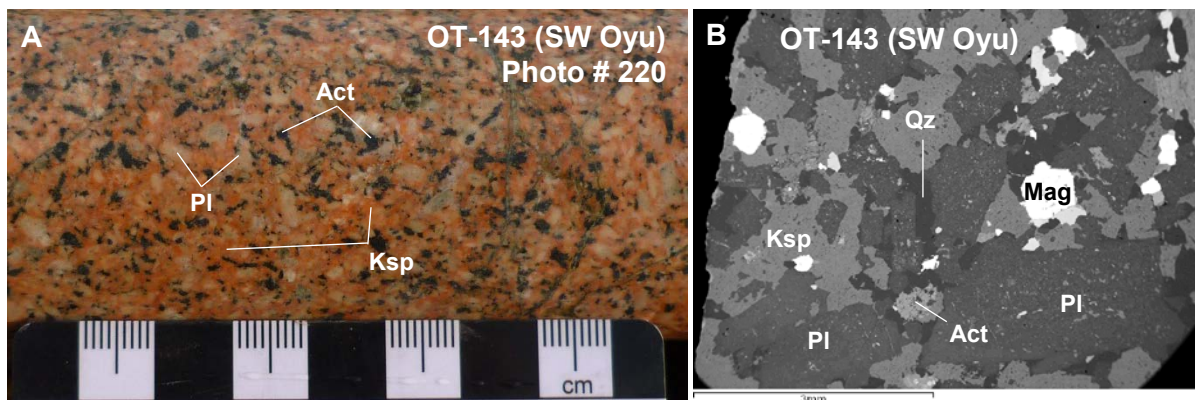


Figure 4.12. Representative images of sample OT-143, equigranular QMD. a) Core photograph, and b) backscatter electron SEM image. Pl = plagioclase, ksp = K-feldspar, Act = actinolite, mag = magnetite, qz = quartz.

#### 4.4.2 Biotite Granodiorite (BiGd)

Of the several generations of post-mineralisation intrusions which cross-cut the deposit, one set is considered to have been intruded immediately after mineralisation at both Heruga and Hugo Dummett (e.g. Wainwright, 2008). This intrusion is a feldspar porphyry, but is texturally distinct from the QMD, and is only weakly altered and unmineralised. It has been referred to in previous published and unpublished literature as a ‘biotite granodiorite’ (BiGd). Mineralised veins are truncated at the contact between the QMD and the BiGd and a distinct drop-off in Cu and Au grade is observed at these boundaries (e.g. Fig. 4.19). The BiGd locally contains small amounts of disseminated sulphides (mainly pyrite) which are likely to have been reworked from the ore body (D. Crane; pers. comm., 2013). U-Pb dating has constrained the age of the BiGd to between  $363 \pm 4$  and  $367 \pm 4$  Ma (Wainwright et al 2011b), which supports an intrusion age immediately post-dating mineralisation.

At Heruga, narrow anastomosing dykes of BiGd cross-cut the footwall Oyu Tolgoi sequence (including the QMD intrusions) but no BiGd has been observed in the hanging wall Heruga sequence (e.g. Fig. 4.5). Some sills of BiGd run between the two sequences along the Contact Fault. At Hugo Dummett, the BiGd also occurs as narrow anastomosing dykes (<10 m width) in the deeper parts of the system, which flare outwards significantly into the Heruga sequence (up to 1 km wide) when crossing the Contact Fault (Figs. 4.8 and 4.9). BiGd outcrops above the Hugo Dummett deposits, and ~ 5 km NE of Hugo Dummett in the area immediately south of the Ulaan Khud prospect (Fig. 4.3)

The BiGd may be subdivided into two textural variants – a fine-grained porphyry with a large number of small feldspar phenocrysts, and a coarser-grained porphyry with sparse (but larger) phenocrysts. In both examples, plagioclase feldspar phenocrysts account for ~40% of the rock volume. In the coarse BiGd porphyry, plagioclase phenocrysts are large (up to 1 cm), equant, and frequently show clear oscillatory zoning in hand specimen (Fig. 4.13 a). In the fine

grained porphyry, plagioclase feldspars are mostly 1-2 mm, and are also equant and euhedral (Fig. 4.13 b). Occasionally, dark cores are observed in the large feldspar phenocrysts (Fig. 4.13 a), which comprise mostly rutile and chlorite. Feldspars are albitic in composition, and are partly altered to sericite (Fig. 4.13 f). Quartz phenocrysts account for ~25% of the rock. They are occasionally observed as rounded subhedral quartz ‘eyes’, but most are prismatic and euhedral, which are mostly < 1mm. Relict mafic phenocrysts (10 – 30 %) range in size from 1 to 3 mm. They are altered to an assemblage of chlorite + calcite + rutile + white mica. White mica is typically observed as ‘fringed’ rims, inter-grown with chlorite (Fig. 4.13 c). Calcite and rutile are present as clots within grains. It is unclear what mafic phase was present in these rocks before the alteration, which is pervasive and no remnant phenocrysts in any of the studied samples. Although previous authors suggest that biotite is the primary mafic phase, the relict habit could also be suggestive of hornblende (e.g. Fig. 4.13 c). The presence of both Ca- and K-bearing phases in the alteration assemblage is ambiguous, and it is likely that both or either of these elements were added during hydrothermal alteration. The groundmass of BiGd comprises an interlocking matrix of small (10 – 50 µm) anhedral K-feldspar, quartz, and subordinate albite (Fig. 4.13 d)

Given the abundance of quartz phenocrysts (>20%) and the multitude of plagioclase phenocrysts, this rock classifies as a granodiorite *sensu stricto*, according to the QAPF classification (Streckeisen, 1974). However, in spite of the mining terminology for this intrusion, no biotite was observed in any sample, and only relict grains are present. Herein, this intrusion type is still referred to as ‘biotite granodiorite’ (or *BiGd*), because a) this is the most reasonable name for the unaltered protolith, and b) to be in accordance with previously published literature.



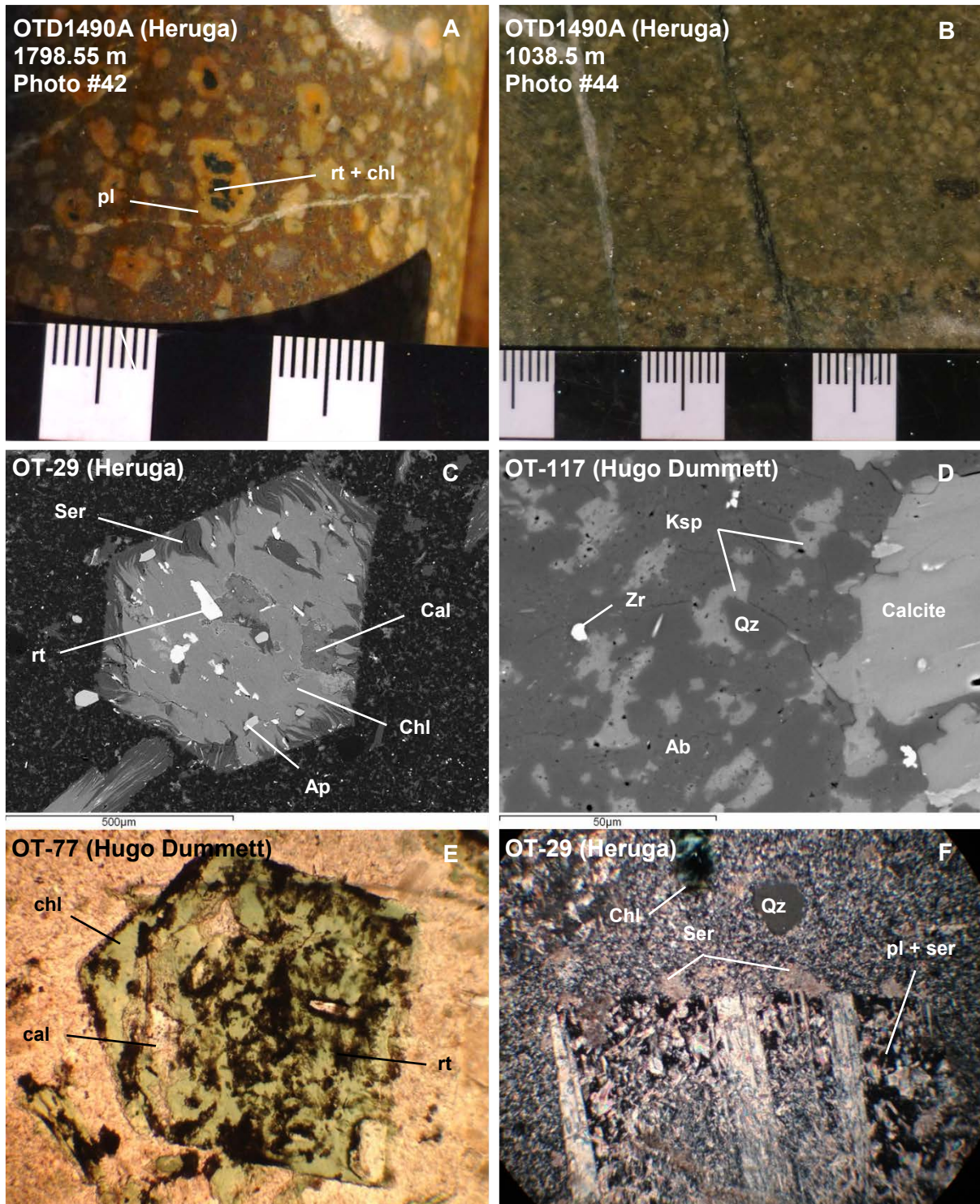


Figure 4.13. Representative images of the biotite granodiorite. a) Inclusions of rutile and chlorite in feldspar phenocryst, b) minor calcite and chlorite veinlets in fine-grained BiGd. c) altered biotite (?) phenocryst, d) typical groundmass of the BiGd intrusions, e) relict biotite phenocryst altered to an assemblage of chlorite, calcite, and rutile, and f) Partially altered plagioclase phenocryst. Rt – rutile, chl – chlorite, - pl – plagioclase, ser – sericite, ap – apatite, - cal – calcite, zr – zircon, qz – quartz, ab – albite.

#### 4.4.3 Devonian volcanic sequence (Dvs)

Overlying the Augite basalt sequence of Devonian volcanic rocks of intermediate composition (hereafter, *Dvs*; c.f. ‘Unmineralised Dacite Sequence’ of Wainwright et al., 2011a). At Heruga, the *Dvs* reach a thickness of ~100 m, and reach a maximum thickness of <500 m above the Hugo Dummett deposit (Fig. 4.9). This unit is considered to represent part of a much thicker sequence of volcanic rocks that has been significantly eroded because a <500 m thick overburden is unlikely to be sufficient to contain a developing porphyry system (Crane and Kavalieris, 2012). The timing of volcanic activity with respect to mineralisation is unclear, although the presence of altered, mineralised igneous clasts at the base of the unit (Wainwright et al., 2011a) indicates that its onset was after at least some mineralisation in the district. These rocks are considered to be co-magmatic with the QMD because they have similar geochemical characteristics and the U-Pb zircon ages of the *Dvs* ( $367 \pm 3$  Ma; Wainwright et al., 2011a) overlap within error of the QMD.

The *Dvs* comprises several volcanic deposits. Described here are the lithologies present in a typical sequence of volcanic rocks from the *Dvs* at Hugo Dummett (OTD447; 639.05 to 801.6 m depth; Fig. 4.14). The three main volcanic units are present: ignimbrite, block-ash tuff, and ash fall tuff. The block-ash tuffs are present as repeated horizons of 10 – 30 m thick, heterolithic, matrix-supported volcanoclastic breccia. The predominant clast type in these breccias is dark brown, uncrowded porphyry with large, tabular feldspar phenocrysts (up to 7 mm) comprising ~25 vol. % of clasts. Smaller clasts of dark, fine-grained, crowded porphyry are also present. Clasts range in size from <1 cm up to 10 cm, and are angular to sub-rounded. The matrix of this unit is fine lapilli. Block-ash tuff sequences are overlain by either ignimbrite or ash fall deposits. A thick (60 m) sequence of ignimbrite (cf. dacite ash flow tuff with fiamme; Crane and Kavalieris, 2012) is found overlying one interval of block-ash tuff at ~730 m (Fig. 4.14).

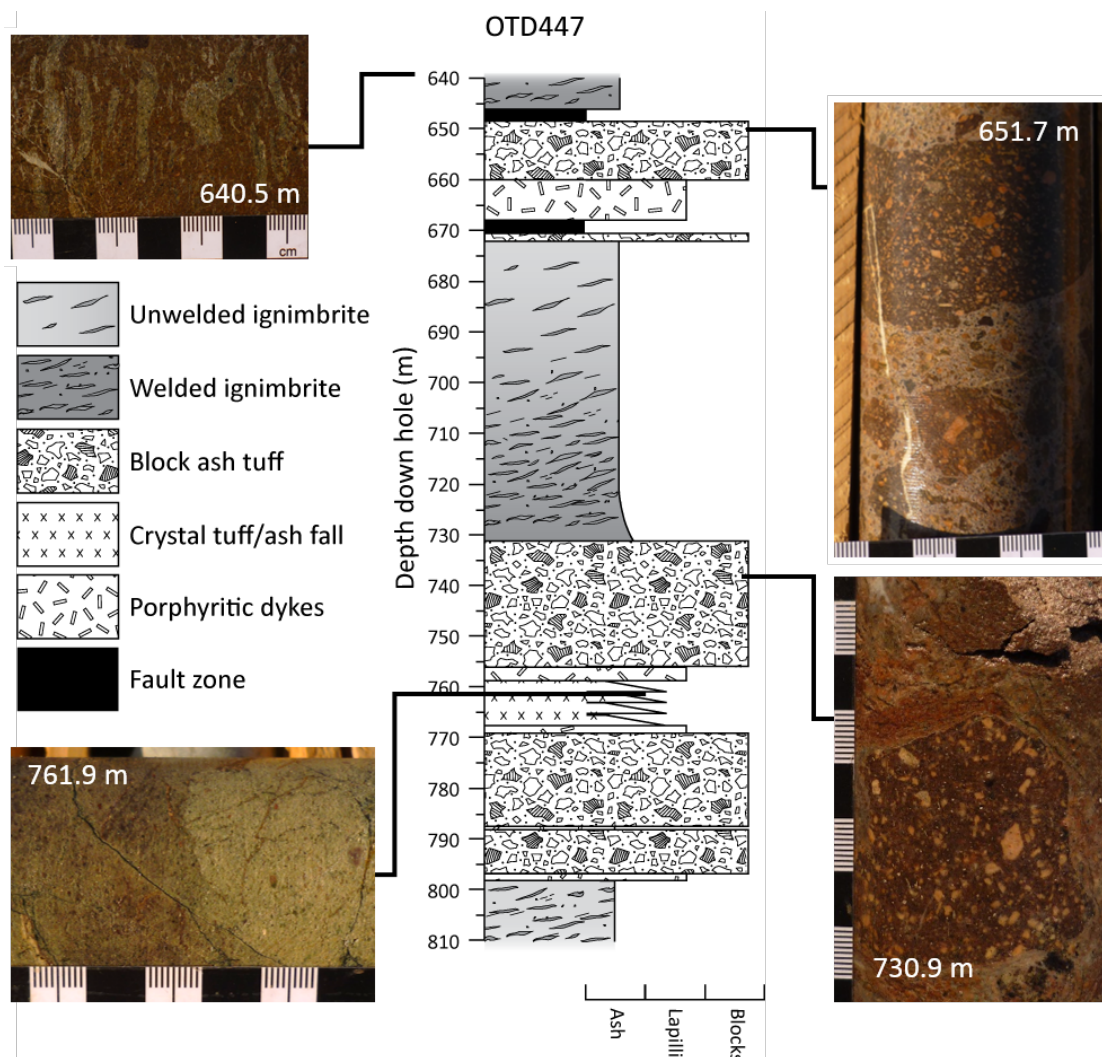


Figure 4.14. Log of 170 m section of Dvs from drill hole OTD447, above the Hugo Dummett deposit. The sequence comprises 2 thick, successive ignimbrite deposits, which have block ash tuffs at their base. Fault zones are minor brecciated drill core intersections, which do not represent large amounts of displacement (based on approximate correlations of thickness with other drill holes).

This unit varies from poorly welded ash flow tuff at the top, to welded ignimbrite at the bottom. Fiamme become increasingly well-developed towards the bottom of this unit, suggesting it represents one volcanic event. Ash fall tuffs (at ~760 m depth) comprise a 10 m thick unit containing several fining-upwards sequences of ash and lapilli tuff (Fig. 4.14). The base of each sequence consists of crystal lapilli tuff, which grades to fine ash tuff at the top.

Ash fall



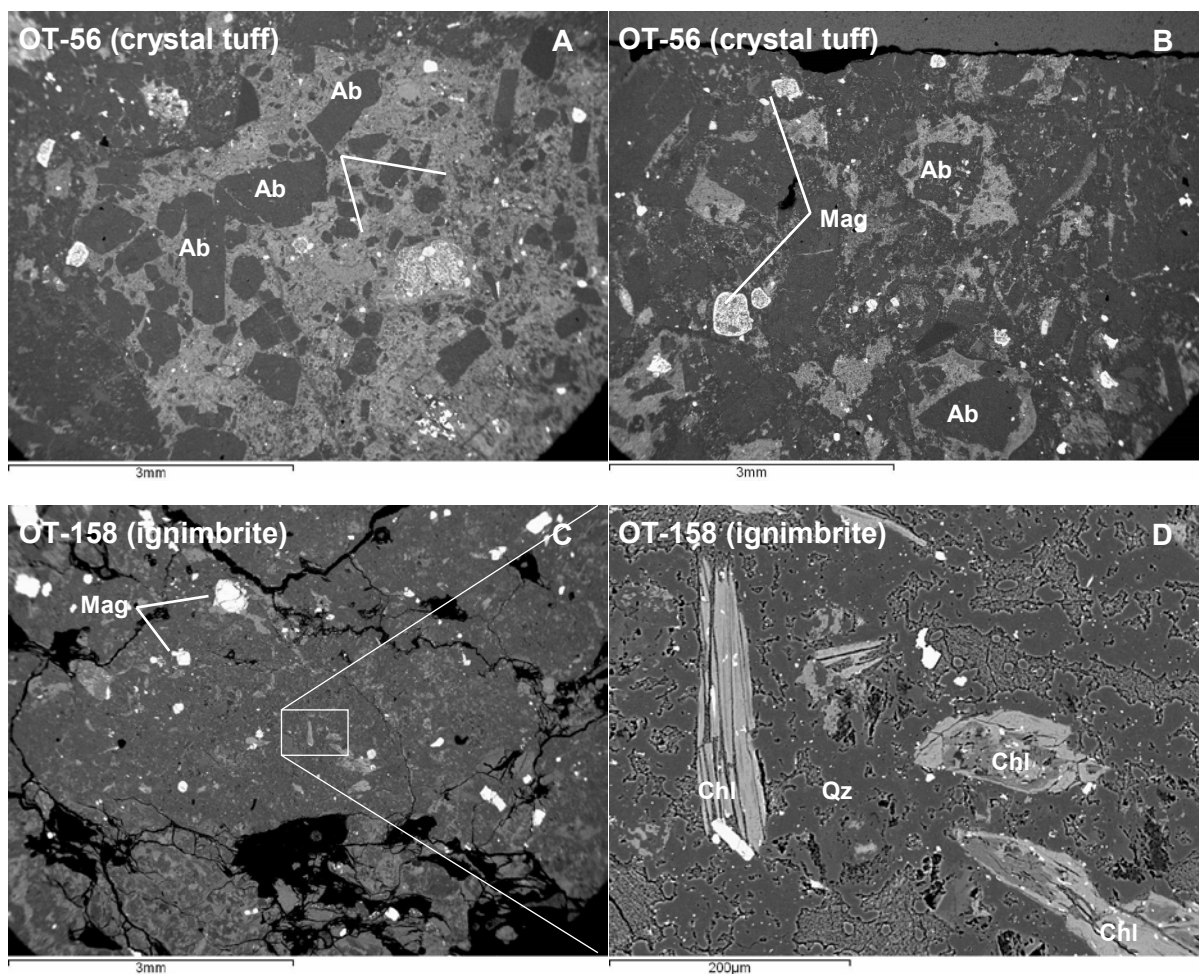


Figure 4.15. (a) Backscatter SEM image of crystal tuff. Plagioclase (albite) crystals in a devitrified matrix. (b) Backscatter electron SEM image of crystal tuff. Magnetite crystals are present in the matrix. (c) Backscatter SEM image of ignimbrite, with magnetite phenocrysts. (d) Small, relict hornblende crystals are common. Chl = chlorite., Qz = quartz, Ab = albite, Mag = magnetite.

tuffs are composed of mildly sericitised albite crystals up to 2 mm in size surrounded by a fine grained matrix of sericite, albite, and quartz. Mafic minerals have been altered to chlorite. The ignimbrite is composed of a fine-grained matrix of albite and quartz (possibly devitrified glass; Fig. 4.15 b,c) with some fractured phenocrysts, mainly Fe-Ti oxides. Small, relict mafic minerals, most likely amphibole based on cleavages, are completely replaced by chlorite (Fig. 4.15 d). Apatite is common in the groundmass of both ignimbrite and ash fall tuff, and is frequently found associated with Fe-Ti oxides. Some coarse-grained, felsic xenoliths are



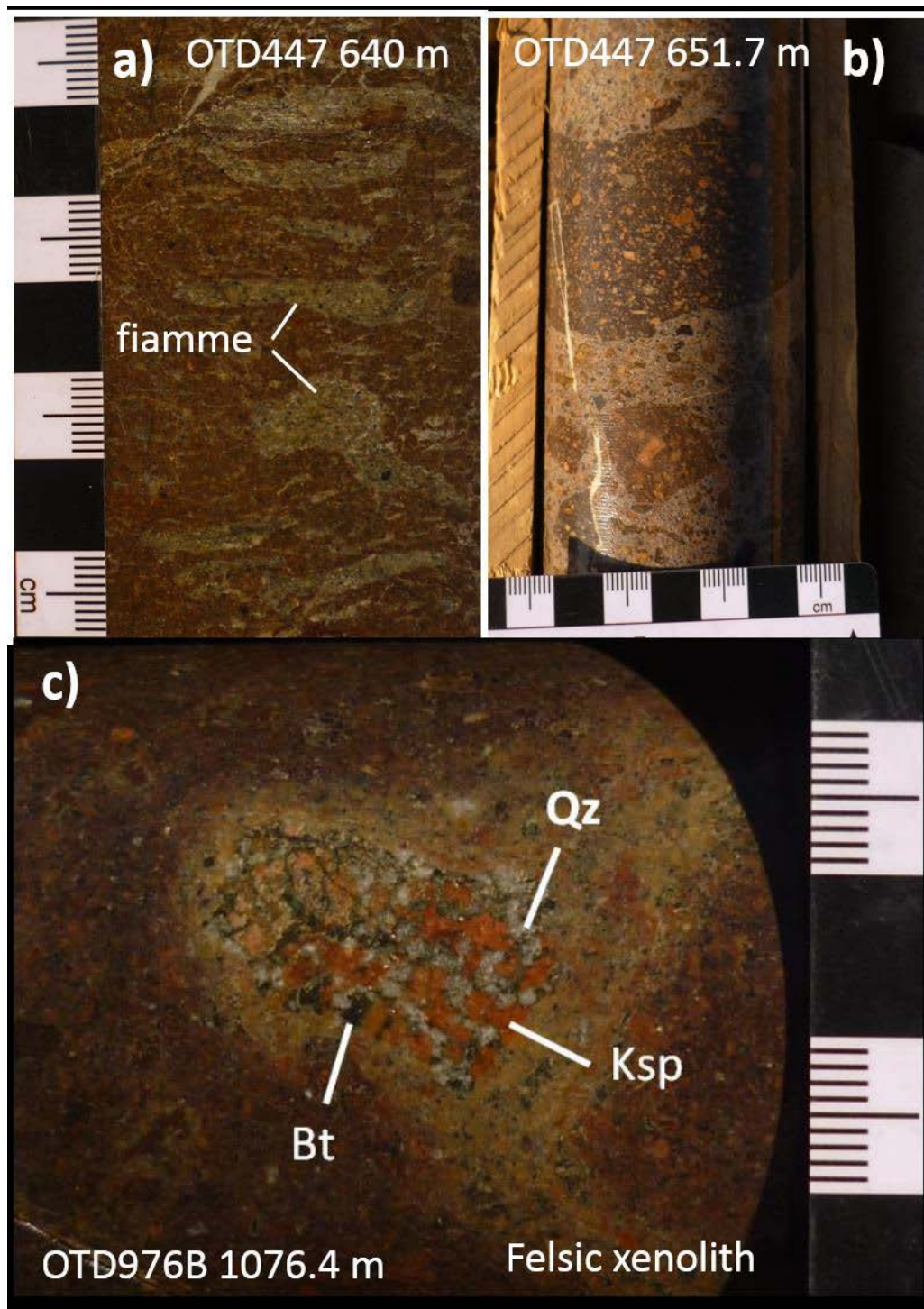


Figure 4.16. Representative images of Dvs rocks. (a) Ignimbrite with fiamme from the Dvs at Hugo Dummett. (b) Block ash tuff from same intersection of Dvs as in (a). Blocks are composed of felsic porphyry, with phenocrysts up to 5 mm. (c) Felsic xenolith in lapilli tuff from Dvs at Hugo Dummett.

observed in the Dvs (Fig. 4.16 c). They range in size from 1 cm to ~15 cm and contain a holocrystalline assemblage of quartz, K-feldspar and biotite. K-feldspars are commonly altered to sericite, and biotite to chlorite. All Dvs rocks are cut by narrow calcite veinlets.

#### 4.4.4 Hydrothermal alteration

The two most abundant alteration styles in the late Devonian intrusions are potassic, and quartz sericitic. Sodic-calcic alteration is also present in some rocks. Other alteration styles (such as biotite-magnetite alteration in the Augite Basalt host rocks, or distal propylitic alteration) are found at Oyu Tolgoi but have not been carefully studied because they do not occur in late Devonian intrusions, are not found in the core of the deposit, or both. Advanced argillic alteration is also present in the shallow portions of some areas of the Hugo Dummett deposit, although it is entirely absent at Heruga, and is not discussed herein.

| Hole ID: EJD0026    |          | Deposit: Heruga        |        |        |                       |          | Depth: 1556 to 1582                                                                                                                                                                                                                                               |          |
|---------------------|----------|------------------------|--------|--------|-----------------------|----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------|
| Hole depth (metres) | Sample # | Lithology (base depth) | Grade  |        | Alteration assemblage |          | Comments (Igneous and hydrothermal texture)                                                                                                                                                                                                                       | #        |
|                     |          |                        | Au g/t | Cu wt% | Ksp 2nd               | Sericite |                                                                                                                                                                                                                                                                   |          |
|                     |          |                        | 1 2    | 1 2    |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1558                | OT-51 →  | QMD                    |        |        |                       |          | Igneous textures largely destroyed (Ser-Sil overprinting K-sil) 'Ghost' fsp (40%, 1-2mm, elongate, euhedral), mafic phase (Bt?, <5%, entirely chloritised) Fragments of mineralised qz + cpy + mo veins. Sulphides primarily cpy (in veins and dissem.), minor py | 64<br>65 |
| 1560                |          | 1561.6                 |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1562                |          | Ba                     |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1564                |          | Aug Bas                |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1566                |          | 1565.4                 |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1568                |          | QMD                    |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1570                |          |                        |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1572                |          | 1573.45                |        |        |                       |          |                                                                                                                                                                                                                                                                   | 66       |
| 1574                |          | Aug Bas                |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1576                |          | 1574.9                 | 3.79>  |        |                       |          |                                                                                                                                                                                                                                                                   |          |
| 1578                |          | QMD                    |        |        |                       |          | Sinuous qz + cpy (+py) veins, strong ser-sil alteration Igneous textures completely obscured                                                                                                                                                                      | 67       |
| 1580                |          |                        |        |        |                       |          |                                                                                                                                                                                                                                                                   |          |

Figure 4.17. Petrological log for drill hole EJD0026 from Heruga, between 1556 and 1582 m depth.

#### 4.4.4.1 Potassic (K-feldspar + quartz + apatite)

In the QMD, potassic alteration is found in the deepest parts of the Heruga and Hugo Dummett deposits (e.g. Figs. 4.21 and 4.24). It is characterised by a brick red colour, and is frequently associated with a dense network of quartz (+ bornite ± chalcopyrite) stockwork veins (Fig. 4.23), giving affected rocks a distinctive pink-red, black and white appearance in hand specimen (Fig. 4.11 a). Potassic alteration typically destroys original igneous textures. Where present, only ‘ghost’ relict feldspar phenocrysts remain (Fig. 4.11 d). Potassic alteration is typically associated with the highest Au grades, and also modest Cu content. (e.g. Fig. 4.23)

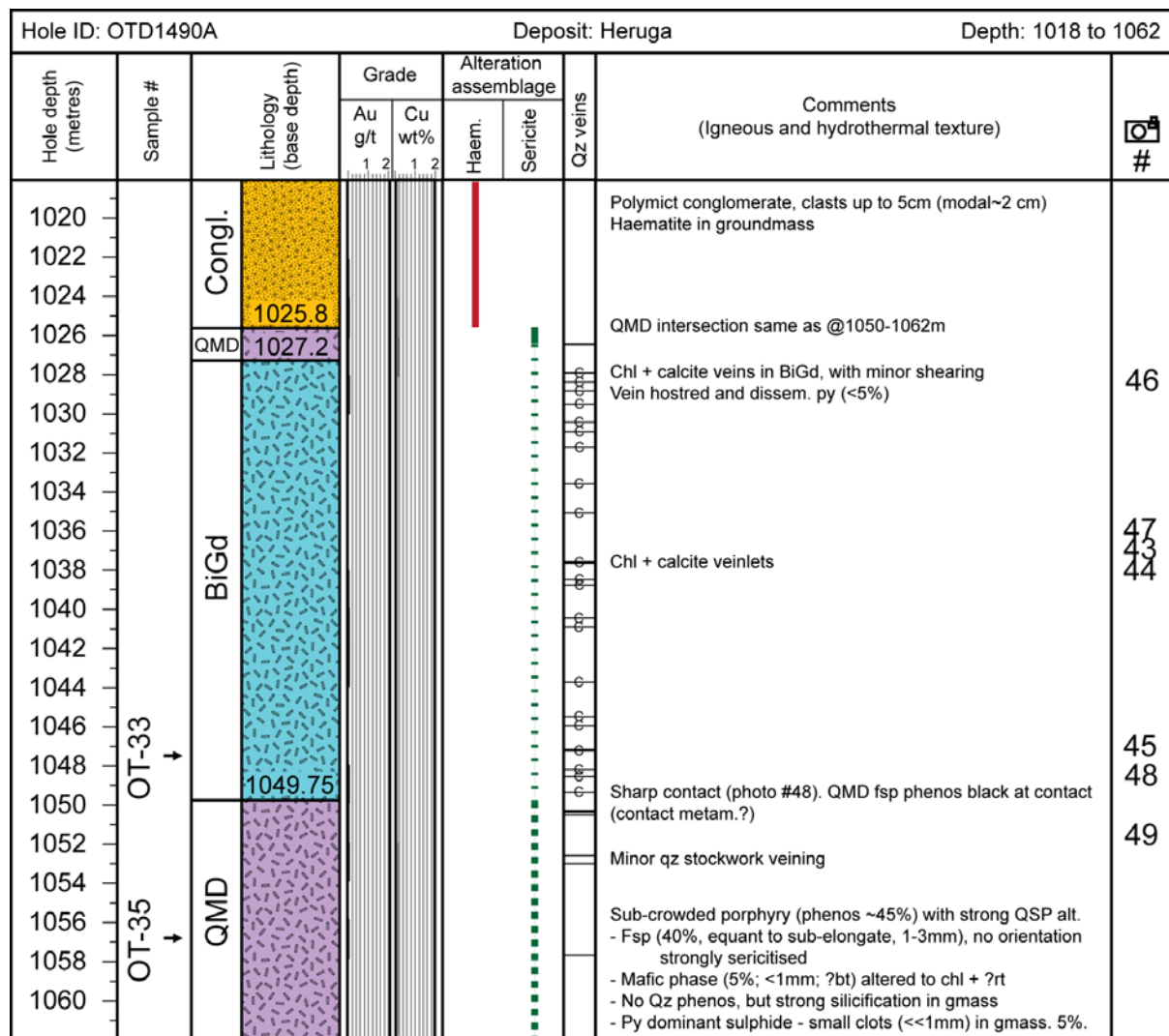


Figure 4.18. Petrological log for drill hole OTD1490A from Heruga, between 1016 and 1062 m depth.

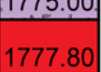
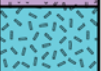
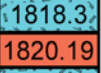
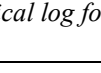
| Hole ID: OTD1490A      |            |                                                                                   | Deposit: Heruga                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                     | Depth: 1706 to 1826                                                                                                          |                                                                                          |  |  |  |  |
|------------------------|------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|--|--|--|--|
| Hole depth<br>(metres) | Sample #   | Lithology<br>(base depth)                                                         | Grade                                                                               |                                                                                     | Alteration<br>assemblage                                                            |                                                                                     | Qz veins                                                                            | Comments<br>(Igneous and hydrothermal texture)                                                                               | <br># |  |  |  |  |
|                        |            |                                                                                   | Au<br>g/t                                                                           | Cu<br>wt%                                                                           | Ksp 2nd                                                                             | Chl Ser                                                                             |                                                                                     |                                                                                                                              |                                                                                          |  |  |  |  |
| 1708                   | OT-25<br>↓ | Fz                                                                                |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                     | Igneous textures obscured by strong potassic alteration                                                                      | 29                                                                                       |  |  |  |  |
| 1710                   |            | QMD                                                                               |    |    |    |    |    | Fsp (50%; <2mm, euhedral, elongate, weak orientation along hole). Altered to dark green (sericite)                           | 30                                                                                       |  |  |  |  |
| 1712                   |            |                                                                                   |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                     | Gmass silicified. Diss. py in gmass replacing mafic phase?                                                                   | 32                                                                                       |  |  |  |  |
| 1714                   |            |                                                                                   |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                                                              |                                                                                          |  |  |  |  |
| 1716                   |            |                                                                                   |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                                                              |                                                                                          |  |  |  |  |
| 1718                   |            |                                                                                   | 1718.1                                                                              |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                                                              |                                                                                          |  |  |  |  |
| 1720                   | Aug Bas    |  |    |    |    |    |                                                                                     |                                                                                                                              |                                                                                          |  |  |  |  |
| 1722                   |            |                                                                                   |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                     |                                                                                                                              |                                                                                          |  |  |  |  |
| 1768                   | OT-27<br>↓ | Aug Bas                                                                           |    |    |    |    |    |                                                                                                                              |                                                                                          |  |  |  |  |
| 1770                   |            | QMD                                                                               |    |    |    |    |    | Igneous texture mostly obscured by strong ser alteration. Looks the same as @1711                                            | 33                                                                                       |  |  |  |  |
| 1772                   |            | QMD                                                                               |    |    |    |    |    | Thick (10 cm) qz + anh 'crackle' vein                                                                                        | 35                                                                                       |  |  |  |  |
| 1774                   |            | Ba                                                                                |   |   |   |   |   | Cpy veinlets cross-cut earlier barren qz veins                                                                               |                                                                                          |  |  |  |  |
| 1776                   |            | QMD                                                                               |  |  |  |  |  | Strong potassic alteration close to contact, diss. py + cpy                                                                  | 36                                                                                       |  |  |  |  |
| 1778                   |            | QMD                                                                               |  |  |  |  |  | 'Crackle' qz + cpy vein (>10cm) cut by calcite vein.                                                                         | 41                                                                                       |  |  |  |  |
| 1780                   | OT-31<br>↓ | QMD                                                                               |  |  |  |  |  | 'Ghost' fsp, 1-2 mm, with blurry edges, 'crowded' texture                                                                    | 37                                                                                       |  |  |  |  |
| 1782                   |            | QMD                                                                               |  |  |  |  |  | Patches of sulphides                                                                                                         | 39                                                                                       |  |  |  |  |
| 1784                   |            | QMD                                                                               |  |  |  |  |  | Thick (3cm) qz + cpy (+?anh) 'crackle' vein w/ chl selvage.                                                                  | 40                                                                                       |  |  |  |  |
| 1786                   |            | QMD                                                                               |  |  |  |  |  | Chl in gmass. Abundant cpy + (qz) stringers                                                                                  | 38                                                                                       |  |  |  |  |
| 1788                   |            | QMD                                                                               |  |  |  |  |  | Qz vein w/ potassic (Ksp) selvage overprinting sericite                                                                      |                                                                                          |  |  |  |  |
| 1790                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1792                   | OT-29<br>↓ | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1794                   |            | QMD                                                                               |  |  |  |  |  | Coarse BiGd                                                                                                                  | 42                                                                                       |  |  |  |  |
| 1796                   |            | QMD                                                                               |  |  |  |  |  | Fsp (30%, up to 7mm, mostly 2-3mm, equant, euhedral) show frequent bimodal zoning. Clots of haem+chl at core of some grains, |                                                                                          |  |  |  |  |
| 1798                   |            | QMD                                                                               |  |  |  |  |  | Mafic phase (?bt) altered to chlorite and FeTi oxides                                                                        |                                                                                          |  |  |  |  |
| 1800                   |            | QMD                                                                               |  |  |  |  |  | Qz 'eye' phenocrysts (<1mm, <5%)                                                                                             |                                                                                          |  |  |  |  |
| 1802                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1804                   | OT-29<br>↓ | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1806                   |            | QMD                                                                               |  |  |  |  |  | Calcite + chl veins throughout this unit                                                                                     |                                                                                          |  |  |  |  |
| 1808                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1810                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1812                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1814                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1816                   | OT-29<br>↓ | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1818                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1820                   |            | Hb/And                                                                            |  |  |  |  |  | Sparsely porphyritic (15%), pyroxene-phyric basaltic intrusion                                                               |                                                                                          |  |  |  |  |
| 1822                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1824                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |
| 1826                   |            | QMD                                                                               |  |  |  |  |  |                                                                                                                              |                                                                                          |  |  |  |  |

Figure 4.19. Petrological log for drill hole OTD1490A, from Heruga, between 1706 and 1826 m depth.



| Hole ID: OTD1502B      |                   |                                                                                    | Deposit: Heruga                         |           |                                                                                    |                                                                                    |          | Depth: 1758 to 1792                                                                                                                                                                                      |                                                                                          |
|------------------------|-------------------|------------------------------------------------------------------------------------|-----------------------------------------|-----------|------------------------------------------------------------------------------------|------------------------------------------------------------------------------------|----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Hole depth<br>(metres) | Sample #          | Lithology<br>(base depth)                                                          | Grade                                   |           | Alteration<br>assemblage                                                           |                                                                                    | Qz veins | Comments<br>(Igneous and hydrothermal texture)                                                                                                                                                           | <br># |
|                        |                   |                                                                                    | Au<br>g/t                               | Cu<br>wt% | Ksp 2nd                                                                            | Sericite                                                                           |          |                                                                                                                                                                                                          |                                                                                          |
| 1760                   | OT-84<br>↓<br>QMD |  | No assay data collected (too low grade) |           |  |  | No data  | Uncrowded porphyry - variably obscured by alteration<br>Fsp (30-40%, 1-5mm, elongate to equant, euhedral)<br>fuzzy 'ghost' edges (ser alteration)<br>Chl in gmass, with diss. py (replacing mafics, ?bt) | 96<br>95<br>94                                                                           |
| 1762                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1764                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1766                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1768                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1770                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          | Tourmaline + Qz + py veins, 1-2cm with strong sericite halos                                                                                                                                             | 98                                                                                       |
| 1772                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1774                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1776                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          | Ksp selvages around miner qz veins (overprinting Ser)                                                                                                                                                    |                                                                                          |
| 1778                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1780                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1782                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1784                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1786                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |
| 1788                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          | Igneous texture same as @1760<br>Py (+ qz) veins with white sericite selvages<br>Veins offset by minor faults, which are infilled by epidote + chl                                                       | 97                                                                                       |
| 1790                   |                   |                                                                                    |                                         |           |                                                                                    |                                                                                    |          |                                                                                                                                                                                                          |                                                                                          |

Figure 4.20. Petrological log for drill hole OTD1502B from Heruga, between 1758 and 1792 m depth.

In thin section, feldspar phenocrysts have a 'cloudy', slightly reddish appearance, which is likely to be due to the presence of small (<1 µm) grains of haematite, which are also abundant in the groundmass. The feldspar phenocrysts are albitic in composition, and often display a weak sericite overprint (Fig. 4.11 d) The groundmass of potassically-altered QMD comprises a fine-grained aggregate of quartz and K-feldspar, and subordinate albite. Grains are anhedral and range in size from < 1 µm to 50 µm, with a mean size of ~10 µm. Biotite is an extremely rare phase which is found as small (<1 mm) shreddy grains in the groundmass, where present. The characteristic red colour is contributed by a combination of the K-feldspar in the groundmass, and by the presence of the haematite grains. In mine reports and literature, potassically altered QMD it is referred to as "Red QMD" or "AuQMD" (e.g. Fig. 4.23) and is considered a separate type of QMD. However, in spite of the obvious differences in colour and

| Hole ID: OTD1502A      |                                                                                     |                                                                                               | Deposit: Heruga                                                                     |           |                                                                                                                              |          | Depth: 2072 to 2136                                                               |                                                                                                                                                                                                                                 |                                                                                          |
|------------------------|-------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-----------|------------------------------------------------------------------------------------------------------------------------------|----------|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Hole depth<br>(metres) | Sample #                                                                            | Lithology<br>(base depth)                                                                     | Grade                                                                               |           | Alteration<br>assemblage                                                                                                     |          | Qz veins                                                                          | Comments<br>(Igneous and hydrothermal texture)                                                                                                                                                                                  | <br># |
|                        |                                                                                     |                                                                                               | Au<br>g/t                                                                           | Cu<br>wt% | Ksp 2nd                                                                                                                      | Sericite |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
|                        |                                                                                     |                                                                                               | 1 2                                                                                 | 1 2       |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2074                   | OT-45<br>↓                                                                          | QMD                                                                                           | No assay data collected (too low grade)                                             |           |                                                                                                                              |          |  | 'Crowded' porphyry<br>Fsp (45%, elongate, weak orientation perp. to drill core axis),<br>altered to ser.<br>Narrow qz + py (+ cpy) veins with assoc. sericite selvages<br>(~1cm wide)                                           | 50<br>to<br>52<br>53                                                                     |
| 2076                   |                                                                                     |              |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2078                   |                                                                                     |              |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2080                   |                                                                                     | BiGd                                                                                          |                                                                                     |           |                                                                                                                              |          |  | Fine grained BiGd<br>Fsp - (30-40%, 1-2 mm, equant) Occasional twinning visible.<br>Mafics - (5-10%, ~1mm, ?bt, altered to chl)<br>Qz - Small grains (<< 1mm) in gmass.<br>Gmass - brown to red colour, minor chl and diss. py. |                                                                                          |
| 2082                   |                                                                                     |                                                                                               |                                                                                     |           |                                                                                                                              |          |  |                                                                                                                                                                                                                                 |                                                                                          |
| 2084                   |                                                                                     |                                                                                               |                                                                                     |           |                                                                                                                              |          |  |                                                                                                                                                                                                                                 |                                                                                          |
| 2086                   |                                                                                     |              |                                                                                     |           |                                                                                                                              |          | 2087.51                                                                           |                                                                                                                                                |                                                                                          |
| 2088                   |                                                                                     | QMD                                                                                           |                                                                                     |           |                                                                                                                              |          |  | Brick red appearance, 'crowded' porphyry texture<br>Fsp - (50-60%, no orientation, mostly elongate,<br>some equant, altered to ksp/ser)<br>Mafics - Clots of chl replacing ?bt or ?hbld, 2-3 mm, 15%<br>Gmass - brick red       | 54                                                                                       |
| 2090                   |                                                                                     |                                                                                               |                                                                                     |           |                                                                                                                              |          |  |                                                                                                                                                                                                                                 |                                                                                          |
| 2092                   |                                                                                     |                                                                                               |                                                                                     |           |                                                                                                                              |          |  |                                                                                                                                                                                                                                 |                                                                                          |
| 2094                   |                                                                                     |                                                                                               |                                                                                     |           |                                                                                                                              |          |  |                                                                                                                                                                                                                                 |                                                                                          |
| 2096                   |    | 2098.45                                                                                       |    |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2098                   |    |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2100                   | BiGd                                                                                | 2102.45                                                                                       |    | 55        |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2102                   |    | Sharp contact between BiGd and QMD, marked by strong<br>sericite alteration                   |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2104                   |    | Same igneous textures as @2090. Chloritised mafics<br>are altered hbld (2-3mm, elongate, 20%) |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2106                   |    |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2108                   |  |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2110                   |  |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2112                   |  | Occasional large (1cm) equant, zoned fsp phenocrysts,<br>altered to ser                       |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2114                   |  |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2116                   |  |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2118                   |  |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2120                   | OT-43<br>↓                                                                          | QMD                                                                                           |  |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2122                   |                                                                                     |                                                                                               |  |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2124                   |                                                                                     |                                                                                               |  |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2126                   |                                                                                     |                                                                                               |  |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2128                   |                                                                                     |                                                                                               |  |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2130                   |                                                                                     |                                                                                               |  |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2132                   | OT-47<br>↓                                                                          |                                                                                               |  |           | Strong sericite-chlorite alteration at 50-75cm intersections,<br>assoc. with calcite + chlorite veining<br>Minor py in gmass |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
| 2134                   |                                                                                     |                                                                                               |  |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |
|                        | OT-41<br>↓                                                                          |                                                                                               |                                                                                     |           |                                                                                                                              |          |                                                                                   |                                                                                                                                                                                                                                 |                                                                                          |

Figure 4.21. Petrological log for drill hole OTD1502A from Heruga, between 2072 and 2136 m depth.

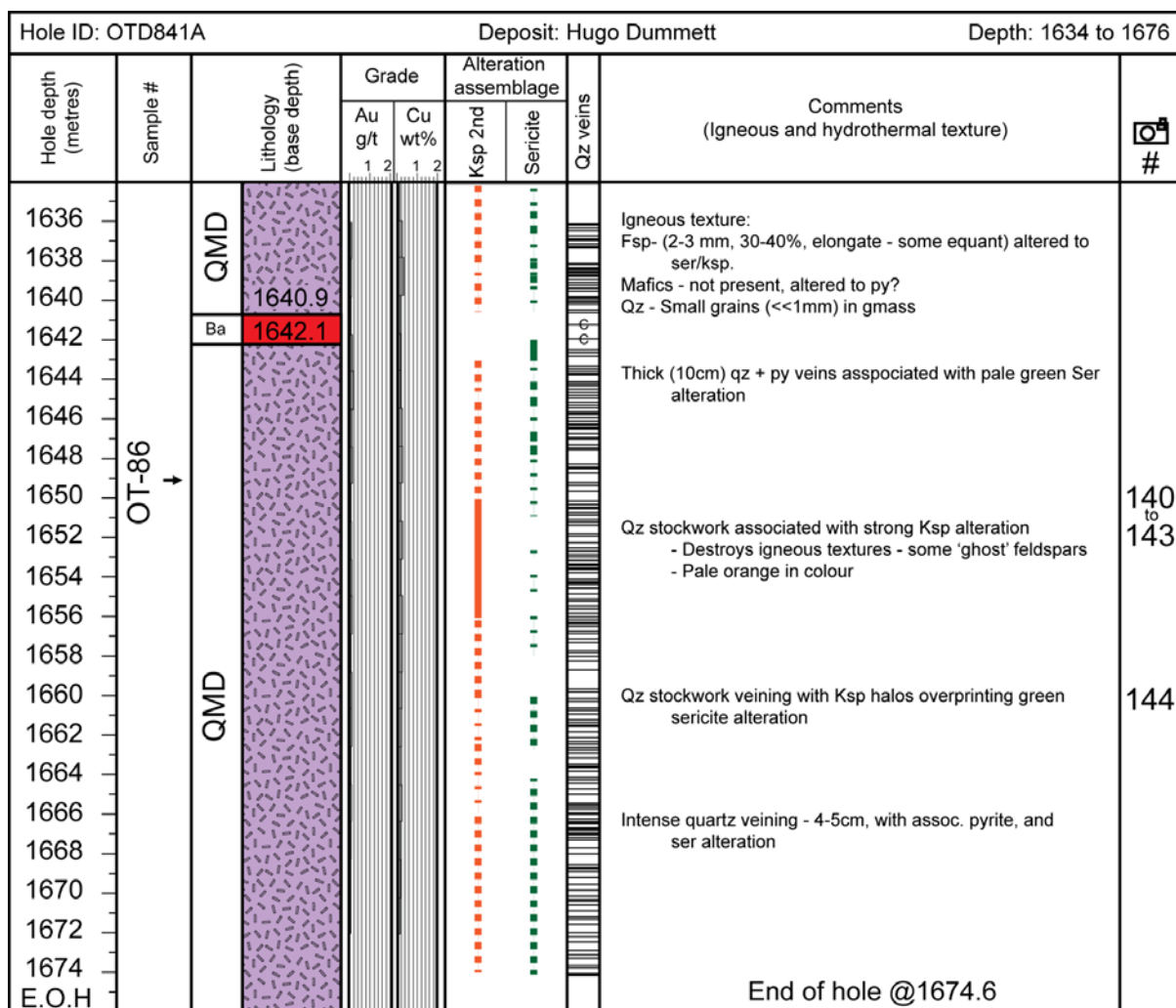


Figure 4.22. Petrological log for drill hole OTD841A from Hugo Dummett, between 1634 and 1676 m depth.

metal grade between the “Red QMD” and any other type, there is practically no difference in terms of their igneous textures, suggests that these differences relate solely to difference in alteration style.

#### 4.4.4.2 Quartz-sericitic (white mica + quartz + pyrite)

Quartz-sericitic alteration is most strongly developed in shallower intersections of QMD (e.g. Fig. 4.25). A transition from quartz-sericitic to potassic alteration with depth was recognised in several drill holes (e.g. Figs. 4.23 and 4.24), and occurs gradually on the scale of 100s of metres. On the 1 – 10 m scale, sericitic alteration is found within potassic zones as

| Hole ID: OTD976A    |          |                        | Deposit: Hugo Dummett |        |                       |          | Depth: 1472 to 1530 |                                                                                                                            |            |
|---------------------|----------|------------------------|-----------------------|--------|-----------------------|----------|---------------------|----------------------------------------------------------------------------------------------------------------------------|------------|
| Hole depth (metres) | Sample # | Lithology (base depth) | Grade                 |        | Alteration assemblage |          | Qz veins            | Comments (Igneous and hydrothermal texture)                                                                                | #          |
|                     |          |                        | Au g/t                | Cu wt% | Ksp                   | Sericite |                     |                                                                                                                            |            |
| 1474                | OT-65    | QMD                    | 1                     | 2      | 1                     | 2        |                     | - Fsp (30%) <1mm - 5mm. Elongate laths, weak orientation. Ubiquitously altered to pale green sericite (illite?)            | 107 to 111 |
| 1476                |          | QMD                    |                       |        |                       |          |                     | - Mafic phase (5-10%; hblid?) largely replaced by cpy (+py).                                                               |            |
| 1478                |          | QMD                    |                       |        |                       |          |                     | - No quartz phenocrysts present, silicification in gmass.                                                                  |            |
| 1480                |          | QMD                    |                       |        |                       |          |                     | - Occasional euhedral relict titanite (<1mm), altered to ?rutile                                                           |            |
| 1482                | OT-67    | QMD                    |                       |        |                       |          |                     | Stringers of cpy (1mm thick) cross-cut thick qz + py + cpy veins                                                           | 112 to 117 |
| 1484                |          | QMD                    |                       |        |                       |          |                     | Igneous texture largely obscured by alteration. Mineralised qz vein fragments account for ~70% vol.                        |            |
| 1486                |          | QMD                    |                       |        |                       |          |                     | Onset of potassic alt (Ksp) - strongly texturally destructive. Mineralised qz vein fragments common                        |            |
| 1488                |          | QMD                    |                       |        |                       |          |                     | Potassic with incomplete sericite overprint. Qz vein fragments with ?chl halos.                                            |            |
| 1490                | OT-69    | QMD                    |                       |        |                       |          |                     | Igneous texture largely obscured. Occasional 'ghost' feldspar phenocrysts (1-2 mm, elongate, euhedral)                     | 120 to 123 |
| 1492                |          | QMD                    |                       |        |                       |          |                     | Potassic with incomplete sericite overprint. Qz vein fragments. Sericite associated with massive qz + cpy veins (3-5 cm)   |            |
| 1494                |          | QMD                    |                       |        |                       |          |                     | Strong potassic alteration, igneous textures entirely obscured. - Vivid orange with dark stringers and patches (cpy + ?bn) |            |
| 1496                |          | QMD                    |                       |        |                       |          |                     | - Anastomosing A-type qz veins                                                                                             |            |
| 1498                | OT-69    | QMD                    |                       |        |                       |          |                     | Igneous textures observed - same as @1474m                                                                                 | 124        |
| 1500                |          | QMD                    |                       |        |                       |          |                     | - Fsp (30%), ~2mm, elongate and aligned. Sericite altered, gmass flooded with Ksp.                                         |            |
| 1502                |          | QMD                    |                       |        |                       |          |                     | - Mafic phase (<5%; <1mm) altered to cpy.                                                                                  |            |
| 1504                |          | QMD                    |                       |        |                       |          |                     | Abundant mineralised qz vein fragments                                                                                     |            |
| 1506                | OT-69    | QMD                    |                       |        |                       |          |                     | Same strong potassic alteration as seen @1501. - Strongly texturally destructive                                           | 124        |
| 1508                |          | QMD                    |                       |        |                       |          |                     | - Qz + cpy stockwork veins cross-cut by narrow calcite veins                                                               |            |
| 1510                |          | QMD                    |                       |        |                       |          |                     | Qz + cpy stockwork veining very well developed (~20% vol)                                                                  |            |
| 1512                |          | QMD                    |                       |        |                       |          |                     |                                                                                                                            |            |

Figure 4.23. Petrological log for drill hole OTD976A from Hugo Dummett, between 1472 and 1530 m depth.

wide selvages surrounding thick (>10 cm) quartz + pyrite ( $\pm$  chalcopyrite) veins (Fig. 4.11 b). This suggests that the quartz-sericite alteration overprinted the earlier potassic alteration in the shallower portions of the system. The down-hole transition from quartz-sericite to potassic alteration is also accompanied by a marked change in metal grade and style, with the low Au, high Cu grades of the quartz-sericitic zone (Fig. 4.24) giving way to lower Cu but higher Au



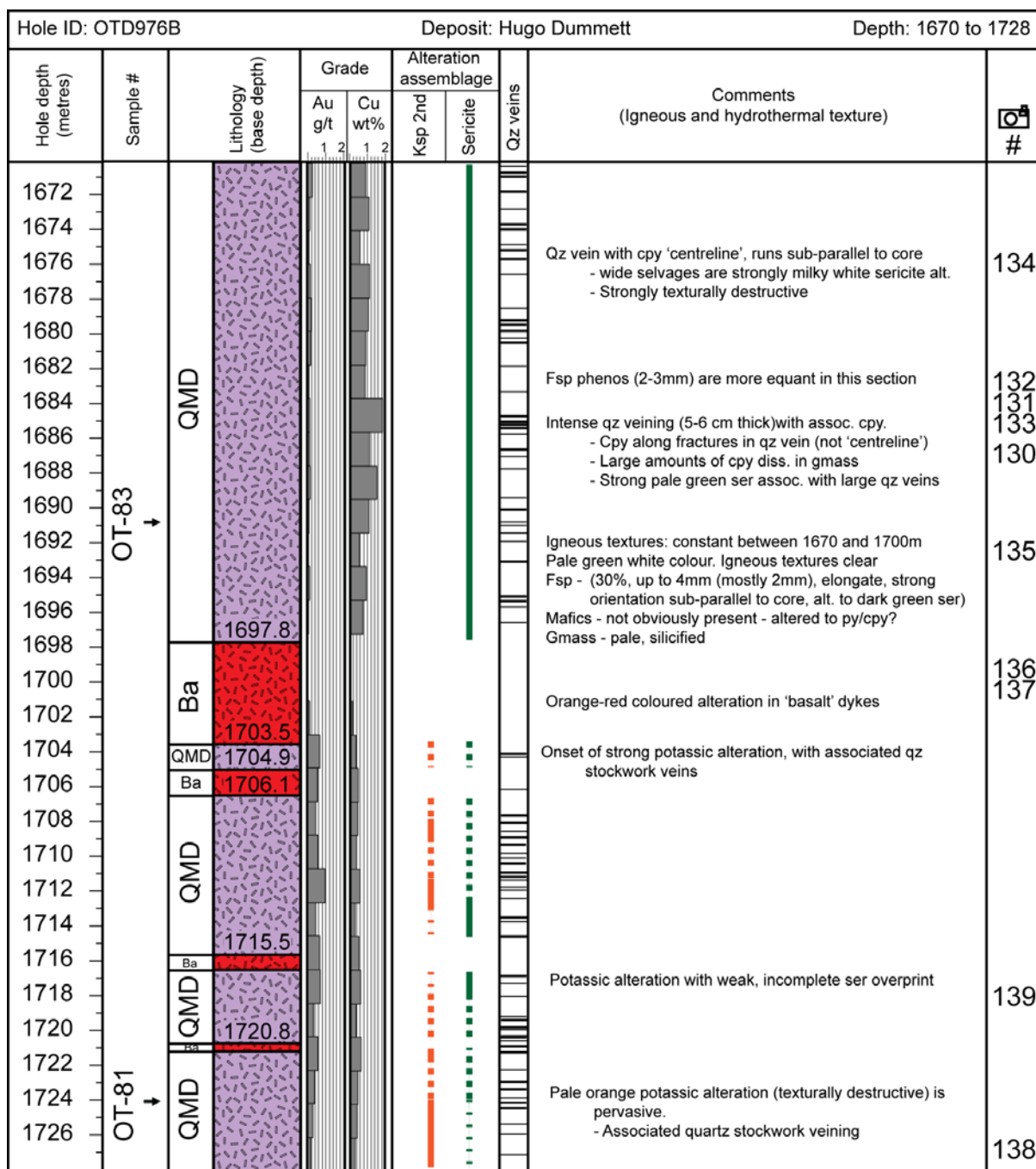


Figure 4.24. Petrological log for drill hole OTD976B from Hugo Dummett, between 1670 and 1728 m depth.

grade in the potassic zone (e.g. Figs. 4.23 and 4.24). This change is likely to be due to remobilisation of the Au during the quartz-sericite overprinting event.

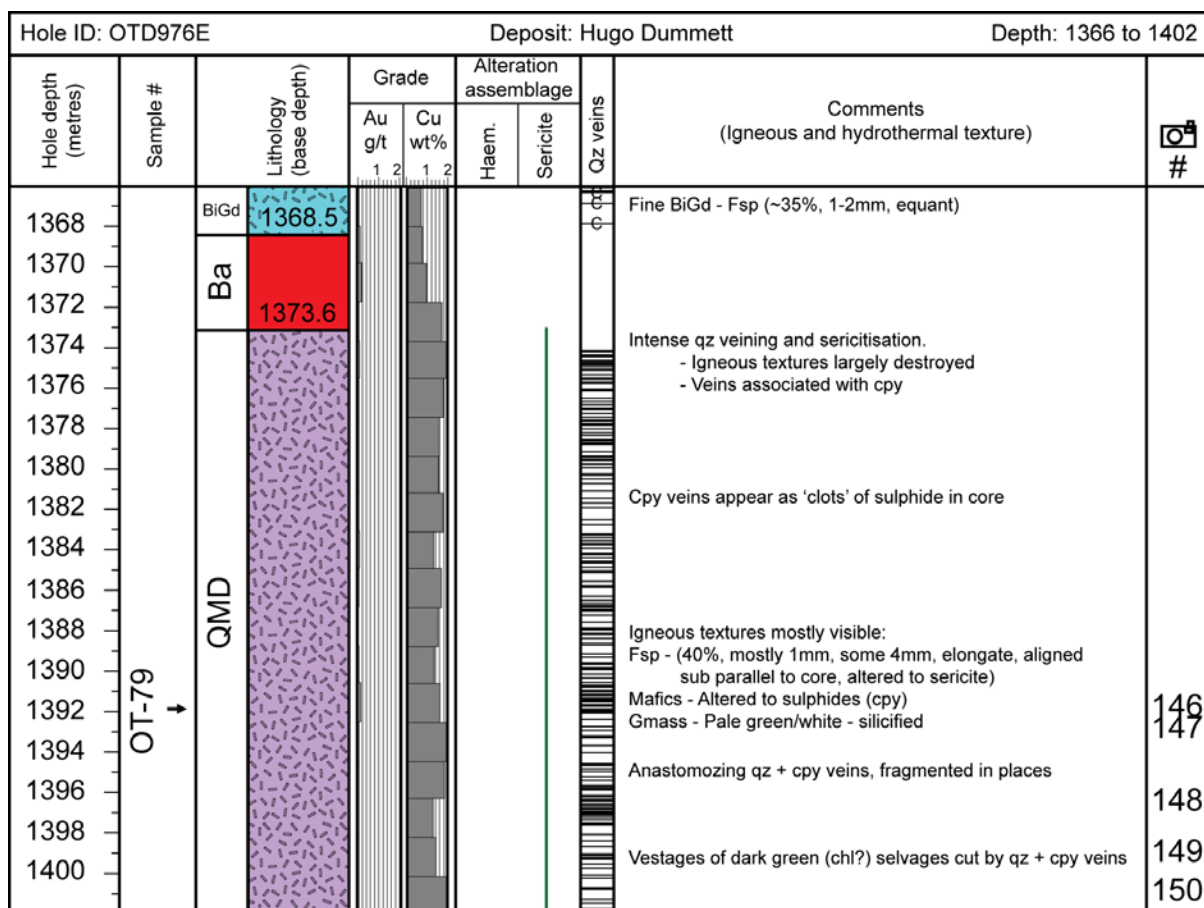


Figure 4.25. Petrological log for drill hole OTD976E from Hugo Dummett, between 1366 and 1402 m depth.

Rocks affected by quartz-sericite alteration are white to pale green colour in hand specimen. Igneous textures are partially destroyed in some intersections, although relict feldspar phenocrysts are frequently observed, and are mostly darker in colour than the surrounding groundmass. Along with the large quartz + pyrite veins, small (<1 cm) mineralised pygmatic quartz vein fragments are common in these rocks (Fig. 4.10). Chalcopyrite and bornite are the most common Cu sulphides, and are found in narrow (<1 cm) chalcopyrite veinlets cross-cut earlier quartz veins, in larger quartz veins (Fig. 4.10 a), and abundantly disseminated in the groundmass (Fig. 4.10 c). In thin section, feldspar phenocrysts are entirely replaced by fine grained sericite (<1 µm), which is occasionally observed as radial 'rosettes' within the feldspar phenocrysts. The groundmass comprises a uniform patchwork of subhedral

quartz and sericitised feldspar, with irregular patches up to 400 µm in size. Larger (1-2 mm), anhedral patches of quartz are also present, which may represent small vein quartz fragments, or silicification of the groundmass. Micas in the groundmass often fringe sericitised feldspar phenocrysts, which causes the edges of the grains to be fuzzy and indistinct. Apatite is a common phenocryst in sericite altered rocks (see Chapter 6).

#### *4.4.4.3 Sodic-calcic (actinolite + albite + magnetite + apatite + titanite)*

Sodic-calcic alteration, while common in the Augite Basalt host rocks from deep portions of the system (Crane and Kavalieris, 2012), is relatively uncommon in the QMD. One sample of sodic-calcic alteration was observed at the deepest level of drilling in the SW Oyu deposit (OT-143). Given that this system is the most deeply eroded (Fig. 4.4 a), and that this sample is coarse-grained and equigranular, this drilled intersection is likely to represent the deepest parts of the Oyu Tolgoi system studied here, and supports suggestions that sodic-calcic alteration forms in the deepest portions of porphyry systems (e.g. Sillitoe, 2010; Sillitoe et al., 2013). In sample OT-143, hornblende is altered to actinolite, with a minor epidote overprint along the relict cleavage planes, and is associated with magnetite, apatite, and titanite (Fig. 4.12). Sulphides are absent from this sample, and whole rock Cu and Au grade is extremely low (~0.02 g/t Au; 200 ppm Cu). Groundmass feldspars are albitised, although rims of oligoclase are present on plagioclase phenocrysts.

|                                |       | BiGd  |        |        |        |       | QMD - potassic alteration |        |        |        |       | QMD - sericitic alteration |        |        |        |       | QMD NaCa | LOD   | Median     |
|--------------------------------|-------|-------|--------|--------|--------|-------|---------------------------|--------|--------|--------|-------|----------------------------|--------|--------|--------|-------|----------|-------|------------|
|                                |       | min   | 1st Q. | median | 3rd Q. | max   | min                       | 1st Q. | median | 3rd Q. | max   | min                        | 1st Q. | median | 3rd Q. | max   | OT-145   |       | Felsic arc |
| SiO <sub>2</sub>               | wt. % | 59.5  | 63.8   | 64.65  | 65.2   | 66.2  | 51.9                      | 60.5   | 62.5   | 64.6   | 68    | 58.9                       | 64.9   | 66.8   | 69.4   | 74.2  | 59.9     | 0.01  | 68.6       |
| Al <sub>2</sub> O <sub>3</sub> | wt. % | 14.7  | 15.1   | 15.3   | 15.6   | 15.9  | 13.35                     | 16.0   | 16.8   | 17.39  | 20.6  | 11.95                      | 15.0   | 16.5   | 17.1   | 18.3  | 18.25    | 0.01  | 15.2       |
| FeOt                           | wt. % | 2.43  | 2.98   | 3.24   | 3.52   | 3.86  | 1.70                      | 2.74   | 3.33   | 4.18   | 12.33 | 0.91                       | 1.94   | 2.39   | 4.05   | 6.30  | 3.31     | 0.01  | 3.29       |
| CaO                            | wt. % | 2.17  | 2.93   | 3.20   | 3.44   | 4.17  | 0.25                      | 0.85   | 1.38   | 2.46   | 3.98  | 0.10                       | 0.36   | 0.72   | 1.72   | 3.49  | 2.75     | 0.01  | 2.43       |
| MgO                            | wt. % | 0.83  | 1.21   | 1.47   | 1.64   | 2.15  | 0.45                      | 0.84   | 1.01   | 1.22   | 2.43  | 0.16                       | 0.49   | 0.69   | 1.28   | 2.17  | 1.34     | 0.01  | 0.92       |
| Na <sub>2</sub> O              | wt. % | 1.01  | 3.27   | 3.88   | 4.60   | 5.51  | 0.10                      | 0.97   | 3.25   | 4.69   | 6.30  | 0.14                       | 0.16   | 0.24   | 5.03   | 5.77  | 6.74     | 0.01  | 4.37       |
| K <sub>2</sub> O               | wt. % | 2.26  | 2.65   | 2.93   | 3.14   | 4.75  | 2.49                      | 4.15   | 5.01   | 6.03   | 6.84  | 1.86                       | 2.82   | 3.59   | 4.44   | 6.34  | 2.35     | 0.01  | 2.61       |
| TiO <sub>2</sub>               | wt. % | 0.42  | 0.44   | 0.50   | 0.52   | 0.55  | 0.25                      | 0.30   | 0.40   | 0.55   | 0.68  | 0.19                       | 0.27   | 0.30   | 0.50   | 0.59  | 0.53     | 0.01  | 0.52       |
| MnO                            | wt. % | 0.04  | 0.06   | 0.085  | 0.1    | 0.23  | 0.01                      | 0.04   | 0.05   | 0.10   | 0.3   | 0.01                       | 0.03   | 0.04   | 0.07   | 0.13  | 0.14     | 0.01  | 0.10       |
| P <sub>2</sub> O <sub>5</sub>  | wt. % | 0.16  | 0.17   | 0.19   | 0.20   | 0.24  | 0.05                      | 0.11   | 0.17   | 0.27   | 0.54  | 0.04                       | 0.08   | 0.09   | 0.21   | 0.30  | 0.21     | 0.01  | 0.14       |
| C                              | wt. % | 0.58  | 0.70   | 0.80   | 1.04   | 1.68  | 0.01                      | 0.11   | 0.35   | 0.62   | 1.02  | 0.01                       | 0.04   | 0.16   | 0.25   | 0.68  | 0.42     | 0.01  | 0.02       |
| S                              | wt. % | 0.03  | 0.06   | 0.17   | 0.43   | 1.54  | 0.04                      | 0.40   | 0.96   | 1.57   | 9.83  | 0.24                       | 0.75   | 1.10   | 1.60   | 4.92  | 0.89     | 0.01  | 0.01       |
| Ba                             | ppm   | 276   | 695    | 886    | 1030   | 1605  | 245                       | 541    | 751    | 1168   | 3020  | 95                         | 379    | 433    | 622    | 938   | 818      | 0.5   | 800        |
| Hf                             | ppm   | 3.7   | 4.0    | 4.1    | 4.2    | 4.4   | 1.9                       | 2.8    | 3.4    | 3.8    | 4.6   | 2.3                        | 2.8    | 3.3    | 4.2    | 4.8   | 3.3      | 0.2   | 5.7        |
| Nb                             | ppm   | 6.8   | 7.1    | 7.8    | 8.1    | 9.9   | 3.7                       | 4.4    | 5.9    | 6.3    | 8.9   | 2.3                        | 5.1    | 5.8    | 7.6    | 9.0   | 6.0      | 0.2   | 7.7        |
| Rb                             | ppm   | 42.3  | 67.2   | 76.1   | 85.8   | 116.0 | 68.8                      | 91.3   | 112.5  | 134.0  | 191.0 | 54.0                       | 76.1   | 85.5   | 108.8  | 207.0 | 56.2     | 0.2   | 62.4       |
| Sr                             | ppm   | 209   | 449    | 566    | 742.25 | 1870  | 91.4                      | 184.6  | 306    | 466    | 958   | 37.7                       | 73.1   | 323    | 437.5  | 1025  | 1040     | 0.1   | 221        |
| Ta                             | ppm   | 0.4   | 0.5    | 0.5    | 0.5    | 0.7   | 0.2                       | 0.3    | 0.3    | 0.4    | 0.7   | 0.2                        | 0.3    | 0.3    | 0.5    | 0.6   | 0.3      | 0.1   | 0.58       |
| Th                             | ppm   | 3.64  | 4.06   | 4.30   | 4.45   | 5.48  | 0.97                      | 2.19   | 2.72   | 3.51   | 5.52  | 1.01                       | 2.11   | 2.88   | 4.64   | 8.76  | 2.32     | 0.05  | 5.53       |
| U                              | ppm   | 1.29  | 1.58   | 1.71   | 1.93   | 3.18  | 0.58                      | 0.81   | 0.96   | 1.76   | 4.66  | 0.35                       | 0.94   | 1.18   | 1.87   | 3.20  | 1.00     | 0.05  | 2.48       |
| V                              | ppm   | 64    | 74.8   | 81.5   | 89.25  | 96    | 57                        | 80.75  | 114.5  | 185.5  | 300   | 39                         | 65     | 86     | 133    | 178   | 142      | 5     | 27.5       |
| Y                              | ppm   | 9.4   | 10.6   | 11.4   | 12.45  | 14.9  | 7.2                       | 10.65  | 16.15  | 20.125 | 26.3  | 3.2                        | 10.5   | 11.7   | 16.45  | 21.9  | 21.1     | 0.5   | 37.7       |
| Zr                             | ppm   | 124   | 128    | 131    | 137.5  | 156   | 66                        | 98     | 107    | 126    | 162   | 65                         | 93.5   | 99     | 133.5  | 156   | 100      | 2     | 178        |
| Ag                             | ppm   | 0.5   | 0.7    | 0.9    | 1.6    | 2.3   | 0.6                       | 1      | 1.4    | 2.65   | 8.7   | 0.5                        | 0.8    | 1.2    | 1.525  | 12.8  | <0.5     | 0.5   | 2.1        |
| Co                             | ppm   | 3     | 6      | 7      | 8      | 11    | 1                         | 3      | 5      | 8      | 26    | 1                          | 2.5    | 6      | 7.5    | 55    | 2        | 1     | 9.71       |
| Cu                             | ppm   | 13    | 37     | 73     | 484    | 9110  | 185                       | 827    | 2850   | 9663   | 28900 | 118                        | 1180   | 2520   | 6340   | 43500 | 299      | 1     | 19         |
| Mo                             | ppm   | 1.0   | 1.0    | 2.0    | 3.5    | 11.0  | 1.0                       | 4.5    | 9.0    | 18.0   | 433.0 | 1.0                        | 3.0    | 9.5    | 42.8   | 116.0 | <1       | 1     | 3.9        |
| Ni                             | ppm   | 3     | 7.3    | 9.5    | 15     | 20    | 1                         | 1      | 2.5    | 4.25   | 8     | 1                          | 1.75   | 2      | 4.25   | 5     | <1       | 1     | 6.3        |
| Pb                             | ppm   | 4.0   | 9.3    | 16.5   | 26.8   | 170.0 | 7.0                       | 9.0    | 14.0   | 21.0   | 191.0 | 2.0                        | 8.0    | 18.0   | 30.5   | 152.0 | 5.0      | 2     | 12.1       |
| Zn                             | ppm   | 36    | 61     | 85     | 121    | 210   | 16                        | 47     | 61     | 91     | 242   | 6                          | 38     | 48     | 114    | 200   | 53       | 2     | 80         |
| Au                             | ppm   | 0.001 | 0.004  | 0.009  | 0.045  | 0.106 | 0.011                     | 0.037  | 0.119  | 0.556  | 1.000 | 0.009                      | 0.021  | 0.054  | 0.108  | 1     | 0.037    | 0.001 | 0.002      |
| Sc                             | ppm   | 4     | 5      | 6      | 6      | 7     | 2                         | 2.25   | 4      | 5      | 14    | 2                          | 2      | 3      | 4.5    | 6     | 5        | 0.1   | 12         |

Table 4.1. Summary of the geochemical characteristics of Oyu Tolgoi intrusions. Coloured cells represent % difference from median felsic arc rock (see Table 3.2)

|                                  |       | BiGd  |        |        |        |       | QMD - potassic alteration |        |        |        |        | QMD - sericitic alteration |        |        |        |       | QMD NaCa | LOD  | Median felsic arc |
|----------------------------------|-------|-------|--------|--------|--------|-------|---------------------------|--------|--------|--------|--------|----------------------------|--------|--------|--------|-------|----------|------|-------------------|
|                                  |       | min   | 1st Q. | median | 3rd Q. | max   | min                       | 1st Q. | median | 3rd Q. | max    | min                        | 1st Q. | median | 3rd Q. | max   | OT-145   |      |                   |
| La                               | ppm   | 15.90 | 17.68  | 18.70  | 20.00  | 25.00 | 5.60                      | 8.70   | 13.80  | 15.78  | 33.60  | 1.90                       | 11.35  | 14.50  | 16.10  | 21.70 | 16.60    | 0.5  | 18.81             |
| Ce                               | ppm   | 33.80 | 36.03  | 38.25  | 40.68  | 46.00 | 10.70                     | 16.63  | 27.90  | 31.53  | 65.20  | 3.60                       | 21.30  | 26.00  | 33.55  | 43.70 | 33.50    | 0.5  | 38.47             |
| Pr                               | ppm   | 3.94  | 4.30   | 4.51   | 5.05   | 5.66  | 1.39                      | 2.13   | 3.69   | 3.92   | 8.14   | 0.43                       | 2.54   | 3.01   | 4.30   | 5.19  | 4.16     | 0.03 | 5.19              |
| Nd                               | ppm   | 16.30 | 17.13  | 17.95  | 20.15  | 22.60 | 5.70                      | 9.68   | 14.90  | 17.18  | 32.50  | 1.90                       | 10.00  | 12.30  | 16.45  | 21.00 | 17.90    | 0.1  | 20.93             |
| Sm                               | ppm   | 3.40  | 3.50   | 3.70   | 4.04   | 4.45  | 1.28                      | 2.22   | 3.03   | 3.83   | 6.64   | 0.46                       | 2.06   | 2.68   | 3.51   | 4.48  | 4.11     | 0.03 | 5.35              |
| Eu                               | ppm   | 0.88  | 0.98   | 1.03   | 1.11   | 1.35  | 0.45                      | 0.63   | 0.92   | 1.11   | 1.66   | 0.24                       | 0.56   | 0.79   | 0.96   | 1.30  | 1.31     | 0.03 | 1.14              |
| Gd                               | ppm   | 2.61  | 2.71   | 2.89   | 3.18   | 3.54  | 1.19                      | 1.97   | 2.84   | 3.56   | 5.17   | 0.56                       | 1.86   | 2.16   | 2.97   | 4.15  | 3.73     | 0.05 | 6.18              |
| Tb                               | ppm   | 0.34  | 0.37   | 0.39   | 0.44   | 0.47  | 0.18                      | 0.30   | 0.43   | 0.55   | 0.74   | 0.08                       | 0.28   | 0.32   | 0.44   | 0.62  | 0.58     | 0.01 | 1.03              |
| Dy                               | ppm   | 1.77  | 2.05   | 2.12   | 2.37   | 2.65  | 1.14                      | 1.72   | 2.62   | 3.38   | 4.46   | 0.54                       | 1.69   | 2.04   | 2.72   | 3.63  | 3.49     | 0.05 | 6.91              |
| Ho                               | ppm   | 0.34  | 0.37   | 0.40   | 0.46   | 0.51  | 0.26                      | 0.37   | 0.55   | 0.70   | 0.91   | 0.11                       | 0.36   | 0.39   | 0.59   | 0.74  | 0.75     | 0.01 | 1.46              |
| Er                               | ppm   | 0.91  | 1.00   | 1.08   | 1.19   | 1.37  | 0.79                      | 1.12   | 1.63   | 2.10   | 2.66   | 0.33                       | 1.02   | 1.22   | 1.68   | 2.15  | 2.12     | 0.03 | 4.19              |
| Tm                               | ppm   | 0.14  | 0.15   | 0.17   | 0.19   | 0.21  | 0.13                      | 0.19   | 0.27   | 0.33   | 0.41   | 0.05                       | 0.17   | 0.21   | 0.28   | 0.34  | 0.35     | 0.01 | 0.65              |
| Yb                               | ppm   | 0.80  | 0.93   | 1.00   | 1.09   | 1.37  | 0.87                      | 1.28   | 1.82   | 2.05   | 2.63   | 0.35                       | 1.14   | 1.46   | 1.83   | 2.21  | 2.09     | 0.03 | 3.89              |
| Lu                               | ppm   | 0.12  | 0.14   | 0.15   | 0.17   | 0.2   | 0.17                      | 0.15   | 0.2175 | 0.3    | 0.3375 | 0.43                       | 0.06   | 0.2    | 0.24   | 0.31  | 0.37     | 0.01 | 0.616             |
| LOI                              | wt. % | 3.73  | 4.22   | 4.56   | 5.34   | 7.74  | 2.51                      | 3.22   | 3.48   | 3.97   | 9.27   | 2.13                       | 3.08   | 3.85   | 4.31   | 7.54  | 3.30     |      | 1.09              |
| Sr/Y                             |       | 18.5  | 36.6   | 48.0   | 66.0   | 188.9 | 6.3                       | 10.7   | 16.9   | 32.4   | 99.2   | 4.2                        | 5.8    | 19.2   | 29.1   | 117.8 | 49.3     |      | 5.6               |
| V/Sc                             |       | 12.1  | 13.2   | 14.5   | 15.7   | 17.0  | 13.5                      | 26.2   | 28.8   | 34.6   | 75.0   | 16.0                       | 19.9   | 29.7   | 34.4   | 46.3  | 28.4     |      | 2.5               |
| Eu/Eu*                           |       | 0.76  | 0.87   | 0.92   | 0.98   | 1.17  | 0.76                      | 0.89   | 0.93   | 1.01   | 1.19   | 0.82                       | 0.87   | 0.95   | 1.01   | 1.29  | 0.93     |      | 0.71              |
| Dy <sub>N</sub> /Yb <sub>N</sub> |       | 1.29  | 1.39   | 1.44   | 1.51   | 1.73  | 0.87                      | 0.92   | 0.97   | 1.03   | 1.16   | 0.73                       | 0.91   | 0.98   | 1.06   | 1.41  | 1.12     |      | 1.12              |
| La <sub>N</sub> /Yb <sub>N</sub> |       | 11.2  | 12.3   | 13.6   | 14.7   | 20.4  | 2.3                       | 4.9    | 5.8    | 6.3    | 9.2    | 3.9                        | 5.5    | 6.0    | 7.0    | 16.0  | 5.70     |      | 3.3               |
| La <sub>N</sub> /Sm <sub>N</sub> |       | 2.90  | 3.15   | 3.26   | 3.36   | 4.26  | 1.52                      | 2.50   | 2.94   | 3.24   | 3.73   | 2.20                       | 2.68   | 3.23   | 3.63   | 4.74  | 2.60     |      | 2.09              |
| ΣREE                             | ppm   | 81.6  | 87.5   | 92.4   | 100.5  | 112.8 | 30.8                      | 51.0   | 78.0   | 83.3   | 165.2  | 10.6                       | 55.6   | 68.3   | 89.4   | 104.1 | 91.0     |      | 106.4             |
| CCPI                             | %     | 33.6  | 37.7   | 39.9   | 44.3   | 50.0  | 19.7                      | 31.5   | 35.8   | 39.1   | 71.6   | 13.7                       | 28.7   | 39.3   | 45.5   | 76.2  | 33.8     |      | 32.0              |
| A.I.                             | %     | 31.4  | 34.2   | 38.2   | 41.9   | 61.4  | 33.4                      | 48.7   | 58.9   | 64.6   | 94.3   | 28.6                       | 38.1   | 79.5   | 90.7   | 94.9  | 28.0     |      | 34.1              |
| ASI                              |       | 0.97  | 1.04   | 1.07   | 1.11   | 1.43  | 0.91                      | 1.01   | 1.08   | 1.38   | 1.87   | 0.87                       | 1.19   | 1.55   | 2.03   | 4.55  | 1.08     |      | 1.05              |

Table 4.1. (contd).

|                                  |       | Dvs (Xtal tuff) | Dvs (Ign) | Dvs (Xtal tuff) | Dvs (felsic xenolith) | Dvs (Ign) | Dvs (Ign) | LOD   | Median felsic arc |
|----------------------------------|-------|-----------------|-----------|-----------------|-----------------------|-----------|-----------|-------|-------------------|
|                                  |       | OT-155          | OT-90     | OT-54           | OT-58                 | OT-152    | OT-154    |       |                   |
| SiO <sub>2</sub>                 | wt. % | 61.9            | 58.5      | 60.6            | 70.4                  | 56.4      | 55.2      | 0.01  | 68.6              |
| Al <sub>2</sub> O <sub>3</sub>   | wt. % | 16.75           | 15.40     | 17.30           | 12.40                 | 15.30     | 18.65     | 0.01  | 15.2              |
| FeOt                             | wt. % | 3.92            | 5.69      | 4.80            | 2.18                  | 4.08      | 5.10      | 0.01  | 3.29              |
| CaO                              | wt. % | 3.02            | 3.94      | 2.97            | 3.97                  | 6.87      | 4.61      | 0.01  | 2.43              |
| MgO                              | wt. % | 0.92            | 1.26      | 1.62            | 0.51                  | 0.62      | 2.07      | 0.01  | 0.92              |
| Na <sub>2</sub> O                | wt. % | 2.58            | 2.80      | 4.36            | 4.00                  | 4.19      | 3.29      | 0.01  | 4.37              |
| K <sub>2</sub> O                 | wt. % | 3.01            | 3.41      | 2.53            | 1.56                  | 2.16      | 1.56      | 0.01  | 2.61              |
| TiO <sub>2</sub>                 | wt. % | 0.44            | 0.48      | 0.53            | 0.12                  | 0.43      | 0.53      | 0.01  | 0.52              |
| MnO                              | wt. % | 0.14            | 0.17      | 0.15            | 0.13                  | 0.21      | 0.11      | 0.01  | 0.10              |
| P <sub>2</sub> O <sub>5</sub>    | wt. % | 0.20            | 0.21      | 0.25            | 0.04                  | 0.19      | 0.26      | 0.01  | 0.14              |
| C                                | wt. % | 1.03            | 0.91      | 0.55            | 0.88                  | 1.84      | 1.14      | 0.01  | 0.02              |
| S                                | wt. % | 0.02            | 0.03      | 0.17            | 0.02                  | 0.14      | 0.04      | 0.01  | 0.01              |
| Ba                               | ppm   | 688             | 312       | 877             | 631                   | 4740      | 668       | 0.5   | 800               |
| Hf                               | ppm   | 3.4             | 4.0       | 4.0             | 2.3                   | 3.1       | 3.6       | 0.2   | 5.7               |
| Nb                               | ppm   | 4.8             | 6.9       | 7.1             | 3.3                   | 6.0       | 6.9       | 0.2   | 7.7               |
| Rb                               | ppm   | 79.6            | 107.0     | 62.9            | 33.2                  | 40.9      | 35.9      | 0.2   | 62.4              |
| Sr                               | ppm   | 227             | 437       | 542             | 447                   | 733       | 732       | 0.1   | 221               |
| Ta                               | ppm   | 0.2             | 0.4       | 0.4             | 0.2                   | 0.4       | 0.4       | 0.1   | 0.58              |
| Th                               | ppm   | 1.90            | 2.63      | 3.06            | 2.14                  | 2.15      | 2.33      | 0.05  | 5.53              |
| U                                | ppm   | 0.70            | 1.17      | 1.19            | 0.90                  | 0.88      | 0.65      | 0.05  | 2.48              |
| V                                | ppm   | 103             | 108       | 111             | 29                    | 77        | 92        | 5     | 27.5              |
| Y                                | ppm   | 15.1            | 20.6      | 21.8            | 7.3                   | 17.6      | 21.5      | 0.5   | 37.7              |
| Zr                               | ppm   | 123             | 132       | 143             | 63                    | 95        | 130       | 2     | 178               |
| Ag                               | ppm   | <0.5            | <0.5      | <0.5            | <0.5                  | <0.5      | <0.5      | 0.5   | 2.1               |
| Co                               | ppm   | 4               | 7         | 12              | 3                     | 5         | 6         | 1     | 9.71              |
| Cu                               | ppm   | 44              | 36        | 71              | 22                    | 49        | 22        | 1     | 19                |
| Mo                               | ppm   | <1              | <1        | <1              | <1                    | <1        | <1        | 1     | 3.9               |
| Ni                               | ppm   | <1              | <1        | 2               | <1                    | <1        | <1        | 1     | 6.3               |
| Pb                               | ppm   | 10.0            | 9.0       | 212.0           | 10.0                  | 17.0      | 17.0      | 2     | 12.1              |
| Zn                               | ppm   | 199             | 91        | 112             | 49                    | 68        | 110       | 2     | 80                |
| Au                               | ppm   | 0.001           | 0.001     | 0.004           | 0.001                 | 0.001     | 0.001     | 0.001 | 0.002             |
| Sc                               | ppm   | 5               | 5         | 6               | 1                     | 4         | 5         | 0.1   | 12                |
| La                               | ppm   | 14.20           | 16.90     | 17.50           | 8.60                  | 17.20     | 14.80     | 0.5   | 18.81             |
| Ce                               | ppm   | 26.90           | 32.50     | 34.80           | 13.60                 | 31.80     | 29.00     | 0.5   | 38.47             |
| Pr                               | ppm   | 3.26            | 3.96      | 4.51            | 1.49                  | 3.86      | 3.67      | 0.03  | 5.19              |
| Nd                               | ppm   | 13.20           | 16.50     | 18.90           | 5.70                  | 15.80     | 15.50     | 0.1   | 20.93             |
| Sm                               | ppm   | 2.68            | 3.78      | 4.23            | 1.20                  | 3.59      | 3.56      | 0.03  | 5.35              |
| Eu                               | ppm   | 0.91            | 1.22      | 1.12            | 0.46                  | 1.06      | 1.22      | 0.03  | 1.14              |
| Gd                               | ppm   | 2.71            | 3.47      | 3.75            | 1.12                  | 3.40      | 3.90      | 0.05  | 6.18              |
| Tb                               | ppm   | 0.44            | 0.55      | 0.57            | 0.17                  | 0.50      | 0.63      | 0.01  | 1.03              |
| Dy                               | ppm   | 2.59            | 3.45      | 3.53            | 1.10                  | 3.07      | 3.69      | 0.05  | 6.91              |
| Ho                               | ppm   | 0.58            | 0.74      | 0.77            | 0.21                  | 0.63      | 0.78      | 0.01  | 1.46              |
| Er                               | ppm   | 1.63            | 2.16      | 2.25            | 0.70                  | 1.80      | 2.20      | 0.03  | 4.19              |
| Tm                               | ppm   | 0.25            | 0.35      | 0.36            | 0.11                  | 0.28      | 0.34      | 0.01  | 0.65              |
| Yb                               | ppm   | 1.73            | 2.22      | 2.45            | 0.84                  | 1.78      | 2.27      | 0.03  | 3.89              |
| Lu                               | ppm   | 11.42           | 13.78     | 16.54           | 6.30                  | 11.02     | 14.96     | 0.01  | 0.616             |
| LOI                              | wt. % | 6.14            | 5.92      | 4.87            | 4.73                  | 8.35      | 7.83      |       | 1.09              |
| Sr/Y                             |       | 15.0            | 21.2      | 24.9            | 61.2                  | 41.6      | 34.0      |       | 5.6               |
| V/Sc                             |       | 20.6            | 21.6      | 18.5            | 29.0                  | 19.3      | 18.4      |       | 2.5               |
| Eu/Eu*                           |       | 0.84            | 0.91      | 1.44            | 1.04                  | 0.96      | 0.83      |       | 0.71              |
| Dy <sub>N</sub> /Yb <sub>N</sub> |       | 1.00            | 1.04      | 0.96            | 0.88                  | 1.15      | 1.09      |       | 1.12              |
| La <sub>N</sub> /Yb <sub>N</sub> |       | 5.9             | 5.5       | 5.1             | 7.3                   | 6.9       | 4.7       |       | 3.3               |
| La <sub>N</sub> /Sm <sub>N</sub> |       | 3.42            | 2.89      | 2.67            | 4.63                  | 3.09      | 2.68      |       | 2.09              |
| ΣREE                             | ppm   | 71.4            | 88.2      | 95.2            | 35.5                  | 85.1      | 81.9      |       | 106.4             |
| CCPI                             | %     | 46.4            | 52.8      | 48.3            | 32.6                  | 42.5      | 59.7      |       | 32.0              |
| A.I.                             | %     | 41.2            | 40.9      | 36.1            | 20.6                  | 20.1      | 31.5      |       | 34.1              |
| ASI                              |       | 1.35            | 1.06      | 1.23            | 0.92                  | 0.83      | 1.40      |       | 1.05              |

Table 4.1. (contd).

## 4.5 Whole Rock Geochemistry

In all cases, whole rock samples were taken from a larger rock sample, the remainder of which was retained for petrological work. Samples were selected to represent a wide variety of rock textures and alteration types. Where possible, large quartz veins were removed from the samples before whole rock analysis. All whole rock geochemistry samples were between 130g and 800g, with an average of approximately 250g. Details of analytical techniques for whole rock geochemistry are outlined in Chapter 2. 70 samples were selected for whole rock analysis, and the lithologies and deposits from which these samples were drawn is summarised in Table 4.1. One of the Dvs samples analysed for whole rock geochemistry is one of the felsic xenoliths. Median whole rock values for each group are presented in Table 4.1. Comparison will be drawn between the data from Oyu Tolgoi and the median value for arc magmas, and the compilation of fertile dataset. See Chapter 2 for the origin of this dataset.

### 4.5.1 Focussing questions

The following questions are considered in the presentation and discussion of the whole rock data.

- How do Oyu Tolgoi intrusions compare to a global dataset of barren magmas?
- Do Oyu Tolgoi magmas contain signatures of fertility?
- Given the reasonably well constrained sequence of intrusions and volcanic rocks at Oyu Tolgoi, how does the whole rock geochemistry evolve temporally? In particular, how does the whole rock geochemistry change in magmas that erupted either side of the period of mineralisation? i.e. from the QMD-Dvs to the BiGd?
- How do different hydrothermal alteration styles affect signatures of fertility?
- Are there differences between intrusions at the Heruga and Hugo Dummett deposits?

#### 4.5.2 Major elements

Silica values for all rocks in this study range from 52 to 74 wt. %  $\text{SiO}_2$ . QMD from Hugo Dummett have higher silica values (60.3 to 74.2, median = 67.1 wt. %  $\text{SiO}_2$ ) than the samples from Heruga (57.4 to 69.5, median = 63 wt. %  $\text{SiO}_2$ ) or Southwest Oyu (59.4 to 65.5, median = 58.9 wt. %  $\text{SiO}_2$ ). Dvs rocks have a range of silica values between 55.2 and 61.9 wt. %  $\text{SiO}_2$ . The felsic xenolith has a higher silica (70.4 wt. %  $\text{SiO}_2$ ) than the rocks that host it. BiGd rocks have a much narrower range of silica contents, with most samples between 62 and 66 wt. %  $\text{SiO}_2$  (median = 64.6 wt. %  $\text{SiO}_2$ ).

Several major elements have been significantly changed from their original composition by hydrothermal alteration, with  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  concentrations particularly affected. Potassically altered rocks show high  $\text{K}_2\text{O}$  concentrations which are atypical of fresh, barren arc rocks, and  $\text{Na}_2\text{O}$  concentrations which range from values typical of barren rocks, to extremely low values ( $<0.1$  wt. %; Fig. 4.26 a,b). Quartz-sericite alteration in the QMD is marked in some samples by a significant depletion in  $\text{Na}_2\text{O}$ , but little change in  $\text{K}_2\text{O}$ . BiGd samples show a narrower range of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , both of which vary between 2 and 5 wt. %.  $\text{CaO}$  values of nearly all rocks are depleted with respect to the fractionation trends observed in the barren dataset, and QMD rocks are more depleted in  $\text{CaO}$  than the BiGd or Dvs samples (Fig. 4.26 g). Nominally immobile elements  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  follow fractionation trends similar to those seen in barren arc rocks (Fig. 4.26 c,d).

#### 4.5.3 Trace elements

MORB-normalised multi-element patterns show that QMD samples from Heruga, Hugo Dummett and SW Oyu have trace element features in common, which deviate from typical felsic arc trace element values (Fig. 4.27). With respect to typical arcs, the QMD samples are depleted in Zr, Hf, Y, Yb, and enriched in Sr. In general, trace element patterns



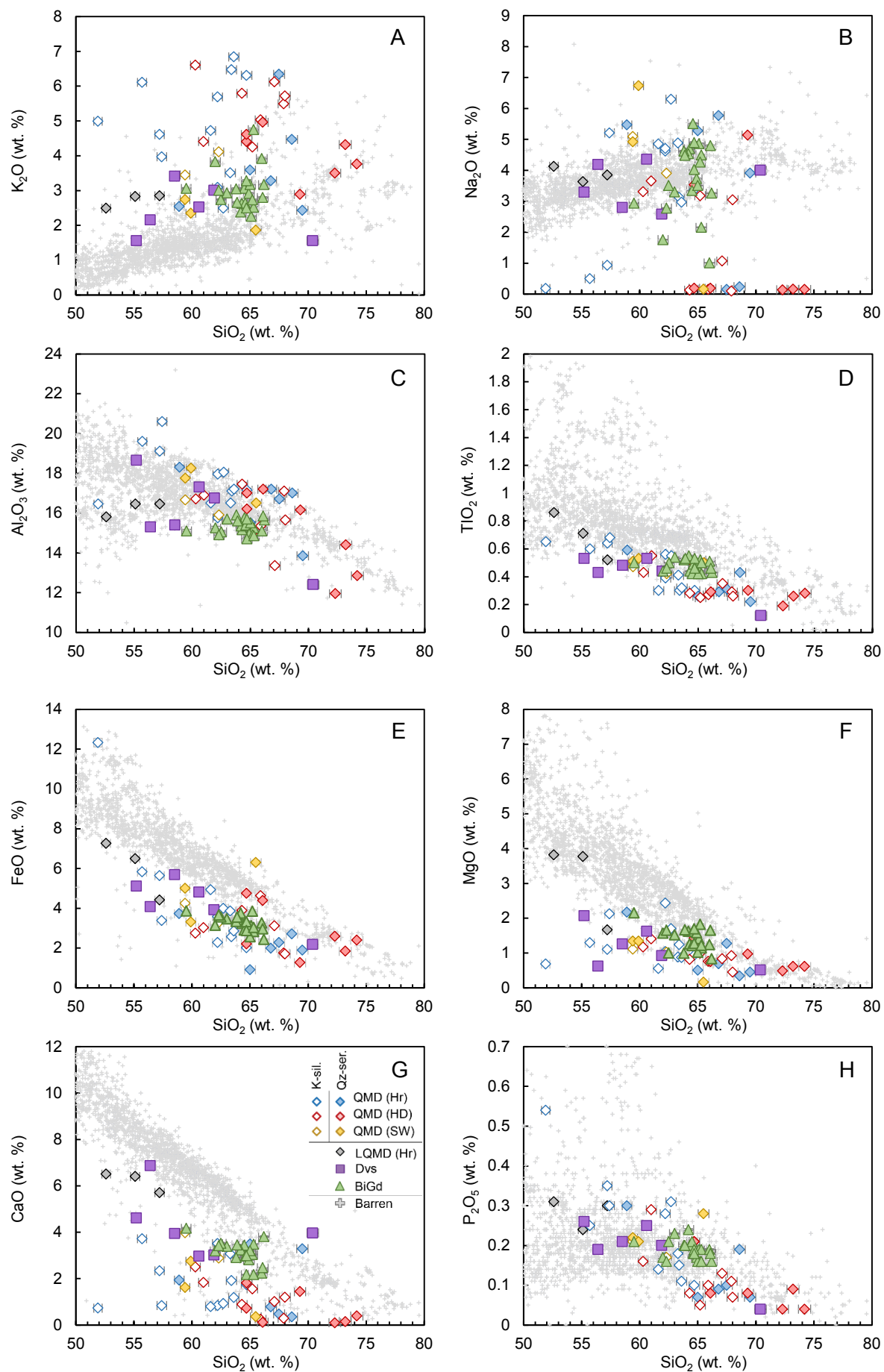


Figure 4.26. (previous page) Harker diagram for major elements: a)  $K_2O$ , b)  $Na_2O$ , c)  $Al_2O_3$ , d)  $TiO_2$ , e)  $FeO$ , f)  $MgO$ , g)  $CaO$ , h)  $P_2O_5$ . Light gray crosses are the barren sample suite from the Aleutians arc. Error bars are smaller than the symbol size for most elements.

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are more depleted in the QMD from Hugo Dummett than Heruga or SW Oyu. This is likely to be because the Hugo Dummett QMD is more fractionated, and would be correspondingly depleted in trace elements whose compatibility is higher in more felsic magmas (e.g., P, Zr). QMD are also more depleted in Ta than Nb compared to average crustal rocks. BiGd shows similar MORB normalised trace element patterns, with a stronger depletion in Y and Yb. The Dvs has similar trace element patterns to the QMD. The felsic xenolith is more strongly depleted in trace elements than the host volcanic rocks, and to normal felsic arc rock values. The exceptions to this are Sr, Ba, and Th, which is enriched compared to average felsic arc rocks, and similarly enriched compared to the host Dvs.

#### 4.5.4 Rare earth elements

Chondrite-normalised REE patterns in QMD and Dvs rocks are broadly similar, in spite of the range of values for  $\Sigma REE$  (10 to 165 ppm; Table 4.10). The patterns are characteristic of porphyry systems, showing enrichment in LREE, and a greater depletion in the MREE than the HREE (QMD median  $Dy_N/Yb_N = 0.98$ ; Fig. 4.28 c-h). Absolute REE abundances broadly decrease with increasing fractionation. For example, the three most primitive QMD samples from the Heruga deposit have the highest  $\Sigma REE$ . Chondrite-normalised patterns of the BiGd are markedly different. REE concentrations from all BiGd samples show very little variability, and chondrite-normalised patterns strongly overlap (Fig. 4.28 a,b). They show a more pronounced HREE depletion than the QMD or Dvs (median  $Dy_N/Yb_N = 1.44$ ). Both QMD/Dvs and BiGd rocks are depleted in M- and HREE with respect to typical felsic arc rocks.

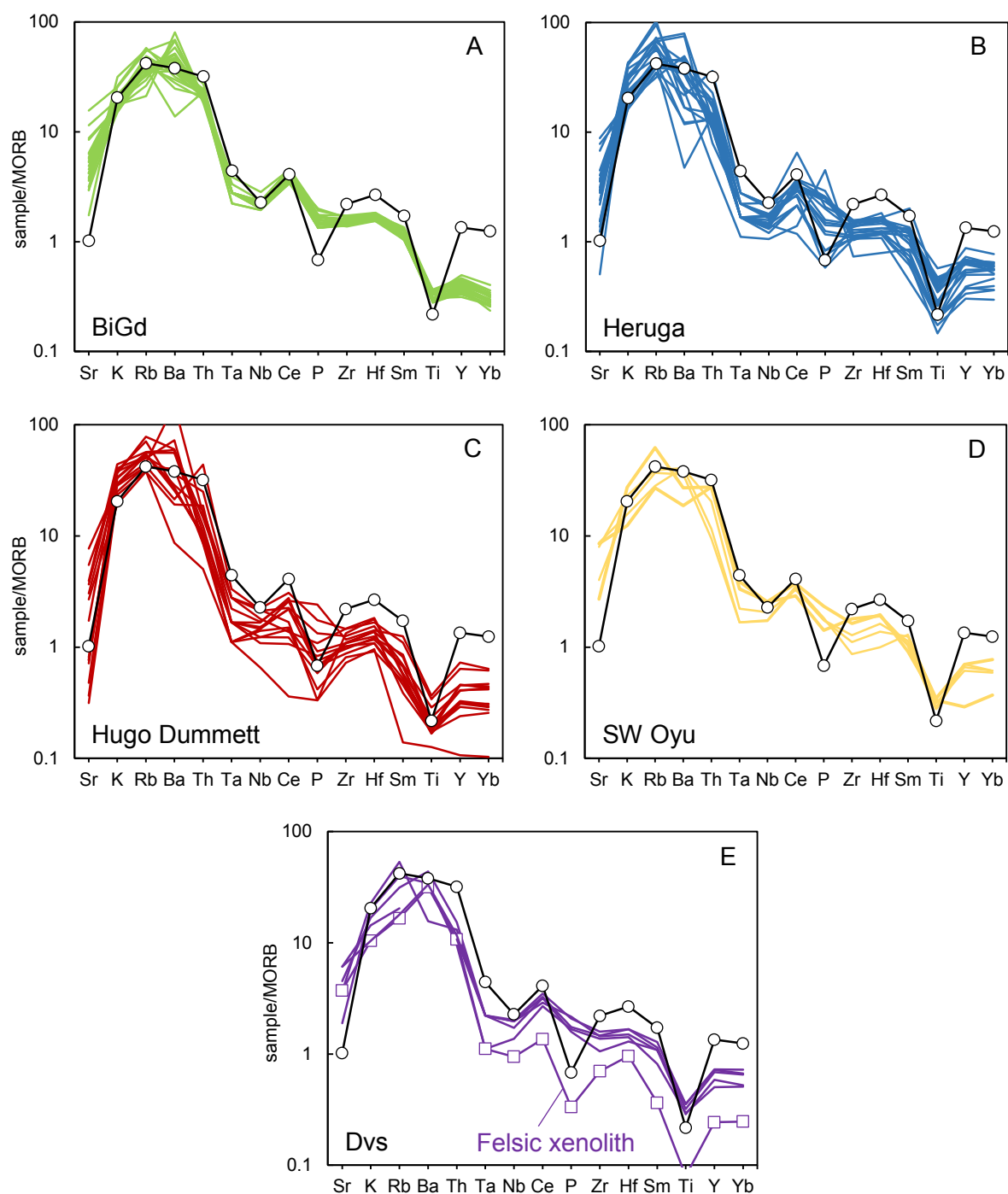


Figure 4.27. MORB-normalised trace element variation diagrams for Oyu Tolgoi rocks. a) Biotite granodiorite, b) Heruga quartz monzodiorite, c) Hugo Dummett quartz monzodiorite, d) SW Oyu quartz monzodiorite, e) Devonian volcanic sequence. Black line with open symbols is the median felsic arc value. Normalising values from Rollinson (1993)

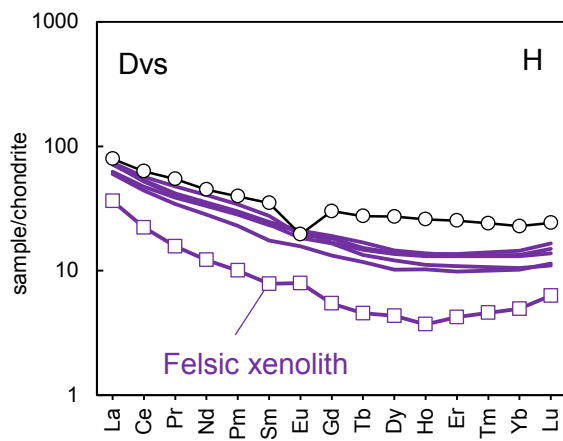
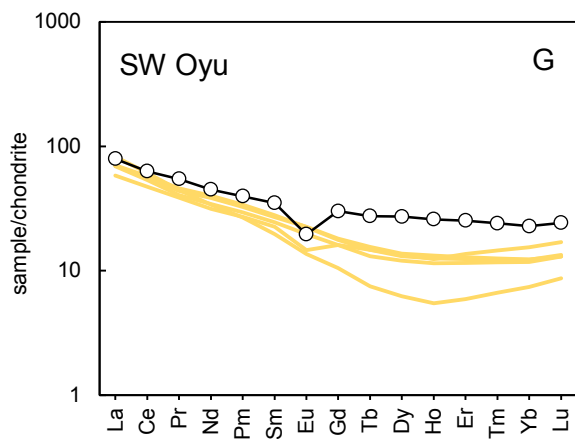
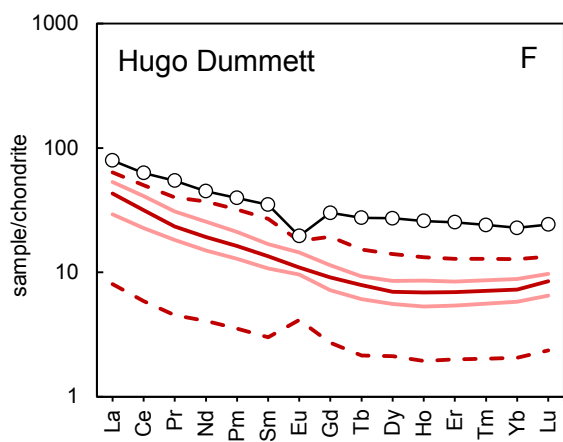
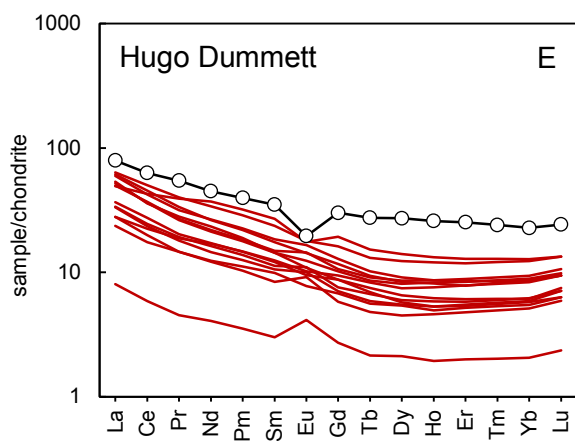
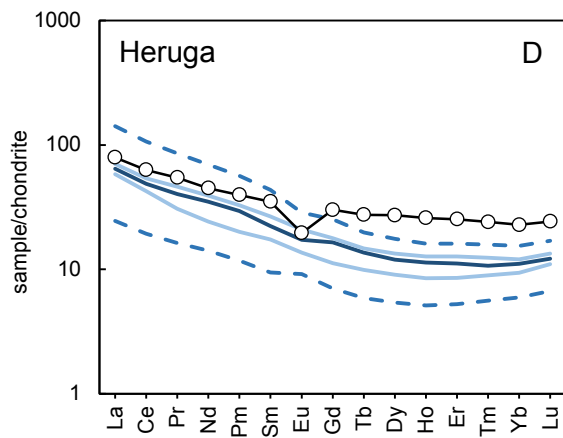
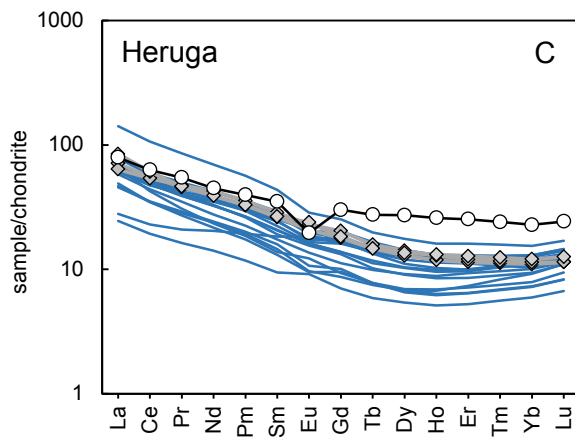
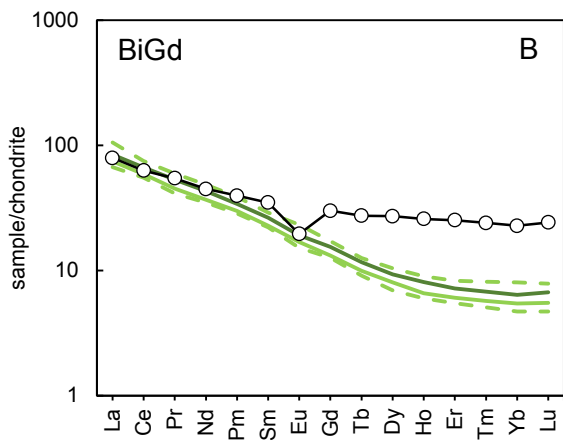
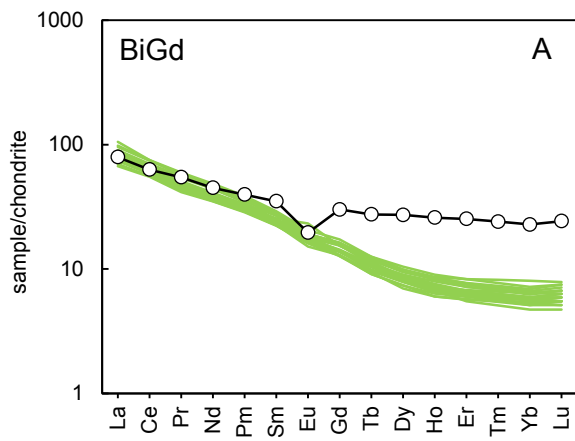


Figure 4.28. (previous page). Chondrite normalised REE patterns for Oyu Tolgoi rocks. a,b) Biotite granodiorite, c,d) Heruga quartz monzodiorite, e,f) Hugo Dummett quartz monzodiorite, g) Devonian volcanic sequence, h) SW Oyu quartz monzodiorite. In b,d and f, dashed lines are minimum and maximum patterns, pale thick lines are upper and lower quartile values, and thick bold line is the median. Black line with open symbols is the median felsic arc value. Normalising values from Sun and McDonough (1989).

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Eu anomalies in all studied rocks are weak or absent, but some slight negative and positive values are seen ( $\text{Eu}/\text{Eu}^*$  between 0.76 and 1.44; Table 4.1). Rocks with the most depleted REE concentrations also typically show the highest values of  $\text{Eu}/\text{Eu}^*$ . For example, the felsic xenolith of the Dvs (sample OT-57) has the highest  $\text{Eu}/\text{Eu}^*$  value of all Dvs samples (Table 4.1). This is a common observation in magmas associated with porphyry systems (e.g. Lang and Titley, 1998; see Chapter 1).

#### 4.5.5 Fertility indicators

Sr/Y values of Oyu Tolgoi rocks are generally higher than typical arc values (median = 5.6). BiGd have the highest Sr/Y (median = 49.9) with values reaching up to 189 (Fig. 4.29 a). This is significantly higher than the Sr/Y values of most typical arc rocks, and plot wholly in the field of adakites-like rocks on plots of Sr/Y vs Y (Fig. 4.29 b). The Sr/Y values of QMD from Heruga and Hugo Dummett show significant overlap with one another, and with the Dvs (median = 24.9), although the felsic xenolith has a high Sr/Y value of 61 (Fig. 4.29 b). Sr/Y values of the BiGd and some QMD samples increase with increasing  $\text{SiO}_2$ , whereas the majority of the QMD and Dvs rocks show decreasing Sr/Y with increasing fractionation, which matches the evolution of typical arc systems.

La/Yb values are also highest in the BiGd compared to the QMD or the Dvs (Fig. 4.29 c). These values for the BiGd are also significantly higher than typical arc rocks and some of the highest La/Yb values plot in the field of adakites-like rocks (Fig. 4.29 d). La/Yb increases

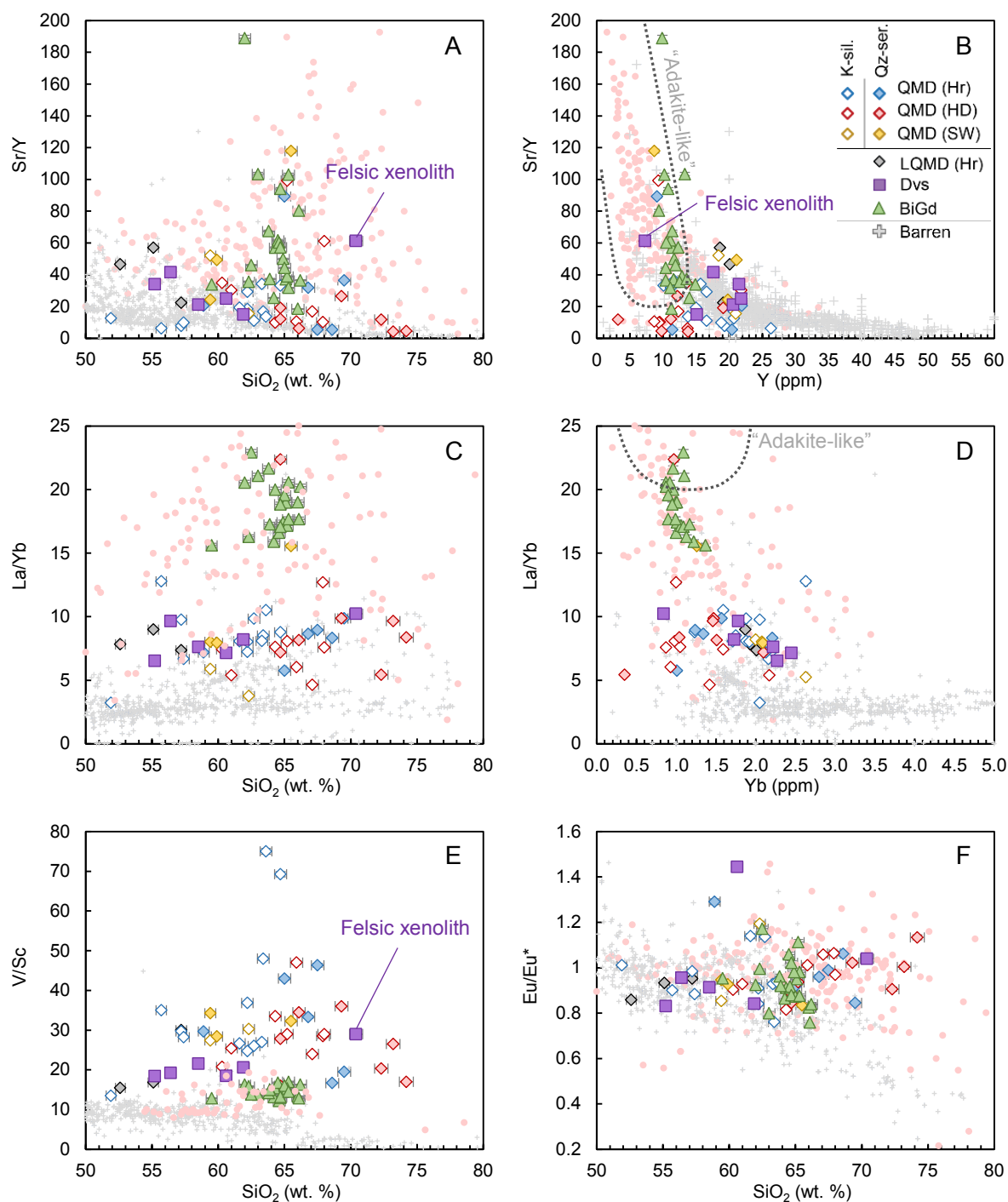


Figure 4.29. Variation of Oyu Tolgoi whole rock geochemistry in terms of certain indicators of magmatic fertility: a,b) Sr/Y, c,d) La/Yb, e) V/Sc and f) Eu/Eu\*. Pink symbols are from the 'fertile' dataset of rocks from other porphyry systems. Fields of 'adakite-like' rocks taken from Richards and Kerrich (2007).

with increased fractionation in the BiGd, whereas the QMD and Dvs show only weak increases in La/Yb that are typical of arc magmas.

Eu/Eu\* shows no apparent decrease with increasing fractionation (Fig. 4.29 e). This is in contrast with the pattern of decreasing Eu/Eu\* with increasing fractionation that is observed in typical arc magmas. Oyu Tolgoi rocks overlap with barren rocks at lower SiO<sub>2</sub> (< ~65 wt. %), and the distinction only becomes apparent at silica values greater than this. There are almost no typical arc rocks from this compilation with Eu/Eu\* > 0.8 at SiO<sub>2</sub> > 65 wt. %, whereas rocks from Oyu Tolgoi commonly have higher Eu/Eu\* values for the same SiO<sub>2</sub>.

All studied rocks from Oyu Tolgoi have V/Sc values that are significantly higher than barren arc rocks. BiGd samples have V/Sc between 12 and 17, which plot in the field defined by the fertile porphyry dataset (Fig. 4.29 e). whereas QMD samples have significantly higher V/Sc than observed in the fertile porphyry dataset (up to 75). These high values are due to low Sc, rather than high V, the latter of which broadly follow the fractionation trends observed in barren rocks (Fig. 4.30).

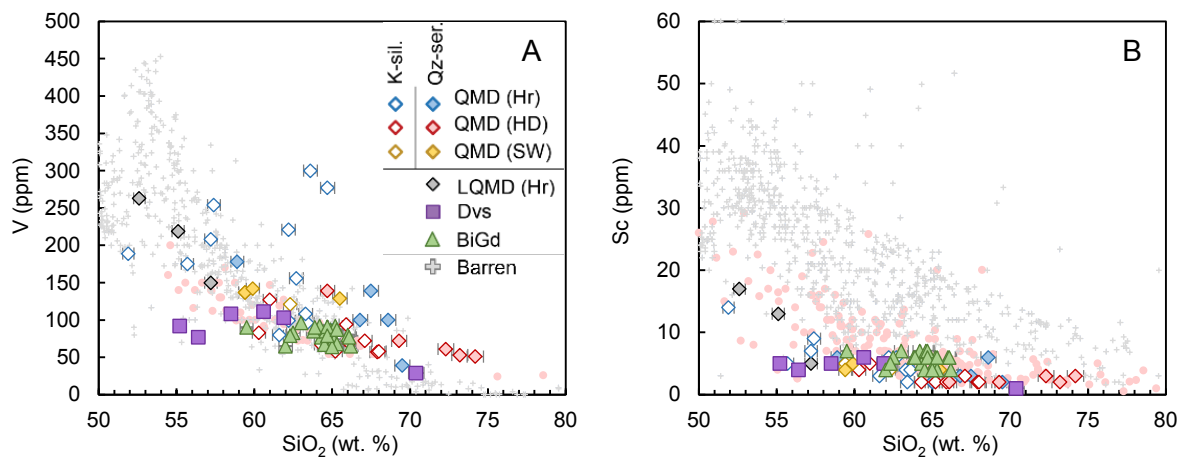


Figure 4.30. Variation of a) V and b) Sc with respect to SiO<sub>2</sub> for Oyu Tolgoi rocks, and 'barren' and 'fertile' datasets. Oyu Tolgoi rocks are typically well below the barren typical fractionation trends for Sc, but are a closer match for V fractionation trends, in spite of some higher values.

#### 4.5.6 Alteration geochemistry

Several techniques are presented here to assess the effects of different styles of hydrothermal alteration on whole rock geochemistry.

##### *4.5.6.1 Isocon method*

The isocon method of Grant (1986; 2005) was applied to QMD whole rock analyses to assess the mass change and mobility of major and selected trace elements during hydrothermal alteration. As all of the QMD in this study is altered, the ‘unaltered’ QMD equivalent was derived from Khashgerel et al. (2008), who determined a value of least altered QMD based on an average of 10 samples from Hugo Dummett. Two samples were selected as representative of the two main alteration styles: OT-65 (sericitic) and OT-69 (potassic). These samples are from the same drill hole, and lie at either end of the transition from potassic to sericitic alteration (see Figs. 4.9 and 4.23). To calculate the isocon, a line passing through the origin, and Zr and  $\text{Al}_2\text{O}_3$  (the conserved elements) was used, the slope of which is hereafter called ‘ $s$ ’. The isocon method is briefly described in section 3.5.6.1.

In both potassic and sericitic rocks, the slope of the isocon is  $<1$ , indicating bulk mass gain (Fig. 4.31), which is greater in sericitic ( $s = 0.875$ ) than in potassic alteration ( $s = 0.972$ ). Calculated values for  $\Delta M$  are +2.9% (potassic) and +14.3% (sericitic).

Potassic alteration is associated with increases in  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , and decreases in FeO and CaO (Fig. 4.32). Depletions occur in all REE, with the strongest depletions occurring in the LREE (La, Ce, and Nd). Notable depletions occur in V (~60 ppm) and Sr (186 ppm). Sericitic alteration is accompanied by silicification (+6 wt. %  $\text{SiO}_2$ ), and loss of  $\text{Na}_2\text{O}$ . In the trace elements, there are mild losses in La and Ce, and enrichments in other REE and Y. As with potassic alteration, there is a striking loss of V (~20 ppm) and an extremely large loss of Sr which accounts for most of the Sr from the unaltered sample.



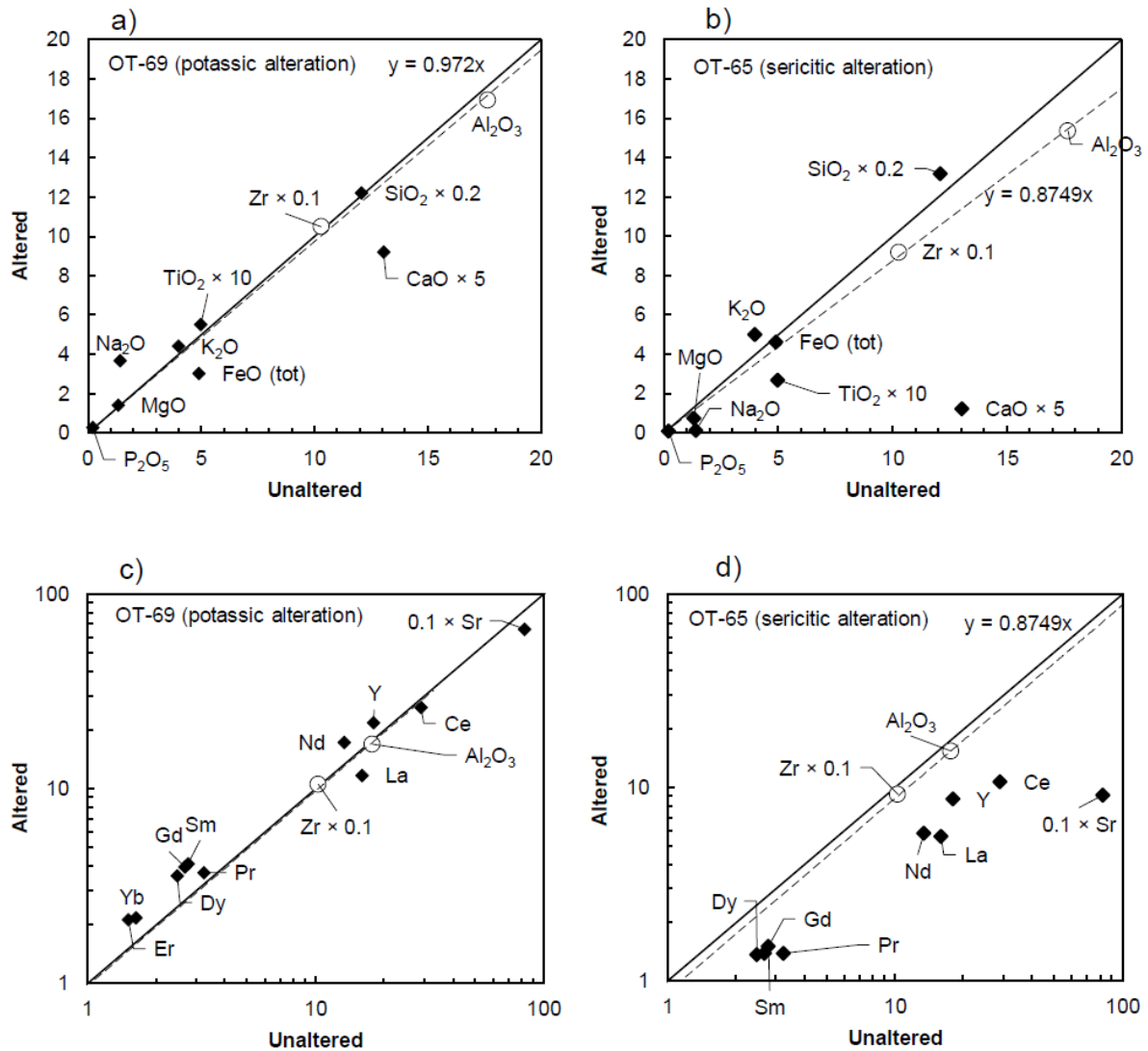


Figure 4.31. Isocon diagrams (after Grant, 1986) for QMD rocks; potassic alteration, major elements (a) and trace elements (c), and sericitic alteration, major elements (b) and trace elements (d). “Unaltered” is least altered QMD, taken from Khashgerel et al. (2008)

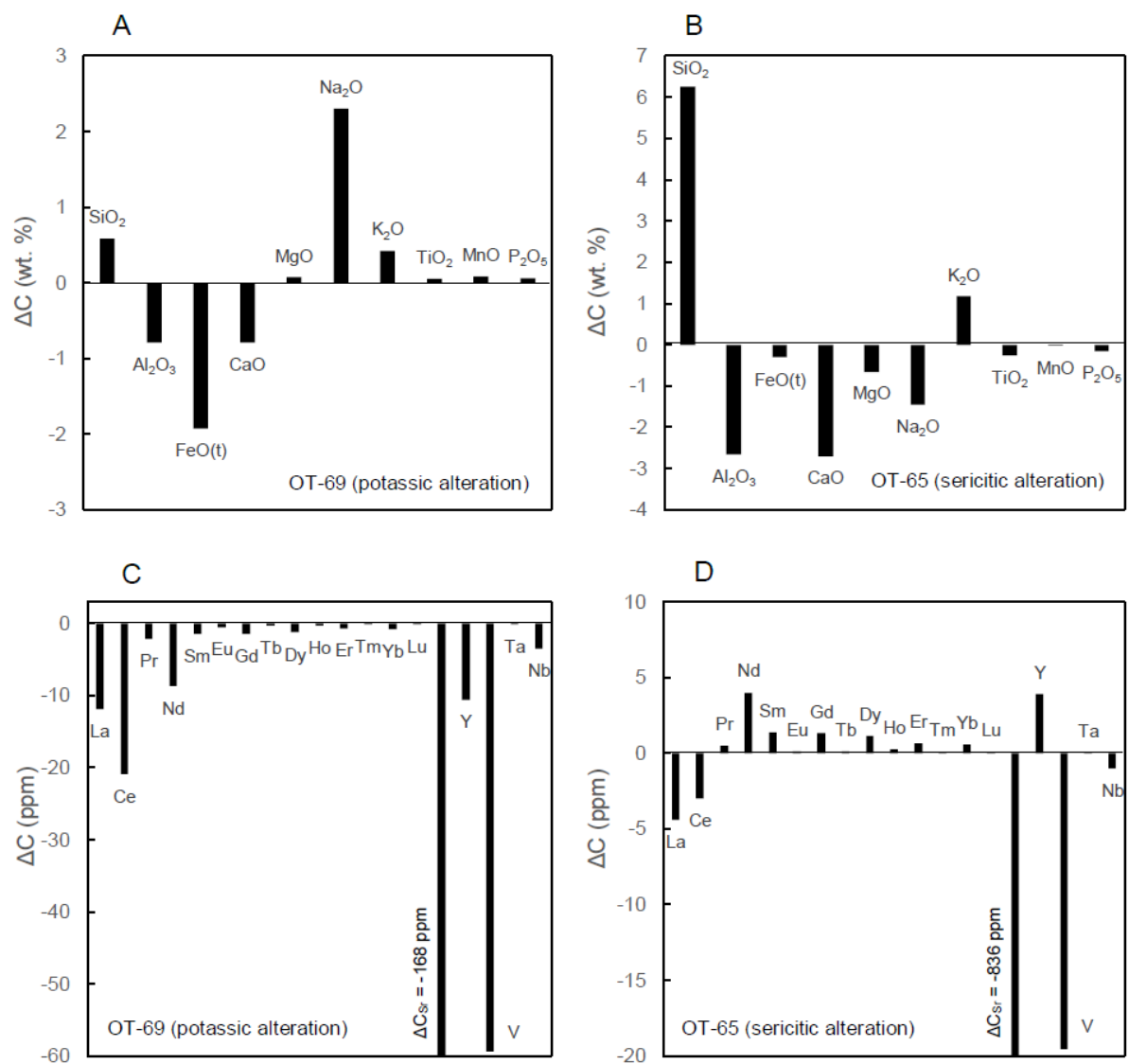


Figure 4.32. Bar charts showing relative losses and gains of (a,b) major elements and (c,d) trace elements in two rocks which are potassically altered (a,c) and sericitically altered (b,d). Values calculated using the isocon method of Grant (1986).

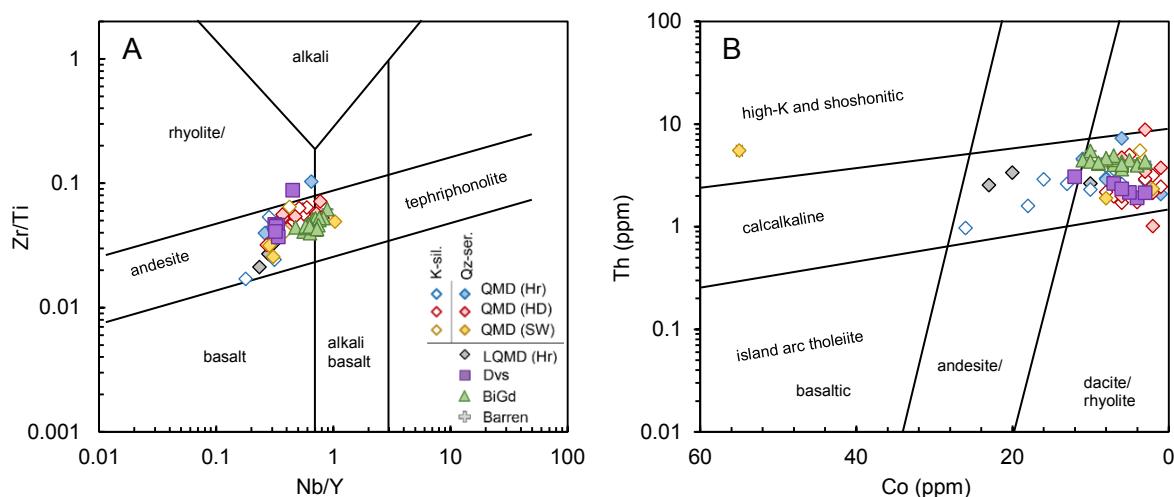


Figure 4.33. Immobility element discriminant diagrams, from a) Pearce (1986), and b) Hastie et al. (2007)

#### 4.5.6.2 Immobility element plots

The presence of extensive hydrothermal alteration, which especially affects  $K_2O$  and  $Na_2O$  concentrations, means that typical methods for determining the geochemical affinity (e.g. total alkali silica) may not be used, and other means are required to categorise the Oyu Tolgoi porphyry rocks, e.g. classifications based on nominally immobile elements. Plots of  $Zr/Ti$  vs.  $Nb/Y$  classify these rocks as andesite/ basaltic andesite, with a minor alkali component (Fig. 4.33 a). The scheme of Hastie et al. (2007) classifies these rocks as calcalkaline, and of andesitic to dacitic/rhyolitic composition (Fig. 4.33 b)

#### 4.5.6.3 Alteration Index and the alteration boxplot

The alteration boxplot (Large et al., 2001) plots two indices of alteration: alteration index (A.I.; Ishikawa et al., 1976) and the chlorite-carbonate-pyrite index (CCPI; see Chapter 2), in order to assess the relative extent of hydrothermal alteration. At Oyu Tolgoi, BiGd and Dvs samples mostly plot within the least altered box, but some Dvs data trend towards the albite + chlorite (+ calcite). Most QMD rocks from Heruga, and a smaller number from Hugo

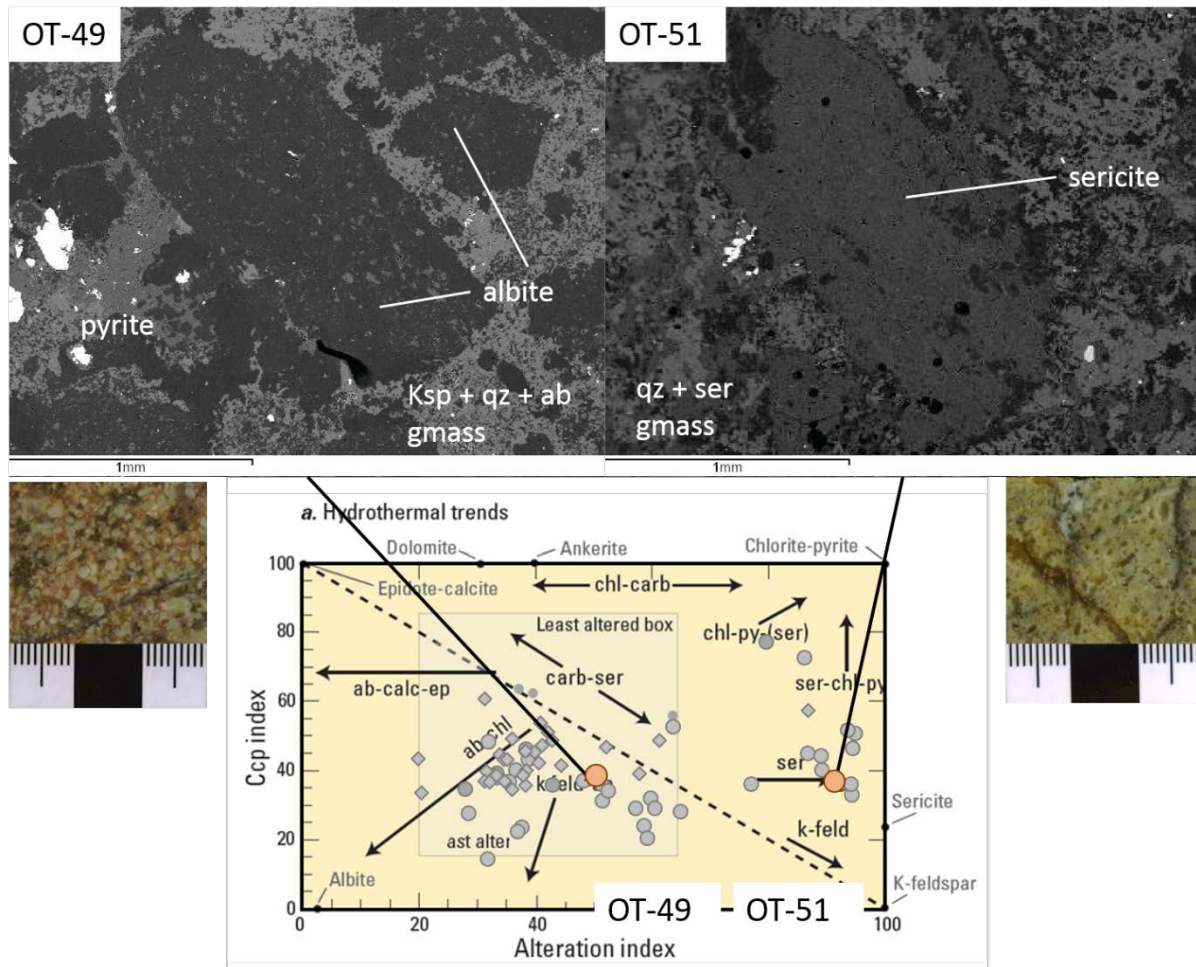


Figure 4.34. The alteration boxplot for Oyu Tolgoi rocks. Highlighted are two samples; OT-49 (potassic alteration) and OT-51 (sericitic alteration). Rocks where feldspar phenocrysts have been extensively altered to sericite tend to have higher values for alteration index (A.I.)

Dummett, plot in the least altered field of the box plot. A group of 9 samples from Hugo Dummett, 3 samples from Heruga, and 1 from SW Oyu plot outside this box, and spread towards the sericite point. Rocks from this group with higher A.I. show stronger sericitisation of plagioclase phenocrysts than rocks with lower A.I. (Fig. 4.34).

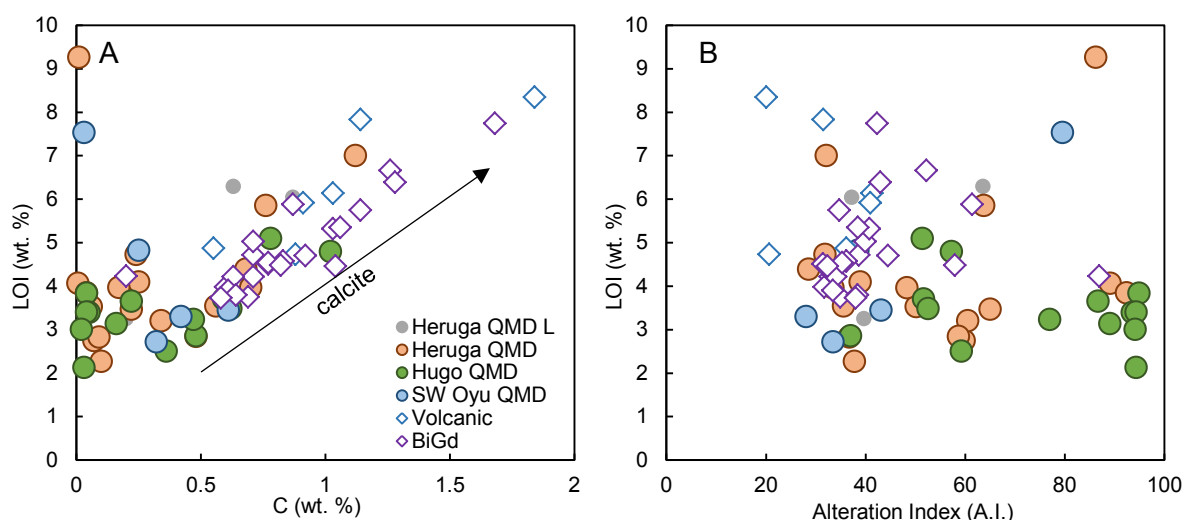


Figure 4.35. Variation of loss on ignition (LOI) with a) elemental C, and b) alteration index. The positive trend of C and LOI is attributed to the presence of calcite in these samples. Error bars are smaller than symbol size.

#### 4.5.6.4 Loss on ignition as an index of alteration

Median loss on ignition values (LOI) for the QMD rocks are between 3.4 and 3.9 wt. %. Median values are higher in the Devonian volcanic rocks (Dvs; 6.1 wt. %) and the Biotite granodiorite (BiGd; 4.6 wt. %) than in the more strongly altered QMD intrusions. LOI also correlate strongly with bulk rock carbon (Fig. 4.35 a). This is probably due to the abundance of carbonates, principally calcite, in the BiGd and Dvs rocks. In both cases calcite is present as veins, and in clots in the groundmass. As such, LOI is a less useful index of alteration for these rocks, because some of the most strongly altered samples have the lowest LOI (Fig. 4.35 b).

## 4.6 Discussion

### 4.6.1 The effect of alteration on whole rock indicators of porphyry fertility

The usefulness of a given whole rock indicator of fertility is partly determined by the ability of that signature to survive the types of hydrothermal alteration which are most common in porphyry systems. This, in turn, is dependent upon a) the ability of the minerals which host

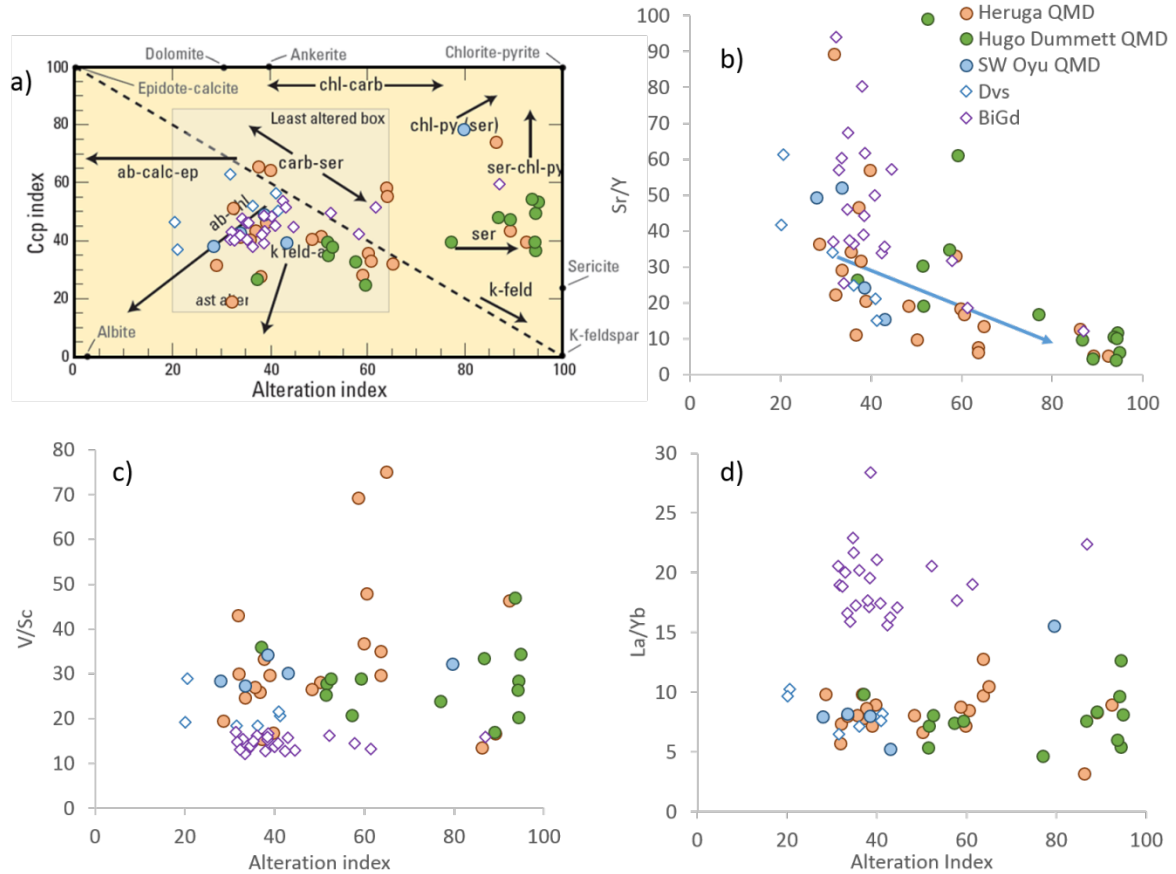


Figure 4.36. a) Alteration boxplot for Oyu Tolgoi rocks. b – d) variation of several indicators of fertility with respect to alteration index (A.I.). Sr/Y (a) shows particular decreases with increased alteration. This is not seen in either V/Sc (b) or La/Yb (c). Error bars are smaller than symbol size.

the elements to resist hydrothermal alteration, and b) the mobility of those elements in saline hydrothermal fluids. The robustness of whole rock indicators of fertility is discussed in this section.

Sr/Y values show strong decreases with increasing A.I., with a cluster of analyses with Sr/Y values <20 ppm (Fig. 4.36 b). This is not seen for either V/Sc or La/Yb, which both have equivalent values in rocks with low and high A.I. Given that the primary sink of Sr in felsic igneous rocks is plagioclase, the replacement of plagioclase with sericite, and the high fluid

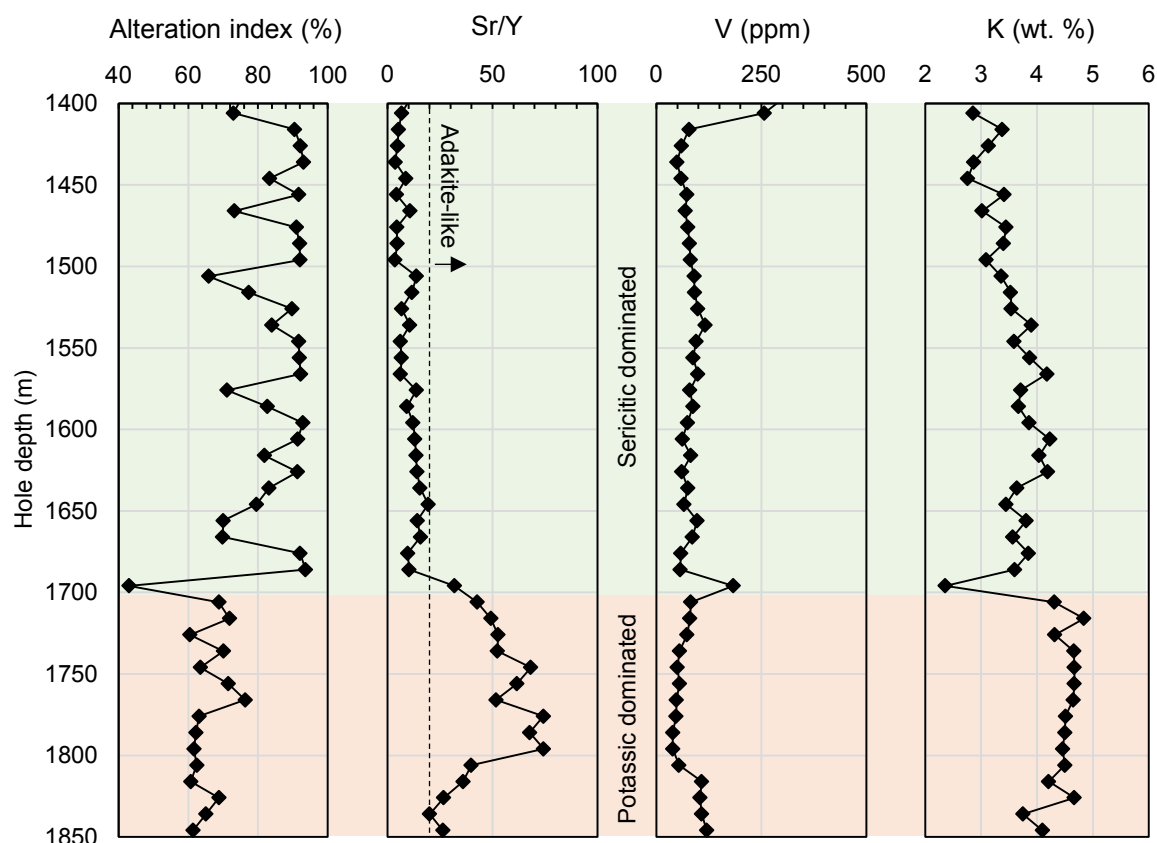


Figure 4.37. Down-hole variation in alteration index (A.I.), Sr/Y, V, and K. A significant change occurs in Sr, K, and A.I. at the boundary between the potassic-dominated zone (pale orange) and the sericitic-dominated zone (pale green). Dotted line on Sr/Y plot is the minimum value required for ‘adakite-like’ rocks, from Richards and Kerrich (2007). Drill hole is OTD976B (see Figs. 4.9 and 4.24).

mobility of Sr, provides a likely mechanism to explain the decreasing Sr/Y values in increasingly sericite-altered QMD rocks.

To assess the relative effects of potassic and sericitic alteration styles on Sr/Y whole rock values, assay data was provided by Oyu Tolgoi for hole OTD976B between 1400 to 1850 (end of hole), and the variation of key parameters with depth is plotted in (Fig. 4.37). This intersection was chosen because: a) apart from minor Carboniferous-age basaltic intrusions, this intersection entirely comprises QMD, and b) this intersection has a sharp distinction

between sericitic-dominated and potassic-dominated alteration (at ~1700 m; Fig. 4.24), which affords a direct comparison.

At the boundary between the two alteration zones, there is a downwards step increase in Sr/Y ratio, and K content, and a decrease in average alteration index, going from the sericite dominated zone into the potassic zone. Sr/Y values in particular are markedly different. In the shallower sericitic zone, they are consistently  $<20$ , which is the value described by Richards and Kerrich (2007) as being the boundary for ‘adakite-like’ rocks. In the potassic zone, however, Sr/Y ratios are consistently well in excess of 20, with values up to ~75 (Fig. 4.37). Given that there is no obvious change in QMD texture at ~1700m (Fig. 4.24) and other compositional sensitive parameters (e.g. Zr/Ti, not presented here) are consistent throughout the length of the core, it is likely that the original intrusion was chemically homogenous. This supports the conclusions that Sr/Y ratios are lower in sericitic zones, highlighted by the fact that there is an inverse relationship between alteration index and Sr/Y ratio. Consequently, the value of whole rock Sr/Y ratios as an indicator of porphyry fertility is compromised by its mobility during strong sericitic alteration (and the concomitant destruction of plagioclase feldspar), and the fluid mobility of Sr.

The absence of a correlation between La/Yb and alteration index implies that this may be a more robust signature. No REE data were available from the Oyu Tolgoi assay data presented in Figure 4.37, so it was not possible to assess the down hole variation in La/Yb ratios and Eu/Eu\* values. However, the net gains and losses of REE determined by the isocon method are relatively small compared to Sr (Fig. 4.32 c,d). La, Yb, Eu, Sm, and Gd (the latter two used to calculate the parameter Eu\*) are typically hosted in phases such as apatite and zircon in granitic rocks (e.g. Jefferies, 1985). These two phases are present in rocks from Oyu Tolgoi, and are more resistant to hydrothermal alteration given their presence in nearly all



rocks (see Chapters 5 and 6). Consequently, La/Yb is likely to be a more robust fertility indicator than Sr/Y.

It was not possible to assess the concentration change of Sc by the isocon method, as these values were not reported in the least altered sample of Khashgerel et al. (2008). V concentrations are depleted in both sericitic and potassic rocks (Fig. 4.32 c,d), with a greater depletion in the potassic zone. In spite of this, there appears to be no significant change in V content of the QMD between the sericitic and potassic zones from the assay data (Fig. 4.37). Also, V concentration appear to be broadly comparable to typical arc rocks (Fig. 4.30) and V/Sc ratios are comparable to those reported from other porphyry systems (e.g. Olson, 2015). Thus, the robustness of the V/Sc ratio during hydrothermal alteration is poorly constrained.

#### 4.6.2 The evolution of the Late Devonian Oyu Tolgoi magmatic system

The Late Devonian magmatic rocks of Oyu Tolgoi may provide a record of the changing conditions of a magma chamber during the formation of a large porphyry systems. Systematic changes in magmas the pre-, syn-, and post-mineralisation intrusions may reflect magma chamber processes which enhance the fertility of the system.

Similarities in whole rock geochemistry and overlapping ages of the QMD and Dvs have led some workers to consider them to be co-magmatic (e.g. Wainwright et al., 2011a; Crane and Kavalieris, 2012). In spite of this conclusion, Crane and Kavalieris (2012) noted some differences between these rock types. In particular, the QMD samples have more strongly depleted in MREE, and contain lower TiO<sub>2</sub> than the volcanic rocks. The same features are seen in the samples from this study (Figs. 4.26 d, and 4.28 h respectively). These differences are due to the more primitive nature of the Dvs compared to most of the QMD rocks. For the REE and immobile major and trace elements, both rock types lie on common fractionation trends, and

the QMD rocks have a composition that is intermediate between the volcanic rocks and the felsic xenoliths found therein. Consequently, the geochemical evidence supports a co-genetic QMD and Dvs, which are hypabyssal and volcanic variants of a common magmatic system.

The fact that crystalline felsic products of this magmatic system (i.e. the felsic xenoliths) are entrained in the more mafic Dvs magmas suggests that the fractionation processes in this system were cyclical, with varying periods of fractionation of melts to more felsic compositions, followed by replenishment of the magma system with more mafic melts. The xenoliths represent the crystalline products of magmas that were the culmination of an earlier cycle of fractionation, and the more mafic magmas into which they were entrained represent the early stages of a subsequent cycle of fractionation. This interpretation is in accordance with the cyclical nature of processes thought to occur in sub-arc magmatic systems (e.g. Annen et al., 2006), including in those associated with porphyry deposits (Rohrlach and Loucks, 2005).

One geochemical feature that the QMD and Dvs rocks have in common is MREE-depleted chondrite-normalised REE patterns, and both rock types lie on common fractionation trends of decreasing  $Dy_N/Yb_N$  ratio with increasing  $SiO_2$  content (Fig. 4.38). This feature has been observed at a number of volcanic arcs, and has previously been attributed to the dominant role of hornblende in controlling the REE characteristics of residual melts during magmatic evolution (e.g. Davidson et al., 2007; see Fig. 1.8). Amphiboles require hydrous magmatic conditions in order to crystallise, ( $> 4$  wt. %  $H_2O$ ; Ridolfi et al., 2010), so the presence of amphibole phenocrysts in some of the least altered QMD rocks, and as small relict grains in Dvs (Fig. 4.15) is a first-order indication that they were  $H_2O$ -rich at the moment of crystallisation.

A significant change in geochemistry of the magmatic system appears to have occurred between the formation of the QMD and Dvs, and the emplacement of the BiGd dykes. These

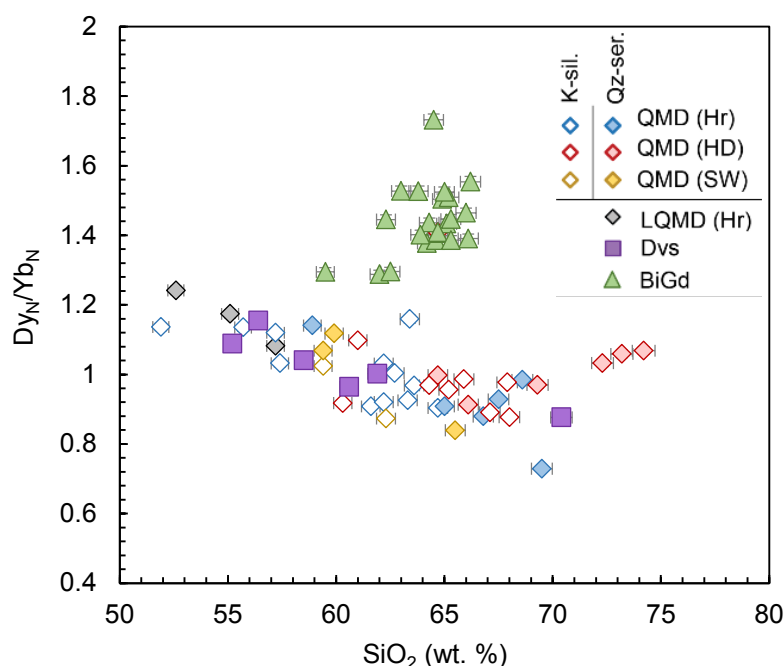


Figure 4.38.  $Dy_N/Yb_N$  vs  $SiO_2$  for rocks from Oyu Tolgoi. QMD and Dvs rocks show decreasing  $Dy/Yb$  with increasing  $SiO_2$ , which is typically associated with hornblende fractionation, whereas BiGd rocks show increasing  $Dy/Yb$ , the latter of which is typically ascribed to garnet fractionation.

changes include the switch to higher  $Sr/Y$ ,  $La/Yb$ , and  $Dy/Yb$  values, the latter two of which is a measure of the changing shape of chondrite-normalised REE patterns (i.e. greater HREE depletion). BiGd rocks show increasing  $Dy_N/Yb_N$  with fractionation. (Fig. 4.38). These REE characteristics are indicative of the involvement of garnet during magmatic evolution (Davidson et al., 2007; see Chapter 1).

Garnet fractionation signatures are thought to be generated in arc magmas in various ways, including as a residual phase during slab melting (e.g. Defant and Drummond, 1990), due to the fractional crystallisation of garnet as an igneous phase during high-pressure magmatic evolution (Alonso-Perez et al., 2009), or by the partial melting of, or melt equilibration with, garnetiferous lower crust/upper mantle, especially in response to crustal thickening (e.g. Hildreth and Moorbath, 1988; Kay and Mpodozis, 2001). Some authors have interpreted the Contact Fault as a thrust fault, and used this as evidence for crustal thickening

around the period of mineralization at Oyu Tolgoi (note that the timing of movement along is well constrained by cross-cutting relationships with the Dvs and BiGd). However, the sense of movement along this fault is poorly constrained as it is only known from drill core, and has also been interpreted as a low angle detachment fault by mine geologists at Oyu Tolgoi (2014, pers. comm.). Therefore, the processes which triggered the fractionation of garnet remain enigmatic, and will be further discussed in Chapter 7.

#### **4.7 Concluding remarks**

Indicators of fertility are present in Oyu Tolgoi intrusions which are spatially and temporally related to mineralisation.

- Some high Sr/Y and La/Yb ( $> 20$  for both) are found in the causative intrusions (quartz monzodiorite), but they mostly occur in the post-mineralisation biotite granodiorite intrusions. This means meaning the relationship between these parameters and the processes which generate mineralisation are likely to be complex.
- Eu/Eu\* values  $\sim 1$  are maintained to high SiO<sub>2</sub> contents, although strong separation from the field of barren rocks is not achieved.
- V/Sc values of all intrusions are between 2 and 6 times higher than barren rocks for a given SiO<sub>2</sub> content. This is especially true of the causative quartz monzodiorite.

The presence of well-developed and spatially well constrained alteration styles affords an investigation of the effects of alteration on whole rock indicators of fertility.

- Sr/Y is not a robust measure of magmatic fertility, because Sr loss is commonly associated with feldspar-destructive hydrothermal alteration, especially sericitic alteration.

- La/Yb ratios are less affected by alteration, probably because these elements are hosted in robust accessory phases (e.g. zircon, apatite)
- The relationship between V/Sc ratios and alteration are poorly constrained. Isocon analysis indicates that V is lost during alteration (especially potassic), but there is no obvious distinction between potassic and sericitic rocks in terms of V. Isocon analysis indicated that Sc is largely immobile during alteration.

Successive intrusions which overlap the period of mineralisation at Oyu Tolgoi have differing trace element geochemistry, which could reflect changes in the magmatic conditions that also drive changes in magmatic fertility.

- A switch from amphibole-dominated fractionation to garnet-dominated fractionation occurs between the emplacement of the QMD (+ Dvs) and the BiGd intrusions.

## Chapter 5: Zircon

### 5.1 Introduction

Zircon ( $\text{ZrSiO}_4$ ) is a common accessory mineral in intermediate to felsic igneous rocks. In spite of its low abundance (<1 modal %), zircon is the major repository of Zr, Hf, U, Th and HREE in igneous rocks (Sawka, 1988; Bea, 1996; O'Hara et al., 2001). Grains of zircon are typically small (<50  $\mu\text{m}$ ) and euhedral grains display a variety of prismatic habits that may vary as a function of the intensive parameters at the time of crystallisation (e.g. Pupin, 1980; Munoz et al., 2012).

The size and scarcity of zircon grains in igneous rocks belie their importance in understanding igneous petrogenesis. Zircon is one of the most popular and robust minerals for radiometric dating, due in part to its high U content, and resistance to high temperature re-equilibration. Zircon chemistry is also sensitive to melt chemistry (e.g. Belousova et al., 2002b), redox conditions (Burnham and Berry, 2012; Trail et al., 2012) and temperature of crystallisation (Ferry and Watson, 2007). Hf and O isotopes may be used to infer the source of melts from which zircons crystallised (e.g. Kemp et al., 2007). Mineral inclusions in detrital or xenocrystic zircon provide a record of co-crystallising phases that is preserved long after the context of the host rock is lost; this is key information for provenance studies of ancient continental crust (e.g. Jennings et al., 2011). In addition, zircon can provide useful petrogenetic information for strongly altered igneous rocks which are otherwise difficult to interpret (e.g. in porphyry Cu systems: Ballard et al., 2002; Munoz et al., 2012).

This chapter contains a description of the petrology, geochronology, and mineral chemistry of zircons from altered porphyry intrusions and coeval volcanic and plutonic rocks at Resolution and Oyu Tolgoi. These data are used to constrain the processes that occurred in

the magmatic systems prior to, during and after porphyry mineralisation. Results are compared with zircons from barren granitoid rocks.

## 5.2 Background

### 5.2.1 Zircon trace element chemistry

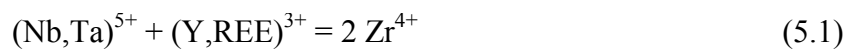
Trace elements substitute into zircon in place of tetrahedral  $\text{Si}^{4+}$  and octahedral  $\text{Zr}^{4+}$ . The commonest substitution is  $\text{Hf}^{4+} = \text{Zr}^{4+}$ . Due to the incompatibility of Hf in most igneous phases,  $\text{Hf}_{\text{melt}}$  increases as melts evolve to more felsic compositions, so  $\text{Hf}_{\text{zircon}}$  is correspondingly higher in zircons from more evolved melts. Thus,  $\text{Hf}_{\text{zircon}}$  is often used as an index of melt fractionation and can be plotted against other trace elements to show their variation in evolving magmas.

Other tetravalent cations (e.g.  $\text{U}^{4+}$ ,  $\text{Th}^{4+}$ ) also substitute directly for  $\text{Zr}^{4+}$ . The partitioning of U is partly controlled by redox conditions, because  $\text{U}^{4+}$ ,  $\text{U}^{5+}$  and  $\text{U}^{6+}$  are likely to exist in terrestrial melts (e.g. Burnham and Berry, 2012).  $\text{Ti}^{4+}$  substitution for  $\text{Si}^{4+}$  in zircon is controlled by the temperature of crystallisation, and Ti-in-zircon is a widely used zircon geothermometer in felsic igneous systems (Ferry and Watson, 2007).

Trivalent cations (e.g.  $\text{Y}^{3+}$ ;  $\text{REE}^{3+}$ ) require a coupled substitution into zircon to maintain charge balance. The most common substitution is:  $\text{Zr}^{4+} + \text{Si}^{4+} = \text{P}^{5+} + (\text{Y}, \text{REE})^{3+}$  (Spear, 1982). This is also called the “xenotime substitution” (xenotime is  $\text{YPO}_4$ ; Hoskin and Schaltegger, 2003). A similar coupled substitution allows for the incorporation of  $\text{Sc}^{3+}$  with  $\text{P}^{5+}$  (Halden et al., 1993). HREE partition more strongly into zircon than LREE because the ionic radius of 8-fold coordinated  $\text{Zr}^{4+}$  (0.84 Å) is most similar to the HREE (e.g.  $\text{Lu}^{3+} = 0.977$  Å). Thus, chondrite-normalised REE patterns for zircon show gradual increase in values from La to Lu, with the exception of anomalously high and low values for Ce and Eu

respectively, which are partly controlled by redox. Zircons from any given rock can show significant REE variability which is due, in part, to varying concentrations in the melt. The substitution of REE<sup>3+</sup> into zircon also varies with temperature, such that  $D_{\text{REE}}$  increases as temperature decreases, and partition coefficients for a given REE can increase up to an order of magnitude between 800 and 900°C (Trail et al., 2012; Burnham and Berry, 2012).

Trivalent cations may also partition into zircon with pentavalent Nb and Ta, by a coupled substitution described by Es'kova (1959):



The chemical similarity of Nb and Ta (8 fold ionic radius = 0.78 Å) means their partitioning behaviour is similar. Nb and Ta partition coefficients into zircon are independent of redox conditions or bulk chemistry of the melt (Burnham, 2012) so their concentrations in zircon are primarily controlled by the melt concentration of Nb and Ta.

### 5.2.2 The redox sensitivity of Ce and Eu

The estimation of redox conditions from Ce and Eu concentrations is a useful application of zircon trace element chemistry. Ce and Eu are unusual amongst the REE in that they may exist in oxidation states other than 3+ under terrestrial conditions (Ce<sup>4+</sup> and Ce<sup>3+</sup>; Eu<sup>2+</sup> and Eu<sup>3+</sup>). Ce<sup>4+</sup> is more compatible in zircon than other REE<sup>3+</sup> (including Ce<sup>III</sup>) due to the similarity of its ionic radius ( $r = 0.97 \text{ Å}$ ) to Zr<sup>4+</sup> ( $r = 0.84 \text{ Å}$ ). Similarly, Eu<sup>3+</sup> ( $r = 1.07 \text{ Å}$ ) is more compatible than Eu<sup>2+</sup> ( $r = 1.13 \text{ Å}$ ). Because typical melts contain Ce and Eu in both of their oxidation states, (Burnham and Berry, 2014; Smythe and Brenan, 2015) these elements are normally enriched and depleted in zircon respectively, leading to positive Ce anomalies



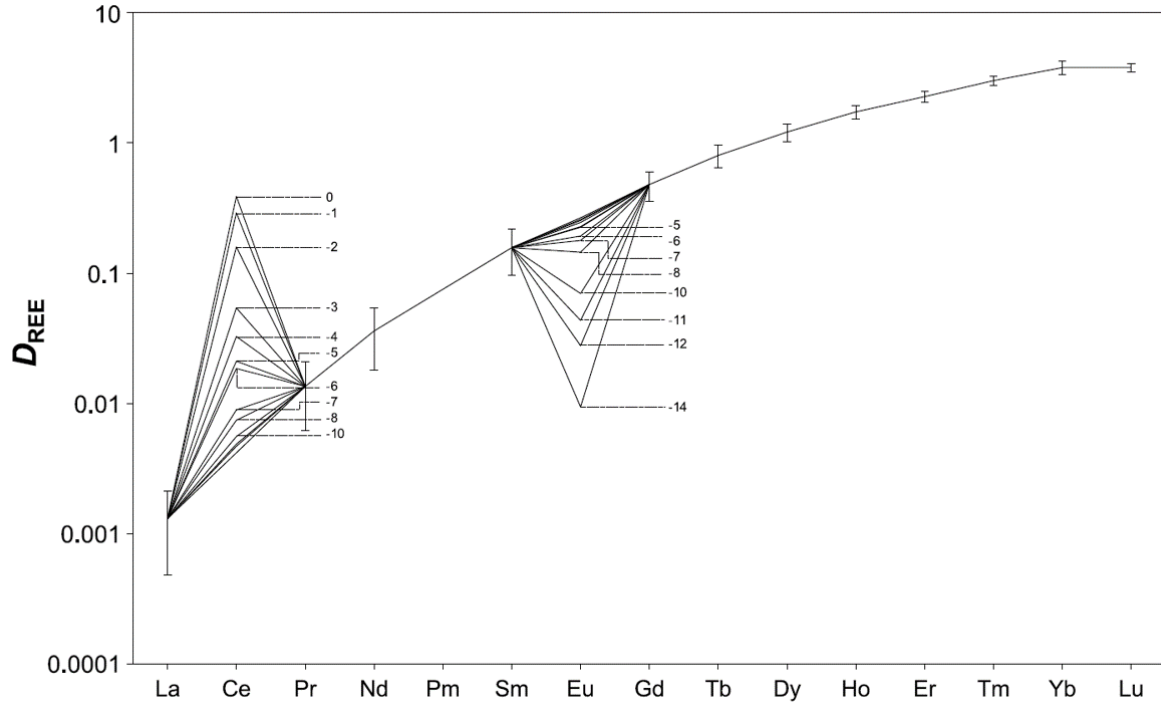


Figure 5.1. Typical chondrite-normalised REE pattern for a magmatic zircon, showing the experimentally determined redox sensitivity of Eu and Ce. The results of each experiment are labelled with log  $fO_2$  conditions (from Burnham and Berry, 2012).

and negative Eu anomalies. The size of each anomaly varies as a function of the redox conditions (Fig. 5.1). However, Eu may also be controlled by the partitioning of  $Eu^{2+}$  into other phases, especially feldspars. As a consequence, oxidised melts may still produce negative Eu anomalies in zircon if feldspar has fractionated extensively. In situations where high magmatic water contents have suppressed feldspar fractionation, the Eu anomaly may be primarily controlled by redox (Dilles et al., 2015). This may explain the apparent decoupling of Ce and Eu anomalies in zircons from natural systems.

The Eu anomaly is quantified using the ratio of measured Eu and ‘expected’ Eu value based on its neighbouring REE ( $Eu^*$ ), and is calculated as:

$$\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N} / \sqrt{(\text{Sm}_\text{N} \times \text{Gd}_\text{N})} \quad (5.2)$$

where the subscript ‘N’ denotes the use of chondrite-normalised values (Sun and McDonough, 1989). The Ce anomaly may be estimated quantitatively in the same way as the Eu anomaly, i.e.  $\text{Ce}/\text{Ce}^* = \text{Ce}_\text{N} / \sqrt{(\text{La}_\text{N} \times \text{Pr}_\text{N})}$ . However, due to the low abundance of LREE in zircon, La and Pr may be below detection limits. Additionally, micro-inclusions of LREE-bearing phase (e.g. apatite) can affect the calculation of  $\text{Ce}^*$ . Instead,  $\text{Ce}/\text{Ce}^*$  may be calculated from normalised Nd and Sm values. Given that the chondrite normalised value for Nd may be estimated from the values for Ce and Sm:

$$\text{Nd}_\text{N} = \sqrt{(\text{Ce}^*_\text{N} \times \text{Sm}_\text{N})} \quad (5.3)$$

Rearranging this equation for  $\text{Ce}^*_\text{N}$  allows for  $\text{Ce}/\text{Ce}^*$  to be calculated from the values of Nd and Sm, which are normally present at detectable levels in zircon and much less strongly affected by LREE contamination. The expression for calculating  $\text{Ce}/\text{Ce}^*$  from Nd and Sm values is as follows:

$$\text{Ce}/\text{Ce}^* = \text{Ce}_\text{N} / \frac{(\text{Nd}_\text{N})^2}{\text{Sm}_\text{N}} \quad (5.4)$$

Although the direct determination of the Ce oxidation state in zircon is problematic (Dilles et al., 2015), it is possible to estimate  $\text{Ce}^{4+}/\text{Ce}^{3+}$  indirectly if the partitioning of other 3+ and 4+ cations is well constrained. Ballard et al. (2002) presented a method for calculating  $\text{Ce}^{4+}/\text{Ce}^{3+}$  which relies on the fundamental premise that the total Ce in the melt and the zircon is a sum of Ce in its two oxidation states:

$$Ce_{zircon} = Ce_{zircon}^{3+} + Ce_{zircon}^{4+} \quad (5.5)$$

$$Ce_{melt} = Ce_{melt}^{3+} + Ce_{melt}^{4+} \quad (5.6)$$

Given that  $Ce^{3+}$  and  $Ce^{4+}$  have separate partition coefficients in zircon, these may be introduced into these equations which, when combined and rearranged, produce the following formula:

$$Ce^{4+}/Ce^{3+} = \frac{Ce_{melt} - \frac{Ce_{zircon}}{D_{Ce(3+)}^{zircon/melt}}}{\frac{Ce_{zircon}}{D_{Ce(4+)}^{zircon/melt}} - Ce_{melt}} \quad (5.7)$$

where  $D_{Ce(3+)}^{zircon/melt}$  and  $D_{Ce(4+)}^{zircon/melt}$  are the partition coefficients between the melt and zircon for  $Ce^{3+}$  and  $Ce^{4+}$  respectively. These parameters are determined by assuming that the partitioning behaviour of  $Ce^{3+}$  and  $Ce^{4+}$  is intermediate between the partition coefficients for its neighbouring 3+ and 4+ cations, i.e. REE for 3+, and Hf, Zr, Th and U for 4+. Partition coefficients for REE and Hf, Th, and U for a given zircon trace element analysis may be determined by using the chemistry of the whole rock as a proxy for melt chemistry. Using the lattice strain model (Blundy and Wood, 1994), plots of  $\ln D^{zircon/melt}$  vs ionic radius for calculated 3+ partition coefficients produce straight line arrays, from which the calculated value of  $D_{Ce}$  will deviate. A trend line may be added to these straight lines, and interpolating between the values of  $D_{La}$  and  $D_{Pr}$  provides an estimate for  $D_{Ce}^{3+}$ . The same process may be used to interpolate a value for  $D_{Ce}^{4+}$  from between  $D_{Hf}$  and  $D_{Th}$ .

### 5.2.3 Ti-in-zircon thermometer

In this study, the calibration of Ferry and Watson (2007) is used, as it takes into account variations in both  $a_{SiO_2}$  and  $a_{TiO_2}$ , which are not accounted for in other thermometers

(e.g. Watson et al., 2006). The activity of  $\text{SiO}_2$  was set at 1, due to the abundant quartz in the groundmass of intrusions at both Oyu Tolgoi and Resolution. The activity of  $\text{TiO}_2$  is likely to be high, because of the presence of titanite in some of these intrusions. An activity of 0.7 was used as a reasonable estimate for titanite-bearing magmas by other workers (Claiborne et al., 2010; Dilles et al., 2015). Rutile in Resolution intrusions is likely to be hydrothermal, so  $a_{\text{TiO}_2}$  at the time of zircon crystallisation  $<1$ , and a value of 0.7 is also used.

Pressure variations provides a large potential source of error in the Ti-in-zircon thermometer. Ferry and Watson (2007) report a Ti-in-zircon pressure dependence of approximately  $5\text{ }^\circ\text{C kb}^{-1}$ . This thermometer was calibrated at 1 GPa (10 kb), meaning that temperature estimates for zircons in this study, which crystallised in shallow crustal environments typical of porphyry systems (100 to 300 MPa; Seedorff et al., 2005), may have been overestimated by up to  $30\text{ }^\circ\text{C}$ . However, as there is unlikely to be a significant difference between the crystallisation pressure of zircons in this study, pressure dependence is not sufficient to generate significant discrepancies between individual temperature analyses. Estimates of error for temperature analyses are  $\pm 12\text{ }^\circ\text{C}$  ( $2\sigma$ ) at temperatures around  $600\text{ }^\circ\text{C}$ , so this error value was applied to all temperature estimates.

#### 5.2.4 Usefulness as an indicator mineral of porphyry Cu fertility

Zircon is a robust mineral that is resistant to breakdown or chemical re-equilibration during hydrothermal alteration, and is commonly preserved in heavy mineral concentrates from stream sediments. As a result, zircon provides a useful tool for investigating the properties of igneous and metamorphic rocks in a particular district. Identifying indicators of fertility in zircons from stream sediments would be useful in focusing regional exploration programs.

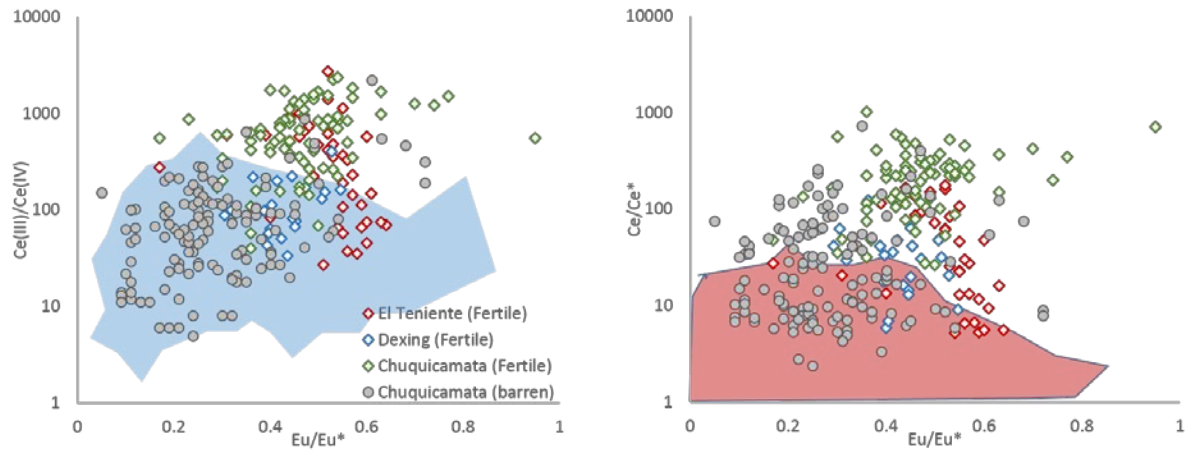


Figure 5.2. Elevated Ce and Eu anomalies in zircon from various porphyry systems. See text for data sources. (a) Calculated  $Ce^{4+}/Ce^{3+}$  ratio plotted against the Eu anomaly. Blue field is barren dataset of Ballard et al. (2002),  $n = 436$ ; (b) Ce anomaly in zircon plotted against the Eu anomaly. Red area is the field occupied by the ostensibly unmineralised global detrital zircon database of Iizuka et al. (2010),  $n = 1,017$ . Dexing data from Liang et al., (2006), El Teniente data from Muñoz et al., 2012, and Chuquicamata data from Ballard et al (2002).

Differences in zircon chemistry between fertile and barren intrusions from porphyry systems have been noted by a number of authors. In particular, zircons from intrusions that are closely related to mineralisation appear to have higher positive Ce anomalies, and smaller negative Eu anomalies than zircons from ostensibly barren granitoids (Fig. 5.2). Ballard et al. (2002) present a comparison between zircons from barren and fertile intrusions at Chuquicamata-El Abra porphyry systems (Chile). They compare these to a data from 436 detrital zircons from Palaeozoic sandstones, and showed that zircons from ore-bearing intrusions have  $Ce^{4+}/Ce^{3+} > 300$  and  $Eu/Eu^* > 0.4$ , whereas zircons from barren intrusions and from the Palaeozoic detrital dataset, do not commonly contain elevated  $Ce^{4+}/Ce^{3+}$  and  $Eu/Eu^*$ . Muñoz et al. (2012) showed that zircons from fertile intrusions at El Teniente (Chile) overlapped with the fertile field of Ballard et al. (2002) in terms of Eu and Ce anomalies. In a

study of zircons from the Dexing porphyry (China), Liang et al. (2006) found that zircons from fertile rocks have  $\text{Ce}^{4+}/\text{Ce}^{3+}$  greater than approximately 120. Dilles et al. (2015) demonstrated that zircons from Yerington, Yanacocha, Carlin, and El Salvador showed increasing  $\text{Eu}/\text{Eu}^*$  in successive intrusions immediately preceding mineralisation, which they linked to progressive oxidation due to the loss of reducing fluids. These geochemical features have been interpreted to indicate oxidised, hydrous melt conditions which may be key characteristics of fertile porphyry magmas (see section 1.3.5).

#### 5.2.5 Focus of this chapter

This chapter focuses on the geochemical and textural characteristics of zircons from Oyu Tolgoi and Resolution, and the associated magmatic rocks from both deposits. In particular, the following questions will be focussed upon:

1. The extent to which  $\text{Ce}^{4+}/\text{Ce}^{3+}$ ,  $\text{Ce}/\text{Ce}^*$ , and  $\text{Eu}/\text{Eu}^*$  of zircon are reasonable approximations of redox conditions of silicate melts;
2. The differences in chemistry between zircons from ore-forming and barren magmas within each deposit (e.g. Resolution vs Schultze Granite or Apache Leap intrusions), and between these rocks and average granitic rocks (global database compiled from the literature);
3. The difference in chemistry between zircons from high- and low-Cu grade porphyry systems (specifically, Hugo Dummett and Heruga at Oyu Tolgoi);
4. The implications of these chemical differences on the assessment of the redox conditions of fertile magmatic systems.

| Sample     | Lithology | Number of Analyses | Metal content (host rock) |     |        |              |
|------------|-----------|--------------------|---------------------------|-----|--------|--------------|
|            |           |                    | Cu                        | Mo  | Au     | Size         |
| Oyu Tolgoi |           |                    |                           |     |        |              |
| OT-11      | BiGd      | 29                 | 13                        | <1  | 0.004  | <50 - 300 μm |
| OT-158     | Dvs       | 32                 | 22                        | <1  | <0.001 | <50 - 400 μm |
| OT-7       | QMD Hr    | 34                 | 1645                      | 43  | 0.021  | 50 - 300 μm  |
| OT-21      | QMD Hr    | 33                 | 2610                      | 6   | 0.145  | 50 - 200 μm  |
| OT-35      | QMD Hr    | 36                 | 854                       | 3   | 0.019  | <50 - 250 μm |
| OT-39      | QMD Hr    | 15                 | 9460                      | 137 | 0.362  | 100 - 500 μm |
| OT-45      | QMD Hr    | 29                 | 185                       | 2   | 0.011  | <50 - 400 μm |
| OT-49      | QMD Hr    | 34                 | 882                       | 13  | 0.101  | <50 - 350 μm |
| OT-65      | QMD HD    | 35                 | 25400                     | 17  | 0.279  | <50 - 500 μm |
| OT-81      | QMD HD    | 33                 | 4100                      | 5   | 0.41   | <50 - 250 μm |
| OT-94      | QMD HD    | 40                 | 2440                      | 47  | 0.063  | 100 - 300 μm |
| OT-103     | QMD HD    | 27                 | 4310                      | 116 | 0.103  | <50 - 350 μm |
| OT-121     | QMD HD    | 33                 | 6990                      | 4   | 0.112  | <50 - 500 μm |
| OT-133     | QMD HD    | 35                 | 12750                     | 24  | 0.834  | <50 - 300 μm |
| OT-139     | QMD HD    | 30                 | 16550                     | 1   | 0.823  | <50 - 250 μm |

|            |                  |    |       |     |        |              |
|------------|------------------|----|-------|-----|--------|--------------|
| Resolution |                  |    |       |     |        |              |
| R-1B-13    | Int. Breccia     | 30 | 5190  | 46  | 0.036  | <50 - 300 µm |
| R-1B-7     | Int. Breccia     | 58 | 9580  | 9   | 0.005  | <50 - 250 µm |
| R-3B-7     | LP               | 34 | 16250 | 59  | 0.026  | 50 - 100 µm  |
| R-13F-2    | QLP              | 29 | 6150  | 160 | 0.006  | <50 - 300 µm |
| R-1B-5     | QLP              | 13 | 3850  | 82  | 0.051  | <50 - 300 µm |
| R-2A-13    | QLP              | 26 | 8630  | 68  | 0.016  | <50 - 300 µm |
| R-2B-6     | QLP              | 18 | 6350  | 113 | 0.016  | <50 - 300 µm |
| R-23D-2    | RDP              | 35 | 1520  | 8   | 0.005  | <50 - 300 µm |
| R-5D-1     | RDP              | 12 | 6030  | 339 | 0.009  | <50 - 250 µm |
| R-7D-3     | RDP              | 48 | 8240  | 63  | 0.024  | <50 - 300 µm |
| R-7D-7     | RDP              | 40 | 121   | 177 | 0.004  | <50 - 400 µm |
| R-9A-4     | RDP              | 34 | 1180  | 17  | 0.002  | <50 - 300 µm |
| R-RF-G     | Apache Leap      | 28 | 69    | <1  | 0.002  | <50 - 300 µm |
| R-S-13     | Schultze Granite | 29 | 4     | <1  | <0.001 | 100 - 300 µm |
| R-S-8      | Schultze Granite | 51 | <1    | <1  | <0.001 | <50 - 300 µm |

Table 5.1. Summary of zircon samples analysed by LA-ICP-MS.

### 5.3 Methods

Zircons from 30 rocks were analysed, covering a range of igneous rock types from both Resolution (15 rocks) and Oyu Tolgoi (15 rocks; (Table. 5.1). Selected samples from Oyu Tolgoi consisted of 6 samples of QMD from Heruga (low grade), 7 QMD from Hugo Dummett (high grade), 1 unmineralised BiGd (13 ppm Cu), and 1 unmineralised Dvs (22 ppm Cu). At Resolution, 2 samples of the Schultze Granite (one of which is R-S-13; the Schultze Granite porphyry), 1 Apache Leap intrusion, and 12 Resolution porphyry intrusions were selected. The Schultze Granite samples are unmineralised (<4 ppm Cu). All zircons were analysed from mineral separates mounted in polished blocks, and a total of 960 LA-ICP-MS trace element analyses were conducted (see section 2.5.3 for analytical methods).

#### 5.3.1 Compilation of literature data

The median composition of zircons from barren felsic arc rocks was determined from a compilation of literature data drawn from the GEOROC mineral database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). These data were filtered on the basis of their rock name. Zircons from rocks codified as andesite, diorite, dacite, granodiorite, monzodiorite, and monzonite were combined, and the median values for these zircons are presented in Table 5.7, and in Table 5.4 under the heading ‘and/dac’. Similarly, the median composition of zircons from rhyolite and granite rock types is combined under the heading ‘granite’. Zircons from granite rocks are enriched in incompatible elements (Hf, Nb, Ta, U, REE), but are depleted in compatible elements (Sr, Ti) with respect to zircons from andesite/dacite. These are geochemical features that are likely to be inherited from the degree of evolution of the associated magmas. In the descriptions of data from this study, comparisons will be drawn with median values for zircons from the andesite/dacite compilation, which shall be referred to as zircons from intermediate rocks.



| \      | Andesite/Dacite |        |        |        |        |        | Granite |        |        |         |         |        | B<br>(2002) |
|--------|-----------------|--------|--------|--------|--------|--------|---------|--------|--------|---------|---------|--------|-------------|
| (ppm)  | Min.            | 1st Q. | median | 3rd Q. | Max.   | n=     | Min.    | 1st Q. | median | 3rd Q.  | Max.    | n=     | median      |
| Sc     | 26              | 57     | 72     | 85.8   | 478    | 16     | 0.1     | 18.3   | 73.4   | 145     | 576     | 267    | 44          |
| Ti     | 1.22            | 7.3    | 11.0   | 16.0   | 587    | 287    | 0.93    | 5.8    | 8.62   | 14.1    | 838     | 550    |             |
| V      | 5.5             | 5.5    | 5.5    | 5.5    | 5.5    | 1      | 0.1     | 0.725  | 2.4    | 5.45    | 15.2    | 34     |             |
| Rb     | 13              | 13     | 13     | 13     | 13     | 1      | 0.32    | 0.69   | 1.01   | 1.955   | 20.5    | 51     |             |
| Sr     | 0.21            | 0.91   | 2.7    | 6.6    | 115    | 46     | 0.21    | 0.48   | 0.84   | 2.09    | 178.6   | 61     |             |
| Y      | 86              | 562    | 954    | 1454   | 29198  | 421    | 7.7     | 991    | 1539   | 2245    | 22190   | 1730   |             |
| Nb     | 0.17            | 1.75   | 3.32   | 6.9    | 176    | 155    | 0.48    | 3.13   | 8.52   | 16.4    | 564     | 317    |             |
| La     | 0.001           | 0.01   | 0.04   | 0.349  | 3037   | 436    | 0.002   | 0.05   | 0.181  | 1.7     | 5253    | 703    | 12          |
| Ce     | 0.8             | 11     | 19.2   | 51.9   | 6176   | 496    | 0.28    | 14.4   | 25.4   | 50.1    | 7011    | 757    | 61          |
| Pr     | 0.002           | 0.1    | 0.1    | 0.48   | 155    | 442    | 0.009   | 0.16   | 0.32   | 1.05    | 78.8    | 415    | 8           |
| Nd     | 0               | 0.6    | 1.6    | 6.5    | 2696   | 489    | 0.04    | 1.8    | 3.6    | 9.0     | 461     | 798    | 44.7        |
| Sm     | 0.1             | 1.4    | 3.2    | 8.6    | 645    | 496    | 0.3     | 3.5    | 6.2    | 11.5    | 337     | 758    | 21.5        |
| Eu     | 0.085           | 0.4    | 0.9    | 2.5    | 368    | 493    | 0.01    | 0.43   | 0.82   | 1.65    | 39.0    | 754    | 2.1         |
| Gd     | 1               | 11.0   | 20.1   | 39.45  | 1174   | 495    | 1.9     | 21.3   | 32.2   | 52.8    | 474     | 578    | 58          |
| Tb     | 0.74            | 4      | 7.29   | 12.4   | 2752   | 430    | 0.73    | 7.95   | 12     | 18.7    | 99.7    | 570    | 224         |
| Dy     | 4               | 53     | 90.7   | 153    | 3224   | 496    | 1.6     | 96     | 149    | 229     | 2156    | 1214   |             |
| Ho     | 2               | 24.08  | 37.9   | 57.5   | 3747   | 435    | 5.0     | 35.6   | 52.5   | 79.3    | 339     | 570    |             |
| Er     | 15.1            | 117    | 178    | 269    | 4123   | 496    | 19.3    | 210    | 408    | 1036    | 8241    | 1022   |             |
| Tm     | 3.8             | 28     | 42     | 59.4   | 7654   | 435    | 2.58    | 32.82  | 50.5   | 71      | 272     | 570    |             |
| Yb     | 42.7            | 258    | 395    | 561    | 10131  | 496    | 4.7     | 335    | 500    | 679     | 7109    | 1097   |             |
| Lu     | 4.78            | 54.5   | 79     | 113    | 8471   | 516    | 2.2     | 57     | 86.0   | 128     | 6513    | 944    |             |
| Hf     | 2688            | 7921   | 9665   | 10854  | 29679  | 443    | 869.6   | 9518   | 10480  | 11649   | 99500   | 1531   | 12800       |
| Ta     | 0.10            | 0.6    | 1.0    | 1.7    | 227    | 108    | 0.1     | 0.9    | 1.3    | 2.8     | 15.2    | 153    | 2.3         |
| Pb     | 0.2             | 7.6    | 26.9   | 83.6   | 6926.3 | 2112   | 0.01    | 8.8    | 24.4   | 74.2525 | 62000   | 2948   | 8.8         |
| Th     | 0               | 72.7   | 135    | 270    | 29193  | 5332   | 0.0051  | 92     | 186    | 391     | 46210   | 7879   | 368         |
| U      | 1               | 118    | 220    | 428    | 22181  | 6879   | 0.0119  | 144    | 283    | 580     | 1798000 | 10494  | 764         |
| Eu/Eu* | 0.02            | 0.31   | 0.42   | 0.59   | 2.00   | 492.00 | 0.01    | 0.10   | 0.17   | 0.27    | 1.62    | 575.00 | 0.2         |
| ΣREE   | 4.8             | 543    | 885    | 1350   | 29277  | 517    | 1.0     | 571    | 1162   | 1856    | 15645   | 1355   | 1813        |
| Yb/Gd  | 1.9             | 14.7   | 21.5   | 34.1   | 190    | 495    | 0.9     | 12.7   | 16.4   | 21.0    | 85.9    | 578    | 13.3        |
| U/Pb   | 0.26            | 2.3    | 10.1   | 28.6   | 9611   | 2097   | 0.12    | 3.0    | 11.8   | 32.5    | 29600   | 2948   | 86.8        |
| Th/Pb  | 0.01            | 2.7    | 13.6   | 37     | 942    | 1447   | 0.02    | 4.5    | 10.5   | 26.4    | 9431    | 1922   | 41.8        |
| Ta/Nb  | 0.04            | 0.27   | 0.34   | 0.42   | 2.61   | 108    | 0.04    | 0.21   | 0.29   | 0.40    | 0.99    | 86     | 0.5         |
| T (°C) | 604             | 750    | 790    | 830    | 1449   | 287    | 586     | 729    | 766    | 816     | 1550    | 551    | 1.5         |
| Ce/Ce* | 0.19            | 18.5   | 55.3   | 174    | 6149   | 487    | 0.60    | 9.1    | 27.5   | 69.8    | 1501    | 736    |             |

Table 5.2. Compilation of literature data from the GEOROC database. 'Min.' and 'Max.' are the minimum and maximum values, and '1<sup>st</sup> Q.' and '3<sup>rd</sup> Q.' are the first and third quartile values. The number of samples, 'n', varies as not all elements were analysed in each literature study. Column 'B (2002)' are median values from Belousova et al (2002b)

These median values are comparable to the median values determined for granitoid zircons by Belousova et al. (2002b) from 154 analyses. In most cases, median values from the GEOROC database for zircons from intermediate rocks are within the same order of magnitude as values from Belousova et al. (2002b). LREE (La, Pr, Nd, and Sm) of the Belousova zircons are unusually high and are an order of magnitude higher than is predicted from experimental studies of trace element partitioning. A compilation of literature data is presented in Table 5.2.

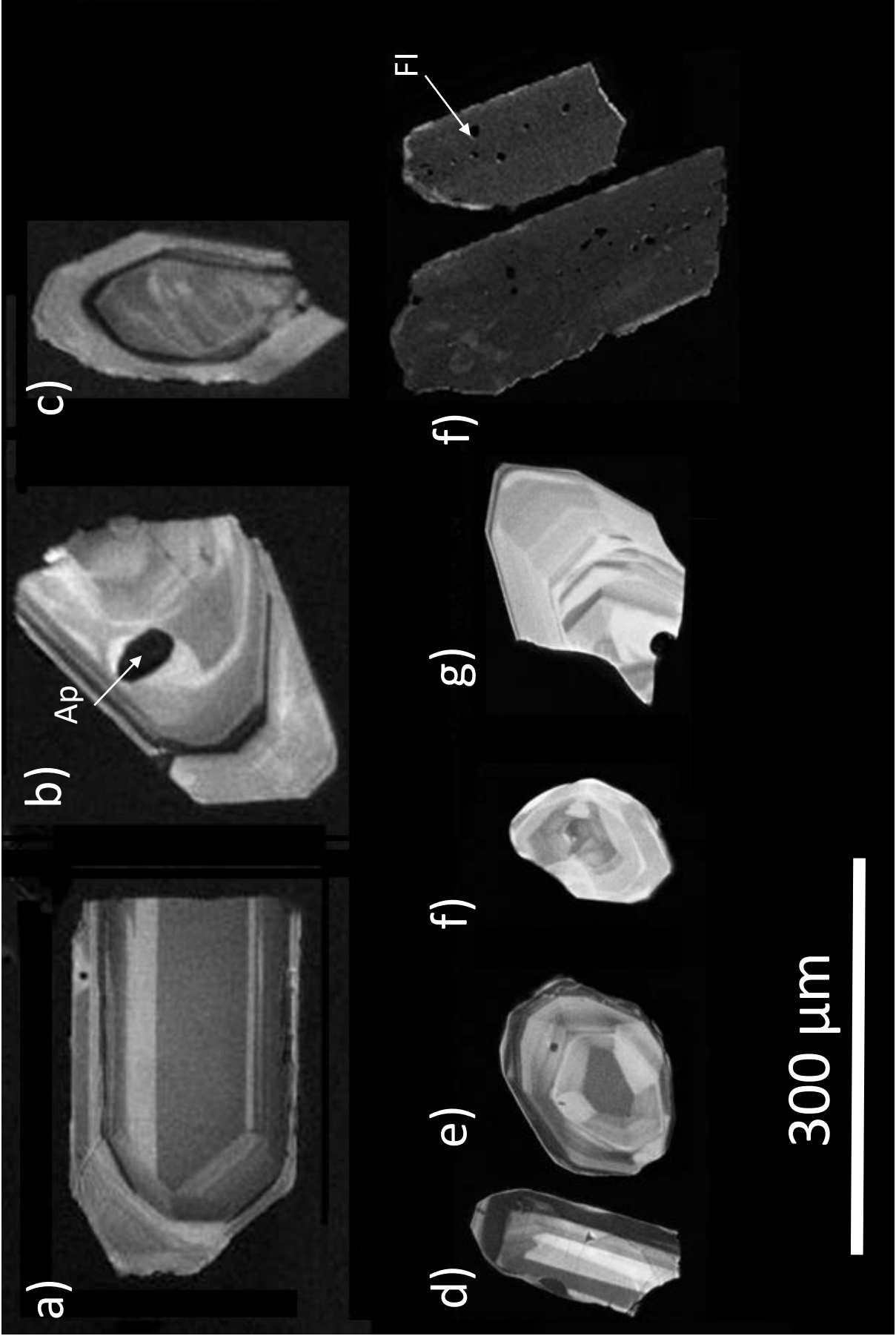
## **5.4 Results – Oyu Tolgoi**

### **5.4.1 Petrography of Oyu Tolgoi zircons**

Of those samples for which mineral separation was conducted, zircon was found in rocks with silica values from 55.2 wt. % SiO<sub>2</sub> (OT-158, ignimbrite) to 69.3 wt. % SiO<sub>2</sub> (Hugo Dummett QMD). Grains analysed in this study ranged in size from ~30  $\mu$ m to <500  $\mu$ m. Smaller grains of zircon exist in the groundmass of porphyry intrusions.

Zoning is common to almost all zircons (Fig. 5.3). In some cases, this zoning is oscillatory and no apparent break in crystal growth is observed. In other examples, cores of zircon have truncated zoning and are overgrown by a rim with different CL characteristics (Fig. 5.3 a-c). Although a range of zoning patterns exists, most rims have a brighter CL response than the cores.

Mineral inclusions in zircon typically have a ‘granitic’ character, i.e. biotite, K-feldspar, quartz and apatite, with subordinate magnetite and titanite. Some ovoid inclusions are truly granitic, in that they contain all (or most) of these phases inter-grown with one another. These may represent crystallised melt inclusions. Growth of sulphides (especially chalcopyrite) along cracks is common in zircons from mineralised intrusions, and cracks are easily distinguishable in CL images.



*Figure 5.3. (previous page). Representative SEM-CL images of zircons from Oyu Tolgoi, showing: (a-c) truncated cores with lighter overgrowth rims; (d-g) oscillatory and sector zoning; (f) zircons with ‘mottled’ texture, with pitted surfaces and dull CL colours. Ap = apatite. FI = fluid inclusion*

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A group of zircons found only in sample OT-103 have a distinctive texture that is different to all other zircons in this study (Fig. 5.3 f). These grains are subhedral and have a mottled appearance which is due to the presence of numerous inclusions (up to 10  $\mu\text{m}$ ). The inclusions appear as pits on the surface of polished samples and are probably opened fluid inclusions. ‘Mottled’ zircons lack the concentric zoning characteristic of the other zircons, and instead have a very dull CL response, with some irregular lighter patches. Sample OT-103 contains both mottled zircons and the more common bright-CL type.

#### 5.4.2 Geochronology of Oyu Tolgoi zircons

Geochronological data are presented in full in Appendix 3. Errors on individual  $^{206}\text{Pb}/^{238}\text{U}$  ages are quite large ( $\pm \sim 10$  Myr). Analyses from two of the QMD intrusions (OT-45 Heruga, and OT-139 Hugo Dummett) yielded concordia ages of  $361.4 \pm 2.8$  and  $362.0 \pm 2.1$  Ma respectively (Fig. 5.4). In both of these samples, older zircon grains (up to  $\sim 372$  Ma) are also found. Sample OT-103 (QMD – Hugo Dummett) has a concordia age of  $366.2 \pm 3.3$ , but from a much smaller number of analyses. These concordia ages are consistent with published dates for the QMD intrusions presented by Dolgoplova et al. (2013) that are within error, between  $359 \pm 8$  and  $367 \pm 7$  Ma. However, Wainwright et al. (2011) published an older age of  $369 \pm 2$  Ma and a Re-Os molybdenite age from Heruga gave a similar age of  $371 \pm 1$  Ma (Ivanhoe Mines, unpublished data).

|             |           | Isotope ratios                   |         |                                  |         |                                   |         |  | Apparent age (Ma)                 |           |                                  |           |                                  |           |
|-------------|-----------|----------------------------------|---------|----------------------------------|---------|-----------------------------------|---------|--|-----------------------------------|-----------|----------------------------------|-----------|----------------------------------|-----------|
| Sample name | Lithology | $^{206}\text{Pb}/^{238}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{235}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{206}\text{Pb}$ | RSD (%) |  | $^{207}\text{Pb}/^{206}\text{Pb}$ | $2\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ | $2\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | $2\sigma$ |
| OT-45       | QMD-Hr    | 0.0567                           | 1.26    | 0.4252                           | 1.61    | 0.05248                           | 1.84    |  | 356                               | 9         | 360                              | 10        | 306                              | 84        |
| OT-45       | QMD-Hr    | 0.0572                           | 1.28    | 0.4272                           | 2.26    | 0.05217                           | 1.90    |  | 359                               | 9         | 361                              | 14        | 292                              | 86        |
| OT-45       | QMD-Hr    | 0.0573                           | 1.27    | 0.4284                           | 1.76    | 0.0524                            | 2.11    |  | 359                               | 9         | 362                              | 11        | 302                              | 96        |
| OT-45       | QMD-Hr    | 0.0575                           | 1.34    | 0.4353                           | 1.93    | 0.0530                            | 2.37    |  | 360                               | 9         | 367                              | 12        | 328                              | 108       |
| OT-45       | QMD-Hr    | 0.0577                           | 1.44    | 0.416                            | 3.56    | 0.05091                           | 3.31    |  | 362                               | 10        | 353                              | 21        | 236                              | 152       |
| OT-45       | QMD-Hr    | 0.0581                           | 1.12    | 0.438                            | 1.36    | 0.05397                           | 1.45    |  | 364                               | 8         | 369                              | 8         | 368                              | 66        |
| OT-45       | QMD-Hr    | 0.0589                           | 0.90    | 0.4332                           | 2.13    | 0.05315                           | 1.79    |  | 369                               | 6         | 365                              | 13        | 334                              | 80        |
| OT-45       | QMD-Hr    | 0.0593                           | 1.70    | 0.4415                           | 2.61    | 0.05326                           | 2.03    |  | 372                               | 12        | 371                              | 16        | 338                              | 92        |
| OT-103      | QMD-HD    | 0.0582                           | 1.53    | 0.438                            | 2.16    | 0.05483                           | 2.41    |  | 365                               | 11        | 369                              | 13        | 404                              | 108       |
| OT-103      | QMD-HD    | 0.0584                           | 1.31    | 0.4384                           | 2.45    | 0.0535                            | 2.17    |  | 366                               | 9         | 369                              | 15        | 348                              | 98        |
| OT-103      | QMD-HD    | 0.0595                           | 1.17    | 0.4474                           | 1.30    | 0.05439                           | 1.45    |  | 373                               | 8         | 375                              | 8         | 386                              | 64        |
| OT-103      | QMD-HD    | 0.0608                           | 1.85    | 0.4463                           | 1.60    | 0.05415                           | 1.66    |  | 380                               | 14        | 375                              | 10        | 376                              | 76        |
| OT-103      | QMD-HD    | 0.0617                           | 1.99    | 0.4542                           | 4.05    | 0.0543                            | 5.38    |  | 386                               | 15        | 380                              | 26        | 384                              | 242       |
| OT-139      | QMD-HD    | 0.0572                           | 1.45    | 0.4283                           | 1.89    | 0.05354                           | 2.03    |  | 359                               | 10        | 362                              | 12        | 350                              | 92        |
| OT-139      | QMD-HD    | 0.0573                           | 1.36    | 0.4346                           | 2.58    | 0.0534                            | 2.18    |  | 359                               | 9         | 366                              | 16        | 346                              | 98        |
| OT-139      | QMD-HD    | 0.0573                           | 1.71    | 0.4236                           | 1.89    | 0.0540                            | 1.71    |  | 359                               | 12        | 359                              | 11        | 370                              | 76        |
| OT-139      | QMD-HD    | 0.0575                           | 1.15    | 0.4233                           | 1.87    | 0.05379                           | 1.86    |  | 360                               | 8         | 358                              | 11        | 362                              | 84        |
| OT-139      | QMD-HD    | 0.0574                           | 1.20    | 0.4351                           | 3.17    | 0.05438                           | 3.03    |  | 360                               | 8         | 367                              | 20        | 386                              | 136       |
| OT-139      | QMD-HD    | 0.0574                           | 1.06    | 0.4299                           | 1.79    | 0.05419                           | 1.50    |  | 360                               | 7         | 363                              | 11        | 378                              | 68        |
| OT-139      | QMD-HD    | 0.0577                           | 1.43    | 0.4291                           | 2.30    | 0.05283                           | 2.25    |  | 362                               | 10        | 363                              | 14        | 320                              | 102       |
| OT-139      | QMD-HD    | 0.0585                           | 1.16    | 0.4392                           | 2.57    | 0.05406                           | 2.00    |  | 366                               | 8         | 370                              | 16        | 372                              | 92        |
| OT-139      | QMD-HD    | 0.0584                           | 1.21    | 0.4376                           | 1.21    | 0.05377                           | 1.25    |  | 366                               | 9         | 369                              | 7         | 360                              | 56        |
| OT-139      | QMD-HD    | 0.059                            | 1.16    | 0.4431                           | 2.07    | 0.05468                           | 1.98    |  | 370                               | 8         | 372                              | 13        | 398                              | 88        |
| OT-139      | QMD-HD    | 0.0593                           | 1.15    | 0.4452                           | 2.88    | 0.05405                           | 2.57    |  | 371                               | 8         | 374                              | 18        | 372                              | 116       |

| Sample name | Lithology | Isotope ratios                   |         |                                  |         |                                   |         | Apparent age (Ma)                 |            |                                  |            |                                  |            |
|-------------|-----------|----------------------------------|---------|----------------------------------|---------|-----------------------------------|---------|-----------------------------------|------------|----------------------------------|------------|----------------------------------|------------|
|             |           | $^{206}\text{Pb}/^{238}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{235}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{206}\text{Pb}$ | RSD (%) | $^{207}\text{Pb}/^{206}\text{Pb}$ | 2 $\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ | 2 $\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | 2 $\sigma$ |
| OT-11       | BiGd      | 0.0577                           | 2.81    | 0.4431                           | 7.27    | 0.05286                           | 6.28    | 361                               | 20         | 372                              | 45         | 322                              | 286        |
| OT-11       | BiGd      | 0.0578                           | 1.85    | 0.4414                           | 2.30    | 0.05441                           | 2.54    | 362                               | 13         | 371                              | 14         | 388                              | 114        |
| OT-11       | BiGd      | 0.0581                           | 1.73    | 0.4300                           | 2.87    | 0.0529                            | 2.75    | 364                               | 12         | 363                              | 18         | 322                              | 124        |
| OT-11       | BiGd      | 0.0581                           | 1.78    | 0.4371                           | 1.93    | 0.05322                           | 1.62    | 364                               | 13         | 368                              | 12         | 338                              | 74         |
| OT-11       | BiGd      | 0.0583                           | 2.04    | 0.4340                           | 1.55    | 0.0549                            | 1.73    | 365                               | 14         | 366                              | 10         | 408                              | 78         |
| OT-11       | BiGd      | 0.0595                           | 1.03    | 0.448                            | 1.22    | 0.05349                           | 1.20    | 373                               | 7          | 376                              | 8          | 348                              | 54         |
| OT-11       | BiGd      | 0.0617                           | 1.31    | 0.4668                           | 1.98    | 0.05545                           | 1.77    | 386                               | 10         | 389                              | 13         | 430                              | 78         |
| OT-11       | BiGd      | 0.0624                           | 0.86    | 0.4727                           | 1.46    | 0.05344                           | 1.35    | 390                               | 7          | 393                              | 10         | 346                              | 60         |
| OT-11       | BiGd      | 0.0676                           | 1.54    | 0.5279                           | 2.26    | 0.05632                           | 1.66    | 421                               | 13         | 430                              | 16         | 464                              | 74         |
| OT-11       | BiGd      | 0.0676                           | 1.55    | 0.5494                           | 0.96    | 0.05669                           | 1.08    | 422                               | 13         | 445                              | 7          | 478                              | 48         |
| OT-11       | BiGd      | 0.0681                           | 1.43    | 0.5433                           | 2.10    | 0.0572                            | 2.22    | 425                               | 12         | 441                              | 15         | 498                              | 98         |
| OT-11       | BiGd      | 0.0683                           | 1.42    | 0.5343                           | 0.91    | 0.0550                            | 1.05    | 426                               | 12         | 435                              | 6          | 410                              | 48         |
| OT-11       | BiGd      | 0.0695                           | 1.20    | 0.5519                           | 1.57    | 0.0561                            | 1.34    | 433                               | 10         | 446                              | 11         | 454                              | 60         |

Table 5.3. Concordant U-Pb data and calculated ages for Oyu Tolgoi zircons. HD = Hugo Dummett, Hr = Heruga

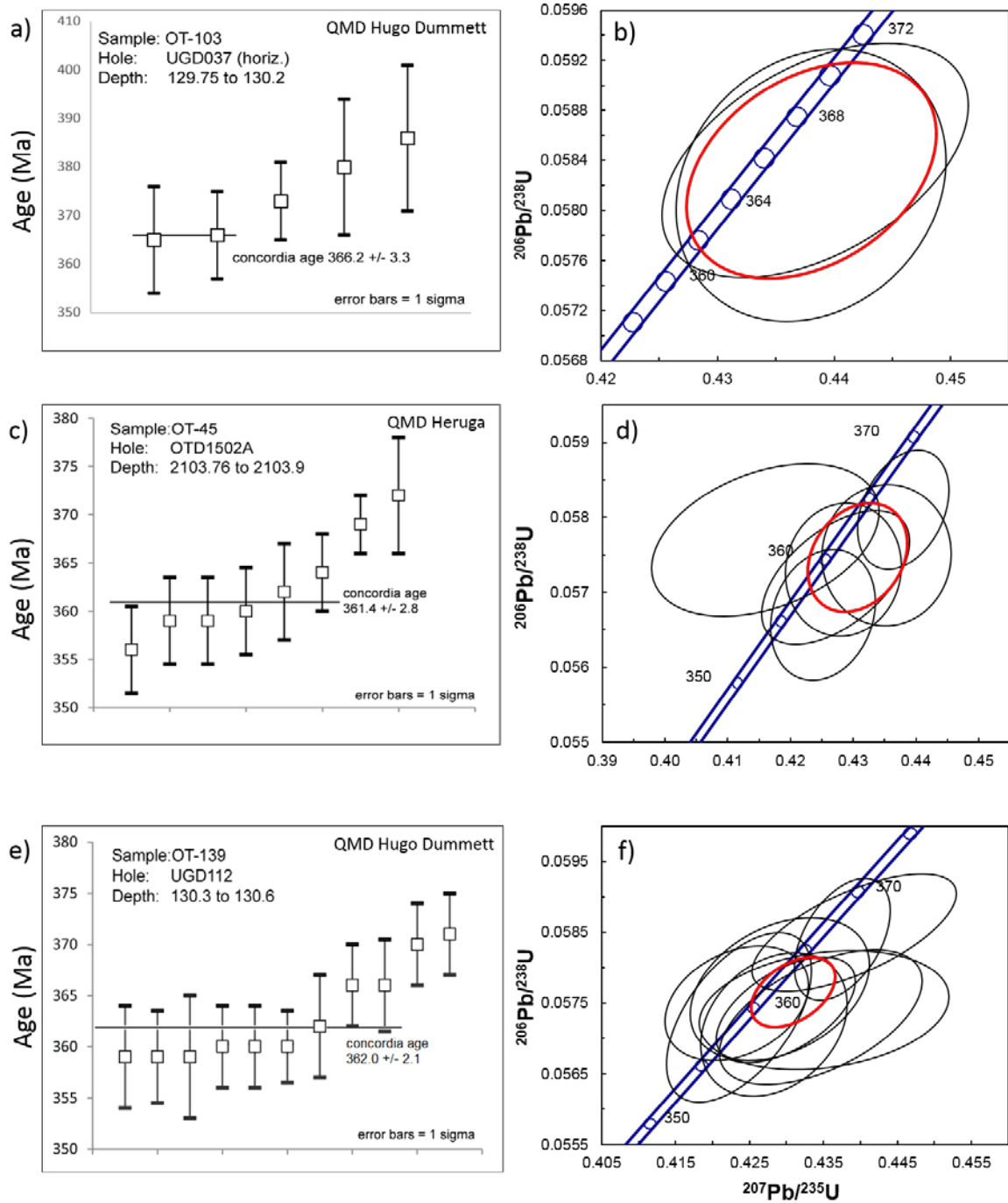


Figure 5.4. (a, c, e) Age arrays for  $^{206}\text{Pb}/^{238}\text{U}$  ages determined for three QMD intrusions by LA-ICP-MS. (b, d, f) Wetherwill concordia plots for the same intrusions, showing the data point error ellipses of the analyses used to calculate concordia ages. Red ellipses are the calculated isochron ages. Error ellipses represent  $2\sigma$ , error bars in a, c, and e represent  $1\sigma$ .

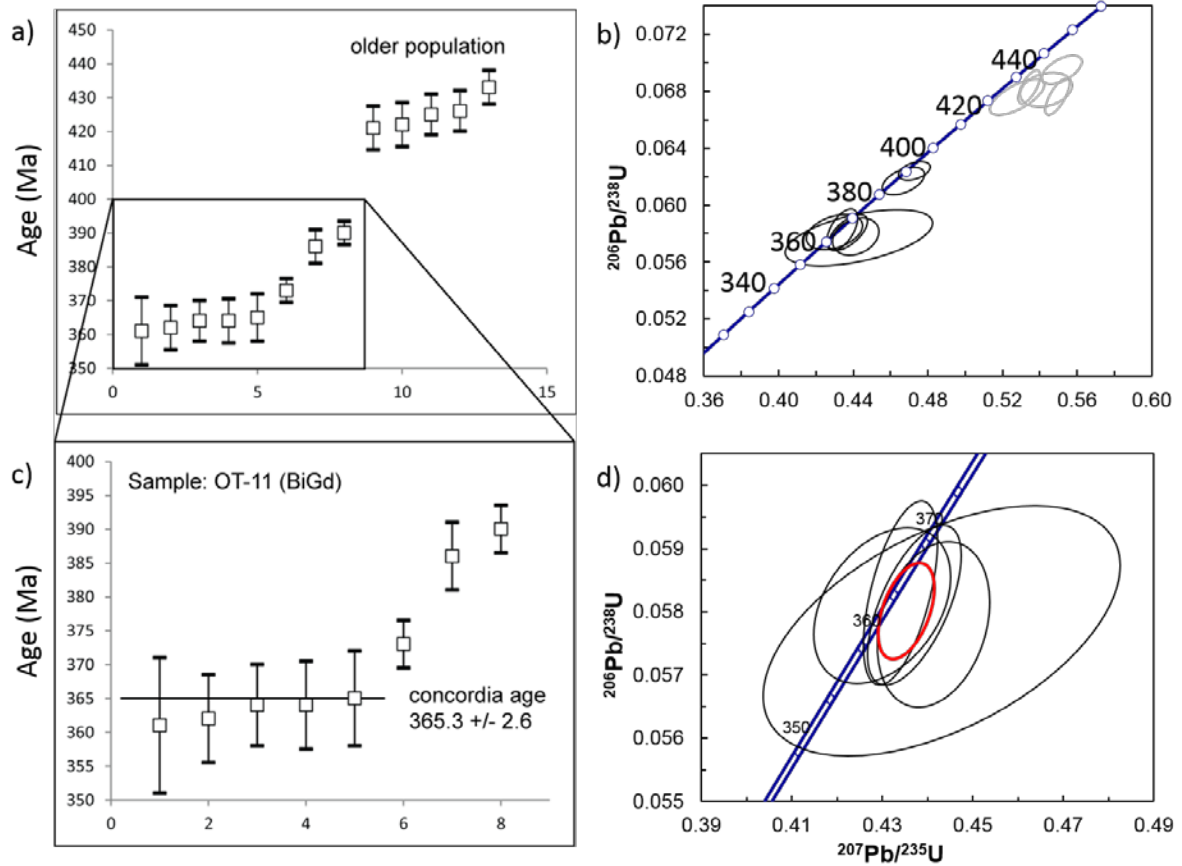


Figure 5.5. (a,c) Arrays for  $^{206}\text{Pb}/^{238}\text{U}$  ages determined by LA-ICP-MS for a sample of BiGd. (b,d) Wetherill concordia plots for the same data, showing the data point error ellipses of the analyses used to calculate concordia ages. Red ellipses represent the calculated isochron ages. Grey ellipses in (b) are discordant inherited ages. Error ellipses represent  $2\sigma$ , error bars in (a) and (c) represent  $1\sigma$ .

BiGd sample OT-11 has a population that yields a concordia age of  $365.3 \pm 2.6$  (Fig. 5.5). This is consistent with previous age estimates of the BiGd of  $\sim 366$  Ma (Wainwright et al., 2011). Older populations of analyses exist at  $\sim 400$  Ma and  $\sim 430$  Ma, the latter being mildly discordant (Fig. 5.5 c,d). Zircons of this age were also noted by Wainwright (2008).



### 5.4.3 Geochemistry of Oyu Tolgoi zircons

A summary of the chemistry of Oyu Tolgoi zircons is presented in Table 5.4, and the full dataset is presented in Appendix 4. The trace element chemistry of Oyu Tolgoi zircons can be divided into two geochemically distinct groups. One group of analyses has lower  $\text{Eu}/\text{Eu}^*$ ,  $\text{Ce}^{4+}/\text{Ce}^{3+}$ , and  $\text{Yb}/\text{Gd}$ , and higher crystallisation  $T$  ( $^{\circ}\text{C}$ ), Ta, Nb, Y, and  $\Sigma\text{REE}$  than another group. Median  $\text{Ce}/\text{Ce}^*$  is similar for both groups. The distinction between these groups is most apparent in Ta values, which are broadly bimodal and have frequency peaks at 0.09 and 0.39 ppm, and a dearth of Ta values between 0.2 and 0.27 ppm (Fig. 5.6 a).

To test the distinction between these groups, Ta values were plotted on a log normal distribution (Fig. 5.6 b), which confirms the presence of two populations of data. The break in slope of the log normal plot occurs at 0.2 ppm Ta, and thus the zircon analyses from QMD

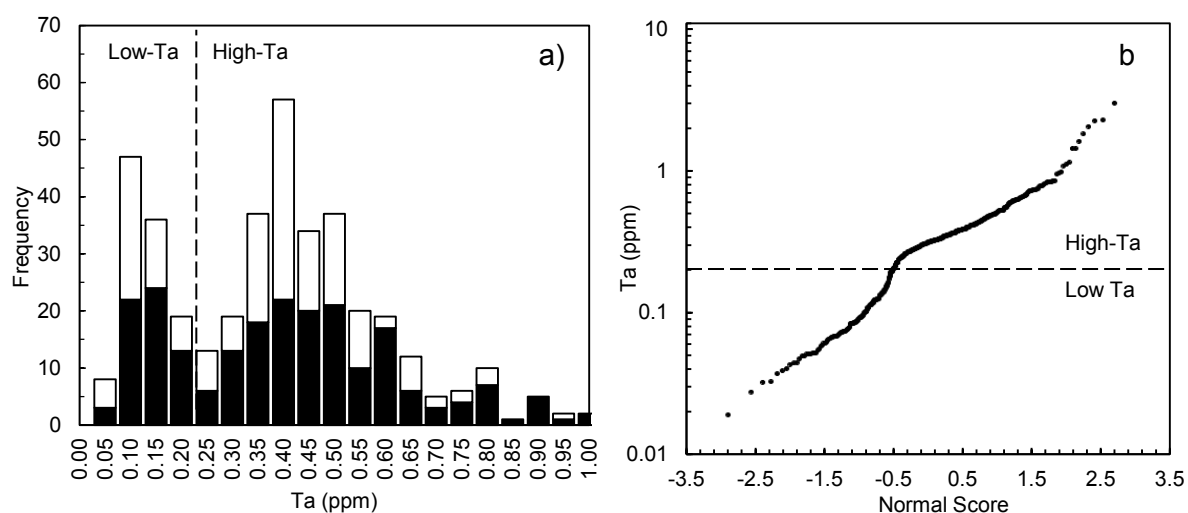


Figure 5.6. a) Frequency distribution, and b) log normal distribution for Ta in zircons from Oyu Tolgoi. The paucity of grains with  $\sim 0.2$  ppm Ta is the basis for discriminating between the geochemically distinct 'low-Ta' and 'high-Ta' groups.

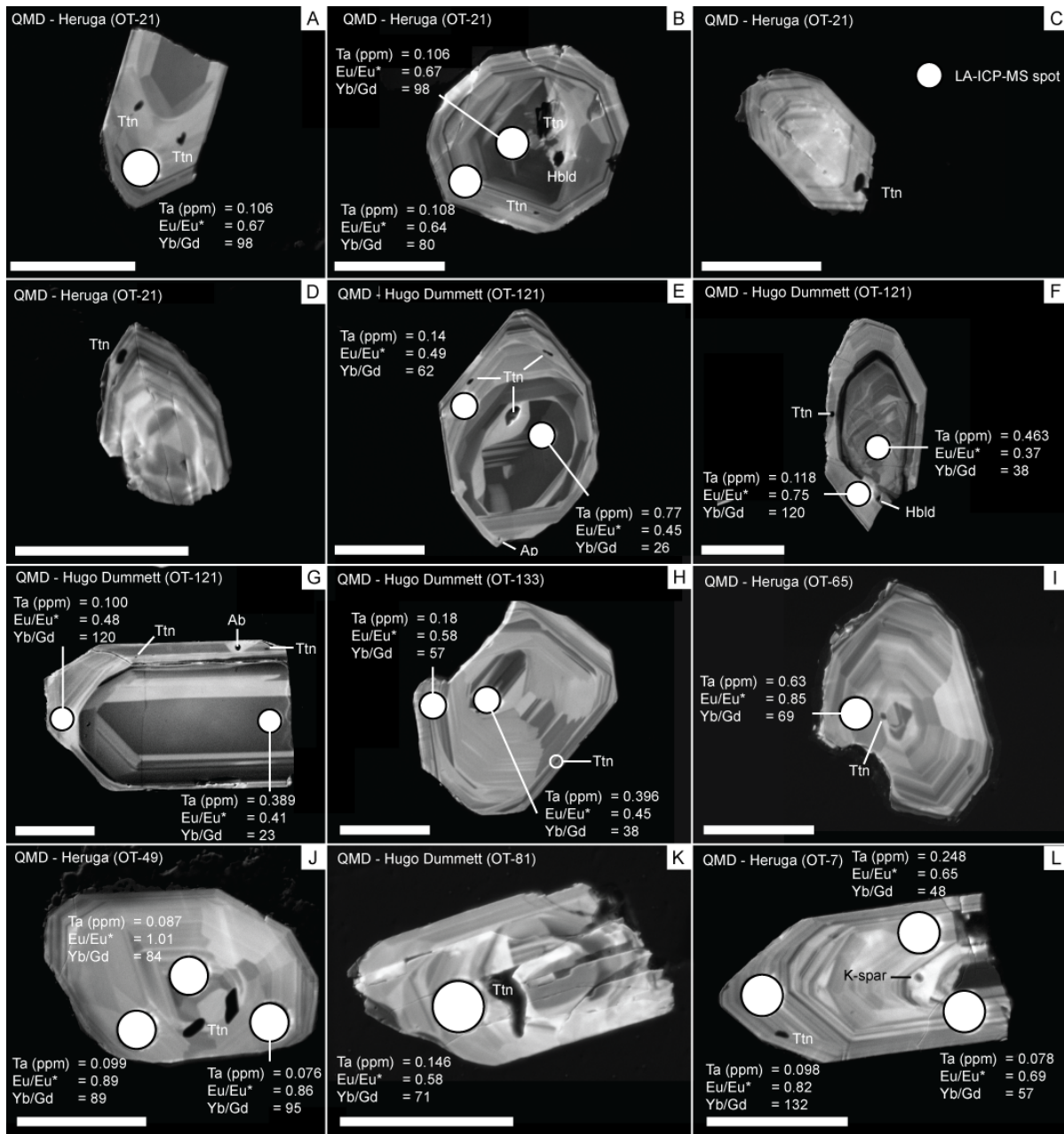


Figure 5.7. Some examples of the distribution of low- and high-Ta analyses in Oyu Tolgoi zircons. Low-Ta values ( $<0.2$  ppm) is commonly observed in the rims of grains that have high-Ta cores, which display truncated zoning patterns (a, e, f, g, h). However, grains with high-Ta cores and rims (j) and low-Ta cores and rims also exist. In all cases, low Ta values are accompanied by high Eu/Eu\* and Yb/Gd values, and zones with these values also contain small inclusions of titanite. Ttn = titanite, K-spar = K-feldspar, Ab = albite, hbl = hornblende

rocks are divided into two groups: *low-Ta* zircon (<0.2 ppm) and *high-Ta* zircon (>0.2 ppm). Both groups are geochemically distinct from the group of *mottled zircons* from sample OT-103, which have the highest Ta values. Note that the terminology of ‘low-Ta’ and ‘high-Ta’ is a relative distinction at Oyu Tolgoi; the median value of Ta for both groups is lower than the median value typical of zircons from both intermediate and granitic rocks.

Low-Ta zircon analyses are commonly found in the rims, overgrowing high-Ta cores, or at the edge of grains with concentric zoning. Some grains have low-Ta values in both core and rim, and some grains have both high-Ta cores and rims (Fig. 5.7).

Low-Ta grains are most common in the QMD, with a near-equal percentage of analyses from Heruga and Hugo Dummett. Of the total number of LA-ICP-MS trace element analyses of zircons the QMD, ~28 % of these analyses are from the low-Ta group. Some zircon analyses from the unmineralised BiGd and Dvs volcanic rocks also have low Ta values (<0.2 ppm), but these analyses will be discussed along with other analyses of zircon from these units.

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*Table 5.4. (next page) Median values for zircons from Oyu Tolgoi. Coloured boxes indicate % difference from andesite/dacite median zircon value. Dark green = >200% difference, light green = >150%, pale red = <50%, dark red = <25%. “And/dac” and “Granite” are median values for typical andesite/dacite and granitic rocks, from GEOROC database (see text). LOD = limit of detection for LA-ICP-MS analyses. “1st Q” and “3<sup>rd</sup> Q” are the 1st and 3rd quartile respectively, and min and max are the minimum and maximum value determined for each group during this study.*

|     | Low Ta |        |        |        |       | High Ta |        |        |        |      | Dys    |        |        |        |       | BiGd   |        |        |        |      | LOD   | And/Dac | Granite |
|-----|--------|--------|--------|--------|-------|---------|--------|--------|--------|------|--------|--------|--------|--------|-------|--------|--------|--------|--------|------|-------|---------|---------|
| ppm | min    | 1st Q. | median | 3rd Q. | max   | min     | 1st Q. | median | 3rd Q. | max  | min    | 1st Q. | median | 3rd Q. | max   | min    | 1st Q. | median | 3rd Q. | max  | ppm   | median  | median  |
| Sc  | 89.6   | 103    | 108    | 115    | 181   | 82.1    | 100    | 108    | 117    | 407  | 121.0  | 126    | 136    | 146    | 164   | 87.4   | 101    | 117    | 137    | 152  | 0.20  | 72      | 73.4    |
| Ti  | 1.81   | 3.50   | 4.43   | 5.31   | 9.66  | b.d.l.  | 5.97   | 7.88   | 10.6   | 25.1 | b.d.l. | 7.34   | 8.78   | 10.4   | 13.50 | b.d.l. | 2.55   | 5.91   | 9.0    | 25.1 | 1.4   | 11      | 8.62    |
| V   | b.d.l. | 0.11   | 0.15   | 0.21   | 0.70  | b.d.l.  | 0.29   | 0.40   | 0.55   | 3.9  | b.d.l. | 0.17   | 0.23   | 0.41   | 1.00  | b.d.l. | 0.083  | 0.21   | 0.32   | 1.9  | 0.061 | 5.5     | 2.4     |
| Rb  | b.d.l. | b.d.l. | 0.045  | 0.07   | 0.2   | b.d.l.  | 0.06   | 0.093  | 0.1    | 0.7  | b.d.l. | 0.1    | 0.22   | 0.3    | 0.4   | b.d.l. | 0.05   | 0.097  | 0.1    | 0.3  | 0.038 | 13      | 1.01    |
| Sr  | 0.043  | 0.086  | 0.11   | 0.14   | 1.0   | 0.051   | 0.11   | 0.13   | 0.17   | 4.8  | 0.085  | 0.18   | 0.23   | 0.31   | 0.87  | 0.051  | 0.11   | 0.12   | 0.18   | 0.55 | 0.024 | 2.7     | 0.84    |
| Y   | 128    | 237    | 276    | 467    | 1151  | 225     | 535    | 725    | 1067   | 5868 | 315    | 917    | 1306   | 1594   | 3013  | 217    | 499    | 798    | 1047   | 3259 | 0.15  | 954     | 1539    |
| Nb  | 0.265  | 0.440  | 0.58   | 0.740  | 2.04  | 0.590   | 1.03   | 1.3    | 1.77   | 37.1 | 0.883  | 1.27   | 1.9    | 4.04   | 13.78 | 0.520  | 0.92   | 1.5    | 4.05   | 37.1 | 0.030 | 3.32    | 8.52    |
| La  | b.d.l. | b.d.l. | b.d.l. | 0.02   | 0.123 | b.d.l.  | b.d.l. | b.d.l. | b.d.l. | 0.3  | b.d.l. | b.d.l. | b.d.l. | 0.04   | 0.142 | b.d.l. | b.d.l. | b.d.l. | 0.03   | 0.3  | 0.020 | 0.04    | 0.181   |
| Ce  | 3.28   | 5.41   | 7      | 9.20   | 28.0  | 1.42    | 8.09   | 10.3   | 14.2   | 116  | 5.53   | 8.06   | 13.0   | 19.96  | 116.3 | 1.42   | 5.88   | 8.02   | 21.3   | 39   | 0.022 | 19.2    | 25.4    |
| Pr  | b.d.l. | b.d.l. | b.d.l. | 0.024  | 0.13  | b.d.l.  | 0.018  | 0.0323 | 0.071  | 0.85 | b.d.l. | 0.0328 | 0.0639 | 0.128  | 0.33  | b.d.l. | b.d.l. | 0.0317 | 0.092  | 0.85 | 0.016 | 0.1     | 0.32    |
| Nd  | b.d.l. | b.d.l. | 0.219  | 0.344  | 1.96  | b.d.l.  | 0.386  | 0.678  | 1.39   | 12.3 | b.d.l. | 0.681  | 1.26   | 2.386  | 4.46  | b.d.l. | 0.364  | 0.566  | 1.27   | 12.3 | 0.19  | 1.6     | 3.6     |
| Sm  | b.d.l. | 0.298  | 0.440  | 0.696  | 3.26  | 0.159   | 1.21   | 1.72   | 3.50   | 25.2 | 0.1595 | 1.992  | 3.44   | 5.256  | 10.37 | 0.330  | 0.97   | 1.70   | 3.14   | 16.7 | 0.11  | 3.2     | 6.2     |
| Eu  | 0.0829 | 0.203  | 0.269  | 0.414  | 1.22  | 0.0720  | 0.402  | 0.606  | 1.10   | 6.77 | 0.0720 | 0.705  | 1.11   | 1.534  | 4.21  | 0.1925 | 0.337  | 0.624  | 1.11   | 3.06 | 0.032 | 0.9     | 0.82    |
| Gd  | 0.957  | 1.91   | 2.75   | 4.25   | 17.1  | 1.28    | 7.73   | 10.8   | 19.4   | 137  | 1.281  | 13.34  | 21.6   | 28.11  | 60.6  | 2.06   | 6.65   | 12.1   | 17.5   | 77   | 0.12  | 20.1    | 32.2    |
| Tb  | 0.422  | 0.776  | 1.06   | 1.70   | 5.43  | 0.668   | 2.94   | 4.11   | 6.97   | 46.8 | 0.668  | 4.882  | 7.95   | 10.23  | 21.17 | 0.867  | 2.67   | 4.53   | 6.32   | 25.7 | 0.019 | 7.29    | 12      |
| Dy  | 6.55   | 12.4   | 15.8   | 24.3   | 73.8  | 14.7    | 40.5   | 54.6   | 89.0   | 557  | 14.69  | 67.3   | 106    | 132.6  | 270.2 | 13.2   | 36.5   | 59.5   | 87.2   | 334  | 0.093 | 90.7    | 149     |
| Ho  | 3.50   | 6.23   | 7.54   | 12.4   | 30.4  | 7.00    | 16.9   | 23.1   | 34.7   | 209  | 9.96   | 27.42  | 42.6   | 51.1   | 101.0 | 6.11   | 15.6   | 24.3   | 31.9   | 119  | 0.027 | 37.9    | 52.5    |
| Er  | 23.9   | 40.7   | 47.1   | 78.9   | 191   | 37.3    | 91.0   | 122    | 173    | 948  | 54.2   | 152.9  | 216    | 257.8  | 486   | 36.7   | 83.5   | 129    | 182    | 523  | 0.12  | 178     | 408     |
| Tm  | 7.78   | 12.8   | 15.1   | 24.0   | 58.4  | 10.6    | 23.5   | 31.1   | 43.7   | 220  | 14.29  | 35.9   | 52.9   | 62.9   | 113.3 | 10.6   | 22.6   | 30.8   | 43.9   | 98   | 0.026 | 42      | 50.5    |
| Yb  | 118    | 184    | 226    | 327    | 860   | 124     | 273    | 356    | 482    | 2179 | 171    | 444    | 612    | 747    | 1290  | 124    | 235    | 321    | 529    | 930  | 0.21  | 395     | 500     |
| Lu  | 24.5   | 38.5   | 52.7   | 69.5   | 199   | 23.2    | 48.1   | 62.0   | 81.0   | 342  | 28.7   | 72.2   | 98.1   | 113.2  | 180   | 23.2   | 43.5   | 65.6   | 99.8   | 189  | 0.032 | 79      | 86      |

|                                    | Low Ta |        |        |        |        | High Ta |        |        |        |       | Dys    |        |        |        |       | BiGd  |        |        |        |       | LOD   | And/Dac | Granite |
|------------------------------------|--------|--------|--------|--------|--------|---------|--------|--------|--------|-------|--------|--------|--------|--------|-------|-------|--------|--------|--------|-------|-------|---------|---------|
| ppm                                | min    | 1st Q. | median | 3rd Q. | max    | min     | 1st Q. | median | 3rd Q. | max   | min    | 1st Q. | median | 3rd Q. | max   | min   | 1st Q. | median | 3rd Q. | max   | ppm   | median  | median  |
| Hf                                 | 6126   | 7187   | 7803   | 8222   | 9492   | 6134    | 7858   | 8370   | 9081   | 11926 | 6324   | 7228   | 7976   | 8608   | 9441  | 6855  | 8148   | 8861   | 9488   | 11792 | 2.0   | 9665    | 10480   |
| Ta                                 | 0.021  | 0.075  | 0.100  | 0.142  | 0.191  | 0.202   | 0.357  | 0.441  | 0.592  | 8.69  | 0.3176 | 0.4389 | 0.612  | 0.852  | 2.232 | 0.097 | 0.293  | 0.432  | 0.878  | 8.69  | 0.019 | 1       | 1.3     |
| Pb                                 | 0.376  | 0.612  | 0.921  | 1.45   | 9.12   | 0.276   | 0.843  | 1.28   | 1.94   | 40.5  | 0.384  | 1.509  | 1.94   | 2.88   | 40.53 | 0.276 | 0.895  | 1.28   | 4.12   | 19.9  | 0.062 | 26.9    | 24.4    |
| Th                                 | 9.32   | 16.6   | 24.7   | 39.1   | 275    | 7.36    | 24.0   | 35.4   | 54.2   | 1047  | 11.04  | 40.0   | 52.7   | 77.0   | 1047  | 7.36  | 24.9   | 33.4   | 126.3  | 505   | 0.061 | 135     | 186     |
| U                                  | 31.8   | 51.4   | 67.1   | 90.1   | 278    | 30.9    | 57.2   | 75.3   | 103    | 780   | 30.9   | 81.2   | 110    | 125.4  | 732   | 36.2  | 59.0   | 124    | 283    | 772   | 0.093 | 220     | 283     |
| Eu/Eu*                             | 0.46   | 0.66   | 0.81   | 0.94   | 2.6    | 0.020   | 0.37   | 0.42   | 0.47   | 0.77  | 0.30   | 0.34   | 0.38   | 0.48   | 0.59  | 0.020 | 0.32   | 0.53   | 0.67   | 0.77  |       | 0.42    | 0.17    |
| ΣREE                               | 201    | 306    | 369    | 568    | 1393   | 228     | 526    | 680    | 954    | 4779  | 313    | 862    | 1176   | 1385   | 2486  | 228   | 511    | 671    | 999    | 2170  |       | 885     | 1162    |
| Yb/Gd                              | 26.1   | 81.5   | 110    | 131    | 191    | 9.55    | 29.1   | 38     | 44.7   | 594   | 22.6   | 27.7   | 38     | 40     | 57    | 9.55  | 26.9   | 36     | 48.6   | 199   |       | 21.5    | 16.4    |
| U/Pb                               | 27.6   | 58.9   | 72     | 85.8   | 120    | 6.34    | 47.4   | 61     | 70.8   | 564   | 18.1   | 47.3   | 50     | 64.7   | 93    | 24.66 | 41.0   | 67     | 110.5  | 564   |       | 10.1    | 11.8    |
| Th/Pb                              | 15.7   | 26.1   | 27     | 29.0   | 33.4   | 4.26    | 26.7   | 28     | 29.6   | 161   | 21.8   | 25.8   | 27     | 27.9   | 29.6  | 21.04 | 25.4   | 28     | 29.4   | 35    |       | 13.6    | 10.5    |
| Ta/Nb                              | 0.077  | 0.14   | 0.17   | 0.20   | 0.34   | 0.094   | 0.30   | 0.34   | 0.39   | 0.54  | 0.12   | 0.23   | 0.28   | 0.35   | 0.48  | 0.094 | 0.19   | 0.29   | 0.35   | 0.44  |       | 0.34    | 0.29    |
| T (°C)                             | 633    | 685    | 704    | 720    | 777    | 554     | 731    | 757    | 786    | 882   | 554    | 750    | 767    | 784    | 811   | 597   | 659    | 730    | 770    | 882   |       | 790     | 766     |
| Ce <sup>4+</sup> /Ce <sup>3+</sup> | 61.6   | 663    | 1102   | 1746   | 8330   | 12.7    | 96.4   | 218    | 445    | 7578  | 26.3   | 50     | 189    | 306    | 583   | 12.7  | 138.7  | 331    | 722    | 7578  |       | N/A     | N/A     |
| Ce/Ce*                             | 2.18   | 102    | 215    | 459    | 907656 | 7.60    | 87.0   | 194    | 418    | 8325  | 24.83  | 62     | 141    | 224    | 1555  | 15.14 | 78.2   | 225    | 505    | 2716  |       | 55      | 28      |

Table 5.4. (contd.)

|                                    | Mottled zircon |                    |        |                    |       | LOD   | And/Dac | Granite |
|------------------------------------|----------------|--------------------|--------|--------------------|-------|-------|---------|---------|
| ppm                                | min            | 1 <sup>st</sup> Q. | median | 3 <sup>rd</sup> Q. | max   | ppm   | median  | median  |
| Sc                                 | 95.9           | 99                 | 124    | 129                | 133   | 0.2   | 72      | 73.4    |
| Ti                                 | 2.18           | 6.36               | 8.46   | 10.73              | 12.22 | 1.4   | 11      | 8.62    |
| V                                  | 0.02           | 0.714              | 1.1    | 1.421              | 1.779 | 0.061 | 5.5     | 2.4     |
| Rb                                 | 0.009          | 0.36               | 0.47   | 0.57               | 0.81  | 0.038 | 13      | 1.01    |
| Sr                                 | 0.3            | 0.4753             | 3.11   | 15.603             | 55.69 | 0.024 | 2.7     | 0.84    |
| Y                                  | 143            | 1154               | 2620   | 3797               | 6188  | 0.15  | 954     | 1539    |
| Nb                                 | 0.89           | 8.699              | 18.6   | 19.026             | 27.8  | 0.03  | 3.32    | 8.52    |
| La                                 | 0.01           | 0.02               | 0.116  | 0.63               | 1.645 | 0.02  | 0.04    | 0.181   |
| Ce                                 | 3.91           | 41.93              | 97.7   | 120.01             | 157.7 | 0.022 | 19.2    | 25.4    |
| Pr                                 | 0.038          | 0.1762             | 0.47   | 2.063              | 4.75  | 0.016 | 0.1     | 0.32    |
| Nd                                 | 0.36           | 3.243              | 5.69   | 15.973             | 38.07 | 0.19  | 1.6     | 3.6     |
| Sm                                 | 0.59           | 8.403              | 12.9   | 15.941             | 30.4  | 0.11  | 3.2     | 6.2     |
| Eu                                 | 0.031          | 1.001              | 1.68   | 2.265              | 4.51  | 0.032 | 0.9     | 0.82    |
| Gd                                 | 1.371          | 29.49              | 57.7   | 74.82              | 141.7 | 0.12  | 20.1    | 32.2    |
| Tb                                 | 0.597          | 8.336              | 19.4   | 24.5               | 47.38 | 0.019 | 7.29    | 12      |
| Dy                                 | 7.83           | 92.6               | 244    | 304.2              | 567.5 | 0.093 | 90.7    | 149     |
| Ho                                 | 3.79           | 37.73              | 91.4   | 123.7              | 207   | 0.027 | 37.9    | 52.5    |
| Er                                 | 28.3           | 214.1              | 429    | 607.1              | 958   | 0.12  | 178     | 408     |
| Tm                                 | 9.06           | 56.5               | 98.6   | 135.4              | 208.5 | 0.026 | 42      | 50.5    |
| Yb                                 | 128            | 747                | 1052   | 1296               | 1999  | 0.21  | 395     | 500     |
| Lu                                 | 37.6           | 129.1              | 167    | 222.5              | 324   | 0.032 | 79      | 86      |
| Hf                                 | 7156           | 8767               | 9207   | 10351              | 12382 | 2     | 9665    | 10480   |
| Ta                                 | 0.4449         | 3.1157             | 3.82   | 4.437              | 6.014 | 0.019 | 1       | 1.3     |
| Pb                                 | 2.416          | 11.194             | 17.7   | 33.96              | 40.42 | 0.062 | 26.9    | 24.4    |
| Th                                 | 60.41          | 321                | 488    | 1007               | 1077  | 0.061 | 135     | 186     |
| U                                  | 586.8          | 837.7              | 1047   | 1376.1             | 2927  | 0.093 | 220     | 283     |
| Eu/Eu*                             | 0.1            | 0.17               | 0.2    | 0.22               | 0.35  |       | 0.42    | 0.17    |
| ΣREE                               | 222            | 1473               | 2285   | 2910               | 4672  |       | 885     | 1162    |
| Yb/Gd                              | 16.5           | 20.5               | 22.1   | 26                 | 146   |       | 21.5    | 16.4    |
| U/Pb                               | 27             | 32                 | 40.1   | 163.5              | 243   |       | 10.1    | 11.8    |
| Th/Pb                              | 23.6           | 26.7               | 27     | 27.6               | 29.7  |       | 13.6    | 10.5    |
| Ta/Nb                              | 0.2            | 0.2                | 0.25   | 0.36               | 0.5   |       | 0.34    | 0.29    |
| T (°C)                             | 647            | 737                | 764    | 787                | 801   |       | 790     | 766     |
| Ce <sup>4+</sup> /Ce <sup>3+</sup> | 5.3            | 54                 | 162    | 327                | 1663  |       | N/A     | N/A     |
| Ce/Ce*                             | 2.12           | 6                  | 32     | 275                | 428   |       | 55      | 28      |

Table 5.4. (contd.)

#### 5.4.3.1 High field strength elements

Nb and Ta increase proportionally with one another, and values for both range over 2 orders of magnitude (Fig. 5.8 a). Analyses of low-Ta zircons, as well as having low Nb (median = 0.58 ppm), also have lower Ta/Nb (median = 0.17) than the high-Ta group (median = 0.34 ppm Ta/Nb). The latter ratios are typical of zircons from felsic rocks (median = 0.34). Mottled zircons from sample OT-103 have higher Nb (median = 18.6) and Ta (median = 3.8) than typical zircons, and slightly lower Ta/Nb (median = 0.25). Both Nb and Ta increase as a function of  $\Sigma\text{REE}$  (Fig. 5.8 b), due to the coupled substitution described above (Eq. 5.1).

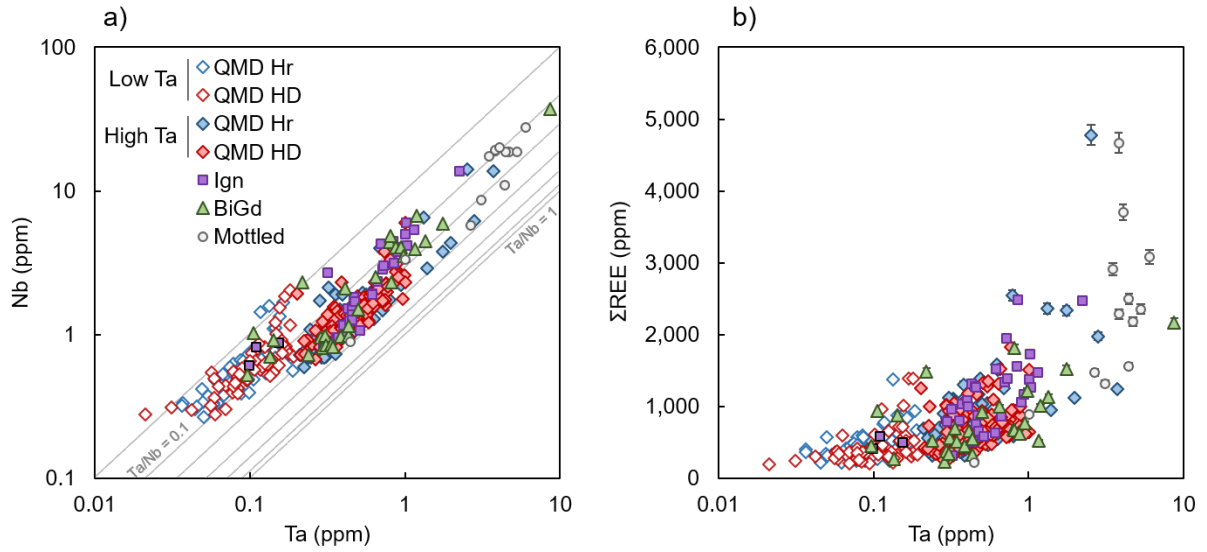


Figure 5.8. Variation of Ta in Oyu Tolgoi zircons with respect to (a) Nb, and (b)  $\Sigma\text{REE}$ . Low-Ta zircons have a lower Ta/Nb ratio than High Ta, BiGd, Dvs and ‘mottled’ zircon analyses. Errors are smaller than the symbol size of all analyses in (a), and most analyses in (b). All analyses conducted by LA-ICP-MS.

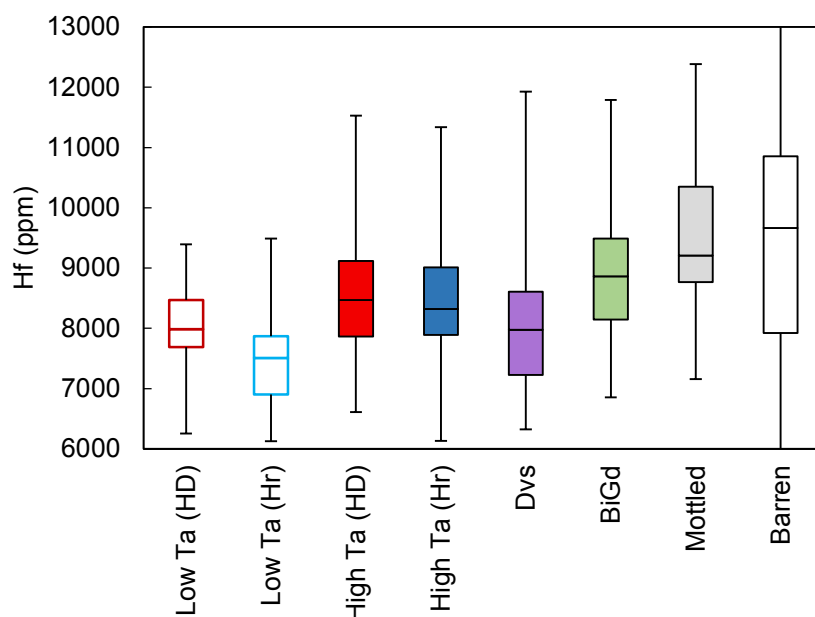


Figure 5.9. Box and whisker diagram showing the median, upper and lower quartiles, and range of Hf contents in zircons from Oyu Tolgoi. HD = Hugo Dummett, Hr = Heruga.

Hafnium values for all zircons range between 6126 and 12382 ppm. Low- and high-Ta groups have similar Hf content, although the high-Ta group tend to have slightly higher median Hf than low-Ta zircons (Fig. 5.9). Both groups have lower median Hf values than typical zircons from intermediate rocks (9665 ppm). Hf contents of the mottled zircons are more similar to zircons from intermediate rocks (median = 9207 ppm).

#### 5.4.3.2 Rare earth elements (REE) and yttrium

Total REE ( $\Sigma$ REE) for all Oyu Tolgoi zircons are at the lower end of the range observed in crustal zircons (250 to 5000 ppm; Hoskin and Schaltegger, 2003), with most zircon analyses (>95%) containing less than 1500 ppm REE. Chondrite-normalised REE patterns are broadly typical of crustal zircon, with strong HREE enrichment and LREE depletion, with 5 to 6 orders



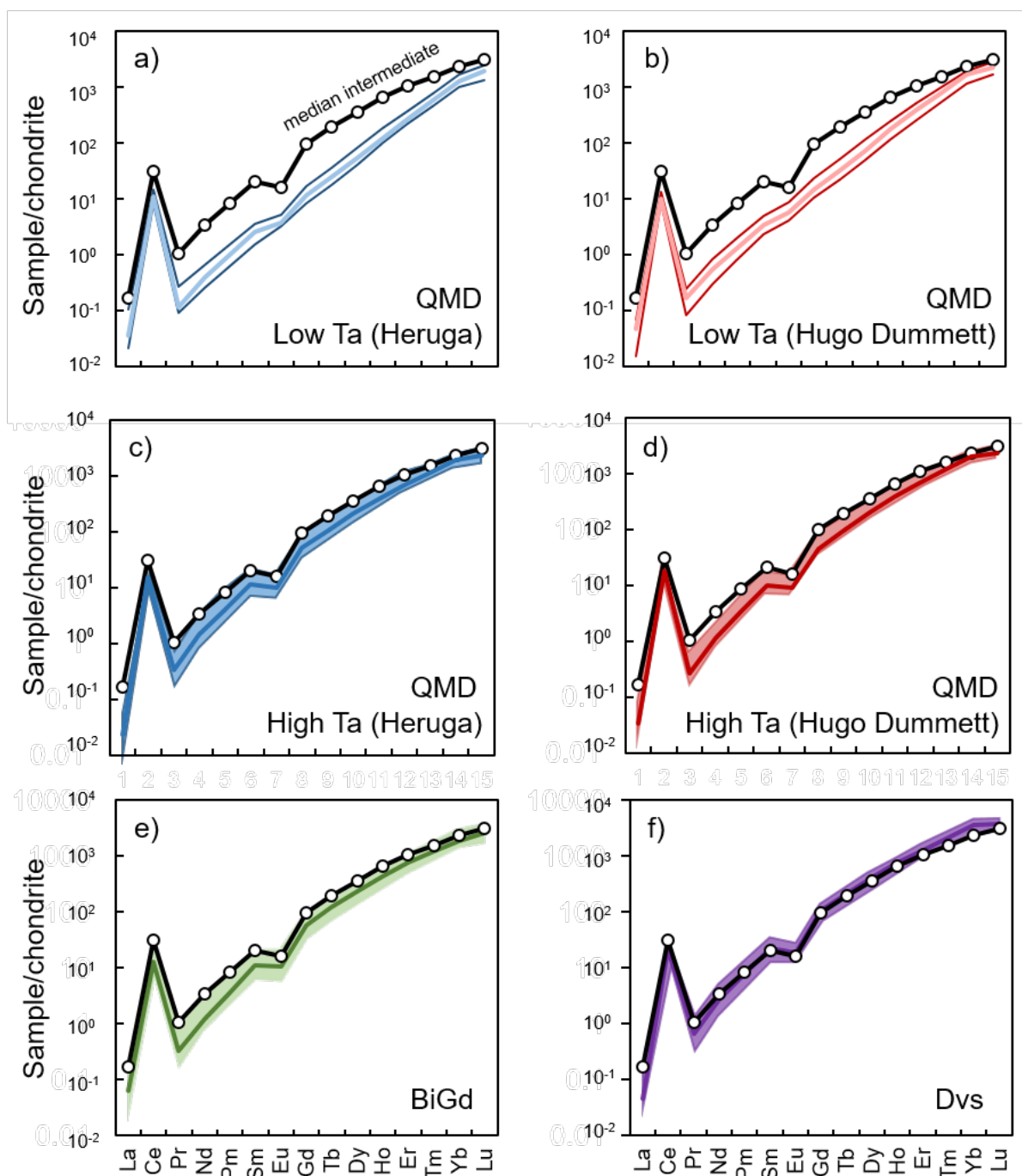


Figure 5.10. Median chondrite-normalised REE patterns of Oyu Tolgoi zircons: a) low Ta group (Heruga), b) low Ta group (Hugo Dummett), c) high Ta group (Heruga), d) high Ta group (Hugo Dummett), e) BiGd, f) Dvs. Black line with open circles labelled 'median intermediate' is the median value of zircons from intermediate rocks. Shaded area on each diagram is the interquartile range. Chondrite values taken from Sun and McDonough (1989).

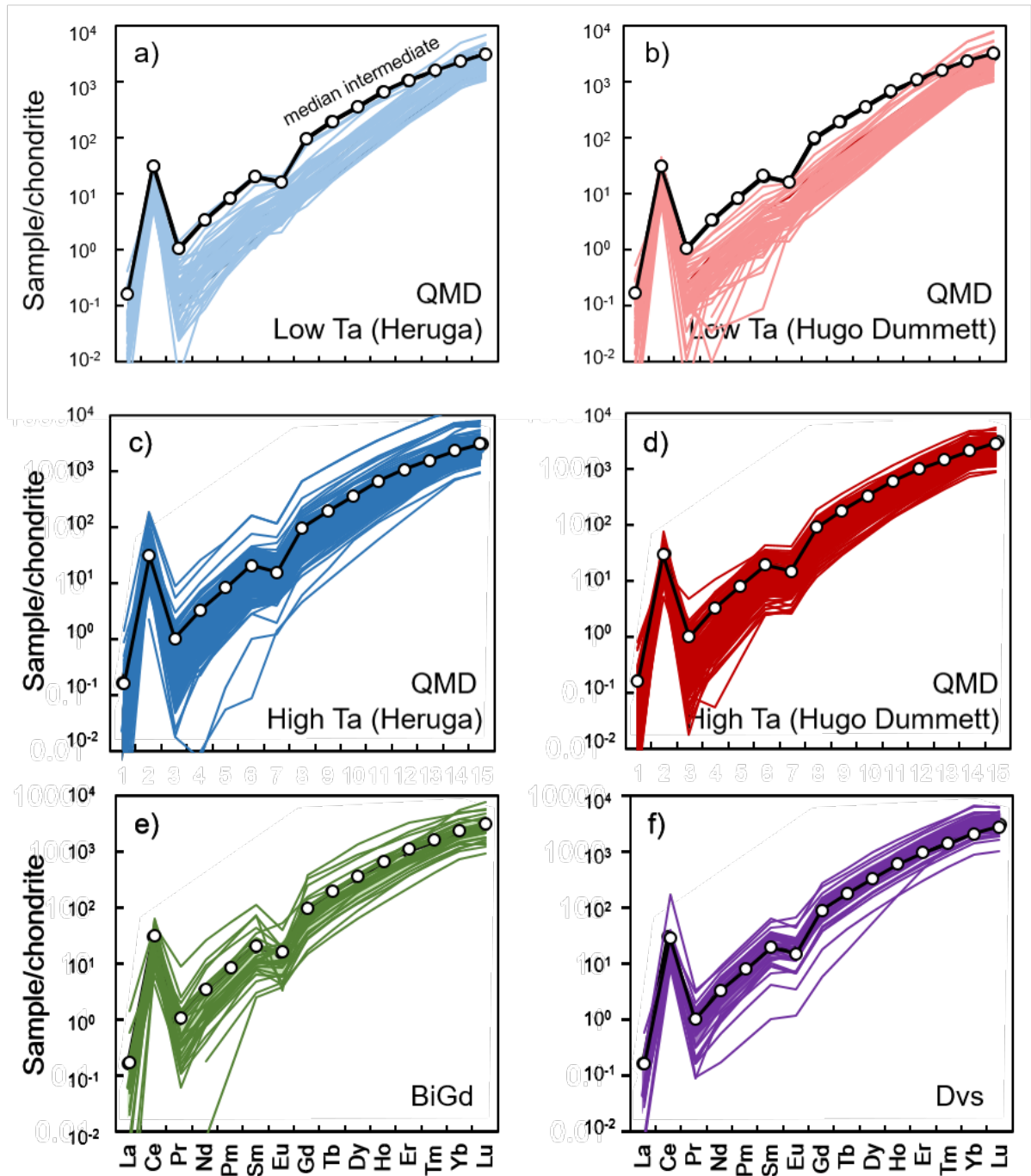


Figure 5.11. Chondrite-normalised REE patterns of Oyu Tolgoi zircons: a) low Ta group (Heruga), b) low Ta group (Hugo Dummett), c) high Ta group (Heruga), d) high Ta group (Hugo Dummett), e) BiGd, f) Dvs. Black line with open circles labelled 'median intermediate' is the median value of zircons from intermediate rocks. Chondrite values taken from Sun and McDonough (1989).

of magnitude difference between  $\text{La}_N$  and  $\text{Lu}_N$ . Zircons from the BiGd, Dvs, and QMD high-Ta group zircons from both Hugo Dummett and Heruga have chondrite-normalised REE patterns that are a close match to that of median zircon from intermediate rocks (Fig. 5.10 c-f). By contrast, the low Ta zircons are strongly depleted in MREE compared to zircons from intermediate rocks, although La, Ce, Yb, and Lu values are more typical (Table 5.4, Fig. 5.10 a,b). Y values are also low for low Ta zircons, (median = 276 ppm) compared to high-Ta grains (median = 725 ppm) or typical zircons (median = 954 ppm). Within both high and low Ta groups, there is little difference between zircons from the QMD from Heruga and Hugo Dummett.

The mottled zircons are enriched in LREE, and depleted in HREE with respect to other zircons from the same rock (Fig. 5.12).

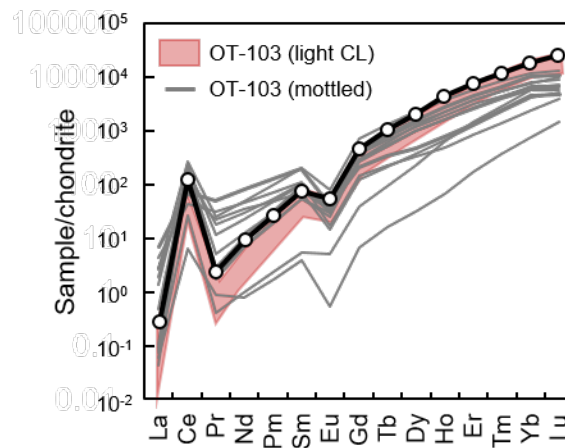


Figure 5.12. Chondrite-normalised REE patterns of dull-CL 'mottled' zircons from QMD sample OT-103 (grey lines). Zircons with light-CL characteristics of the high-Ta group from the same sample are plotted for comparison (red shaded field). Black line with white circles is the median value of zircons from intermediate rocks. In general, mottled zircons are enriched in LREE and depleted in HREE with respect to both the median intermediate zircons, and the high-Ta zircons from sample OT-103. Chondrite values taken from Sun and McDonough (1989).

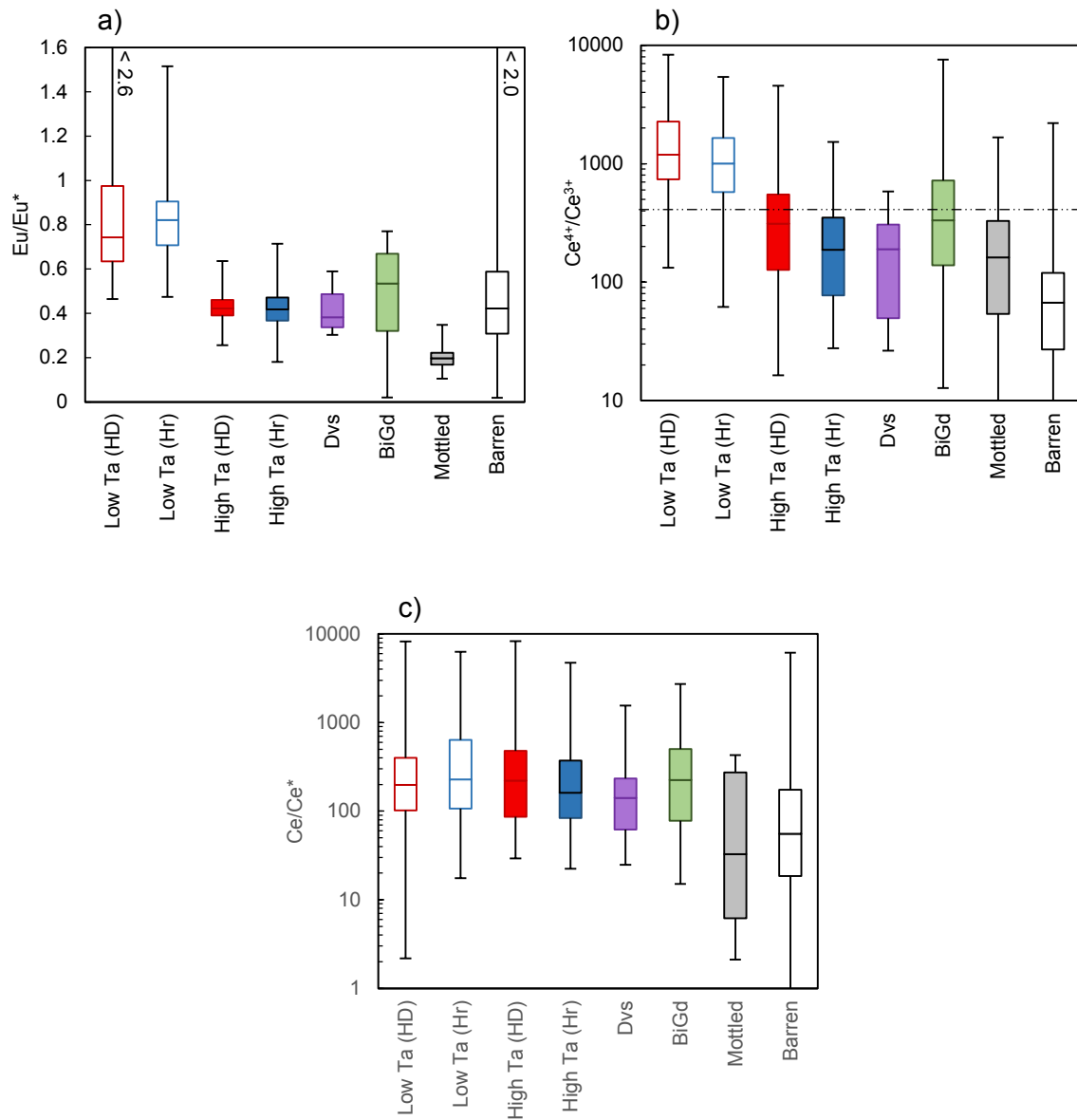


Figure 5.13. Box and whisker diagrams showing the median, interquartile range, and range of a)  $Eu/Eu^*$  values, b)  $Ce^{4+}/Ce^{3+}$ , and c)  $Ce/Ce^*$  for Oyu Tolgoi zircons. Data for zircons from "barren" intrusions in b) are of 131 analyses from Ballard et al. (2002). These values were used because  $Ce^{4+}/Ce^{3+}$  is difficult to calculate for other zircons from barren rocks from the literature, because of the lack of whole rock data, which is necessary in the calculation of  $Ce^{4+}/Ce^{3+}$ . The horizontal dashed line in b) is the suggested upper limit of zircons from "barren" rocks ( $Ce^{4+}/Ce^{3+} = 300$ ). All Oyu Tolgoi data collected by LA-ICP-MS.

#### 5.4.3.3 *Eu and Ce anomalies*

The high-Ta group has median  $\text{Eu}/\text{Eu}^*$  values that are closely similar to zircons from intermediate rocks (median = 0.42). By contrast, the low-Ta group has substantially higher  $\text{Eu}/\text{Eu}^*$  values than zircons from intermediate rocks, with median values  $>0.7$ , and several values in excess of unity (Fig. 5.13 a). There is no substantive difference in the Eu anomaly of zircons from Heruga and Hugo Dummett in either low or high Ta groups. Dvs zircons have similar Eu anomalies to typical zircons from intermediate rocks, with  $\text{Eu}/\text{Eu}^*$  values consistently  $<0.6$ . BiGd zircons have moderately high  $\text{Eu}/\text{Eu}^*$  (median = 0.53), although still largely within the interquartile range of zircons from intermediate rocks (Fig. 5.13 a). The mottled zircons have the largest negative Eu anomalies (i.e. smallest  $\text{Eu}/\text{Eu}^*$  values) of all Oyu Tolgoi zircons, with  $\text{Eu}/\text{Eu}^*$  values (median = 0.2) less than zircons from intermediate rocks.

$\text{Ce}^{4+}/\text{Ce}^{3+}$  for the low-Ta group are substantially higher than values for the high-Ta group (Fig. 5.13 b), which mostly have values  $<300$  (the upper limit of  $\text{Ce}^{4+}/\text{Ce}^{3+}$  values in zircons from barren rocks according to Ballard et al., 2002). As with the Eu anomaly, BiGd zircons are moderately high, compared to the Dvs, mottled zircons, and zircons from “barren” rocks (data from Ballard et al., 2002; see caption in Figure 5.13 for details).

There is little difference in the  $\text{Ce}/\text{Ce}^*$  values of all groups of zircons (Fig. 5.13 c), with the exception of the mottled zircons, which have low  $\text{Ce}/\text{Ce}^*$  values (median = 32). All other groups have mildly higher median  $\text{Ce}/\text{Ce}^*$  (median = 55) compared to zircons from intermediate rocks, but lie within the range of values of these zircons.

#### 5.4.3.4 *Uranium, Lead, Thorium*

For a given group of zircons, the relative abundance of these elements is as follows:  $\text{U} > \text{Th} > \text{Pb}$ . There is little difference between the U, Th, and Pb content of zircons between low and high Ta groups, or between Heruga and Hugo Dummett (Fig. 5.14). Dvs and BiGd zircons

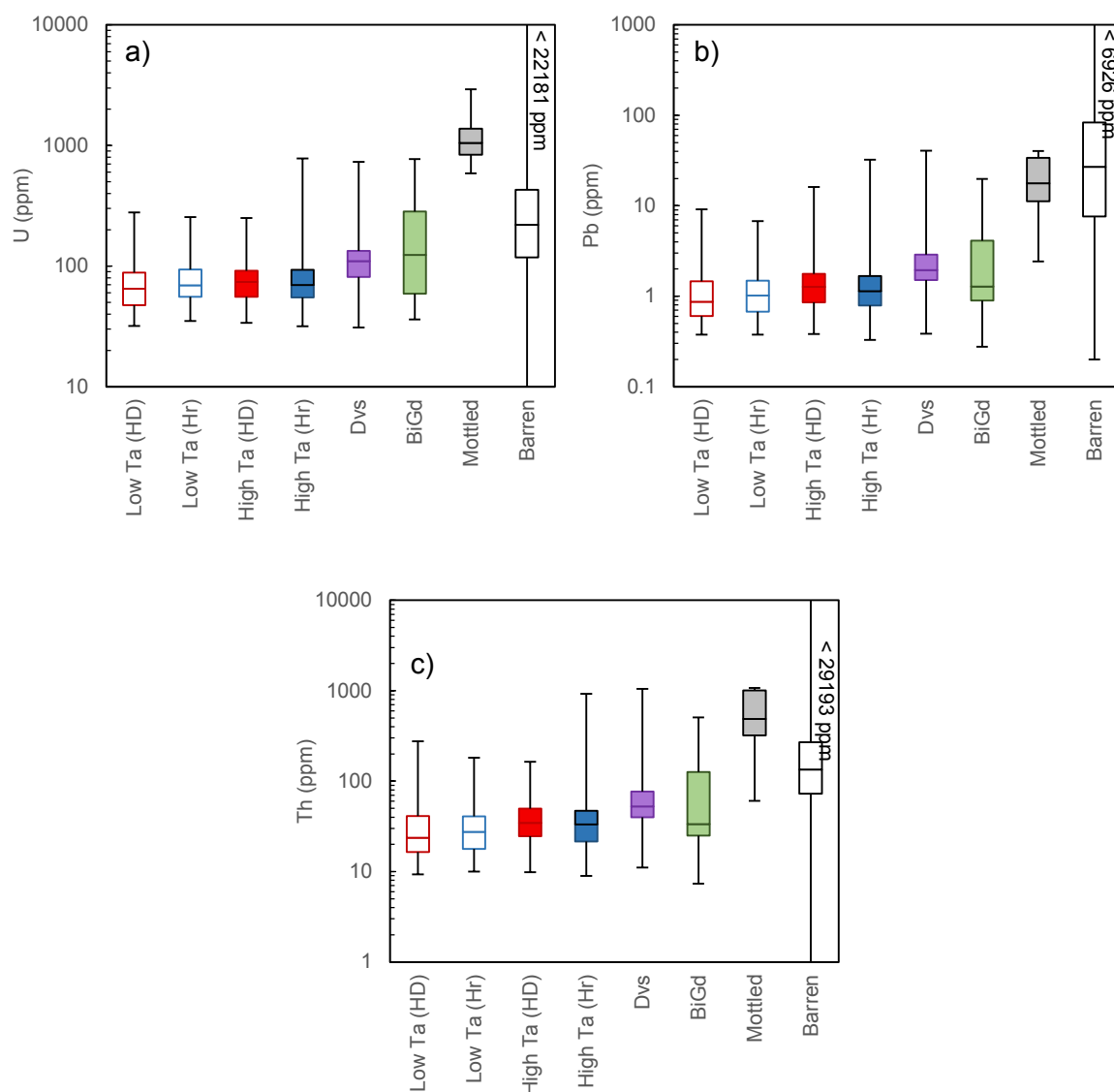


Figure 5.14. Box and whisker diagrams showing the median, interquartile range, and range of a) U, b) Pb, and c) Th concentrations in Oyu Tolgoi zircons. All data collected by LA-ICP-MS.

also have a similar range of U, Th, and Pb concentrations to the low and high Ta groups. All of these groups are depleted in these elements with respect to zircons from intermediate rocks. This is especially true of Pb, which is typically enriched by an order of magnitude in zircons from intermediate rocks (median = 27 ppm) compared to most groups of zircons from Oyu Tolgoi (<2 ppm; Fig. 5.14 b).

Mottled zircons are enriched in U, Th, and Pb by an order of magnitude with respect to other groups of zircon from Oyu Tolgoi. Median U and Th values are higher than zircons from intermediate rocks, but median Pb values are similar (Fig. 5.14 b).

#### 5.4.3.5 Crystallisation temperature (*Ti-in-zircon*)

Temperatures of crystallisation were calculated from Ti values using the calibration of Ferry and Watson (2007) (see section 5.2.3 for details of assumptions and initial parameters). Low Ta zircons have significantly lower median temperature estimates ( $\sim 700^{\circ}\text{C}$ ) than other zircon groups, or than zircons from intermediate rocks (median =  $790^{\circ}\text{C}$ ; Fig. 5.15). Median temperature estimates for the high Ta, Dvs, and mottled zircons are all similar, and are moderately lower than the estimates for zircons from intermediate rocks. BiGd zircons show the widest interquartile range of temperature estimates, with some values as low as the low Ta group. There is no difference in temperature estimate between zircons from low and high Ta groups.

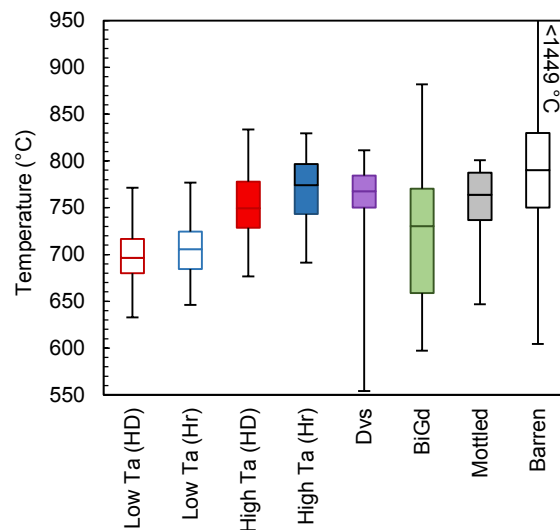


Figure 5.15. Box and whisker diagrams showing the median, interquartile range, and range of *Ti-in-zircon* temperature estimates for Oyu Tolgoi zircons. The thermometer of Ferry and Watson (2007) was used for temperature estimates, and Ti values were determined by LA-ICP-MS.

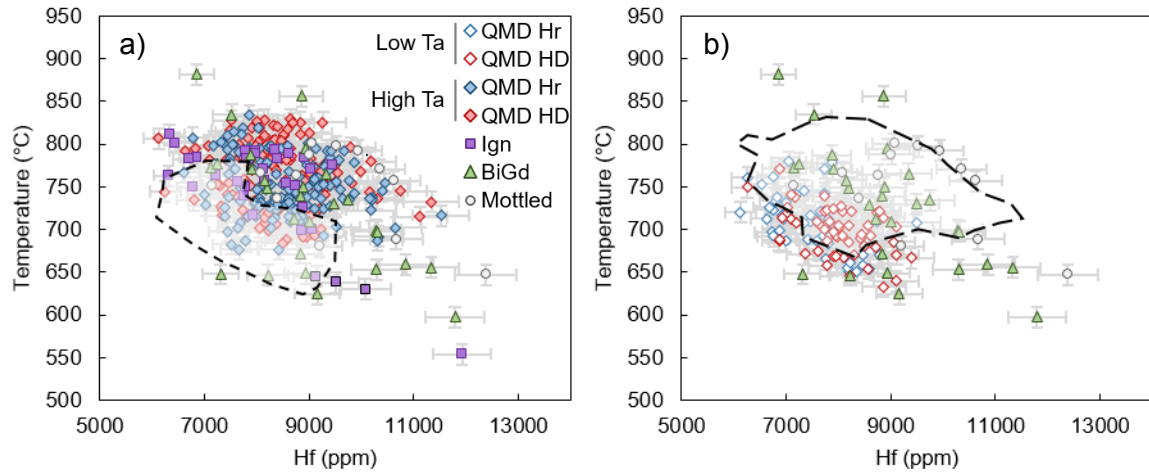


Figure 5.16. Variation of temperature estimates with Hf content of Oyu Tolgoi zircons. Low Ta zircons have been removed in a), and high Ta zircons have been removed in b), for clarity. In both cases, the black dashed outline shape represents the field of the removed data points.

Hf concentrations generally show a weak negative correlation with temperature (Fig. 5.16). Low Ta zircons have a lower T for a given Hf concentration, when compared to high Ta, Dvs and mottled zircons.

#### 5.4.3.6 Variation of zircon chemistry with U-Pb ages and degree of fractionation

It has not been possible to distinguish clear trends in the evolution of zircon trace element chemistry on timescales typical of magmatic-hydrothermal systems (1-2 m.y.; e.g. von Quadt et al., 2011), or on slightly larger timescales related to igneous processes (e.g. 5 - 10 m.y.; e.g. Annen et al., 2006) due to the large overlapping errors of individual U-Pb analyses ( $2\sigma = \sim 10$  Ma). High-Ta group zircons are associated with the entire range of ages of Oyu Tolgoi zircons (426 to 353 Ma), but the small number of low-Ta group zircons exclusively occur between 360 and 366 Ma, and are within error of one another (Fig. 5.17 a). Consequently, there is a specific group of late Devonian zircons that is characterised by high Ce/Ce\* (>250),



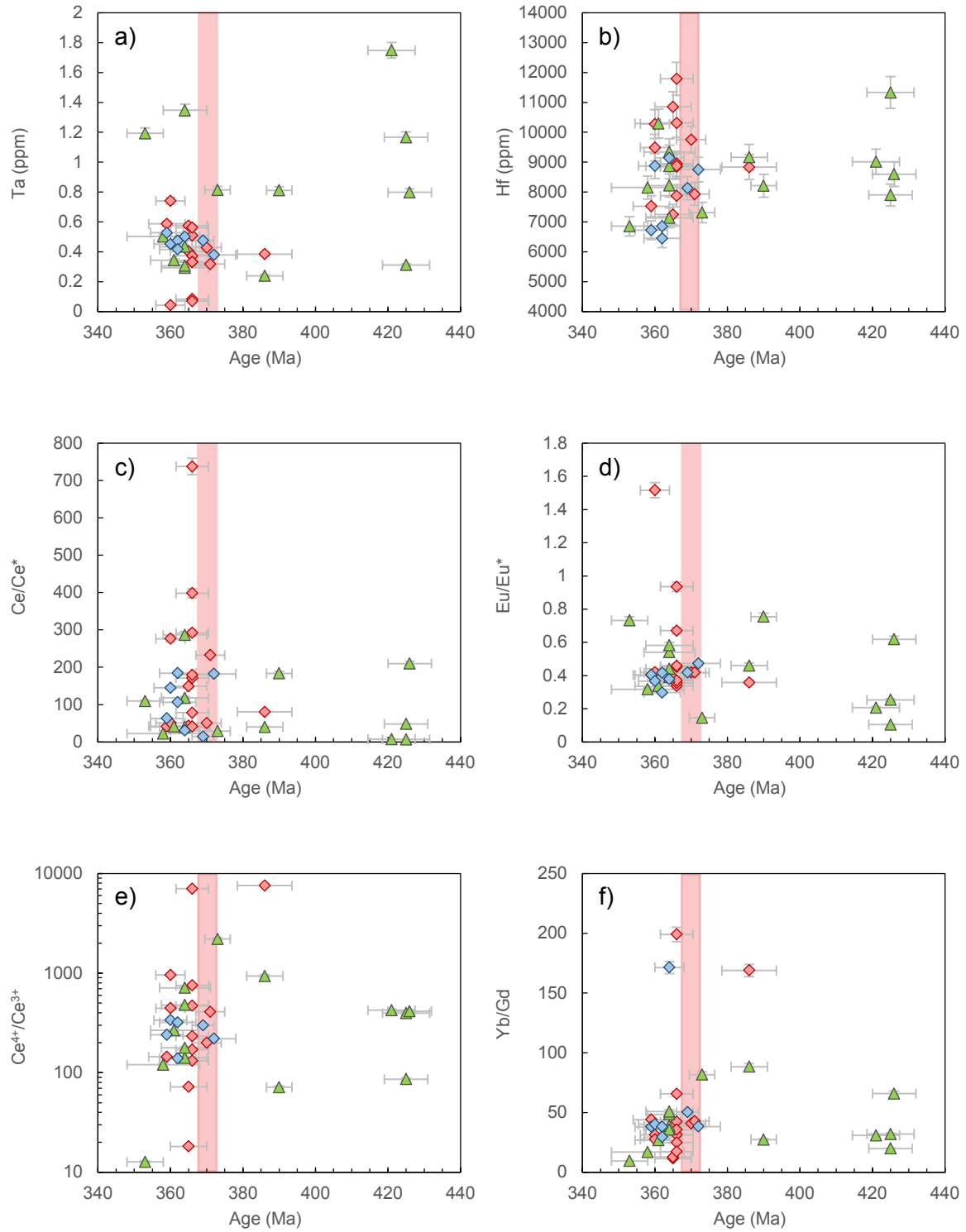


Figure 5.17. Variation in certain trace element variables with calculated  $^{206}\text{Pb}/^{238}\text{U}$  zircon age. a) Ta, b) Hf, c) Ce/Ce\*, d) Eu/Eu\*, e)  $\text{Ce}^{4+}/\text{Ce}^{3+}$ , f) Yb/Gd Pink shaded area represents the period of mineralisation, as determined by Re-Os molybdenite dating (Stein, unpublished dates). All data collected by LA-ICP-MS. Error bars for  $^{206}\text{Pb}/^{238}\text{U}$  ages are  $1\sigma$ .

high  $\text{Eu}/\text{Eu}^*$  ( $>0.5$ ) and MREE depletion ( $\text{Yb}/\text{Gd} >100$ ), which coincide with the period of mineralisation (Fig. 5.17 c,d,f), as determined by Re-Os molybdenite dating ( $370$  to  $373 \pm 1.2$ ). A peak in zircon Hf concentration also occurs at this time (Fig. 5.17 b).

With the exception of weak correlations with crystallisation temperature (Fig. 5.16), most trace elements and other variables (e.g.  $\text{Eu}/\text{Eu}^*$ ) show no clear correlations with Hf concentration (Fig. 5.18).

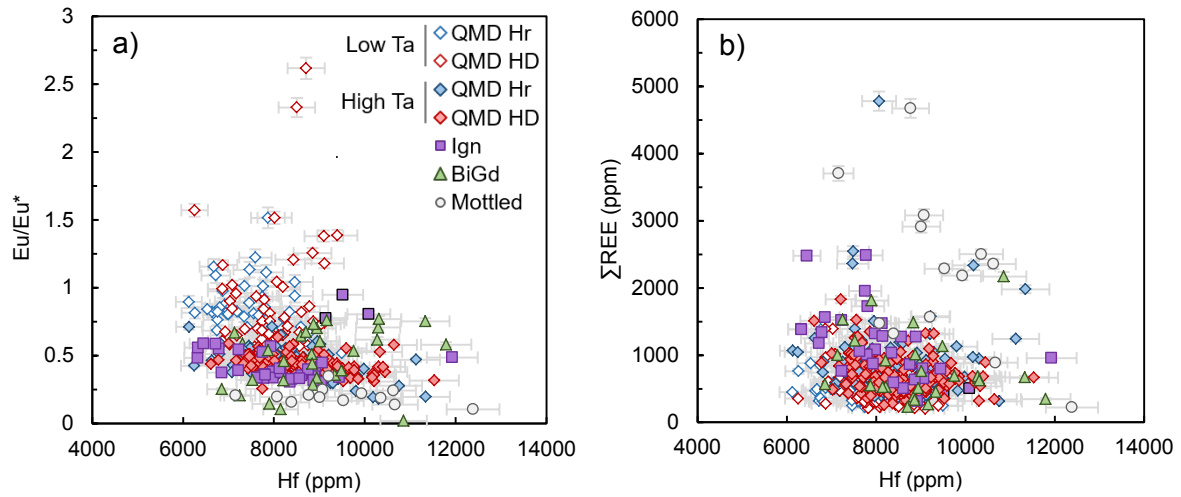


Figure 5.18. Variation of a)  $\text{Eu}/\text{Eu}^*$ , and b)  $\Sigma\text{REE}$  with Hf of Oyu Tolgoi zircons. There is no clear correlation with increasing Hf in terms of these (and most other) trace elements in Oyu Tolgoi zircons. Figure a) highlights the elevated  $\text{Eu}/\text{Eu}^*$  of the low Ta zircons with respect to all other groups.

## 5.5 Results - Resolution

### 5.5.1 Petrography of Resolution zircons

Zircons from Resolution range in size from  $<10\ \mu\text{m}$  grains in porphyry intrusions, commonly associated with biotite phenocrysts, to larger grains up to  $400\ \mu\text{m}$ . Zircons are typically euhedral grains. In the Resolution porphyry intrusions, some zircons are more elongate than zircons from the Schultze Granite. Grains from the Schultze Granite also tend to be larger ( $\sim 300\ \mu\text{m}$ ) when compared to grains from the Resolution intrusions ( $\sim 150\ \mu\text{m}$ ) but in general, the textures of zircons from both rocks are similar (Fig. 5.19).

A large number of zircons from all studied intrusions in the Resolution district contain distinct cores and rims, which are most clearly seen in CL images. Cores have different CL response to rims and, in some cases, the zoning patterns seen in the cores are truncated by overgrowth rims (Fig. 5.19) which suggests that these are inherited xenocrystic zircons. Inherited cores of zircons may also be observed in transmitted light because the cores commonly contain many more inclusions than the rims. Rims typically show very fine dark and light oscillatory growth zones in CL, and many crystals show a zone of brighter CL between the inherited core and the rim. In some cases, the boundary of the inherited core is outlined by a ring of small mineral inclusions. Apatite is the most common inclusion in zircon, with grains normally  $<20\ \mu\text{m}$  in size, and so too small to be analysed by laser ablation (Fig. 5.20 a). Other REE-rich phosphate minerals (monazite, xenotime) account for a very small number of inclusions. Aside from apatite, the most common included phases in both cores and rims are quartz and albite.

Small sulphide grains ( $<10\ \mu\text{m}$ ) are also found within zircons. Those from mineralised intrusions contain sulphides which appear to have grown in cracks within the grains (Fig. 5.20 c). These cracks may be seen in CL images and are defined by trails of small inclusions. Chalcopyrite and bornite are the predominant sulphides in these cracks. Zircons from the

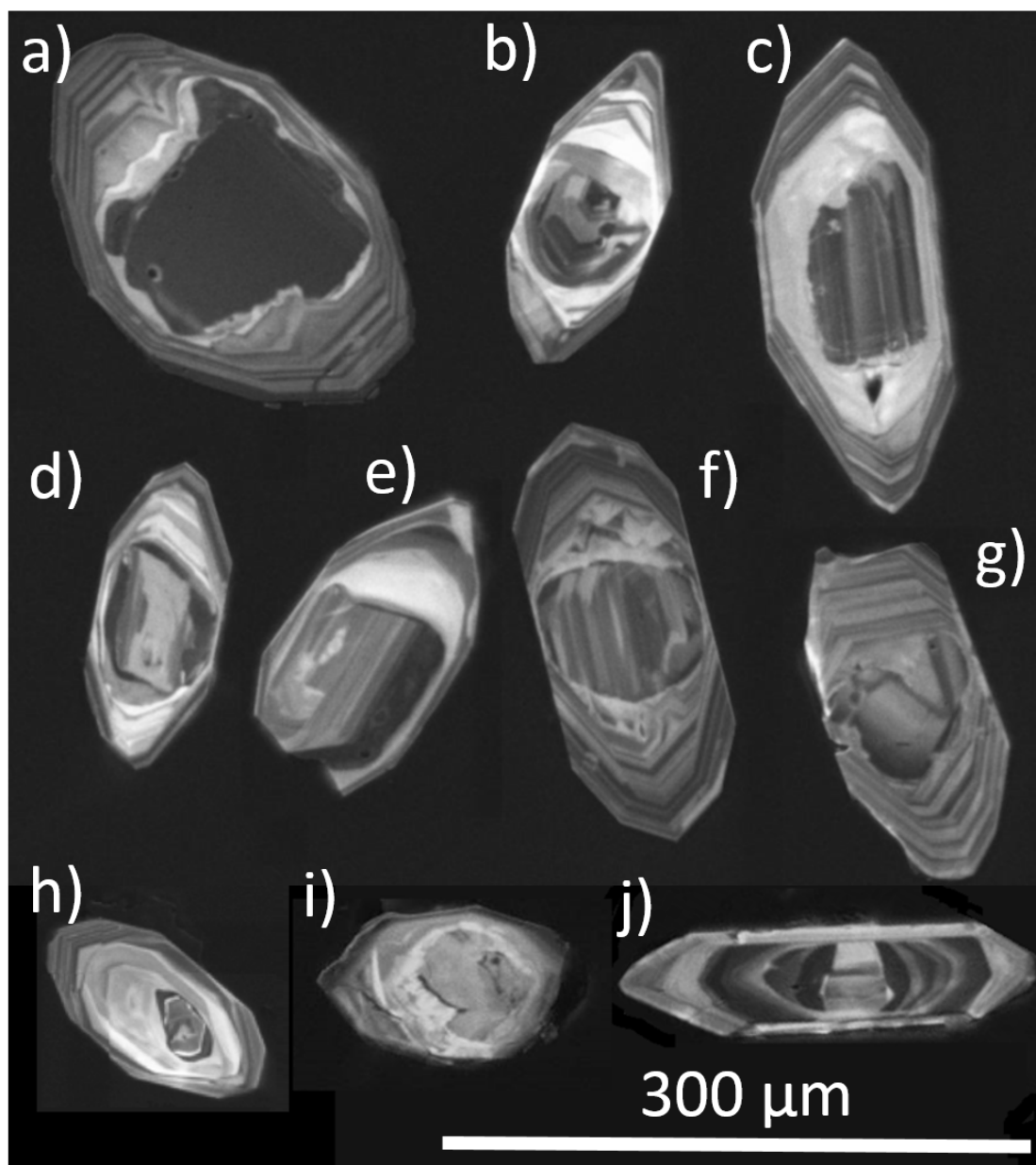
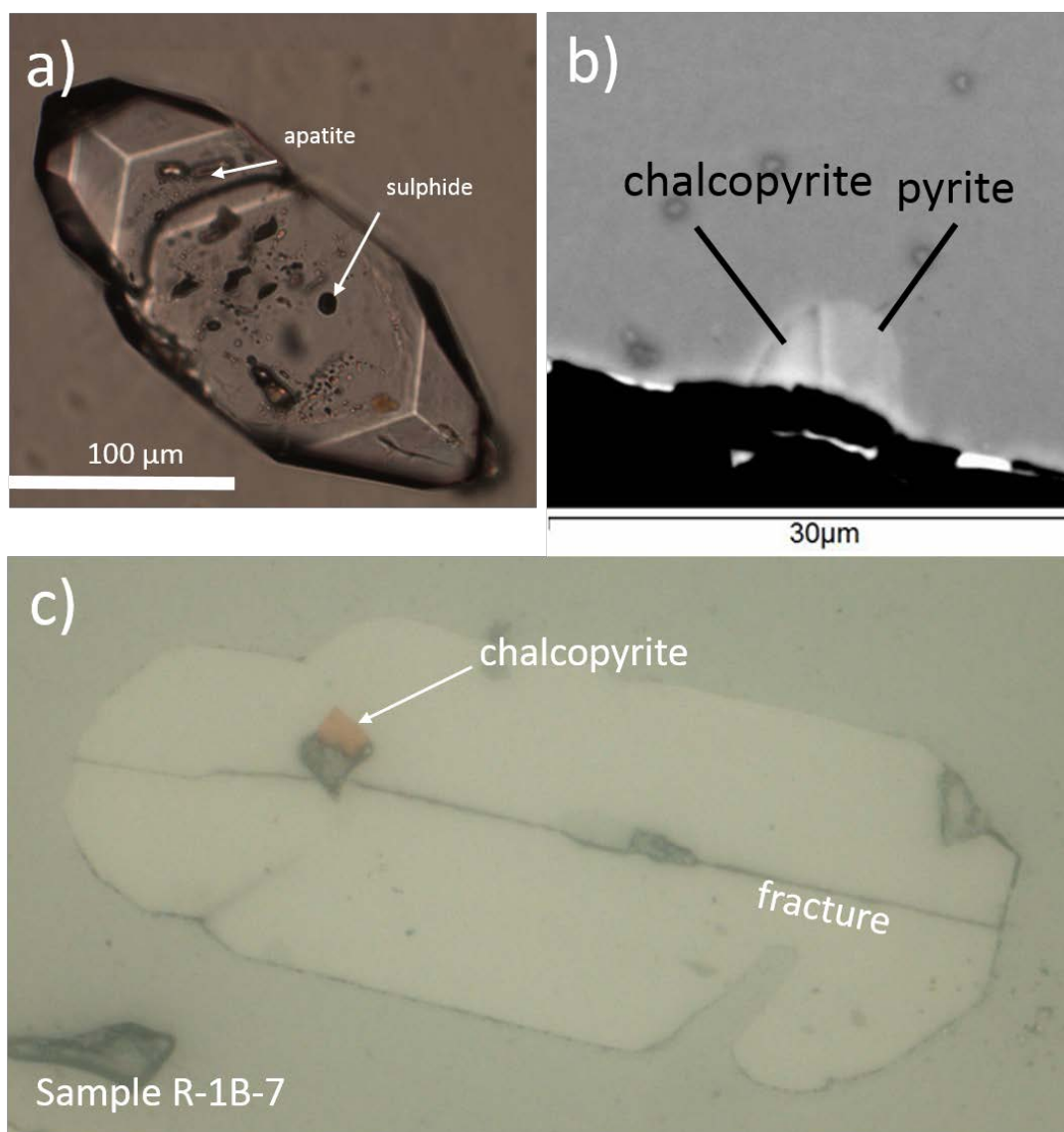


Figure 5.19. Representative SEM-CL images of zircons from the Resolution district. Most zircon grains contain inherited cores, which have different CL patterns to the rims (a-g). In some cases, inherited cores are more subtle (h-j). a-g from the Schultze Granite sample R-S-13, h-j from Resolution intrusions.



*Figure 5.20. Sulphide inclusions in zircon grains. (a) Transmitted light image of sulphide inclusions in zircon from the Schultze Granite. Outline of inherited core clearly visible. (b) Backscatter SEM image of co-existing chalcopyrite and pyrite in sulphide melt inclusion within zircon from the Apache Leap intrusion. Black outline at bottom of image is U-Pb date spot. (c) Reflected light image of chalcopyrite inclusion situated on a crack in zircon from mineralised Resolution intrusion.*

unmineralised Schultze granite and the felsic Apache Leap intrusions also contain sulphide inclusions. These occur as spherical to ovoid blebs containing two or more sulphide minerals,

typically chalcopyrite and pyrite, and are not found along cracks (Fig. 5.20 a,b). They are found exclusively in the cores of grains; no examples have been seen in zircon rims. Five verifiable examples have been observed including those in (Fig. 5.20).

### 5.5.2 Geochronology of Resolution district zircons

Several U-Pb zircon dates from Resolution district rocks were rejected from the calculation of concordia ages due to discordance. The discordance is partly due to the mixing of zones of different ages during analysis because of the presence of inherited cores. Concordant ages of inherited cores show that they are much older than the rims, with individual  $^{206}\text{Pb}/^{238}\text{U}$  ages between  $1.36 \pm 0.057$  and  $1.81 \pm 0.066$  Ga. The ages of the inherited cores have clusters of ages at  $\sim 1.65$  and  $\sim 1.40$  Ma (Fig. 5.21 b). Concordant Proterozoic U-Pb analyses are presented in Table 5.5.

Concordia ages were calculated from zircons from 2 out of the 4 rock samples that were dated. The concordia age of  $70.66 \pm 0.66$  Ma for sample R-2B-6 (Fig. 5.22 b) should be treated with caution due to the small number of analyses used for the calculation. Samples R-7D-3 (Resolution) and R-RF-G (Apache Leap intrusion) yielded 2 and 3 concordant ages respectively, which do not overlap within error ( $2\sigma$  error ellipses; Fig. 5.22 a, d). Grains from the Schultze Granite span a range from  $65 \pm 2$  to  $61 \pm 5$  Ma, yielding a concordia age of  $63.47 \pm 0.42$  Ma based on 4 concordant analyses (Fig. 5.22 c). This age lies within the range of ages previously determined for the Schultze Granite ( $66.9 \pm 2.9$  to  $61.3 \pm 1.4$  Ma; Stavast et al., 2006). Concordant Laramide U-Pb analyses are presented in Table 5.6.

| Sample name | Location        | Isotope ratios                   |         |                                  |         |                                   |         | Apparent age (Ma)                 |           |                                  |           |                                  |           |
|-------------|-----------------|----------------------------------|---------|----------------------------------|---------|-----------------------------------|---------|-----------------------------------|-----------|----------------------------------|-----------|----------------------------------|-----------|
|             |                 | $^{206}\text{Pb}/^{238}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{235}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{206}\text{Pb}$ | RSD (%) | $^{207}\text{Pb}/^{206}\text{Pb}$ | $2\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ | $2\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | $2\sigma$ |
| R-S-13      | Schultze porph. | 0.2352                           | 2.33    | 2.9235                           | 1.31    | 0.08977                           | 1.73    | 1420                              | 66        | 1388                             | 20        | 1362                             | 57        |
| R-S-13      | Schultze porph. | 0.2491                           | 1.91    | 3.1092                           | 1.88    | 0.09036                           | 1.68    | 1432                              | 64        | 1435                             | 29        | 1434                             | 49        |
| R-S-13      | Schultze porph. | 0.2513                           | 0.98    | 3.1364                           | 1.65    | 0.091                             | 0.85    | 1446                              | 32        | 1442                             | 25        | 1445                             | 25        |
| R-S-13      | Schultze porph. | 0.2604                           | 1.75    | 3.4064                           | 1.80    | 0.09436                           | 1.65    | 1514                              | 64        | 1506                             | 28        | 1492                             | 47        |
| R-S-13      | Schultze porph. | 0.271                            | 1.39    | 3.628                            | 1.48    | 0.09673                           | 0.85    | 1562                              | 32        | 1556                             | 24        | 1546                             | 38        |
| R-S-13      | Schultze porph. | 0.2982                           | 3.17    | 4.3324                           | 2.75    | 0.10075                           | 1.73    | 1636                              | 64        | 1700                             | 45        | 1682                             | 94        |
| R-S-13      | Schultze porph. | 0.3011                           | 1.23    | 4.3267                           | 0.93    | 0.10348                           | 1.18    | 1686                              | 44        | 1698                             | 15        | 1697                             | 37        |
| R-S-13      | Schultze porph. | 0.2945                           | 1.10    | 4.2267                           | 0.87    | 0.10359                           | 0.86    | 1688                              | 32        | 1679                             | 14        | 1664                             | 32        |
| R-S-13      | Schultze porph. | 0.3239                           | 2.08    | 5.0911                           | 1.97    | 0.11292                           | 1.78    | 1846                              | 64        | 1835                             | 34        | 1809                             | 66        |
| R-RF-G      | fels. ALi       | 0.2419                           | 1.55    | 3.0434                           | 1.15    | 0.09042                           | 1.54    | 1434                              | 58        | 1419                             | 18        | 1396                             | 39        |
| R-RF-G      | fels. ALi       | 0.2451                           | 1.21    | 3.0599                           | 1.47    | 0.0917                            | 1.13    | 1460                              | 42        | 1423                             | 22        | 1413                             | 31        |
| R-13F-2     | QLP             | 0.2548                           | 0.73    | 3.1621                           | 1.00    | 0.08964                           | 0.90    | 1416                              | 34        | 1448                             | 15        | 1463                             | 19        |
| R-13F-2     | QLP             | 0.2612                           | 1.78    | 3.3653                           | 2.09    | 0.09247                           | 1.14    | 1476                              | 44        | 1496                             | 33        | 1496                             | 48        |
| R-13F-2     | QLP             | 0.2868                           | 1.65    | 4.063                            | 1.08    | 0.10022                           | 0.96    | 1628                              | 34        | 1647                             | 18        | 1626                             | 47        |
| R-13F-2     | QLP             | 0.2924                           | 2.89    | 4.0459                           | 3.29    | 0.09718                           | 2.19    | 1570                              | 82        | 1643                             | 54        | 1654                             | 84        |
| R-7D-3      | RDP             | 0.2419                           | 1.52    | 2.9958                           | 1.60    | 0.08893                           | 1.45    | 1402                              | 56        | 1407                             | 24        | 1396                             | 38        |
| R-7D-3      | RDP             | 0.2924                           | 1.11    | 4.1435                           | 1.66    | 0.10305                           | 1.20    | 1678                              | 44        | 1663                             | 27        | 1654                             | 32        |
| R-7D-3      | RDP             | 0.2947                           | 1.71    | 4.2539                           | 1.31    | 0.1013                            | 1.24    | 1648                              | 46        | 1684                             | 21        | 1665                             | 50        |
| R-2B-6      | QLP             | 0.2918                           | 1.73    | 4.0712                           | 1.38    | 0.10012                           | 1.15    | 1626                              | 42        | 1649                             | 23        | 1651                             | 50        |

Table 5.5. Concordant U-Pb data and calculated ages for Proterozoic cores of Resolution zircons. Fels. ALi = felsic Apache Leap intrusion.

| Sample name | Location        | Isotope ratios                   |         |                                  |         |                                   |         | Apparent age (Ma)                 |           |                                  |           |                                  |           |
|-------------|-----------------|----------------------------------|---------|----------------------------------|---------|-----------------------------------|---------|-----------------------------------|-----------|----------------------------------|-----------|----------------------------------|-----------|
|             |                 | $^{206}\text{Pb}/^{238}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{235}\text{U}$ | RSD (%) | $^{207}\text{Pb}/^{206}\text{Pb}$ | RSD (%) | $^{207}\text{Pb}/^{206}\text{Pb}$ | $2\sigma$ | $^{207}\text{Pb}/^{235}\text{U}$ | $2\sigma$ | $^{206}\text{Pb}/^{238}\text{U}$ | $2\sigma$ |
| R-13F-2     | QLP             | 0.0113                           | 3.33    | 0.0786                           | 3.99    | 0.05301                           | 5.21    | 72                                | 5         | 77                               | 6         | 328                              | 236       |
| R-2B-6      | QLP             | 0.0108                           | 2.62    | 0.0692                           | 4.45    | 0.04722                           | 4.60    | 69                                | 4         | 68                               | 6         | 60                               | 166       |
| R-2B-6      | QLP             | 0.0111                           | 1.74    | 0.0716                           | 2.13    | 0.04576                           | 2.26    | 71                                | 2         | 70                               | 3         | 1                                | 38        |
| R-2B-6      | QLP             | 0.0111                           | 1.52    | 0.0723                           | 2.41    | 0.04675                           | 2.69    | 71                                | 2         | 71                               | 3         | 36                               | 98        |
| R-7D-3      | RDP             | 0.0099                           | 1.16    | 0.0682                           | 1.55    | 0.0478                            | 1.53    | 64                                | 1         | 67                               | 2         | 88                               | 72        |
| R-7D-3      | RDP             | 0.0102                           | 1.21    | 0.0668                           | 2.02    | 0.04624                           | 2.05    | 65                                | 2         | 66                               | 3         | 8                                | 58        |
| R-7D-3      | RDP             | 0.0105                           | 1.19    | 0.0701                           | 2.15    | 0.04818                           | 2.53    | 67                                | 2         | 69                               | 3         | 108                              | 120       |
| R-RF-G      | fels. ALi       | 0.0099                           | 2.47    | 0.0646                           | 8.33    | 0.04608                           | 8.50    | 64                                | 3         | 64                               | 10        | 0                                | 194       |
| R-RF-G      | fels. ALi       | 0.0107                           | 1.92    | 0.07                             | 3.23    | 0.04707                           | 3.32    | 68                                | 3         | 69                               | 4         | 52                               | 130       |
| R-RF-G      | fels. ALi       | 0.0113                           | 1.60    | 0.0745                           | 3.05    | 0.04787                           | 3.40    | 72                                | 2         | 73                               | 4         | 92                               | 160       |
| R-S-13      | Schultze porph. | 0.0095                           | 4.25    | 0.064                            | 6.63    | 0.04842                           | 4.67    | 61                                | 5         | 63                               | 8         | 120                              | 220       |
| R-S-13      | Schultze porph. | 0.0098                           | 1.28    | 0.0645                           | 1.86    | 0.04651                           | 2.12    | 63                                | 2         | 63                               | 2         | 24                               | 74        |
| R-S-13      | Schultze porph. | 0.0098                           | 1.16    | 0.0654                           | 2.07    | 0.04825                           | 2.23    | 63                                | 1         | 64                               | 3         | 110                              | 106       |
| R-S-13      | Schultze porph. | 0.0101                           | 1.76    | 0.0671                           | 1.89    | 0.04817                           | 2.08    | 65                                | 2         | 66                               | 2         | 106                              | 98        |

Table 5.6. Concordant U-Pb isotope data and calculated ages for Laramide zircons from Resolution and associated lithologies.



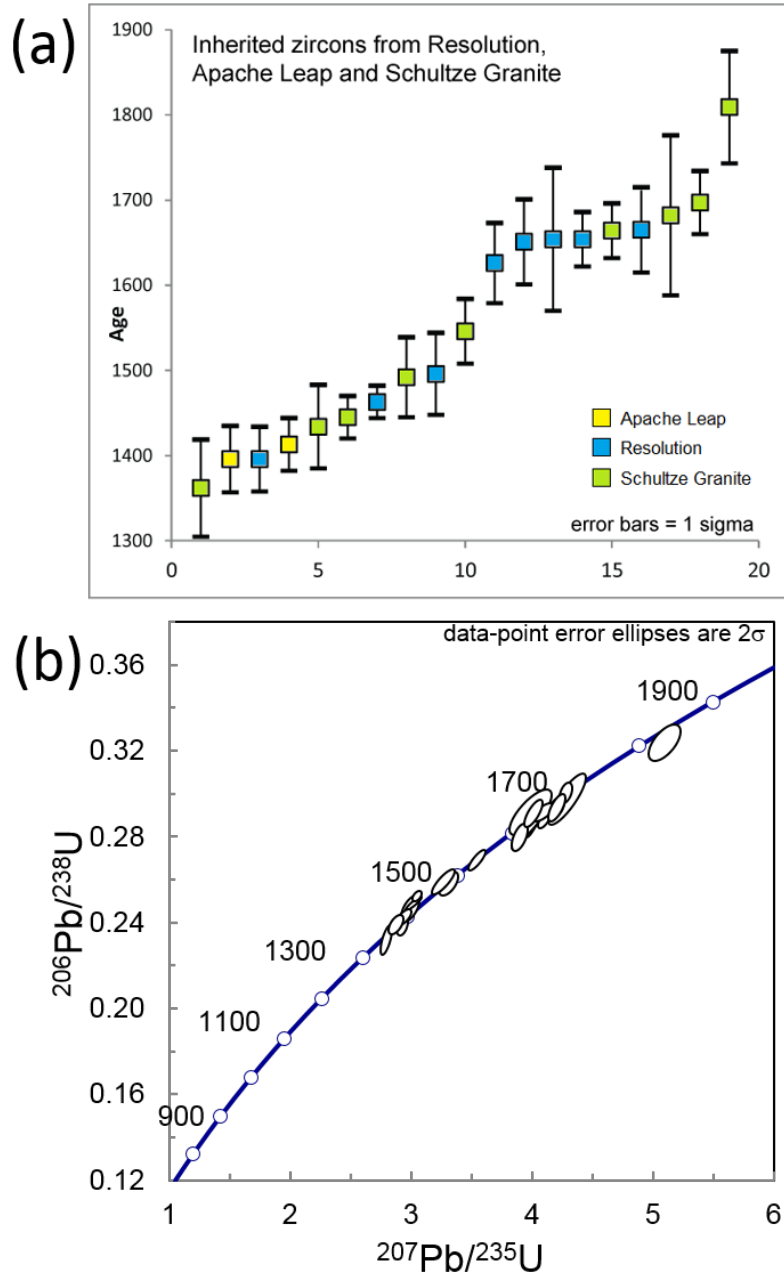


Figure 5.21. a) Age arrays for  $^{206}\text{Pb}/^{238}\text{U}$  ages determined for inherited cores of Resolution, Schultze Granite and Apache Leap samples, by LA-ICP-MS. (b) Wetherill concordia plots for the grains, showing the bimodal distribution of Proterozoic ages. Error ellipses represent  $2\sigma$ , error bars in Figure a) represent  $1\sigma$ .

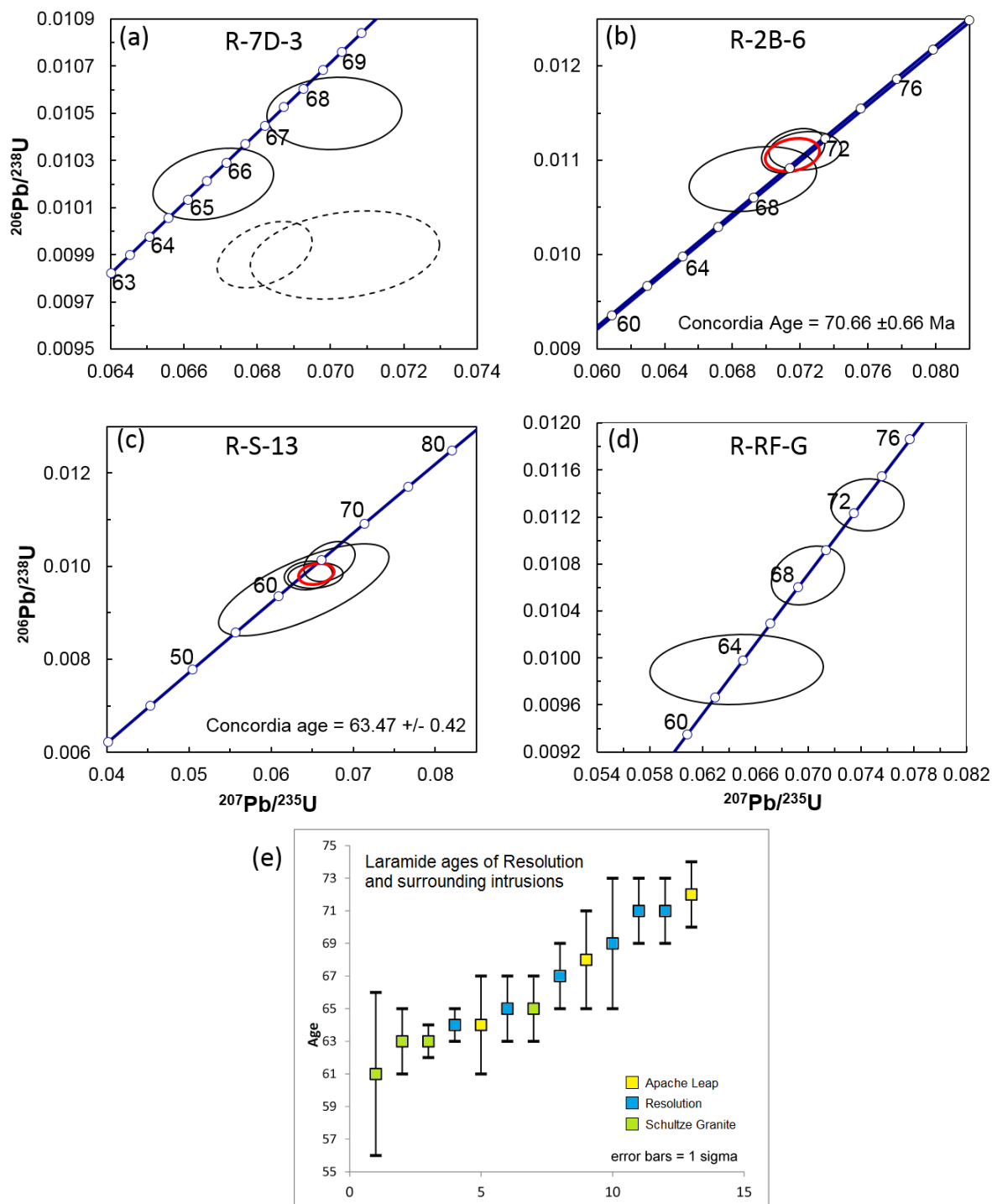


Figure 5.22. (a-d) Wetherill concordia plots for Laramide zircon rims, showing the data point error ellipses of the analyses used to calculate concordia ages. Red ellipses are the calculated isochron ages. Dotted ellipses in figure a) are not concordant in Error ellipses represent  $2\sigma$ , error bars Figure e) represent  $1\sigma$ .

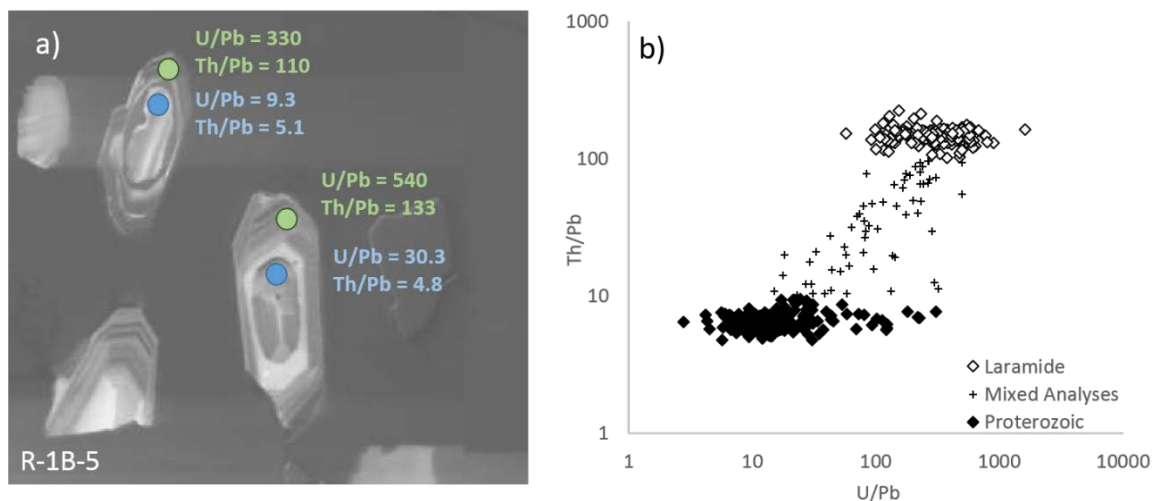


Figure 5.23. (a) Proterozoic cores of zircon have lower Th/Pb ( $<10$ ) and U/Pb (mostly  $<100$ ) than Laramide rims, which have values of  $>100$  for both ratios. These differences are due to the decay of U and Th to Pb, and the large difference in age between cores and rims. (b) On the basis of their geochemistry, Proterozoic cores may be easily distinguished from the rims, without the need for U-Pb dating. Data collected by LA-ICP-MS.

### 5.5.3 Geochemistry of Resolution district zircons

As well as being distinguishable on textural grounds, the Proterozoic inherited cores are distinct from Laramide rims in terms of their geochemistry (Fig. 5.23 a). In particular, plots of the ratios of radiogenic parent and daughter elements (U/Pb and Th/Pb) show two distinct populations, with some scatter between them (Fig. 5.23 b). Proterozoic analyses typically have Th/Pb values  $<10$ , whereas the Laramide zircons have Th/Pb values  $>100$ ; these values can therefore be used to divide the dataset into Laramide and Proterozoic analyses. The scattered data between the two main populations are likely to be analyses of mixed old and young material. As they are a small number of analyses, they are discarded and are not discussed further. The older population is found in zircons from all samples and will be discussed together as the ‘Proterozoic zircons’.

| ppm                                    | QLP    |                    |        |                    |       | RDP    |                    |        |                    |       | Intrusion Breccia |                    |        |                    |       | LOD   | And/Dac | Granite |
|----------------------------------------|--------|--------------------|--------|--------------------|-------|--------|--------------------|--------|--------------------|-------|-------------------|--------------------|--------|--------------------|-------|-------|---------|---------|
|                                        | min    | 1 <sup>st</sup> Q. | median | 3 <sup>rd</sup> Q. | max   | min    | 1 <sup>st</sup> Q. | median | 3 <sup>rd</sup> Q. | max   | min               | 1 <sup>st</sup> Q. | median | 3 <sup>rd</sup> Q. | max   | ppm   | median  | median  |
| <b>Sc</b>                              | 107.5  | 209                | 276    | 346                | 913   | 122.2  | 211                | 284    | 359                | 749   | 169.4             | 261                | 296    | 341                | 1089  | 0.20  | 72      | 73.4    |
| <b>Ti</b>                              | b.d.l. | 2.89               | 3.70   | 7.30               | 26.23 | b.d.l. | 2.70               | 4.28   | 7.4                | 16.1  | b.d.l.            | 2.61               | 3.54   | 5.2                | 15.78 | 1.4   | 11      | 8.62    |
| <b>V</b>                               | b.d.l. | 0.145              | 0.202  | 0.319              | 2.464 | 0.0637 | 0.135              | 0.188  | 0.268              | 1.52  | b.d.l.            | 0.132              | 0.216  | 0.287              | 1.075 | 0.061 | 5.5     | 2.4     |
| <b>Rb</b>                              | b.d.l. | 0.1057             | 0.1535 | 0.2323             | 1.500 | b.d.l. | 0.1177             | 0.1609 | 0.246              | 0.870 | 0.0681            | 0.1338             | 0.1843 | 0.224              | 0.359 | 0.038 | 13      | 1.01    |
| <b>Sr</b>                              | 0.0476 | 0.1572             | 0.1910 | 0.286              | 0.81  | 0.0584 | 0.170              | 0.215  | 0.304              | 1.76  | 0.0711            | 0.175              | 0.231  | 0.276              | 0.42  | 0.024 | 2.7     | 0.84    |
| <b>Y</b>                               | 197    | 685                | 1178   | 1742               | 8498  | 243    | 849                | 1429   | 1790               | 4611  | 413               | 1103               | 1370   | 1719               | 2958  | 0.15  | 954     | 1539    |
| <b>Nb</b>                              | 0.339  | 3.194              | 5.393  | 11.794             | 31.75 | 1.046  | 3.28               | 8.14   | 13.77              | 32.3  | 0.958             | 5.29               | 10.17  | 17.56              | 27.15 | 0.030 | 3.32    | 8.52    |
| <b>La</b>                              | b.d.l. | b.d.l.             | b.d.l. | 0.03               | 0.153 | b.d.l. | b.d.l.             | b.d.l. | 0.05               | 0.3   | b.d.l.            | b.d.l.             | b.d.l. | 0.02               | 0.100 | 0.020 | 0.04    | 0.181   |
| <b>Ce</b>                              | 6.84   | 14.69              | 23.45  | 39.87              | 216.5 | 2.15   | 22.49              | 28.35  | 40.7               | 75    | 15.70             | 23.26              | 32.51  | 40.47              | 73.2  | 0.022 | 19.2    | 25.4    |
| <b>Pr</b>                              | b.d.l. | 0.0269             | 0.0454 | 0.083              | 1.15  | b.d.l. | 0.031              | 0.053  | 0.107              | 0.31  | b.d.l.            | 0.0266             | 0.0379 | 0.082              | 0.42  | 0.016 | 0.1     | 0.32    |
| <b>Nd</b>                              | b.d.l. | 0.694              | 1.013  | 1.590              | 24.14 | b.d.l. | 0.697              | 0.997  | 1.81               | 7.1   | 0.3055            | 0.587              | 0.829  | 1.430              | 6.81  | 0.19  | 1.6     | 3.6     |
| <b>Sm</b>                              | 0.6267 | 1.978              | 3.753  | 5.252              | 64.00 | 0.681  | 2.35               | 3.59   | 5.91               | 16.7  | 1.1386            | 2.576              | 3.676  | 5.415              | 12.68 | 0.11  | 3.2     | 6.2     |
| <b>Eu</b>                              | 0.4390 | 0.980              | 1.567  | 2.226              | 28.76 | 0.3876 | 0.968              | 1.517  | 2.27               | 8.12  | 0.5140            | 1.231              | 1.588  | 2.340              | 5.95  | 0.032 | 0.9     | 0.82    |
| <b>Gd</b>                              | 5.572  | 13.80              | 20.69  | 32.76              | 289.4 | 5.89   | 17.03              | 24.54  | 35.0               | 87    | 6.754             | 16.94              | 27.00  | 34.03              | 55.2  | 0.12  | 20.1    | 32.2    |
| <b>Tb</b>                              | 2.093  | 4.775              | 7.313  | 12.70              | 85.92 | 2.614  | 6.04               | 9.19   | 13.32              | 30.6  | 2.643             | 6.639              | 9.854  | 11.82              | 21.13 | 0.019 | 7.29    | 12      |
| <b>Dy</b>                              | 28.65  | 55.0               | 100.0  | 161.5              | 890.9 | 32.0   | 74.2               | 117.0  | 173.6              | 410   | 31.82             | 87.5               | 119.1  | 154.0              | 268.6 | 0.093 | 90.7    | 149     |
| <b>Ho</b>                              | 6.26   | 21.75              | 38.95  | 56.6               | 306.4 | 8.77   | 28.1               | 46.3   | 60.7               | 158   | 12.59             | 33.67              | 42.76  | 55.9               | 101.8 | 0.027 | 37.9    | 52.5    |
| <b>Er</b>                              | 16.8   | 112.0              | 171.2  | 275.6              | 1174  | 26.6   | 138.7              | 222.9  | 282                | 738   | 61.9              | 171.4              | 218.9  | 268.2              | 449   | 0.12  | 178     | 408     |
| <b>Tm</b>                              | 2.43   | 27.2               | 41.5   | 64.8               | 235.1 | 4.4    | 34.5               | 53.3   | 64.9               | 170   | 16.46             | 40.0               | 54.1   | 61.5               | 103.0 | 0.026 | 42      | 50.5    |
| <b>Yb</b>                              | 18     | 312                | 455    | 670                | 2274  | 37     | 382                | 577    | 679                | 1635  | 188               | 436                | 589    | 700                | 1037  | 0.21  | 395     | 500     |
| <b>Lu</b>                              | 2.5    | 54.1               | 77.8   | 105.7              | 273   | 5.0    | 62.1               | 85.5   | 104.0              | 234   | 26.0              | 70.8               | 86.7   | 103.9              | 152   | 0.032 | 79      | 86      |
| <b>Hf</b>                              | 6474   | 9390               | 10600  | 11070              | 14423 | 6770   | 9990               | 10658  | 11544              | 15807 | 6817              | 10353              | 11146  | 11926              | 14972 | 2.0   | 9665    | 10480   |
| <b>Ta</b>                              | 0.0257 | 0.8644             | 1.5237 | 2.464              | 6.581 | 0.251  | 0.882              | 1.913  | 3.266              | 9.16  | 0.1578            | 1.2377             | 2.1129 | 3.497              | 6.875 | 0.019 | 1       | 1.3     |
| <b>Pb</b>                              | b.d.l. | 0.544              | 0.950  | 1.78               | 13.45 | b.d.l. | 0.815              | 1.378  | 1.99               | 5.2   | 0.225             | 0.833              | 1.357  | 2.42               | 6.92  | 0.062 | 26.9    | 24.4    |
| <b>Th</b>                              | 9.94   | 73.8               | 138.4  | 285.6              | 2074  | 7.63   | 114.8              | 206.5  | 305.0              | 803   | 41.18             | 122.5              | 193.0  | 378.8              | 1106  | 0.061 | 135     | 186     |
| <b>U</b>                               | 7.1    | 220.9              | 356.5  | 537.2              | 1388  | 15.9   | 263.0              | 499.3  | 684                | 1593  | 25.6              | 331.3              | 480.1  | 720.3              | 2744  | 0.093 | 220     | 283     |
| <b>Eu/Eu*</b>                          | 0.35   | 0.49               | 0.57   | 0.66               | 0.91  | 0.09   | 0.46               | 0.53   | 0.60               | 0.87  | 0.35              | 0.49               | 0.52   | 0.57               | 0.77  |       | 0.42    | 0.17    |
| <b>ΣREE</b>                            | 119    | 684                | 954    | 1506               | 5864  | 155    | 789                | 1182   | 1435               | 3504  | 378               | 900                | 1197   | 1373               | 2244  |       | 885     | 1162    |
| <b>Yb/Gd</b>                           | 1.1    | 19.2               | 28.5   | 36                 | 74    | 2.64   | 21.2               | 27.6   | 33.1               | 48    | 5.0               | 22.4               | 27.6   | 36                 | 50    |       | 21.5    | 16.4    |
| <b>U/Pb</b>                            | 18.3   | 199.8              | 320.4  | 420.9              | 771   | 92.21  | 225.0              | 312.6  | 446.0              | 1600  | 114.1             | 211.7              | 335.2  | 455.3              | 650   |       | 10.1    | 11.8    |
| <b>Th/Pb</b>                           | 20.1   | 133.4              | 142.9  | 153.3              | 224.1 | 107.10 | 140.0              | 149.6  | 159.2              | 215   | 103.1             | 144.3              | 155.6  | 159.4              | 183.3 |       | 13.6    | 10.5    |
| <b>Ta/Nb</b>                           | 0.08   | 0.18               | 0.22   | 0.27               | 0.49  | 0.14   | 0.21               | 0.25   | 0.30               | 0.67  | 0.11              | 0.19               | 0.21   | 0.25               | 0.34  |       | 0.34    | 0.29    |
| <b>T (°C)</b>                          | 601    | 669                | 689    | 749                | 887   | 608    | 664                | 701    | 751                | 830   | 563               | 661                | 685    | 718                | 828   |       | 790     | 766     |
| <b>Ce<sup>4+</sup>/Ce<sup>3+</sup></b> | 1.3    | 112                | 230    | 366                | 1252  | 5.6    | 63.2               | 143.0  | 230                | 583   | 7.2               | 176                | 287    | 472                | 816   |       | N/A     | N/A     |
| <b>Ce/Ce*</b>                          | 10.42  | 113                | 251    | 385                | 1323  | 8.57   | 95.7               | 182.8  | 399                | 1064  | 15.77             | 205                | 377    | 585                | 842   |       | 55.3    | 27.5    |

| ppm                                | Schultze Granite |                    |        |                    |        | Apache Leap |                    |        |                    |       | Proterozoic |                    |        |                    |        | LOD   | And/Dac | Granite |
|------------------------------------|------------------|--------------------|--------|--------------------|--------|-------------|--------------------|--------|--------------------|-------|-------------|--------------------|--------|--------------------|--------|-------|---------|---------|
|                                    | min              | 1 <sup>st</sup> Q. | median | 3 <sup>rd</sup> Q. | max    | min         | 1 <sup>st</sup> Q. | median | 3 <sup>rd</sup> Q. | max   | min         | 1 <sup>st</sup> Q. | median | 3 <sup>rd</sup> Q. | max    | ppm   | median  | median  |
| Sc                                 | 163.8            | 255                | 319    | 407                | 730    | 119.6       | 150                | 223    | 434                | 660   | 83.8        | 152                | 187    | 241                | 776    | 0.20  | 72      | 73.4    |
| Ti                                 | b.d.l.           | 2.82               | 3.88   | 7.13               | 14.11  | b.d.l.      | 3.11               | 3.69   | 6.1                | 15.6  | 2.436       | 5.96               | 7.83   | 10.0               | 27.75  | 1.4   | 11      | 8.62    |
| V                                  | b.d.l.           | 0.113              | 0.165  | 0.247              | 2.183  | 0.0664      | 0.107              | 0.152  | 0.199              | 2.53  | b.d.l.      | 0.234              | 0.441  | 0.836              | 11.582 | 0.061 | 5.5     | 2.4     |
| Rb                                 | b.d.l.           | 0.1790             | 0.3018 | 0.4814             | 1.195  | b.d.l.      | 0.0550             | 0.0714 | 0.258              | 0.446 | b.d.l.      | 0.1191             | 0.1709 | 0.229              | 1.985  | 0.038 | 13      | 1.01    |
| Sr                                 | 0.0668           | 0.2177             | 0.3316 | 0.470              | 1.04   | 0.0471      | 0.081              | 0.143  | 0.288              | 0.50  | 0.0576      | 0.156              | 0.201  | 0.286              | 3.84   | 0.024 | 2.7     | 0.84    |
| Y                                  | 263              | 1211               | 2180   | 3147               | 8203   | 228         | 397                | 824    | 2738               | 3486  | 272         | 842                | 1157   | 1567               | 4381   | 0.15  | 954     | 1539    |
| Nb                                 | 1.115            | 4.126              | 13.926 | 25.693             | 48.05  | 0.786       | 2.28               | 3.65   | 15.53              | 36.1  | 0.902       | 2.52               | 4.05   | 5.89               | 83.34  | 0.030 | 3.32    | 8.52    |
| La                                 | b.d.l.           | b.d.l.             | b.d.l. | 0.05               | 0.539  | b.d.l.      | b.d.l.             | b.d.l. | 0.04               | 0.1   | b.d.l.      | b.d.l.             | b.d.l. | 0.04               | 1.073  | 0.020 | 0.04    | 0.181   |
| Ce                                 | 4.77             | 20.83              | 26.71  | 33.60              | 60.4   | 1.73        | 8.59               | 17.93  | 24.4               | 38    | 1.35        | 13.01              | 22.58  | 34.25              | 164.1  | 0.022 | 19.2    | 25.4    |
| Pr                                 | b.d.l.           | 0.0242             | 0.0514 | 0.171              | 0.86   | b.d.l.      | b.d.l.             | 0.024  | 0.033              | 0.69  | b.d.l.      | 0.0427             | 0.0707 | 0.137              | 1.19   | 0.016 | 0.1     | 0.32    |
| Nd                                 | b.d.l.           | 0.608              | 1.016  | 1.824              | 13.50  | b.d.l.      | 0.271              | 0.814  | 1.01               | 10.5  | b.d.l.      | 0.783              | 1.230  | 2.358              | 16.98  | 0.19  | 1.6     | 3.6     |
| Sm                                 | 0.5299           | 2.906              | 4.156  | 6.783              | 22.01  | 0.185       | 1.17               | 2.14   | 4.62               | 17.1  | 0.4928      | 2.118              | 3.204  | 5.152              | 24.68  | 0.11  | 3.2     | 6.2     |
| Eu                                 | 0.2495           | 0.904              | 1.252  | 1.749              | 9.76   | 0.1295      | 0.540              | 1.312  | 1.90               | 8.12  | 0.0796      | 0.389              | 0.679  | 1.198              | 8.38   | 0.032 | 0.9     | 0.82    |
| Gd                                 | 5.170            | 19.69              | 29.92  | 48.10              | 83.8   | 1.81        | 7.53               | 18.06  | 35.3               | 64    | 2.754       | 13.19              | 18.92  | 29.59              | 111.2  | 0.12  | 20.1    | 32.2    |
| Tb                                 | 2.606            | 7.628              | 12.896 | 20.26              | 41.89  | 0.978       | 2.81               | 5.61   | 15.71              | 20.4  | 1.260       | 5.069              | 7.254  | 10.99              | 33.15  | 0.019 | 7.29    | 12      |
| Dy                                 | 27.38            | 100.5              | 179.7  | 261.5              | 641.0  | 15.9        | 34.8               | 63.4   | 225.2              | 283   | 17.52       | 69.4               | 97.2   | 145.6              | 394.7  | 0.093 | 90.7    | 149     |
| Ho                                 | 8.99             | 39.65              | 70.46  | 103.0              | 260.8  | 7.08        | 13.3               | 26.1   | 93.7               | 122   | 8.16        | 27.39              | 38.18  | 53.8               | 149.9  | 0.027 | 37.9    | 52.5    |
| Er                                 | 38.4             | 186.3              | 355.1  | 535.9              | 1288   | 40.1        | 64.1               | 126.1  | 438                | 671   | 47.4        | 142.5              | 187.3  | 260.1              | 720    | 0.12  | 178     | 408     |
| Tm                                 | 8.16             | 45.4               | 86.8   | 130.5              | 307.7  | 9.0         | 13.8               | 26.0   | 101.0              | 158   | 12.92       | 32.5               | 46.0   | 59.5               | 185.3  | 0.026 | 42      | 50.5    |
| Yb                                 | 83               | 478                | 860    | 1364               | 3129   | 95          | 138                | 238    | 997                | 1930  | 154         | 364                | 500    | 656                | 2105   | 0.21  | 395     | 500     |
| Lu                                 | 13.2             | 69.6               | 128.3  | 175.4              | 439    | 15.6        | 25.7               | 39.5   | 155.2              | 277   | 22.7        | 58.5               | 77.9   | 102.2              | 314    | 0.032 | 79      | 86      |
| Hf                                 | 6323             | 9874               | 11872  | 13219              | 19108  | 8019        | 9618               | 10940  | 11921              | 16151 | 6736        | 9045               | 9706   | 10727              | 14639  | 2.0   | 9665    | 10480   |
| Ta                                 | 0.2785           | 1.5700             | 5.1972 | 7.725              | 13.853 | 0.135       | 0.629              | 1.611  | 3.785              | 6.05  | 0.3807      | 1.0939             | 1.7701 | 2.807              | 44.246 | 0.019 | 1       | 1.3     |
| Pb                                 | 0.174            | 0.581              | 0.986  | 1.73               | 3.74   | b.d.l.      | 0.217              | 0.409  | 0.90               | 1.2   | 1.051       | 9.694              | 15.832 | 31.73              | 231.78 | 0.062 | 26.9    | 24.4    |
| Th                                 | 25.10            | 86.6               | 150.7  | 274.4              | 554    | 5.71        | 40.6               | 65.3   | 132.2              | 209   | 8.09        | 65.4               | 101.8  | 195.7              | 1334   | 0.061 | 135     | 186     |
| U                                  | 25.8             | 186.7              | 709.6  | 1074.6             | 2373   | 41.8        | 81.5               | 234.1  | 340                | 826   | 25.8        | 158.5              | 278.3  | 480.4              | 3856   | 0.093 | 220     | 283     |
| Eu/Eu*                             | 0.19             | 0.28               | 0.35   | 0.49               | 0.79   | 0.40        | 0.47               | 0.64   | 0.71               | 0.75  | 0.02        | 0.21               | 0.28   | 0.37               | 0.79   |       | 0.42    | 0.17    |
| ΣREE                               | 212              | 997                | 1740   | 2741               | 6232   | 230         | 334                | 646    | 2097               | 3470  | 311         | 732                | 1015   | 1335               | 3870   |       | 885     | 1162    |
| Yb/Gd                              | 7.9              | 28.8               | 40.1   | 44                 | 122    | 4.29        | 17.8               | 37.6   | 45.7               | 88    | 8.1         | 21.2               | 29.5   | 37                 | 143    |       | 21.5    | 16.4    |
| U/Pb                               | 98.1             | 326.9              | 581.4  | 819.7              | 1820   | 137.58      | 209.2              | 575.6  | 954.7              | 2227  | 2.8         | 9.8                | 13.7   | 22.3               | 305    |       | 10.1    | 11.8    |
| Th/Pb                              | 102.9            | 139.8              | 154.2  | 163.0              | 179.5  | 104.36      | 134.8              | 171.3  | 184.6              | 207   | 4.8         | 6.0                | 6.5    | 7.2                | 9.6    |       | 13.6    | 10.5    |
| Ta/Nb                              | 0.20             | 0.27               | 0.31   | 0.39               | 0.59   | 0.15        | 0.18               | 0.29   | 0.44               | 0.68  | 0.21        | 0.38               | 0.44   | 0.51               | 1.38   |       | 0.34    | 0.29    |
| T (°C)                             | 582              | 667                | 693    | 747                | 816    | 578         | 675                | 688    | 732                | 827   | 655         | 731                | 756    | 780                | 894    |       | 790     | 766     |
| Ce <sup>4+</sup> /Ce <sup>3+</sup> | 4.7              | 83                 | 204    | 260                | 1678   | 2.2         | 53.0               | 149.6  | 220                | 705   | 0.4         | 43                 | 97     | 219                | 8653   |       | N/A     | N/A     |
| Ce/Ce*                             | 11.44            | 111                | 265    | 434                | 2989   | 13.66       | 105.9              | 180.1  | 318                | 1283  | 2.16        | 45                 | 89     | 173                | 1771   |       | 55.3    | 27.5    |

Table 5.7. (previous page) Median values for zircons from Resolution. Colour code as in Table 5.4. “And/dac” and “Granite” are median values for typical andesite/dacite and granitic rocks, from GEOROC database (see text). LOD = limit of detection for LA-ICP-MS analyses. “1st Q” and “3<sup>rd</sup> Q” are the 1st and 3rd quartile respectively, and min and max are the minimum and maximum value determined for each group during this study.

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Laramide-age rims are discussed separately on the basis of whether they are from Resolution, the Schultze Granite, or the Apache Leap intrusions. “Resolution intrusions” will be used as a broad term for QLP, RDP, and intrusion breccia samples.

#### 5.5.3.1 High Field Strength Elements

Nb and Ta increase proportionally with one another (Fig. 5.24 a) and values increase with increasing  $\Sigma\text{REE}$  in zircons of all groups (Fig. 5.24 b), as is also seen in Oyu Tolgoi zircons (Fig. 5.8 b). Zircons from the Resolution intrusions (QLP, RDP, intrusion breccia), Apache Leap intrusion, and Proterozoic zircons all have similar median Ta and Hf concentrations, which are comparable to the median Ta and Hf concentrations of zircons from intermediate

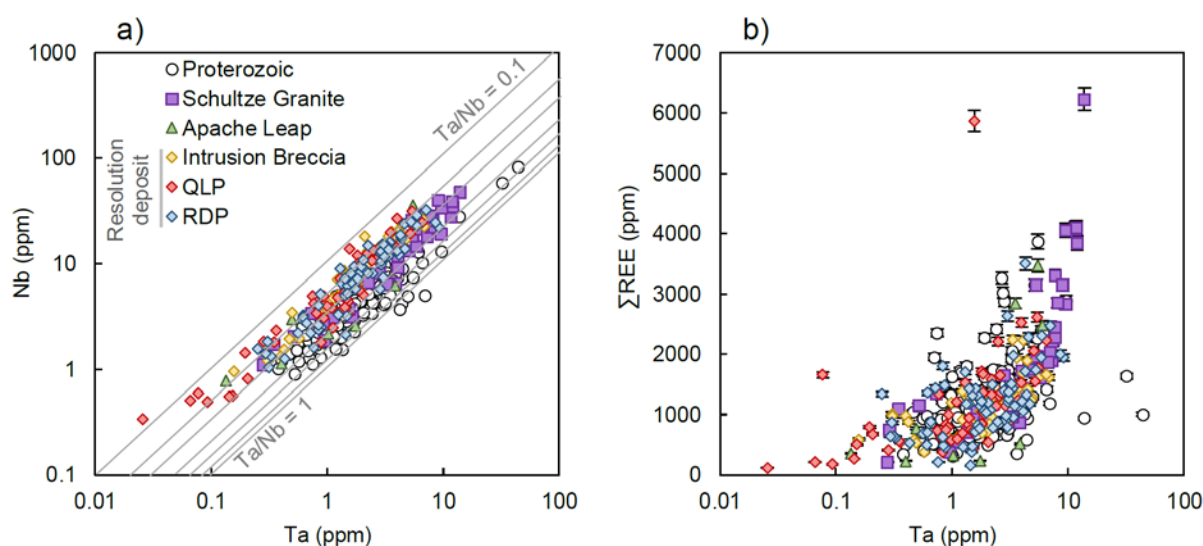


Figure 5.24. Variation of Ta in Resolution zircons with respect to (a) Nb, and (b)  $\Sigma\text{REE}$ . a) Ta/Nb ratios of all types of zircon are broadly similar. b) Ta increases with increasing  $\Sigma\text{REE}$ . Errors are smaller than the symbol size of all analyses in (a), and most analyses in (b). All analyses conducted by LA-ICP-MS.

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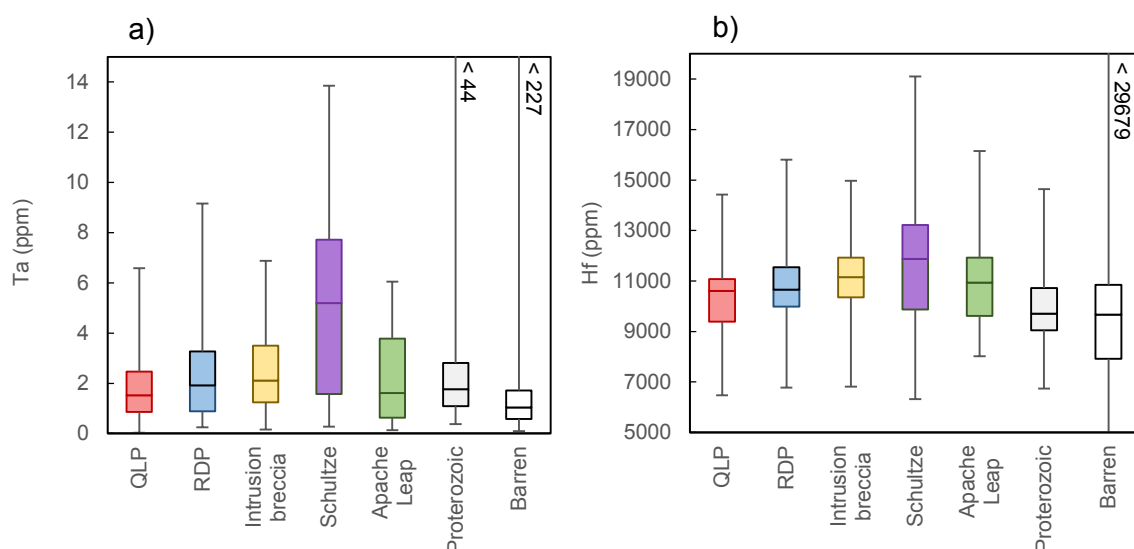


Figure 5.25. Box and whisker diagram showing the median, upper and lower quartiles, and range of a) Ta, and b) Hf contents in zircons from Resolution.

rocks (Fig. 5.25). Zircons from the Schultz Granite have higher Ta and Hf, which is likely due to the more fractionated nature of the granite.

### 5.5.3.2 Rare earth elements (REE) and yttrium

In all types of studied zircon from the Resolution district, median chondrite-normalised REE patterns are closely similar to median patterns of zircons from intermediate granitoids. Zircons from the Felsic Apache Leap intrusion are mildly depleted in both L- and HREE with respect to the intermediate granitoid values. Median Schultz Granite zircons are weakly enriched in HREE with respect to median intermediate granitoids. There is little difference in the range, interquartile range, and median REE patterns of zircons from the three Resolution intrusion types (QLP, RDP, intrusion breccia).

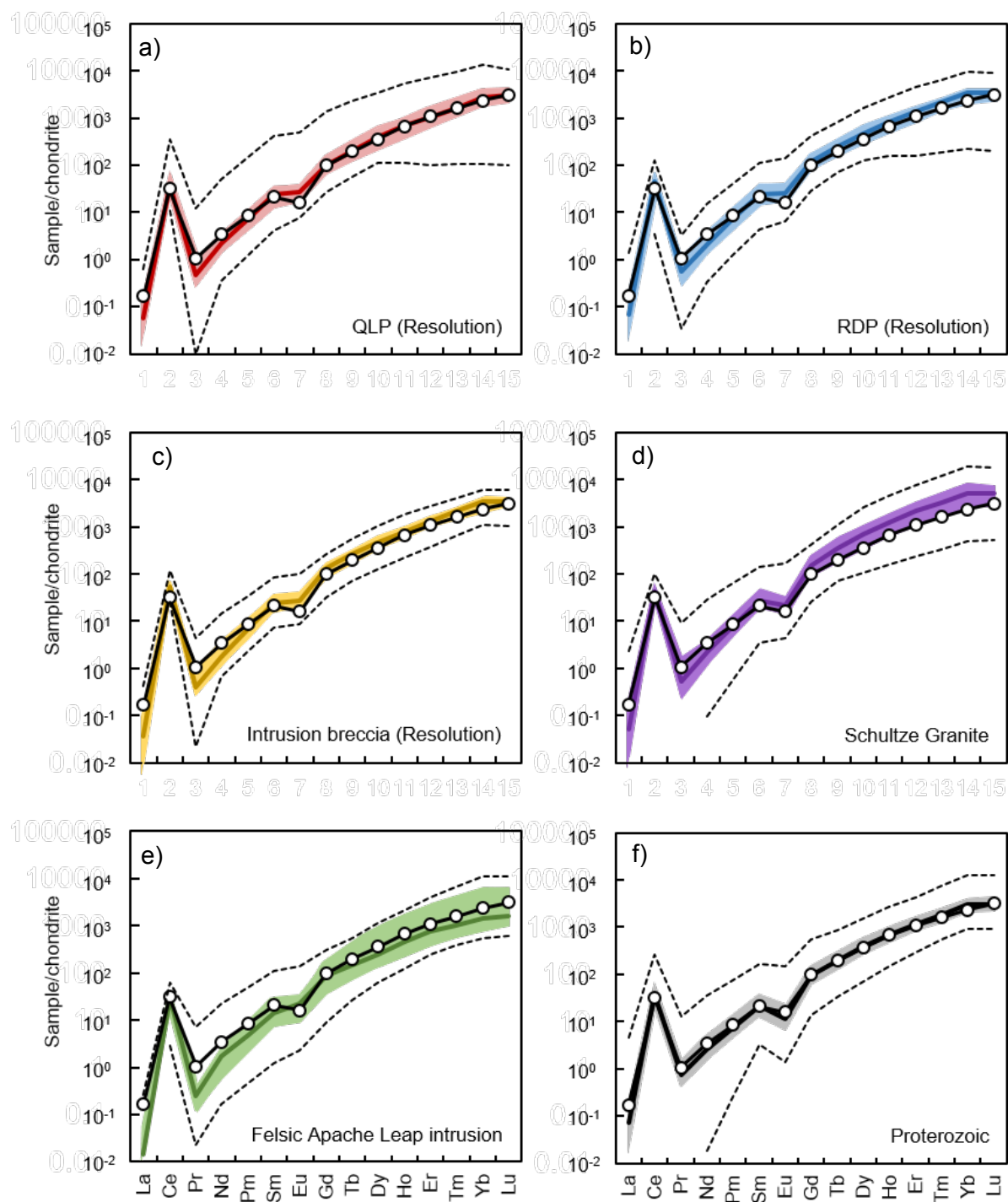


Figure 5.26. Chondrite normalised REE patterns for Resolution zircons. Dotted lines represent maximum and minimum values. Coloured areas are the interquartile range. Black line with open circles is the median chondrite normalised REE pattern for zircons from barren, intermediate rocks. Data collected by LA-ICP-MS. Chondrite values taken from Sun and McDonough (1989).



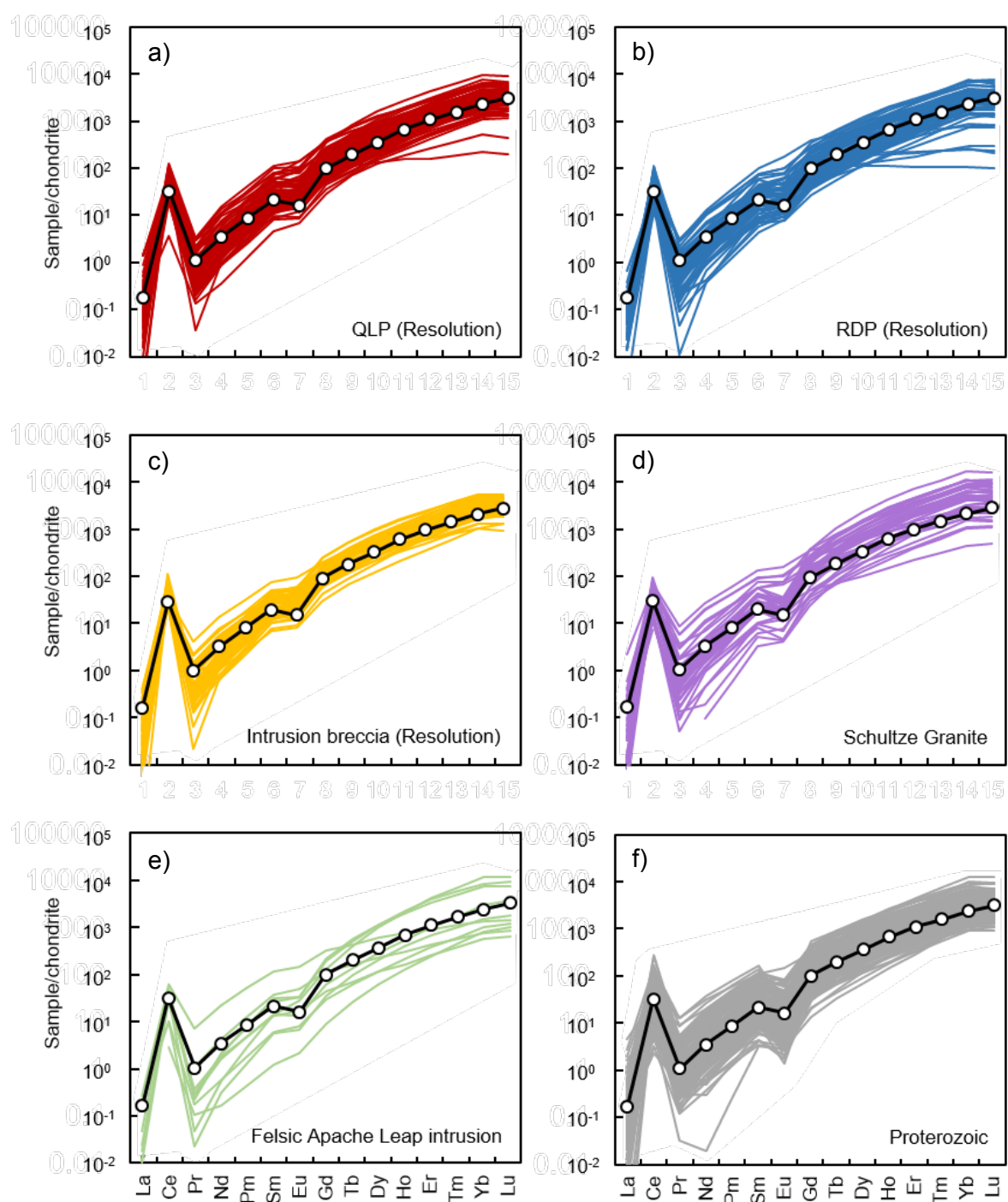


Figure 5.27. Chondrite normalised REE patterns for Resolution zircons. Black line with open circles is the median chondrite normalised REE pattern for zircons from barren, intermediate rocks. Data collected by LA-ICP-MS. Chondrite values taken from Sun and McDonough (1989).

### 5.5.3.3 Eu and Ce anomalies

The Schultze Granite and Proterozoic zircons have Eu/Eu\* values that are respectively similar to or lower than zircons from intermediate granitoids. The Resolution intrusion (QLP, RDP, intrusion breccia) have zircons with similar, moderately high Eu/Eu\* (median values ~0.55), with some values reaching Eu/Eu\* ~0.9. The highest median Eu/Eu\* values are found in zircons from the felsic Apache Leap sample (Fig. 5.28 a).

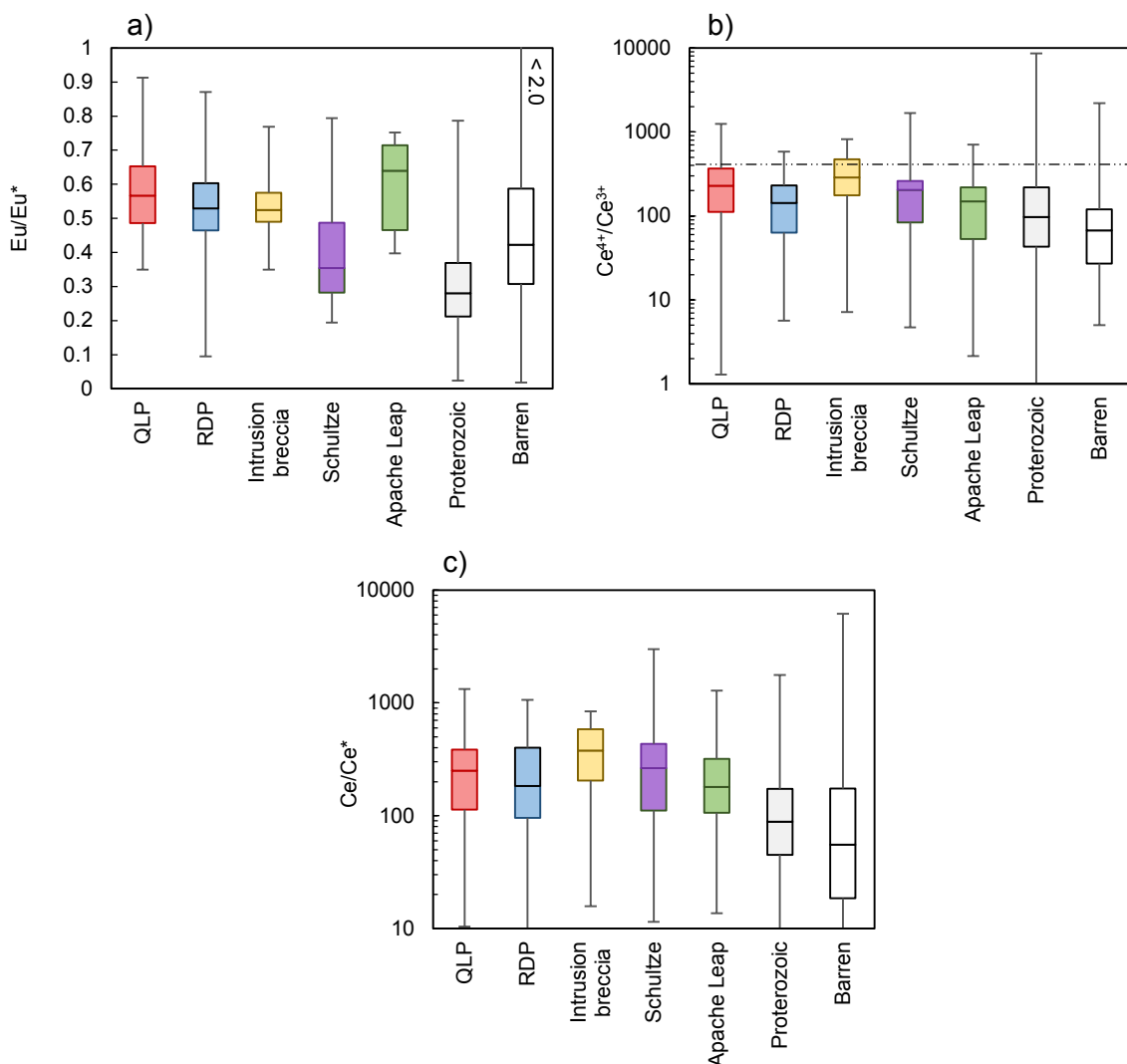


Figure 5.28. Box and whisker diagrams showing the median, interquartile range, and range of a) Eu/Eu\* values, b)  $Ce^{4+}/Ce^{3+}$ , and c)  $Ce/Ce^*$  for Resolution district zircons. Data for zircons from “barren” intrusions in b) are of 131 analyses from Ballard et al. (2002). The horizontal dashed line in b) is the suggested upper limit of zircons from “barren” rocks ( $Ce^{4+}/Ce^{3+} = 300$ ). All data collected by LA-ICP-MS.

Median  $\text{Ce}^{4+}/\text{Ce}^{3+}$  values of Resolution District zircons are all below the value of 300 suggested by Ballard et al. (2002) to separate zircons from fertile and barren intrusions (Fig. 5.28 b), and all  $\text{Ce}^{4+}/\text{Ce}^{3+}$  values are within the range of zircons from Barren intrusion (with the exception of some Proterozoic zircons). Zircons from the intrusion breccia have mildly higher median  $\text{Ce}^{4+}/\text{Ce}^{3+}$  compared to zircons from other Resolution intrusion (QLP or RDP).

Median  $\text{Ce}/\text{Ce}^*$  values of Laramide zircons from the Resolution intrusion (QLP, RDP, intrusion breccia), the Schultze Granite, and the Apache Leap intrusion are at least twice as high as median values for zircons for typical intermediate rocks, although the interquartile ranges of these zircon groups overlap with the typical intermediate zircons (Table 5.7; median = 55).

#### *5.5.3.4 Uranium, Lead, Thorium*

All Laramide zircons are significantly depleted in Pb with respect to both the typical zircons from intermediate rocks, and the Proterozoic zircons (Fig. 5.29 b). As with the U, Th, and Pb concentrations of zircons from Oyu Tolgoi (Fig. 5.14), this observation is likely to be due to the age of zircons from the literature dataset. By contrast, Proterozoic zircons have higher Pb due to the ingrowth of Pb over the much longer period of time since their crystallisation.

Th and U show increases with increasing Hf in all samples. U concentrations of the Proterozoic zircons (median = 278 ppm) and Apache Leap intrusions (median = 289 ppm) are typical of zircons in felsic crustal rocks (median = 222 ppm). U and Th both attain much higher concentrations in the Schultze Granite and Resolution intrusion zircons (Fig. 5.29 a,c).

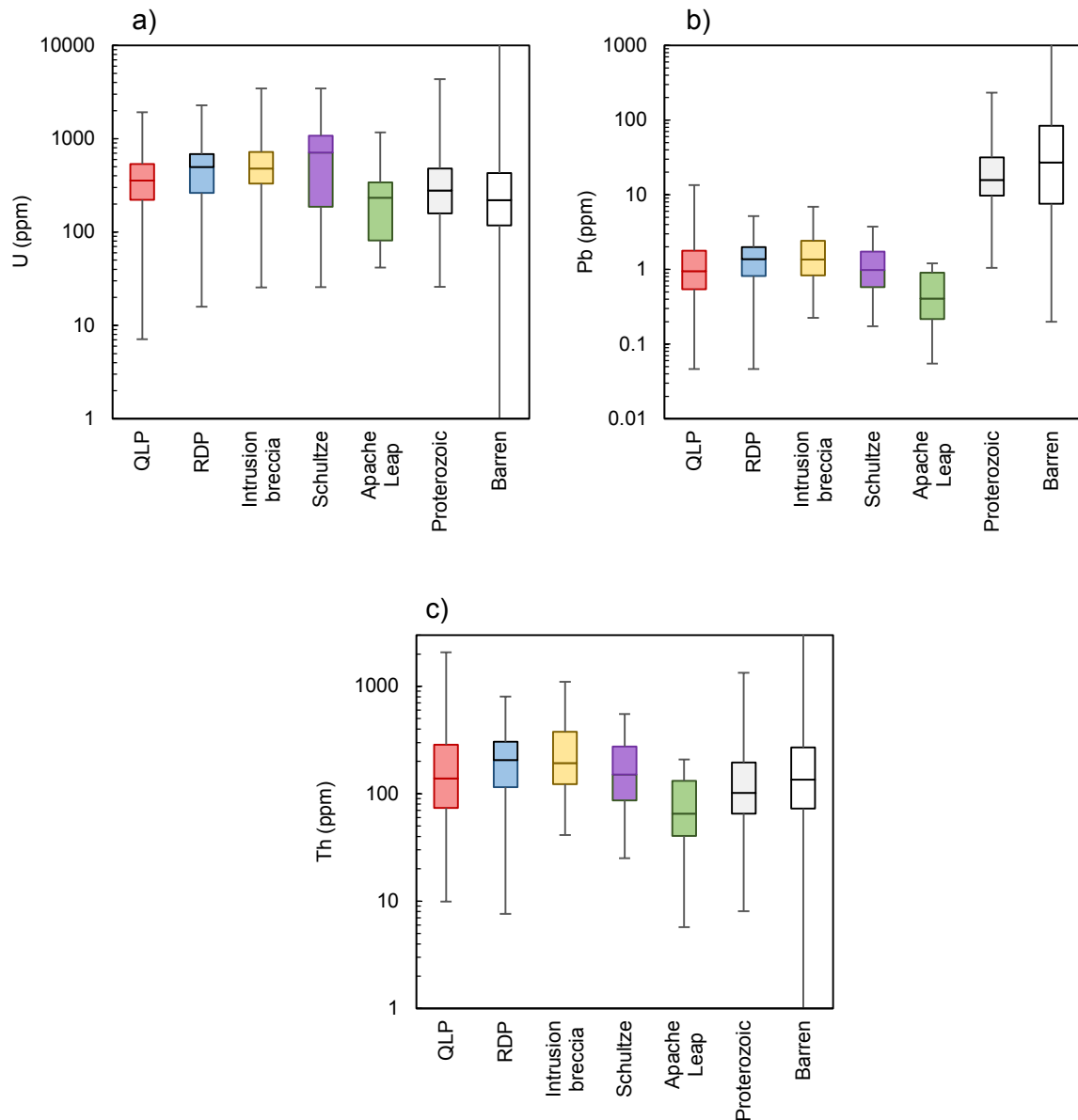


Figure 5.29. Box and whisker diagrams showing the median, interquartile range, and range of a) U, b) Pb, and c) Th concentrations of Resolution district zircons. All data collected by LA-ICP-MS.

#### 5.5.3.5 Crystallisation temperature (*Ti-in-zircon*)

Crystallisation temperatures of the Resolution, Schultze Granite, and Apache Leap zircons were calculated by the method of Ferry and Watson (2007).  $\text{TiO}_2$  and  $\text{SiO}_2$  activities were set at 1 and 0.7 respectively (see section above). Temperature estimates for low (median = 654, 658 and 648°C respectively), and are lower than average felsic rock zircon (median =

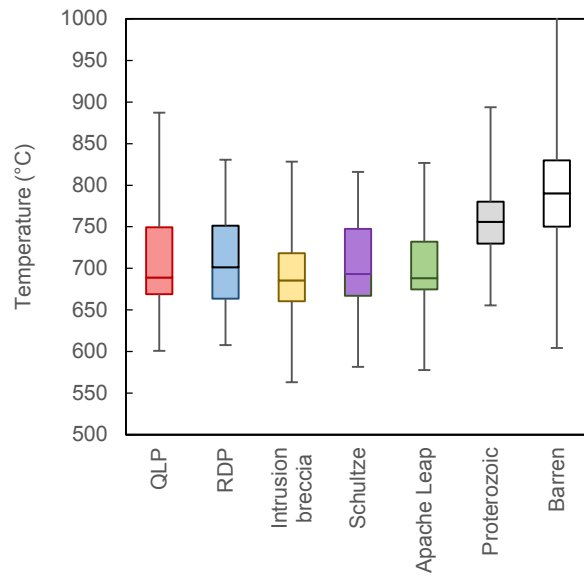


Figure 5.30. Box and whisker diagrams showing the median, interquartile range, and range of temperatures calculated by the Ti-in-zircon method (Ferry and Watson, 2007) of Resolution district zircons. Ti analysed by LA-ICP-MS.

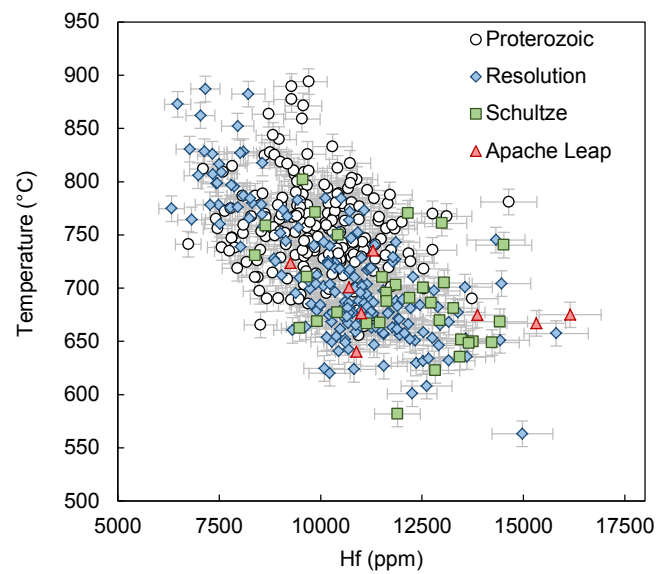


Figure 5.31. Variation in calculated temperature with Hf content for Resolution zircons.

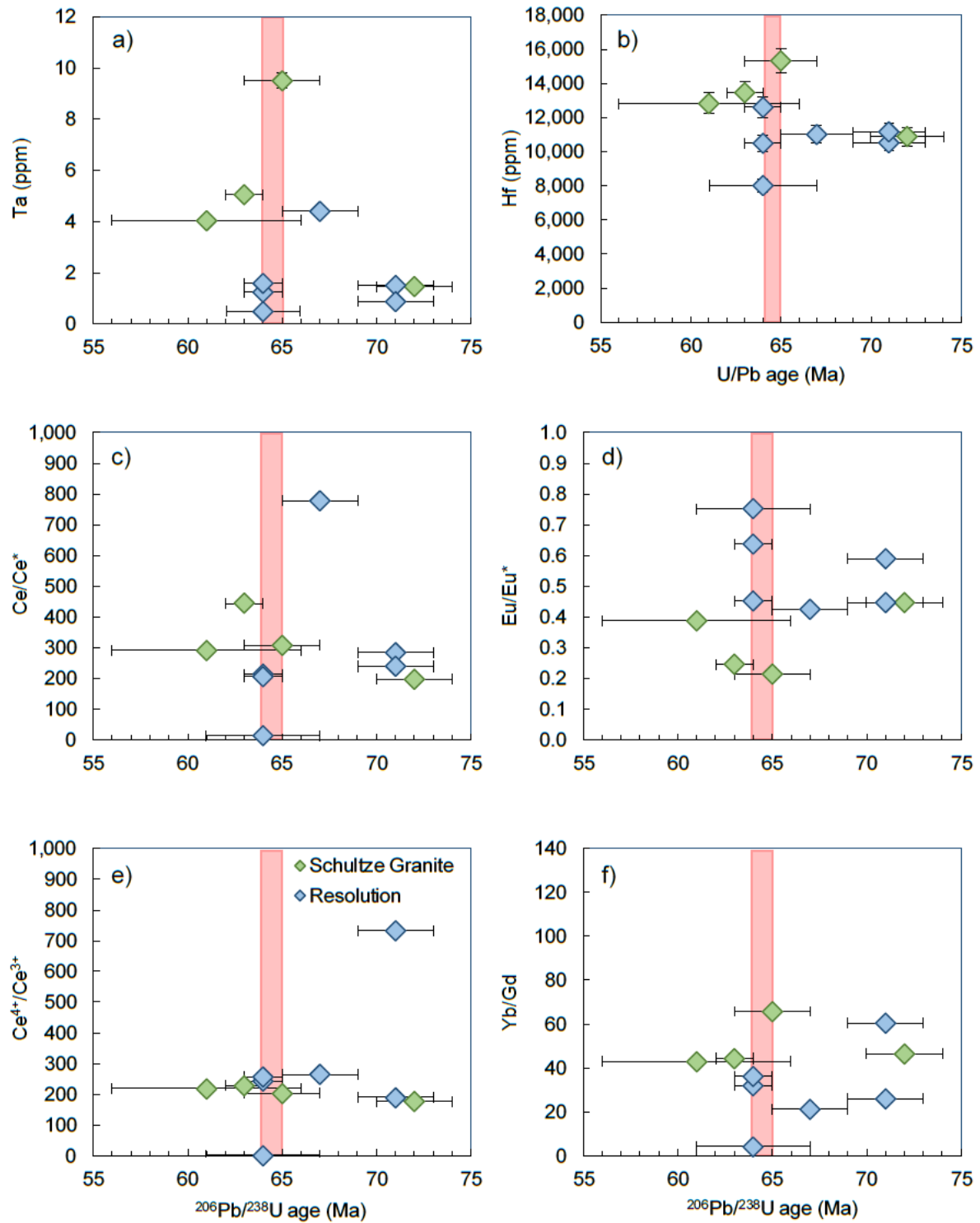


Figure 5.32. Variation in certain trace element variables with calculated  $^{206}\text{Pb}/^{238}\text{U}$  zircon age. a) Ta, b) Hf, c) Ce/Ce\*, d) Eu/Eu\*, e)  $\text{Ce}^{4+}/\text{Ce}^{3+}$ , f) Yb/Gd Pink shaded area represents the period of mineralisation, as determined by Re-Os molybdenite dating (Hehnke et al., 2012). All data collected by LA-ICP-MS. Error bars for  $^{206}\text{Pb}/^{238}\text{U}$  ages are  $1\sigma$ .

749°C). Proterozoic zircons have a higher crystallisation temperature (Fig. 5.30) Increasing Hf content corresponds loosely to decreasing temperature (Fig. 5.31).

#### *5.5.3.6 Variation of zircon chemistry with U-Pb ages and degree of fractionation*

Due to the limited number of concordant U-Pb dates, the evolution of zircon trace element chemistry with absolute age is poorly constrained (Fig. 5.32). The evolution of the system may be considered in terms of fractionation processes by plotting trace elements against an internal index of fractionation (i.e. Hf).

## **5.6 Discussion**

### **5.6.1 The origin of low-Ta zircons at Oyu Tolgoi**

The low-Ta group zircons at Oyu Tolgoi have geochemical features that are not commonly observed in crustal zircons. Values of <0.2 ppm Ta and <1 ppm Nb are rare in zircons from arc rocks and occur primarily in dolerite and lamproite (Belousova et al., 2002b). The exceptionally high Eu/Eu\* and Ce<sup>4+</sup>/Ce<sup>3+</sup> values of the low-Ta group (Fig. 5.13) are especially interesting because such high values have previously been used to distinguish between barren and fertile intrusions (e.g. Ballard et al., 2002; Dilles et al., 2015). The frequent occurrence of the low-Ta group as rims on high-Ta cores separated by a dissolution boundary could be interpreted as recording the transition from typical (barren) arc magmatism to a more fertile magmatic system from core to rim.

#### *5.6.1.1 Mafic input into a felsic magma chamber?*

One explanation is that an influx of mafic melt into a felsic magma chamber caused both the partial dissolution of pre-existing zircons, and the change in chemistry of subsequent new zircon rim growth. This is because the influx of mafic melt would cause the Hf, Ta, Nb of the melt to decrease, and the Eu/Eu\* to increase, all of which are characteristics of the low-Ta group

zircons. An increase in temperature would cause the melt to become undersaturated in Zr, and for pre-existing zircons to resorb. This process would cause the temperature of the magma to rise. However, temperature estimates for the low-Ta group zircons are lower than the high-Ta cores, and also lower than is typical for temperature estimates of crustal zircons (Fig. 5.15). Also, the low Ta/Nb ratio of the low-Ta group (Fig. 5.8) cannot be explained by the influx of mafic melts, which are likely to have higher Ta/Nb ratio (Stepanov and Hermann, 2013). For these reasons, and influx of mafic melt is unlikely to cause the core to rim variation in these samples.

#### *5.6.1.2 Equilibration with titanite?*

The depleted MREE, Ta, Nb, lower Ta/Nb and the weakly negative to positive Eu anomalies of the low-Ta group may all be explained by the co-crystallisation of titanite. Although relatively rare in altered QMD intrusions, titanite is commonly found associated with magnetite and quartz in less altered samples (e.g. OT-143). In moderately altered samples, titanite is partially replaced by an assemblage of rutile + anhydrite + quartz, which is a typical alteration assemblage (e.g. Rabbia et al., 2002). Inclusions of titanite in zircon are also observed in many samples of altered QMD (Fig. 5.7) suggesting that titanite was more abundant in the QMD prior to alteration.

Ta and Nb are both strongly compatible in titanite and Ta is more compatible than Nb ( $D_{Nb} = 7.26$ ,  $D_{Ta} = 84$ ; Prowatke and Klemme, 2005). As a result, the crystallisation of titanite during late-stage magmatic evolution would deplete the residual melt in Nb and Ta, and decrease the Ta/Nb ratio (Stepanov and Hermann, 2013; Stepanov et al., 2014). Low Ta and Nb values are unlikely to be influenced directly by melt redox conditions because both elements occur exclusively as  $Nb^{5+}$  and  $Ta^{5+}$  in terrestrial melts (Burnham et al., 2012) and Nb and Ta partitioning into zircon has been shown experimentally to be independent of  $fO_2$  (Burnham and Berry, 2012). Because partitioning of both elements into zircon is controlled by Henry's Law, zircons would inherit low Nb, Ta, and Ta/Nb from melts that have fractionated titanite.



The co-crystallisation of titanite may also explain why clear fractionation trends are not seen in zircon chemistry with respect to Hf (Fig. 5.18). The usefulness of Hf as an index of fractionation relies on the fact that it is incompatible in residual melts, and so its abundance increases with fractionation. However, Hf is compatible in titanite ( $D_{\text{Hf}} = 18.7$ ; Bachmann et al., 2005), so fractionation of titanite would increase the compatibility of Hf in the crystallising assemblage, and may even generate Hf depletion in residual melts.

Although high  $\text{Eu}/\text{Eu}^*$  values in zircons may occur under oxidising conditions (see 5.2.2),  $\text{Eu}/\text{Eu}^*$  values in excess of 1, as is observed in the low-Ta group, cannot be accounted for by changes in redox alone. Even under highly oxidised conditions,  $D_{\text{Eu}}$  would have partition coefficients intermediate between  $D_{\text{Sm}}$  and  $D_{\text{Gd}}$  (Burnham and Berry, 2012; Trail et al., 2012), so  $\text{Eu}/\text{Eu}^*$  values in excess of 1 must be due, at least in part, to melts and/or fluids that are enriched in Eu with respect to Sm and Gd. REE are strongly compatible in titanite, and MREE are more compatible than LREE ( $D_{\text{Sm}}/D_{\text{La}} = 8.2$ ) or HREE ( $D_{\text{Sm}}/D_{\text{Yb}} = 2.4$ ). Also, Eu ( $D_{\text{Eu}} = 661$ ) is less compatible than Sm or Gd ( $D_{\text{Sm}} = 930$ ;  $D_{\text{Gd}} = 855$ ; Bachmann et al., 2005) so that crystallisation of titanite could relatively enrich the residual melt in Eu.

Simulating the removal of small volumes of titanite from melts of average QMD composition produces hypothetical residual melts with lower  $\text{Dy}/\text{Yb}$  and  $\Sigma\text{REE}$ , and mild positive Eu anomalies (Fig. 5.33 a). Zircons calculated to be in equilibrium with these titanite-fractionated residual melts have REE patterns that closely resemble those of the low-Ta group zircons, with the removal of only 0.2% titanite required to generate these signatures. Zircons calculated to be in equilibrium with melts of average QMD composition more closely match the REE patterns of zircons from the high-Ta group (Fig. 5.33 b).

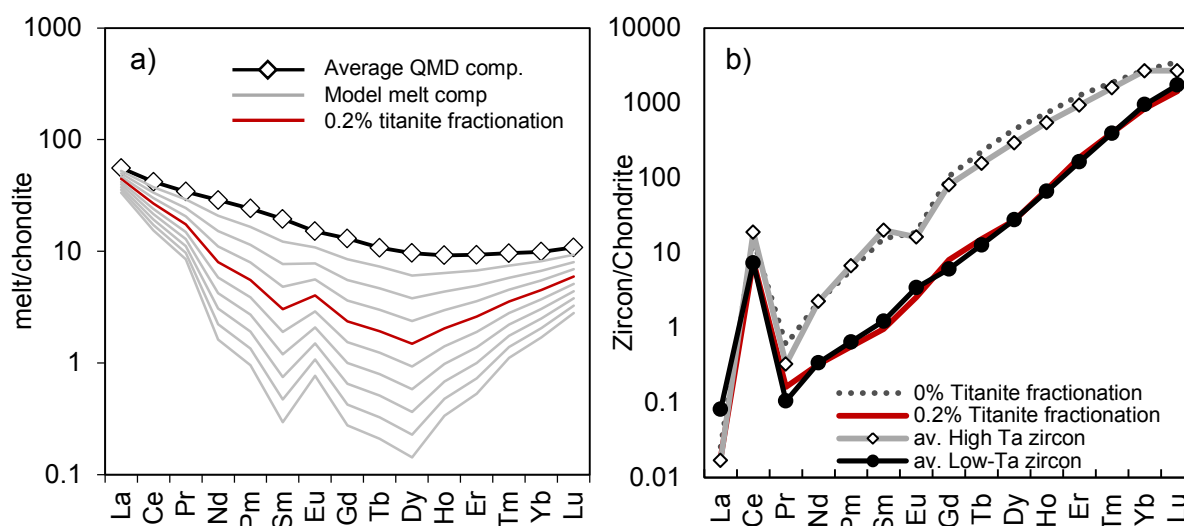


Figure 5.33. Rayleigh fractionation modelling results. a) Chondrite normalised titanite fractionated model melts (grey lines). Each line represents 0.05% titanite crystallisation from the average QMD composition (black line with white diamonds), with 0.2% titanite fractionation highlighted in red. b) Chondrite normalised REE compositions in equilibrium with the average QMD (i.e. 0% titanite fractionated; black dotted line) and 0.2% titanite fractionation (red line). These model patterns are strikingly similar to the observed average REE contents of high- and low-Ta group zircons respectively. Zircon partition coefficients from Sano et al (2002).

These results suggest that co-crystallisation with titanite can exercise a strong control on zircon Ta and REE chemistry, especially Eu anomalies. There is strong petrographic and geochemical evidence for this processes occurring at Oyu Tolgoi. Zircon analyses from zones with titanite inclusions ubiquitously have low Ta, high Eu/Eu\* values, and are depleted in MREE (Yb/Gd), whereas titanite free zones show high Ta, low Eu/Eu\* and low Yb/Gd (Fig. 5.7). Although titanite is only found in oxidised granodioritic rocks (Fig. 5.34), there is no significant difference in Ce/Ce\* ratio between the low- and high-Ta groups (Fig. 5.13 c) so differences in oxidation state are unable to explain such dramatically different Eu/Eu\* values between the two groups. Consequently, the ability of Eu/Eu\* in zircon to record melt redox conditions is compromised by the crystallisation of titanite.

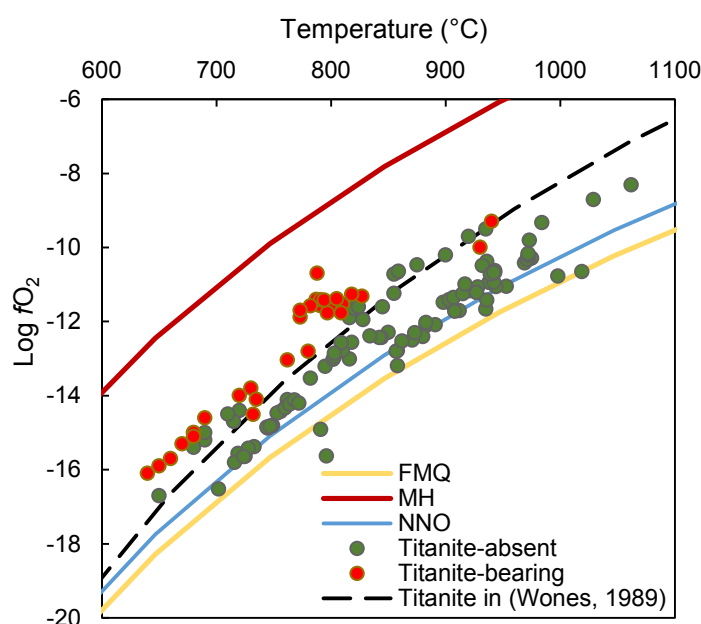


Figure 5.34. A literature compilation of  $T$  and  $fO_2$  data for titanite-bearing and titanite-absent volcanic rocks. Titanite is associated with rocks with redox conditions greater than  $FMQ + 2$ . Dashed line is experimentally-determined titanite stability field of Wones (1989). Sources of data are taken from after Ackerson (2011), after whom the diagram was modified.

It remains unclear what prompted the crystallisation of titanite at Oyu Tolgoi. Other mechanisms for titanite crystallisation which do not involve changes in redox conditions have previously been suggested, such as changes in the Ca/Al ratio of melts (Frost et al., 2000).

### 5.6.2 Determining $Ce^{4+}/Ce^{3+}$ in zircon: theory and practice

The method of Ballard et al. (2002) for calculating  $Ce^{4+}/Ce^{3+}$  faces several practical challenges to its application. The main problem lies in selecting appropriate melt compositions to use for  $Ce_{melt}$  and for calculating  $D_{Ce(3+)}^{zircon/melt}$  and  $D_{Ce(4+)}^{zircon/melt}$ . This is less problematic for zircons in glassy volcanic rocks (Marshall et al., 2009) or where melt inclusions are abundant and may be easily analysed (Thomas et al., 2002), but in plutonic rocks where zircons record a

protracted and complex history of fractional crystallisation, it may not be possible to estimate melt compositions. Ballard et al. (2002) proposed the use of bulk rock geochemistry in place of melt values, but the bulk rock trace element budget does not necessarily reflect melt composition at the time of zircon crystallisation and the disparity between the two may be difficult to estimate. For example, late-stage fractional crystallisation of REE-rich accessory phases (e.g. apatite, titanite) may have a profound effect on the trace element budget of residual melts, although bulk rock values will remain unchanged if those phases are not fractionated (e.g. Glazner et al., 2008). Furthermore, in the case of xenocrystic or detrital zircons (e.g. the Proterozoic inherited zircons from the Resolution rocks), or zircons from strongly hydrothermally altered rocks, not even the context of the bulk rock chemistry remains.

$\text{Ce}^{4+}/\text{Ce}^{3+}$  values calculated by the method of Ballard et al. (2002) are much more sensitive to  $D_{\text{Ce}^{3+}}$  than either of the other melt-dependent variables ( $D_{\text{Ce}^{4+}}$  or  $\text{Ce}_{\text{melt}}$ ; Fig. 5.35 a-c), and therefore constraining  $D_{\text{Ce}^{3+}}$  is critical to the successful estimation of  $\text{Ce}^{4+}/\text{Ce}^{3+}$  using this method. Ballard et al. (2002) calculated  $D_{\text{Ce}^{3+}}$  by assuming its partitioning behaviour is intermediate between neighbouring trivalent cations ( $D_{\text{La}}$  and  $D_{\text{Pr}}$ ), and similarly  $D_{\text{Ce}^{4+}}$  is calculated as intermediate between tetravalent  $D_{\text{Zr}}$ ,  $D_{\text{Hf}}$ ,  $D_{\text{U}}$ , and  $D_{\text{Th}}$ . In the absence of melt compositions, bulk rock values of REE, Hf, Th, U and Zr are used to calculate these partition coefficients. Because zircons from a given rock sample have a wide range of REE concentrations, and these values are all divided by the same bulk rock value, the range of  $D_{\text{Ce}^{3+}}$  values calculated using this approach can vary by up to 3 orders of magnitude for a particular rock (Fig. 5.35 b)

With the exception of Ce and Eu,  $D_{\text{REE}}^{\text{Zircon}}$  values are not sensitive to  $f\text{O}_2$  but do increase with decreasing temperature (Burnham and Berry, 2012; Trail et al., 2012). This can

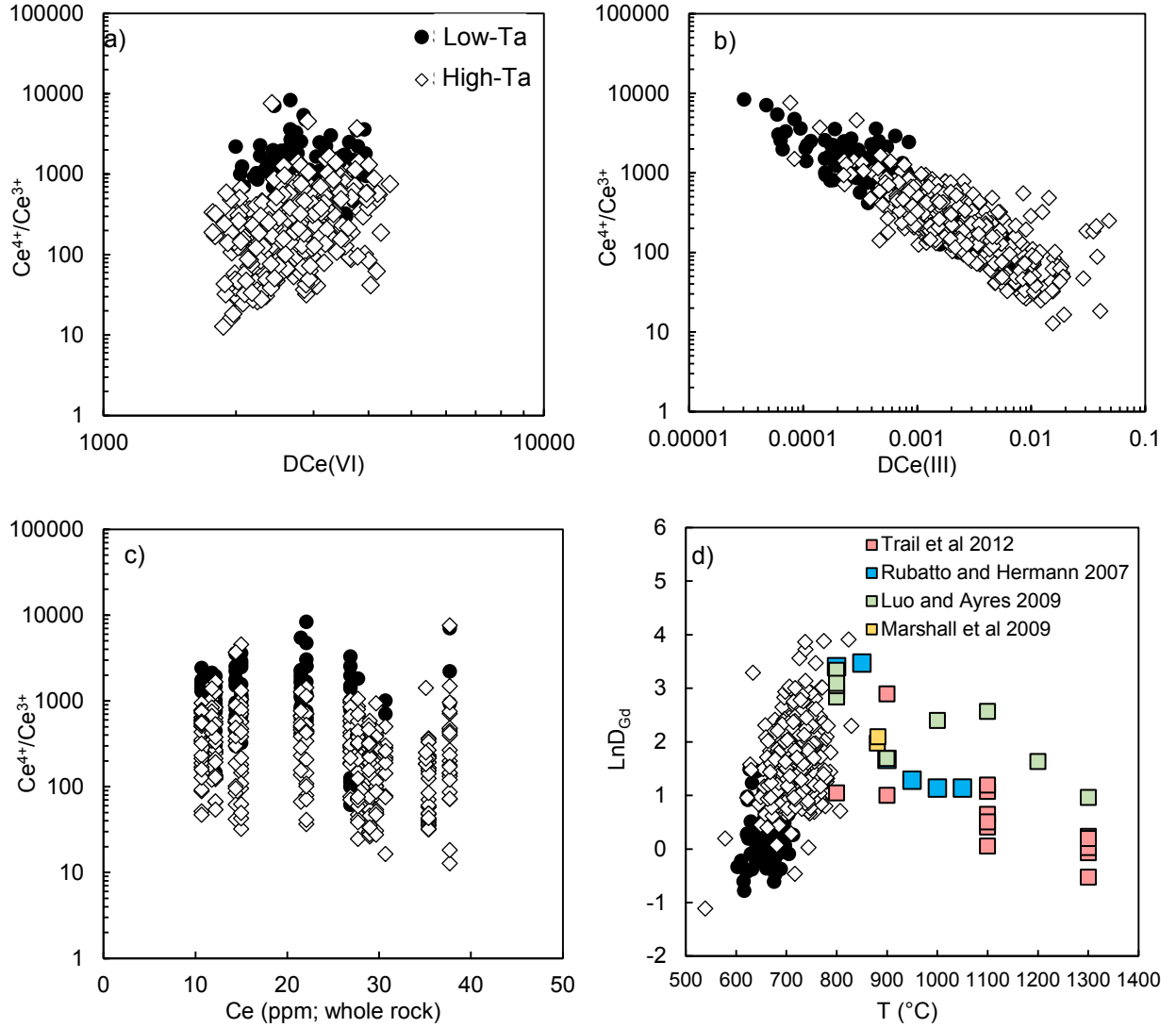


Figure 5.35. (a-c) Calculated  $Ce^{4+}/Ce^{3+}$  for quartz monzodiorite zircons plotted against the parameters which are used in its calculation; (a)  $D_{Ce(VI)}$ , (b)  $D_{Ce(III)}$ , (c) Ce (ppm; whole rock). Of these parameters, the value of  $Ce^{4+}/Ce^{3+}$  is most strongly influenced by  $D_{Ce(III)}$  values. (d)  $LnD_{Gd}$  (zircon/whole rock) calculated for Oyu Tolgoi zircons are not comparable to experimentally-determined  $LnD_{Gd}$  values from the literature. This suggests that using whole rock REE as a proxy for melt leads to unrealistic  $D_{REE}$  partition coefficients, which in turn leads to incorrect values for  $Ce^{4+}/Ce^{3+}$ . Gd is chosen for comparative purposes because it is not redox sensitive. Low-Ta zircons (black circles) and high-Ta zircons (white diamonds) are shown.

be shown by looking at experimental partition coefficients for redox-insensitive REE, such as Gd (Fig. 5.35 d). However, values for  $D_{\text{Gd}}$  calculated by zircon/bulk rock from Oyu Tolgoi decrease with increasing temperature, reaching low  $D_{\text{Gd}}$  values that are more commonly associated with zircons at  $\sim 1200^\circ\text{C}$ . Low-Ta group zircons show especially low  $D_{\text{Gd}}$  values. Because these values do not match experimentally calculated partition coefficients for these temperatures, they are therefore unlikely to represent realistic partition coefficients between the zircons and their parental melts. The explanation for these low values is due to the difference between bulk rock REE content and the actual melt REE content. In the case of the low-Ta zircons, melt  $\Sigma\text{REE}$  was likely to be lower than bulk rock  $\Sigma\text{REE}$  because of the co-crystallisation of titanite (Fig. 5.33 a), perhaps crystallising in small pockets of evolved melt at lower temperature. This would lead to anomalously low values of  $D_{\text{Ce}^{3+}}$ , and correspondingly high values of  $\text{Ce}^{4+}/\text{Ce}^{3+}$ . Any difference between the bulk rock REE content and the actual REE content of the melts from which a given zircon crystallised causes an under or overestimate in  $\text{Ce}^{4+}/\text{Ce}^{3+}$ , which is proportional to the magnitude of the difference between these values. Thus, in cases where the REE content of the bulk rock is not a good approximation for the REE content of the melt (e.g. where titanite has crystallised, but not fractionated), calculated zircon  $\text{Ce}^{4+}/\text{Ce}^{3+}$  may vary considerably without any change in  $f\text{O}_2$ .

A possible solution to this problem is to consider  $D_{\text{Ce}^{3+}}$  as an intermediate value between experimentally determined partition coefficients for La and Pr. However, selecting appropriate partition coefficients is difficult because published values for  $D_{\text{REE}}$  may vary over 3 orders of magnitude at a given temperature (Fig. 5.35 d) which suggests that some melt compositional control on  $D_{\text{REE}}$  zircon may exist.

### 5.6.3 Ce/Ce\*: A measure of melt redox conditions?

A more robust measure of the Ce anomaly is Ce/Ce\*, which produces a quantitative estimation of the Ce anomaly directly from zircon chemistry, with no reference to bulk rock or melt values. Ce/Ce\*, unlike either Eu/Eu\* or Ce<sup>4+</sup>/Ce<sup>3+</sup>, is likely to be independent of melt chemistry in terrestrial magmas because Ce anomalies are rare in igneous melts, and the calculation of Ce/Ce\* does not rely on knowledge of the partitioning behaviour of other REE into zircon.

It has been suggested that the crystallisation of LREE-rich phases (e.g. monazite, titanite) could remove trivalent cations (including Ce<sup>3+</sup>) from the melt, thereby increasing the melt Ce<sup>4+</sup>/Ce<sup>3+</sup> ratio, and driving Ce/Ce\* zircon ratios to high values without any change in melt redox conditions (Claiborne et al., 2010). However, the oxidation state of the melt is likely to be buffered by Fe such that the Ce<sup>4+</sup>/Ce<sup>3+</sup> ratio would be unaffected by minor Ce<sup>3+</sup> removal. The fact that there is no clear variation of Ce/Ce\* with any proxy for titanite fractionation supports this notion (Fig. 5.36). Consequently, Ce/Ce\* ratio is likely to be the most robust measure of ambient magma redox conditions in zircon. Despite this, the difficulties in determining Ce/Ce\* precisely preclude it from being an accurate oxybarometer. For example, experimentally calibrated estimates of  $fO_2$  which use the Ce anomaly (e.g. Trail et al., 2012) produce values of  $fO_2$  derived from zircons from this study that have an unrealistically wide interquartile range and high median (c.f. Dilles et al., 2015). We therefore suggest that zircon Ce/Ce\*, calculated using Eq. 5.4, may be used but only as a semi-quantitative measure of magma redox conditions.

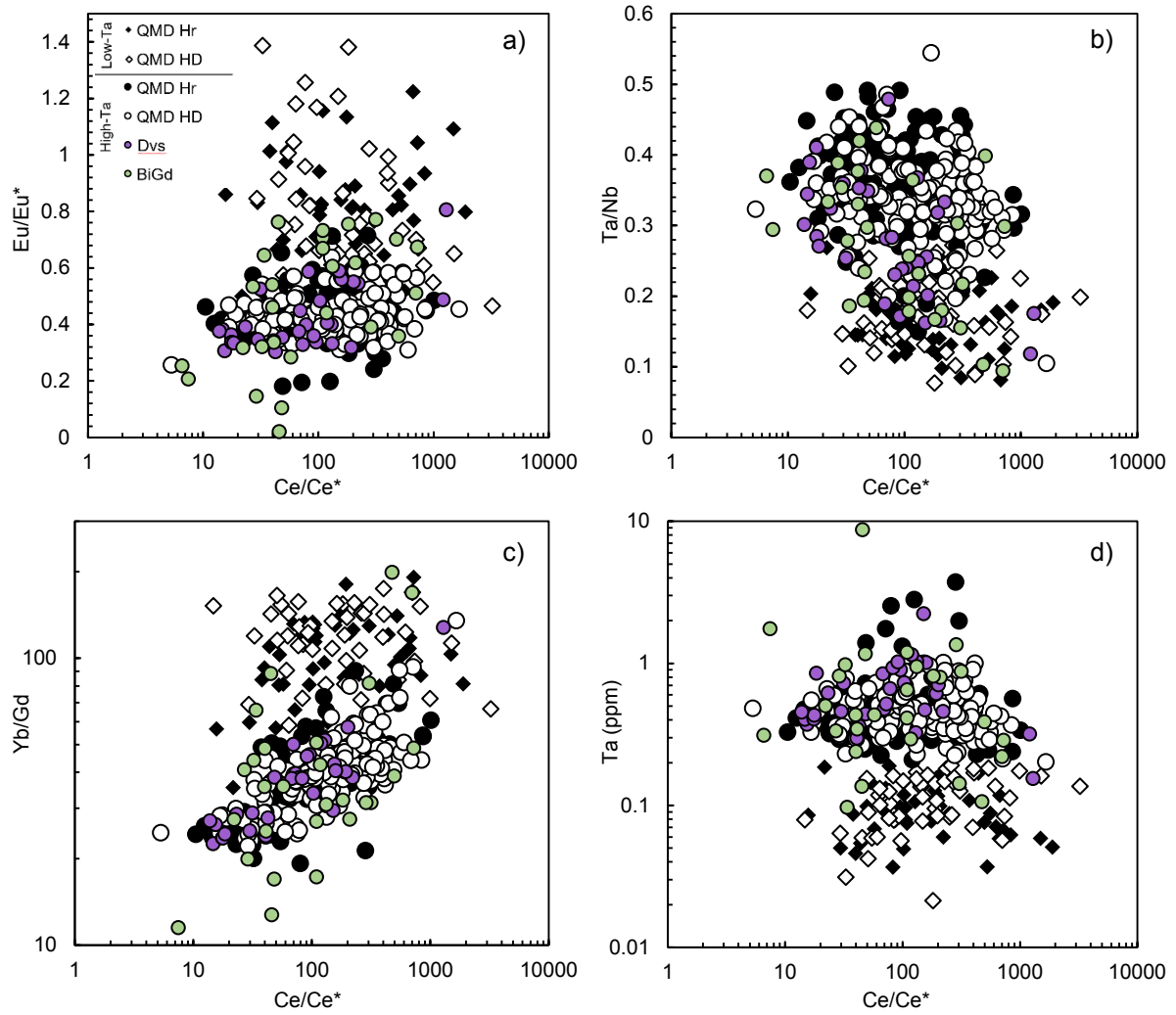


Figure 5.36. Variation of  $Ce/Ce^*$  with parameters which are strongly controlled by titanite crystallisation: (a)  $Eu/Eu^*$ , (b)  $Ta/Nb$ , (c)  $Yb/Gd$ , and (d)  $Ta$ , for Oyu Tolgoi zircons. Strong correlations do not exist for these elements, suggesting that titanite crystallisation does not affect  $Ce/Ce^*$  values, and is not triggered by (or accompanied by) a large increase in oxidation state.

#### 5.6.4 Zircon chemical evolution: a case study from the Resolution

Unlike at Oyu Tolgoi, clear fractionation trends are seen in zircon chemistry with respect to Hf (e.g. Fig. 5.31), which allows the temporal evolution of zircon chemistry (including fertility indicators) to be assessed.



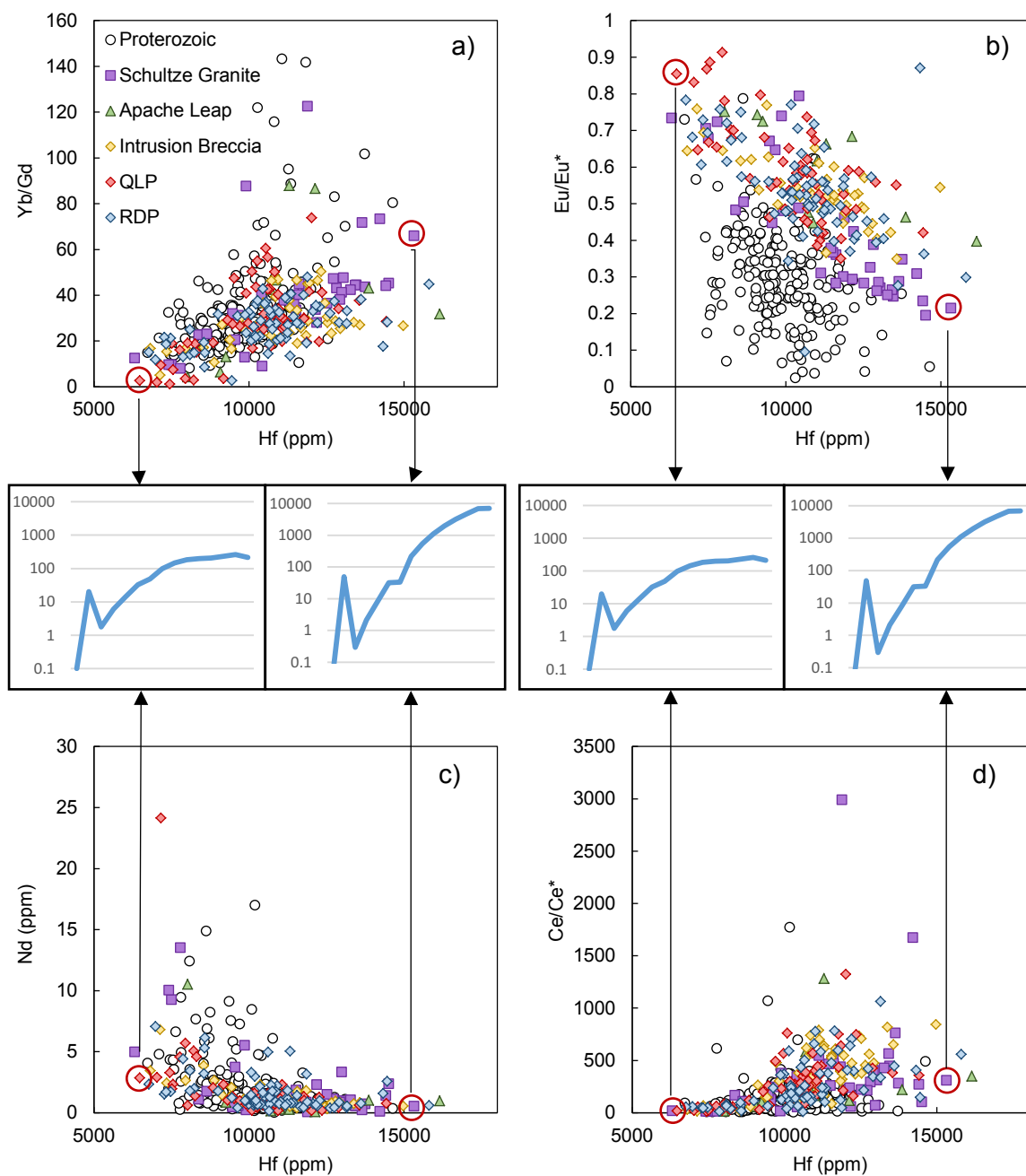


Figure 5.37. The evolution of REE patterns with increased Hf (as a proxy for melt fractionation). a) Yb/Gd, a measure of the extent of HREE enrichment with respect to MREE, b) Eu/Eu\*, c) Nd (LREE), d) Ce/Ce\*. Chondrite normalised REE patterns for selected analyses at either end of the fractionation sequence are presented to show how REE patterns vary from 'primitive' (low Hf) to 'fractionated' (high Hf). All data collected by LA-ICP-MS.

In general, REE decrease with increased fractionation in the whole rock data for Resolution (see Chapter 3). At lower temperature, REE partition mores strongly into zircon (e.g. Trail et al., 2012, Burnham and Berry, 2012) which may explain why the concentration of HREE increases with fractionation (Fig. 5.37 a). However, this may not account for decreases in LREE with increased fractionation (Fig. 5.37 c). These observations have been made of zircons from other systems (e.g. Claiborne et al., 2010). The relative magnitude of LREE and HREE partition coefficients do not change with decreasing temperature (e.g. Trail et al., 2012), so this divergence in the behaviour of L- and HREE is likely due to significant depletion in the melt concentration of LREE with respect to HREE. Melt depletions have to be significant enough to overcome the effects of increasing LREE compatibility at lower temperature.

One likely reason for the LREE depletion is the co-crystallisation of monazite, which is a common accessory phase in in the Schultze Granite, and is less common but still present in the Resolution intrusions. Co-precipitation of monazite would cause the melt to become significantly depleted in L- to MREE, due to their strong compatibility in monazite ( $D_{Gd}$  up to 1900; Stepanov et al., 2012). Partition coefficients for HREE into monazite are two orders of magnitude smaller, so the effect of monazite crystallisation on HREE chemistry of residual melts will be significantly less. As a result, zircons crystallising in progressively fractionated magmas would become depleted in LREE, but may become enriched in HREE due to its increased compatibility in zircon at lower temperature.

Eu/Eu\* values change systematically with fractionation such that the most primitive zircon concentrations (i.e. lowest Hf) have the highest Eu/Eu\* values (Fig. 5.37 b). This likely reflects the small Eu anomalies of primitive melts (MORB Eu/Eu\*  $\approx$  1; Rollinson, 1993). Progressive fractionation of feldspar would cause a decrease in melt Eu/Eu\*, which is mirrored in the zircon chemistry. Although monazite may cause some fractionation between Eu and

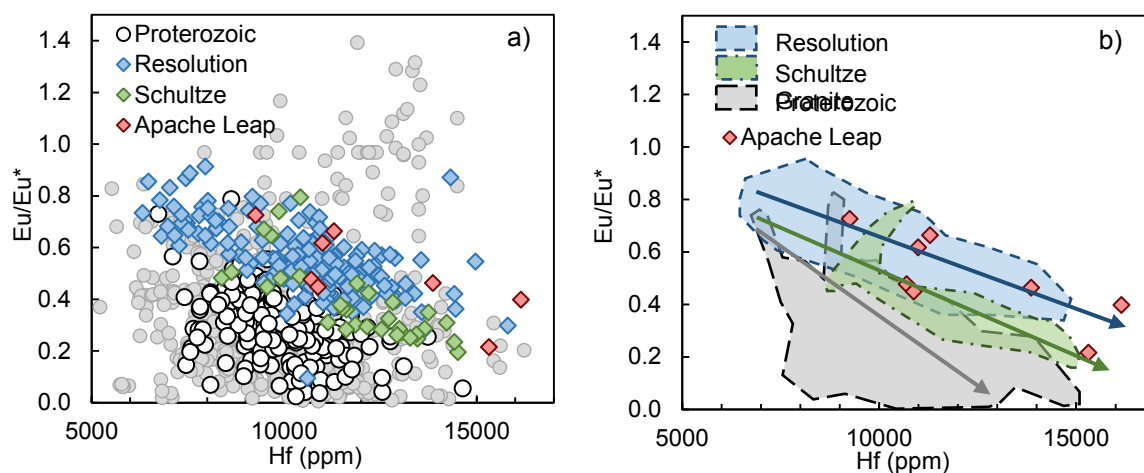


Figure 5.38. Decreasing  $Eu/Eu^*$  with increasing Hf for Resolution zircons. (a) Grey circles are data from the literature, which broadly follow the trend for the Proterozoic zircons. (b) The data fields for zircons from this study. At a given Hf content, Proterozoic zircons have lower  $Eu/Eu^*$  than Schultze Granite zircon, which have lower  $Eu/Eu^*$  values than zircons from the Resolution intrusions. Sparse data from the felsic Apache Leap intrusions follow the trend of the Resolution data. Arrows indicate evolutionary trends for each group.

other REE (Stepanov et al., 2012), the effect is much smaller than for titanite, meaning Eu anomalies are largely controlled by the crystallisation of plagioclase. Zircons from the barren dataset and the Proterozoic inherited zircons at Resolution, have lower  $Eu/Eu^*$  values for a given Hf content compared to zircons from the Resolution intrusions, Apache Leap intrusions, or Schultze Granite (Fig. 5.38). These same trends are seen in zircons from other porphyry systems (Dilles et al., 2015), where zircons from barren intrusions show steeper trends of decreasing  $Eu/Eu^*$  with increasing fractionation than zircons from fertile intrusions.

In summary, the evolution of zircon trace element chemistry is strongly influenced by co-precipitation with (or equilibrium with) other mineral phases, especially REE-bearing accessory phases. At Resolution, monazite causes LREE depletion in zircon with increasing fractionation. At Oyu Tolgoi, the co-precipitation of titanite causes a depletion in MREE, and an increase in  $Eu/Eu^*$  values.

### 5.6.5 Hydrothermal zircons at Oyu Tolgoi

The group of ‘mottled’ zircons from sample OT-103 are chemically and texturally unlike any other zircons sampled in this study, and are also dissimilar to other zircon populations (the low- and high-Ta group) found in the same rock. However, they are very similar to hydrothermal zircons in altered granitic rocks, thought to have precipitated from fluid-saturated melts (e.g. Hoskin and Schaltegger, 2003; Pettke et al., 2005). Zircons that are unequivocally of hydrothermal origin are found as small mineral inclusions in vein quartz in association with fluid inclusions (Schaltegger et al., 2007), although a hydrothermal origin for zircon grains in igneous rocks may be inferred from texture (containing abundant fluid inclusions), host rock composition (i.e. hydrothermally altered mafic rocks may carry zircons) and by chemical comparison with magmatic zircons from the same rock.

Hydrothermal zircons are rare with respect to magmatic zircons, and previous studies have shown them to have a diverse and unsystematic range of chemical characteristics. For example, hydrothermal zircons from the Boggy Plain pluton have elevated REE, Nb, and Ta compared to igneous zircon from the same rocks (Hoskin et al., 1998), whereas hydrothermal zircon from the Mole Granite are depleted in REE, Nb, and Ta with respect to local igneous zircon (Pettke et al., 2005; Fig. 5.39 a,b).

Most hydrothermal zircons from sample OT-103 have the same elevated REE seen in the Boggy Plain pluton, except for 2 analyses which display REE patterns that are more similar to igneous zircon (Fig. 5.39 c). Pb is strongly incompatible in zircon crystallising from melt (e.g. Finch et al., 2001), so the elevated common Pb contents observed in these mottled zircons (Table 5.4) is likely to be the result of crystallisation from fluids that are enriched in Pb (Pettke et al., 2005). High common Pb contents have been generated in synthetic zircon grown from Pb-rich hydrothermal solutions (e.g. Watson et al., 1997). Pb partitions strongly into high-salinity hydrothermal fluids, due to its propensity to form aqueous chloride complexes (Audétat

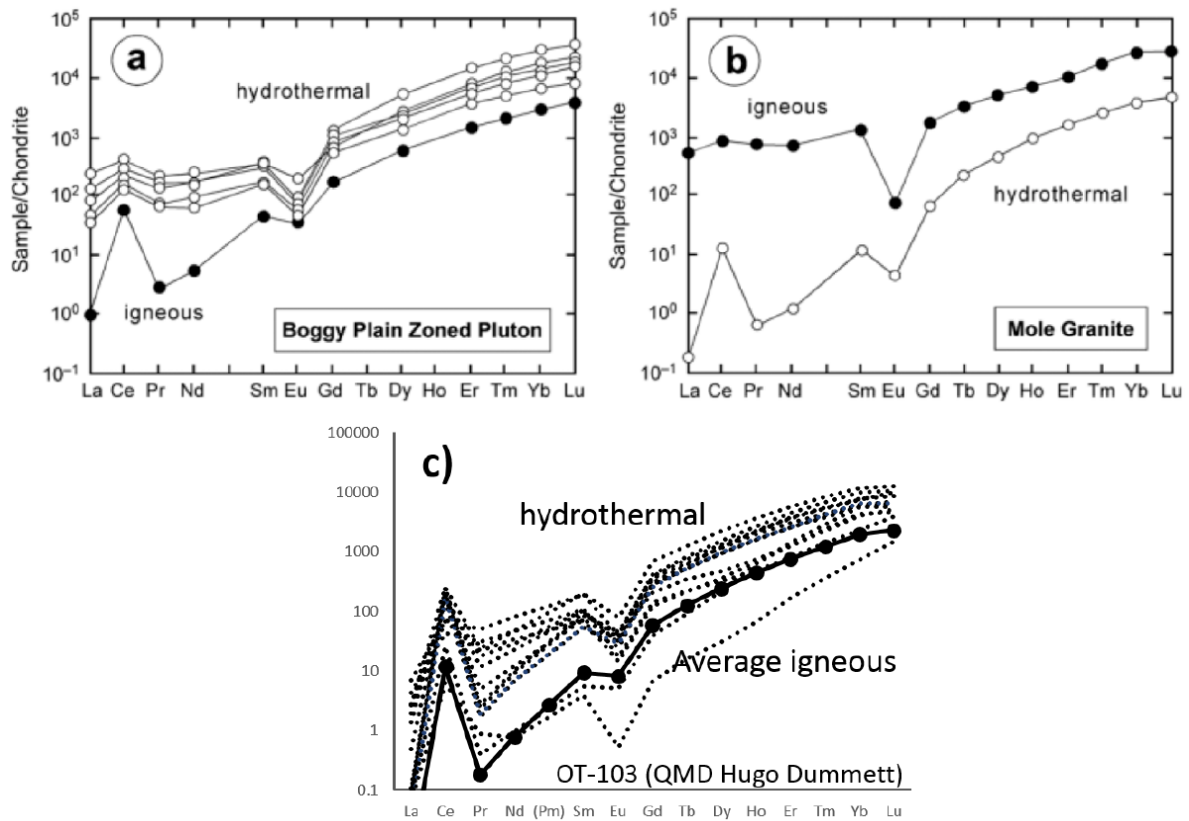


Figure 5.39. Comparison between the REE patterns of igneous and hydrothermal zircons from literature data. (a) the Boggy Plain Pluton; (b) the Mole Granite; and (c) the mottled hydrothermal zircons from OT-103. The latter most closely resemble the Boggy Plain Pluton hydrothermal zircons, including a small Ce anomaly and similarly elevated Pb, Nb and Ta (not shown). Hydrothermal zircon is rare at Oyu Tolgoi, and only found in one sample. Literature data from Pettke et al (2005).

et al., 2008; Zajacz et al., 2008) and REE are also compatible in high-salinity hydrothermal fluids, in particular the LREE (Reed et al., 2002). Such fluids may also preferentially partition Sm and Gd over Eu, causing them to carry a negative Eu anomaly that may be passed on to subsequent minerals. The chemistry of the hydrothermal zircon at Oyu Tolgoi is thus consistent with precipitation from a high-salinity fluid. Fluid inclusion data for Oyu Tolgoi are sparse and, although no data exist for Hugo Dummett, fluids with up to 22.6 wt. % NaCl equivalent have been observed in A-type quartz veins at Central Oyu (Muller et al., 2010).

## 5.7 Concluding remarks

Zircons from Oyu Tolgoi and Resolution contain elevated  $\text{Eu}/\text{Eu}^*$ ,  $\text{Ce}/\text{Ce}^*$ , and  $\text{Ce}^{4+}/\text{Ce}^{3+}$  compared to zircons from barren rocks. The conventional interpretation of such signatures would be that they indicate highly oxidised conditions in porphyry magmas. However, there are some problems with such an interpretation.

- $\text{Eu}/\text{Eu}^*$  at Oyu Tolgoi are often in excess of 1. This cannot be achieved by redox conditions alone, as the most oxidised system would have no Eu anomaly (i.e.  $\text{Eu}/\text{Eu}^* = 1$ ). Values in excess of unity must indicate melt enriched in Eu.
- Significant titanite is present as micro-inclusions in zircons from Oyu Tolgoi. This is significant because titanite has the potential to locally, drastically increase melt  $\text{Eu}/\text{Eu}^*$  ratios, because of the unequal partitioning of Sm and Gd over Eu. If titanite crystallises but is not fractionated, then such changes in melt chemistry would not be observed in whole rock geochemistry (i.e. whole rock REE  $\neq$  melt REE if titanite crystallises).
  - In the zones where titanite inclusions are found, zircons have elevated  $\text{Eu}/\text{Eu}^*$ ,  $\text{Ce}^{4+}/\text{Ce}^{3+}$ , and Yb/Gd (i.e. MREE depletion). Modelling zircon compositions in equilibrium with variably titanite-crystallised melts demonstrates that such characteristics may be expected of zircons in equilibrium with small amounts of titanite ( $\sim 0.2$  vol. %).
- As the calculation of  $\text{Ce}^{4+}/\text{Ce}^{3+}$  relies on the assumption that whole rock REE = melt REE, the crystallisation of titanite may also cause overestimates in this parameter.
- These results demonstrate that calculated  $\text{Ce}^{4+}/\text{Ce}^{3+}$  and  $\text{Eu}/\text{Eu}^*$  values of zircon are not *necessarily* useful proxies for the oxidation state of granitic magmas because both values may be affected by the crystallisation of REE-bearing accessory phases. Crystallising small volumes of these phases (e.g. titanite) can cause a large changes in

these parameters in zircon which are potentially unrelated to changes in redox conditions.

- $\text{Ce}/\text{Ce}^*$  is unlikely to be affected by the crystallisation of any REE-bearing phase, because no phase preferentially takes Ce from the melt over La or Pr (or vice versa), with the exception of zircon itself, which does not crystallise in significant abundances. Thus,  $\text{Ce}/\text{Ce}^*$  may represent the most faithful measure of melt redox. However, there are significant difficulties in measuring this ratio, as La and Pr are frequently below detection limit in zircon.

## Chapter 6: Apatite

### 6.1 Introduction

Apatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH},\text{Cl})$ ] is the most abundant phosphate mineral in a wide variety of rock types and is a common accessory phase in intermediate to silicic igneous rocks. The classification of apatite is based on halogen chemistry, with three main end members: fluorapatite, chlorapatite, and hydroxyapatite. A complete solid solution is thought to exist between these end members, with fluorapatite being by far the most common type found in terrestrial rocks (Deer et al., 1992). Apatite contains a diverse range of trace elements due to several permissible anion and cation substitutions. REE are all strongly compatible in apatite, especially La and Ce (Prowatke and Klemme, 2006) which, together with Si, Mn, Fe, and Na, may account for 1000s of parts per million for each element (Belousova et al., 2002a).

Apatite plays an important role in understanding igneous petrogenesis because the crystallisation and fractionation of apatite significantly depletes melts in  $\text{P}_2\text{O}_5$  (e.g. Hoskin et al., 2000) and it can account for a significant proportion of the REE and Y budget of granitic rocks (e.g. Jefferies, 1985). Apatite also hosts appreciable concentrations of radiogenic elements (U, Pb, and Th). U-Pb and Th-Pb dating of apatite by LA-ICP-MS is becoming more widely used in geochronological studies as methods are developed to overcome the problems of its low U and Th concentrations and relatively high common Pb content (e.g. Chew et al., 2011). Fission track dating of apatite is already widely used to investigate the tectonic and thermal history of rocks in a large number of environments, including in porphyry systems (Maksaev and Zentilli, 1999; McInnes et al., 1999). Apatite may also provide a robust record of melt redox conditions (Miles et al., 2014) and trace element evolution (e.g. Chu et al., 2009), which makes it especially useful in provenance studies (Jennings et al., 2011).



In porphyry Cu deposits, apatite occurs as both primary igneous phenocrysts and hydrothermal grains. It is found in deposits from a variety of arcs and tectonic settings, including Chuquicamata (Maksaev and Zentilli, 1999; McInnes et al., 1999), Los Pelambres (Bertens et al., 2006; Perelló et al., 2012), Pebble (Lang and Gregory, 2012), Grasberg (Weiland and Cloos, 1996; Leys et al., 2012), and many examples from southwestern North America (Dilles et al., 1987; Streck and Dilles, 1998; Levielle and Stegen, 2012).

## 6.2 Background

### 6.2.1 Substitution mechanisms in apatite

Apatite consists of phosphate tetrahedra linked to two calcium polyhedral sites, bound to 9 oxygens (Ca1) or 6 oxygens and the halogen group (Ca2). The most common cation substitution in natural apatites is direct divalent cation substitution for  $\text{Ca}^{2+}$ , in which  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Pb}^{2+}$  are the most common cations involved. Some of these, especially  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , and  $\text{Pb}^{2+}$ , show strong preference for the Ca2 site, although this decreases as the concentration of substituting divalent cations increases (Pan and Fleet, 2002; and references cited therein). Conversely, Mn has a preference for the Ca1 site, although this also decreases with increasing Mn concentration. Results of investigations into  $\text{Fe}^{2+}$  substitution are ambiguous, showing a random distribution at low  $\text{Fe}^{2+}$  concentrations, and preference for Ca1 (Khudolozhkin et al., 1974) or Ca2 (Hughes et al., 1993) at higher Fe.

Trivalent cations ( $\text{REE}^{3+}$ ), and monovalent cations ( $\text{Na}^+$ , subordinate K, Li, Rb) require coupled substitutions to maintain charge balance. A common substitution is:



REE<sup>3+</sup> cations may also form part of a coupled substitution with tetravalent cations (e.g. Si<sup>4+</sup>) in the following coupled relationship:



Tetravalent cations (Th<sup>4+</sup>, U<sup>4+</sup>) can also substitute into apatite at the expense of Ca<sup>2+</sup>, as follows:



where  $\square$  indicates the presence of a Ca-deficiency vacancy.

Sulphur (S<sup>6+</sup>) and Si<sup>4+</sup> substitute into apatite in a coupled substitution involving P (Rouse and Dunn, 1982; Core, 2004), and with Na<sup>+</sup> in a coupled substitution for Ca and P (Liu and Comodi, 1993). Both substitutions are likely to be important in igneous systems (Peng et al., 1997; Streck and Dilles, 1998). As sulphur only substitutes into apatite as sulphate (S<sup>6+</sup>), only apatites crystallising from oxidised magmas may contain significant S (Parat et al., 2011). In such magmas, the sulphur content of apatite directly reflects that of the melt (Peng et al., 1997; Streck and Dilles, 1998).

### 6.2.2 Redox sensitivity

Several potentially redox sensitive cations substitute into apatite. Mn partitioning may be independent of melt composition, and largely redox controlled (Miles et al., 2014). This is because Mn<sup>2+</sup> has a more similar ionic radius to Ca<sup>2+</sup> than Mn<sup>3+</sup>, so apatite from more reduced melts may have higher Mn contents. Miles et al. (2014) determined the following expression for the redox sensitivity of Mn in apatite:

$$\log fO_2 = -0.0022 (\pm 0.0003) \times \text{Mn (ppm)} - 9.75 (\pm 0.46) \quad (6.4)$$

$\text{Eu}^{3+}$  has an ionic radius closer to  $\text{Ca}^{2+}$  than  $\text{Eu}^{2+}$  does (Sha and Chappell, 1999; Prowatke and Klemme, 2006) so oxidised melts or fluids with high  $\text{Eu}^{3+}/\text{Eu}^{2+}$  will partition Eu more strongly into apatite. Although no experimental work on Fe redox sensitivity in apatite has been produced to date,  $\text{Fe}^{2+}$  has been predicted to partition into apatite in a similar way to Mn (Miles et al., 2014), and the presence of  $\text{Fe}^{2+}$  has been determined by Mössbauer spectroscopy (Khudolozhkin et al., 1974). However, the concentration of Fe and Eu in apatite may also be controlled by the crystallisation of other phases that are Fe- (magnetite, biotite, hornblende) or Eu-rich (plagioclase, monazite, titanite). Phases that partition Mn (magnetite, hornblende, biotite) either do not partition Mn strongly enough, or do not crystallise abundantly enough to significantly affect the partitioning of Mn into apatite over typical ranges of silica content (Miles et al., 2014).

### 6.2.3 Halogen cation exchange between apatite and fluids

The partitioning of halogens between aqueous fluids or melts and apatite has been studied extensively (e.g. Zhu and Sverjensky, 1992; Korzhinsky, 1981; Piccoli and Candela, 1994). Based on experimental data, the fluid and melt Cl content can be estimated. The Cl content of a fluid in equilibrium with apatite ( $C_{Cl}^{aq}$ ) varies as a function of the molar fraction of apatite composition, temperature, and pressure:

$$C_{Cl}^{aq} = \frac{\frac{X_{Cl}^{Ap}}{X_{OH}^{Ap}} \cdot \frac{3.54 \times 10^7}{18} \cdot \frac{1}{10^{[0.04661 + \frac{2535.8}{T} - \frac{0.0303 \cdot (P-1)}{T}]}}}{10^{(-0.63 - 0.00035 \cdot P)}} \quad (6.5)$$

where  $X_{Cl}^{Ap}$  and  $X_{OH}^{Ap}$  are the mole fractions of Cl and OH in apatite, T is temperature in Kelvin, and P is pressure in bars. The melt concentration of Cl ( $C_{Cl}^l$ ) may also be estimated in a similar fashion, using:

$$C_{Cl}^l = \frac{\frac{X_{Cl}^{Ap}}{X_{OH}^{Ap}} \cdot \frac{3.54 \times 10^7}{18} \cdot \frac{1}{10 \left[ 0.04661 + \frac{2535.8}{T} - \frac{0.0303 \cdot (P-1)}{T} \right]}}{D_{Cl}^{aq/l} \cdot 10^{(-0.63 - 0.00035 \cdot P)}} \quad (6.6)$$

where  $D_{Cl}^{aq/l} = 3.75 + 19.8 \cdot P$  (kbars).

Experimental studies have demonstrated that halogen re-equilibration in apatite is very slow at sub-solidus temperatures (500 to 600°C: Ekstrom, 1973; Latil and Maury, 1977). Oscillatory zoning is typically absent in apatites from plutonic rocks that have a protracted post-crystallisation thermal history, an observation which could indicate sub-solidus re-equilibration. However, the absence of zoning is also common in apatites from volcanic rocks, which cool much more rapidly, suggesting that post-crystallisation re-equilibration is not an issue (see Piccoli and Candela, 1994).

#### 6.2.4 Stability in igneous and hydrothermal systems

The solubility of  $P_2O_5$  in silicate melts is low which, along with the low compatibility of  $P_2O_5$  in other major rock forming minerals, accounts for the relative abundance of apatite as an accessory phase in igneous rocks (Piccoli and Candela, 2002). Apatite saturation in igneous systems may be induced by decreasing the temperature, or increasing the  $P_2O_5$  and  $SiO_2$  content of magmas. These competing variables may be described by the following expression, from Harrison and Watson (1984):

$$T = \frac{[26400 \cdot C_{SiO_2}^l - 4800]}{[12.4 \cdot C_{SiO_2}^l - \ln(C_{P_2O_5}^l) - 3.97]} \quad (6.7)$$

where  $T$  is the temperature of apatite saturation (K), and  $C_{SiO_2}^l$  and  $C_{P_2O_5}^l$  are the fractions of  $SiO_2$  and  $P_2O_5$  in the melt at the moment of apatite saturation. As a result of this relationship, apatite is a relatively late-crystallising phase in mafic systems, and crystallises more readily in lower temperature, higher  $SiO_2$  melts (e.g. granitic systems). Studies of purely hydrothermal apatite are rarer than those of igneous apatite, and tend to focus on its occurrence in magnetite-apatite deposits (e.g. Bath et al., 2013) or in pegmatites (e.g. Ámli, 1975; Liu and Zhang, 2005), although its occurrence in hydrothermal systems associated with porphyry deposits has been noted (e.g. Williams and Cesbron, 1977).

#### 6.2.5 Apatites from I-type and S-type granites

Previous studies have noted differences between apatites from I-type intermediate rocks, and S-type or fractionated (felsic) I-type granites (with silica values up to 76 wt. %  $SiO_2$ ; Sha and Chappell, 1999; Hsieh et al, 2008; Chu et al, 2009). The primary differences are seen in the LREE, which are depleted in apatite from S-type and felsic I-type granites relative to intermediate I-type rocks. This has been linked to the co-crystallisation of LREE-enriched monazite, which is more stable and less soluble in peraluminous melts (Sha and Chappell, 1999). Also, apatites from S-type and felsic I-type granites have higher Mn and Fe contents and lower  $Eu/Eu^*$ , owing to the fact that these magmas are typically more reduced than metaluminous, less fractionated I-type magmas. Apatites from S-type granites also tend to have lower Cl, Sr, and higher F (e.g. Chu et al., 2009).

## 6.2.6 Usefulness as an indicator mineral of porphyry Cu fertility

Apatite is a potentially important mineral indicator of porphyry fertility for a variety of reasons. First, its abundance in igneous rocks means grains may be analysed *in situ* from thin section. Consequently, chemical analyses can be understood in the textural context of the grain within the rock, and this also avoids the need for costly mineral separation. Apatite also crystallises in purely magmatic, magmatic-hydrothermal, and purely hydrothermal environments and, as a result, it has the potential to record the geochemical conditions of a fertile magmatic-hydrothermal system through much of its lifetime, although late-stage acidic alteration can be apatite-destructive. Critically, apatite contains elements that have been identified as displaying systematically different behaviour in whole rock data from barren and fertile systems (e.g. Sr, Y, Eu) and apatite itself has been shown to vary in terms of its Cl and S contents. Many of these trace elements are sufficiently abundant in apatite to be analysed by EPMA.

Given that igneous rocks from fertile porphyry intrusions are typically elevated in Sr compared to barren arc magmas at a given SiO<sub>2</sub> (see Chapter 1), and that the Sr content of apatite is strongly sensitive to melt concentrations of Sr (e.g. Jennings et al., 2011), apatites from fertile porphyry systems may be predicted to be Sr-rich, and could preserve this signature even if the chemistry of the whole rock has been compromised by hydrothermal alteration.

Apatite may also provide a record of the evolution of halogens in melts and hydrothermal fluids. This has implications for the potential of apatite as an indicator of fertility, because Cl-bearing fluids are likely to play an important role in the transport of metals in porphyry systems and other ore deposits (see Chapter 1). Limited studies of apatite in felsic rocks associated with porphyry deposits have shown that this tends to have high Cl (>5 molar % of halogen site; Piccoli and Candela, 2002), thought to reflect the high salinity of the fluids in equilibrium with it during formation. Hydrothermal apatites from mineralised granitic

systems may also contain elevated Cl contents compared to barren granites (Roegge et al., 1974).

#### 6.2.7 Focus of this chapter

The textural and geochemical characteristics of apatite from mineralised porphyry intrusions and associated unmineralised igneous rocks at Resolution and Oyu Tolgoi are the primary focus of this chapter. In addition, these characteristics are compared with literature data on apatite from other arcs worldwide. In particular, this chapter considers:

1. The textural and chemical differences between magmatic and hydrothermal apatite;
2. The extent to which apatite records the host bulk rock chemistry, especially elements that are considered to be important in porphyry fertility studies (e.g. Sr, Y, Eu);
3. The differences between the chemistry and texture of apatites from barren and fertile arcs or arc segments;
4. The differences between the chemistry and texture of apatites from high- and low-Cu grade porphyry systems (specifically, Hugo Dummett and Heruga at Oyu Tolgoi).

### 6.3 Methods

A summary of the analytical work carried out on apatites from Resolution and Oyu Tolgoi is presented in Table 6.1. At Resolution, EPMA analyses were conducted for one sample from the Schulte Granite (R-S-11), felsic Apache Leap apatite (R-RF-G), 6 Resolution porphyry intrusion samples (dominant-type, vein-type and dull-CL apatite), and apatites from the hydrothermal breccia matrix. LA-ICP-MS analyses were done on 11 samples containing apatite from the Resolution intrusions; 4 from the QLP, and 6 from the RDP (one of which was a clast of RDP in the hydrothermal breccia). Apatites were also analysed from 4 rocks from the

| Sample Name       | Rock type | Apatite type | # analyses |      | analysed from     | Whole rock chemistry |          |          | Vol. % (from CIPW) |
|-------------------|-----------|--------------|------------|------|-------------------|----------------------|----------|----------|--------------------|
| <b>Oyu Tolgoi</b> |           |              | LA-ICP-MS  | EPMA |                   | Cu (ppm)             | Mo (ppm) | Au (ppm) |                    |
| OT-11             | BiGd      |              | 24         | 31   | mounted separates | 13                   | <1       | 0.004    | 0.39               |
| OT-77             | BiGd      |              | 17         |      | thin section      | 39                   | <1       | 0.003    | 0.36               |
| OT-117            | BiGd      |              | 21         |      | thin section      | 5690                 | 1        | 0.094    | 0.45               |
| OT-13             | BiGd      |              | 23         |      | thin section      | 76                   | 1        | 0.052    | 0.50               |
| OT-56             | Dvs       |              | 20         | 27   | thin section      | 71                   | <1       | 0.004    | 0.52               |
| OT-158            | Dvs       |              | 20         | 23   | thin section      | 22                   | <1       | <0.001   | 0.57               |
| OT-125            | QMD HD    | S-Ap         | 11         | 22   | thin section      | 28900                | 2        | 1        | 0.28               |
| OT-67             | QMD HD    | S-Ap         | 20         |      | thin section      | 9730                 | 3        | 0.072    | 0.24               |
| OT-69             | QMD HD    | S-Ap         | 25         | 24   | mounted separates | 12450                | 0.5      | 0.604    | 0.62               |
| OT-94             | QMD HD    | S-Ap         | 19         |      | mounted separates | 2440                 | 47       | 0.063    | 0.16               |
| OT-139            | QMD HD    | S-Ap         | 25         | 25   | mounted separates | 16550                | 1        | 0.823    | 0.10               |
| OT-133            | QMD HD    | S-Ap         | 18         | 21   | mounted separates | 6990                 | 4        | 0.112    |                    |
| OT-121            | QMD HD    | S-Ap         | 10         | 35   | mounted separates | 12750                | 24       | 0.834    | 0.16               |
| OT-81             | QMD HD    | S-Ap         | 25         | 25   | mounted separates | 4100                 | 5        | 0.41     | 0.14               |
| OT-51             | QMD HD    | S-Ap         | 14         | 26   | thin section      | 2520                 | 78       | 0.395    | 0.20               |
| OT-19             | QMD Hr    | S-Ap         | 10         |      | mounted separates | 1845                 | 17       | 0.091    |                    |
| OT-49             | QMD Hr    | S-Ap         | 12         | 11   | thin section      | 882                  | 13       | 0.101    | 0.28               |
| OT-37             | QMD Hr    | S-Ap         | 19         | 16   | thin section      | 3770                 | 75       | 0.137    | 0.62               |
| OT-21             | QMD Hr    | S-Ap         | 23         | 28   | mounted separates | 2610                 | 6        | 0.145    |                    |
| OT-40             | QMD Hr    | S-Ap         | 21         |      | mounted separates | 9460                 | 137      | 0.362    |                    |
| OT-149            | QMD SW    | S-Ap         | 14         | 12   | thin section      | 118                  | 2        | 0.009    | 0.45               |
| OT-146            | QMD SW    | S-Ap         | 20         |      | thin section      | 299                  | 0.5      | 0.037    | 0.43               |
| OT-143            | QMD SW    | M-Ap         | 24         | 26   | thin section      | 391                  | <1       | 0.011    | 0.44               |
| OT-45             | QMD Hr    | M-Ap         | 44         | 44   | thin section      | 185                  | 2        | 0.011    | 0.36               |

Table 6.1. Summary of analytical work conducted on apatite.



| Sample Name       | Rock type            | Apatite type               | # analyses |      | analysed from     | Whole rock chemistry |          |          | Vol. % (from CIPW) |
|-------------------|----------------------|----------------------------|------------|------|-------------------|----------------------|----------|----------|--------------------|
| <b>Resolution</b> |                      |                            | LA-ICP-MS  | EPMA |                   | Cu (ppm)             | Mo (ppm) | Au (ppm) |                    |
| R-2A-16           | QLP                  | Dominant                   | 13         | 17   | thin section      | -                    | -        | -        |                    |
| R-2A-17           | QLP                  | Dominant                   | 16         |      | thin section      | -                    | -        | -        |                    |
| R-2B-6            | QLP                  | Dominant                   | 46         |      | thin section      | 6350                 | 113      | 0.016    |                    |
| R-13F-2           | QLP                  | Dominant, vein and dull CL | 24         | 25   | mounted separates | 6150                 | 160      | 0.006    | 0.48               |
| R-2A-12           | RDP                  | Dominant                   | 21         |      | thin section      | -                    | -        | -        |                    |
| R-23D-1           | RDP                  | Dominant                   | 14         | 87   | mounted separates | 1520                 | 8        | 0.005    | 0.20               |
| R-1B-9            | QLP                  | Dominant                   | 24         |      | thin section      | 1960                 | 451      | 0.005    | 0.35               |
| R-9A-1            | RDP                  | Dominant                   | 17         | 20   | thin section      | 1180                 | 7        | <0.002   | 0.16               |
| R-9A-2            | RDP                  | Dominant                   | 13         |      | thin section      | 1290                 | 58       | 0.002    | 0.18               |
| R-9A-4            | RDP                  | Dominant                   | 20         | 33   | thin section      | 1180                 | 17       | 0.002    | 0.16               |
| R-7D-3            | RDP                  | Dominant, vein, dull CL    | 24         | 26   | mounted separates | 8240                 | 63       | 0.024    | 0.24               |
| R-RF-A            | Mafic ALi            |                            | 7          |      | thin section      | 136                  | 1        | 0.005    | 0.32               |
| R-RF-G            | Felsic ALi           |                            | 25         | 109  | mounted separates | 69                   | <1       | 0.002    | 0.39               |
| R-S-8             | Schultze             |                            | 22         |      | thin section      | <1                   | <1       | <0.001   | 0.17               |
| R-S-9             | Schultze             |                            | 19         |      | thin section      | 2                    | 1        | 0.003    | 0.17               |
| R-S-10            | Schultze             |                            | 25         |      | thin section      | <1                   | <1       | <0.001   | 0.17               |
| R-S-11            | Schultze             |                            | 22         | 12   | thin section      | 1                    | 1        | <0.001   | 0.16               |
| R-S-12            | Bt enclave           |                            | 23         |      | thin section      | 68                   | <1       | <0.001   | 0.70               |
| R-S-13            | Schultze P           |                            | 11         |      | thin section      | 4                    | <1       | <0.001   | 0.17               |
| R-SF-2            | Ksp megacryst        |                            | 24         |      | thin section      | -                    | -        | -        |                    |
| R-2A-10m          | Hydrothermal Breccia |                            |            | 8    | thin section      | -                    | -        | -        |                    |

Table 6.1. (contd.)

Schultze Granite (main phase), 1 sample of the biotite-rich enclave, 1 sample of Schultze Granite porphyry, and 1 sample of a K-feldspar megacryst. Apatite was analysed from 1 sample each of the mafic and felsic Apache Leap intrusions. Most LA-ICP-MS analyses were conducted on polished thin sections, with a subset done on apatite separates mounted in polished blocks.

At Oyu Tolgoi, EPMA analyses were conducted on apatites from one BiGd sample (OT-11), two samples from the Dvs (OT-158 and OT-56), 7 from the QMD at Hugo Dummett, 4 from the QMD at Heruga, and 2 from the QMD at SW Oyu. LA-ICP-MS analysis was done on apatites from 4 samples of the BiGd, 2 samples of Dvs, 8 QMD samples from Hugo Dummett, 7 QMD samples from Heruga, and 3 QMD samples from SW Oyu.

Most apatite crystals were located by transmitted light microscopy of polished thin sections. In thin section, apatite is recognised by its high relief, habit (hexagonal when cut perpendicular to the C-axis, tabular and elongate when parallel to C-axis), and very low birefringence (low 1<sup>st</sup> order). Some populations of apatite, especially those in highly altered rocks, were difficult to identify by transmitted light microscopy, and were instead identified by a combination of CL microscopy and SEM techniques in polished thin sections. In some samples, apatites found in thin section were too small to analyse, so larger grains were picked from dense mineral separates and mounted in polished resin blocks. Apatite is the most abundant phosphate in these rocks due to the relative scarcity of monazite and xenotime. As a result, the estimates of apatite abundance quoted herein have been derived from normative analysis of bulk rock data (CIPW norm; Table 6.1).

### 6.3.1 Compilation of literature data

In order to compare the chemistry of the studied porphyry-related apatites with those from barren arc rocks, a compilation of literature data was made (data sources are: Sha and Chappell et al, 1999; Hoskin et al., 2000; Hsieh et al., 2008; Chu et al., 2009; Miles et al., 2014). All rocks are ostensibly unrelated to mineralisation. Apatites from the literature come from a diverse range of rock chemistry, between 49.7 and 77.8 wt. % SiO<sub>2</sub>, which include apatites from S-type and I-type intermediate and felsic rocks (ASI. between 0.7 and 1.5).

A median value was generated for all apatite data for rocks > 60 wt. % SiO<sub>2</sub> (referred to as ‘median granitoid’; Table 6.2). In addition, the same literature data was divided into two categories; ‘S-type and felsic I-type’ granites and ‘intermediate’ granites, and medians were generated for both of these groups. This was done in order to draw out the strong systematic differences between apatites from I-type intermediate rocks (cf. ‘mafic’ I-type of Sha and Chappell, 1999; <70 wt. % SiO<sub>2</sub>), and apatites from felsic I-type rocks (>70 % SiO<sub>2</sub>) and S-type rocks (>65 wt. % SiO<sub>2</sub>; Sha and Chappell, 1999; Chu et al., 2009). For example, apatites from intermediate I-type rocks have low Mn contents (<1000 ppm), whereas apatites from S-type and felsic I-type rocks show Mn contents which increase with whole rock SiO<sub>2</sub>, up to 2 wt. % Mn (Fig. 6.1 a; Table 6.2). A similar pattern is seen in Fe content (Fig. 6.1 b). These differences are independent of the whole rock Mn and Fe concentration, which follow similar fractionation trends for all groups (Sha and Chappell, 1999). For the calculation of medians, classification of these rocks as S-type, felsic I-type, and intermediate I-type igneous rocks are taken from the authors of the original studies.

Most of these median granitoid values are comparable with the median apatite values determined from 669 samples by Belousova et al. (2002a), and mean values for 475 analyses of apatites not related to ore deposits, taken from Piccoli and Candela (2002) (Table 6.2).

|                               | Median Granitoid |           |        |           |       |     | B.<br>(2002) | P&C. (2002)         | S-type &<br>felsic I-type | Int. I-type |
|-------------------------------|------------------|-----------|--------|-----------|-------|-----|--------------|---------------------|---------------------------|-------------|
|                               | Min              | 1st<br>Q. | Median | 3rd<br>Q. | Max   | n=  | Median       | Mean $\pm$ $\sigma$ | Median                    | Median      |
| <b>F (wt. %)</b>              | 1.89             | 2.34      | 2.77   | 3.50      | 5.13  | 51  | 2.77         | 2.74 $\pm$ 0.59     | 3.572                     | 2.75        |
| <b>Cl (wt. %)</b>             | ---              | 0.01      | 0.05   | 0.09      | 1.11  | 59  | 0.46         | 0.27 $\pm$ 0.37     | 0.06                      | 0.14        |
| <b>S (ppm)</b>                | 140              | 150       | 155    | 238       | 620   | 26  |              | 1121 $\pm$ 961      | 150                       | 475         |
| <b>Ca (wt. %)</b>             | 36.1             | 37.5      | 38.15  | 38.6      | 39.5  | 75  |              | 37.9 $\pm$ 1.3      | 38.22                     | 38.75       |
| <b>Na (ppm)</b>               | 100              | 504       | 799    | 1111      | 4100  | 246 |              |                     | 1060                      | 670         |
| <b>Mg</b>                     |                  |           |        |           |       |     | 27.8         | 422 $\pm$ 422       |                           |             |
| <b>Si</b>                     | 51               | 570       | 1041   | 1742      | 77177 | 293 |              | 1963 $\pm$ 3366     |                           | 1486        |
| <b>V</b>                      | 1                | 173       | 529    | 1605      | 5817  | 232 | 7.5          |                     | 2734                      | 449         |
| <b>Mn</b>                     | 190              | 527       | 922    | 2426      | 25187 | 476 | 308          | 1936 $\pm$ 3872     | 3830                      | 724         |
| <b>Fe</b>                     | 107              | 419       | 1005   | 2308      | 10300 | 198 | 312          | 2332 $\pm$ 2876     | 3400                      | 465         |
| <b>Sr</b>                     | 19               | 188       | 346    | 464       | 1850  | 485 | 135          | 592 $\pm$ 422       | 92                        | 405         |
| <b>Y</b>                      | 14               | 266       | 634    | 1679      | 5974  | 570 | 1079         | 1858 $\pm$ 2005     | 2711                      | 499         |
| <b>Zr</b>                     | 0.098            | 0.385     | 0.632  | 1.13      | 8.65  | 196 | <2.3         |                     | 0.365                     | 0.701       |
| <b>Ba</b>                     | 0.035            | 0.57      | 1.6    | 8         | 140   | 168 |              |                     | 0.625                     | 3.585       |
| <b>La</b>                     | 5.6              | 272       | 731    | 1310      | 4006  | 323 | 704          | 3845 $\pm$ 7599     | 258                       | 1102        |
| <b>Ce</b>                     | 12               | 797       | 1531   | 2502      | 7692  | 332 | 2165         | 6535 $\pm$ 12890    | 782                       | 2023        |
| <b>Pr</b>                     | 2.1              | 130       | 195    | 290       | 997   | 332 | 265          | 1336 $\pm$ 1748     | 134                       | 229         |
| <b>Nd</b>                     | 0.09             | 427       | 676    | 1012      | 3761  | 331 | 1032         | 3490 $\pm$ 5714     | 686                       | 757         |
| <b>Sm</b>                     | 15               | 107       | 186    | 277       | 882   | 329 | 215          | 557 $\pm$ 1211      | 281                       | 152         |
| <b>Eu</b>                     | 2                | 9.55      | 14     | 17        | 94.6  | 331 | 23           | 19 $\pm$ 9          | 9                         | 16          |
| <b>Gd</b>                     | 12               | 84.3      | 165    | 334       | 1016  | 324 | 208          | 155 $\pm$ 71        | 388                       | 132         |
| <b>Tb</b>                     | 1.6              | 5.55      | 17.6   | 60.8      | 184   | 332 |              |                     | 79                        | 17          |
| <b>Dy</b>                     | 7.4              | 55.6      | 119    | 365       | 1164  | 305 | 172          | 229 $\pm$ 341       | 509                       | 90          |
| <b>Ho</b>                     | 1.9              | 5.64      | 20.5   | 66.6      | 217   | 332 | 36           |                     | 89                        | 18          |
| <b>Er</b>                     | 4.3              | 30.3      | 58.8   | 169       | 542   | 288 | 97           | 110 $\pm$ 98        | 221                       | 45          |
| <b>Tm</b>                     | 0.51             | 4         | 7.55   | 22.9      | 163   | 290 | 14           | 6 $\pm$ 4           |                           |             |
| <b>Yb</b>                     | 4                | 25.3      | 47.2   | 139       | 543   | 290 | 85           | 75 $\pm$ 70         | 182                       | 35          |
| <b>Lu</b>                     | 0.75             | 3.8       | 6.8    | 18        | 69.1  | 290 | 13           | 6 $\pm$ 4           | 22                        | 6           |
| <b>Pb</b>                     | 0.98             | 3.87      | 6.62   | 12.6      | 1734  | 315 | 8.9          |                     | 7.27                      | 4           |
| <b>Th</b>                     | 0.23             | 13.5      | 31     | 63.2      | 649   | 332 | 46           | 26 $\pm$ 11         | 5.82                      | 39.85       |
| <b>U</b>                      | 0.16             | 13.4      | 29     | 53.7      | 330   | 305 | 20           | 169 $\pm$ 1078      | 58.3                      | 20          |
| <b>La/Yb</b>                  | 0.061            | 1.15      | 13.3   | 33.1      | 393   | 332 |              |                     | 0.94                      | 20.51       |
| <b>Sm/Yb</b>                  | 0.18             | 2.1       | 3.96   | 6.2       | 21.5  | 332 |              |                     | 1.88                      | 4.67        |
| <b><math>\Sigma</math>REE</b> | 311              | 3093      | 4122   | 5679      | 16964 | 331 |              |                     | 3439                      | 4217        |
| <b>Sr/Y</b>                   | 0.0044           | 0.082     | 0.571  | 1.3       | 10.1  | 330 |              |                     | 0.04                      | 0.78        |
| <b>Eu/Eu*</b>                 | 0.011            | 0.121     | 0.299  | 0.513     | 1.65  | 332 |              |                     | 0.09                      | 0.36        |

Table 6.2. Calculated median values for apatites from barren rocks. Median values for granitoids from the literature dataset are here compared to median values determined by Belousova et al. (2002a), and mean values from Piccoli and Candela (2002), under the labels “B. (2002)” and “P&C. (2002)”. The literature dataset is further divided into apatites from intermediate I-type, and S-type/Felsic I-type rocks, and medians for these subdivisions were also calculated.

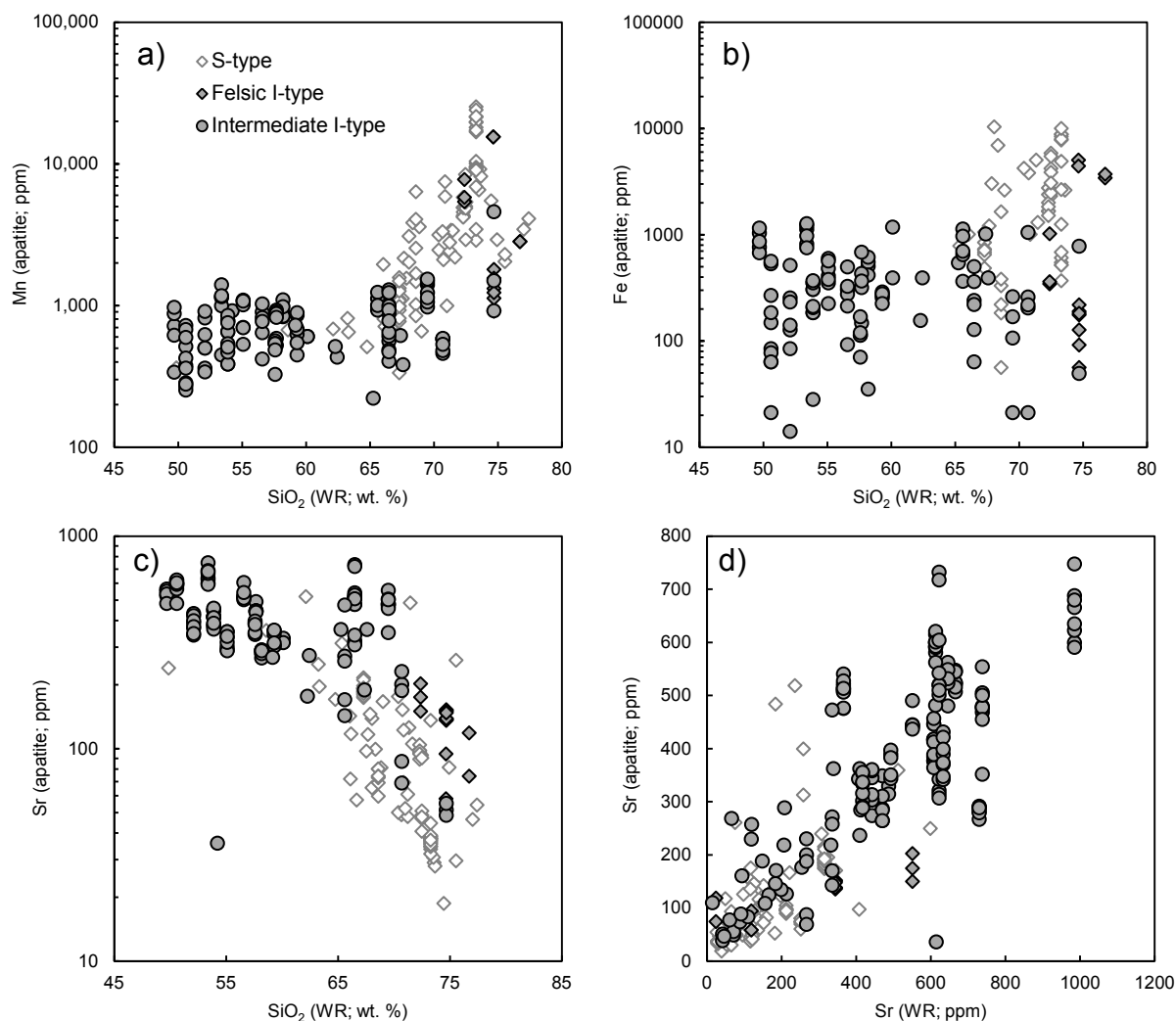


Figure 6.1. A summary of the divergent characteristics of apatites from S- and felsic I-type granites, and those from intermediate I-type granites. (a-b) Mn and Fe content in S-type granites increases with increasing fractionation. (c) Sr in apatites from S-type granites decreases to low values (~10 ppm) with increasing whole rock fractionation. All literature apatite data have Sr values <750 ppm. (d) Sr in apatite closely mirrors the Sr content of whole rocks. For sources of literature data, see Section 0.

S concentrations from Piccoli and Candela (2002) are an order of magnitude higher (mean = 1121 ppm) than the medians calculated for either S-type or I-type granites (150 ppm) or intermediate I-type rocks (475 ppm). This wide range of median S concentrations could represent undersampling and/or the natural variability of S in granite-hosted apatites. Median Cl values (0.27 wt. %) reported by Piccoli and Candela (2002) are lower than some reported

Cl concentrations of apatites from barren volcanic rocks, such as Santorini (1.04 wt. %), Pinatubo (1.17 wt. %) and Mt. St Helens (0.72 wt. %; data from Webster et al., 2009). Median F concentrations for apatites from S-type and felsic I-type rocks are very high (median = 3.57 wt. %). This value is close to the stoichiometric limit for F in apatite (3.76 wt. %), and is likely to be due to incorrect analytical procedures used when analysing for F in apatite (Pyle et al., 2002). Nonetheless, these high values are considered to be a qualitative reflection of strong F-enrichment in apatites from S-type and felsic I-type granites. F contents of apatite from intermediate I-type rocks are lower (median = 2.75 wt. %). Apatites from S-type and felsic I-type rocks have lower median Sr (92 ppm), LREE (La/Yb = 258) and Th (5.82 ppm) and have higher median Mn (3830 ppm), Fe (3400 ppm) and Y (2711 ppm) than intermediate I-type rocks.

## **6.4 Results – Oyu Tolgoi**

In the following sections, each group of apatites will be assigned a classification (hydrothermal or igneous) based on their textures and mineral associations. These classifications will be presented separately at the end of each section.

### **6.4.1 Petrography of Oyu Tolgoi apatites**

A summary of the textural characteristics of Oyu Tolgoi apatites is found in Table 6.3. Apatite is a common accessory mineral in the QMD, and accounts for 0.2 to 0.7 vol. % of rocks from Heruga, Hugo Dummett, and SW Oyu. It is particularly common to rocks which have been strongly affected by potassic alteration (Red QMD). Apatite is largely absent from rocks which have been strongly affected by sericitic alteration.

Apatites from the QMD may be broadly characterised into two groups, depending upon the minerals they are found associated with. In the least altered and weakly mineralised QMD, some apatites are found inter-grown with magnetite phenocrysts. In addition, apatites are found as isolated grains in the groundmass, although these are considered to be similar to

the magnetite-associated apatites based on their texture and habit. Apatites from magnetite-bearing rocks shall be referred to as 'M-Ap'. In mineralised rocks, apatite is found inter-grown with sulphides. Apatites from these rocks shall be referred to as 'S-Ap'. These types of apatite will be discussed separately.

#### *6.4.1.1 Sulphide-associated apatite (S-Ap)*

S-Ap grains vary in size from sub-micron to ~400  $\mu\text{m}$ , and most of those analysed were ~100  $\mu\text{m}$  in size. Grains are typically subhedral to anhedral, are found in the groundmass, and also occur in granular clots that are inter-grown with sulphide minerals: pyrite and subordinate chalcopyrite at Heruga and SW Oyu; chalcopyrite and occasionally bornite and chalcocite at Hugo Dummett (Fig. 6.2 a-f). Apatites from some rocks (e.g. OT-67) are heavily fractured, and cracks are infilled with sulphides (Fig. 6.2 e,f). Apatite has also replaced mafic minerals (probably mostly hornblende, based on the relict habit) as part of an assemblage of chlorite, sulphides, rutile and occasionally calcite (Fig. 6.2 c,d). Apatites inter-grown with sulphides commonly have a dull CL response, although some examples show very thin, bright CL rims (<10  $\mu\text{m}$ ). S-Ap is most commonly associated with strong, texturally-destructive potassic alteration, which imparts a brick red colour on rocks (i.e. Red QMD). It is much less common in rocks that have been affected by strong sericitic or advanced argillic alteration, although is present in rocks with only a partial sericitic overprint.

S-Ap are considered to be hydrothermal in origin. This is because of their intimate mineral association with other hydrothermal minerals, especially chalcopyrite and bornite. The in-filling of sulphides along cracks indicates that in some cases, S-Ap crystallised before sulphides. However, the apparent local equilibrium and close spatial distribution between S-Ap and sulphide minerals suggest it is part of the same mineral association (cf. Seedorff et al., 2005).

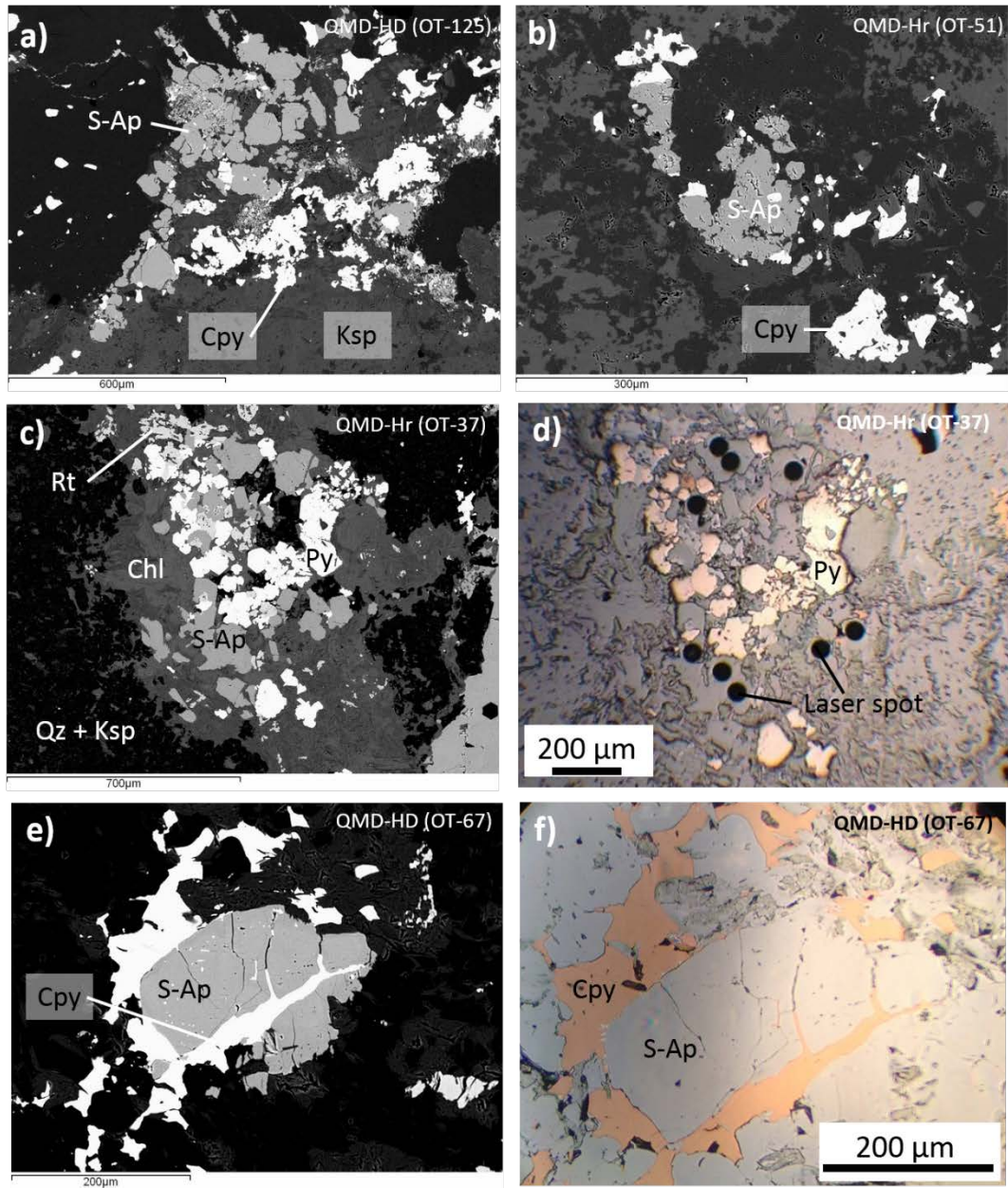


Figure 6.2. Representative images of sulphide-associated apatite (S-Ap) from QMD intrusions. (a-b) Inter-grown chalcopyrite and anhedral S-Ap from Hugo Dummett and Heruga. (c-d) SEM and reflected light microscopy images of S-Ap forming part of an alteration assemblage of pyrite, chlorite and rutile, replacing a hornblende phenocryst in QMD from Heruga. (e-f) SEM and reflected light microscopy images inter-growths of chalcopyrite and S-Ap in QMD from Hugo Dummett. Cpy = chalcopyrite, Py = pyrite, Rt = rutile, Qz = quartz, Ksp = K-feldspar.



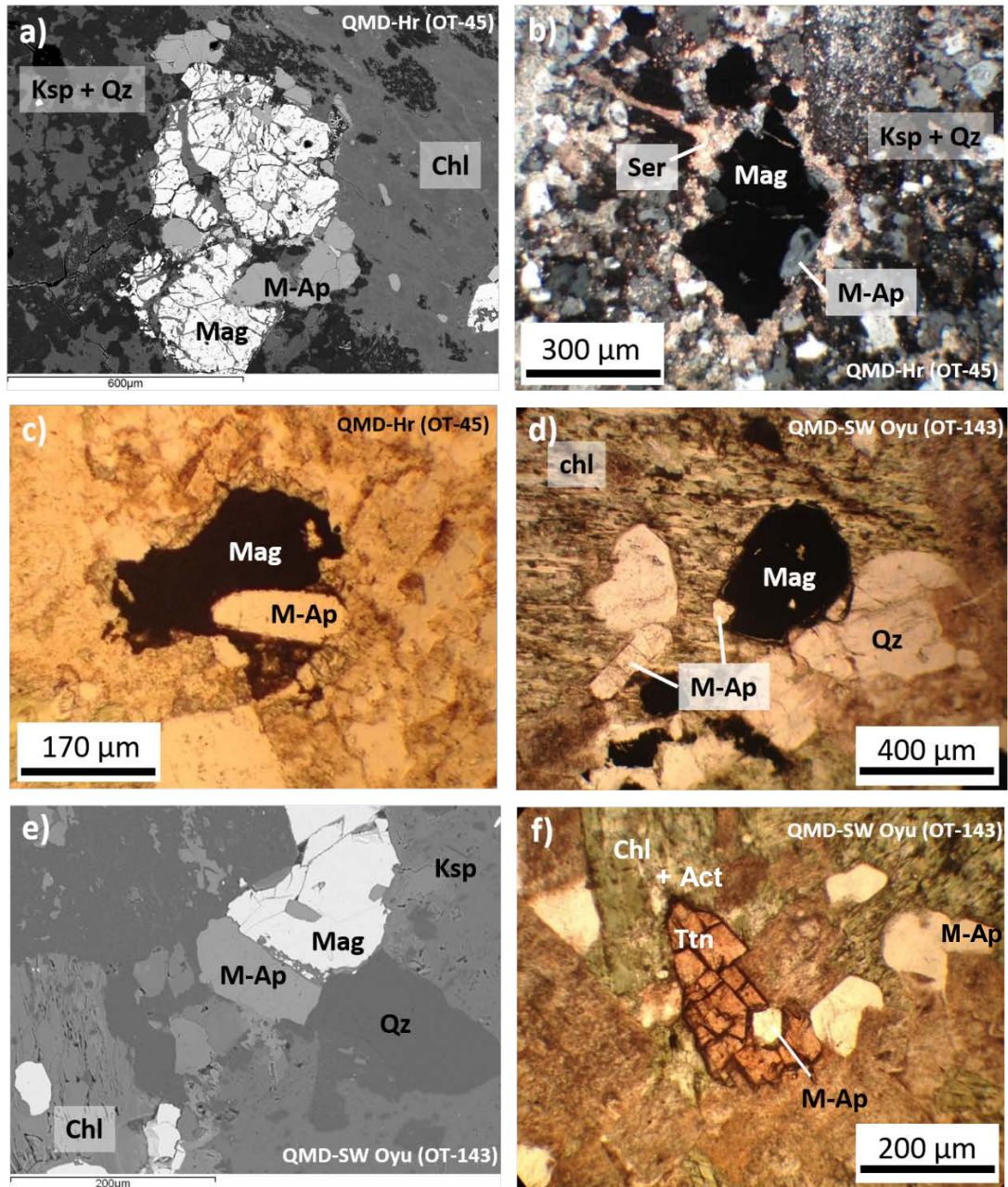


Figure 6.3. Representative images of (M-Ap). (a) A cluster of M-Ap and magnetite adjacent to a chloritised hornblende phenocryst in Heruga. (b) M-Ap and magnetite, surrounded by a halo of sericite in a groundmass of K-feldspar and quartz (QMD Heruga). (c) M-Ap and magnetite (QMD Heruga). (d-e) M-Ap inter-grown with magnetite at the edge of chloritised hornblende phenocryst (QMD SW Oyu). (f) M-Ap grains with titanite on margins of chloritised hornblende phenocryst. Mag = magnetite, Qz = quartz, Ksp = K-feldspar, Ttn = titanite, Ser = sericite.

#### 6.4.1.2 Magnetite-associated apatite (*M-Ap*)

In two samples of QMD, one from Heruga (OT-45) and one from SW Oyu (OT-143), apatites are texturally distinct from those described above, and account for ~0.4 vol. % of each rock. These apatites are not found associated with sulphides, but are inter-grown instead with magnetite (Fig. 6.3 a-e), or titanite (Fig. 6.3 f) as well as being found as isolated examples in the groundmass, and occasionally as inclusions in chloritized hornblende. These two QMD samples are less strongly altered and mineralised compared to other QMD rocks (<400 ppm Cu; Table 1) and sulphide grains are very rare. Feldspars are only partly sericitised, although hornblende phenocrysts are completely replaced by chlorite + actinolite (Fig. 6.3 a, d, e-f). Apatites from these rocks are euhedral to subhedral and range in size from <10  $\mu\text{m}$  to 300  $\mu\text{m}$ . They have a brighter CL response than S-Ap.

M-Ap are most likely to be primary igneous in origin. It is unclear whether the magnetite with which these grains are inter-grown are primary or secondary. In the SW Oyu sample (OT-143), M-Ap is also inter-grown with a sodic-calcic assemblage including titanite, suggesting possible re-equilibration with high-temperature hydrothermal fluids.

#### 6.4.1.3 Dvs apatite

The textural characteristics of M-Ap are similar to those observed for apatite in the unmineralised Dvs samples. Apatites from these rocks (OT-56 and OT-158) are euhedral, up to 300  $\mu\text{m}$  in length and are commonly inter-grown with magnetite (Fig. 6.4 a) or occur as isolated crystals in the devitrified groundmass (Fig. 6.4 b). Some of these grains show crenulated edges, which are inter-grown with the groundmass minerals. CL response in these grains is bright and flat, with no zoning (Fig. 6.4 b).

Dvs apatite are considered to be primary igneous, due in part to their presence in weakly altered and unmineralised volcanic rocks. There is an apparent textural similarity between Dvs and M-Ap, in terms of mineral associations and crystal habit.

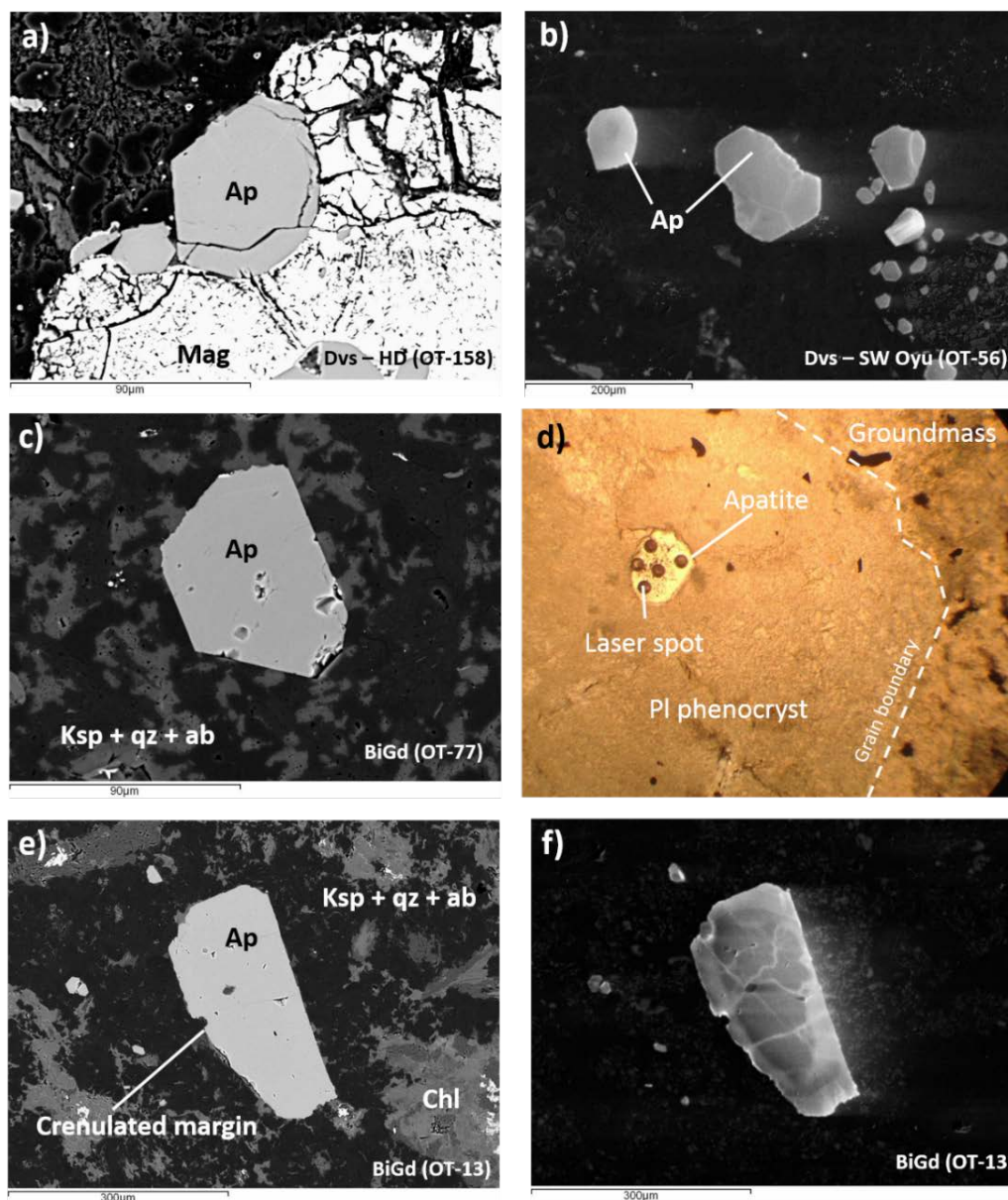


Figure 6.4. Representative images of apatite from Dvs and BiGd. (a) SEM backscatter image of Dvs apatite with magnetite grain. (b) SEM-CL image of unzoned, flat-CL response of Dvs apatite. (c) SEM backscatter image showing euhedral BiGd apatite in quartz, K-feldspar and albite groundmass. (d) Reflected light image showing inclusion of apatite near the core of plagioclase phenocryst in the BiGd. (e-f) SEM backscatter and SEM-CL images of BiGd apatite microphenocryst in K-feldspar, quartz and albite groundmass. Bright CL lines in the core of the crystal are annealed cracks not visible in backscatter image. Ap = apatite, Ksp = K-feldspar, Qz = quartz, ab = albite, pl = plagioclase, Chl = chlorite.



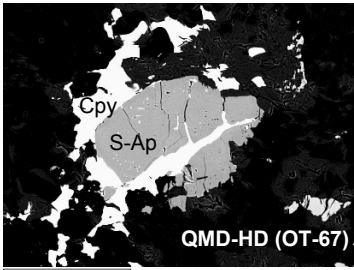
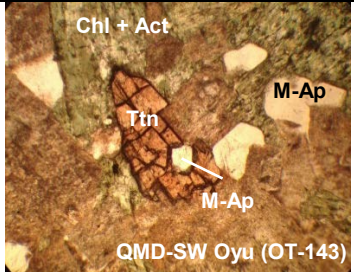
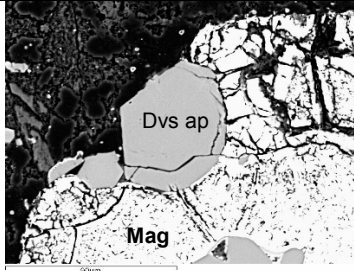
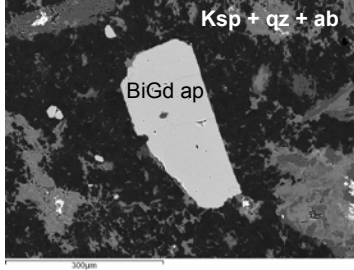
|                                                                                                                             | Occurrence                                                                                                              | Mineral associations                                                                 | Texture                                                                                                                                                                    | Origin                                                                                          | Representative image                                                                 |
|-----------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| <b>S-Ap</b><br><i>sulphide-associated apatite from QMD</i>                                                                  | QMD (Heruga, Hugo Dummett, SW Oyu). Found in strongly altered and mineralised rocks                                     | Chalcopyrite, bornite, pyrite (latter mostly at Heruga)                              | Anhedral, containing lots of cracks (frequently infilled with Cu sulphides). Up to 500 µm, but most between 200-300 µm. Dull CL response.                                  | Hydrothermal - close association with sulphides suggests equilibration with ore-forming fluids. |   |
| <b>M-Ap</b><br><i>magnetite-associated apatite from QMD</i>                                                                 | QMD (Heruga, SW Oyu). Not observed in rocks from Hugo Dummett, although weakly altered rocks are rarer at this deposit. | Magnetite, K-feldspar, titanite, chlorite and actionlite (after hornblende?), quartz | Euhedral to subhedral                                                                                                                                                      | Igneous, or high-T hydrothermal (sodic-calcic). Found in least-altered QMD.                     |   |
| <b>Dvs apatite</b><br><i>apatites from volcanic rocks co-genetic with QMD</i>                                               | Ubiquitous in the devitrified groundmass of late Devonian volcanic rocks, and as inclusions in magnetite                | Magnetite, albite, chlorite                                                          | Euhedral, between 50 and 300 µm. Unzoned.                                                                                                                                  | Igneous – observed in weakly altered and unmineralised co-genetic volcanic rocks.               |   |
| <b>BiGd apatite</b><br><i>apatites from post-mineralisation intrusion which cross-cut mineralisation, Dvs, and the QMD.</i> | Ubiquitous in the groundmass of BiGd intrusions (diagnostic).                                                           | K-feldspar, quartz, albite, calcite                                                  | Euhedral to subhedral, up to 400 µm (mostly 100 – 200 µm). Typically elongate laths. Strong zoning in CL images, with some minor cracks showing strong CL characteristics. | Hydrothermal – in equilibrium with assemblage of chlorite and calcite, and occasional sericite. |  |

Table 6.3 (previous page). Summary table of the textural characteristics of Oyu Tolgoi apatites. Mag = magnetite., Ttn = titanite, chl = chlorite, act = actinolite, ksp = K-feldspar, qz = quartz, ab = albite, cpy = chalcopyrite.

#### 6.4.1.4 BiGd apatite

BiGd samples contain abundant microphenocrysts of apatite. These grains are euhedral, with subordinate subhedral grains, and are typically 100 to 200  $\mu\text{m}$  in size, although much smaller grains are also present (Fig. 6.4 c-f). Although most apatites are pristine, some grains show crenulated edges inter-grown with surrounding minerals, similar to the Dvs apatites. They occur as randomly distributed and oriented microphenocrysts in the groundmass, or in small clusters of minerals replacing mafic phases (with chlorite and calcite, after biotite). Some large apatite grains (up to 250  $\mu\text{m}$ ) are found as inclusions in the cores of plagioclase feldspar crystals (Fig. 6.4 d). Apatites from BiGd have a bright CL response and very occasionally show irregular, concentric zoning, with bright rims and dark cores being the most common pattern (Fig. 6.4 f). The fact that BiGd apatite is observed replacing mafic phases with calcite and chlorite is indicative of a propylitic alteration assemblage.

#### 6.4.2 Geochemistry of Oyu Tolgoi apatites

All apatite data from this study is present in Appendix 5.

##### 6.4.2.1 Fluorine, chlorine, and sulphur

Nearly all analyses of F from Oyu Tolgoi are within the stoichiometric limit of F in apatite, with only 6 exceptions from 454 analyses. It should be noted that F values reported herein are qualitative only, due to analytical problems in measuring F by EPMA (see Section 2.4.2). OH was calculated by difference from 2 apfu (atoms per formula unit), *i.e.*  $\text{OH} = 2 - \text{F} - \text{Cl}$ , where F (apfu) and Cl (apfu) are calculated from EPMA data on the basis of 26 oxygens. Because they rely on knowledge of F values, OH values herein must also be treated as qualitative estimates.

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*Table 6.4. (next page) Summary of the geochemical characteristics of Oyu Tolgoi apatites. Coloured cells represent % difference from median granitoid apatite (For colour code, see Table 5.4).*

|                   | S-Ap (QMD Hugo Dummett) |        |        |        |         | S-Ap (QMD Heruga) |        |        |        |         | S-Ap (QMD SW Oyu) |         |        |        |         | M-Ap (Heruga) |        |        |        |        |       | Median<br>Granitoid |
|-------------------|-------------------------|--------|--------|--------|---------|-------------------|--------|--------|--------|---------|-------------------|---------|--------|--------|---------|---------------|--------|--------|--------|--------|-------|---------------------|
|                   | Min.                    | 1st Q. | Median | 3rd Q. | Max     | Min.              | 1st Q. | Median | 3rd Q. | Max     | Min.              | 1st Q.  | Median | 3rd Q. | Max     | Min.          | 1st Q. | Median | 3rd Q. | Max    | LOD   |                     |
| <b>F (wt.%)</b>   | 1.92                    | 2.55   | 2.83   | 3.15   | 4.26    | 2.16              | 2.71   | 2.91   | 3.15   | 3.79    | 2.62              | 2.715   | 2.735  | 2.8    | 3.03    | 2.18          | 2.36   | 2.46   | 2.55   | 2.93   | 0.12  | 2.77                |
| <b>Cl (wt.%)</b>  | b.d.l.                  | 0.18   | 0.22   | 0.275  | 0.83    | b.d.l.            | 0.09   | 0.16   | 0.44   | 0.91    | 0.21              | 0.315   | 0.35   | 0.3675 | 0.46    | 0.08          | 0.56   | 0.65   | 0.71   | 0.85   | 0.06  | 0.05                |
| <b>S (wt.%)</b>   | b.d.l.                  | b.d.l. | b.d.l. | 0.08   | 0.94    | b.d.l.            | b.d.l. | b.d.l. | b.d.l. | b.d.l.  | b.d.l.            | b.d.l.  | b.d.l. | b.d.l. | 0.17    | b.d.l.        | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.05  | 0.015               |
| <b>Ca (wt.%)</b>  | 33.21                   | 38.78  | 39.03  | 39.28  | 39.89   | 37.8              | 39.0   | 39.3   | 39.5   | 40.1    | 39.25             | 39.3475 | 39.48  | 39.64  | 39.73   | 38.3          | 38.6   | 38.8   | 39.1   | 39.6   | 0.05  | 38.15               |
| <b>Na (ppm)</b>   | 183.8                   | 958.9  | 1122.6 | 1252.9 | 1965.0  | 284.9             | 903.0  | 1072.0 | 1309.5 | 2416.2  | 184.4             | 401.3   | 596.7  | 852.5  | 1340.3  | 466.2         | 1009.3 | 1198.6 | 1454.0 | 2081.0 | 11.65 | 799                 |
| <b>Mg (ppm)</b>   | 95.7                    | 241.0  | 422.2  | 626.7  | 1522.6  | 54.5              | 170.8  | 288.8  | 500.4  | 1539.7  | 50.5              | 83.0    | 373.9  | 626.3  | 1083.3  | 50.8          | 113.3  | 138.9  | 164.3  | 286.6  | 0.40  |                     |
| <b>Si (ppm)</b>   | b.d.l.                  | 763.9  | 1234.3 | 1639.3 | 10156.7 | b.d.l.            | b.d.l. | 1025.6 | 1552.1 | 87304.1 | 758.2             | 1222.9  | 1514.5 | 1845.1 | 6349.2  | 1462.1        | 1916.1 | 2106.2 | 2311.9 | 3819.3 | 456   | 1041                |
| <b>Mn (ppm)</b>   | 588.9                   | 3033.0 | 4032.4 | 5604.5 | 14096.1 | 315.1             | 689.2  | 1063.8 | 3228.7 | 12056.1 | 748.5             | 1005.1  | 1521.8 | 2822.6 | 13039.9 | 1202.1        | 1710.5 | 1941.5 | 2173.7 | 2419.6 | 4.49  | 922                 |
| <b>Fe (ppm)</b>   | 554.9                   | 1500.7 | 2052.5 | 3010.2 | 5556.2  | 234.2             | 603.4  | 1153.5 | 2334.4 | 4585.7  | 134.5             | 185.7   | 461.1  | 1174.6 | 13613.8 | 365.5         | 599.7  | 683.2  | 808.5  | 1177.2 | 13.35 | 1005                |
| <b>Sr (ppm)</b>   | 181.3                   | 429.7  | 517.7  | 677.2  | 3802.2  | 364.5             | 484.5  | 529.5  | 649.5  | 2087.9  | 296.2             | 429.5   | 609.3  | 1003.4 | 1472.3  | 227.0         | 258.7  | 285.5  | 306.9  | 1051.0 | 0.65  | 346                 |
| <b>Y (ppm)</b>    | 380.1                   | 1010.6 | 1436.2 | 1738.0 | 3249.0  | 154.3             | 723.2  | 1120.1 | 1445.2 | 3240.2  | 34.9              | 529.5   | 819.8  | 1077.9 | 1652.9  | 252.2         | 574.1  | 808.9  | 905.6  | 1622.8 | 1.57  | 634                 |
| <b>Zr (ppm)</b>   | b.d.l.                  | 0.05   | 0.09   | 0.21   | 3.83    | b.d.l.            | 0.03   | 0.06   | 0.14   | 35.42   | b.d.l.            | 0.04    | 0.09   | 0.16   | 4.05    | 0.05          | 0.50   | 0.83   | 1.29   | 3.01   | 0.03  | 0.632               |
| <b>Ba (ppm)</b>   | 0.10                    | 0.36   | 0.64   | 1.26   | 59.64   | 0.09              | 0.30   | 0.46   | 1.10   | 20.74   | 0.54              | 0.99    | 1.51   | 2.90   | 5.21    | 0.24          | 0.62   | 0.77   | 1.22   | 70.32  | 0.08  | 1.6                 |
| <b>La (ppm)</b>   | 79.4                    | 223.6  | 338.1  | 424.9  | 1185.0  | 75.6              | 211.2  | 297.5  | 406.7  | 731.3   | 37.5              | 127.4   | 183.2  | 247.8  | 710.1   | 454.5         | 784.2  | 951.6  | 1180.2 | 1952.4 | 0.29  | 731                 |
| <b>Ce (ppm)</b>   | 216.0                   | 642.1  | 998.0  | 1417.1 | 3098.8  | 203.7             | 600.5  | 861.1  | 1181.1 | 1860.0  | 138.3             | 401.7   | 584.2  | 744.1  | 1702.6  | 1350.0        | 1859.5 | 2771.7 | 3271.1 | 4840.7 | 1.44  | 1531                |
| <b>Pr (ppm)</b>   | 31.6                    | 91.1   | 138.7  | 183.0  | 330.4   | 28.1              | 88.3   | 123.8  | 160.3  | 237.6   | 22.15             | 58.5    | 88.8   | 110.5  | 223.9   | 116.2         | 200.2  | 287.8  | 326.5  | 474.1  | 0.18  | 195                 |
| <b>Nd (ppm)</b>   | 151.6                   | 426.3  | 645.2  | 830.6  | 1315.8  | 138.4             | 409.6  | 594.3  | 757.9  | 1075.8  | 85.24             | 278.8   | 414.8  | 518.9  | 1005.4  | 355.5         | 792.8  | 1014.8 | 1237.2 | 1798.2 | 0.97  | 676                 |
| <b>Sm (ppm)</b>   | 46.7                    | 138.9  | 182.5  | 225.8  | 358.5   | 33.7              | 131.2  | 168.9  | 206.2  | 294.1   | 19.76             | 93.3    | 124.7  | 168.8  | 252.1   | 51.8          | 159.8  | 197.9  | 224.0  | 345.6  | 0.32  | 186                 |
| <b>Eu (ppm)</b>   | 14.3                    | 30.2   | 36.3   | 44.0   | 115.0   | 14.8              | 33.6   | 38.8   | 43.2   | 77.4    | 9.19              | 24.0    | 37.1   | 43.0   | 59.8    | 6.9           | 13.5   | 15.1   | 17.3   | 27.3   | 0.06  | 14                  |
| <b>Gd (ppm)</b>   | 60.2                    | 177.2  | 234.1  | 275.6  | 446.8   | 35.9              | 157.4  | 199.3  | 244.4  | 316.3   | 16.55             | 110.4   | 142.8  | 219.9  | 299.0   | 47.0          | 157.8  | 182.2  | 213.4  | 341.1  | 0.38  | 165                 |
| <b>Tb (ppm)</b>   | 9.1                     | 25.8   | 37.7   | 43.8   | 72.0    | 5.5               | 23.9   | 31.0   | 37.8   | 63.7    | 2.12              | 16.9    | 22.3   | 33.4   | 45.8    | 6.2           | 18.7   | 22.7   | 27.9   | 43.8   | 0.05  | 17.6                |
| <b>Dy (ppm)</b>   | 59.6                    | 179.1  | 243.3  | 290.6  | 519.4   | 33.1              | 146.1  | 207.1  | 257.4  | 514.2   | 10.70             | 102.3   | 145.9  | 211.3  | 295.8   | 37.2          | 106.3  | 134.9  | 154.9  | 246.3  | 0.35  | 119                 |
| <b>Ho (ppm)</b>   | 12.3                    | 36.0   | 50.4   | 61.5   | 111.1   | 6.1               | 27.7   | 42.6   | 54.8   | 124.7   | 1.56              | 20.0    | 29.3   | 42.0   | 61.4    | 7.9           | 20.9   | 27.2   | 30.9   | 50.6   | 0.07  | 20.5                |
| <b>Er (ppm)</b>   | 39.5                    | 104.7  | 150.7  | 193.4  | 365.6   | 15.6              | 85.8   | 130.0  | 170.8  | 417.2   | 3.86              | 56.3    | 84.8   | 117.4  | 178.3   | 22.6          | 57.0   | 77.9   | 86.5   | 154.8  | 0.20  | 58.8                |
| <b>Tm (ppm)</b>   | 4.9                     | 14.8   | 21.6   | 28.1   | 52.7    | 1.7               | 11.6   | 18.0   | 23.0   | 62.8    | 0.52              | 7.1     | 11.5   | 16.0   | 25.6    | 3.0           | 7.0    | 9.6    | 10.9   | 20.7   | 0.03  | 7.55                |
| <b>Yb (ppm)</b>   | 23.6                    | 96.3   | 147.1  | 190.6  | 366.5   | 10.9              | 77.6   | 119.5  | 156.9  | 428.9   | 2.36              | 43.4    | 73.6   | 100.4  | 173.1   | 20.6          | 42.4   | 59.6   | 67.6   | 128.0  | 0.15  | 47.2                |
| <b>Lu (ppm)</b>   | 3.0                     | 14.3   | 21.4   | 27.7   | 55.5    | 1.3               | 10.6   | 16.3   | 22.5   | 61.4    | 0.36              | 5.7     | 10.0   | 14.4   | 24.3    | 3.6           | 6.4    | 8.3    | 9.6    | 19.6   | 0.02  | 6.8                 |
| <b>Pb (ppm)</b>   | 0.96                    | 2.35   | 3.36   | 4.74   | 53.69   | 0.48              | 0.96   | 2.23   | 3.60   | 19.18   | 0.29              | 0.69    | 1.05   | 2.11   | 18.34   | 0.62          | 1.30   | 1.52   | 1.95   | 5.92   | 0.14  | 6.62                |
| <b>Th (ppm)</b>   | 0.91                    | 6.99   | 14.85  | 22.31  | 90.31   | 0.89              | 5.18   | 8.02   | 13.51  | 49.99   | 0.17              | 2.32    | 4.66   | 9.66   | 39.54   | 7.41          | 11.50  | 18.36  | 23.04  | 142.31 | 0.02  | 31                  |
| <b>U (ppm)</b>    | 1.34                    | 7.37   | 12.32  | 18.58  | 143.36  | 0.42              | 3.55   | 5.31   | 9.70   | 43.48   | 0.43              | 1.38    | 3.26   | 6.91   | 40.99   | 2.71          | 7.61   | 14.05  | 18.66  | 90.61  | 0.03  | 29                  |
| <b>La/Yb</b>      | 0.55                    | 1.14   | 1.44   | 1.81   | 16.35   | 0.67              | 1.51   | 1.81   | 2.33   | 8.08    | 0.29              | 1.21    | 1.48   | 2.61   | 10.52   | 5.22          | 10.54  | 11.98  | 15.46  | 26.38  |       | 13.3                |
| <b>Sm/Yb</b>      | 0.46                    | 1.23   | 1.48   | 1.72   | 9.42    | 0.36              | 1.33   | 1.51   | 2.01   | 6.02    | 0.75              | 1.58    | 1.91   | 2.50   | 9.29    | 2.54          | 3.26   | 3.61   | 4.17   | 7.78   |       | 3.96                |
| <b>ΣREE (ppm)</b> | 796                     | 2463   | 3295   | 4095   | 7327    | 634               | 2155   | 2873   | 3772   | 5410    | 616               | 1383    | 1996   | 2707   | 4424    | 2648          | 4279   | 5911   | 6653   | 10271  |       | 4122                |
| <b>Sr/Y</b>       | 0.13                    | 0.26   | 0.38   | 0.59   | 3.82    | 0.20              | 0.37   | 0.47   | 0.88   | 6.88    | 0.30              | 0.44    | 0.58   | 1.46   | 39.86   | 0.18          | 0.31   | 0.37   | 0.60   | 1.73   |       | 0.571               |
| <b>Eu/Eu*</b>     | 0.27                    | 0.40   | 0.58   | 0.76   | 1.93    | 0.42              | 0.54   | 0.66   | 0.85   | 2.10    | 0.45              | 0.56    | 0.63   | 0.81   | 1.34    | 0.15          | 0.20   | 0.26   | 0.31   | 0.46   |       | 0.299               |

|                   | M-Ap (SW Oyu) |        |        |        |        | BiGd   |        |        |        |        | Dvs    |        |        |        |        |       | Median<br>Granitoid |
|-------------------|---------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|---------------------|
|                   | Min.          | 1st Q. | Median | 3rd Q. | Max    | Min.   | 1st Q. | Median | 3rd Q. | Max    | Min.   | 1st Q. | Median | 3rd Q. | Max    | LOD   |                     |
| <b>F (wt.%)</b>   | 2.22          | 2.645  | 2.975  | 3.26   | 3.51   | 1.46   | 1.55   | 1.69   | 1.985  | 2.54   | 1.46   | 1.65   | 1.82   | 1.98   | 3.85   | 0.12  | 2.77                |
| <b>C (wt. %)</b>  | b.d.l.        | 0.1525 | 0.37   | 0.60   | 0.75   | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.13   | 0.51   | 1.00   | 1.36   | 1.55   | 0.06  | 0.05                |
| <b>S (wt.%)</b>   | b.d.l.        | b.d.l. | 0.07   | 0.13   | 0.19   | b.d.l. | b.d.l. | 0.06   | 0.085  | 0.27   | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.05  | 0.015               |
| <b>Ca (wt.%)</b>  | 38.68         | 39.26  | 39.47  | 39.675 | 40.29  | 39.36  | 39.74  | 39.85  | 39.975 | 40.22  | 38.1   | 38.7   | 38.9   | 39.4   | 40.1   | 0.05  | 38.15               |
| <b>Na (ppm)</b>   | 116.7         | 219.5  | 341.6  | 476.2  | 1006.7 | 30.8   | 346.2  | 488.3  | 727.6  | 1579.9 | 429.8  | 593.7  | 764.8  | 835.5  | 1300.8 | 11.65 | 799                 |
| <b>Mg (ppm)</b>   | 15.2          | 36.1   | 55.6   | 90.2   | 611.6  | 24.3   | 115.2  | 163.5  | 237.6  | 471.8  | 237.4  | 381.9  | 421.4  | 694.5  | 2749.8 | 0.40  |                     |
| <b>Si (ppm)</b>   | 668.8         | 1411.4 | 1869.1 | 2097.8 | 4210.7 | b.d.l. | 924.0  | 1345.3 | 1719.2 | 2902.4 | 1482.8 | 1819.3 | 2063.6 | 2253.1 | 3277.2 | 456   | 1041                |
| <b>Mn (ppm)</b>   | 238.0         | 410.6  | 621.3  | 911.5  | 1240.1 | 137.5  | 702.3  | 806.2  | 915.6  | 1073.7 | 1256.1 | 1368.4 | 1857.6 | 2288.4 | 2718.8 | 4.49  | 922                 |
| <b>Fe (ppm)</b>   | 174.4         | 269.7  | 377.8  | 465.3  | 1312.0 | 126.9  | 614.1  | 769.7  | 942.6  | 2082.6 | 1015.8 | 1172.8 | 1397.8 | 2413.4 | 4051.4 | 13.35 | 1005                |
| <b>Sr (ppm)</b>   | 233.4         | 322.0  | 378.8  | 431.3  | 489.5  | 201.5  | 859.4  | 1014.1 | 1231.8 | 6596.4 | 494.6  | 612.3  | 743.4  | 880.0  | 1023.8 | 0.65  | 346                 |
| <b>Y (ppm)</b>    | 63.3          | 145.2  | 240.8  | 303.0  | 559.7  | 12.4   | 139.9  | 199.3  | 237.3  | 925.2  | 259.3  | 460.9  | 756.3  | 856.3  | 982.5  | 1.57  | 634                 |
| <b>Zr (ppm)</b>   | 0.05          | 0.55   | 0.80   | 1.53   | 2.48   | b.d.l. | 0.22   | 0.71   | 1.24   | 10.10  | 0.22   | 1.29   | 2.19   | 3.31   | 4.78   | 0.03  | 0.632               |
| <b>Ba (ppm)</b>   | b.d.l.        | 0.15   | 0.34   | 0.42   | 0.74   | 0.21   | 1.21   | 1.85   | 2.53   | 9.23   | 0.61   | 2.36   | 4.52   | 7.46   | 20.54  | 0.08  | 1.6                 |
| <b>La (ppm)</b>   | 195.0         | 318.3  | 366.4  | 512.1  | 758.0  | 0.4    | 79.3   | 138.4  | 223.6  | 902.3  | 393.2  | 658.3  | 737.7  | 834.8  | 956.2  | 0.29  | 731                 |
| <b>Ce (ppm)</b>   | 247.7         | 554.1  | 709.6  | 961.1  | 1545.9 | b.d.l. | 259.9  | 435.3  | 661.2  | 1571.4 | 932.5  | 1299.8 | 2132.0 | 2380.4 | 2663.7 | 1.44  | 1531                |
| <b>Pr (ppm)</b>   | 18.6          | 45.4   | 80.8   | 99.5   | 129.4  | 0.18   | 32.4   | 59.6   | 96.4   | 213.9  | 92.5   | 136.2  | 254.9  | 277.1  | 308.9  | 0.18  | 195                 |
| <b>Nd (ppm)</b>   | 66.8          | 176.4  | 290.2  | 386.7  | 573.2  | 1.13   | 145.5  | 280.1  | 423.7  | 950.3  | 325.4  | 538.2  | 1066.2 | 1190.8 | 1320.8 | 0.97  | 676                 |
| <b>Sm (ppm)</b>   | 11.6          | 30.2   | 49.3   | 66.8   | 126.0  | 0.36   | 35.6   | 62.2   | 93.8   | 216.0  | 52.8   | 104.9  | 217.1  | 242.4  | 268.1  | 0.32  | 186                 |
| <b>Eu (ppm)</b>   | 2.8           | 5.0    | 5.9    | 8.5    | 11.1   | 0.22   | 10.4   | 14.9   | 19.1   | 48.5   | 11.9   | 23.5   | 25.8   | 28.3   | 49.9   | 0.06  | 14                  |
| <b>Gd (ppm)</b>   | 12.6          | 31.4   | 49.4   | 67.9   | 137.6  | 0.85   | 39.5   | 60.7   | 82.5   | 251.3  | 50.2   | 100.2  | 197.3  | 224.6  | 262.1  | 0.38  | 165                 |
| <b>Tb (ppm)</b>   | 1.4           | 3.7    | 6.0    | 8.1    | 16.2   | 0.15   | 4.7    | 7.0    | 9.5    | 32.8   | 6.1    | 12.7   | 24.7   | 28.1   | 31.5   | 0.05  | 17.6                |
| <b>Dy (ppm)</b>   | 9.0           | 21.4   | 36.4   | 46.7   | 96.0   | 1.27   | 26.0   | 37.0   | 52.5   | 186.4  | 35.9   | 76.5   | 138.8  | 161.2  | 176.3  | 0.35  | 119                 |
| <b>Ho (ppm)</b>   | 1.8           | 4.7    | 8.1    | 10.0   | 20.4   | 0.31   | 4.6    | 7.0    | 8.8    | 35.8   | 8.0    | 15.8   | 26.5   | 31.3   | 34.9   | 0.07  | 20.5                |
| <b>Er (ppm)</b>   | 5.7           | 14.6   | 24.4   | 31.4   | 57.4   | 1.90   | 12.1   | 17.9   | 21.0   | 95.5   | 25.6   | 45.3   | 71.5   | 81.8   | 92.4   | 0.20  | 58.8                |
| <b>Tm (ppm)</b>   | 0.8           | 1.9    | 3.1    | 4.2    | 7.0    | 0.27   | 1.5    | 2.0    | 2.5    | 10.9   | 3.4    | 5.6    | 8.6    | 9.8    | 11.5   | 0.03  | 7.55                |
| <b>Yb (ppm)</b>   | 5.5           | 13.4   | 22.4   | 27.5   | 40.2   | 2.11   | 8.5    | 11.1   | 14.2   | 59.0   | 23.1   | 33.4   | 50.6   | 59.0   | 72.5   | 0.15  | 47.2                |
| <b>Lu (ppm)</b>   | 1.1           | 2.4    | 3.8    | 4.9    | 5.9    | 0.34   | 1.2    | 1.5    | 1.9    | 7.7    | 3.2    | 5.4    | 6.8    | 8.0    | 11.3   | 0.02  | 6.8                 |
| <b>Pb (ppm)</b>   | b.d.l.        | 0.65   | 1.18   | 1.65   | 2.58   | 1.08   | 3.40   | 4.01   | 4.82   | 35.44  | 1.32   | 1.58   | 1.87   | 2.24   | 3.77   | 0.14  | 6.62                |
| <b>Th (ppm)</b>   | 2.96          | 10.51  | 12.46  | 15.19  | 22.58  | b.d.l. | 0.86   | 2.25   | 5.14   | 76.68  | 3.64   | 6.45   | 9.26   | 11.07  | 18.93  | 0.02  | 31                  |
| <b>U (ppm)</b>    | 1.63          | 2.58   | 3.48   | 4.83   | 7.96   | b.d.l. | 1.44   | 2.18   | 3.32   | 26.40  | 1.21   | 2.89   | 3.41   | 4.00   | 10.97  | 0.03  | 29                  |
| <b>La/Yb</b>      | 5.44          | 12.71  | 16.11  | 19.03  | 29.41  | 0.07   | 4.37   | 9.07   | 12.80  | 143.90 | 6.63   | 9.74   | 10.78  | 12.24  | 17.08  |       | 13.3                |
| <b>Sm/Yb</b>      | 2.22          | 2.30   | 2.58   | 2.81   | 3.48   | 0.09   | 4.22   | 5.66   | 8.12   | 22.98  | 1.76   | 4.11   | 4.58   | 4.76   | 5.40   |       | 3.96                |
| <b>ΣREE (ppm)</b> | 581           | 1272   | 1714   | 2197   | 3154   | 17     | 680    | 1129   | 1849   | 4022   | 2153   | 2997   | 4988   | 5518   | 6196   |       | 4122                |
| <b>Sr/Y</b>       | 0.54          | 1.17   | 1.63   | 2.37   | 7.01   | 0.94   | 4.24   | 5.28   | 8.08   | 95.95  | 0.58   | 0.80   | 0.95   | 1.67   | 3.29   |       | 0.571               |
| <b>Eu/Eu*</b>     | 0.19          | 0.34   | 0.45   | 0.53   | 0.93   | 0.25   | 0.69   | 0.76   | 0.80   | 1.57   | 0.31   | 0.36   | 0.38   | 0.69   | 1.36   |       | 0.299               |

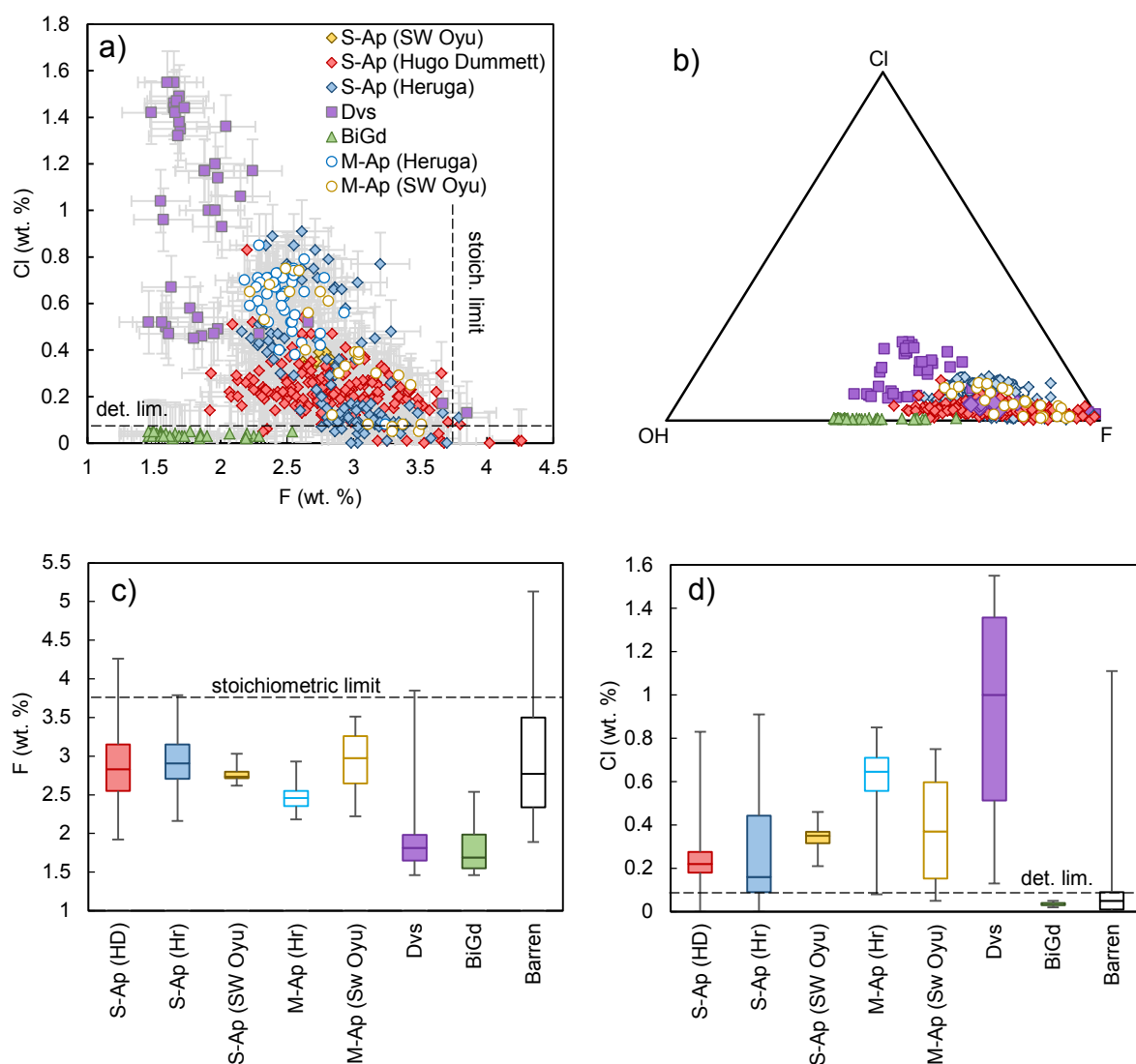


Figure 6.5. Halogen chemistry of Oyu Tolgoi apatites. a) Cl and F contents generally show an inverse relationship. b) Halogen ternary diagram, showing the propensity of apatites from Oyu Tolgoi to be enriched in F over Cl and OH. c-d) Box and whisker diagrams showing the median, interquartile range, and range of F and Cl concentrations. Note the extremely low Cl content of apatites from the post-mineralisation BiGd intrusions. All data collected by EPMA.

Cl and F contents in Oyu Tolgoi apatite generally show an inverse relationship (Fig. 6.5 a). S-Ap from QMD rocks is mostly fluorapatite, with F accounting for >50% of the halogen site, and in some cases up to 98% (Fig. 6.5 b). Median F values for S-Ap from Heruga, Hugo Dummett, and SW Oyu are all similar, and comparable with apatites from barren granitoids. BiGd and Dvs apatites are relatively depleted in F (Fig. 6.5 c).



Cl values for all groups are close to the limit of detection (Fig. 6.5 d). In general, S-Ap have lower Cl values than M-Ap. The highest Cl values are found in the Dvs apatite, with median values in excess of 1 wt. %. By contrast, the post mineralisation BiGd apatites have extremely low Cl contents, with all reported values below the limit of detection (Fig. 6.5 d). The median Cl value for apatites from all rock types are higher than the median value determined for apatites from barren granitoids, but they lie well within the range of median values for barren granitoids determined by other studies (e.g. Belousova et al., 2002a; Piccoli and Candela, 2002; Table 6.2).

Sulphur concentrations are close to the limit of detection, and all groups of apatite have some analyses below this value (549 ppm). Most S-Ap analyses are below LOD, although some analyses are up to 1 wt. % S. These especially high S analyses are likely due to the interaction between the electron beam and small inclusions of sulphides, especially bornite (Fig. 6.6 b). M-Ap typically have higher S values, mostly between LOD and 0.2 wt. % S. This is a higher

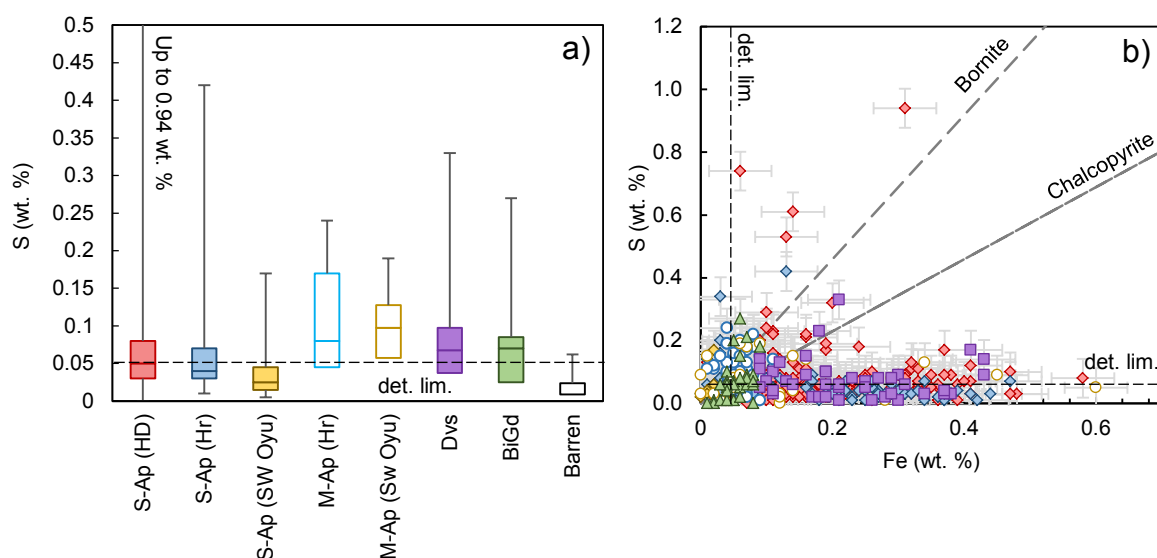


Figure 6.6. a) Box and whisker diagrams showing the median, interquartile range, and range of S concentrations in apatites from Oyu Tolgoi. b) S vs. Fe content. Some S-Ap analyses with high S have Fe:S ratios which indicate small inclusions of sulphide minerals were also analysed. Data from a) and b) collected by EPMA.

S content than median granitoids from the literature survey produced for this study, but within the range of S values determined by other workers (e.g. mean  $\pm \sigma = 0.11 \pm 0.10$  wt. %; Piccoli and Candela, 2002; see Table 6.2) The maximum values reported here are similar to the high S concentrations reported by Streck and Dilles (1998) for apatites from the mineralised Yerington batholith ( $\leq 0.4$  wt. % S).

#### 6.4.2.2 Monovalent cations

Median Na concentrations of Oyu Tolgoi apatites are broadly similar to those for granitoid apatites, although S-Ap has higher Na (median = 1123 and 1072 ppm for Hugo Dummett and Heruga respectively) and the BiGd has lower Na (486 ppm) than typical granitoids ( $\sim 799$  ppm). Na concentrations in M-Ap from the QMD (median = 997 ppm) are broadly typical of apatites from granitoids. Na from all apatites shows a correlation with REE (Fig. 6.7 a), indicating the importance of the coupled substitution by which REE and Na are partitioned into apatite (see Equation 6.1). The deviation of the Dvs apatite from this trend highlights the role other substitution mechanisms play in REE and Na partitioning. Na does not

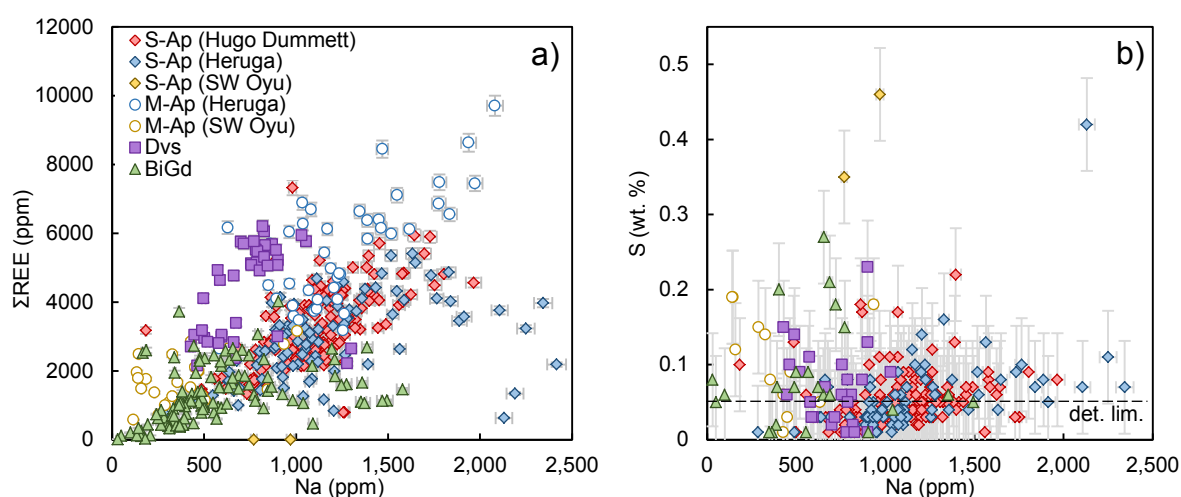


Figure 6.7. Variation of Na with respect to elements which form a coupled substitution with Na into apatite: a)  $\Sigma$ REE, and b) S. There is a near-absence of a correlation between S and Na (unlike in apatites from Resolution – see Figure 6.21). S values in b) were determined by EPMA, all other data was collected by LA-ICP-MS.

show a strong correlation with S (Fig. 6.7 b), so the coupled substitution involving Na and S may not be important at this locality (Liu and Comodi, 1993).

#### *6.4.2.1 Divalent cations*

In terms of median concentrations, the order of abundance of divalent trace element cations in S-Ap, M-Ap and Dvs apatite is  $Mn > Fe > Sr > Mg > Pb > Ba$ , although, in a given rock, divalent cation concentrations in apatites may vary by up to an order of magnitude. Sr is the most abundant divalent trace element in apatites from the post mineralisation BiGd (Fig. 6.8 a)

All groups of apatite have median values that are enriched in Sr with respect to median granitoid apatite concentrations (median = 346 ppm), with the exception of the M-Ap samples, which have similar Sr content (median = 299 ppm). The BiGd is particularly enriched in Sr (median = 980 ppm), and Sr concentrations reach up to 3190 ppm, which is an order of magnitude more than the median values for apatites from granitoid rocks. The maximum Sr content of granitoid apatites from the literature dataset is ~750 ppm Sr.

Hydrothermal S-Ap have high Mn contents, with maximum values >1 wt. %. In particular, S-Ap from Hugo Dummett are significantly enriched in Mn with respect to S-Ap from Heruga and SW Oyu, and with respect to most apatites from median granitoid rocks (Fig. 6.8 b). Such high values of Mn in apatite are more typically associated with apatites from S-type granitoids, and are extremely rare in intermediate I-type rocks (e.g. Fig. 6.1 a). M-Ap, Dvs and BiGd apatites have lower Mn, which are more typical of intermediate granitoids.

Fe values of Dvs apatite, and S-Ap from Heruga and Hugo Dummett are higher than is typical apatites from barren granitoids, whereas S-Ap (SW Oyu), M-Ap and BiGd apatites have more typical apatite Fe values. Pb values for all apatite groups are mostly lower than typical granitoid apatites.

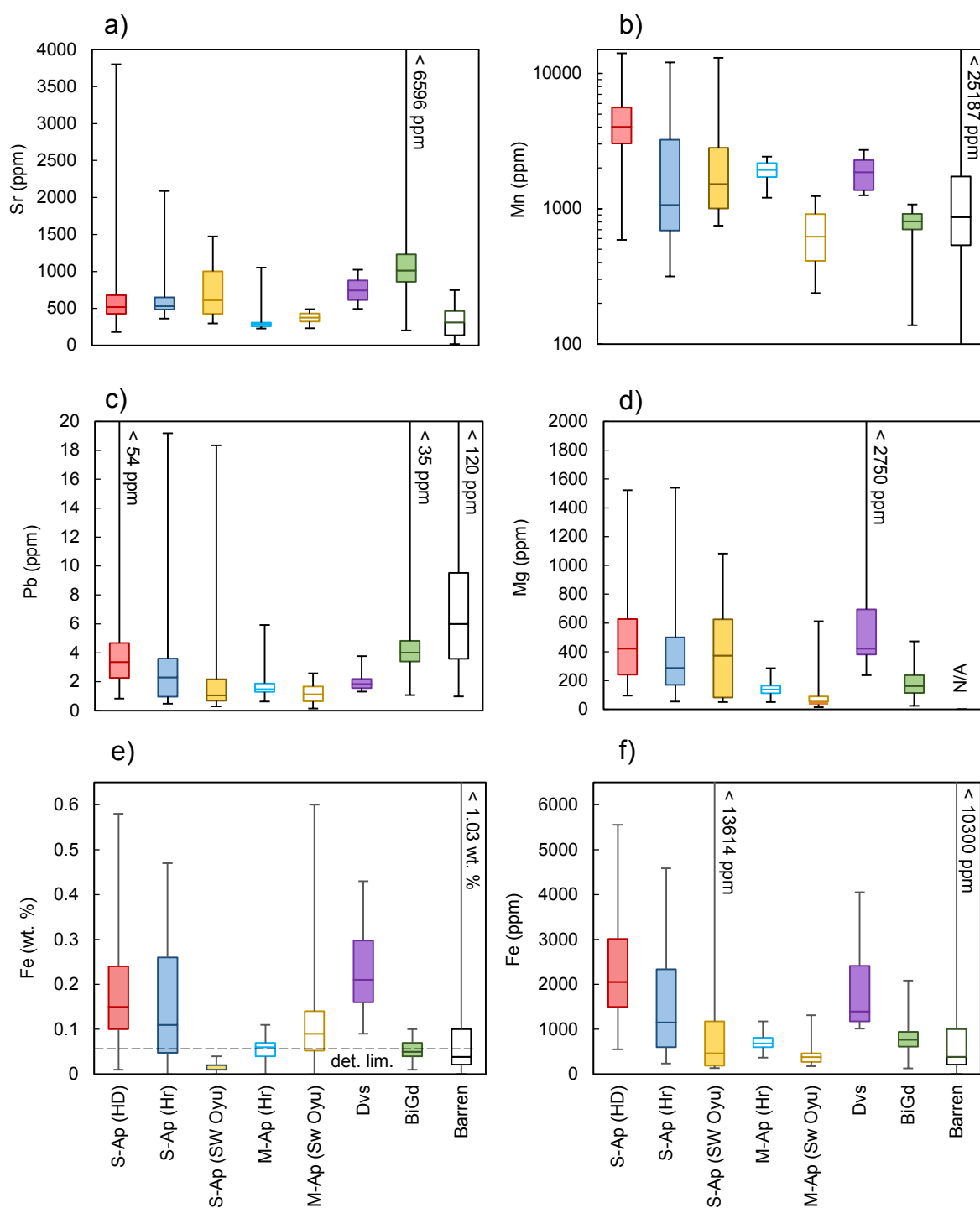


Figure 6.8. Box and whisker diagrams showing the median, interquartile range, and range of divalent cations in Oyu Tolgoi apatites. a) Sr, b) Mn (N.B. logarithmic scale) c) Pb, d) Mg, e-f) Fe contents in Oyu Tolgoi apatites. Data collected by LA-ICP-MS, except data in e), which was collected by EPMA. Note that insufficient literature data exist for Mg to make a comparison to barren granitoid apatites.

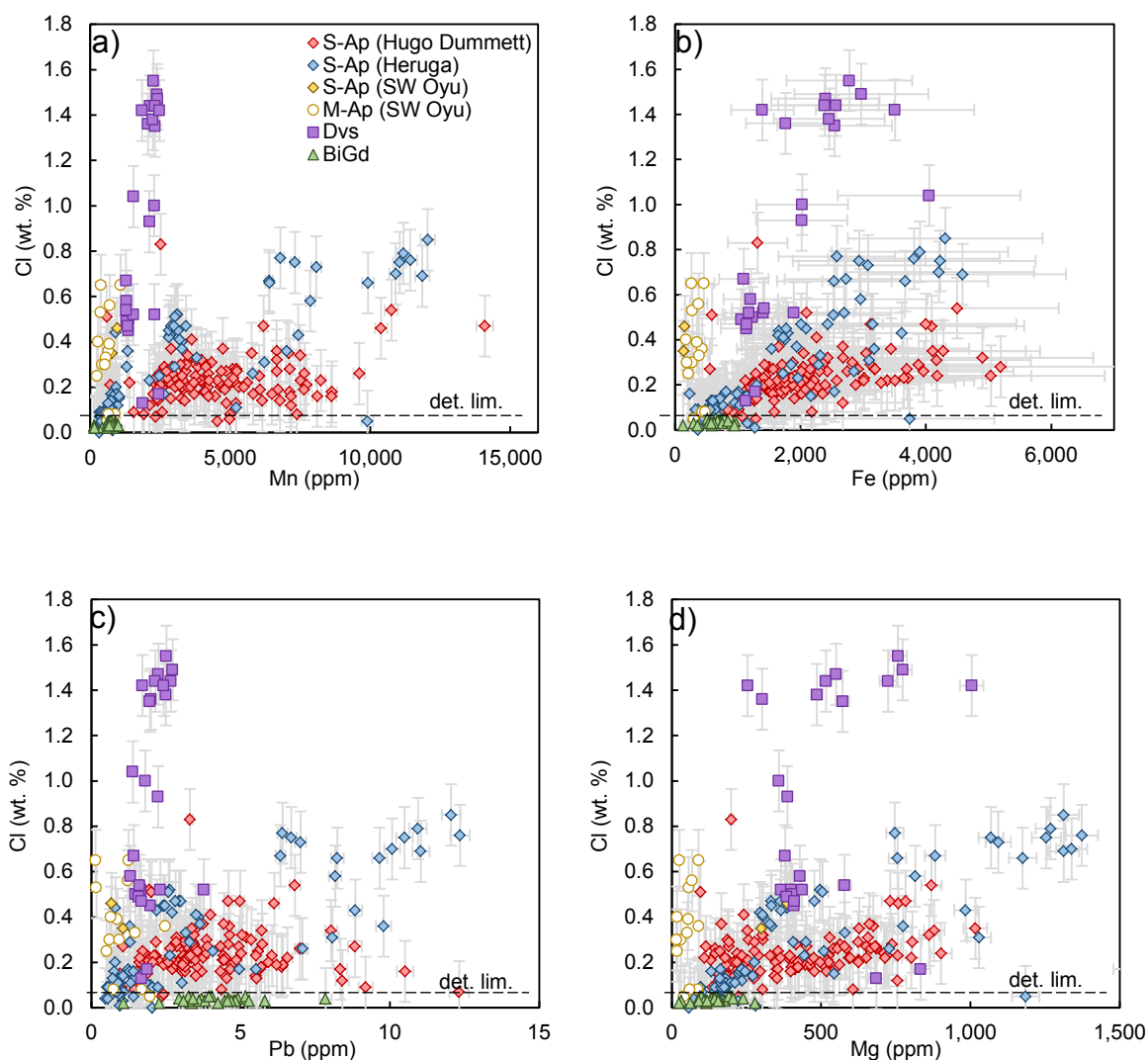


Figure 6.9. Variability of Cl with respect to various divalent cations: a) Mn, b) Fe, c) Pb, d) Mg. Cl values determined by EPMA, all cation data collected by LA-ICP-MS.

The concentrations of some divalent cations in certain groups of Oyu Tolgoi apatite show positive correlations with Cl concentration (Fig. 6.9 a-d). These trends are most clear in hydrothermal apatites (S-Ap) from Heruga and Hugo Dummett, which show Mg, Mn, Pb, and Fe increasing with Cl concentration. No such correlations exist between Cl and Sr or Ba.

Apatites of igneous origin (Dvs and M-Ap) also show weak correlations between these elements and Cl, but the  $M^{2+}/Cl$  ratio of these is much lower, i.e. a very large increase in Cl is accompanied by a smaller increase in Mn, Fe, and Pb relative to S-Ap. This is manifest as

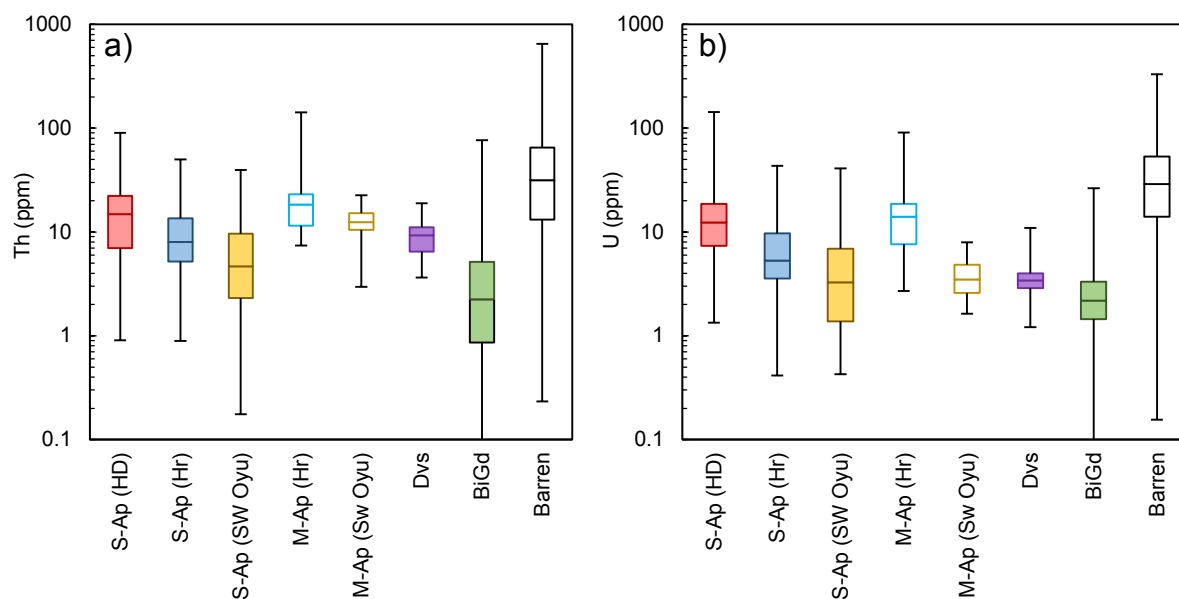


Figure 6.10. Box and whisker diagrams showing the median, interquartile range, and range of a) Th, and b) U in Oyu Tolgoi apatites. Data collected by LA-ICP-MS.

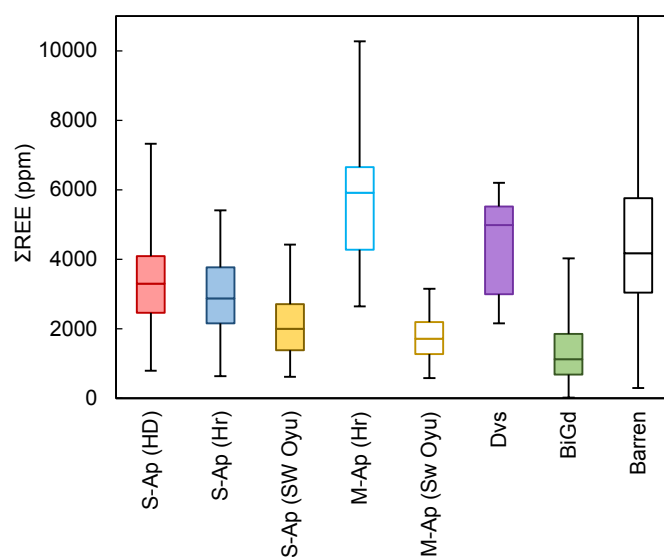


Figure 6.11. Box and whisker diagrams showing the median, interquartile range, and range of  $\Sigma\text{REE}$  in apatites from Oyu Tolgoi. All data collected by LA-ICP-MS.

steeper trends on  $M^{2+}$  vs Cl diagrams (Fig. 6.10). BiGd apatite, containing low Cl, generally have low Mn, Fe, and Mg, and plot close to the origin on such diagrams.

#### *6.4.2.2 Thorium and uranium*

Median concentrations of both thorium and uranium contents in all groups are significantly lower than median values for granitoid apatites (~31 ppm for both Th and U; Fig. 6.10). BiGd apatites are especially depleted in Th and U, and M-Ap are the most enriched.

#### *6.4.2.3 Rare earth elements*

Oyu Tolgoi apatites broadly contain similar  $\Sigma$ REE to typical granitoid apatites. S-Ap  $\Sigma$ REE concentrations are at the low of these values. M-Ap (SW Oyu) and BiGd are both depleted in REE with respect to typical granitoids, whereas M-Ap (Heruga) and Dvs apatites have similar  $\Sigma$ REE, comparable to granitoid apatites (Fig. 6.11).

Chondrite normalised REE patterns of S-Ap from all deposits are mostly enriched in HREE and depleted in LREE with respect to median granitoid apatite values (Fig. 6.12 a-c) and have low  $La_N/Yb_N$  values (1.44 to 1.88; Table 6.4). S-Ap have less pronounced Eu anomalies (median  $Eu/Eu^*$  0.58 to 0.66) than median granitoid apatites ( $Eu/Eu^* = 0.3$ ). BiGd apatites are depleted in all REE with respect to median granitoid apatites, with a more strongly depletion in HREE ( $La_N/Yb_N =$  Table 6.4). Negative Eu anomalies are very small (median  $Eu/Eu^* = 0.76$ ). Dvs apatite and M-Ap (Heruga) have similar chondrite-normalised REE patterns, which are strongly similar to typical granitoid patterns (Fig. 6.13) except for their smaller Eu anomalies (median  $Eu/Eu^* = 0.38$  and 0.45 respectively). However, M-Ap (SW Oyu) are more strongly depleted in all REE, with a particular depletion in MREE (Fig. 6.13 e).

$Eu/Eu^*$  broadly increases with decreasing  $\Sigma$ REE (Fig. 6.14 a), a correlation which is independent of the deposit or type of apatite. This is also the case for apatite from the literature

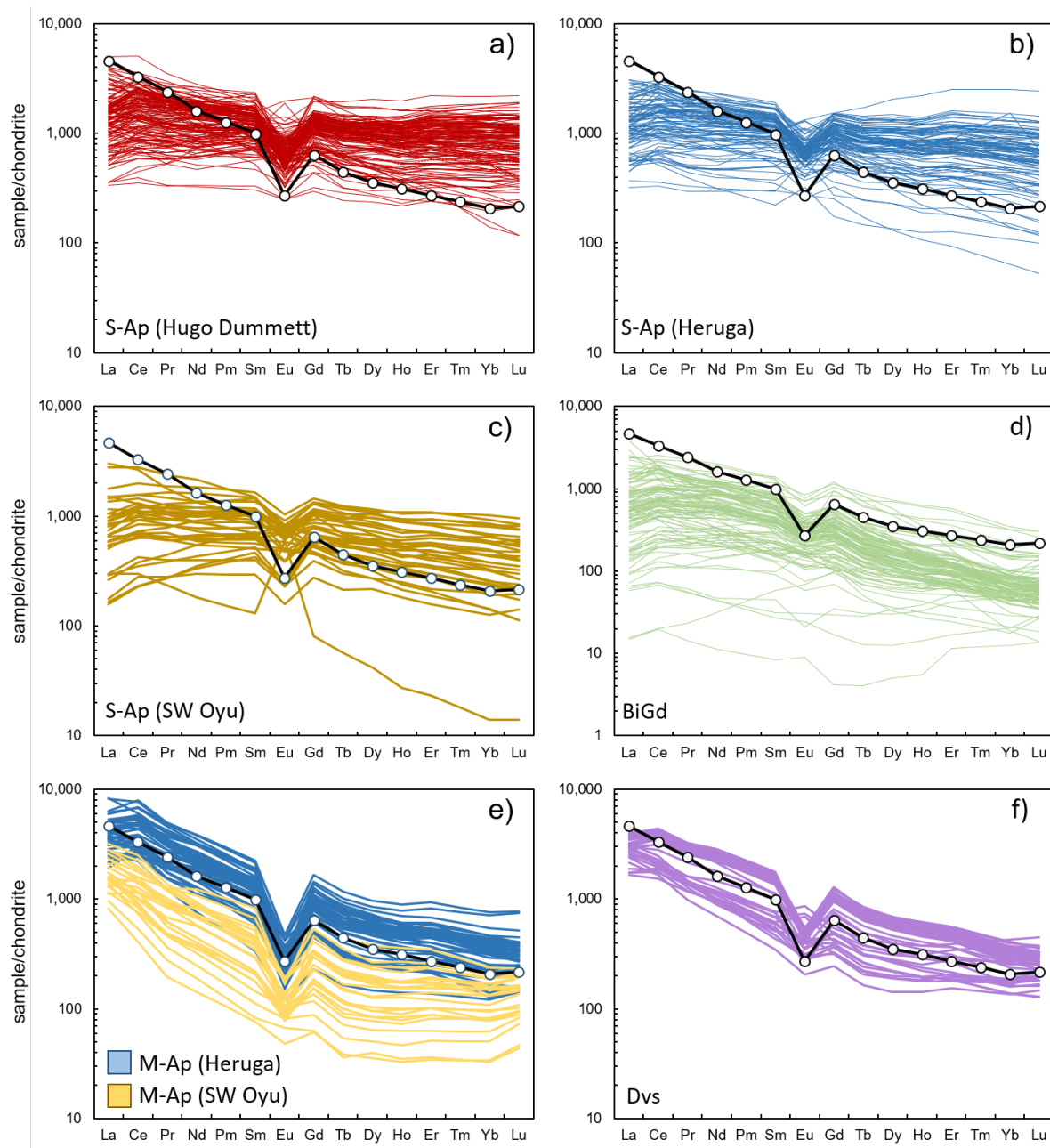


Figure 6.12. Chondrite-normalised REE patterns for apatites from Oyu Tolgoi, showing the raw individual REE analyses. a-c) S-Ap, d) BiGd apatite (note the change in y-axis scale), e) M-Ap, f) Dvs apatite. Black line with white circles is the median value for granitoid apatites. Normalising values from Sun and McDonough (1989). All REE data collected by LA-ICP-MS.



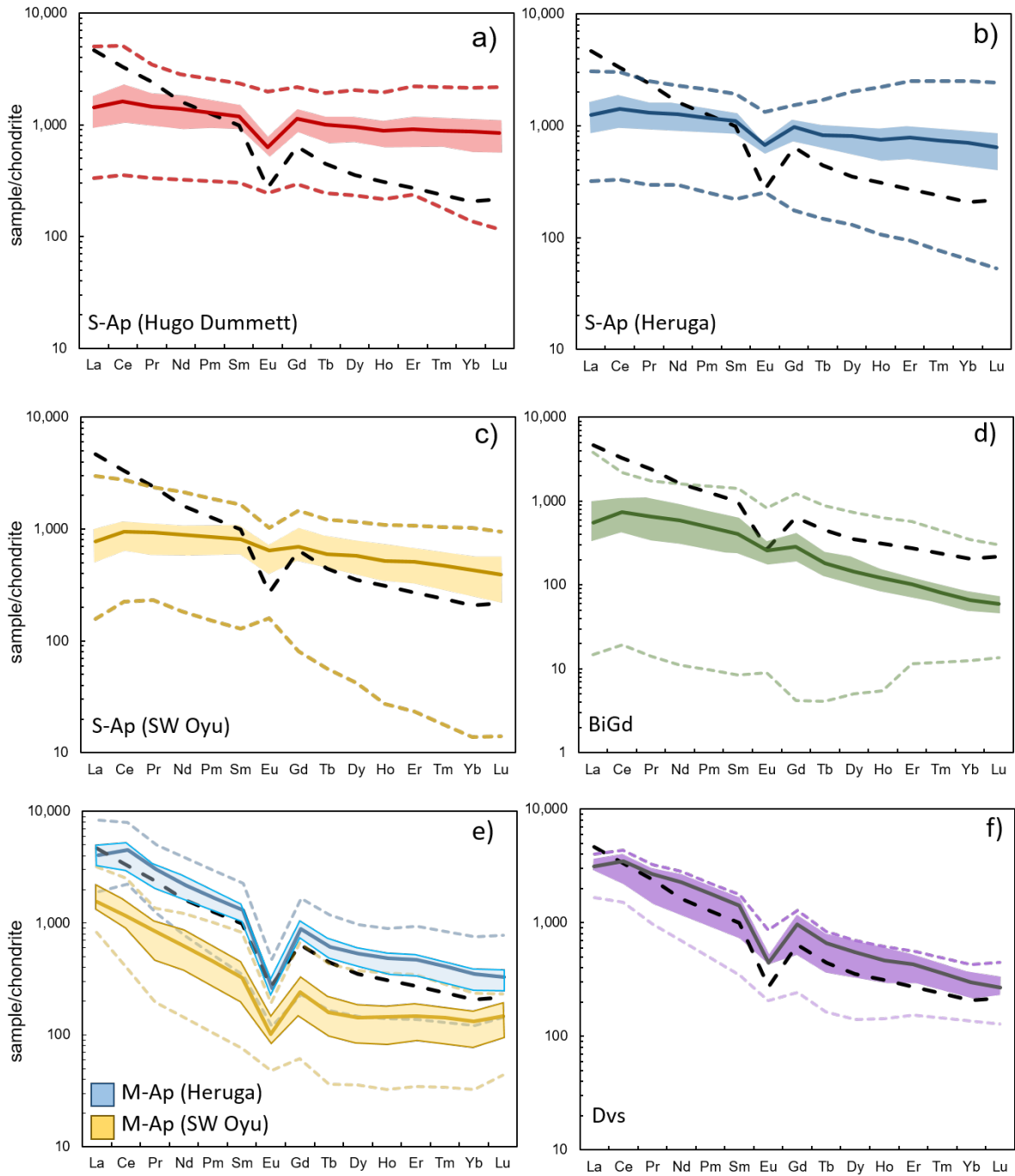


Figure 6.13. Chondrite-normalised REE patterns for apatites from Oyu Tolgoi. a-c) S-Ap, d) BiGd apatite (note the change in y-axis scale), e) M-Ap, f) Dvs apatite. Dashed lines are the maximum and minimum values, shaded areas are the interquartile range, and thick coloured lines are the median values. Black dashed line is the median value for granitoid apatites. Normalising values from Sun and McDonough (1989). All REE data collected by LA-ICP-MS.

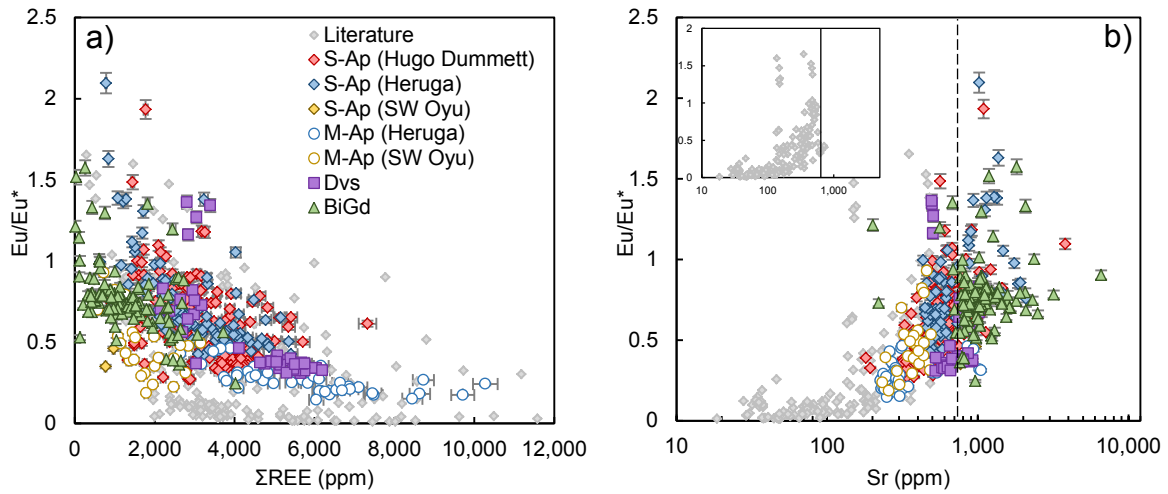


Figure 6.14. The Eu anomaly ( $Eu/Eu^*$ ) shows a) a negative correlation with  $\Sigma REE$ , and b) a positive correlation with Sr. These correlations are also seen in the literature data. Oyu Tolgoi data extend above the upper limit of  $\sim 750$  ppm Sr observed in the literature dataset (see b), inset). All data collected by LA-ICP-MS.

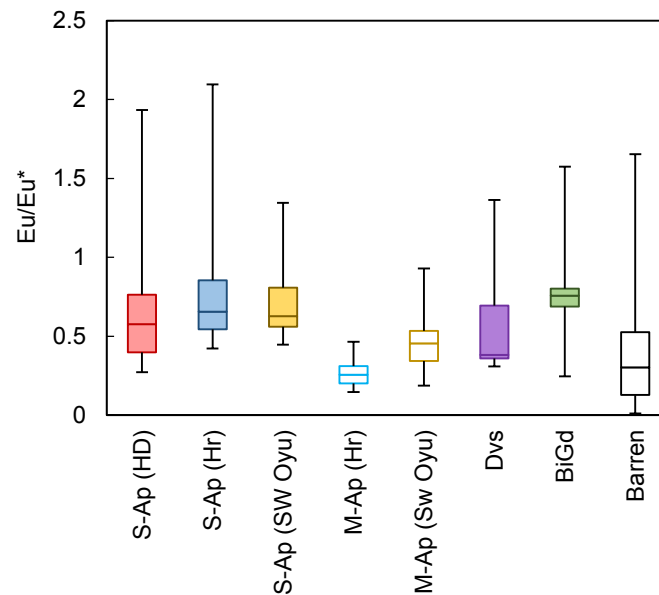


Figure 6.15. Box and whisker diagrams showing the median, interquartile range, and range of  $Eu/Eu^*$  values in Oyu Tolgoi apatites. Data collected by LA-ICP-MS.

dataset. Eu/Eu\* also shows positive correlations with Sr (Fig. 6.14 b), with the weakly mineralised M-Ap bearing rocks at the low Sr and low Eu/Eu\* end of the trend, and the mineralised S-Ap bearing rocks at the upper end with the barren, post-mineralisation BiGd apatites.

## **6.5 Results – Resolution**

### **6.5.1 Petrography of Resolution, Schultze Granite, and associated intrusions**

#### *6.5.1.1 Resolution intrusions*

Apatite is common in the Resolution porphyry intrusions, except those that have been strongly affected by sericitic alteration. Apatite accounts for up to 0.6 vol. % of the samples. There is no consistent textural distinction between apatite from the QLP and RDP, but there are at least three texturally distinct populations of apatite present in these rocks. The volumetrically dominant population of apatites occurs in the groundmass of the porphyry intrusions, or as occasional inclusions in primary biotite (Fig. 6.16 a,b) Grains have a variety of habits, from anhedral grains to pristine, euhedral crystals. All grains are found as part of an interlocking matrix of groundmass minerals, primarily K-feldspar, quartz, secondary biotite, and anhydrite (Fig. 6.16 c). These apatites also frequently contain inclusions of these groundmass phases, and also occasionally monazite. Most grains are ~100 µm in length and some grains are up to 400 µm, although many smaller grains are found in the groundmass. The CL response from these apatites is bright, with pale green colours (Fig. 6.16 d). These apatites shall be referred to as the “dominant-type” apatites. Their apparent equilibrium with the potassic groundmass, and absence in strongly sericitised rocks, suggests they are hydrothermal in origin, and form part of a potassic alteration assemblage.

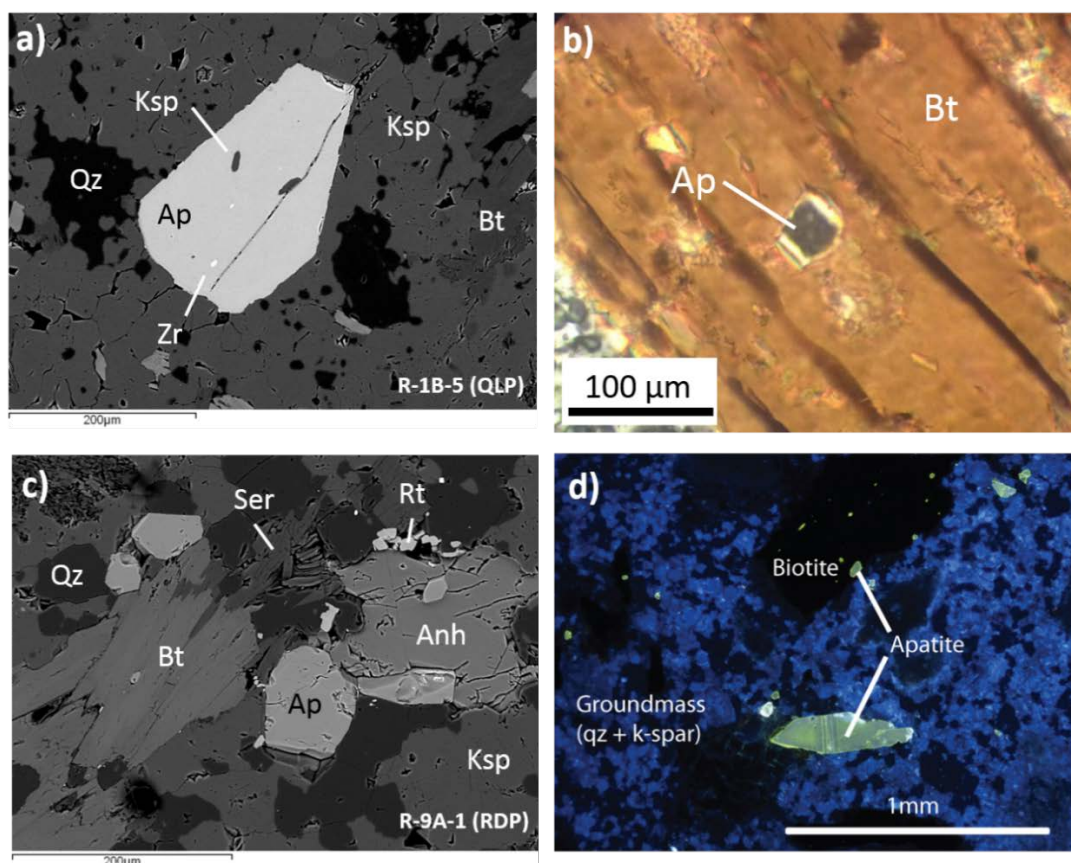


Figure 6.16. Representative images of dominant-type apatite from Resolution porphyry intrusions. (a) apatite in a K-feldspar, quartz, and secondary biotite groundmass; (b) apatite inclusion in biotite crystal; (c) apatite with associated secondary biotite, sericite, quartz, K-feldspar, anhydrite, and rutile. (d) Cold-cathode CL image of large apatite grain (pale green) in a groundmass of quartz (no CL) and K-feldspar (blue). Apatite grains are also included in biotite crystal. Ap = apatite, Ksp = K-feldspar, Qz = quartz, Bt = biotite, Ser = sericite, Rt = rutile, Anh = anhydrite. (a,c) backscatter SEM images, (b) transmitted light, (d) CL microscope

Another much rarer type of apatite was observed in only 2 rocks from this study; R-13F-2 and R-7D-3 (both QLP). This type of apatite has a characteristically dull CL response compared to the bright CL of dominant-type apatite. It is observed in microveinlets cutting

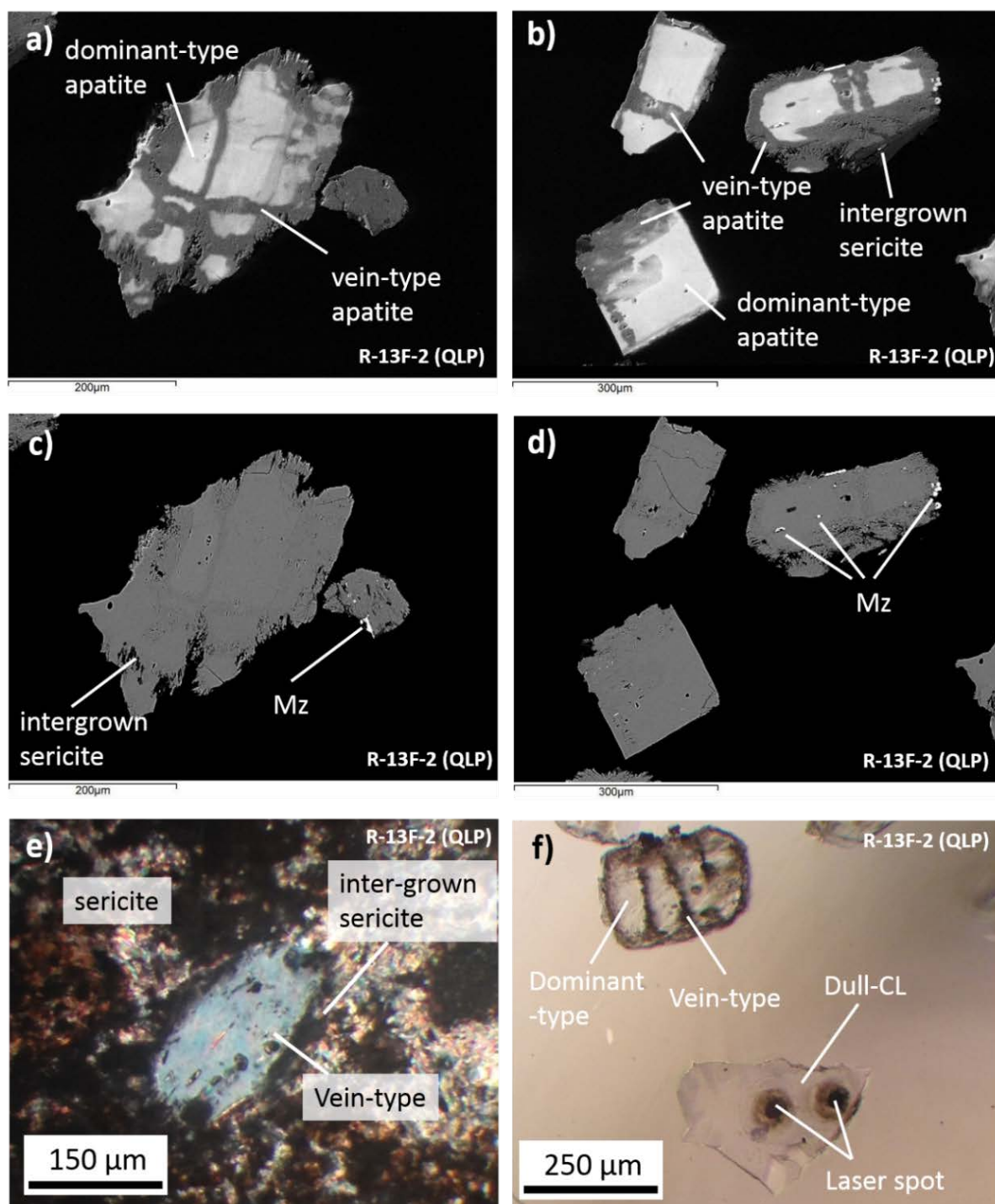


Figure 6.17. Texture of vein-type and dull-CL type apatite. (a,b) SEM-CL images of vein-type apatite as rims on dominant-type apatite, and cross-cutting it. Vein-type apatite is intergrown with sericite. (c,d) SEM backscatter images of monazite inclusions in vein-type apatite zones. CL response is duller surrounding monazite grains. (e) Transmitted light image of vein-type apatite in situ, intergrown with sericite. (f) Reflected light image of pristine, anhedral dull-CL apatite grain. Mz = monazite.

grains of the dominant-type, and also appears to replace them (Fig. 6.17 a-d). This type of apatite (hereafter, “*vein-type*”) has a different texture to the host crystal, displaying a pitted, mottled surface, and containing frequent small inclusions of monazite (Fig. 6.17 c,d). Microveinlets are typically <40 µm in width, and most are <10 µm. Vein-type apatites and their host dominant-type apatites are found in the sericitised groundmass of these two samples (Fig. 6.17 e). These vein-type apatites are very likely to be hydrothermal, as they appear to be re-setting the texture of early (potassic) dominant-type grains. Their presence only in sericitised rocks indicates they form part of a later hydrolytic assemblage.

Rare, large (~200-500 µm) grains of apatite with a flat, dull CL response were also observed in the same rocks as the patchy and vein-type apatite. These tend to be anhedral and do not have the pitted surface seen in the vein-type (Fig. 6.17 f). They are referred to herein as the “*dull CL*” apatites. They were only observed in the apatite mineral concentrates for both samples, so their textural origin is less well constrained. However, they are only found in sericitised rocks that also contain vein-type and no dominant-type apatite, and have a similarly weak CL response with the vein-type apatite. On this basis, they are likely to form during sericitic hydrothermal alteration.

#### 6.5.1.2 *Schultze Granite (main phase)*

Apatite is a common accessory phase in all samples from the Schultze Granite, accounting for 0.17 vol. %. Grains are typically subhedral and are found at the boundaries of larger biotite, plagioclase, K-feldspar, and quartz crystals (Fig. 6.18 a) and also as inclusions in biotite. Apatites are also commonly found inter-grown with large clusters of magnetite and ilmenite. Some grains (or clusters of grains) are very large, up to ~1 mm, but most are ~200 µm. The CL response from Schultze Granite apatites is a bright, pale green colour with little zoning, similar to the dominant-type apatites of the Resolution intrusions.



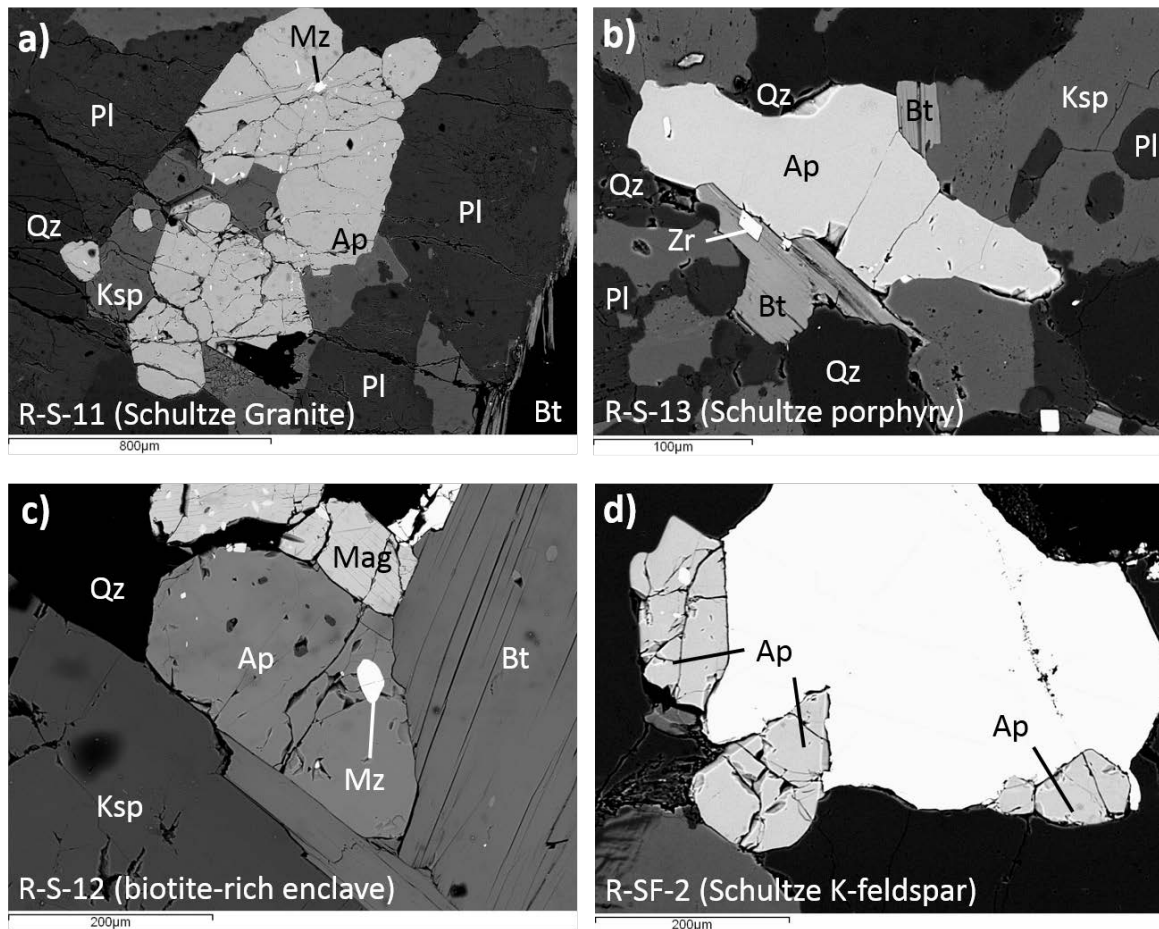


Figure 6.18. Representative SEM backscatter images of apatite from the Schultze Granite and related lithologies. (a) Cluster of apatite crystals with monazite inclusions from the main phase of the Schultze Granite. (b) Apatite from the Schultze Granite porphyry. (c) Apatite with monazite inclusion intergrown with biotite, magnetite, K-feldspar and quartz. (d) apatite intergrown with magnetite from the core of a K-feldspar megacryst of the Schultze Granite. Ap = apatite, Mz = monazite, Zr = zircon, Ksp = K-feldspar, Mag = magnetite, Qz = quartz, Pl = plagioclase, Bt = biotite.

#### 6.5.1.3 Schultze Granite porphyry

Apatite accounts for 0.17 % of the Schultze Granite porphyry sample R-S-13. It has similar textural characteristics to apatites found in the Schultze Granite main phase. Grains are subhedral, up to 300 µm in size, and are often found intergrown with (or included within) biotite and magnetite (Fig. 6.18 b). Isolated examples in the groundmass are also observed.

#### *6.5.1.4 Biotite-rich enclave*

Apatite is an abundant accessory phase within biotite-rich enclave sample R-S-12, accounting for 0.7 vol. % of this sample. It is found as subhedral to euhedral grains, mostly between 100 and 200  $\mu\text{m}$ , although some grains reach 600  $\mu\text{m}$  in size. Apatites in this rock are found associated with biotite and magnetite in nearly all cases, either on the margins of large biotite crystals, or as inclusions within them (Fig. 6.18 c). Apatite inclusions in biotite rarely exceed  $\sim 250$   $\mu\text{m}$  in size. Grains are equant and hexagonal, or elongate lozenge-shaped laths depending on the crystal orientation in which they have been cut. CL characteristics are the same as in the Schultze Granite main phase.

#### *6.5.1.5 K-feldspar megacrysts*

Apatite in the K-feldspar megacryst sample (R-SF-2) shows a similar association with magnetite and biotite as is observed in the main phase of the granite (Fig. 6.18 d). Isolated grains within the megacryst are very rare; they are usually found both at the margins of, and as inclusions within, large grains or clusters of magnetite. Apatites are up to 250  $\mu\text{m}$  with some smaller grains  $< 50$   $\mu\text{m}$ . Grains are mostly euhedral, with subhedral habits less common, and are equant to elongate. CL characteristics

Their intimate association of igneous phases (magnetite, plagioclase), with of Schultze Granite apatites from all lithologies, and the near absence of alteration in these rocks suggests that these apatites are primary igneous.

#### *6.5.1.6 Mafic Apache Leap intrusion*

Apatite is an accessory phase in the mafic Apache Leap intrusion, comprising 0.32 vol. % of sample R-RF-A. It is typically found in clusters of several small grains in close proximity to magnetite and/or relict hornblende crystals. Grains are small (mostly  $< 100$   $\mu\text{m}$  in size), and have euhedral habits, with subordinate subhedral grains. They are found mostly as thin, needle-



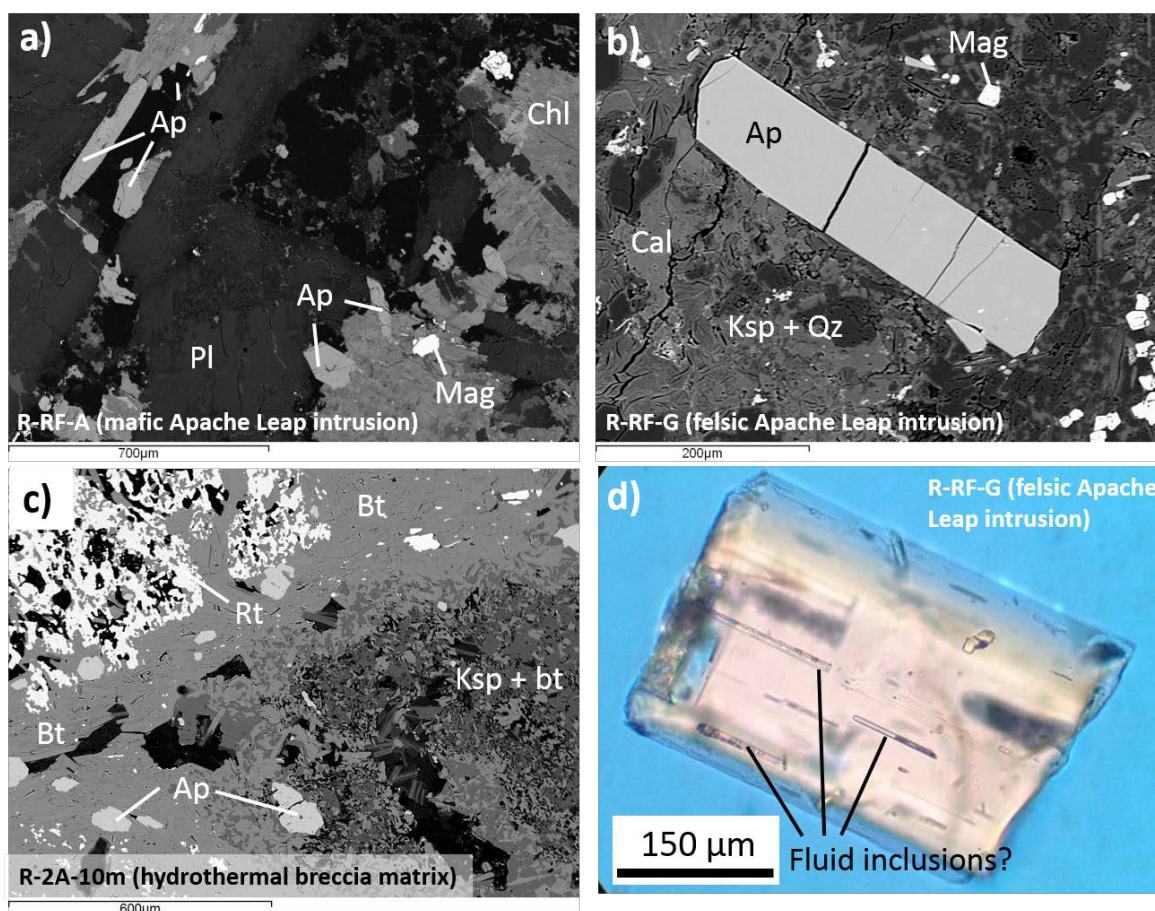


Figure 6.19. Representative images of apatite from the Apache Leap intrusions and the matrix of the hydrothermal breccia at Resolution. (a) SEM backscatter image showing needle-like apatite grains in the mafic Apache Leap intrusion, with plagioclase and chloritised hornblende. (b) SEM backscatter image showing euhedral apatite from the groundmass of the felsic Apache Leap intrusion. Groundmass comprises inter-grown K-feldspar, quartz, and occasional magnetite grains, with patches of calcite. (c) SEM backscatter image showing apatite in the matrix of the hydrothermal breccia, inter-grown with secondary biotite in clots with rutile. (d) Transmitted light image of apatite from the felsic Apache Leap intrusion, showing narrow channels parallel to the C-axis, possibly fluid inclusions. Ap = apatite, Pl = plagioclase, Chl = chlorite, Cal = calcite, Mag = magnetite, Rt = rutile, Ksp = K-feldspar.

like crystals, as well as more tabular grains (Fig. 6.19 a). Apatites in this rock are not found as inclusions in other minerals, but rather occur at the grain boundaries of other phases. The needle-like habit of these grains, and their association with chloritised relict hornblende grains suggest that these grains are secondary, forming as a result of the breakdown of primary mafic phases.

#### *6.5.1.7 Felsic Apache Leap intrusion*

Apatite from sample R-RF-G accounts for 0.39 vol. % of this rock. Apatites are typically located in the groundmass of this porphyry intrusion, sometimes associated with clots of calcite (Fig. 6.19 b). Some examples of apatite grains in altered biotite phenocrysts were observed. Apatites are euhedral, and mostly around 100  $\mu\text{m}$  in size, reaching up to 400  $\mu\text{m}$ . Grains are prismatic and hexagonal in cross section. For this sample, apatite was analysed from separated grains mounted in polished blocks. Narrow, elongate fluid inclusions up to 150  $\mu\text{m}$  long are frequently seen parallel to the *c*-axis (Fig. 6.19 d).

The association of these apatites with chloritised mafic minerals and clots of calcite in the groundmass suggest they are hydrothermal, and form part of a propylitic assemblage.

#### *6.5.1.8 Hydrothermal breccia*

A small set of EPMA analyses were collected for sample R-2A-10m, the matrix of the hydrothermal breccia (see Section 3.4.2.2), which contains abundant apatite grains. They are large (up to 1 mm, mostly 300 to 500  $\mu\text{m}$ ), subhedral, tabular laths inter-grown with (and containing inclusions of) biotite, rutile and sulphides in clots of crystals (Fig. 6.19 c). The association of these grains with secondary biotite suggests that they are hydrothermal in origin.

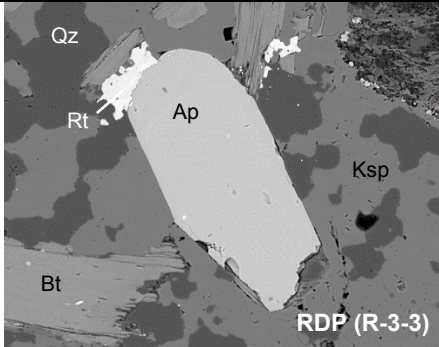
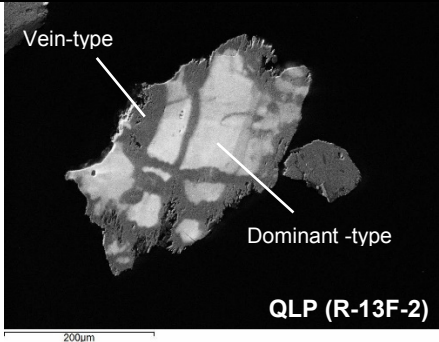
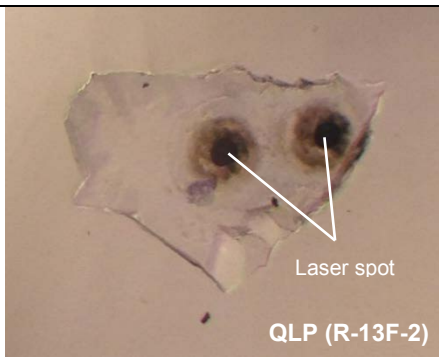
|                                                                                                                                           | Occurrence                                                                                                                                                                                       | Mineral associations                                                      | Texture                                                                                                                                                                                                                      | Origin                                                                                                                                                                                         | Representative image                                                                 |
|-------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| <b>Resolution porphyry intrusions – “dominant-type”</b><br><br><i>Most abundant apatite population in QLP and RDP porphyry intrusions</i> | Ubiquitous in all potassic-sericitic altered porphyry intrusions, absent in strongly sericite altered rocks. Primarily found in groundmass of porphyry intrusions, also as inclusions in biotite | K-feldspar (ksp), quartz (Qz), Biotite (bt), Rutile (rt), anhydrite (anh) | Euhedral to subhedral, 200-700 µm, forms part of an interlocking groundmass mosaic (with qz + ksp ± bt ± anh). Weak green CL characteristics, minor concentric zoning.                                                       | Hydrothermal - associated with high temperature potassic (+ sericite) alteration. Abundant evidence of equilibrium with other hydrothermal potassic minerals (such as K-feldspar and biotite). |   |
| <b>Resolution porphyry intrusions – “vein-type”</b><br><br><i>Rare apatite microveinlets replacing dominant-type apatite</i>              | Found only in two samples (R-13F-2, and R-7D-3) of sericite-altered QLP. Always observed as veinlets in dominant-type apatite.                                                                   | Sericite, dominant-type apatite, monazite (inclusions within apatite)     | Narrow veins (<50 µm) crossing dominant-type apatite. Veins are normally ‘ragged’ (containing multiple fluid inclusions, and are inter-grown with sericite and monazite. Some gradation from dominant- to vein-type apatite. | Hydrothermal – associated with sericitic alteration. Related to fluid re-equilibration and unmixing of dominant apatite to an assemblage of vein-type apatite + monazite                       |   |
| <b>Resolution porphyry intrusions – “dull CL-type”</b><br><br><i>Rare grains of optically clear apatite found in sample R-13F-2</i>       | Only in sample R-13F-2 (sericite-altered QLP)                                                                                                                                                    | Unknown – only observed in mineral separates. No mineral inclusions       | Optically clear, subhedral, up to 400 µm. Dull CL characteristics, which give its name                                                                                                                                       | Hydrothermal – only found in sericite altered sample R-13F-2, so likely associated with hydrolytic alteration.                                                                                 |  |

Table 6.5. Summary of the textural characteristics of Resolution apatites

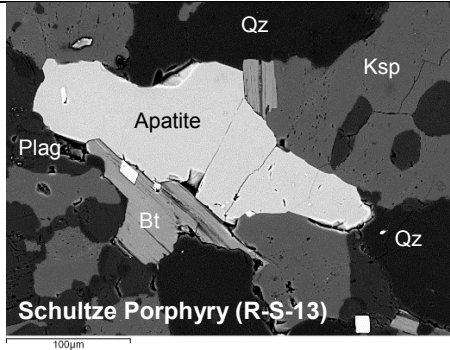
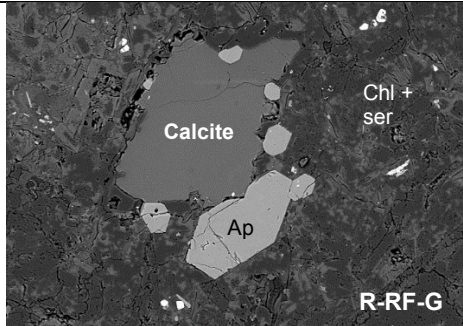
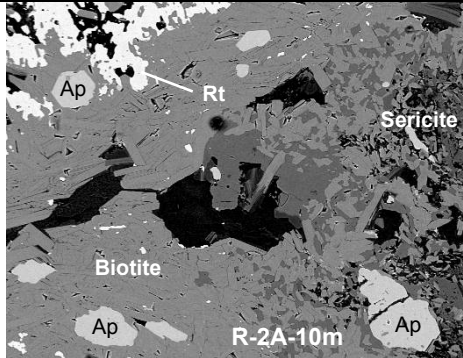
|                                                                                                                                   | Occurrence                                                                                                                                      | Mineral associations                                                                                                 | Texture                                                                                                                                                                    | Origin                                                                                               | Representative image                                                                 |
|-----------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| <b>Schultze Granite</b><br><i>Apatites in unmineralised late Cretaceous granite and associated lithologies.</i>                   | Ubiquitous mineral in all Schultze Granite samples. Includes in biotite-rich enclave, Schultze porphyry, and inclusions in K-feldspar megacryst | K-feldspar (including megacrysts), magnetite-ilmenite, biotite, plagioclase, quartz, subordinate monazite inclusions | Sub- to anhedral, between 50 and 800 µm, in mafic clots with biotite and magnetite. Green CL colour, and weakly zones. Associated with minor monazite inclusions.          | Igneous – associated with unaltered, unmineralised rocks.                                            |   |
| <b>Felsic Apache Leap</b><br><i>Apatites from unmineralised, weakly altered felsic porphyry intrusions outside of the deposit</i> | Common accessory mineral in the groundmass of felsic Apache Leap intrusions.                                                                    | Chlorite, albite, sericite, calcite                                                                                  | Euhedral to subhedral, large (up to 500 µm). Occasionally found as inclusions in altered hornblende phenocrysts.                                                           | Hydrothermal – close intergrown association with calcite and sericite (see right)                    |   |
| <b>Hydrothermal breccia</b><br><i>Syn-mineral, mineralised hydrothermal breccia. Strongly biotitised</i>                          | A common mineral in the one hydrothermal breccia sample studied herein.                                                                         | Rutile, secondary (hydrothermal) biotite, sericite                                                                   | Subhedral to anhedral, up to 500 µm in size, but mostly ~300 µm. often containing inclusions of shreddy secondary biotite. Apatite mostly found close to 'clots' of rutile | Hydrothermal – found in a hydrothermal breccia, associated with shreddy secondary biotite and rutile |  |

Table 6.5. (contd.)



|                  | QLP (dominant) |        |        |        |        | RDP (dominant) |        |        |        |         | Schultze Granite |        |        |        |         | Felsic Apache Leap |        |        |        |        |       |              |
|------------------|----------------|--------|--------|--------|--------|----------------|--------|--------|--------|---------|------------------|--------|--------|--------|---------|--------------------|--------|--------|--------|--------|-------|--------------|
|                  | Min.           | 1st Q. | Median | 3rd Q. | Max    | Min.           | 1st Q. | Median | 3rd Q. | Max     | Min.             | 1st Q. | Median | 3rd Q. | Max     | Min.               | 1st Q. | Median | 3rd Q. | Max    | LOD   | Median       |
| <b>F (wt.%)</b>  | 3.03           | 3.57   | 3.75   | 3.89   | 4.19   | 2.04           | 3.12   | 3.44   | 3.68   | 4.44    | 2.64             | 2.88   | 3.01   | 3.12   | 3.42    | 1.70               | 2.09   | 2.31   | 2.45   | 2.68   | 0.12  | 2.77         |
| <b>Cl (wt.%)</b> | b.d.l.         | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l.         | b.d.l. | b.d.l. | b.d.l. | 0.22    | b.d.l.           | b.d.l. | b.d.l. | 0.07   | 0.17    | b.d.l.             | b.d.l. | b.d.l. | 0.11   | 0.41   | 0.06  | <b>0.05</b>  |
| <b>S (wt.%)</b>  | b.d.l.         | b.d.l. | 0.07   | 0.17   | 0.40   | b.d.l.         | b.d.l. | b.d.l. | b.d.l. | 0.57    | b.d.l.           | b.d.l. | 0.08   | 0.10   | 0.11    | b.d.l.             | b.d.l. | b.d.l. | 0.08   | 0.43   | 0.05  | <b>0.015</b> |
| <b>Ca (wt.%)</b> | 37.9           | 38.5   | 38.7   | 38.9   | 39.2   | 35.4           | 39.0   | 39.1   | 39.3   | 39.9    | 37.6             | 38.1   | 38.2   | 38.3   | 38.5    | 37.5               | 39.0   | 39.2   | 39.3   | 39.6   | 0.05  | <b>38.15</b> |
| <b>Na</b>        | 337.8          | 596.1  | 667.3  | 796.2  | 1221   | 379.4          | 600.4  | 674.2  | 808.3  | 9547    | 350.9            | 949.0  | 1137   | 1242   | 2317    | 481.6              | 628.4  | 692.2  | 793.3  | 1347   | 11.65 | 799          |
| <b>Mg</b>        | 39.3           | 101.2  | 211.9  | 314.9  | 530.2  | 47.1           | 82.5   | 118.4  | 203.9  | 2642.7  | 22.7             | 134.7  | 229.9  | 336.9  | 2115.3  | 146.6              | 155.2  | 166.6  | 171.8  | 241.7  | 0.40  |              |
| <b>Si</b>        | 638.3          | 907.5  | 1061   | 1196   | 2147   | 620.8          | 978.3  | 1137   | 1296   | 103164  | 547.9            | 846.3  | 974.3  | 1293   | 6643    | 924.3              | 1020   | 1186   | 1268   | 1813   | 456   | 1041         |
| <b>Mn</b>        | 329.4          | 819.9  | 1169   | 1621   | 8065   | 265.2          | 683.3  | 915.1  | 1278   | 3142.8  | 1884             | 5503   | 6793   | 9120   | 11860   | 771.8              | 1274   | 1376   | 1569   | 2556   | 4.49  | 922          |
| <b>Fe</b>        | 285.0          | 430.6  | 768.6  | 1042   | 1567   | 275.7          | 482.9  | 637.3  | 1016   | 1559    | 282.0            | 813.4  | 1198   | 1591   | 5199    | 869.2              | 968.9  | 1061   | 1120   | 1378   | 13.35 | 1005         |
| <b>Sr</b>        | 169.9          | 283.4  | 346.8  | 400.9  | 1340   | 190.5          | 310.8  | 371.8  | 418.2  | 953.4   | 250.3            | 370.1  | 425.2  | 461.8  | 685.2   | 308.8              | 493.1  | 524.1  | 569.0  | 730.5  | 0.65  | 346          |
| <b>Y</b>         | 246.0          | 641.5  | 759.0  | 1322   | 2340   | 404.8          | 689.1  | 908.2  | 1172   | 1984    | 693.4            | 1700   | 2017   | 2377   | 3465    | 419.3              | 695.7  | 758.0  | 876.3  | 2084   | 1.57  | 634          |
| <b>Zr</b>        | b.d.l.         | 0.08   | 0.12   | 0.32   | 24.72  | b.d.l.         | 0.10   | 0.20   | 0.48   | 2033.96 | b.d.l.           | 0.04   | 0.10   | 0.21   | 4373.91 | b.d.l.             | 0.08   | 0.10   | 1.02   | 4.82   | 0.03  | 0.632        |
| <b>Ba</b>        | b.d.l.         | 0.09   | 0.14   | 0.22   | 1.10   | b.d.l.         | 0.16   | 0.30   | 0.48   | 449.92  | b.d.l.           | 0.19   | 0.34   | 0.57   | 81.93   | 0.15               | 0.64   | 0.77   | 0.95   | 1.68   | 0.08  | 1.6          |
| <b>La</b>        | 55.1           | 180.1  | 200.5  | 248.2  | 419.8  | 77.3           | 202.2  | 256.0  | 297.7  | 533.6   | 52.1             | 130.4  | 200.5  | 252.4  | 389.2   | 110.3              | 209.1  | 226.3  | 240.3  | 352.8  | 0.29  | 731          |
| <b>Ce</b>        | 303.8          | 718.8  | 824.9  | 1107   | 2039   | 249.4          | 842.6  | 1100   | 1295   | 2310.9  | 247.0            | 692.7  | 1005   | 1251   | 1931.0  | 415.5              | 794.6  | 897.6  | 952.8  | 1350   | 1.44  | 1531         |
| <b>Pr</b>        | 39.6           | 106.3  | 123.4  | 156.6  | 248.9  | 43.3           | 127.2  | 150.5  | 176.3  | 305.3   | 47.2             | 108.8  | 141.4  | 168.1  | 266.0   | 72.9               | 126.7  | 146.1  | 155.2  | 211.3  | 0.18  | 195          |
| <b>Nd</b>        | 170.3          | 559.1  | 648.6  | 807.5  | 1204.1 | 217.2          | 639.6  | 786.8  | 908.2  | 1526.5  | 263.3            | 580.4  | 720.3  | 853.7  | 1277.1  | 374.5              | 662.6  | 766.0  | 795.8  | 1133.0 | 0.97  | 676          |
| <b>Sm</b>        | 42.1           | 180.9  | 206.2  | 259.1  | 392.5  | 60.0           | 195.0  | 241.5  | 279.5  | 391.6   | 121.1            | 229.5  | 266.0  | 310.3  | 413.1   | 114.9              | 215.9  | 243.5  | 256.5  | 327.9  | 0.32  | 186          |
| <b>Eu</b>        | 16.7           | 28.9   | 32.8   | 39.5   | 54.2   | 20.2           | 28.5   | 32.7   | 39.6   | 130.6   | 18.4             | 27.5   | 30.9   | 36.2   | 68.9    | 18.7               | 31.1   | 32.3   | 35.7   | 42.6   | 0.06  | 14           |
| <b>Gd</b>        | 43.5           | 208.0  | 222.5  | 264.5  | 421.5  | 75.8           | 199.6  | 245.7  | 282.0  | 472.1   | 184.5            | 287.7  | 329.1  | 370.3  | 455.5   | 118.6              | 228.7  | 247.1  | 274.0  | 354.4  | 0.38  | 165          |
| <b>Tb</b>        | 7.4            | 26.6   | 29.7   | 37.7   | 61.1   | 12.5           | 27.4   | 31.9   | 37.3   | 54.7    | 32.8             | 48.5   | 55.6   | 61.0   | 81.6    | 16.0               | 28.7   | 32.6   | 35.8   | 60.1   | 0.05  | 17.6         |
| <b>Dy</b>        | 44.0           | 144.5  | 161.5  | 227.6  | 376.2  | 80.4           | 145.9  | 179.8  | 207.7  | 334.8   | 185.0            | 295.6  | 342.5  | 389.1  | 558.8   | 83.2               | 156.6  | 170.0  | 190.2  | 391.0  | 0.35  | 119          |
| <b>Ho</b>        | 7.9            | 24.2   | 28.0   | 41.1   | 68.8   | 14.5           | 25.6   | 31.4   | 37.0   | 69.0    | 26.7             | 54.0   | 64.2   | 72.2   | 105.6   | 14.6               | 25.9   | 28.8   | 32.8   | 76.7   | 0.07  | 20.5         |
| <b>Er</b>        | 22.7           | 58.7   | 67.8   | 106.7  | 186.4  | 37.0           | 63.3   | 77.8   | 98.7   | 183.3   | 55.4             | 137.3  | 165.1  | 194.8  | 292.9   | 34.1               | 59.1   | 64.6   | 76.5   | 203.4  | 0.20  | 58.8         |
| <b>Tm</b>        | 3.4            | 6.3    | 7.5    | 13.9   | 25.4   | 4.2            | 7.5    | 9.0    | 11.9   | 23.3    | 4.9              | 15.9   | 19.6   | 23.8   | 38.2    | 3.9                | 6.0    | 6.8    | 7.8    | 26.3   | 0.03  | 7.55         |
| <b>Yb</b>        | 22.1           | 32.3   | 41.1   | 83.7   | 154.9  | 23.6           | 40.1   | 51.8   | 74.1   | 156.3   | 22.2             | 88.4   | 108.7  | 139.3  | 232.1   | 19.5               | 28.4   | 34.1   | 37.5   | 155.0  | 0.15  | 47.2         |
| <b>Lu</b>        | 2.6            | 3.6    | 4.7    | 10.3   | 20.2   | 2.8            | 4.8    | 6.4    | 9.2    | 21.5    | 2.1              | 10.0   | 12.5   | 16.0   | 26.5    | 2.3                | 3.1    | 3.9    | 4.2    | 20.7   | 0.02  | 6.8          |
| <b>Pb</b>        | 0.6            | 1.6    | 2.1    | 2.5    | 11.9   | 0.7            | 1.4    | 1.7    | 2.1    | 77.4    | 1.7              | 2.7    | 3.0    | 3.4    | 10.3    | 3.1                | 3.8    | 4.1    | 4.3    | 6.3    | 0.14  | 6.62         |
| <b>Th</b>        | 0.9            | 2.1    | 3.7    | 5.1    | 14.0   | 1.0            | 3.3    | 5.2    | 8.3    | 154.5   | 0.1              | 0.5    | 1.4    | 3.4    | 37.1    | 0.2                | 1.2    | 1.5    | 1.8    | 4.3    | 0.02  | 31           |
| <b>U</b>         | 1.0            | 2.7    | 5.1    | 8.5    | 88.4   | 1.4            | 3.2    | 6.1    | 11.6   | 314.9   | 0.7              | 7.5    | 13.0   | 24.2   | 83.3    | 0.4                | 0.9    | 1.0    | 1.1    | 5.0    | 0.03  | 29           |
| <b>La/Yb</b>     | 0.85           | 2.30   | 3.15   | 4.28   | 9.29   | 0.89           | 2.50   | 3.47   | 4.35   | 12.39   | 0.66             | 1.00   | 1.10   | 1.31   | 3.18    | 0.51               | 3.95   | 4.87   | 5.93   | 9.26   |       | 13.3         |
| <b>Sm/Yb</b>     | 1.49           | 3.28   | 4.85   | 7.09   | 10.23  | 1.21           | 3.48   | 5.14   | 6.73   | 8.63    | 1.67             | 2.26   | 2.65   | 3.63   | 6.05    | 1.55               | 7.03   | 7.91   | 8.75   | 11.15  |       | 3.96         |
| <b>ΣREE</b>      | 924            | 2352   | 2573   | 3249   | 5063   | 1132           | 2680   | 3116   | 3710   | 6059    | 1263             | 2800   | 3536   | 4190   | 5550    | 1492               | 2638   | 2894   | 3152   | 4123   |       | 4122         |
| <b>Sr/Y</b>      | 0.09           | 0.20   | 0.46   | 0.59   | 5.45   | 0.11           | 0.29   | 0.43   | 0.55   | 1.78    | 0.10             | 0.16   | 0.21   | 0.28   | 0.63    | 0.15               | 0.55   | 0.68   | 0.79   | 1.74   |       | 0.571        |
| <b>Eu/Eu*</b>    | 0.20           | 0.32   | 0.47   | 0.62   | 1.79   | 0.22           | 0.36   | 0.42   | 0.54   | 1.85    | 0.23             | 0.28   | 0.33   | 0.37   | 0.87    | 0.36               | 0.38   | 0.42   | 0.46   | 0.59   |       | 0.299        |

Table 6.6. Summary of the geochemical characteristics of Resolution apatites. For colour code, see Table 5.4

|                  | Vein type apatite |        |         |         |        | Dull-CL apatite |        |        |        |        | Hydrothermal Breccia |        |        |        |        |       |              |
|------------------|-------------------|--------|---------|---------|--------|-----------------|--------|--------|--------|--------|----------------------|--------|--------|--------|--------|-------|--------------|
|                  | Min.              | 1st Q. | Median  | 3rd Q.  | Max    | Min.            | 1st Q. | Median | 3rd Q. | Max    | Min.                 | 1st Q. | Median | 3rd Q. | Max    | LOD   | Median       |
| <b>F (wt.%)</b>  | 2.23              | 2.47   | 2.86    | 2.90    | 3.27   | 2.42            | 4.53   | 4.58   | 4.88   | 5.66   | 3.43                 | 3.51   | 3.58   | 3.65   | 3.75   | 0.12  | 2.77         |
| <b>Cl (wt.%)</b> | b.d.l.            | b.d.l. | b.d.l.  | 0.11    | 0.11   | b.d.l.          | b.d.l. | b.d.l. | 0.02   | 0.10   | b.d.l.               | b.d.l. | 0.06   | 0.07   | 0.08   | 0.06  | <b>0.05</b>  |
| <b>S (wt.%)</b>  | b.d.l.            | 0.18   | 0.50    | 0.61    | 0.62   | b.d.l.          | b.d.l. | b.d.l. | 0.12   | 0.16   | b.d.l.               | b.d.l. | b.d.l. | b.d.l. | b.d.l. | 0.05  | <b>0.015</b> |
| <b>Ca (wt.%)</b> | 39.28             | 39.45  | 39.63   | 39.70   | 39.77  | 39.63           | 40.27  | 40.34  | 40.44  | 40.67  | 39.27                | 39.37  | 39.42  | 39.49  | 39.63  | 0.05  | <b>38.15</b> |
| <b>Na</b>        | 1447              | 1922   | 2528    | 2731.85 | 2849   | 78.70           | 402.77 | 532.60 | 639.17 | 731.26 |                      |        |        |        |        | 11.65 | 799          |
| <b>Mg</b>        | 10.76             | 20.38  | 33.16   | 77.96   | 120.51 | 6.89            | 12.06  | 16.12  | 16.74  | 18.54  |                      |        |        |        |        | 0.40  |              |
| <b>Si</b>        | 955.83            | 991.78 | 1071.14 | 1161.58 | 1321   | 473.99          | 803.98 | 925.45 | 1007   | 1075   |                      |        |        |        |        | 456   | 1041         |
| <b>Mn</b>        | 282.68            | 314.84 | 359.37  | 448.36  | 2178   | 191.65          | 229.81 | 269.39 | 303.78 | 357.51 |                      |        |        |        |        | 4.49  | 922          |
| <b>Fe</b>        | 212.56            | 260.78 | 363.04  | 447.99  | 1033   | 112.77          | 129.98 | 138.63 | 149.61 | 160.76 |                      |        |        |        |        | 13.35 | 1005         |
| <b>Sr</b>        | 14.83             | 40.34  | 88.37   | 168.15  | 331.00 | 529.58          | 780.03 | 851.09 | 956.94 | 1139   |                      |        |        |        |        | 0.65  | 346          |
| <b>Y</b>         | 678.32            | 764.80 | 1163    | 1765    | 2898   | 603.78          | 992.82 | 1325   | 2152   | 3286   |                      |        |        |        |        | 1.57  | 634          |
| <b>Zr</b>        | b.d.l.            | 0.12   | 0.48    | 0.72    | 3.07   | b.d.l.          | b.d.l. | b.d.l. | 0.03   | 0.08   |                      |        |        |        |        | 0.03  | 0.632        |
| <b>Ba</b>        | 7.04              | 10.47  | 12.52   | 18.26   | 70.76  | 0.35            | 2.06   | 3.21   | 5.90   | 9.72   |                      |        |        |        |        | 0.08  | 1.6          |
| <b>La</b>        | 3.9               | 10.3   | 20.0    | 47.0    | 180.8  | b.d.l.          | b.d.l. | 0.4    | 0.6    | 1.2    |                      |        |        |        |        | 0.29  | 731          |
| <b>Ce</b>        | 18.8              | 31.0   | 66.7    | 179.3   | 537.8  | 2.1             | 2.9    | 4.8    | 5.5    | 10.2   |                      |        |        |        |        | 1.44  | 1531         |
| <b>Pr</b>        | 2.7               | 5.0    | 10.5    | 30.8    | 78.9   | 0.8             | 1.3    | 1.9    | 2.4    | 3.5    |                      |        |        |        |        | 0.18  | 195          |
| <b>Nd</b>        | 20.3              | 31.2   | 61.3    | 173.2   | 356.6  | 13.8            | 23.6   | 26.1   | 33.8   | 40.4   |                      |        |        |        |        | 0.97  | 676          |
| <b>Sm</b>        | 28.2              | 44.5   | 66.2    | 88.3    | 143.1  | 87.1            | 123.2  | 145.8  | 170.6  | 207.6  |                      |        |        |        |        | 0.32  | 186          |
| <b>Eu</b>        | 26.2              | 38.7   | 43.2    | 55.6    | 75.3   | 73.9            | 93.2   | 148.3  | 171.0  | 223.8  |                      |        |        |        |        | 0.06  | 14           |
| <b>Gd</b>        | 135.4             | 178.2  | 248.0   | 386.8   | 446.3  | 278.1           | 343.2  | 628.2  | 677.7  | 869.2  |                      |        |        |        |        | 0.38  | 165          |
| <b>Tb</b>        | 28.1              | 34.8   | 48.7    | 90.2    | 110.8  | 35.4            | 45.0   | 66.4   | 86.1   | 113.5  |                      |        |        |        |        | 0.05  | 17.6         |
| <b>Dy</b>        | 159.3             | 182.0  | 282.5   | 545.5   | 652.6  | 159.9           | 221.7  | 275.4  | 416.6  | 582.1  |                      |        |        |        |        | 0.35  | 119          |
| <b>Ho</b>        | 25.9              | 27.9   | 48.9    | 75.8    | 115.1  | 24.4            | 34.8   | 45.3   | 64.8   | 99.6   |                      |        |        |        |        | 0.07  | 20.5         |
| <b>Er</b>        | 53.7              | 64.7   | 110.4   | 169.1   | 274.4  | 54.2            | 85.9   | 106.0  | 166.4  | 265.4  |                      |        |        |        |        | 0.20  | 58.8         |
| <b>Tm</b>        | 5.5               | 6.4    | 10.5    | 17.6    | 31.1   | 5.3             | 8.7    | 12.6   | 20.4   | 30.9   |                      |        |        |        |        | 0.03  | 7.55         |
| <b>Yb</b>        | 26.1              | 31.1   | 49.1    | 91.6    | 160.8  | 23.7            | 43.2   | 65.4   | 109.9  | 170.7  |                      |        |        |        |        | 0.15  | 47.2         |
| <b>Lu</b>        | 2.9               | 3.4    | 5.1     | 10.4    | 18.7   | 2.0             | 4.5    | 7.0    | 11.7   | 18.2   |                      |        |        |        |        | 0.02  | 6.8          |
| <b>Pb</b>        | 16.4              | 26.3   | 50.0    | 55.4    | 96.8   | b.d.l.          | 0.2    | 0.2    | 0.4    | 0.6    |                      |        |        |        |        | 0.14  | 6.62         |
| <b>Th</b>        | 5.6               | 12.4   | 21.6    | 26.7    | 54.7   | 0.5             | 1.2    | 3.2    | 4.7    | 10.7   |                      |        |        |        |        | 0.02  | 31           |
| <b>U</b>         | 9.4               | 27.4   | 29.9    | 32.3    | 58.1   | 10.7            | 28.5   | 61.9   | 102.5  | 149.6  |                      |        |        |        |        | 0.03  | 29           |
| <b>La/Yb</b>     | 0.04              | 0.18   | 0.27    | 0.69    | 1.50   | 0.00            | 0.00   | 0.00   | 0.01   | 0.01   |                      |        |        |        |        |       | 13.3         |
| <b>Sm/Yb</b>     | 0.76              | 0.94   | 1.02    | 1.42    | 3.81   | 1.30            | 1.88   | 2.09   | 2.89   | 5.47   |                      |        |        |        |        |       | 3.96         |
| <b>ΣREE</b>      | 560               | 859    | 1300    | 1553    | 3172   | 889             | 1018   | 1462   | 2029   | 2598   |                      |        |        |        |        |       | 4122         |
| <b>Sr/Y</b>      | 0.01              | 0.04   | 0.05    | 0.11    | 0.49   | 0.23            | 0.33   | 0.65   | 0.81   | 1.88   |                      |        |        |        |        |       | 0.571        |
| <b>Eu/Eu*</b>    | 0.87              | 0.92   | 1.11    | 1.31    | 1.33   | 1.31            | 1.42   | 1.50   | 1.54   | 1.66   |                      |        |        |        |        |       | 0.299        |

Table 6.6. (contd.)

## 6.5.2 Geochemistry of Resolution, Schultze Granite, and associated intrusions

### 6.5.2.1 Fluorine, chlorine, and sulphur

Several analyses of apatite from Resolution have F values in excess of the stoichiometric limit for apatite (Fig. 6.20 a,c). For example, F concentrations of apatite from the QLP and RDP have median values of 3.75 and 3.44 wt.% respectively, but maximum F values in excess of 3.76 wt.% (4.19 and 4.44 wt.% respectively). Dull-CL apatite has extremely high F concentrations, with median values higher than the stoichiometric limit for apatite (4.58 wt. %), and maximum values well in excess of it (5.66 wt.%; (Fig. 6.20 c). Vein-type apatite, Schultze Granite, and Apache Leap apatite have lower median F concentrations (Fig. 6.20 c). The high F content of these apatites are similar to those from S-type and felsic I-type magmas, and highlights the problems in measuring F in apatite by electron microprobe. Values presented in this study should be considered as qualitative, but are evidence nonetheless for relatively high F concentrations in Resolution apatites.

Chlorine concentrations for nearly all apatites from Resolution and associated lithologies are very low, with most below the limit of detection (Fig. 6.20 a,d). Cl in some apatites from the felsic Apache Leap intrusions reaches 0.41 wt. %, and the maximum Cl value for the Schultze Granite apatite is 0.17 wt.%. F and Cl values are broadly inversely proportional to each other (Fig. 6.20 a).

Sulphur concentrations of most Resolution apatites are close to the limit of detection. Although median S values of QLP and RDP dominant-type apatites are generally low, S values in these apatites may reach up to ~0.55 wt. % (Fig. 6.21 a). The vein-type apatite have extremely high S concentrations, with median values of 0.50 wt. %, and a maximum value of 0.62 wt. %. These values are higher than the S-rich apatites of Streck and Dilles (1998), which reached <0.4 wt. % S. These high S values are unlikely to be due to the interaction between electron beam and small sulphide inclusions during EPMA, as there is no correlation between

Fe and S (Fig. 6.21 c). Instead, S values show a close correspondence with Na concentration (Fig. 6.21 b), suggesting that S in these apatites is crystallographically controlled, and incorporated by the couple substitution suggested by Liu and Comodi (1993). Apatite from the hydrothermal breccia have S values consistently below detection limits.

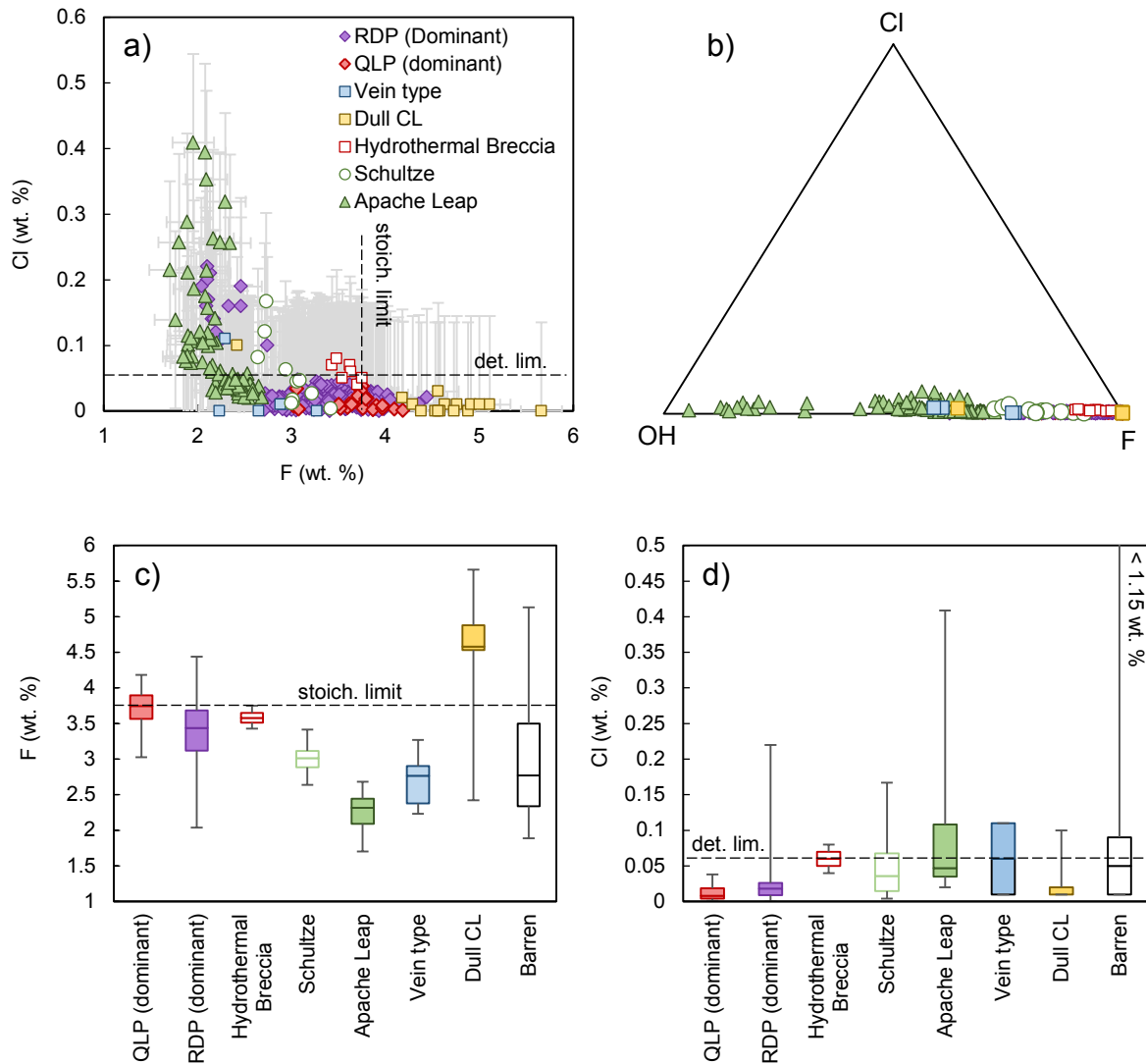


Figure 6.20. Halogen chemistry of Resolution apatites. a) Cl and F contents generally show an inverse relationship. b) Halogen ternary diagram, showing the strong depletion in Cl with respect to OH and, especially, F. c-d) Box and whisker diagrams showing the median, interquartile range, and range of F and Cl concentrations. Many analyses of F, especially in the “dominant-type” and “dull-CL” apatites, are above the stoichiometric limit for F (c), so all F data should be treated qualitatively. All data collected by EPMA.



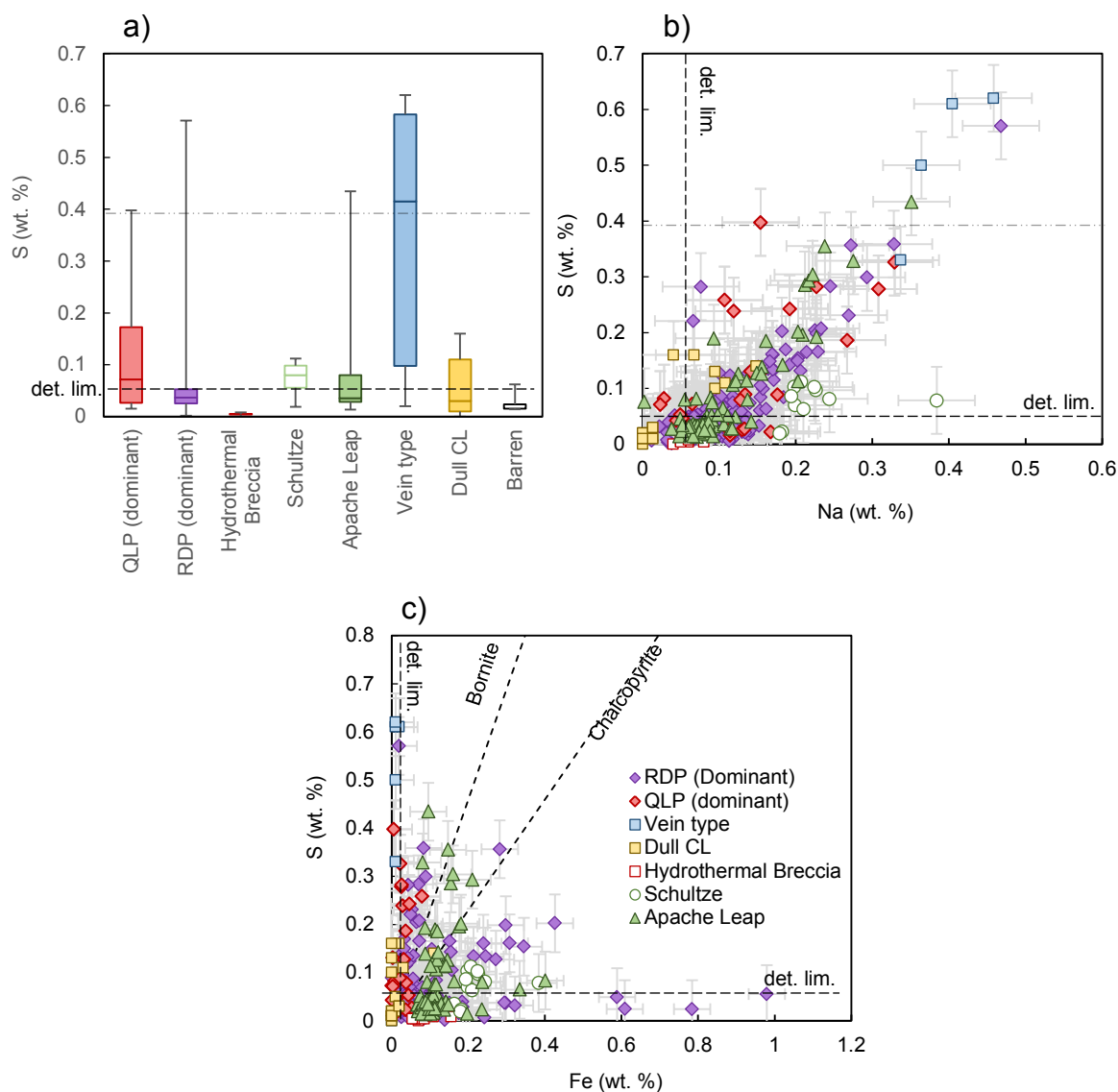


Figure 6.21. a) Box and whisker diagrams showing the median, interquartile range, and range of S concentrations in apatites from Resolution. b) Na vs. S content, showing the clear positive correlation between these two elements. c) Fe vs. S. High S contents of "vein type" apatites cannot be explained by the presence of small inclusions of sulphides, as there is no correlation between S and Fe for these analyses. All data collected by EPMA.

#### 6.5.2.2 Monovalent cations

With the exception of vein type variety, apatites from Resolution have concentrations of Na that are broadly within the range of values observed in apatites from intermediate granitoids (Fig. 6.22 a). Vein type apatites have very high Na values (median = 2528 ppm) compared to apatites from intermediate granitoids (median = 799 ppm). These high Na contents

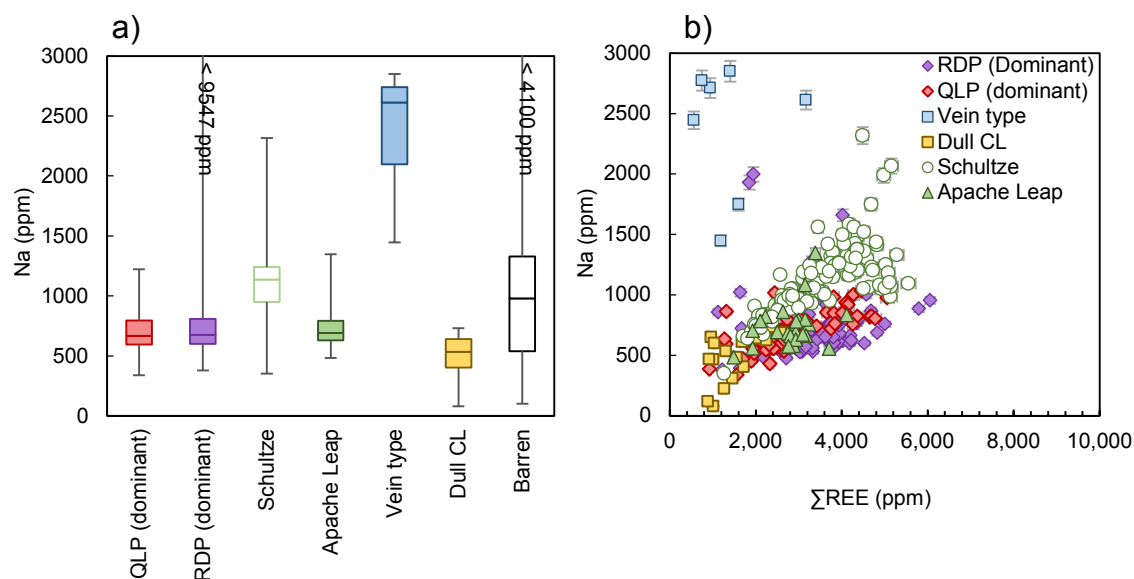


Figure 6.22. a) Box and whisker diagrams showing the median, interquartile range, and range of Na in Resolution apatites. b) the variation of Na with  $\Sigma\text{REE}$ . Error bars in b) are mostly smaller than the symbol size. All data collected by LA-ICP-MS.

also correspond to high S content (Fig. 6.21 b). Na in apatite shows a broad positive correlation with  $\Sigma\text{REE}$ , with the exception again of vein-type apatite, which have lower and higher Na respectively than this trend (Fig. 6.22 b).

### 6.5.2.3 Divalent cations

Sr concentrations in Resolution apatites are mostly lower than the maximum Sr content of apatites from intermediate granitoids (750 ppm). Dull CL apatites have a higher median Sr content (median = 851 ppm), and maximum values in excess of 1000 ppm (Fig. 6.23 a).

Mn contents for dominant-type RDP and QLP, and felsic Apache Leap apatites are similar to one another (Fig. 6.23 b), and correspond to the median Mn values for apatites from barren intermediate I-type rocks (median = 724 ppm; Table 6.2). Vein type and dull-CL type apatites have lower Mn, with median values lower than ~300 ppm. Schultze Granite apatites are enriched in Mn with respect to other Resolution apatites, (median = 8748 ppm), an order of magnitude greater than median granitoid apatites (median = 922 ppm) but are consistent

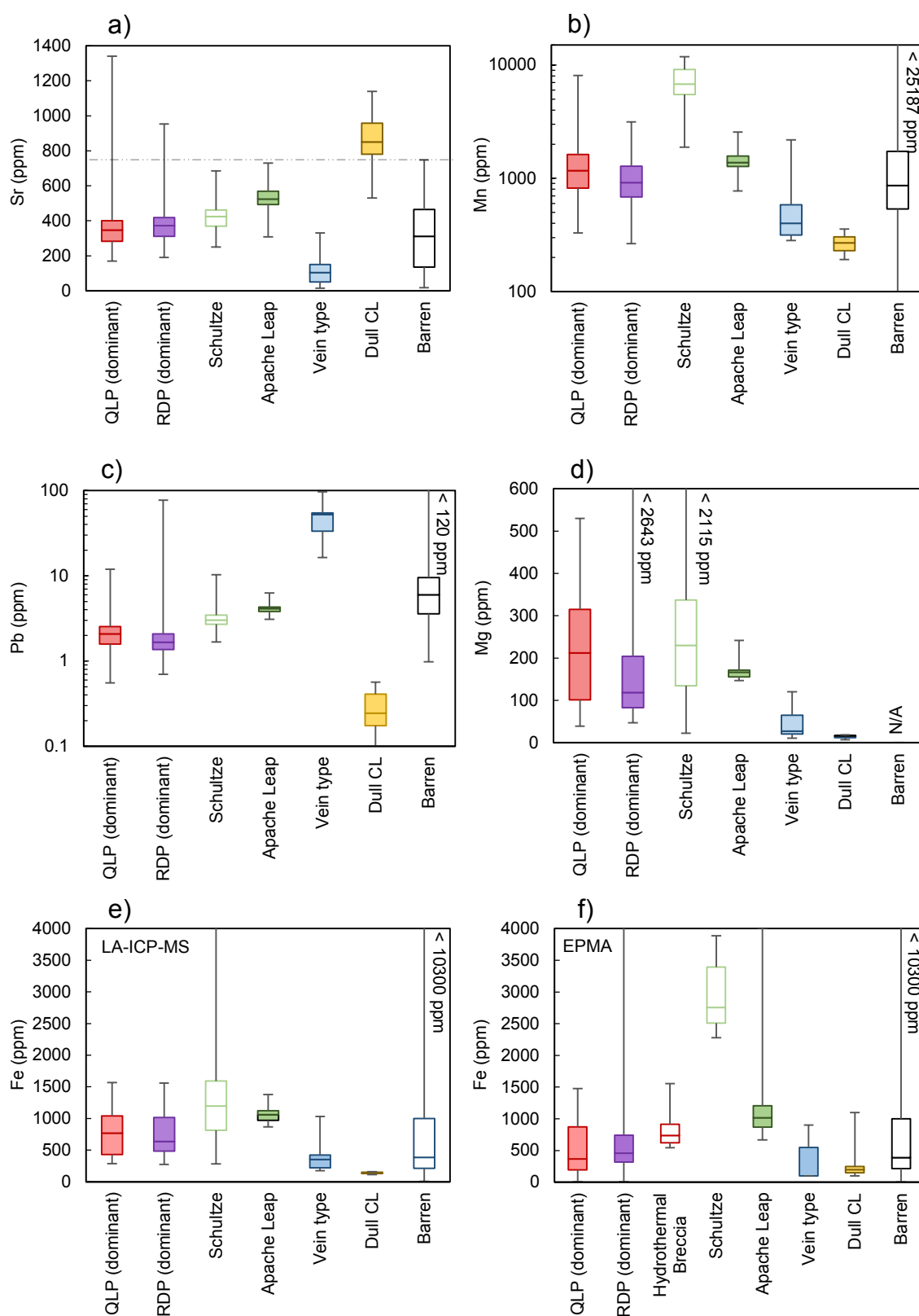


Figure 6.23. Box and whisker diagrams showing the median, interquartile range, and range of a) Sr, b) Mn, c) Pb, d) Mg, and e,f) Fe concentrations in Resolution apatites. Data from a-e) collected by LA-ICP-MS; data from f) collected by EPMA. Horizontal dashed line in a) represents the approximate maximum Sr content of apatites from barren rocks (see Table 6.2).

with apatites from fractionated I-type or S-type granites, which reach Mn values of up to 2 wt.%.

Pb concentrations of dominant-type RDP and QLP apatites are similar, and median values are typically lower than apatites from barren granitoids (Fig. 6.23 c). Late-stage hydrothermal vein-type and dull-CL type apatites have exceptionally high and low Pb respectively, compared to apatites from barren granitoids.

Mg concentrations in the late-stage hydrothermal vein-type and dull-CL apatites are much lower than Mg contents of igneous and high-temperature hydrothermal apatites (Schultze Granite, felsic Apache Leap, and dominant QLP/RDP types; Fig. 6.23 d).

With the exception of the Schultze Granite, the Fe concentrations of Resolution apatites are broadly similar to apatites from barren granitoids (Fig. 6.23 e,f). There is very little difference between dominant-type apatites from the QLP and RDP. Apatites from the felsic Apache Leap are weakly enriched in Fe with respect to later-stage hydrothermal apatites (vein-type and dull-CL type). There is a considerable disparity between the Fe contents determined by EPMA and LA-IC-PMS for apatites from the Schultze granite. Concentrations determined by EPMA are higher than those determined by LA-ICP-MS by ~2000 ppm. This is likely to be due to the analytical problems identified in determining Fe by LA-ICP-MS (see Section 2.5.2). Where possible, the EPMA value for Fe will be used hereafter.

#### *6.5.2.4 Thorium and uranium*

Th contents of both igneous and hydrothermal apatites at Resolution apatites are lower than those found in apatites from typical granitoids. As an exception, vein-type apatites have more typical Th values.

Dominant-type RDP and QLP apatites and (especially) felsic Apache Leap apatites have U concentrations well below apatites found in typical granitoids. Later-stage

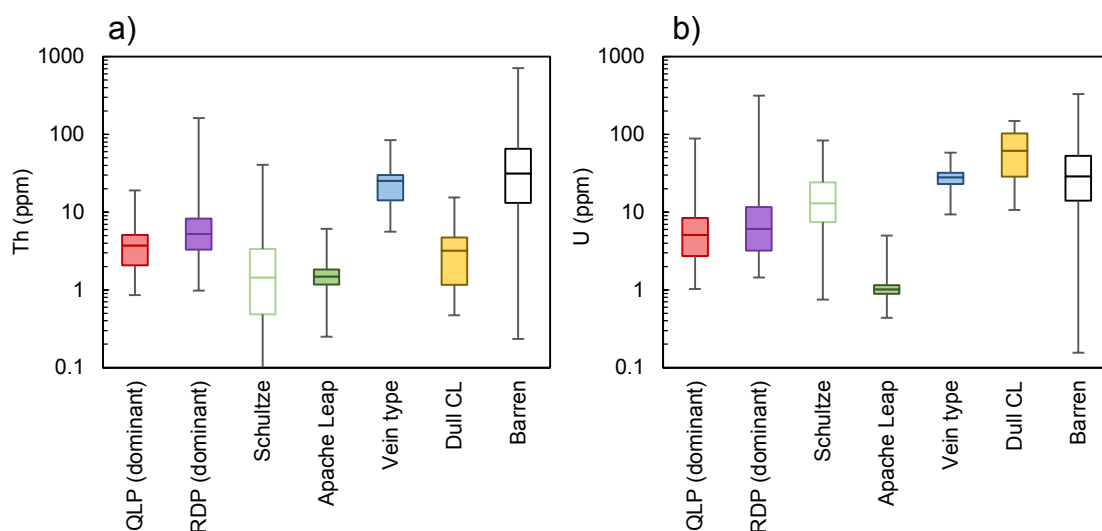


Figure 6.24. Box and whisker diagrams showing the median, interquartile range, and range of a) Th, and b) U concentrations in Resolution apatites. Data collected by LA-ICP-MS.

hydrothermal apatites (dull-CL and vein-type) have higher U, with median values similar to apatites from typical granitoids. Dominant-type RDP and QLP apatites have closely similar Th and U contents.

#### 6.5.2.5 Rare earth elements

Median  $\Sigma$ REE values of Resolution apatites are lower than apatites from typical barren granitoids. Dominant type QLP and RDP have similar median  $\Sigma$ REE values to one another, and to apatites from the Schultze granite and felsic Apache Leap intrusion. Later-stage hydrothermal apatites (dull-CL and vein-type) have lower  $\Sigma$ REE concentrations.

By contrast to some of the apatites from Oyu Tolgoi (Fig. 6.13), the shape of chondrite-normalised REE patterns of apatites from Resolution are significantly different to those found in typical barren granitoids (Fig. 6.27). In particular, they are mostly depleted in LREE and enriched in MREE, and have similar HREE concentrations. Although dissimilar to apatites from typical intermediate I-type granitoids, these patterns are more similar to those observed in apatites from S-type and felsic I-type granitoids, which typically display a LREE depletion

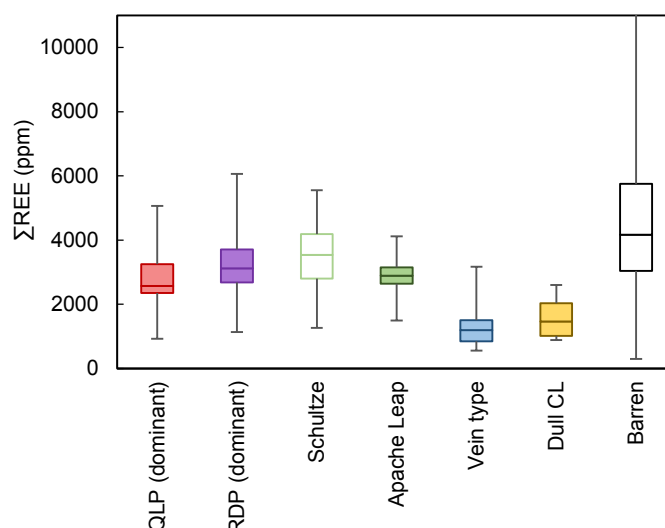


Figure 6.25. Box and whisker diagrams showing the median, interquartile range, and range of  $\Sigma\text{REE}$  in Resolution apatites. All data collected by LA-ICP-MS.

with respect to MREE (Sha and Chappell, 1999; Table 6.2).

Dominant-type QLP and RDP apatites, and felsic Apache Leap apatites have similar chondrite-normalised REE patterns to one another (Fig. 6.27 a-c). Schultze Granite apatites also have similar patterns to these groups, but are more strongly enriched in M- to HREE. Eu anomalies for these types of apatite are mostly negative (i.e.  $\text{Eu}/\text{Eu}^* < 1$ ; Fig. 6.28), and median values are similar to median  $\text{Eu}/\text{Eu}^*$  values of apatites from typical barren granitoids (Fig. 6.29). However, QLP and RDP dominant-type apatites do have some  $\text{Eu}/\text{Eu}^*$  values in excess of 1, and these analyses correspond to some of the lowest REE and the highest Sr contents in Resolution apatites (Fig. 6.28).

Vein-type and (especially) dull-CL type apatites have chondrite-normalised REE patterns which are both strongly different to both other Resolution apatites, and to apatites from typical barren granitoids. In particular, they show significant depletion in LREE (Fig. 6.27 e,f)

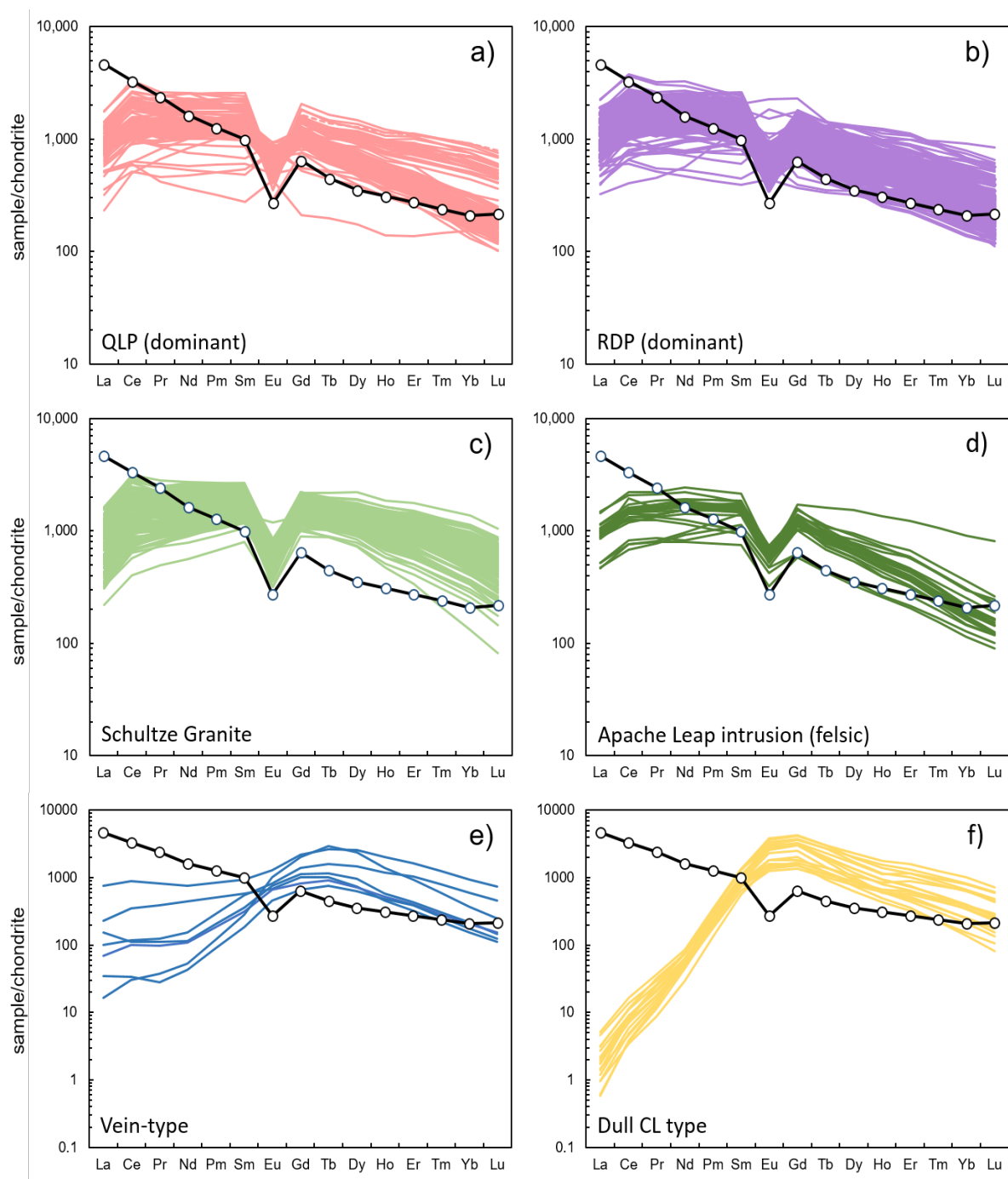


Figure 6.26. Raw chondrite-normalised REE patterns for Resolution apatites. a,b) dominant-type apatites from QLP and RDP intrusions, c) Schultze Granite, d) felsic Apache Leap intrusions, e) vein-type, and f) dull-CL apatite.. Black line with open symbols is the median value for granitoid apatites. Normalising values from Sun and McDonough (1989). All REE data collected by LA-ICP-MS.

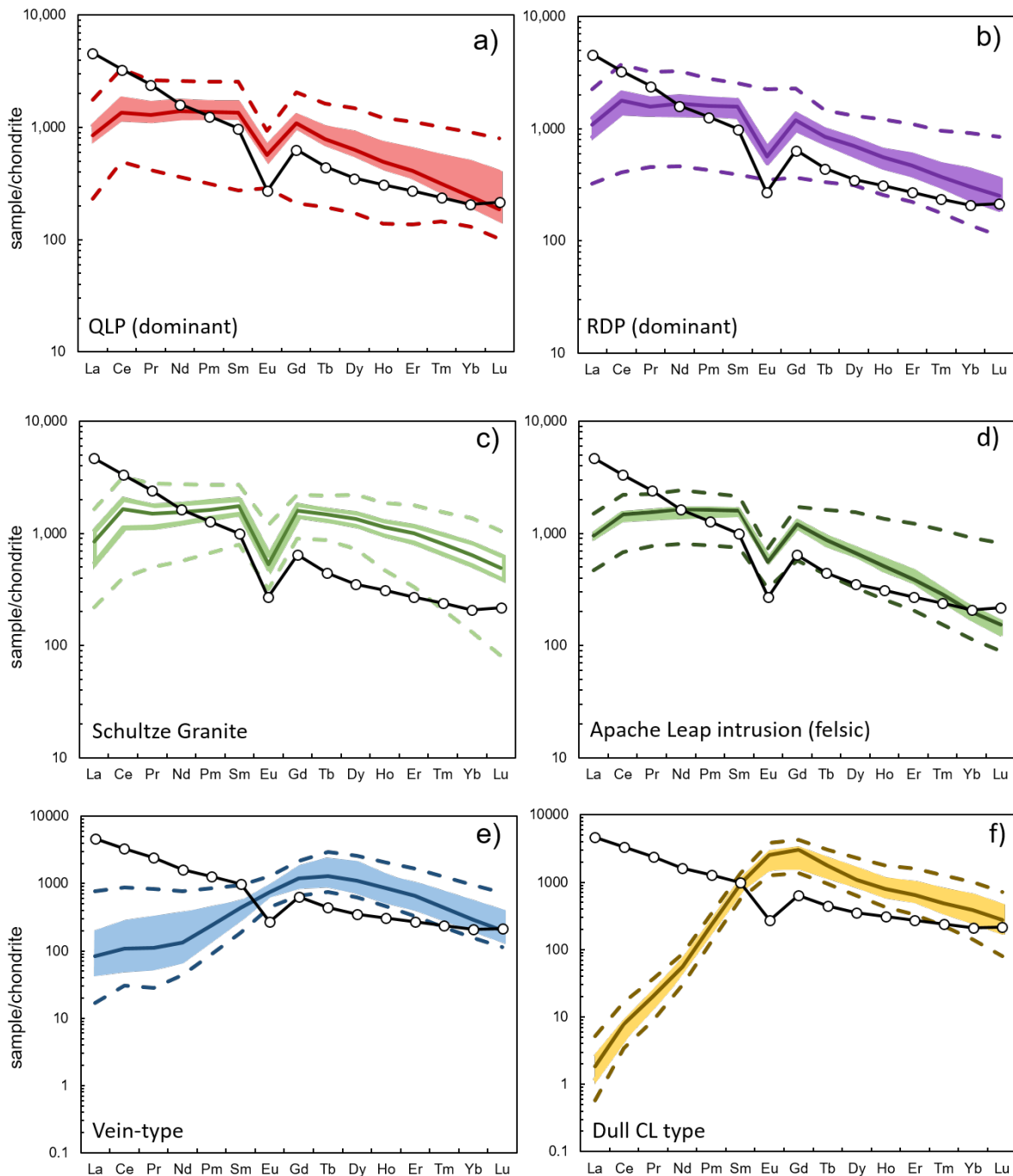


Figure 6.27. Median, minimum, maximum, and interquartile range of chondrite-normalised REE patterns for apatites from Resolution. a,b) dominant-type apatites from QLP and RDP intrusions, c) Schultze Granite, d) felsic Apache Leap intrusions, e) vein-type, and f) dull-CL apatite. Dashed lines are the maximum and minimum values, shaded areas are the interquartile range, and thick darker coloured lines are the median values. Black line with open symbols is the median value for granitoid apatites. Normalising values from Sun and McDonough (1989). All REE data collected by LA-ICP-MS.



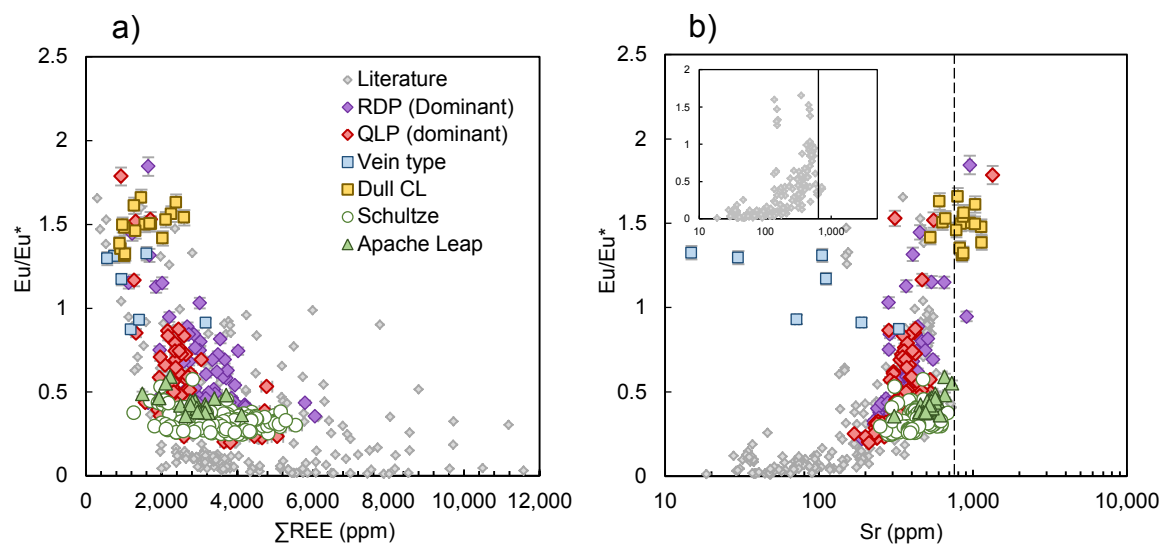


Figure 6.28. Correlations between the Eu anomaly ( $Eu/Eu^*$ ) and a)  $\Sigma REE$ , and b) Sr concentration of Resolution apatites. A small number of Resolution apatite data extend above the upper limit of  $\sim 750$  ppm Sr observed in the literature dataset (see b), inset). All data collected by LA-ICP-MS.

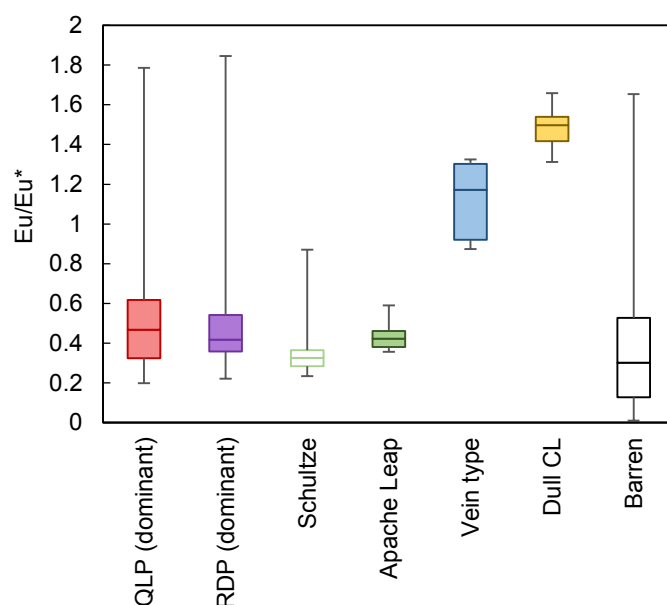


Figure 6.29. Box and whisker diagram showing the median, interquartile range, and range of  $Eu/Eu^*$  values for Resolution apatites. Data collected by LA-ICP-MS.

and the highest Eu/Eu\* values of all analysed Resolution apatites which are nearly all in excess of unity (Figs. 6.28 and 6.29).

The Eu anomalies of most Resolution apatites show the same positive correlation with Sr content (Fig. 6.28 b) as is seen in apatites from Oyu Tolgoi (Fig. 6.14 b). One stark exception to this is the vein-type apatites which, although they have exceptionally high Eu/Eu\*, have the lowest Sr contents of all analysed Resolution apatites.

## **6.6 Estimates of intensive parameters**

### **6.6.1 Apatite saturation temperatures**

Apatite saturation temperatures (AST) were calculated using the method of Harrison and Watson (1984) for magmatic apatites only (i.e. Dvs, M-Ap, and BiGd at Oyu Tolgoi, and the felsic Apache Leap and Schultze Granite apatites at Resolution). AST for BiGd rocks is between 910°C and 937°C, and Dvs has AST of between 834°C and 901°C. At Resolution, the felsic Apache Leap intrusion has an AST of 963°C. AST calculated for the Schultze Granite are between 892°C and 927°C, although the biotite-rich enclave sample has an AST of the 1018°C.

### **6.6.2 Oxygen fugacity**

Log  $fO_2$  was estimated from apatites using the Mn-in-apatite (Miles et al. 2014), and combined with AST to produce estimates for  $\Delta FMQ$  of crystallisation. Log  $fO_2$  was only calculated for apatites that are considered to be magmatic (see 6.6.1), as the model of Miles et al. (2014) is not calibrated to estimate redox conditions from hydrothermal apatite. For Oyu Tolgoi apatites, BiGd apatites yielded redox values between FMQ +2.1 and -0.1. M-Ap (Heruga) produced values between FMQ +0.6 and -2.1. M-Ap (SW Oyu; sample OT-143) produced slightly higher values, between FMQ +2.9 and +0.7. Redox conditions for sample

OT-143 were also estimated from the chemistry of amphibole phenocryst cores using the method of Ridolfi et al. (2010; see Appendix 6 for amphibole data and full model results). FMQ estimates from hornblende (+3.6 to +2.6) overlap with those for Mn-in-apatite for sample OT-143 (Fig. 6.30 a).

For Resolution apatites, Schultze Granite redox estimates extend to unrealistically low  $fO_2$  values, ranging between FMQ -23.3 and -1.2 (Fig. 6.30 b). This is in contrast to estimates of  $fO_2$  for the Schultze Granite determined from sparse hornblende found in the granite, using the method of Ridolfi et al. (2010), and Schultze Granite hornblende data from Stavast (2006), which yield values between FMQ +1.3 and +1.8 (Fig. 6.30 b). This disparity is likely due to the fact that the model of Miles et al. (2014) was not calibrated for apatites with Mn values >4000 ppm. Felsic Apache Leap sample apatites yield redox estimates of between FMQ +0 to -3.9.

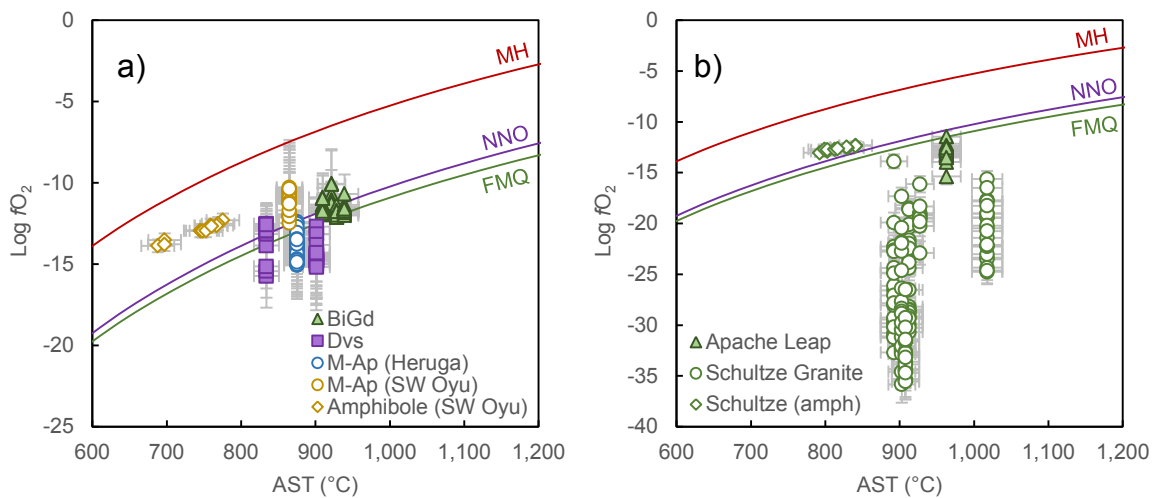


Figure 6.30. Estimates of  $\log fO_2$  (Mn-in-apatite; Miles et al., 2014) and temperature of crystallisation (AST; Harrison and Watson, 1984) from a) Oyu Tolgoi, and b) Resolution. Also plotted are estimates of  $\log fO_2$  and temperature determined from amphiboles (Ridolfi et al., 2010) from the same rocks (open triangles). Errors determined after original experimental studies in all cases. Note that the Schultze Granite sample with high AST (1,018 °C) in b) is the biotite-rich enclave sample. Hornblende data in b) from Stavast (2006). Note the different scales for  $fO_2$  in a) and b).

## 6.7 Discussion

### 6.7.1 Controls on the trace element characteristics of hydrothermal and igneous apatite

It has been demonstrated that the trace element characteristics of apatites from a variety of igneous rock types may be explained in terms of the co-crystallisation of other trace element-rich phases (Sha and Chappell, 1999; Chu et al 2009, Miles et al., 2013). In particular, the crystallisation of monazite, xenotime, and titanite can significantly deplete residual melts in LREE, HREE, and MREE respectively, due to their enrichment in these elements (Fig. 6.31). This sensitivity of apatite to the precipitation of accessory phases makes it a useful tracer of residual melt chemistry during the later stages of crystallisation in rocks that have similar bulk chemical characteristics. Due to the relative paucity of geochemical studies on hydrothermal apatite, this approach is less frequently applied to hydrothermal systems, but it may also be used to infer the chemistry of fluids and the nature of co-precipitating phases in hydrothermal environment.

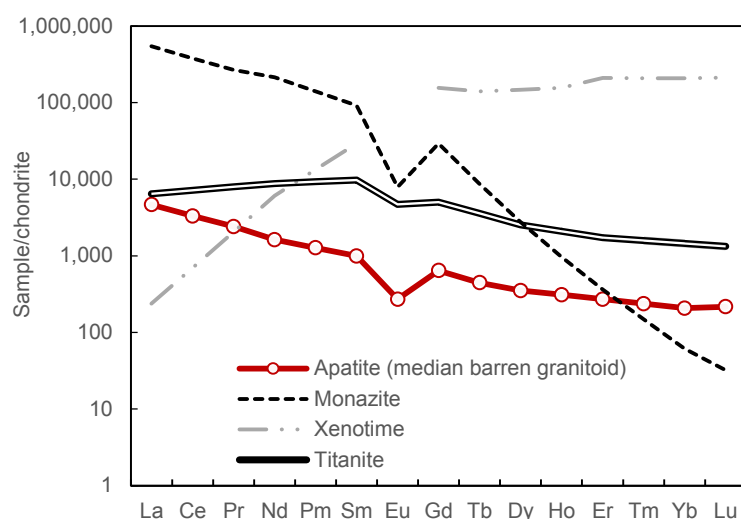


Figure 6.31. Representative REE compositions of monazite, xenotime, and titanite from Harlov (2010). By contrast, apatite from barren granitoids may have REE concentrations that are up to 3 orders of magnitude less than one or other of these phases. Consequently, if apatite crystallises from melts or fluids after (or during) the precipitation of any of these phases, the REE patterns of apatite may be affected, and each phase would impart a characteristic signature.

#### *6.7.1.1 Monazite control on REE and Th in Resolution hydrothermal and igneous apatites*

The chemistry of dominant-type apatites from Resolution (potassic, hydrothermal), and the Schultze Granite (igneous), bear many of the characteristics of apatites from felsic I-type magmas, especially the high Mn and F, and low La/Sm and Cl contents. This is in accord with the bulk chemical characteristics of these rocks, which are highly evolved (70.9 to 73.4 wt.% SiO<sub>2</sub>) It also suggests that the fluids in equilibrium with dominant-type apatites possibly inherited some of their geochemical characteristics from the melts from which they exsolved.

For example, LREE depletions in apatites from S-type and felsic I-type granites are a consequence of the co-precipitation of monazite because it has a strong preference for LREE, and so imposes pronounced LREE depletion on residual melts and resultant phases that crystallise from them (Fig. 6.31). Monazite crystallisation also produces negative Nd anomalies ( $Nd/Nd^* = Nd_N/[Ce_N \times Sm_N]^{0.5}$ ; Miles et al., 2014) due to the preference of monazite for Nd over neighbouring REE. Th contents of monazite are also high (up to 1 wt.% ThO<sub>2</sub>; Harlov et al., 2011), causing Th depletions in residual melts and fluids, and mineral phases in equilibrium with them.

Monazite is present in the Resolution, felsic Apache Leap and Schultze Granite intrusions. It is rarer in the Resolution porphyry intrusions, but is occasionally observed in the groundmass. Both hydrothermal and igneous apatites from Resolution and the Schultze Granite rocks show Nd anomalies that become increasingly negative as La/Sm decreases (Fig. 6.32 a), and both La/Sm and Nd/Nd\* decrease with increasing melt fractionation (whole rock SiO<sub>2</sub> as a proxy; Fig. 6.32 b). Th also decreases with increasing fractionation, consistent with the co-precipitation of monazite (Fig. 6.32 c).

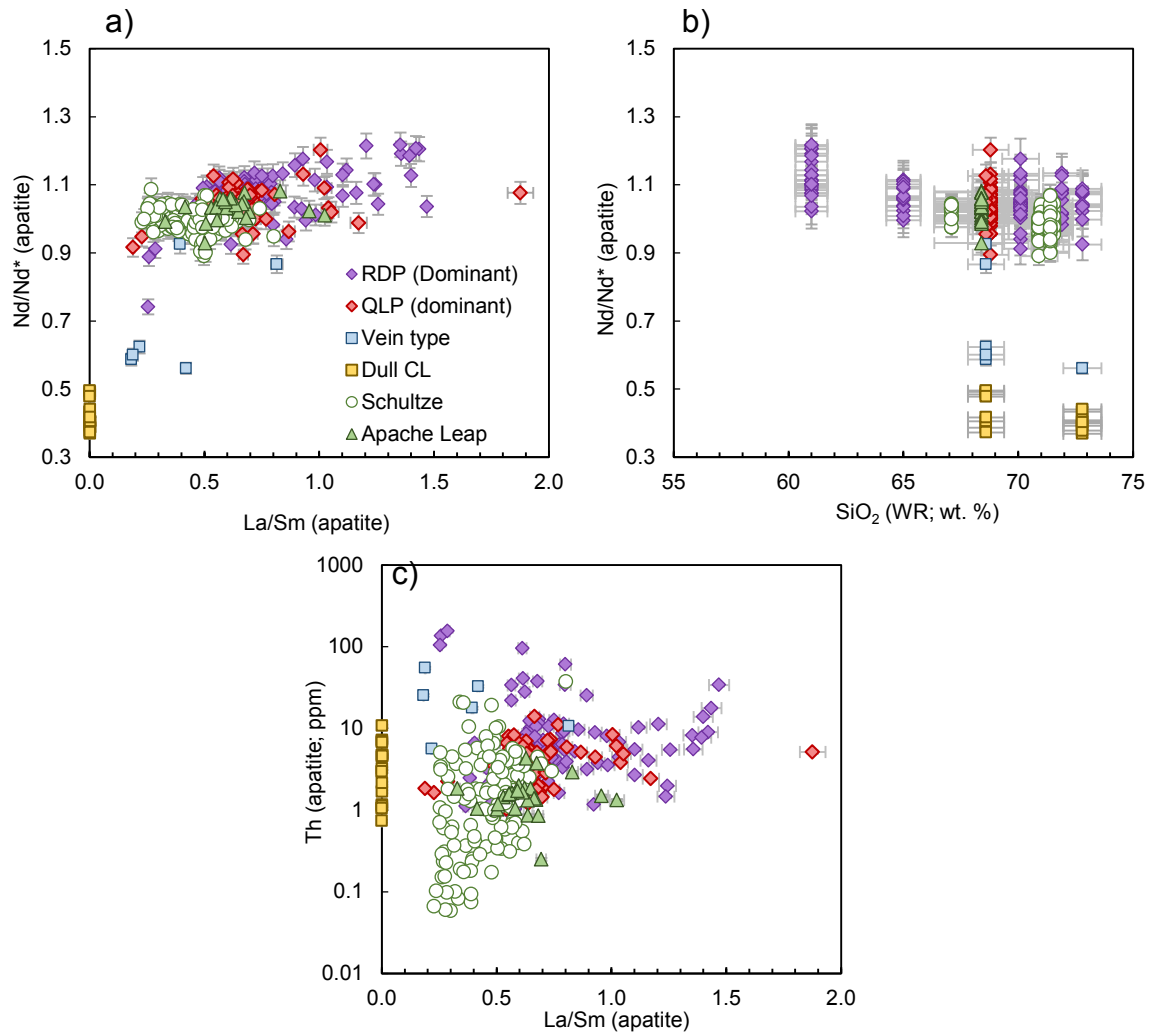


Figure 6.32. The variation of  $Nd/Nd^*$  with indices of fractionation; a)  $La/Sm$  in apatite, and b) whole rock  $SiO_2$ . The smallest  $Nd/Nd^*$  values are found in apatites with the lowest  $La/Sm$ , and highest  $SiO_2$ , as would be expected of apatites crystallising from melts (or fluids) from which progressively larger amounts of monazite have been crystallised. c) The same relationship is seen in apatite Th contents (c), which may also be ascribed to monazite fractionation.

Vein-type and dull-CL apatites show the strongest negative Nd anomalies and lowest  $La/Sm$ . The vein-type apatite contains small inclusions of monazite, which are surrounded by patches of dull CL apatite (Fig. 6.17 a-d). Apatite with similar textures and with comparable LREE-depleted chemistry have been briefly described from other porphyry systems (e.g. Hernandez et al., 2004). These have been interpreted as resulting from the exsolution of

monazite from apatite grains during post-crystallisation re-equilibration with hydrothermal fluids, a process that also occurs during hydration of metamorphic rocks (e.g. Harlov and Förster, 2002). The origin of dull-CL apatite REE chemistry remains unclear. No monazite inclusions are found in these grains, which are pristine and devoid of inclusions (Fig. 6.17 f). Nonetheless, the strongly negative Nd anomalies and low La/Sm ratios of these apatites are suggestive of a monazite-controlled REE budget, either by post-crystallisation equilibration, or by crystallisation from fluids that have saturated monazite.

#### *6.7.1.2 Titanite control on REE in Oyu Tolgoi M-Ap and Dvs apatite*

The co-precipitation of titanite exerts a different control on apatite REE chemistry to that of monazite. REE are strongly compatible in titanite, especially MREE ( $D_{\text{Sm}}/D_{\text{La}} = 8.2$ ,  $D_{\text{Sm}}/D_{\text{Yb}} = 2.4$ ; Bachmann et al., 2005), but titanite contains 2 orders of magnitude less LREE than monazite (Fig. 6.31), so the strong LREE depletion seen in apatites from monazite-bearing granites is not seen in apatites from titanite-bearing rocks. Titanite is typically found in oxidised I-type magmas with higher Ca contents, i.e. for compositions less evolved than granite (e.g. Wones, 1989).

In the M-Ap from sample OT-143 (SW Oyu), apatites are commonly inter-grown with titanite (Fig. 6.3 f), and these apatites are depleted in REE with respect to M-Ap and Dvs apatites from other samples that have no titanite association (e.g. OT-45, Heruga; Fig. 6.13 e). The effects of titanite crystallisation on melts of average QMD composition can be modelled to generate a series of hypothetical melts, to which apatite/melt partition coefficients can be applied in order to predict the composition of coeval apatites. This approach is also applied in Chapter 5 to investigate the effect of titanite crystallisation on the REE chemistry of zircons (Fig. 5.33). The results of this modelling shows that M-Ap from the titanite-absent QMD

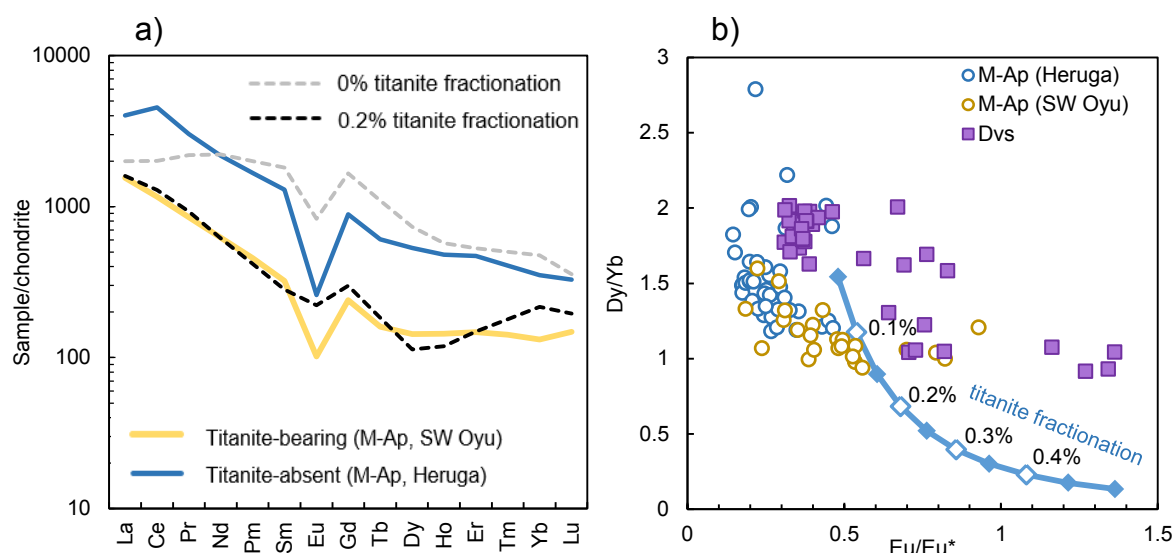


Figure 6.33. Modelling the effects of titanite crystallisation in apatites from Oyu Tolgoi. (a) Apatite in equilibrium with average QMD compositions (grey dashed line) is similar to median M-Ap REE patterns from titanite-absent rock (Heruga; OT-45). Apatite in equilibrium with model melts where 0.2 % titanite (black dashed line) has been removed are a close match for median REE patterns of M-Ap from titanite bearing sample OT-143. (b) Decreasing Dy/Yb with increasing Eu/Eu\* is predicted for apatites in equilibrium with increasingly titanite-fractionated melts (blue line), and these trends are broadly observed in apatites from Dvs and M-Ap, albeit for different initial conditions. Partition coefficients for apatite from Sano *et al.*, (2002), and titanite from Bachmann *et al.* (2005).

(Heruga sample OT-45) has broadly similar REE characteristics to apatites in equilibrium with average QMD compositions. However, model melts that have undergone 0.2% titanite crystallisation, and are depleted in REE as a result, are a close match for the median REE patterns of M-Ap from the titanite-present QMD (SW Oyu sample OT-143). For full details of model and results, see Appendix 7. This result suggests that REE patterns of igneous apatites from Oyu Tolgoi are strongly affected by the crystallisation of small amounts titanite.

The model is not able to closely reproduce the LREE-enrichment, nor the exact Eu anomalies observed in the samples, which is likely due to subtle differences between partitioning behaviour used in the model (Sano *et al.*, 2002) and the actual behaviour.



Published partition coefficients for LREE into apatite are highly variable, with  $D_{La}$  ranging from 4.8 (Prowatke and Klemme, 2006) to 36 (Sano et al., 2002). Nonetheless, the general principle that titanite crystallisation can cause REE depletion, and in particular MREE depletion, in residual melts and resultant phases appears to be valid. The model predicts the increase in  $Eu/Eu^*$  with decreasing  $Dy/Yb$  seen in apatite from the Dvs and QMD M-Ap, albeit from different starting  $Eu/Eu^*$  (Fig. 6.33 b).  $Eu/Eu^*$  increases with titanite crystallisation due to the greater uptake of Sm and Gd with respect to Eu in titanite (Bachmann et al., 2005).

Redox conditions calculated from Mn in igneous apatite and from hornblende for sample OT-143 (Fig. 6.30 a) are in accord with experimental estimates of the  $fO_2$  required to stabilise titanite ( $\sim FMQ + 2.5$ ; Fig. 5.34). Also, the textural relationship between hornblende, titanite, and apatite in sample OT-143 suggests they are co-crystallising phases (Fig. 6.3). However, redox estimates for other samples from either Oyu Tolgoi or Resolution are difficult to make, due to the absence of fresh hornblende in all other rocks from Oyu Tolgoi, and the absence of equilibrium magnetite-ilmenite pairs.

#### *6.7.1.3 Melt chemistry controls on REE in BiGd apatite*

The HREE depletion seen in BiGd apatites ( $Sm/Yb$  up to 22; Table 6.4) mirrors the REE characteristics of the BiGd rocks, which are depleted in HREE compared to other Oyu Tolgoi intrusions (Dvs, QMD). The HREE depletion in the BiGd rocks is thought to have been caused by the deep crustal fractionation of an assemblage of garnet + amphibole + subordinate plagioclase (see Fig. 4.38). Fractionation of garnet in particular leaves the melt depleted in HREE, due to their high partition coefficients into garnet ( $D_{Lu} = 7.1$ ; Johnson et al, 1994). This HREE-depleted characteristic is suggested to be the likely cause of HREE depletion in apatites that crystallised from these magmas.

## 6.7.2 Distinguishing barren and fertile magmatic and hydrothermal systems

### 6.7.2.1 Elevated Sr contents in igneous and hydrothermal apatite

Apatites from ostensibly barren intermediate to felsic igneous rocks rarely have Sr concentrations in excess of ~750 ppm (Figs. 6.14 b, and 6.28 b). The data of Belousova et al. (2002a) comprise 669 analyses of apatite from I-type granitoids, which have a median of 135 ppm Sr and a maximum value of 628 ppm Sr. Piccoli and Candela (2002) presented an average Sr content of 0.07 wt.% SrO (592 ppm Sr) for apatites of intermediate-felsic rocks not associated with ore deposits. The median Sr concentration from the literature survey conducted for this study is 310 ppm, with a maximum value of 747 ppm.

This is in stark contrast to the Sr content of apatite from this study, particularly igneous apatite from Oyu Tolgoi, which frequently contains Sr in excess of 1000 ppm (Figs. 6.8 a, and 6.23 a). For example, the maximum Sr content of apatites from the BiGd is 3190 ppm. At Resolution, maximum Sr contents of the dominant-type QLP and RDP are >1000 ppm. These elevated Sr contents appear to represent a divergence from typical arc-related apatite, reflecting differences in magmatic evolution in the mineralised settings.

Two factors are likely to affect the Sr content of apatites crystallising in the shallow crust. First, the Sr content of the melts ascending into the shallow crustal from deep crustal MASH or hot zones. This is partly controlled by the composition of the melt source, but in most arcs is mainly a function of crystal fractionation processes occurring at depth (e.g. Loucks, 2014). The relative proportions of phases crystallising in deep crustal environments is in turn a function of pressure and melt H<sub>2</sub>O. The generation of Sr-rich melts in the deep crust is discussed in detail in Chapter 1 (Section 1.3.4).

High Sr melt concentrations are a necessary factor for generating Sr-rich apatite, but are not sufficient on their own. The relative timing of plagioclase and apatite crystallisation in the

shallow crust plays a critical role. In typical arc rocks, Sr concentrations in igneous apatite are not normally greater than the Sr content of the rocks in which it occurs, i.e.  $Sr_{Ap}/Sr_{WR}$  values are less than unity ( $Sr_{WR}$  = whole rock Sr content). However, experimental partitioning studies show that Sr is compatible in apatite, ( $D_{Sr} > 1$ ; Prowatke and Klemme, 2006). The apparent disparity between observational and experimental data is due to the timing of plagioclase crystallisation during the cooling of these magmas (e.g. Jennings et al., 2011). As apatite is not commonly a liquidus phase in mafic to intermediate arc magmas (e.g. Piccoli and Candela, 2002), a significant amount of plagioclase may crystallise from the melt before the onset of apatite crystallisation, depleting the melt in Sr. If plagioclase is not segregated from the melt, then the whole rock composition will be unchanged, but the residual melt will be depleted in

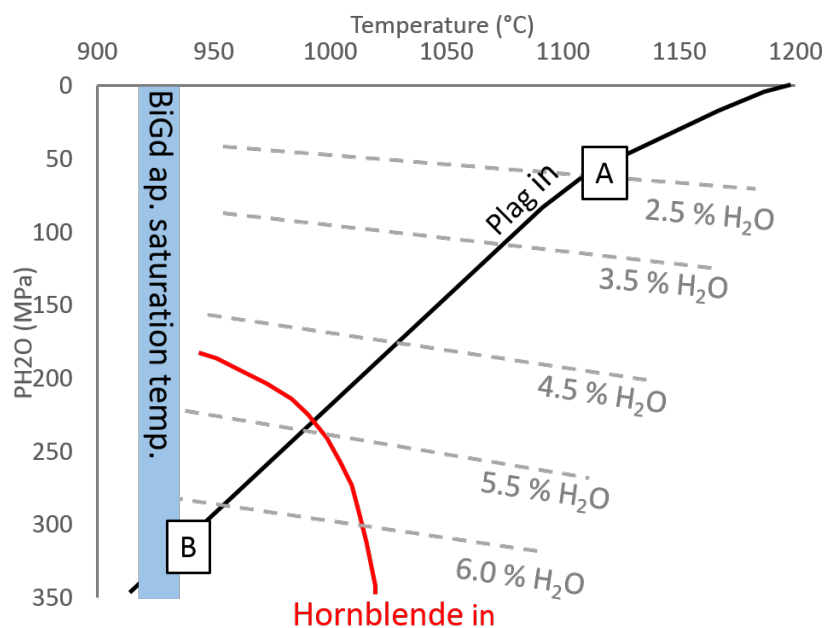


Figure 6.34. Phase diagram showing the  $H_2O$ -dependence of plagioclase saturation temperature. Magmas  $\sim 2.5$  wt. %  $H_2O$  will begin to crystallise plagioclase at point [A], well in advance of the onset of apatite crystallisation, which is (blue box). This will result in the depletion of Sr in the melt, and low Sr apatites. Melts with higher  $H_2O$  (around 6 wt. %) will begin to crystallise plagioclase much later at point [B], at the same time as apatite, meaning no depletion in Sr will occur in the melt, and apatite may reach high Sr. Modified after Blatter and Carmichael (1998)

Sr. Apatites subsequently crystallising from these melts, although enriched in Sr relative to the melt, will not be enriched relative to the whole rock.

Plagioclase is a ubiquitous phase in arc rocks, including porphyry intrusions. Although the crystallisation of plagioclase is an inevitable consequence of cooling silicate melts containing alumina, the timing of plagioclase crystallisation with respect to other phases is highly variable. Experimental studies of water-saturated crystallisation of intermediate silicate melts show that the stability of plagioclase in the shallow crust varies strongly as a function of melt H<sub>2</sub>O. Under anhydrous conditions, plagioclase is the first phase to crystallise at 1200°C, whereas the temperature of plagioclase crystallisation is suppressed to ~900°C where melt H<sub>2</sub>O content is >6.5 wt.% (Fig. 6.34) in which case, hornblende saturates before plagioclase (Loucks, 2014). These experimental studies are supported by the presence of hornblende-bearing, plagioclase-free andesites in some arc rocks (e.g. Blatter and Carmichael, 1998).

The crystallisation of apatite is independent of pressure and melt H<sub>2</sub>O. Instead, it varies as a function of temperature and melt SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> composition (Harrison and Watson, 1984). The saturation temperature of apatite from the BiGd samples studied here is inferred to have been between 910 and 939°C. If correct, this would mean that if these magmas were hydrous (>6.5 wt.% H<sub>2</sub>O), apatite could begin to crystallise just before, or at the same time as the onset of, plagioclase crystallisation (Fig. 6.34, point “B”), before melts were depleted in Sr. Most apatite grains are found in the groundmass of BiGd rocks, but large apatite crystals are occasionally observed as inclusions within the cores of and rims of large plagioclase crystals (Fig. 6.4 d) suggesting that apatite was present throughout the period of feldspar crystallisation.

The Sr content of hydrothermal apatite would vary largely as a function of the Sr content of fluids from which it precipitated, assuming no other Sr-rich phases are also crystallising simultaneously. During partitioning between silicate melts and aqueous fluids, Sr

is generally compatible in the melt, with fluid/melt partition coefficients  $\sim 0.1$  in Cl-bearing fluids (Borchert, 2009). This means melts with a Sr content of 1870 ppm (the maximum Sr content of BiGd rocks) would coexist with a fluid of only  $\sim 190$  ppm Sr. This is in agreement with Sr compositions measured from fluid inclusions in granitic hydrothermal systems (Zajacz et al., 2008). However, Sr is strongly compatible in apatite during fluid/apatite partitioning, with similar partition coefficients to apatite/melt ( $D_{\text{Sr}} = 15$  to 33; Ayers and Watson, 1993). Thus, a hydrothermal fluid would only need to contain 115-253 ppm Sr to precipitate an apatite with  $\sim 3800$  ppm Sr, the maximum Sr concentration observed in S-Ap. Generating Sr-rich apatite (containing several thousand ppm Sr) from hydrothermal fluids is therefore theoretically possible if the magmas from which the mineralising fluids exsolved are already enriched in Sr.

#### *6.7.2.2 Elevated Eu/Eu\* values for igneous and hydrothermal apatite*

Apatites from typical I-type rocks have median Eu/Eu\* values of 0.36; more fractionated I-type and S-type granites have much lower values (median = 0.09). It has been suggested that apatites crystallised from more reduced melts have more negative Eu anomalies due to the preference of apatite for  $\text{Eu}^{3+}$  over  $\text{Eu}^{2+}$  and because the former will be less abundant when  $f\text{O}_2$  is low. Another factor that can affect the Eu anomaly of apatite is the intrinsic Eu anomaly of the melt. For example, melts that have fractionated titanite have smaller negative, or even positive, Eu anomalies due to the preferential uptake of Sm and Gd over Eu in titanite. Consequently, apatites that crystallise from such melts can inherit this characteristic.

The correlations of Sr with REE and Eu/Eu\* (Figs. 6.14 and 6.28) are common to apatites in this study, and suggest that the processes controlling elevated Sr in apatite may also exert some control over Eu/Eu\*. As well as generating high Sr melt concentrations, hydrous, deep-crustal fractionation of an amphibole/garnet-rich assemblage generates melts that have high Eu/Eu\*, and are depleted in REE with respect to typical arc magmas. This is because

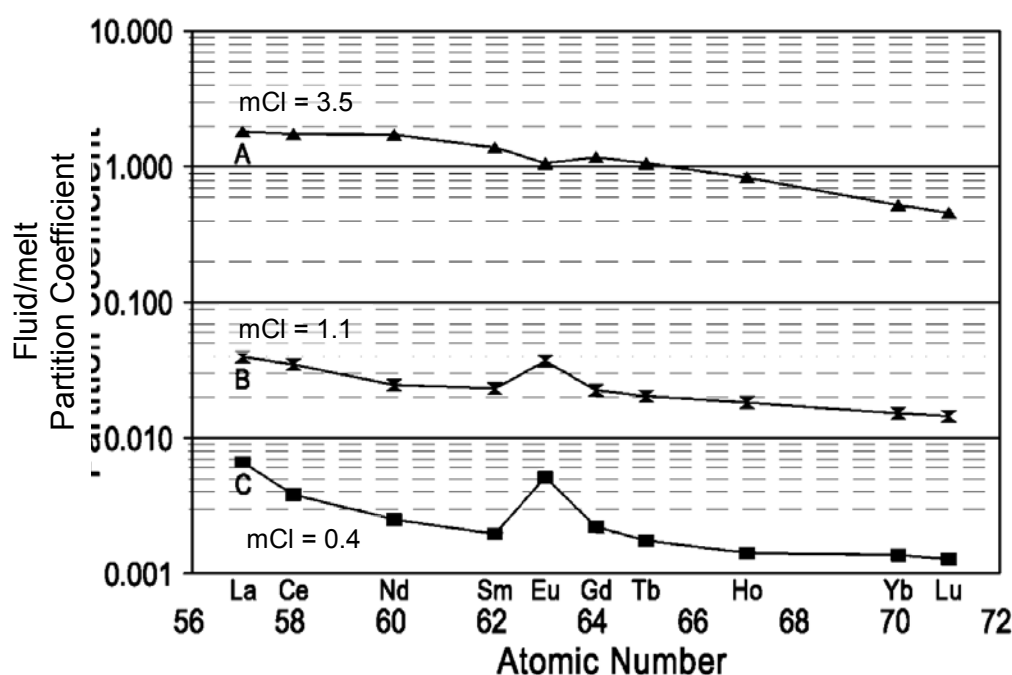


Figure 6.35. Experimentally determined fluid/melt partition coefficients for REE between aqueous fluids and silicate melts. Partition coefficients increase with increasing fluid Cl content, from “C” (lowest salinity) to “A” (highest salinity). Eu is more compatible than Sm and Gd in fluids with  $mCl < 3.5$ , meaning these fluids will carry a positive Eu anomaly, which may be imparted onto hydrothermal phases which precipitate from them. From Reed et al. (2000).

plagioclase crystallisation and fractionation is suppressed under these conditions, reducing the loss of Eu from the residual melt, and M- to HREE are compatible in amphibole  $\pm$  garnet, and Sm and Gd are more compatible than Eu. Oxidised conditions can help to limit loss of Eu from the melt even if plagioclase does fractionate because of its preference for  $Eu^{2+}$  over  $Eu^{3+}$ . These processes lead to neutral or weakly positive Eu anomalies in magmas from porphyry systems (e.g. Lang and Titley, 1988; Richards et al., 2012), and these relatively elevated Eu contents can be transferred into the apatite that crystallises from them.

In the case of hydrothermal apatite, the Eu anomaly of the mineral is likely to be inherited from the fluid. Experimental studies on the partitioning of REE between

monzogranitic melts and aqueous fluids show that REE are mostly compatible in melts, but their compatibility in fluids increases with increasing fluid Cl content (Reed et al., 2000). At  $m_{\text{Cl}} < 3.5$  (equivalent to  $< 20.5$  wt.% NaCl), Eu is more compatible in fluids ( $D_{\text{Eu}} \sim 0.035$ ) than Sm or Gd ( $D_{\text{Sm}}$  or  $D_{\text{Gd}} \sim 0.025$ ; Fig. 6.35). Thus, for apatites crystallizing from low to moderate salinity fluids, the value of Eu/Eu\* in the fluid is likely to be increased over the parent melt. This could give an unrepresentative impression of melt fertility if the Eu anomaly of hydrothermal apatite is assumed to reflect that of the associated magma.

In summary, Sr and Eu/Eu\* of igneous apatites from mineralised porphyry systems are elevated with respect to apatites from barren granitoids. These characteristics are inherited from their host magmas which, for porphyry magmas, are proposed to develop by hydrous, deep crustal fractionation. Hydrothermal fluids exsolving from Sr and Eu rich magmas are likely to acquire these signatures, and will transfer them into hydrothermal apatites. Where brines are the dominant fluids exsolving from magmas and precipitating hydrothermal apatite, then elevated Eu/Eu\* in this phase can also be taken as a positive indicator of melt fertility.

High Sr and Eu/Eu\* cannot be used to distinguish igneous apatites from low-grade or high-grade porphyry systems, nor is it a guaranteed indicator of significant Cu mineralisation. For example, the intrusions with the highest Sr-in-apatite at Oyu Tolgoi is the BiGd (Fig. 6.8), which postdates mineralisation and does not contribute to it. Instead, these chemical characteristics indicate the *potential* for the magmatic system in which they crystallised to generate mineralisation. This potential may not be fulfilled for numerous reasons, including magma stagnation and crystallisation, loss of volatiles and metals during an earlier stage of mineralisation, or eruption and loss of these to the atmosphere (e.g. Pasteris, 1996).

### 6.7.3 Distinguishing low and high-grade porphyry systems using hydrothermal apatite: a case study from Oyu Tolgoi

In this section, the chemistry of hydrothermal apatite inter-grown with sulphides (i.e. S-Ap) from low- and high-grade systems at Oyu Tolgoi is compared and discussed. There is little difference between Heruga and Hugo Dummett S-Ap in terms of more typical indicators

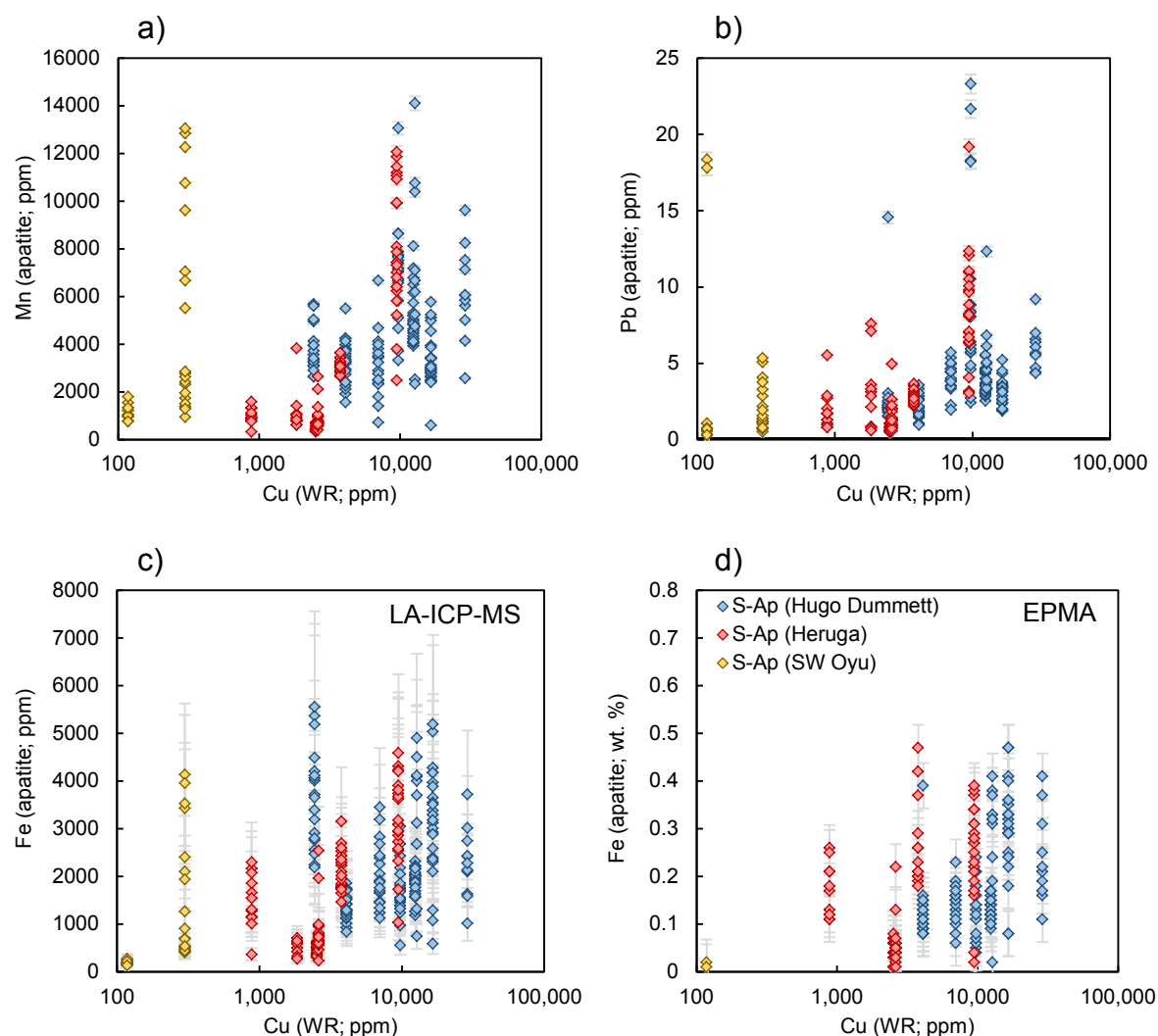


Figure 6.36. Variation of selected divalent cations a) Mn, b) Pb, c,d) Fe, with respect to the Cu content of the rocks from which they were derived. Concentrations of these elements are higher in Heruga than in Hugo Dummett. The highest values of Mn and Pb from Heruga are found in the rocks with the greatest Cu concentration. Mn, Pb and Fe (c) data collected by LA-ICP-MS, Fe (d) collected by EPMA. WR = whole rock data.



of fertility; i.e. Sr (Fig. 6.8 a) and Eu/Eu\* (Fig. 6.15). This suggests that the factors that control these parameters (see 6.7.2.1 and 6.7.2.2) may be capable of increasing the fertility of magmatic systems, but do not necessarily control any subsequent enrichment in Cu during ore formation.

The primary difference between S-Ap from Heruga and Hugo Dummett is the enrichment of some divalent cations, especially Mn, and Pb, in S-Ap from Hugo Dummett with respect to Heruga (Fig. 6.8). This difference is easy to discern when the Mn or Pb content of apatite is compared to the Cu content of the rocks in which they are found (Fig. 6.36). Fe also may also distinguish Heruga from Hugo Dummett, although the distinction is less clear, and may be masked by the analytical issues in determining Fe.

There is some considerable overlap in Mn, Pb (and Fe) contents of S-Ap from the two deposits. For example, Heruga QMD sample OT-39 contains S-Ap with Mn and Pb contents that are significantly higher than other Heruga S-Ap, and more similar to Hugo Dummett S-Ap (Fig. 6.36). However, this sample is atypically enriched in Cu (0.94 wt. % Cu) compared to other rocks from Heruga (typically <0.4 wt. % Cu). When S-Ap are instead subdivided on the basis of the Cu content of their host rocks, the distinction between S-Ap from low-grade and high-grade rocks becomes more apparent (Fig. 6.37). Significantly, rocks that have >0.75 wt. % Cu seldom contain apatites with <1000 ppm Fe, <2500 ppm Mn, or <2.5 ppm Pb (Fig. 6.37).

One interpretation of these differences in S-Ap geochemistry is that they reflect different redox conditions during crystallisation because Mn and Fe are increasingly partitioned into apatite under more reducing conditions, at least for igneous apatites (Miles et al., 2014). However, this would not account for the high Pb contents of S-Ap at Hugo Dummett, as Pb is

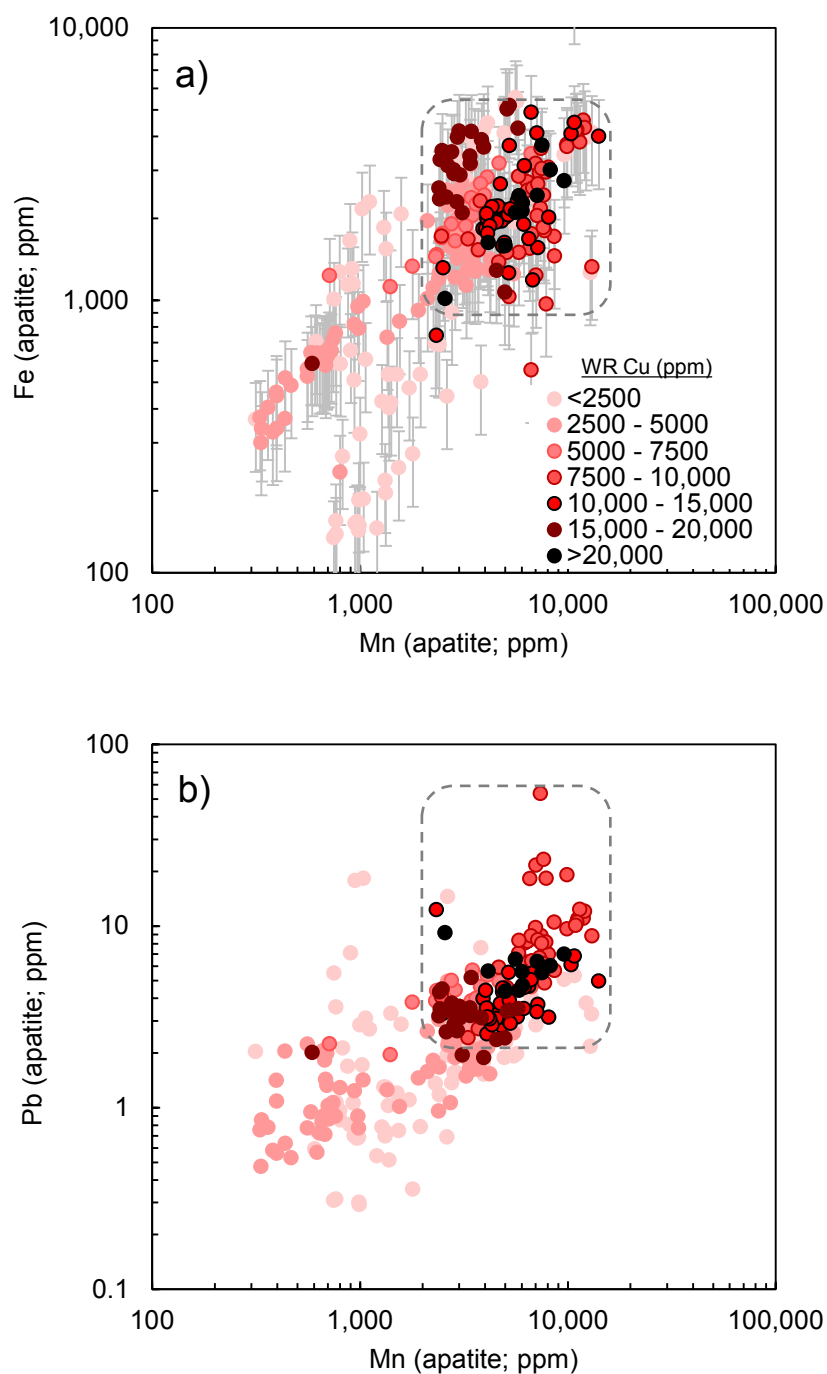


Figure 6.37. The variability of Fe (a) and Pb (b) with respect to Mn in hydrothermal S-Ap from Oyu Tolgoi. The colours indicate the Cu concentration of the rocks from which these apatites were found, such that darker colours are rocks with higher Cu concentration. Dashed box encloses nearly all S-Ap analyses from rocks containing >0.75 wt. % Cu. Both sets of error bars in b) are smaller than symbol size. All data collected by LA-ICP-MS.

not directly redox controlled. Also, the elevated Eu/Eu\* values preclude especially reducing conditions.

Fluid composition is likely to exercise a strong control over hydrothermal apatite chemistry. The observed correlations between Cl and Mn, Fe, and Pb in S-Ap (Fig. 6.9) suggest that apatites with higher divalent metal contents were precipitated from more Cl-rich fluids. This would imply that the fluids involved were moderately more Cl-rich at Hugo Dummett than at Heruga or SW Oyu. Evidence from experimental studies (Webster et al., 1989; Ayers and Eggler, 1995; Bai and van Groos, 1999), and observations from fluid inclusions in mineralized granitic rocks (Audétat et al., 2000; Audétat and Pettke, 2003; Audétat et al., 2008), have demonstrated that Cl-rich fluids are able to transport higher concentrations of cations such as Mn, Pb, and Fe, due to the greater formation of metal chloride complexes (see Seward et al., 2013). The presence of elevated Cl in hydrothermal fluids may also increase the ability of the fluid to transport Cu (Candela and Holland, 1984; Simon et al., 2006). Thus, Cl-rich fluids, carrying elevated Mn, Pb, Fe and Cu, could account for the high Mn, Pb and Fe content of apatite in rocks with high Cu content.

Estimations of the fluid Cl content in equilibrium with these apatite crystals using the method of Piccoli and Candela (1994) is difficult because the equilibrium is strongly dependent on temperature, for which accurate estimates are difficult to make. Piccoli and Candela (1994) used the AST to calculate the Cl content of fluids in equilibrium with apatite-bearing melts. However, because the AST is calculated from melt chemistry (or whole rock chemistry as a proxy), it only applies to igneous apatite. Hydrothermal apatite is likely to crystallise at lower temperatures, and no robust thermometer exists for it. However, approximate estimates of crystallisation temperature may be made by considering the nature of the associated alteration assemblage. For example, S-Ap at Oyu Tolgoi is associated with strong potassic alteration, which typically occurs at temperatures between ~700 and 400°C.

Appendix 8 summarises the results of calculating  $Cl_{\text{fluid}}$  for selected apatite analyses for a range of temperatures at 2 kb. There is approximately a factor of 2 difference in calculated  $Cl_{\text{fluid}}$  contents between 700 and 600°C, irrespective of the Cl/OH ratio of the apatite. Assuming a temperature of 600°C, fluids in equilibrium with S-Ap contain a range of Cl contents between 0.05 wt.% and 4.6 wt.% (equivalent to 0.08 to 7.6 wt.% NaCl and  $m_{\text{Cl}}$  of up to 1.3). A melt-fluid partition coefficient for Cu may be estimated (Candela and Holland, 1994) and a copper concentration for the fluid calculated, assuming the fluid exsolved from a melt with a typical Cu concentration of 50 ppm. These estimates suggest that fluids in equilibrium with S-Ap had modest Cl contents, typical of intermediate density porphyry fluids that would have enabled them to carry <0.05 wt.% Cu as copper chloride complexes. This is an order of magnitude less than Cu concentrations measured in fluid inclusions from porphyry ore deposits, which typically vary between 0.1 and 1 wt.% Cu (e.g. Ulrich et al, 1999; Audetat et al., 2008). This suggests either that the fluids which precipitated the S-Ap at Oyu Tolgoi were not anomalously Cu rich or, probably more likely, that ligands other than Cl were involved in Cu transport.

## **6.8 Concluding remarks**

Apatites from both Resolution and Oyu Tolgoi may be classified as hydrothermal or igneous, depending on the minerals with which they are associated, the nature of the rock in which they are found (i.e. how altered it is), and on their habit. Several generations of hydrothermal apatite are observed at Resolution, some of which (the ‘vein-type’) are observed to replace earlier apatite populations. At Oyu Tolgoi, igneous and hydrothermal apatites may be broadly distinguished in terms of their La/Yb ratio (> 5 for igneous apatite).

The trace element chemistry (especially REE) of both igneous and hydrothermal apatites are strongly controlled by the precipitation of other trace element-enriched phases from

melts or fluids, or the unmixing of these phases from apatite during sub-solidus hydrothermal re-equilibration. At Resolution, equilibration with monazite may be invoked to explain strong LREE depletion, negative Nd/Nd\* and low Th contents. In the case of ‘vein-type’ apatite, monazite appears to have crystallised *in situ* from apatite during hydrothermal re-equilibration. At Oyu Tolgoi, titanite equilibration is able to explain the depleted REE characteristics of igneous apatites and, in particular, the depletion of MREE with respect to HREE (i.e. decreasing Dy/Yb ratios). Monazite or titanite are present either as inclusion within apatite, in the rock itself, or as inclusions preserved in zircon grains from rocks that are otherwise heavily affected by hydrothermal alteration.

Hydrothermal and igneous apatites from Oyu Tolgoi and Resolution mostly have higher median Sr and Eu/Eu\* than apatites from barren rocks, and the correlation of Sr and Eu/Eu\* suggests that these two parameters may be controlled by the same factor, which is likely to be a combination of inheritance from Sr- and Eu-rich melts, and the delay in plagioclase crystallisation with respect to apatite due to high magmatic H<sub>2</sub>O.

Hydrothermal apatites associated with sulphides (or, *S-Ap*) from Hugo Dummett and Heruga are considered to be in equilibrium with fluids that contributed to significant sulphide mineralisation. In spite of their textural similarities, S-Ap from both deposits have significant differences in terms of their Mn, Pb, and Fe contents, namely that Hugo Dummett S-Ap has significantly higher Mn, Pb, and Fe than Heruga. These high values are associated with high Sr and Eu/Eu\* in apatite. These signatures are apparently unique to apatites from porphyry systems. High Mn and Fe in igneous apatites from S-type granitoids are typically associated with low Sr and Eu/Eu\*, meaning hydrothermal apatite from porphyry systems may be distinguished on plots of Sr (or Eu/Eu\*) vs. Mn (or Fe, or Pb).

These signatures show some sensitivity to whole rock Cu content. Although apatites from Oyu Tolgoi rocks with <0.75 wt. % Cu may have a range of Mn, Fe, Pb, and Sr values, apatites from rocks with >0.75 wt. % Cu are exclusively enriched in Mn or Fe (>2000 ppm of either), Sr (>500 ppm), and have high Eu/Eu\* (>0.5). As a result, identifying an abundance of apatite carrying such signatures (e.g. in stream sediments) increases the probability that the rocks from which they derived contained significant mineralisation.

Given the relationship between these divalent cations and the apatite Cl content, it is suggested that the primary control on the Mn, Fe, and Pb of hydrothermal apatite in these systems is the salinity of the fluid with which they are in equilibrium. Highly saline fluids are able to carry high Mn, Fe, Pb, and Cu, as these metals form chloride complexes, affording them a greater ore-forming potential.

## **Chapter 7: Discussion**

### **7.1 Introduction**

Previous chapters have described the chemistry of rocks and minerals at Oyu Tolgoi and Resolution with comparison to barren igneous systems, and accounted for any differences in terms of the divergent processes by which fertile and barren magmas are thought to be generated. This chapter contains a synthesis of these results and considers their implications for the processes by which large porphyry deposits are formed. Important aspects of this discussion are the length and time scales at which various processes operate. Some signatures may be more applicable to regional-scale exploration over 100s of kilometres and millions of years because they broadly identify fertile arc belts and magmatic epochs. At the other end of the exploration scale, processes affecting the distribution of sulphides in the hydrothermal environment may vary between intrusions or hydrothermal systems.

This chapter will discuss the whole rock and mineral indicators identified in the previous chapters, and argue over which length and time scales these signatures may operate, in order to position their use in a regional- to deposit-scale exploration program. The discussion will be framed with reference to the broader geological literature and, where possible, will make reference to geochemical data from a range of other porphyry systems provided by Rio Tinto, to determine the broader applicability of the signatures identified at Resolution and Oyu Tolgoi. Finally, a critical assessment is made of the practical applications of whole rock and mineral fertility indicators to exploration for giant porphyry systems. Recommendations for the implementation of these findings in exploration are made, as are suggestions for future work stemming from the results of this study.

## 7.2 Whole rock geochemistry – tracking deep crustal igneous processes

One key observation from Oyu Tolgoi is the switch in REE geochemistry (Fig. 4.38) and Sr/Y between the syn-mineralisation QMD intrusions and co-magmatic Dvs volcanic rocks (MREE depleted, moderate Sr/Y, La/Yb ratios), and the immediately post-mineralisation BiGd intrusions (HREE depleted, high Sr/Y, La/Yb ratios). These rocks are broadly similar in terms of their major element chemistry and could be comagmatic, and so a subtle switch in trace element chemistry suggests some change in the deeper magmatic system. Significantly, this switch coincides closely with the period of mineralisation, and may thus explain some features of a typical, calc-alkaline arc that is evolving into a magmatic system capable of producing a large porphyry deposit.

### 7.2.1 Garnet fractionation in porphyry magmas

Although HREE depletion with respect to MREE in arc magmas is typically ascribed to the involvement of garnet during magmatic evolution (see section 1.3.4), the specifics of how garnet is involved, and the mechanisms which trigger its involvement, remain unclear. To begin with, fractionation of garnet is less often inferred than amphibole, but it has been considered a likely process in a number of arcs, including the Andes (e.g. Richards and Villeneuve, 2001; 2002; Richards et al., 2013) and the Philippines (Macpherson et al., 2006). Garnet is rarely present in arc rocks, so the inference that garnet has been involved in magmatic evolution is based entirely on whole rock geochemistry, and implies that some residual “cryptic” garnet remains at lower levels in the crust. Cryptic garnet crystallization has also been proposed for magmas associated with several large porphyry Cu deposits, especially in Chile (e.g. Kay and Mpodozis, 2001).

The formation of cryptic garnet signatures is typically ascribed to high pressure, either by fractional crystallization of magmas trapped at the base of thickened arc crust or in the upper mantle (e.g. Macpherson et al., 2006), or by the interaction between primary melts and



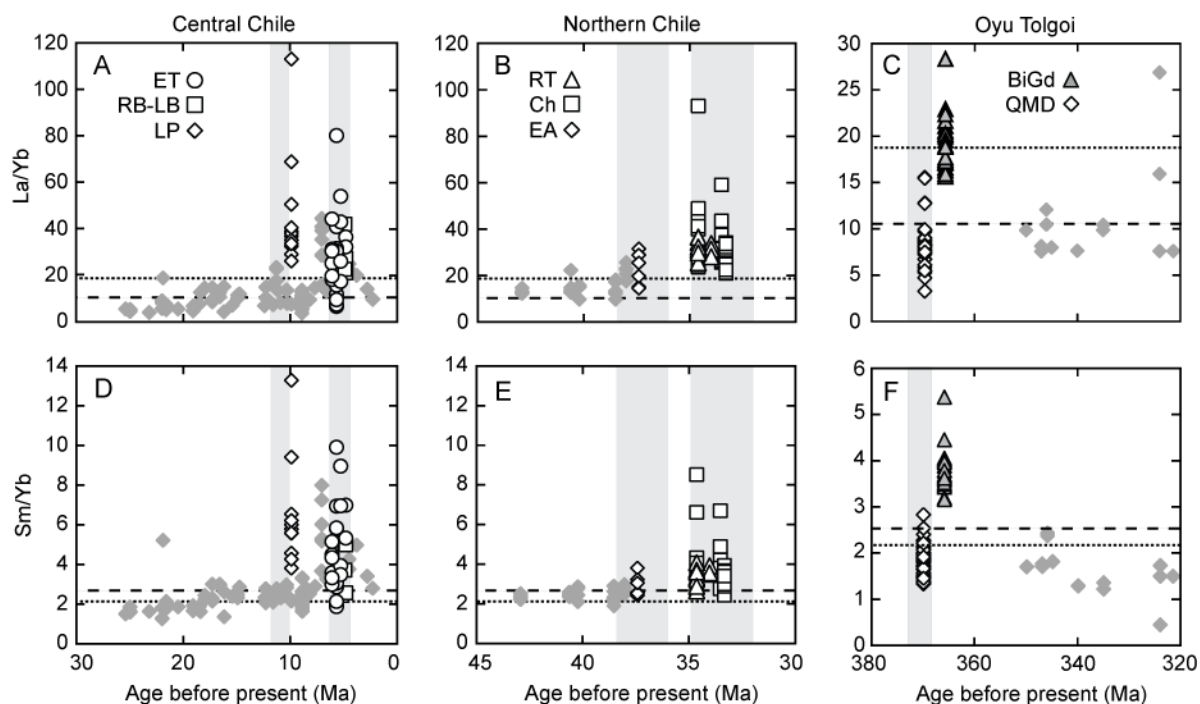


Figure 7.1. Temporal evolution of La/Yb and Sm/Yb ratios in igneous rocks from major porphyry districts over time periods preceding and/or succeeding mineralization. Light gray diamonds are unmineralised country rocks, open symbols are from intrusions associated with mineralization. Gray shaded areas represent periods of mineralization. Horizontal lines represent the maximum modeled values of La/Yb and Sm/Yb due to 40% fractionation of pure amphibole (dotted) and clinopyroxene (dashed). Values above the upper line are best explained by garnet fractionation. Literature data sources are: El Teniente (ET; Stern and Skewes, 1995, Kay et al., 2005; Stern et al., 2011), Rio Blanco-Los Bronces (RB-LB; Stern and Skewes, 1995), Los Pelambres (LP; Reich et al., 2003), Radomiro Tomic (RT), Chuquicamta, (Ch), and El Abra (EA; Ballard, 2002). Unmineralised rocks from Central Chile (Stern and Skewes, 1995; Kurtz et al., 1997; Nystrom et al., 2003; Hollings et al., 2005; Kay et al., 2005; Deckart et al., 2010; Stern et al., 2011), Northern Chile (Ballard, 2002), and Oyu Tolgoi (Wainwright, 2008).

the thickened garnetiferous lower crust or upper mantle (e.g. Hildreth and Moorbath, 1988). This is based on experimental studies which have shown that garnet is a stable igneous phase only at high pressure (1.2 GPa, ~40 km; Muentener et al., 2001). Several studies have recognised the switch from cryptic amphibole to cryptic garnet magmatism occurring close to

the period of mineralisation at a number of giant Andean porphyry systems (Fig. 7.1), and crustal thickening (i.e. increased pressure) has been invoked to explain these changes.

However, there remain some puzzling aspects of cryptic garnet signature magmatism. Although there is a suggested correlation between crustal thickness and garnet fractionation in some magmatic centres (e.g. Kay et al., 1999), areas of thin arc crust are also capable of producing cryptic garnet signatures (Macpherson et al., 2006). Conversely, in some areas of very thick modern arc crust (up to 60 km), cryptic amphibole signatures can predominate in erupted volcanic rocks (e.g. Richards et al., 2013). Significantly, cryptic garnet signature magmatism is often short lived, and localized to one volcanic edifice and/or only one eruption in areas where cryptic amphibole signatures are more typical. To give an example from the Chilean Andes, cryptic garnet signature dacitic tuffs at the Pliocene Cerro Abra Grande volcano are preceded and succeeded by cryptic amphibole signature volcanism within ~10 km and ~2 Myr (Richards et al., 2013). At Cerro Llullaillaco, Late Miocene to Pliocene magmas of cryptic amphibole affinity are succeeded by Pleistocene magmas of cryptic garnet affinity, the latter of which are broadly coeval with cryptic amphibole signature magmas of the nearby Cerro Escorial, just 40 km away (Richards and Villeneuve, 2001; 2002). In these cases, consistent crustal thickness in these areas preclude crustal thickening as a viable interpretation, and has required these authors to invoke polybaric fractionation pathways from deep to mid crust to explain such rapid geochemical switches.

Geochemical switches observed at porphyry systems are typically limited both to the period of mineralisation, and only affect magmas close to the deposit. For example, ore-related intrusions at Rio Blanco-Los Bronces and El Teniente show cryptic garnet signatures (~5 Ma;  $\text{Sm/Yb} = 3$  to 13.3) even though plutonic rocks of similar age around 40 km from El Teniente display cryptic amphibole signatures (6.5 to 5.5 Ma;  $\text{Sm/Yb} = 2.8$  to 3.3; Kurtz et al., 1997). Although crustal thickening may have occurred in these areas, it is difficult to imagine how

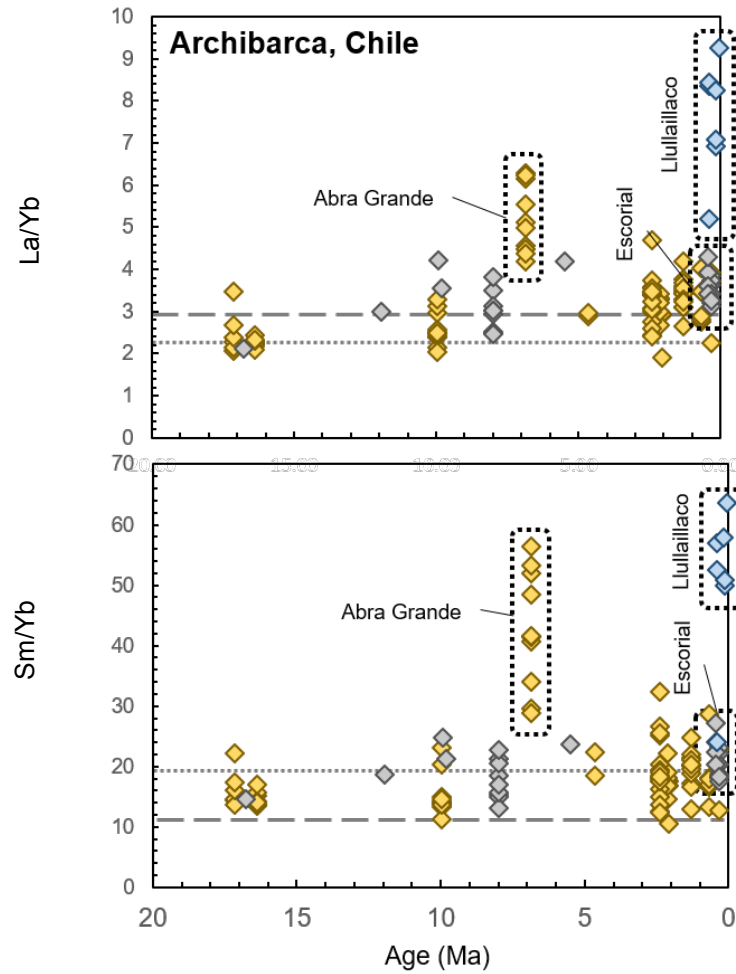


Figure 7.2. Temporal evolution of La/Yb and Sm/Yb ratios from the Archibarca region of Northern Chile. Horizontal lines represent the maximum modelled values of La/Yb and Sm/Yb due to 40% fractionation of pure amphibole (dotted) and clinopyroxene (dashed). Values above the upper line are best explained by garnet fractionation. Data from Richards and Villeneuve (2001; 2002), Richards et al. (2006), and Richards et al. (2013).

such a broad-scale arc process would affect only very narrow time windows and specific sections of a volcanic arc. Geochemical changes associated with crustal thickening have been demonstrated elsewhere (e.g. Bissig et al., 2003), but are normally associated with gradual changes in Sm/Yb over 20-30 Myr, and these are not seen in the regional volcanic rocks in these arcs (e.g. Hollings et al., 2005). Consequently, a different mechanism may be required to

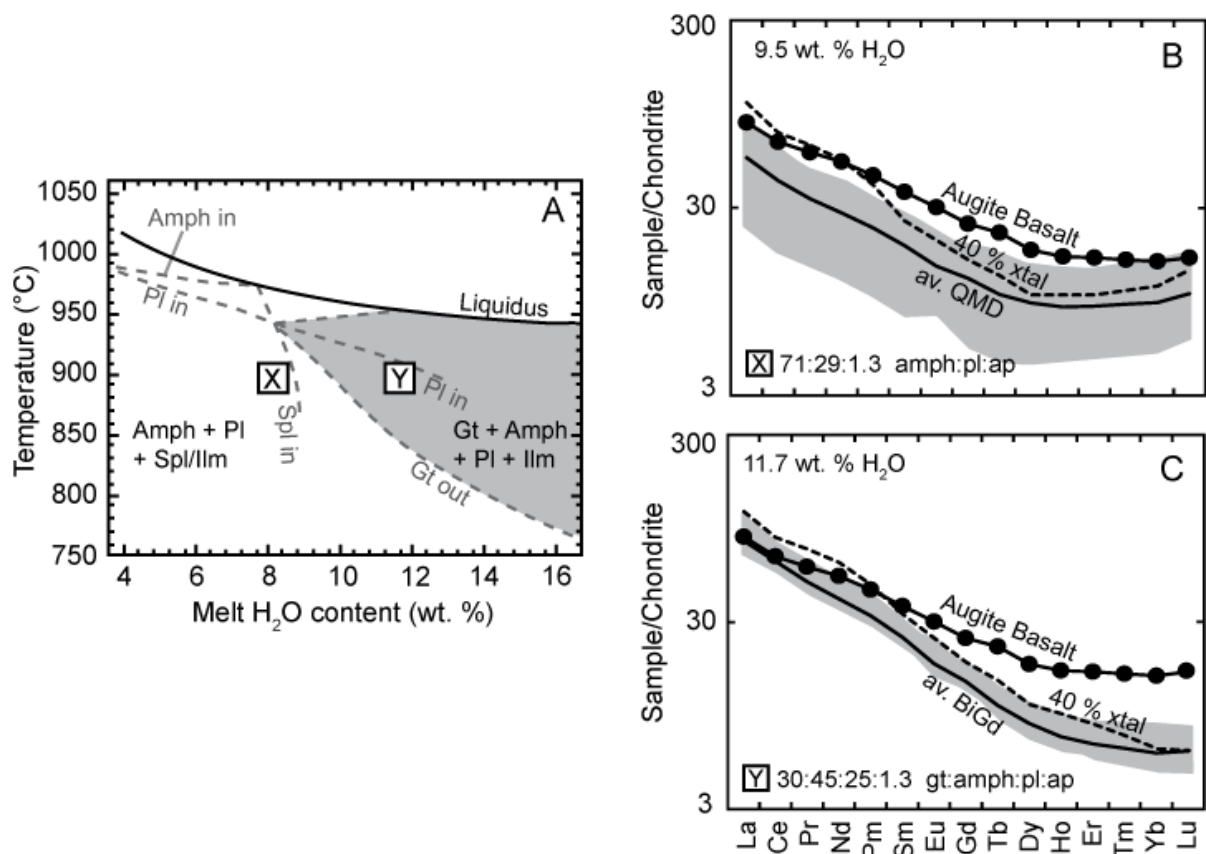


Figure 7.3. a) Andesitic phase relations at 0.8 GPa as a function of temperature and melt H<sub>2</sub>O content, after Alonso-Perez et al. (2009). Garnet stability field is shaded gray. b,c) Comparison between average BiGd and QMD REE patterns, and model results of 40% fractional crystallization (dashed line) of an augite basalt starting composition at lower and higher H<sub>2</sub>O. Shaded fields represent the range of REE patterns at Oyu Tolgoi.

explain the observed geochemical signatures at a variety of porphyry Cu deposits, including Oyu Tolgoi.

#### 7.2.1.1 H<sub>2</sub>O-induced garnet fractionation

As well as being stable at high pressures, recent experimental studies have showed that garnet is a stable igneous phase at lower pressures (0.8 GPa, ~24 km) in very hydrous magmas (Fig. 7.3; Alonso-Perez et al., 2009). At 0.8 GPa, the minimum H<sub>2</sub>O content at which garnet becomes stable increases with decreasing temperature and, at 900°C, garnet is stable in melts >9.5 wt. % H<sub>2</sub>O. In order to investigate the effect of H<sub>2</sub>O-induced garnet crystallisation,

Rayleigh fractionation models were constructed, modelling the fractionation of an augite basalt starting composition using the phase proportions reported by Alonso-Perez et al. (2009) under isothermal, isobaric conditions (900°C; 0.8 GPa) at high  $H_2O_{\text{melt}}$  (11.7 wt. %, 30:45:25 gt:amph:pl) and lower  $H_2O$  melt (9.5 wt. %, 71:29 amph:pl). Partition coefficients are presented in Table 1.1. Although Alonso-Perez et al. (2009) did not record the presence of apatite in their experiments, 1.3 vol. % apatite is included in both models. This is to reflect the decrease in  $P_2O_5$  with  $SiO_2$  in the BiGd, QMD, and Dvs rocks, and is calculated by backward extrapolation of the  $SiO_2$  vs  $P_2O_5$  fractionation trend (Fig. 7.4). Where this line intersects the tie line between apatite (42 wt. %  $P_2O_5$ , 0 wt. %  $SiO_2$ ) and hornblende (0 wt. %  $P_2O_5$ ; ~50 wt. %  $SiO_2$ ), the lever rule was used to determine the fractions of both phases.

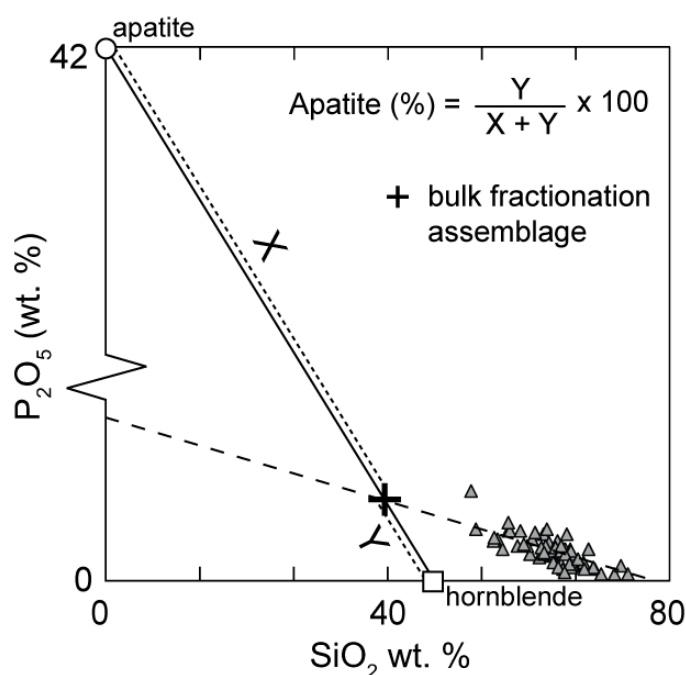


Figure 7.4.  $SiO_2$  vs  $P_2O_5$  for Oyu Tolgoi rocks. The proportion of apatite used in the Raleigh fractionation models was determined by using the lever rule on the tie line between pure apatite and pure hornblende, with the fulcrum of the lever where the tie line intersects the backward-extrapolated fractionation trend (marked with a cross).

The lower  $H_2O$  models show MREE depletion typical of amphibole fractionation, and are similar to the REE patterns of the QMD and Dvs. The higher  $H_2O$  models have HREE depletion indicative of garnet fractionation and they reproduce the key geochemical characteristics of the BiGd (Fig. 7.3 b,c). These results suggest that the BiGd could have formed by isobaric fractionation of a common augite basalt parental magma, but at higher  $H_{2O_{melt}}$  than the QMD. The presence of abundant relict biotite and amphibole phenocrysts in both QMD and BiGd rocks suggests hydrous magmatic conditions throughout the latter stages of magmatic evolution. Based on these models,  $H_2O$  contents would have had to exceed  $\sim 10$  wt.% for garnet to crystallize during the evolution of the BiGd. Switches in REE geochemistry at Cerro Llullaillaco and Cerro Escorial can also be reproduced by modelling the isobaric fractionation of a common parent melt at different  $H_{2O_{melt}}$  (Fig. 7.5).

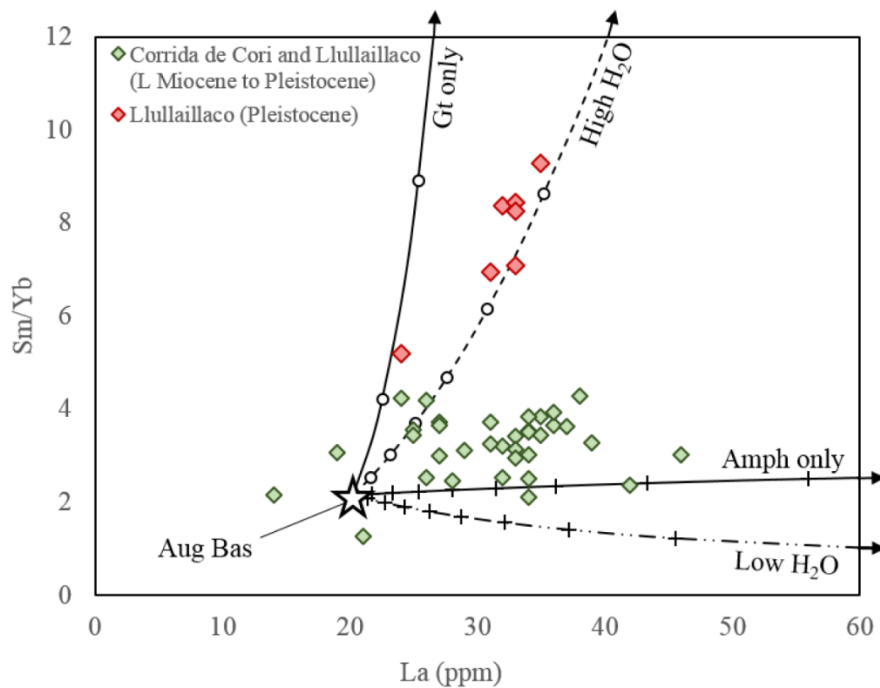


Figure 7.5. Comparison between modelled fractionation paths from this study (dotted and dashed lines), and selected Tertiary volcanic rocks of Central Chile (data from Richards and Villeneuve, 2001; 2002). Green diamonds are the Late Miocene to Pleistocene rocks of the Corrida de Cori, including Late Miocene rocks from Cerro Llullaillaco. Red diamonds are the Pleistocene rocks from Cerro Llullaillaco.

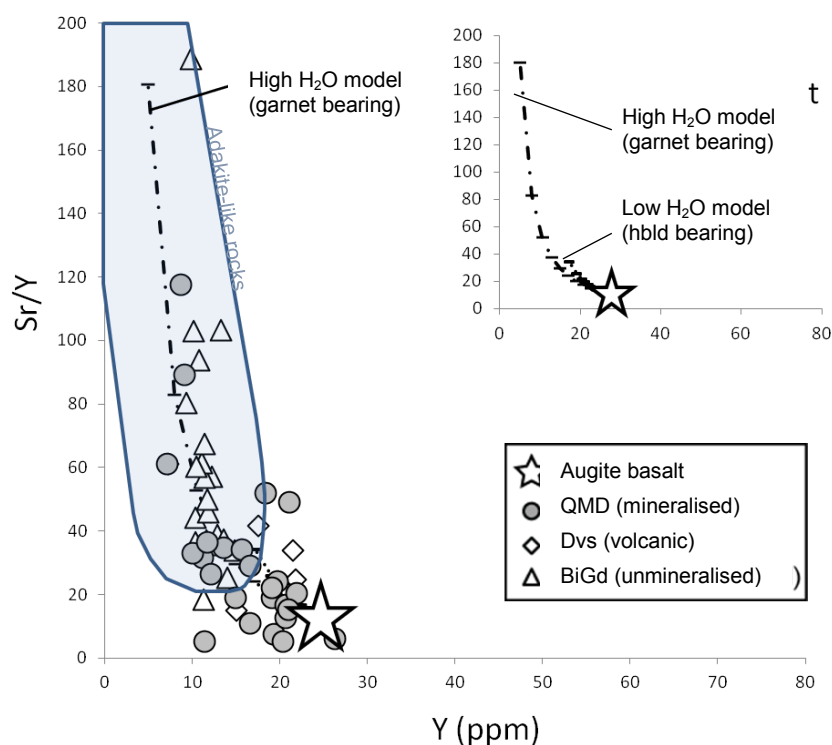


Figure 7.6. Comparison between modelled fractionation paths from this study (dotted and dashed lines), and selected rocks from Oyu Tolgoi, in Sr/Y vs Y space. The field of ‘adakite-like rocks’ (Richards and Kerrich, 2007) is marked on, High H<sub>2</sub>O (garnet bearing)

The high Sr/Y values of the BiGd (mostly > 40) and the lower Sr/Y ratios of the QMD and Dvs (mostly < 40) are also replicated by the high H<sub>2</sub>O (garnet bearing) and low H<sub>2</sub>O (garnet absent) models respectively (Fig. 7.6).

#### 7.2.1.2 Implications for the generation of Sr/Y and La/Yb ratios

It is widely held that Sr/Y and La/Yb ratios are controlled by the fractionation of amphibole ± garnet, and the suppression of plagioclase (e.g. Richards, 2011). The results presented in section 7.2.1.1 highlight three important points about the generation of these signatures. The first point is that although Sr/Y and La/Yb are thought to be generated under conditions where plagioclase is suppressed, there is no necessity for plagioclase fractionation to be stopped entirely. Both the low and high H<sub>2</sub>O models contain significant plagioclase as a

percentage of the fractionating assemblage (29 and 25 vol. % respectively), and both still generate increasing Sr/Y and La/Yb with fractionation.

The second point is that garnet exerts a stronger influence on Sr/Y and La/Yb than amphibole does because, compared to hornblende, garnet has higher and lower  $K_{DS}$  for Y, Kb and Sr, La respectively (Table 1.1). Indeed, the models suggest that to reach  $Sr/Y > 40$ , and  $La/Yb > 20$ , the fractionation of garnet is *required*, as hornblende or clinopyroxene fractionation alone are not sufficient (Figs. 7.2 and 7.6).

The third point is that the onset of cryptic garnet signatures may be induced by increasing magmatic  $H_2O$  to extremely high values, a process already considered to be important in the generation of large porphyry systems (e.g. Richards, 2011). The coincidence between the onset of cryptic garnet signatures and periods of mineralisation may be significant in this regard.

#### *7.2.1.3 Episodic $H_2O$ influx as a trigger for ore formation*

One mechanism for achieving high magmatic  $H_2O$  content is repeated cycles of fractionation of anhydrous silicate phases and replenishment by hydrous magmas in lower crustal sills trapped in compressive tectonic regimes. This process has been proposed to generate magmas with up to 8 wt.%  $H_2O$  over  $\sim 7$  My (Rohrlach and Loucks, 2005). However, the narrow spatial and temporal distribution of cryptic garnet signatures in volcanic rocks and in porphyry systems imply that high water contents are controlled by more localised processes.

Small-scale, along-arc variability in magmatic volatile contents have been observed in modern settings (Parman et al., 2011), which may be due to heterogeneous flux of volatiles from tears or other localised features on the subducting slab (Miller et al., 2006). Thus, it is suggested that spatially and temporally restricted garnet fractionation is related to locally



enhanced volatile flux from the subducting slab which generated unusually hydrous magmatic systems in the overlying arc segment.

The subduction of aseismic ridges and seamounts with high degrees of serpentinization provides an enriched source of H<sub>2</sub>O for arc magmas and could even trigger slab melting (e.g. Richards and Holm, 2013). Subduction of such sea floor anomalies can also generate the compressive tectonic conditions that favour storage and fractionation of magmas in the crust. A temporal link between this process and the formation of Tertiary porphyry deposits has been noted (e.g. Hollings et al., 2005) but the nature of the links to ore formation have remained speculative. Subduction of blocks of anomalously hydrous oceanic crust could lead to elevated volatile flux through the arc, thereby producing magmas that are transiently unusually H<sub>2</sub>O-rich. In turn, this could lead to the crystallization of hornblende, and ultimately garnet, in their crustal transit. Such progressions are broadly coincident with porphyry mineralization not only at Oyu Tolgoi, but also in other large porphyry systems, including the Cenozoic deposits of the Chilean Andes. In this region, mineralization has been linked to the subduction of the Juan Fernandez Ridge. This is only a ~50 km wide anomaly so the compression and water injection that could be associated with its subduction would be restricted to a limited section of the arc (Dominguez et al., 1998). Ridge subduction has been mildly oblique since 12 Ma, and the locus of ridge subduction has migrated south ~23 km Ma<sup>-1</sup> (Yáñez et al., 2002), meaning it would influence a particular section of the arc for only 2-3 Ma. Thus, the subduction of seafloor anomalies provides an appropriate tectono-magmatic framework to explain rapid magmatic H<sub>2</sub>O increases (and concomitant changes in geochemistry) in narrow arc sections.

## 7.2.2 Utility of whole rock geochemistry for porphyry exploration

The following questions, previously laid out in Chapter 1, must be considered when assessing the utility of whole rock indicators of fertility:

- How are fertility signatures affected by hydrothermal alteration?
- How unique are the signatures? i.e. do they only occur in porphyry systems?
- How well, if at all, do they distinguish low from high grade deposits?

### *7.2.2.1 Robustness of whole rock signatures*

In Chapters 3 and 4, a relationship is demonstrated between feldspar-destructive hydrothermal alteration (quantified by the alteration index), and low whole rock values for Sr/Y in rocks from Resolution and Oyu Tolgoi. This is due to the destruction of feldspar, and the fluid mobility of Sr. This relationship appears to be a common phenomenon, being observed in many other porphyry systems. (Fig. 7.7 a). However, Eu/Eu\* and La/Yb are largely independent of alteration intensity (Fig. 7.7 b,d), a factor which is likely due to the occupancy of REE in more robust accessory mineral phases (e.g. monazite, titanite, apatite).

Exceptionally high V/Sc values of porphyry rocks from both Oyu Tolgoi and Resolution are puzzling, because they are not only in excess of the barren reference suite data (Figs. 3.21 e and 4.29 e), but also well in excess of the data for other “fertile” rocks. V/Sc do not show a clear variation with alteration index in the fertile reference suite (Fig. 7.7 c), which is unsurprising given that neither V nor Sc are hosted in feldspar, the destruction of which the alteration index most appropriately measures.

Isocon analysis of rocks from Resolution, where V values are higher than typical arc rocks for a given SiO<sub>2</sub> show V depletion in potassic alteration and V enrichment in sericitic alteration (Fig. 3.24). Sc shows little change in both cases. This accords with the fact that V/Sc

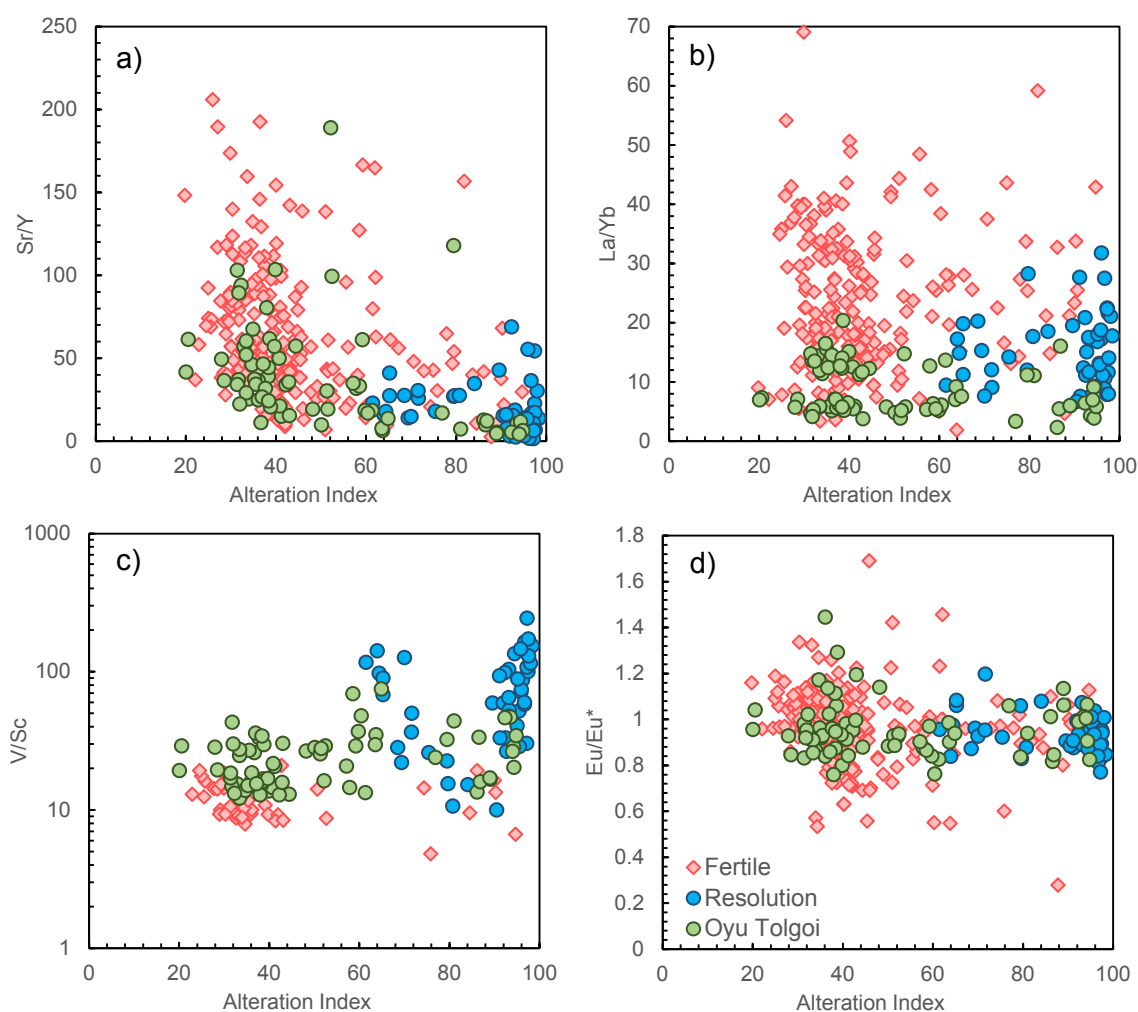


Figure 7.7. Variation of alteration index with a) Sr/Y, b) La/Yb, c) V/Sc, and d) Eu/Eu\* for rocks from the fertile dataset, and Oyu Tolgoi (QMD) and Resolution porphyry intrusion samples from this study. Note the logarithmic scale in c). The origin of the 'fertile' dataset is outlined in Chapter 1.

values are much higher in sericitically-altered rocks than in potassically-altered rocks here, although the latter are still exceptionally high.

Isocon analysis of rocks from Oyu Tolgoi show only strong depletion in V in both sericitic and potassic alteration (Fig. 4.32), which does not square with the observed high V/Sc. Given the apparent mobility of V, it is considered likely that V/Sc is affected by the hydrothermal alteration. However, the magnitude and mechanism of this effect remains unclear.

It should be noted that the least altered rocks studied herein from Oyu Tolgoi (BiGd, Dvs) and Resolution (Schultze Granite) have the lowest V/Sc ratios, which more closely match the V/Sc ratios of rocks from the fertile reference suite.

#### *7.2.2.2 Uniqueness of whole rock signatures*

Given that high Sr/Y, and La/Yb may be largely controlled by the fractionation of (or equilibration with) garnet, it is possible for these signatures to be generated in volcanic arc segments which are not prospective from an exploration standpoint. This is reinforced by the presence of such signatures associated with volcanic and intrusive rocks which are ostensibly unrelated to porphyry mineralisation, such as the Cerro Llullaillaco and Cerro Abra Grande volcanic rocks from the modern High Andes (Fig. 7.8 a,b). These volcanic centres also plot within the fertile region for V/Sc and Eu/Eu\* (Fig. 7.8 c,d). These rocks are interpreted to be derived from magmas which were in equilibrium with garnet in the deep crust (Richards and Villeneuve, 2001; Richards et al., 2006).

Deep crustal fractionation may be a pre-requisite for the generation of fertile magmas but alone it is not sufficient. After these magmas have been generated in the deep crust, a whole range of other processes are required to produce a porphyry system, including (but not limited to) the timing of sulphide saturation, an appropriate tectonomagmatic framework, effective fluid focussing, receptive host rock chemistry, and the absence of extensive volcanic activity (Richards 2003; Sillitoe, 2010; Wilkinson, 2013; Richards, 2013). Consequently, it is likely that the intrusive or extrusive products of some magmatic centres may share certain unusual geochemical signatures with porphyry systems, but be unrelated to mineralisation. These results therefore highlight the potential for false positives in using these signatures in exploration.

The overlap between the barren and fertile fields in all of the whole rock parameters discussed is highest in low silica rocks, meaning that these signatures are not very effective discriminators for  $\text{SiO}_2$  values  $< 55$  wt. % (Fig. 7.8). Uniquely high values of these parameters only occur at silica contents greater than this value. In particular, there is a large degree of overlap between barren and fertile data in terms of  $\text{Eu}/\text{Eu}^*$  (Fig. 7.8 d), making this parameter less useful in distinguishing fertile and barren systems.

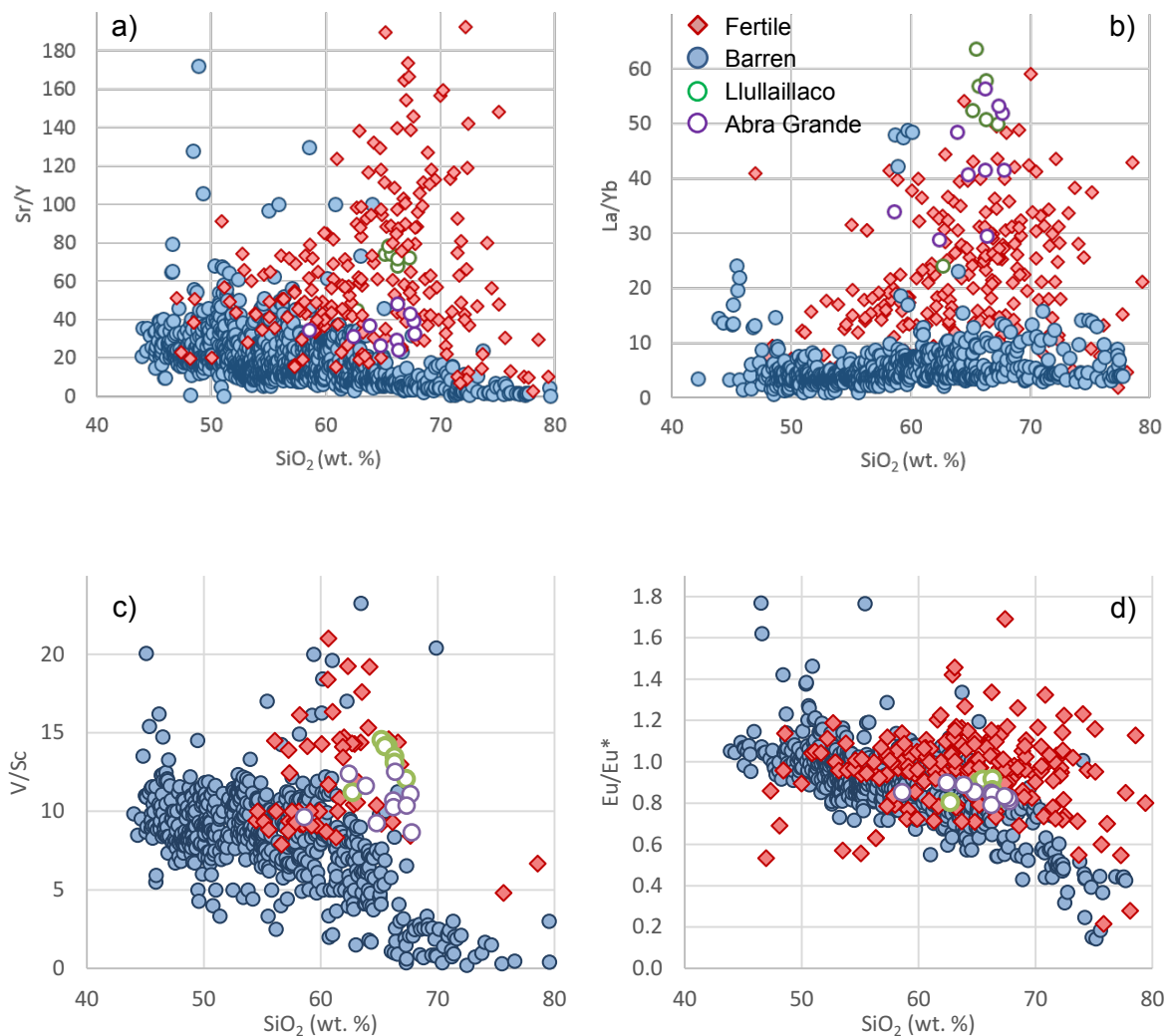


Figure 7.8. A comparison between barren and fertile reference suites with two Tertiary volcanic centres in northern Chile (Llullaillaco and Abra Grande), in terms of a)  $\text{Sr}/\text{Y}$ , b)  $\text{La}/\text{Yb}$ , c)  $\text{V}/\text{Sc}$ , and d)  $\text{Eu}/\text{Eu}^*$ . See text for discussion. Data from Richards and Villeneuve (2001) and Richards et al. (2006).

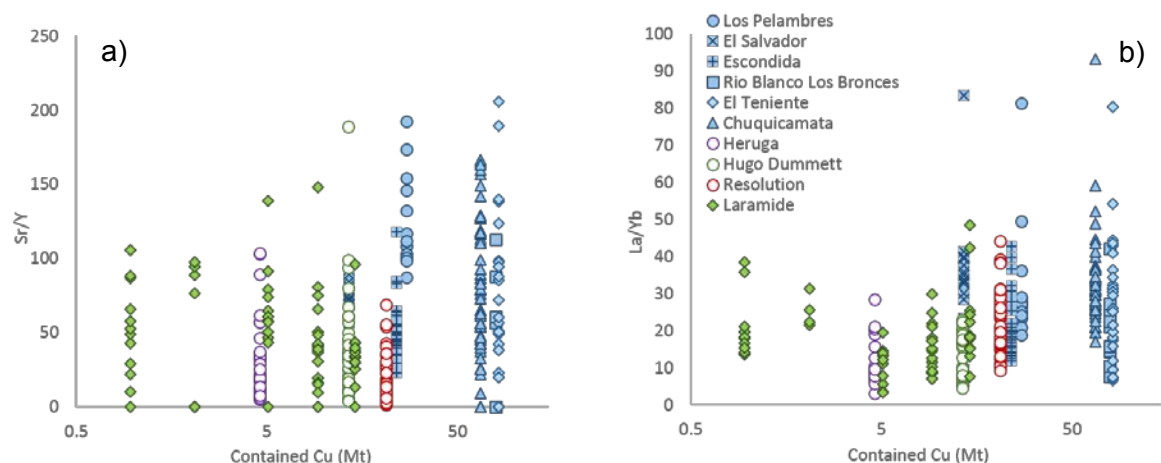


Figure 7.9. Variability of whole rock a) Sr/Y and b) La/Yb ratios with respect to contained Cu content of the deposit from which they were derived. Note that V/Sc is not plotted due to lack of available V data.

#### 7.2.2.3 Distinguishing deposit size with whole rock indicators of fertility

The whole rock Sr/Y and La/Yb ratio of these rocks also appear to be independent of deposit size (in terms of contained Cu; Fig. 7.9). It is difficult to assess the deposit size sensitivity for V/Sc due to the lack of available data.

#### 7.2.2.4 Criteria for distinguishing fertile and barren systems

Based on the above discussion, the following criteria for distinguishing between barren and fertile porphyry rocks is proposed. The Sr/Y and La/Yb values of 20 which were used by other authors to distinguish ‘adakite-like’ rocks from typical arc rocks (e.g. Richards and Kerrich, 2007) are also used here to distinguish fertile from barren rocks. This is because the processes associated with increased magmatic fertility overlap with those that generate adakite-like rocks (e.g. Richards, 2012; Chiaradia et al., 2012; Loucks, 2014). In addition, V/Sc values of >12 are able to describe most of the porphyry Cu-related whole rock data.

As Eu/Eu\* is a weak indicator of magmatic fertility, no single threshold criterion is applied. Instead, a range of values (0.8 to 1.2) is suggested, between which lies the majority

of data from fertile systems from this study, and from the published literature (Fig. 7.8 d). This parameter should not be considered on its own, due to the potential for false positives, and must always be used in conjunction with other fertility indicators.

### **7.3 Zircon – a robust and reliable indicator of magmatic fertility?**

#### **7.3.1 Utility of zircon geochemistry for porphyry exploration**

In the following section, data from this study and from the published literature are combined to determine which geochemical signatures can be useful for distinguishing fertile and barren systems based on zircon chemistry. Recommendations are then made on the relative merits of the discriminatory parameters and the general fitness of zircon as a mineral indicator, based on the categories outlined in Section 1.4, is considered. The specific processes which form fertility signatures are discussed, and the length and timescales of these processes are described. A summary of the utility of zircon as a mineral indicator of porphyry fertility is found in Table 7.5.

##### *7.3.1.1 Robustness of zircon signatures*

Zircon is extremely resilient not only to high temperature re-equilibration in the igneous environment (see section 5.1), but also in rocks that have been altered. In this study, unaltered zircons were extracted from rocks which had undergone extensive hydrolytic alteration. This extreme robustness has both positive and negative aspects in the assessment of fertility. On the positive side, igneous signatures are preserved through an extensive history of hydrothermal and, potentially, tectonic and erosional processes, which makes zircon an ideal target mineral for studies of detrital minerals.

The robustness of zircon can also have drawbacks when considering fertility signatures. For example, several generations of zircon may exist in a rock, some of which

relate to the period of mineralisation, and some which are unrelated. Examples of this include the ubiquitous presence of Proterozoic cores in zircons from Resolution. In this case, it is possible to distinguish the unrelated and related populations based on the Th/Pb and U/Pb ratios of the zircons (Fig. 5.23 b), although more time-consuming U-Pb dating may be necessary if the two zircon populations are closer in age. Thus, indiscriminate analysis of zircon from a given rock could lead to a diluted signature, mixed, or completely misleading signature. As a result, it is recommended that textural analysis is conducted during zircon analysis to interpret the nature of the chemistry of different zones, and statistical analysis of the data be undertaken to distinguish discrete populations.

#### *7.3.1.2 Uniqueness of zircon signatures*

Given the likelihood that Eu/Eu\* values may be affected by the co-crystallisation of other mineral phases, especially titanite (Fig. 5.33), it would appear that high Eu/Eu\* values are not necessarily indicative of oxidised (assumed fertile) conditions in the magma. Titanite is extremely common in unaltered rocks associated with porphyry systems, but is also a common phase in oxidised intermediate I-type barren granitoids, which raises the possibility of false positives when using Eu/Eu\*. Ce/Ce\* is unlikely to be affected by titanite co-crystallisation (section 5.6.3), so high values of this parameter are likely to reflect oxidised conditions, and may be considered an unequivocal proxy for elevated  $fO_2$ .

#### *7.3.1.3 Distinguishing deposit size with zircon indicators of fertility*

The magnitude of the Eu and Ce anomalies in zircon appears to be independent of deposit size or grade, and these parameters can also display a very wide range within individual systems. For example, at Oyu Tolgoi, there is no significant distinction between zircons from Hugo Dummett (high Cu grade and tonnage), and Heruga (lower Cu grade and tonnage; Fig. 5.13). It is worth noting that both systems are hosted in the same rocks and formed during the same magmatic epoch, i.e. broadly under the same geodynamic conditions



and probably derived from the same or similar magma source. Thus, the divergent grade and size of these deposits is unlikely to be due to deep crustal igneous processes, and may be due to other shallow crustal igneous or hydrothermal processes, including fluid chemistry and/or fluid focussing (Richards, 2013).

#### *7.3.1.4 Criteria for distinguishing fertile and barren systems*

Several problems are associated with using  $\text{Eu}/\text{Eu}^*$ ,  $\text{Ce}/\text{Ce}^*$ , and  $\text{Ce}^{4+}/\text{Ce}^{3+}$  as accurate measures of magma redox state in natural systems (Section 5.6). Nonetheless, an empirical relationship between fertile porphyry systems and the occurrence of zircons with higher than average values for these parameters has been recognised in several studies (Table 5.7). Accordingly, zircon may still be a useful indicator of fertility.

Table 7.2 outlines the percentile values of the barren and fertile data for  $\text{Eu}/\text{Eu}^*$  and  $\text{Ce}/\text{Ce}^*$ . 80% of zircons from the barren dataset have  $\text{Eu}/\text{Eu}^* < 0.5$ , whereas almost 80% of the zircons from the fertile dataset are in excess of this value. Thus,  $\text{Eu}/\text{Eu}^*$  of 0.5 is a reasonable criterion for distinction between fertile and barren systems. Similarly, 82% of the barren dataset have  $\text{Ce}/\text{Ce}^*$  values  $< 50$ , whereas 75% of the fertile dataset have values  $> 50$ . As a result, a  $\text{Ce}/\text{Ce}^*$  value of 50 is useful for distinguishing fertile from barren systems.

Insufficient  $\text{Ce}^{4+}/\text{Ce}^{3+}$  exist in the published literature (especially for barren systems, where this parameter is seldom considered) for a proper comparison between fertile and barren systems to be drawn. In addition,  $\text{Ce}^{4+}/\text{Ce}^{3+}$  is likely to be incorrectly estimated for rocks from porphyry systems, as it is calculated using whole rock REE concentration as a proxy for melt REE concentration; an assumption that is inappropriate in the very likely case that titanite has co-crystallised, or the whole rock sample is altered (Section 5.6.2). Accordingly,  $\text{Ce}^{4+}/\text{Ce}^{3+}$  is not considered a useful parameter for porphyry exploration, and  $\text{Ce}/\text{Ce}^*$  is likely to be a more appropriate measure of oxidation.

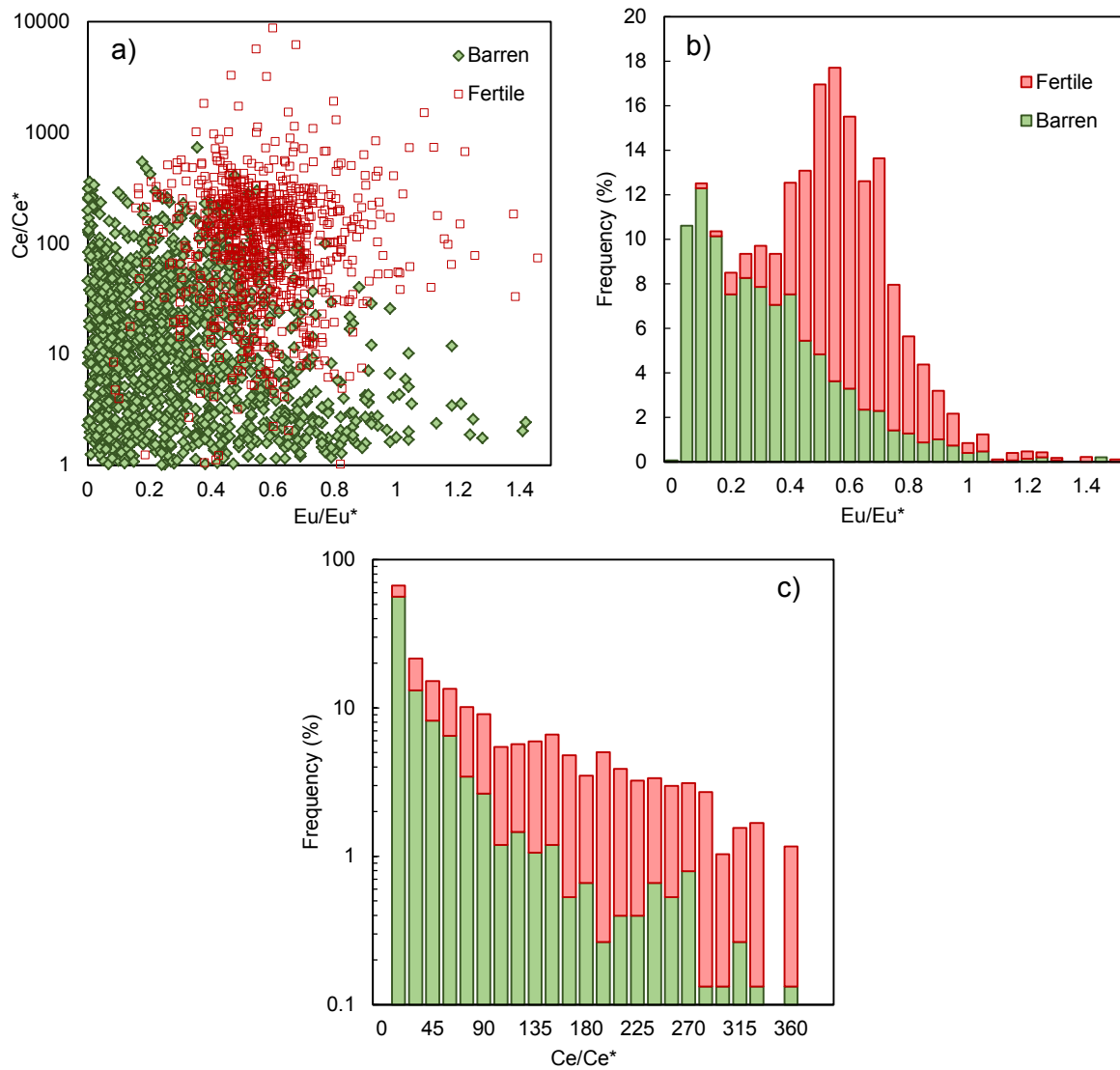


Figure 7.10. a)  $Ce/Ce^*$  vs.  $Eu/Eu^*$  values of zircons from barren and fertile rock suites. b-c) frequency distribution of the same data. Sources of barren data are: Ballard (2001) - Chuquicamata district (Pajonal diorite, Apolo leucogranite, central diorite, dark diorite, aplite, Equis monzodiorite, south granodiorite, Los Picos diorite, Fortuna Gris, Fortuna Clara, Fortuna Leucogranite, San Lorenzo porphyry, Montecristo intrusive, Elena granodiorite); Iizaku et al. (2010) - Various, detrital; Wang et al. (2013) - Various, China (DMC-1, FJZ-1, QTJ-2); Lu et al. (2016) - Various systems, global (Yellowstone, Bandelier, Bishop Tuff, Lucerne pluton – USA; Kadoona and Hawkins – Australia). Sources of fertile data are: Lee (2008) - El Salvador porphyry (A, K, R, X, and L ppy, latite, latite quartz porphyry, quartz porphyry); Munoz et al. (2012) - El Teniente (A porphyry, Sewell Stock, Central diorite, Northern diorite, Teniente porphyry, Late dacite dyke); Ballard (2001) - Chuquicamata (El Abra Mine porphyry, East porphyry, West porphyry, Bench porphyry, Radomiro Tomic minor facies porphyry, Opache Mine porphyry); Lu et al. (2016) - Various systems (Tampakan, Philippines; Batu Hijau, Indonesia; Jiama, Dexing, Qulong, Nannihu, Yuchiling – China; Sar Cheshmeh and Sungun – Iran); Wang et al. (2013) - Various, China (TLS01 FS07, WS02, TGS-7); Zhang et al (2013) – Dexing; This study - low-Ta zircons, (Oyu Tolgoi, Mongolia).

| Deposit               | Country   | Deposit type                         | n=             | Eu/Eu* |      |             | Ce/Ce* |      |           | Ce <sup>4+</sup> /Ce <sup>3+</sup> |      |           | Titanite present? | Reference                                   |
|-----------------------|-----------|--------------------------------------|----------------|--------|------|-------------|--------|------|-----------|------------------------------------|------|-----------|-------------------|---------------------------------------------|
|                       |           |                                      |                | Mean   | ± 1σ | min - max   | Mean   | ± 1σ | min - max | Mean                               | ± 1σ | min - max |                   |                                             |
| South America         |           |                                      |                |        |      |             |        |      |           |                                    |      |           |                   |                                             |
| El Salvador           | Chile     | Porphyry Cu (+ Mo)                   | 172            | 0.57   | 0.13 | 0.24 - 0.85 | 169    | 126  | 6 - 680   |                                    |      |           | Yes               | Lee (2008)                                  |
| El Teniente           | Chile     | Porphyry Cu-Mo                       | 37             | 0.52   | 0.09 | 0.17 - 0.64 | 54     | 52   | 5 - 177   | 432                                | 516  | 28 - 2718 | Yes               | Muñoz et al. (2012)<br>Rabbia et al. (2009) |
| Chuquicamata          | Chile     | Porphyry Cu-Mo                       | 79             | 0.47   | 0.12 | 0.17 - 0.95 | 235    | 172  | <1 - 1006 | 757                                | 526  | 40 - 2341 | Yes, inferred     | Ballard et al. (2002)                       |
| Bajo de la Alumbraera | Argentina | Porphyry Cu-Au                       | 529            | 0.56   | 0.05 | 0.11 - 0.73 | 241    | 128  | 19 - 1138 |                                    |      |           | Yes               | Buret et al. (2016)                         |
| Corocochuayco         | Peru      | Porphyry-skarn                       | 54             | 0.6    | 0.14 | 0.24 - 0.90 | 129    | 97   | 12 - 373  |                                    |      |           | Yes               | Chelle-Michou et al. (2014)                 |
| Asia                  |           |                                      |                |        |      |             |        |      |           |                                    |      |           |                   |                                             |
| Various               | China     | Porphyry Cu                          | 58             | 0.65   | 0.22 | 0.05 - 1.87 | 34     | 26   | 6 - 122   | 411                                | 462  | 36 - 2736 | Yes               | Wang et al. (2013)                          |
| Dexing                | China     |                                      | 22             | 0.43   | 0.07 | 0.29 - 0.56 |        |      |           | 127                                | 84   | 33 - 398  | Not rep.          | Zhang et al. (2013)                         |
| Yulong                | China     |                                      | 77             |        |      |             |        |      |           | 204                                | 19   | 5 - 756   | Not rep.          | Liang et al. (2006)                         |
| Zhanaga               | China     |                                      | 47             |        |      |             |        |      |           | 334                                | 36   | 26 - 729  | "                 | Liang et al. (2006)                         |
| Mangzong              | China     |                                      | 24             |        |      |             |        |      |           | 201                                | 52   | 18 - 1230 | "                 | Liang et al. (2006)                         |
| Duoxiasongduo         | China     |                                      | 47             |        |      |             |        |      |           | 250                                | 37   | 10 - 1314 | "                 | Liang et al. (2006)                         |
| Malasongduo           | China     |                                      | 38             |        |      |             |        |      |           | 258                                | 47   | 17 - 1304 | "                 | Liang et al. (2006)                         |
| CAOB porphyry         | Various   | Porphyry Cu (Au Mo)                  | 76             | 0.48   | 0.12 | 0.24 - 0.79 | 70     | 42   | 12 - 139  | 184                                | 119  | 28 - 592  | N/A               | Shen et al. (2015)                          |
| Oyu Tolgoi            | Mongolia  | Porphyry Cu-Au                       | Low-Ta<br>117  | 0.84   | 0.31 | 0.46 - 2.62 | 322    | 516  | 15 - 3252 | 1435                               | 1300 | 62 - 8330 | Yes               | This study                                  |
|                       | Mongolia  | Porphyry Cu-Au                       | High-Ta<br>343 | 0.43   | 0.09 | 0.02 - 0.77 | 173    | 217  | 5 - 2140  | 365                                | 572  | 13 - 7578 | No                | This study                                  |
|                       | Mongolia  | Post-mineralisation (BiGd)           | High-Ta<br>29  | 0.48   | 0.22 | 0.02 - 0.77 | 170    | 204  | 7 - 725   | 372                                | 358  | 13 - 1482 | No                | This study                                  |
|                       | Mongolia  | Coeval unmineralised volcanics (Dvs) | High-Ta<br>32  | 0.46   | 0.16 | 0.3 - 0.95  | 164    | 302  | 15 - 1294 | 193                                | 148  | 26 - 583  | No                | This study                                  |
| Barren                |           |                                      |                |        |      |             |        |      |           |                                    |      |           |                   |                                             |
| Detrital zircons      | Global    | Barren (detrital)                    | 1015           | 0.37   | 0.3  | 0.01 - 3.14 | 22     | 40   | <1 - 475  |                                    |      |           | Unknown           | Iizaku et al. (2010)                        |
| GEOROC                | Global    | Barren (literature)                  | 492            | 0.30   | 0.24 |             | 157    |      |           |                                    |      |           | Unknown           | GEOROC                                      |
| Yulong                | China     | Non-ore producing                    | 68             |        |      |             |        |      |           | 101                                | 30   | 28 - 112  | Not rep.          | Liang et al. (2006)                         |
| Various               | China     | Barren (adakites)                    | 39             | 0.44   | 0.09 | 0.31 - 0.61 |        |      |           | 84                                 | 76   | 16 - 371  | Not rep.          | Wang et al. (2013)                          |
| Chuquicamata          | Chile     | Not ore associated                   | 131            | 0.29   | 0.13 | 0.05 - 0.72 | 50     | 84   | 2 - 728   | 122                                | 224  | 5 - 2205  | Yes, inferred     | Ballard et al. (2002)                       |

Table 7.1 Mean values of Eu/Eu\*, Ce/Ce\* and Ce<sup>4+</sup>/Ce<sup>3+</sup> for zircons from barren and fertile rocks. Data drawn from a range of literature sources. Titanite is common (although not ubiquitous) in intrusions associated with porphyry systems. "Not rep." = not reported in original study. Barren data also derived from the GEOROC database, filtered to remove analyses from porphyry systems (<http://georoc.mpch-mainz.gwdg.de/>).

| Percentile                | Eu/Eu* |         | Ce/Ce* |         |
|---------------------------|--------|---------|--------|---------|
|                           | Barren | Fertile | Barren | Fertile |
| <i>n</i> =                | 1497   | 923     | 1311   | 856     |
| 10 <sup>th</sup>          | 0.05   | 0.39    | 1.69   | 15.6    |
| 20 <sup>th</sup>          | 0.09   | 0.46    | 2.46   | 35.1    |
| 50 <sup>th</sup> (median) | 0.26   | 0.57    | 9.66   | 123     |
| 80 <sup>th</sup>          | 0.49   | 0.71    | 45.2   | 252     |
| 90 <sup>th</sup>          | 0.65   | 0.81    | 82.9   | 370     |

Table 7.2. Table showing the percentile values (10<sup>th</sup>, 20<sup>th</sup>, 50<sup>th</sup>, 80<sup>th</sup>, 90<sup>th</sup>) for zircon Eu/Eu\* and Ce/Ce\* values from fertile and barren systems. Data sources as in Table 7.1

## 7.4 Apatite – sensitive to shallow hydrothermal processes?

### 7.4.1 Fertility indicators in hydrothermal apatite

One key aim of this study was to determine if it is possible to distinguish low- and high-grade porphyry systems on the basis of the chemistry of hydrothermal or igneous minerals. The most fruitful result in this regard is the observation that extremely high Mn (and Fe) contents are found in hydrothermal apatites from rocks with high Cu content from Hugo Dummett compared to Heruga (see section 6.7.3). This section contains further consideration of this result in order to address the following points:

- a) If high Mn and Fe are a feature of hydrothermal apatites from high-grade porphyry systems, it is important to demonstrate that they may be distinguished geochemically from other apatites (igneous or hydrothermal) with similarly high Mn and Fe that are unrelated related to mineralisation. This is important in exploration, as apatites from stream sediments (i.e. heavy mineral concentrates) lack textural context, and must be distinguishable geochemically.
- b) If these geochemical signatures are only observed at Oyu Tolgoi, or if they are common to high-grade porphyry systems worldwide.

#### 7.4.1.1 Distinguishing high-grade porphyry-hydrothermal apatite from other Mn- and Fe-rich apatite

Although igneous apatites from intermediate I-type rocks typically have low Mn and Fe contents (<1500 and <1300 ppm respectively; Table 6.3), S-type and felsic I-type granitoids may also have contain high Mn apatite, up to 2 wt. %. The Mn and Fe content of igneous apatites from S-type and felsic I-type granites increase with increasing whole rock SiO<sub>2</sub> content

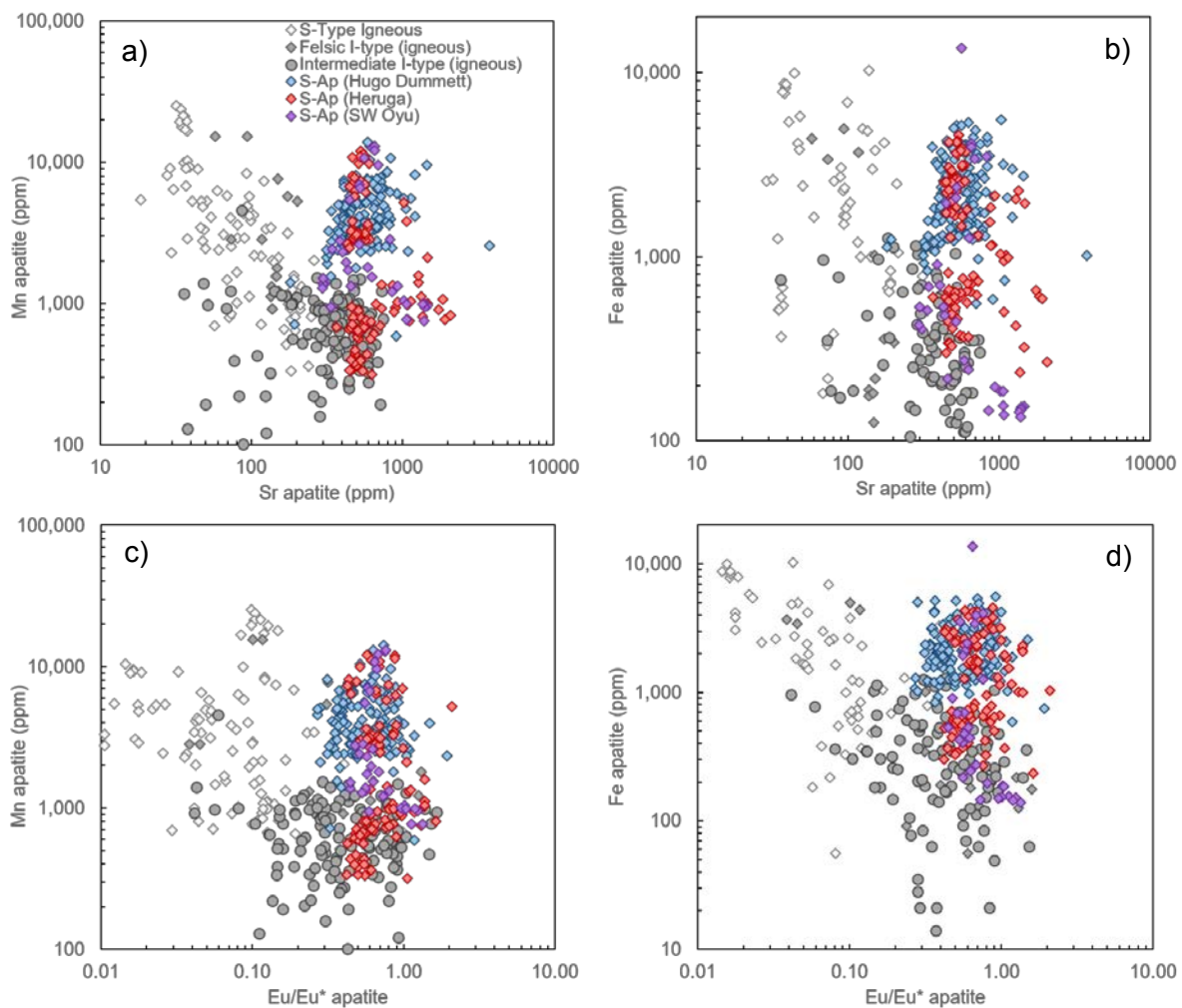


Figure 7.11. Variation of Mn with a) Sr, and c) Eu/Eu\*, and Fe with b) Sr and d) Eu/Eu\* for Oyu Tolgoi S-Ap (hydrothermal apatite) compared with literature data for igneous apatite from S- and I-type granitoids. High Mn and Fe values are common to both igneous apatites from S-type granites, and hydrothermal apatites from primarily Hugo Dummett. However, they may be distinguished on the basis of their Sr content and Eu/Eu\* values.

(Sha and Chappell, 1999). Conversely, the Sr content decreases with increasing  $\text{SiO}_2$ , mirroring the decrease in Sr of the rocks (Fig. 6.1). Consequently, igneous apatites from peraluminous rocks show trends of increasing Mn and Fe with decreasing apatite Sr content (e.g. Belousova et al., 2002a). The low-Sr content of apatites from S-type granites is inherited from the source rocks, which are typically Sr-deficient. This in turn is thought to be inherited from the sedimentary protolith of S-type granites, which has Sr removed by weathering (see Sha and Chappell, 1999). Another distinguishing feature of apatites from S-type felsic rocks is their

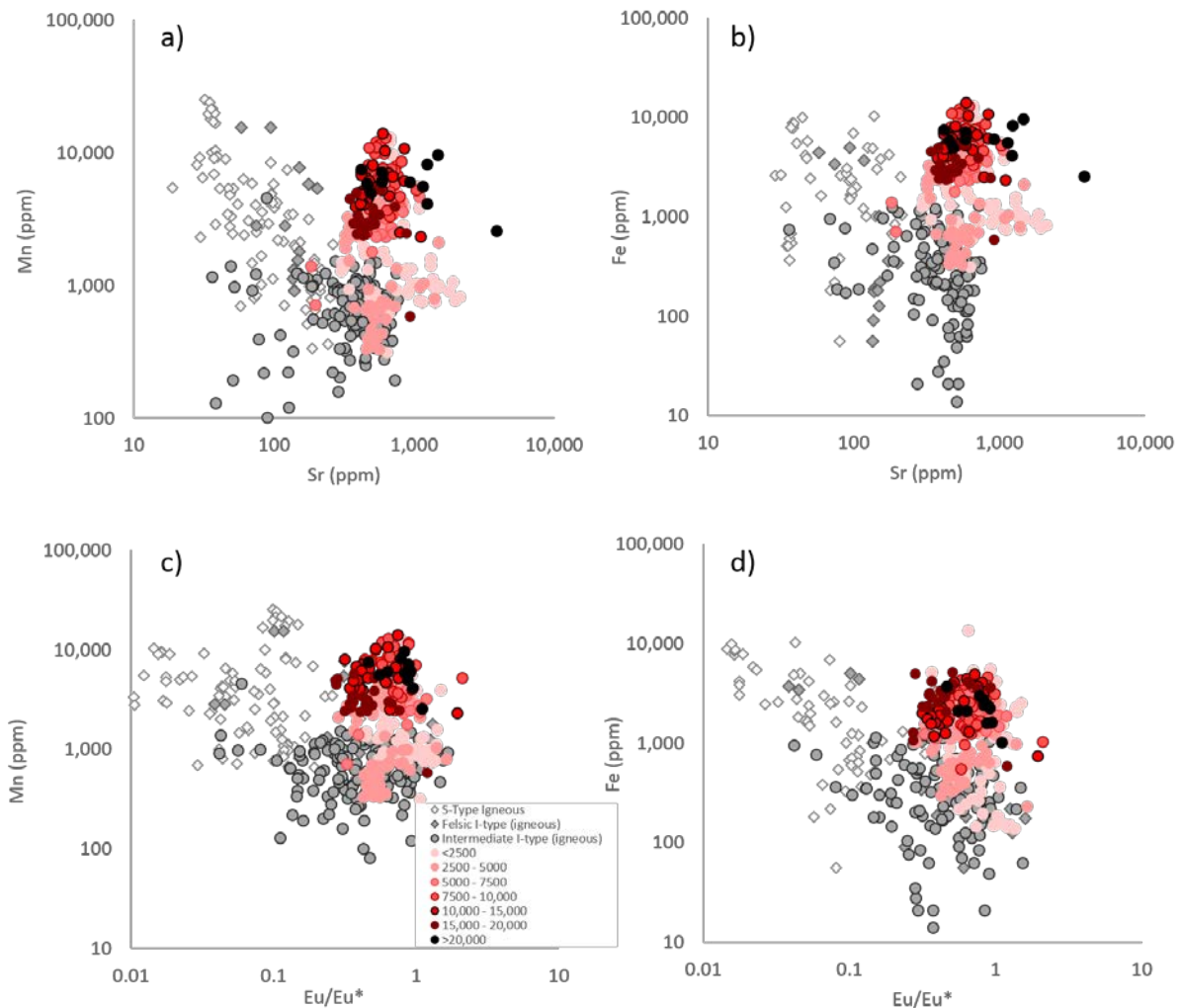


Figure 7.12. Same as Figure 7.11, with Oyu Tolgoi data now binned in terms of the Cu content of the rock from which they were derived. Dark colours indicate higher Cu contents. Legend showing limits of each bin is provided in c), with whole rock Cu values in ppm.

strong negative Eu anomaly (i.e. low Eu/Eu\*) which can frequently extend below 0.1.

By contrast, hydrothermal apatites from Oyu Tolgoi with high Mn and Fe also have high Sr and Eu/Eu\*, and may thus be easily distinguished from apatites from S-type granites on plots of Mn vs. Sr (or Eu/Eu\*). There exists some overlap between igneous I-type apatites and hydrothermal apatites from low-grade rocks, primarily those from Heruga on plots of Mn (or Fe) vs Eu/Eu\* (or Sr). However, all hydrothermal apatites from rocks with >0.75 wt. % Cu plot outside this field (Fig. 7.12).

#### *7.4.1.2 The Rio Tinto apatite dataset – Oyu Tolgoi and Resolution data*

A database of apatite analyses was provided by Rio Tinto Exploration (hereafter, the ‘RTX database’) which contains the major and trace element chemistry of apatites from several porphyry systems ranging in size and grade, as well as a number of ostensibly unmineralised stocks in the vicinity of large porphyry systems. These data were analysed by LA-ICP-MS at the Rio Tinto laboratory in Bundoora, using the same methods as outlines in Chapter 2. Apatite data from the following porphyry systems will be discussed here: La Granja (Peru), Zaldivar, Chuquicamata, El Teniente, El Abra (Chile), and Bingham Canyon (Utah, USA). Also included in this database are analyses of apatites from Resolution and Oyu Tolgoi. The latter provides an opportunity to test the extent to which geochemical relationships in Chapter 6 for apatites from Resolution and Oyu Tolgoi still apply when a larger dataset is considered.

The Oyu Tolgoi apatite analyses in the RTX database are from Heruga QMD (n = 287), Hugo Dummett QMD (97), and SW Oyu QMD (84), as well as samples of the BiGd (306) and Dvs (322). Chondrite normalised REE patterns of the RTX apatite data are very similar to those described in Chapter 6. Specifically, two main groups of data exist – patterns with LREE ≈ HREE (La/Yb ~1-2) with small negative Eu anomalies, and MREE-depleted patterns (La/Yb > 10). These correspond to the REE patterns of S-Ap and M-Ap respectively (Fig. 7.13). This

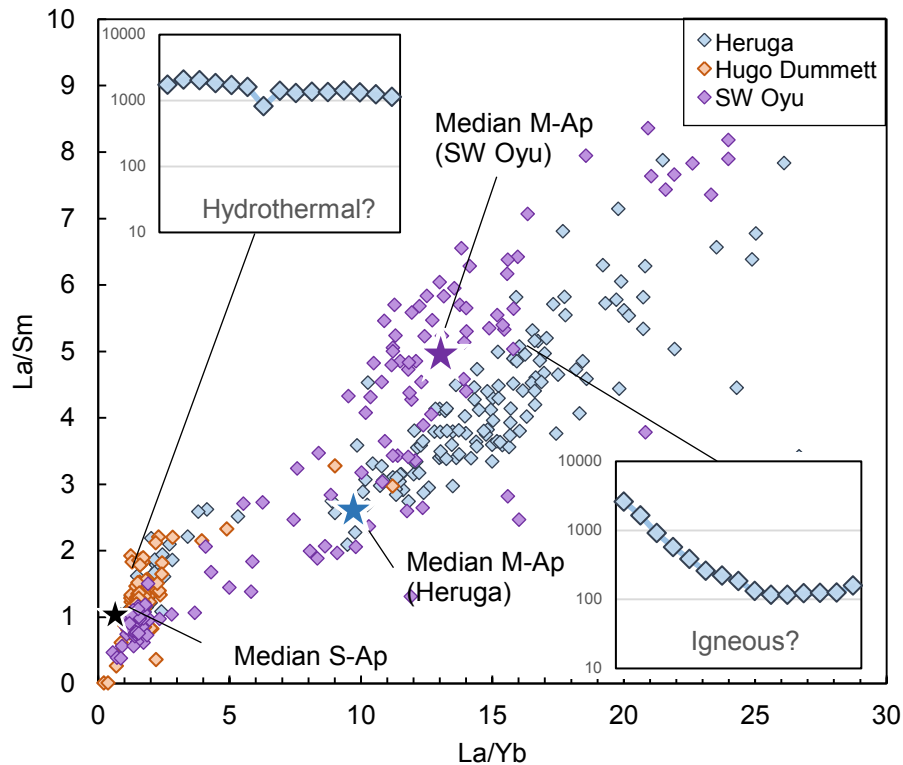


Figure 7.13.  $\text{La/Yb}$  and  $\text{La/Sm}$  apatite data from Oyu Tolgoi from the RTX database. Two main populations are seen: low  $\text{La/Yb}$  and  $\text{La/Sm}$  ('flat' REE patterns; top left inset), and high  $\text{La/Yb}$  and  $\text{La/Sm}$  (bottom right inset). These correspond to the S-Ap (hydrothermal; black star) and M-Ap (igneous; blue and purple stars) from this study. Thus, a  $\text{La/Yb}$  ratio of  $\sim 5$  may distinguish igneous and hydrothermal apatite at Oyu Tolgoi.

shows that, at least in the case of Oyu Tolgoi, it is possible to distinguish hydrothermal from igneous apatite purely on the basis of REE chemistry, and that a  $\text{La/Yb}$  ratio of  $> 5$  is typical of igneous apatite. In the majority of cases, only one type of apatite REE pattern is found in a given rock sample from the RTX dataset.

The S-Ap hydrothermal apatites are considered in this section. The vast majority of Hugo Dummett hydrothermal apatites from the RTX database lie between 2000 and 10,000 ppm Mn, and this strongly overlaps with the data presented in Chapter 6 (Fig. 7.14 b). More dispersion is seen in the hydrothermal apatite data from Heruga, with values as high as 10,000



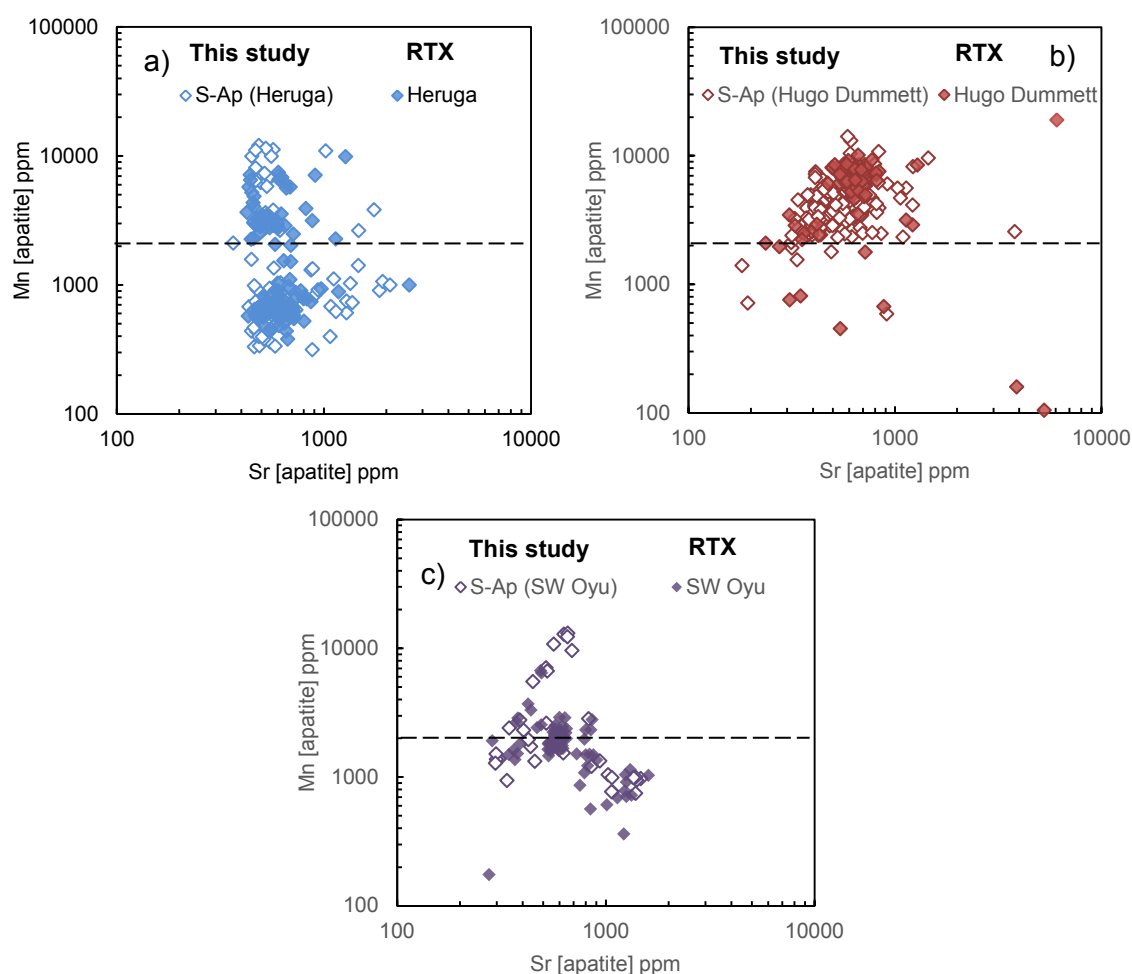


Figure 7.14. A comparison between the RTX apatite database and apatite data from this study. Plots of Mn and Sr are shown for apatites from a) Heruga, b) Hugo Dummett, and c) SW Oyu. There is a close accordance between the data from both studies, indicating that the results are likely to be representative and analytically reproducible. The horizontal dashed line represents 2000 ppm Mn; the vast majority of apatite analyses from Hugo Dummett have Mn concentrations greater than this value.

ppm Mn, but the majority of analyses are <2000 ppm (Fig. 7.14 a). SW Oyu apatites also have a mix of Mn values above and below 2000 ppm. The same is seen in the data for Fe.

In summary, Oyu Tolgoi apatites from the RTX database bear out the observations of Chapter 6, that hydrothermal and igneous apatites may be distinguished by their REE

geochemistry, and that hydrothermal apatites from Hugo Dummett are enriched in Mn and Fe to levels which are not commonly attained by Heruga hydrothermal apatite.

Resolution apatite analyses in the RTX database are from the QLP (124), RDP (36), diabase host rock (435) and the Kvs (Cretaceous volcanoclastic basin fill; 206). The distinction between hydrothermal and igneous apatite based on chondrite normalised REE patterns is less clear at Resolution. This is partly due to the difficulty in recognising truly igneous apatite in this system. Dominant-type apatite in the Resolution intrusions is most likely related to high temperature potassic alteration, and the vein- and dull-CL types are more unambiguously hydrothermal in origin (Table 6.5). Apatites from the felsic Apache Leap intrusion are inter-grown with calcite, so likely formed during some hydrothermal episode (possibly propylitic) although this could be unrelated to the hydrothermal system which generated mineralisation at Resolution. All of these hydrothermal apatites have La/Yb ratios  $<5$  (Table 6.6). The only clear igneous apatite is found in the unaltered, unmineralised Schultze Granite, but La/Yb apatite ratios are also  $<5$  and chondrite normalised REE patterns are similar to 'dominant-type' apatites from the Resolution deposit. The LREE concentration of apatite in these systems is controlled by the presence of monazite, which is common in these intrusions (see section 6.7.1.1). Monazite is more typical of felsic peraluminous igneous rocks (Sha and Chappell, 1999), so it is possible that La/Yb is only a useful distinction between hydrothermal and igneous apatites where the igneous rocks in question are intermediate and I-type.

Apatites with strong LREE depletion ( $\text{La/Yb} \ll 1$ ), as observed in this study (Fig. 6.26 e,f) are also seen in the RTX database (Fig. 7.15). They occur in both the RDP and in the host diabase intrusions, and have a strong similarity in chemistry to the 'vein-type' apatite of Chapter 6 (interpreted as forming by monazite exsolution from apatite during post-crystallisation re-equilibration with hydrothermal fluids. Observing the same geochemical

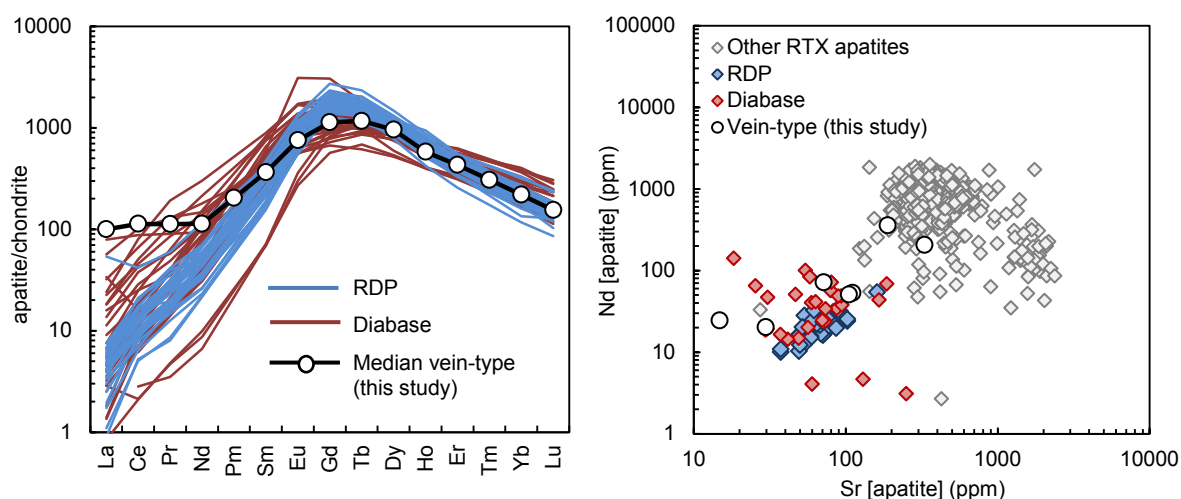


Figure 7.15. Comparison of the RTX dataset and results of this study for apatites from Resolution. a) Chondrite-normalised REE patterns and b) Nd vs. Sr (Nd as a proxy for LREE). Strong LREE depletion observed in the RTX dataset are similar to vein-type apatite from this study. All data collected by LA-ICP-MS.

population of apatite in rocks with very different bulk chemistry supports the notion that these apatites are hydrothermal in origin.

In general, there is a strong overlap in terms of key fertility parameters between the ‘dominant-type’ apatite data from this study, and Resolution apatite from the RTX database (Fig. 7.16). However, there is a population of apatite data which are observed in the RTX dataset, but not in this study. This population is found predominantly in QLP rocks, but is also seen in the Kvs volcanoclastic rocks, and the host diabase (i.e. likely hydrothermal in origin, due to its presence in a diversity of rock types). It has the same high Mn, Sr, and Eu/Eu\* as seen in apatites from Hugo Dummett data. The absence of this population of apatites in the Resolution data presented in Chapter 6 may be explained by the different analytical approach between this study and the RTX dataset. Apatites analysed in this study needed to be free from inclusions and large enough for LA-ICP-MS analysis. In a given thin section, only a small

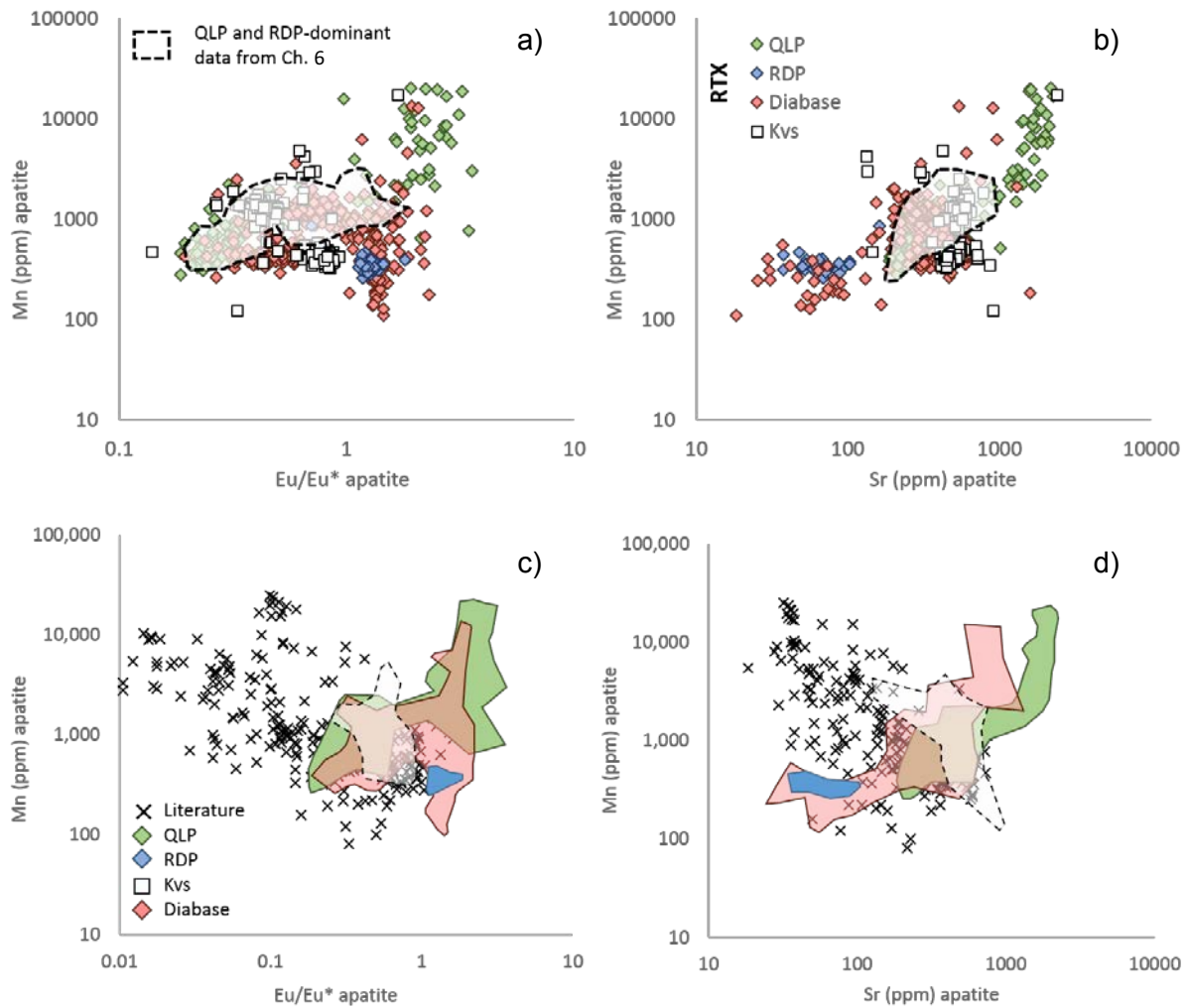


Figure 7.16. Plots of Mn vs. Eu/Eu\* (a-c) and Mn vs. Sr (b-d) for Resolution apatites from the RTX dataset. Raw data points are shown in a) and b), and the fields corresponding to those data are shown in c), and d). The field of 'dominant-type' apatites from this study is present in a) and b) (pale shaded area, surrounded by a dashed line). A population of QLP apatites with high Mn, Sr, and Eu/Eu\* which was not observed in this study, is seen in the RTX database. 'Diabase' = 1.1 Ga mafic intrusions which host mineralisation. 'Kvs' = Cretaceous volcanoclastic rocks found only within the Resolution block. Note the change of scale between a) and c).

number of apatites match these criteria. However, when analysing grains from mineral separates, as is the case for the RTX database, a much larger number of grains may be identified and analysed, thereby providing a more complete representation of the variability present in a given rock sample.

In summary, the key indicators of fertility noted in Chapter 6 for hydrothermal apatites at Oyu Tolgoi are also seen in a range of rock types at Resolution, and are found not only in the causative intrusions, but also in the host rocks.

#### *7.4.1.3 The Rio Tinto apatite dataset – other porphyry systems*

In this section, the key fertility indicators of hydrothermal apatites observed at Resolution and Oyu Tolgoi are investigated in the RTX database for the following porphyry systems: La Granja, Zaldivar, Chuquicamata, Bingham Canyon, El Abra, and El Teniente. These apatite analyses do not have any textural context, although those from La Granja were provided with the grade of the rock from which they were derived. No comment is made on whether these apatites from the RTX database are hydrothermal or igneous in origin.

Apatites from all these porphyry systems display the same trends observed in apatites from Resolution and Oyu Tolgoi; increasing Sr and Eu/Eu\* with Mn content (Figs. 7.17 and 7.18). Some overlap is observed between apatites from porphyry systems and barren igneous rocks where Mn concentrations are low, but these two groups become more distinct at higher Mn concentrations. Apatites from Chuquicamata show exclusively high Mn, Sr, and Eu/Eu\*, which is likely due to undersampling, as these apatites were derived from one rock sample. The absence of high Mn, Sr, and Eu/Eu\* in apatites from El Teniente, which are also derived from one rock sample, is also likely due to undersampling. Further data collection from these two deposits may expand the field of apatite compositions to include the full range of low and high Sr, Mn, and Eu/Eu\* compositions seen at other deposits.

For La Granja deposit, the RTX database contains information on the Cu concentrations of rocks from which apatites were derived. These analyses can be used to test the other major result from Chapter 6; that apatites from rocks containing high Cu concentrations also contain anomalously high Mn, Sr, and Eu/Eu\*.

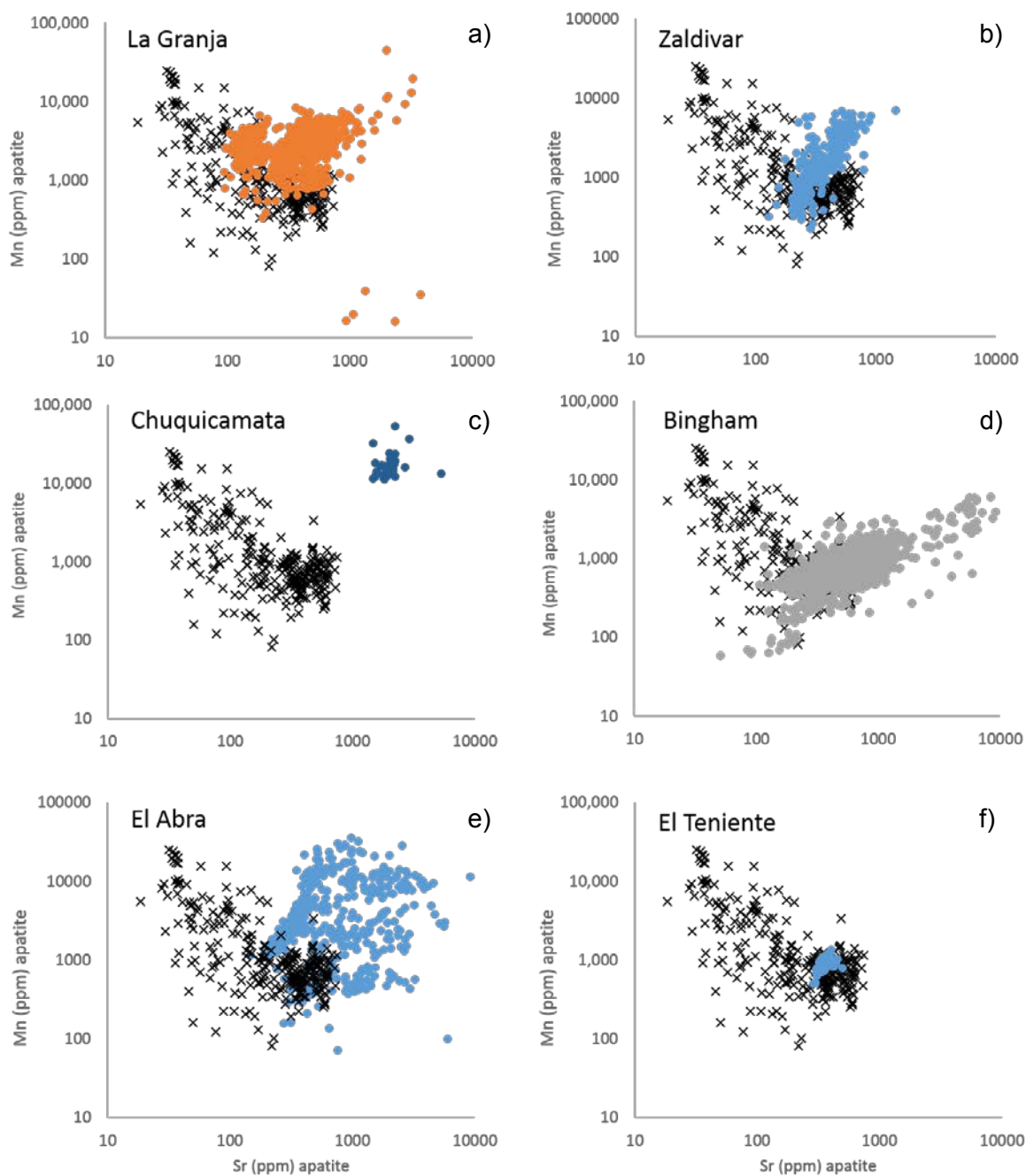


Figure 7.17. Mn vs. Sr contents for apatites from various porphyry systems from the RTX dataset. Apatites are from a) La Granja, b) Zaldivar, c) Chuquicamata, d) Bingham Canyon, e) El Abra, and f) El Teniente. Black crosses represent apatites from the literature dataset of apatites from barren rocks.

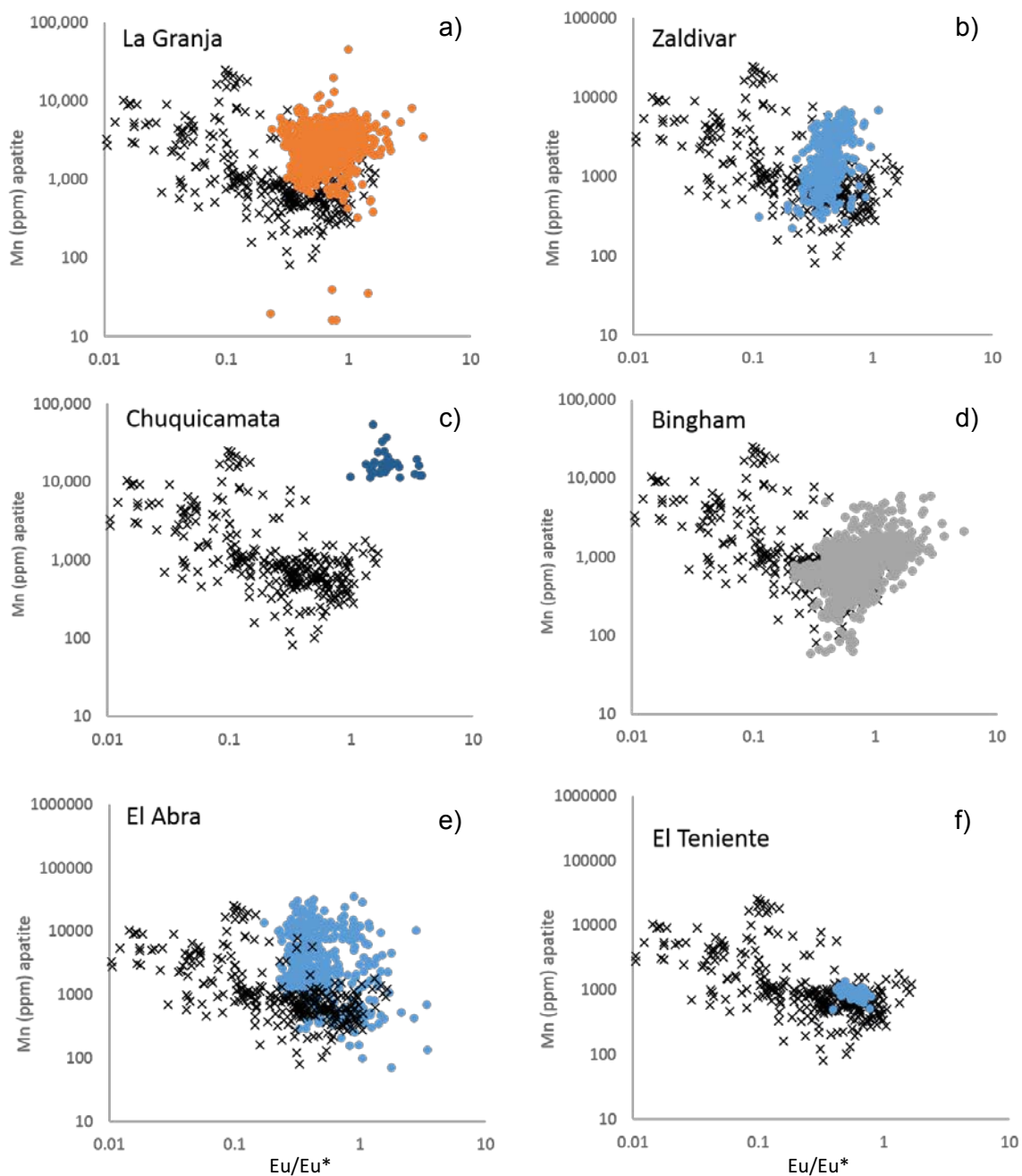


Figure 7.18. Mn vs.  $Eu/Eu^*$  for apatites from various porphyry systems from the RTX dataset. Apatites are from a) La Granja, b) Zaldivar, c) Chuquicamata, d) Bingham Canyon, e) El Abra, and f) El Teniente. Black crosses represent apatites from the barren literature dataset.

These analyses are grouped in terms of the grade of the host rocks: low grade (0.1 – 0.5 wt. % Cu), medium grade (0.5 – 1 wt. % Cu), and high grade (1 – 1.5 wt. % Cu). In general, apatites from low and medium grade rocks at La Granja typically contain lower Sr, Mn, and Eu/Eu\* than apatites from rocks with Cu contents in excess of 1 wt. % (Fig. 7.19). The apatites from high grade rocks show Mn values in excess of 2000 ppm, accompanied by high Sr (>300 ppm) and Eu/Eu\* (>0.5). These observations are in close agreement with those of Chapter 6, and those presented in Figure 7.12.

#### 7.4.1.4 Summary and practical considerations

Hydrothermal apatites from all studied porphyry systems (with the exception of El Teniente – see above) contain some geochemical signatures which provide a clear distinction between

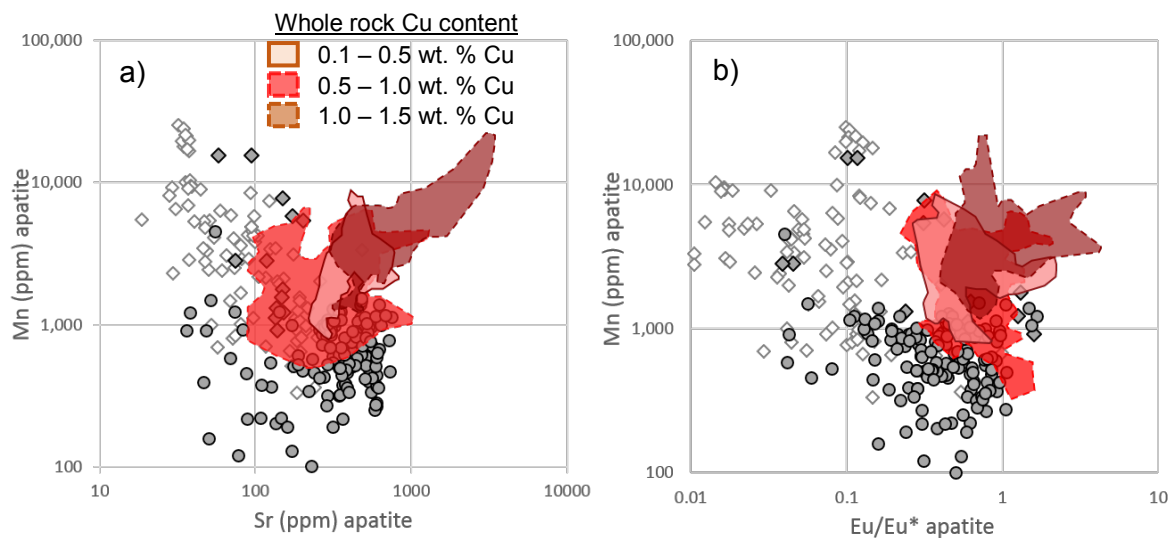


Figure 7.19. Apatite data from La Granja porphyry Cu deposit (Peru) taken from the RTX dataset. Fields shown for a) Mn vs. Sr, and b) Mn vs. Eu/Eu\*. Data are split in terms of Cu content of the host rock. Apatites from rocks with > 1 wt. % Cu do not have Mn concentrations less than 2000 ppm, and rarely have Sr values < 300 ppm. Mn concentrations reach ~2 wt. %. Symbols for barren data (gray and open symbols) as in Figure 7.12.



between porphyry systems and barren rocks. These distinctions are clearest in plots of Mn (or Fe, or Pb) vs. Sr (or Eu/Eu\*). In addition, these signatures may be able to broadly distinguish low-grade from high-grade porphyry systems. Apatites from rocks with high Cu content typically have Mn and Fe values >2000 ppm in concert with high Sr (>300) and Eu/Eu\* (>0.5).

These results have significant implications for exploration, because these signatures appear to be: (a) unique to porphyry systems, with no overlap between the barren and fertile fields where Mn contents are high, and (b) sensitive to the Cu content of host rock. In the case of point (b), this is the first identified instance of a fertility indicator which is potentially sensitive to the metal content of the host rock.

One potential problem in using the Mn, Sr, Fe (and Pb) content of hydrothermal apatite is that, in this study at least, these signatures are a) found in the core of porphyry systems, and (b) are inter-grown with sulphides. This means that mineralisation would already have been recognised during drilling, potentially removing the necessity for apatite to be analysed, and undermining its usefulness as a mineral indicator. As a result, this method would be most useful prior to a drilling campaign when exploring by analysing stream sediments, where the context of the rock is removed and potential mineralisation is unknown.

Another practical consideration is the potential for false positives. At both Oyu Tolgoi and La Granja, apatites from rocks with low Cu content may also have high Mn, Fe, and Sr values. This may be explained by considering the broader system. Firstly, although these individual rocks have lower Cu content, they form part of a deposit where high grade Cu mineralisation is present. These hydrothermal apatites are inferred to be recording the chemistry of a fluid with a high ore forming potential (see section 6.7.3), although the physicochemical conditions of the fluid may not have been appropriate for sulphide

precipitation to occur simultaneously with apatite on the scale of a hand sample. In other words, the same fluids in equilibrium with some hydrothermal apatite from Cu-poor rocks may have generated significant mineralisation elsewhere in the deposit, once the correct fluid conditions (temperature, acidity, sulphidation state, etc.) had been met. What is most significant is, when rocks have high Cu content and apatite is present, these apatites invariably carry elevated fertility signatures.

#### 7.4.2 Fertility indicators in igneous apatite

To establish the appropriate criteria for distinguishing barren and fertile rocks on the basis of their apatite chemistry, igneous apatites from this study and the RTX dataset for Oyu Tolgoi are here compared with apatites from the barren dataset. Igneous apatites from the RTX dataset were drawn from QMD intrusions (i.e. M-Ap), and Dvs rocks, and were identified based on La/Yb ratios  $> 5$  (see Fig. 7.13)

All apatites from the barren dataset have Sr contents  $< 750$  ppm (Fig. 7.20), and 80% of the data are  $< 500$  ppm (Table 7.4). By contrast, the majority of igneous apatite from fertile rocks have Sr concentrations  $> 500$  ppm (median = 656 ppm). Consequently, a value of 500 ppm is considered a reasonable discriminator of fertile and barren systems. It is worth noting that igneous apatites with  $> 750$  ppm Sr are extremely unusual in barren igneous systems, so the identification of such values would be of particular interest for exploration.

There is a much greater overlap between apatites from fertile and barren rocks in terms of their Eu/Eu\* values (Fig. 7.20 b,d; Table 7.4), so this value is deemed not to be useful in distinguishing fertile and barren systems. However, there is a clear distinction between S-type and I-type apatite which could be useful in poorly exposed terrains and when using stream sediments where the geological record is not well known.

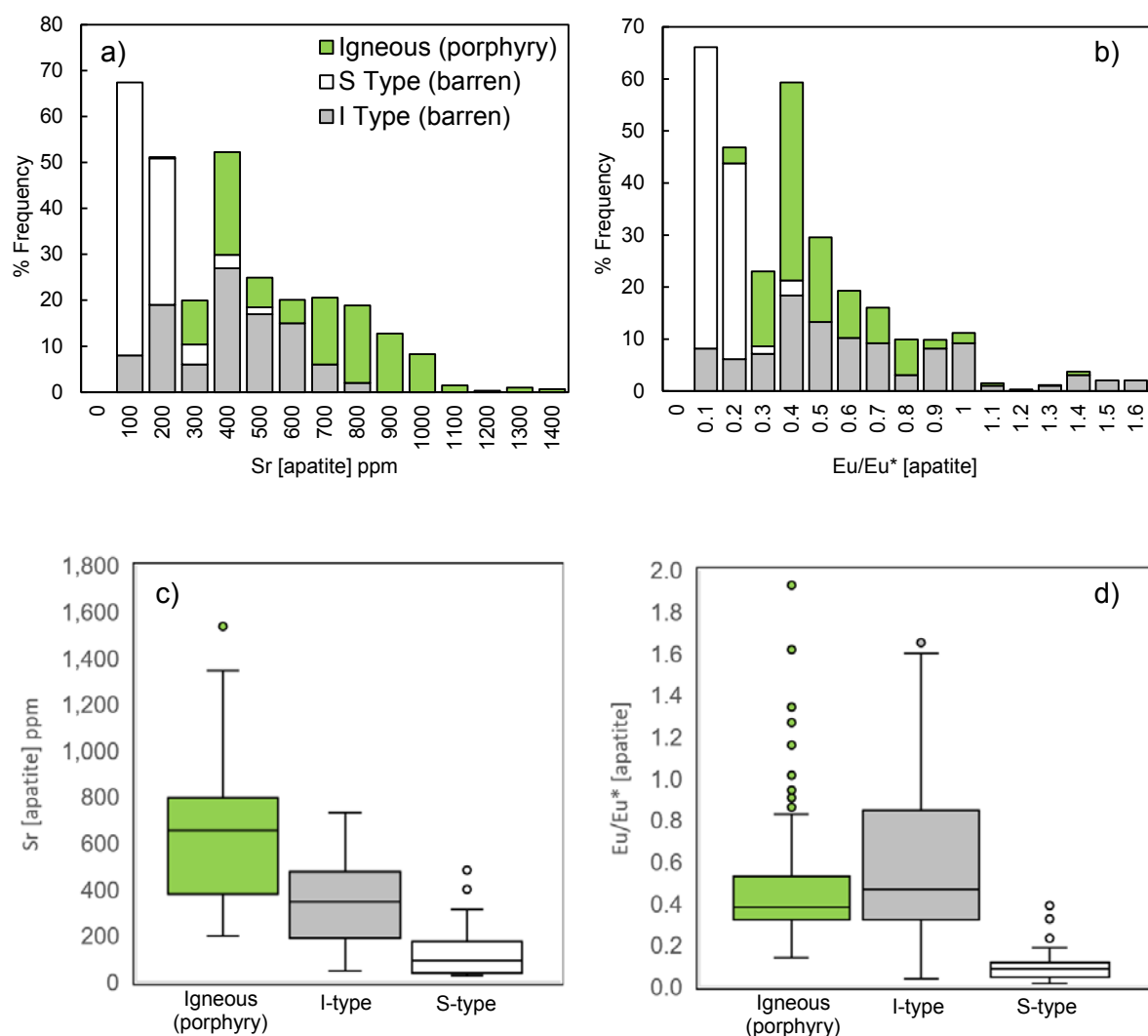


Figure 7.20. Histograms showing the distribution for a) Sr, and b) Eu/Eu\* in igneous apatite from barren and fertile systems. The same data are shown as box and whisker plots in (c,d).

| Percentile                | Sr     |         | Eu/Eu* |         |
|---------------------------|--------|---------|--------|---------|
|                           | Barren | Fertile | Barren | Fertile |
| <i>n</i> =                | 352    | 604     | 353    | 603     |
| 10 <sup>th</sup>          | 50     | 305     | 0.05   | 0.28    |
| 20 <sup>th</sup>          | 97     | 360     | 0.11   | 0.31    |
| 50 <sup>th</sup> (median) | 311    | 656     | 0.30   | 0.38    |
| 80 <sup>th</sup>          | 500    | 829     | 0.59   | 0.60    |
| 90 <sup>th</sup>          | 547    | 921     | 0.82   | 0.73    |

Table 7.3. Table showing the percentile values (10<sup>th</sup>, 20<sup>th</sup>, 50<sup>th</sup>, 80<sup>th</sup>, 90<sup>th</sup>) for apatite Sr and Eu/Eu\* values from fertile and barren systems. “Barren” data from both I-type and S-type granitoids.

|                                                                                                                                    |                                                                                                                                                                                |                                                                                                                                                                                                                         |                                                                                                                                                                                |                                                                                                                                                                                                      |                                                                                                                                                                                                                                                |
|------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>Surface</p> <p>Porphyry deposit</p> <p>Shallow magma chamber</p> <p>Magma ascent</p> <p>Deep crustal equilibration/anatexis</p> |                                                                                                                                                                                | Whole rock                                                                                                                                                                                                              |                                                                                                                                                                                |                                                                                                                                                                                                      |                                                                                                                                                                                                                                                |
|                                                                                                                                    |                                                                                                                                                                                | Sr/Y                                                                                                                                                                                                                    | La/Yb                                                                                                                                                                          | V/Sc                                                                                                                                                                                                 | Eu/Eu*                                                                                                                                                                                                                                         |
|                                                                                                                                    | Porphyry (hydrothermal)                                                                                                                                                        | <b>Potassic and sericitic alteration (possibly propylitic too) decreases Sr/Y due to mobility of Sr, and the destruction of plagioclase feldspar</b>                                                                    | Largely unaffected by hydrothermal alteration.                                                                                                                                 | <b>Potentially affected by hydrothermal alteration?</b>                                                                                                                                              | Largely unaffected by hydrothermal alteration.                                                                                                                                                                                                 |
|                                                                                                                                    | Shallow magma chamber                                                                                                                                                          | Unlikely to be strongly affected by shallow magmatic processes.<br><br>Possibly late stage volatile exsolution induces plagioclase fractionation?                                                                       | Unlikely to be strongly affected by shallow magmatic processes.                                                                                                                | - Minor magnetite fractionation in the shallow crust? Would decrease this ratio.                                                                                                                     | - The fractionation of titanite, which prefers Eu to Sm or Gd.<br>- Late stage volatile exsolution inducing plagioclase fractionation.<br>- Unequal partitioning of Sm, Eu, and Gd between silicate melts and brines upon volatile exsolution. |
|                                                                                                                                    | Mid-crust                                                                                                                                                                      | - Amphibole fractionation and suppression of plagioclase in lower- to mid-crust can strongly increase Sr/Y.<br><b>Garnet fractionation? Induced in the mid crust (~24 km) by extremely high magmatic H<sub>2</sub>O</b> | - Amphibole fractionation in lower- to mid-crust can increase Sr/Y<br><b>Garnet fractionation? Induced in the mid crust (~24 km) by extremely high magmatic H<sub>2</sub>O</b> |                                                                                                                                                                                                      | - Plagioclase fractionation, potentially related to mid crustal volatile exsolution could lower Eu/Eu*?                                                                                                                                        |
| upper mantle - lower crust                                                                                                         | - Partial melting of plagioclase-rich lower crust, or residual garnet in partially melted down-going ocean plate.<br><br>- Equilibrium with garnet (± amph) in the lower crust | - Partial melting of plagioclase-rich lower crust, or residual garnet in partially melted down-going ocean plate.<br><br>- Equilibrium with garnet (± amph) in the lower crust                                          | - Promotion of hornblende fractionation (causing depletion in Sc) due to high H <sub>2</sub> O causes suppression of magnetite, (and enrichment in V).                         | High Eu/Eu* retained by:<br>- suppression of plagioclase by high magmatic H <sub>2</sub> O<br>- Redox conditions. (Oxidised melts have Eu <sup>3+</sup> , which does not partition into plagioclase) |                                                                                                                                                                                                                                                |

|  |                            |                                                                                                                                                   |                                                                                                                                                 |                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                         |
|--|----------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|  |                            | Zircon                                                                                                                                            |                                                                                                                                                 | Apatite                                                                                                                                                                                                     |                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                         |
|  |                            | Eu/Eu*                                                                                                                                            | Ce/Ce*                                                                                                                                          | Sr                                                                                                                                                                                                          | Eu/Eu*                                                                                                                                                                                                                                                             | Mn, Fe, Pb,                                                                                                                                                                                             |
|  | Porphyry (hydrothermal)    | - Co-crystallisation of titanite (during Ca-metasomatism?) causes increase in zircon Eu/Eu*                                                       | - Largely unaffected by the co-crystallisation of other REE-bearing phases<br>- Potentially affected by melt oxidation upon volatile exsolution | - High Sr in hydrothermal apatite inherited from Sr-rich fluids, which derived from Sr-rich melts.                                                                                                          | - Co-crystallisation of titanite (during Ca-metasomatism?)                                                                                                                                                                                                         | Enriched in apatites hydrothermal apatites from high grade systems                                                                                                                                      |
|  | Shallow magma chamber      | Increased by co-crystallisation of titanite, which may be induced by oxidation or increase in melt Ca/Al ratio.                                   |                                                                                                                                                 | - Timing of apatite crystallisation with respect to plagioclase                                                                                                                                             | - Co-crystallisation of titanite increases Eu/Eu*                                                                                                                                                                                                                  | - Mn (and Fe) partitioning controlled by redox conditions.<br>- Oxidising condition result in low Mn ( $Mn^{2+}$ partitions more strongly than $Mn^{3+}$ ). Same likely true for $Fe^{2+}$ vs $Fe^{3+}$ |
|  | Mid crust                  |                                                                                                                                                   | - Fractionation of $Fe^{2+}$ bearing phases in closed systems (lower to mid-crustal process)                                                    |                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                    |                                                                                                                                                                                                         |
|  | upper mantle - lower crust | - High values inherited from melts with high Eu/Eu*, formed by hydrous, oxidised deep crustal fractionation (garnet + amphibole, not plagioclase) | - Oxidised fluids from the down-going slab influence redox conditions of arc magmas.                                                            | - High values inherited from Sr-rich melts formed by hydrous deep crustal fractionation (garnet + amphibole, not plagioclase)<br><br>- Low values inherited from Sr-deficient protolith in S-type granites. | - High values inherited from melts with high Eu/Eu*, formed by hydrous, oxidised deep crustal fractionation (garnet + amphibole, not plagioclase)<br><br>- Low values inherited from Eu-deficient protolith in S-type granites. Indicative of unprospective areas. | - Enriched in igneous apatites from S-type granites. Reduced protolith? Indicative of unprospective areas.                                                                                              |

Table 7.4. (previous two pages). A summary of the main processes which influence signatures of fertility in whole rock, zircon, and apatite geochemistry, divided on the basis of the crustal levels at which they occur. Text in bold represents interpretations based on evidence from this study. Arc crust cross-section figure modified from Cooke et al. (2013).

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## 7.5 Fertility signatures: length and timescales, and use in exploration

In general, processes which occur in the deep crust or upper mantle are likely to affect a broader area of an arc, and may occur over relatively long timescales (c.  $10^0 - 10^1$  Myr). These processes, such as compositional heterogeneity in the down-going slab or mantle wedge (Parman et al., 2011), angle of subduction (Kay and Mpodozis, 2001; Kay et al., 2005), thermal conditions in the slab (potentially related to age and spreading rate), and crustal thickening (Kay and Mpodozis, 2002), may influence large volumes of magma, and be manifested at (or near) the surface in several intrusive or volcanic centres in several epochs of magmatism. Conversely, geochemical processes which occur *in situ* in shallow crustal intrusions are likely to only affect those individual intrusions and (in the case of hydrothermal processes) the country rocks in the immediate vicinity. Furthermore, such shallow processes which occur at near-solidus conditions (e.g. volatile exsolution, the sequestration of metals into hydrothermal fluids) may only exercise a geochemical control over the final mineral phases to crystallise in an intrusion.

For fertility signatures, the length and timescales over which they form has important implications for their use in exploration. Signatures that develop at deep crustal levels and occur on broad length and timescales may only be useful for indicating broad time periods and arc segments with high ore forming potential, and would therefore only be useful to exploration on regional scales. On the other hand, signatures which are generated as part of the mineralising processes and occur in the shallow crustal may provide a very focussed tool

for exploration, as they indicate the likelihood of mineralisation (or high grade mineralisation) in the vicinity. In this section, each of the identified mineral and whole rock signatures will be assessed in terms of the scales over which they form, and the resultant implications for their use in exploration.

#### 7.5.1 Whole rock signatures

Current models of arc magma genesis highlight the different crustal levels at which particular textures and chemical characteristics may be developed. For an intrusive or extrusive igneous rock in the shallow crust, its “essential” geochemical characteristics are largely controlled by lower crustal fractionation, assimilation, and hybridisation, whereas the textural characteristics are determined by processes occurring in the shallow crust (e.g. Hildreth and Moorbath, 1988; Annen et al., 2006). These models do not preclude the influence of shallow crustal processes (e.g. assimilation; modest fractional crystallisation) on whole rock chemistry, but suggest that such a process does not exert a dominant control over whole rock geochemistry, in particular the major elements. In addition to this, shallow crustal processes which are specific to magmatic-hydrothermal mineral deposits (e.g. strong hydrothermal alteration) may also influence the geochemistry of igneous rocks in the shallow crust. Here, the locus of various processes which affect magmatic fertility signatures are identified and discussed.

The control of garnet on La/Yb and Sr/Y ratios (Figs. 7.1 and 7.6; section 7.1.1.1), either by high pressure equilibrium with garnetiferous lower crust (e.g. Kay and Mpodozis, 2001) or lower pressure fractionation in exceptionally hydrous melts (section 7.1.1.1), requires that the minimum pressure at which these signatures are generated is ~0.8 GPa (Fig. 7.3 a) corresponding to a depth of ~24 km. This means that these signatures are most probably developed in the mid- to lower crust.

Similarly, the retention of elevated whole rock Eu/Eu\* values is primarily affected by moderate to high pressure, hydrous fractionation of garnet  $\pm$  amphibole and the suppression of plagioclase (e.g. Richards et al., 2012). In addition, the redox conditions of the melt during plagioclase fractionation can influence Eu anomalies in rocks, due to the preferential uptake of Eu<sup>2+</sup> into plagioclase, although this effect is likely to be small in systems where plagioclase is suppressed. Titanite fractionation can also have a strong influence on Eu/Eu\* values (e.g. Glazner et al., 2008). This process typically occurs at relatively low temperatures in silica-rich magmas, so probably does not affect magmas that form porphyry Cu deposits.

V/Sc ratios are also largely controlled by hydrous fractionation. High H<sub>2</sub>O contents are required in the melt in order to promote hornblende fractionation (scavenging Sc from the melt), and delay magnetite crystallisation, (enriching V in the melt, and increasing V/Sc ratios; Loucks, 2014). High H<sub>2</sub>O concentrations require high pressure or else volatile saturation will occur, so the V/Sc ratio is probably also controlled by the same deep crustal processes as the other whole rock fertility indicators.

The fact that these signatures do not vary with deposit size (Fig. 7.9), that they frequently occur in post-mineralisation intrusions (Fig. 7.1), or even in entirely unmineralised systems (e.g. Fig. 7.2) highlights the fact that although hydrous, lower crustal fractionation is likely a pre-requisite for porphyry formation, it is not sufficient on its own. It must be accompanied by the optimisation of several subsequent processes which occur during the transit of these magmas from the lower crust into shallow crustal ore-forming environments. As a result, these parameters may only indicate an increased ore-forming potential of magmas associated with a particular magmatic epoch and arc segment. For this reason, these signatures are principally useful for broad scale regional exploration.



### 7.5.2 Zircon fertility signatures

Due to the low temperatures of crystallisation (e.g. Fig. 5.15) and the evolved composition of the melts from which zircon crystallises (e.g. Boehnke et al., 2013), zircons present in porphyry systems (excluding xenocrystic grains) mostly crystallised in the shallow crust. However, the geochemical signatures present in “shallow” zircon may be inherited from the melt in part, and these melt signatures were generated at a variety of crustal pressures.

The Ce/Ce\* ratio records the oxidation state at the moment of zircon crystallisation (i.e. in the shallow crust). However, redox conditions in shallow crustal magmas may be partly inherited by processes which occur at greater depth, e.g. the onset of magnetite crystallisation (Jenner et al., 2010). They may also be influenced by degassing processes occurring in the shallow crust, e.g. the reduction of sulphate (Dilles et al., 2015), or the loss of H<sub>2</sub> (Czamanske and Wones, 1973; Burnham, 1979; Czamanske, 1988). Zircon crystallises at the right temperature to record any change in redox conditions in near-solidus shallow crustal environments. However, the lack of significant differences in Ce/Ce\* between, for example, Heruga and Hugo Dummett, or between low- and high-Ta zircons at Oyu Tolgoi suggests that either these processes are not occurring (at least, in the case of Oyu Tolgoi) or that zircon is not sensitive to them. In either case, this makes Ce/Ce\* primarily useful for recording broader redox conditions and, as a result, it is proposed that Ce/Ce\* is most useful for distinguishing zircons from potentially porphyry-forming epochs from other unprospective suites (i.e. exploration over a regional or district scale).

Eu/Eu\* is also strongly influenced by melt redox conditions (Burnham and Berry, 2012). However, the lack of strong correlation between Ce/Ce\* and Eu/Eu\* (e.g. Fig. 7.10 a) highlights the extent to which the latter is affected by other processes, which may occur at various crustal levels. High Eu/Eu\* values may be inherited from the melt, which in turn are

a consequence of deep crustal processes (see above). The co-crystallisation of zircon with (or after) other phases, especially titanite, can also exercise a strong influence over zircon Eu anomalies. This is likely to occur at lower temperatures, based on the presence of titanite inclusions in zircon (Fig. 5.7), and Ti-in-zircon thermometry (e.g. Fig. 5.15), and so is likely to also occur *in situ* in shallow crustal intrusions. As a result, zircon Eu/Eu\* must be used with caution in geochemical exploration to insure that shallow processes have not exercised a dominant control. Filtering on the basis of Ta (>0.2 ppm) may be useful in this regard.

### 7.5.3 Apatite fertility signatures

The chemistry of igneous apatite broadly reflects the melt chemistry, which is determined primarily by deep processes (Table 7.4), making this a potentially useful tool in identifying magmatic epochs or arc segments which are more likely to host mineralisation. Significantly, the signatures it acquires may be observed in unmineralised volcanic cover rocks (e.g. the Dvs at Oyu Tolgoi). In exploration, coeval or immediately post-mineralisation volcanic rocks have a higher sampling potential than porphyry intrusions, because they occupy shallower (near-surface) stratigraphic levels, and are spread over a wide area.

The chemical attributes of hydrothermal apatite occur are developed over the narrowest length and timescale of any signature investigated in this study, and consequently represent the most focussed potential tool for exploration discussed herein. However, implicit in this, is that they will also have the most limited spatial distribution and so would be less likely to be encountered in large scale exploration programmes. These apatites acquired their geochemical characteristics as a result of equilibrium with fluids in porphyry ore-forming environments (<1-7 km depth, <5 km wide; Sillitoe, 2010), over timescales typical of hydrothermal processes (<<1 Myr; von Quadt et al., 2011). As a result, they have the potential to distinguish between mineralised/unmineralised, and low/high-grade deposits which are in close proximity to one another.

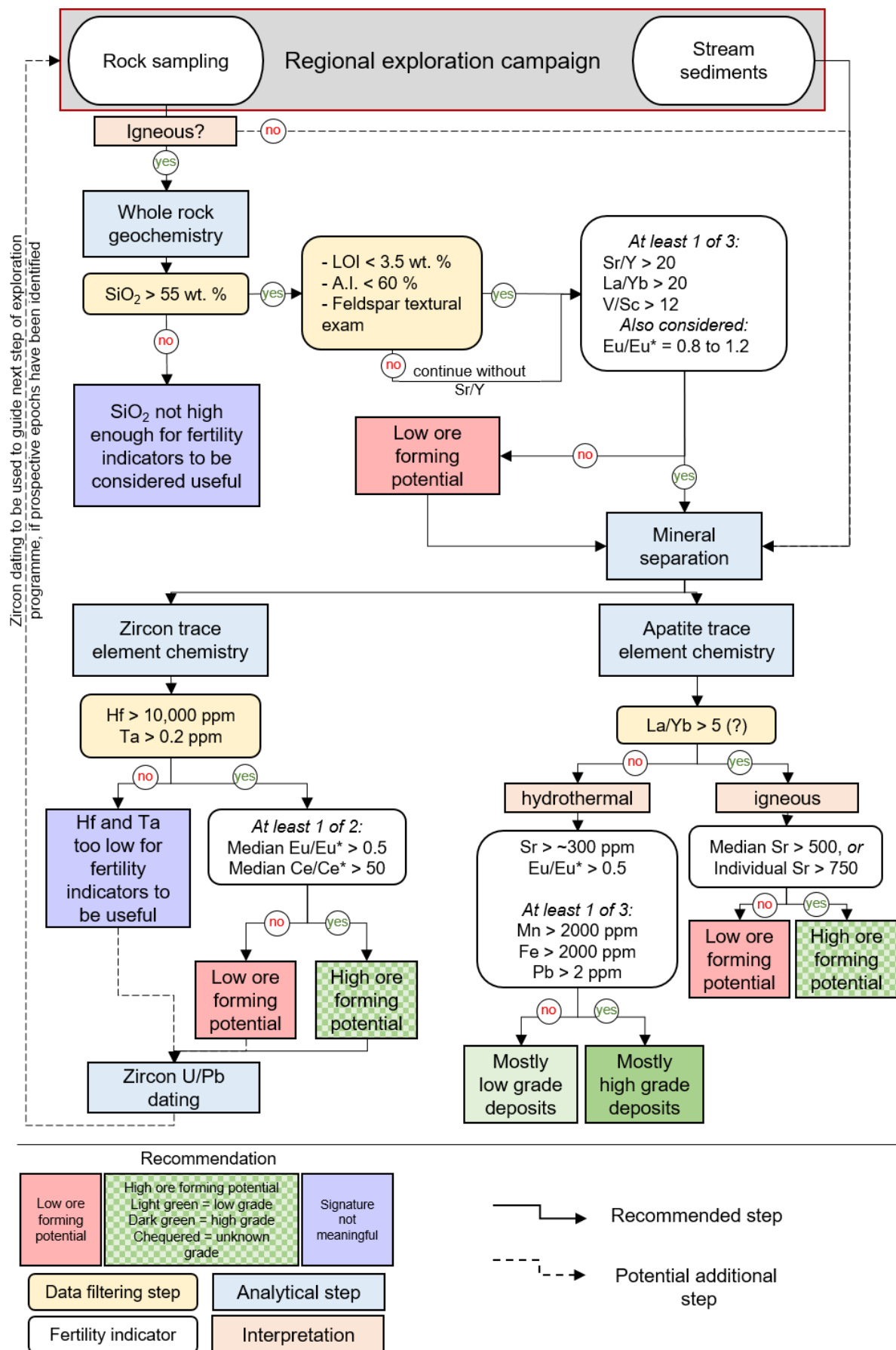
These fertility signatures may be used during exploration of areas where ore-forming potential is already known to be high. For example, areas along-arc from known porphyry mineralisation, or where other regional fertility signatures have been observed (e.g. whole rock, zircon, or igneous apatite chemistry). This tool could be used to identify the potential for large deposits, and especially, to eliminate time spent investigating hydrothermal systems that have little chance of being related to high-grade mineralisation.

## **7.6 Recommendations for exploration**

### **7.6.1 Exploration work flow**

A synthesis of the results which pertain to exploration are presented in Figure 7.21, in the form of a workflow. The workflow is designed to consider an exploration program starting from a regional scale, which would utilise geochemical techniques based on rock sampling during field mapping or drilling, and stream sediment sampling. For the rock sampling, representative samples would be selected from outcrop or from drill core. The workflow assumes that igneous rocks, either volcanic or intrusive, are available. If other rocks of interest (e.g. hydrothermal breccias, post-mineralisation sedimentary cover) are selected, whole rock geochemistry would not be useful but these rocks may warrant mineral separation and further analysis as they may contain relevant chemical information or reworked porphyry-related material.

For igneous rocks, whole rock geochemistry is the first step in the workflow because analysis is (a) relatively cheap (e.g. lithogeochemistry package from ALS Minerals is ~70 USD), and (b) does not require the preparation of thin sections or polished blocks, or time-consuming mineral separation, so that (c) results can be returned relatively quickly. When the whole rock data are received, some filtering is necessary before fertility indicators may be



*Figure 7.21. (previous page) A recommended exploration workflow for the implementation of the geochemical fertility indicators identified in this study in a regional exploration program. See text for discussion.*

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assessed. First, the divergence between fertile and barren populations is greatest in more evolved samples (e.g. Fig. 1.7), so rocks with  $\text{SiO}_2$  values less than ~55 wt. % are not useful for fertility discrimination. The more primitive rocks would also be unlikely to contain zircon, making mineral separation and analysis unnecessary.

Fertility indicators (especially Sr/Y) may be compromised in samples which are strongly affected by hydrothermal alteration (Fig. 7.7), so additional screening for alteration is necessary. Loucks (2014) lists a series of criteria for whole rock filtering, including loss on ignition (LOI) values < 3.5 wt. %, analytical totals between 97.5 and 101.5 wt. %, and the absence of plagioclase destruction (from petrographic observations). The results herein suggest that L.O.I. should not be used as the sole criterion to measure alteration, as it is not sensitive to the kind of alteration (e.g. strong potassic) which is likely to affect fertility indicators. In addition, weakly altered samples containing calcite or anhydrite can have extremely high LOI (up to 9 wt. %; Fig. 4.35). The use of the alteration index is recommended as it more reliably measures feldspar destruction (see Figs. 4.33 and 3.27). Values of Sr/Y from rocks with A.I. > 60% (the limit of 'least altered samples' from Large et al. (2001)) should not be considered, although V/Sc, Eu/Eu\*, and La/Yb may still be used, as they do not appear to vary with A.I. The distinguishing whole rock criteria listed in Figure 7.21: Sr/Y > 20, V/Sc > 12, La/Yb > 20 and Eu/Eu\* between 0.8 and 1.2. It is likely that these criteria will be met simultaneously in the same rock because, for example, Y and Yb are geochemically similar, so high Sr/Y is commonly associated with high La/Yb. At least 1 out of 3 values (Sr/Y, La/Y, and V/Sc) would indicate ore-forming potential. Eu/Eu\*, showing the weakest separation between barren and fertile, is a parameter which may reinforce the

other 3 parameters when they occur in conjunction (see section 7.2.2.4). Rocks which do not meet these criteria should still be considered for mineral chemistry fertility parameters.

The next analytical step would be mineral separation. This would also be the first step applied to samples collected from stream sediments or other surficial cover, or samples from non-igneous rocks of interest (such as conglomerates that might have reworked porphyry-related material). In this study, only apatite and zircon are considered, although other minerals (e.g. magnetite, titanite, rutile, trace sulphides) may also be easily isolated at this stage.

All zircon analysis should be guided by basic petrographic work to identify mineral inclusions and zones within grains, as these are typically extremely relevant to the interpretation of the results. Zircons typically show decreasing  $\text{Eu}/\text{Eu}^*$  with increasing Hf, meaning zircons with the most primitive chemistry also have the highest  $\text{Eu}/\text{Eu}^*$ . This is observed at Resolution (Fig. 5.33) as well as several other systems (e.g. Dilles et al., 2015). The utility of  $\text{Eu}/\text{Eu}^*$  as a fertility indicator lies in the fact that  $\text{Eu}/\text{Eu}^*$  values are high even at high Hf values. As a result, analyses should be filtered so that grains with low Hf values ( $<10,000$  ppm Hf) are not considered. In addition, the effects of titanite crystallisation must be countered. It is not sufficient to discount the possibility of titanite co-crystallisation based solely on petrography, Inclusions of titanite are easily missed because they are rare and typically small ( $<10$   $\mu\text{m}$ ; Fig. 5.7), but have a disproportionate effect on zircon chemistry, especially  $\text{Eu}/\text{Eu}^*$  values. Ta concentration may be used as a guide, such that zircons with Ta values  $<0.2$  ppm should also be discounted (Fig. 7.21).

The criteria for zircons from fertile systems, as described in section 7.3.1.4, are  $\text{Eu}/\text{Eu}^* > 0.5$ , and  $\text{Ce}/\text{Ce}^* > 50$ . In a given rock, there is likely to be a significant range for both of these values, so statistical analysis of the data would be required to resolve any

distinct populations (e.g. cluster analysis). If any population (or indeed, the entire population) of zircons in a given rock have an average value in excess of either one of these criteria (but preferably both), it is likely that these zircons were sourced from magmatic rocks with a high ore forming potential.

U/Pb dating may be conducted on all zircons at this point, including those which have low Hf or Ta, and those with low Eu/Eu\* and Ce/Ce\*. This would allow fertility signatures, both in zircon, and in the whole rock geochemistry, to be constrained to particular geological epochs. This information could then be used in a follow-up cycle of work to target specific field areas or stratigraphic horizons of particular interest.

Apatite trace element analysis may be conducted by LA-ICP-MS from polished thin sections, polished blocks, or from mineral separates. Distinguishing between hydrothermal and igneous apatites is a critical first step in terms of assessing fertility signatures. Texturally, this may be done by the associations of apatite with other mineral phases (e.g. apatites intergrown with sulphides or secondary biotite are likely to be hydrothermal). Geochemically, the distinction can be drawn using the La/Yb ratio (for intermediate I-type rocks), with La/Yb < 5 indicative of hydrothermal apatite.

As hydrothermal apatites (or, indeed, any apatites) with Sr values > ~300 ppm, in addition to Mn > 2000 ppm, Fe > 2000 ppm, and Pb > 2 ppm, appear to be unique to porphyry systems, their identification would be the most significant finding of any geochemical exploration program based on the minerals studied herein (note that apatites from S-type granitoids with similarly high Mn and Fe exclusively have low Sr; see 6.3.1). In addition to high Sr, it is suggested that at least one of the other three criteria (elevated Mn, Fe, or Pb) should be recognised for a positive fertility assessment, although data from this study and the RTX database indicate that high Mn, Fe, and Pb values typically occur

together. If, in a given area, and if sufficient grains are analysed (100s to 1000s of individual LA-ICP-MS analyses), only hydrothermal apatites that do not meet these criteria are found, it is unlikely that a high grade deposit is present. If a mixture of apatites (those which do, and those which do not meet the criteria) are found, the probability of a high grade deposit increases significantly.

During an exploration campaign, if hydrothermally altered rocks are observed which may or may not contain minor amounts of disseminated Cu sulphides, it is currently difficult to determine if these rocks are the distal or shallow extent of a large, high-grade system, or are representative of an underlying uneconomic deposit, without more detailed mapping and initial drilling. However, analysing hydrothermal apatites from these rocks and assessing the fertility signatures presented in Figure 7.21 would provide a quicker and cheaper method for prioritising districts or areas. The same approach could apply to apatites derived from stream sediments, or detrital apatites in post-mineralisation cover.

## 7.6.2 Retrospective exploration

In assessing the utility of mineral and whole rock indicators of fertility developed during this study, it is useful to pose the following question: would either of these blind deposits (Resolution or Oyu Tolgoi) have been easier to detect in the light of the results of this study? In this hypothetical situation, it is assumed that there is no access to geophysical techniques, or other alteration vectoring, or that such techniques have not yet been employed.

### *7.6.2.1 Resolution*

During regional exploration, the Apache Leap intrusions may have been selected for particular scrutiny. This decision would be based partly on their age, as before the discovery of the Resolution deposit, these intrusions had been mapped and assigned a Laramide age (H. Martin, pers. comm., 2012). They also follow a regional tectonic fabric, and strike in the



direction of a large area of unconstrained Palaeozoic and Proterozoic sediments, covered by a thick Tertiary overburden, which would entirely mask any mineralisation that could be present. As such, they may represent part of a broader magmatic sequence under Tertiary cover, possibly even a shallow portion of the western extent of the Schultze Granite.

These rocks have a clear igneous hypabyssal texture, and so would have qualified for whole rock geochemistry. All rocks are sufficiently enriched in  $\text{SiO}_2$  to meet the “evolved character” threshold (61.0 to 68.9 wt. %), apart from the mafic Apache Leap intrusion (51.3 wt. %  $\text{SiO}_2$ ) which would therefore no longer be considered as per Figure 7.21. Given that the felsic Apache Leap intrusions have A.I. values which are mostly  $<60$  (Table 3.2) and textural inspection shows that feldspars are not strongly altered to sericite, they pass the filtering criteria in Figure 7.21.

Apache Leap intrusions mostly have high Sr/Y and La/Yb values ( $> 20$ ). The La/Yb values in particular are intriguing as they are at the upper limit of La/Yb values defined by the fertile dataset. V/Sc values significantly exceed both barren and fertile datasets, and Eu anomalies are mostly absent ( $\text{Eu}/\text{Eu}^* \sim 1$ ). These positive signatures (Fig. 3.21) would provide justification for conducting analyses of mineral separates.

In this study, the only Apache Leap zircons to be analysed were from sample R-RF-G, so the following discussion is based on this rock. Analysis of Apache Leap zircons would show that U/Pb and Th/Pb trace element ratios show a bimodal population which correspond to cores and rims of grains (see Fig. 5.23 b). This immediately suggests a bimodal population of zircon ages, likely to be inherited Proterozoic cores with Laramide age rims, consistent with zircons from other intrusions in Arizona. The younger ‘Laramide’ population (i.e. higher Th/Pb) would mostly have Hf values in excess of 10,000 ppm, and Ta values  $> 0.2$  ppm (Fig. 5.25) thereby passing the filtering gate.

The median  $\text{Eu}/\text{Eu}^*$  value of the inferred Laramide population of zircons from R-RF-G (0.64) is approximately equal to the 90<sup>th</sup> percentile of the barren dataset (0.65; Table 7.2) and falls between the 50<sup>th</sup> and 80<sup>th</sup> percentile of the fertile dataset. This provides a reasonable fertility signature. The median  $\text{Ce}/\text{Ce}^*$  value (180) for the inferred Laramide population is significantly greater than the 90<sup>th</sup> percentile of the barren dataset (82; Table 7.2), and falls between the 50<sup>th</sup> and 80<sup>th</sup> percentile of the fertile dataset. These results place this rock fairly confidently in the fertile domain for both parameters. Zircon U-Pb dating would confirm the Laramide age of this sample, with the youngest concordant age for this rock at  $64 \pm 3$  (2 $\sigma$ ; Fig. 5.22 d), in line with the age of other deposits in the area (Lang and Titley, 1998).

A textural examination would indicate that apatite from these rocks appears to be hydrothermal in origin, which may be confirmed by the REE geochemistry (median  $\text{La}/\text{Yb} < 5$ ; Table 6.6). Median Sr values are high (524 ppm), but  $\text{Eu}/\text{Eu}^*$ , Mn, and Fe concentrations are lower than the criteria in Figure 7.21. This would indicate that the hydrothermal fluids that generated these apatites were not directly related to high-grade mineralisation elsewhere.

In summary, the evidence from whole rock and zircon chemistry of the Apache Leap intrusions would point to an igneous system with a high ore forming potential. Hydrothermal signatures in apatite are more ambiguous, although this may be expected from the rocks, which are not strongly altered. On this basis, the area surrounding Apache Leap (especially the area along strike of the trend of the intrusions) could have been selected for further scrutiny. Sampling of the Laramide volcanic rocks in the vicinity (such as the Kvs, which may be exposed or encountered in shallow drilling) could have been carried out to test further fertile signals

#### 7.6.2.2 *Oyu Tolgoi*

At Oyu Tolgoi, the causative QMD is mostly buried underneath the Contact Fault, and crops out only in a small area above the Central deposit (rocks from which are not studied herein). As a result, the QMD is not considered in this retrospective exploration analysis. The BiGd intrudes above the Contact Fault to crop out above the Hugo Dummett deposit, and is exposed further north in the area around Ulaan Khud (Fig. 4.7). The Dvs is a widespread unit which lies beneath the Contact Fault, but above the alteration and mineralisation. Nearly all drill holes which ultimately intersect the ore body first pass through Dvs rocks (Figs. 4.5 to 4.9), meaning that once intersected, and given their age (which could be easily determined if unknown), they could inform a decision on whether to continue drilling. Both of these two units will be considered here. Both have easily identifiable igneous textures, and so would qualify for whole rock geochemical analysis. All Dvs and BiGd rocks are in excess of 55 wt. % SiO<sub>2</sub> (Table 4.1) and have A.I. values < 60, thus passing the first filtering criteria.

All BiGd and most Dvs samples have Sr/Y values in excess of 20, V/Sc values well in excess of 8, and Eu/Eu\* values mostly within the required range (Fig. 4.29 b,e,f). However, the La/Yb values of the Dvs are low (<10) and for the BiGd, are on the boundary between barren and fertile (Fig. 4.29 d). In spite of this, the other fertility indicators are present, meaning that further mineral separation and analysis could be justified.

Zircons from one BiGd sample (OT-11) and one Dvs sample (OT-158) were studied for this thesis. They have Hf and Ta values which are in excess of the minimum criteria for both elements in most cases Table 5.4. The median Dvs zircon Eu/Eu\* value (0.38) is lower than the minimum threshold value given in Figure 7.21. The median BiGd value (0.53) is higher, and is just in excess of this threshold values. On the other hand, the median Ce/Ce\* for both the Dvs (141) and BiGd (225) are both well in excess of the 90<sup>th</sup> percentile for the barren dataset (82; Table 7.2) and are between the 50<sup>th</sup> and 80<sup>th</sup> percentile for the fertile

dataset. This would lend support to a fertile assessment for the magmatic system responsible for these units. U-Pb dating would reveal a concordia age of  $365.3 \pm 2.6$  Ma for the BiGd which is similar to that of the Dvs ( $369 \pm 1$  Ma; Wainwright, 2008), indicating that the Late Devonian Gurvansayhan terrane should be prospective for porphyry deposits. Note that zircons from Carboniferous rocks, which post-date mineralisation by  $>20$  Myr, have median Eu/Eu\* (0.25) and Ce/Ce\* (40; data from Wainwright, 2008) which are lower than the proposed threshold criteria for zircons from mineralisation-associated magmas, and are below the 10<sup>th</sup> and 50<sup>th</sup> percentiles respectively of all the data from the fertile dataset.

Apatite La/Yb values in excess of 5 for both BiGd (median = 9.1) and Dvs (median = 10.8; Table 6.4) suggest an igneous origin, although textural relationships in the BiGd are more likely to point to a hydrothermal origin. High median Sr values are found in apatites from both units (BiGd = 1014, Dvs = 743), which are close to or exceed the maximum Sr value indicative of apatites from barren igneous systems (750 ppm), and are well above the 80<sup>th</sup> percentile for barren data (500 ppm). The BiGd is above the 90<sup>th</sup> percentile for the fertile dataset. These results would provide further indication of the fertility of the magmatic systems associated with these rocks. The presence of apatite with fertile signatures (namely high Sr) in unmineralised volcanic and intrusive rock in a hitherto underexplored area would draw attention to, not only this area, but the Late Devonian magmatic epoch.

In summary, the whole rock, zircon, and igneous apatite geochemistry of the outcropping intrusive and volcanic rocks at Oyu Tolgoi, even though they are actually slightly post-mineralisation, would indicate the high ore-forming potential of the Late Devonian arc sequence. When considered with evidence from other approaches (e.g. geophysical techniques, and the evidence for ancient copper mining in the area; Crane and Kavalieris, 2012), these results could encourage further exploration in this area, and in other Late Devonian Mongolian sequences.

|            |        |  | Robust                                                                                                                                                                                                                                                                                     | Abundant/<br>Widespread | Easy to identify<br>/isolate | Contain unequivocal signatures                                                                                                                                                                                                                                     | Easy to analyse                                                                                                                                           |
|------------|--------|--|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------|------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Whole Rock | Sr/Y   |  | <b>Poor.</b> Sr is extremely mobile and is affected by significant loss during plagioclase-destructive hydrothermal alteration.<br><br>Sr/Y values decrease with alteration index (Fig. 7.7)                                                                                               | N/A                     | N/A                          | <b>Moderate.</b> Good separation between barren and fertile signatures at SiO <sub>2</sub> values >55 wt. %<br><br>Some ostensibly barren volcanic rocks also display high Sr/Y. Signature can therefore also be generated by processes that produce barren rocks. | <b>Good.</b> Both Sr and Y are routinely included in commercial whole rock geochemistry packages, and are significantly greater than limits of detection  |
|            | La/Yb  |  | <b>Moderate.</b> Although La is subject to modest loss during potassic and sericitic alteration, Yb is largely conserved. There is no relationship between La/Yb and any index of alteration (Fig. 7.7)                                                                                    |                         |                              | <b>Moderate.</b> Similar issues to Sr/Y.                                                                                                                                                                                                                           | <b>Good.</b> Both La and Yb are routinely included in commercial whole rock geochemistry packages, and are significantly greater than limits of detection |
|            | V/Sc   |  | <b>Moderate.</b> - <b>?poor?</b> Isocon analysis indicates significant loss in potassic, and either a loss (Oyu Tolgoi) or a gain (Resolution) in sericitic alteration (Figs. 3.24 and 4.32). V likely to be affected by alteration, but mechanism and magnitude of effect remain unclear. |                         |                              | <b>Good - moderate.</b> Good separation between barren and fertile signatures at SiO <sub>2</sub> values >55 wt. %. Values are exceptionally high at Resolution and Oyu Tolgoi.<br><br>Some ostensibly barren volcanic rocks also display high V/Sc (Fig. 7.8)     | <b>Poor-moderate.</b> V and Sc are only present in trace abundances in igneous rocks, and may not be included in whole rock analytical menus.             |
|            | Eu/Eu* |  | <b>Moderate.</b> There is no relationship between Eu/Eu* and any index of alteration (Fig. 7.7)                                                                                                                                                                                            |                         |                              | <b>Poor.</b> As with Sr/Y and La/Yb, this signature may be generated by processes which are not exclusive to porphyry formation.<br><br>In addition, separation between barren and fertile rocks is weak (Fig. 7.8).                                               | <b>Good.</b> Eu, Sm and Gd are routinely included in commercial whole rock geochemistry packages, and are significantly greater than limits of detection. |

Table 7.5. A summary of the usefulness of whole rock and mineral fertility indicators which have been identified in this study, in terms of the criteria outlined in Chapter 1.

Continued on next page.

|         |                                    |  | Robust                                                                                                                                                                                                                                                                 | Abundant/<br>Widespread                                                                                                                                                                                                                                                                                                                                           | Easy to identify<br>/isolate                                                                                                                                                                                                                                                                                                                                                                                           | Contain unequivocal signatures                                                                                                                                                                  | Easy to analyse                                                                                                                                                                                      |
|---------|------------------------------------|--|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Zircon  | Eu/Eu*                             |  | <b>Excellent.</b> Zircon is very resistant to diffusive re-equilibration, even at high temperatures                                                                                                                                                                    | <b>Moderate.</b> Zircon is only found in sufficiently fractionated igneous rocks, and is only present in low volumetric abundances. However, most porphyry intrusions are intermediate to felsic in composition, which is sufficiently fractionated                                                                                                               | <b>Moderate.</b> Extensive analysis of zircon requires mineral separation. However, separation by density is fairly routine.                                                                                                                                                                                                                                                                                           | <b>Moderate.</b> Signatures may also be generated by co-crystallisation with titanite                                                                                                           | <b>Good.</b> High precision analysis of REE in zircon is routine by LA-ICP-MS. However, complex zoning/multi-age zircon can be problematic and grains must first be imaged using cathodoluminescence |
|         | Ce/Ce*                             |  | <b>Excellent.</b> Zircon is very resistant to diffusive re-equilibration, even at high temperatures                                                                                                                                                                    |                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>Good.</b> Ce/Ce* values in barren rock suites show a good separation from fertile suites (Fig. 7.10)                                                                                         | <b>Poor.</b> La and Pr (required to calculate Ce*) are frequently less than LOD for LA-ICP-MS. La and Pr data can also be compromised by accidental analysis of LREE-rich micro-inclusions.          |
|         | Ce <sup>4+</sup> /Ce <sup>3+</sup> |  | <b>Poor.</b> Ce contents resistant to re-equilibration, but this parameter is calculated using whole rock REE data, which are subject to hydrothermal modification. In addition, whole rock REE content may not equal melt REE which is an assumption of the approach. |                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>Poor.</b> Signatures may also be generated by co-crystallisation with titanite, or in any case where melt REE does not equal whole rock REE.                                                 | <b>Poor.</b> REE in zircon mostly easy to analyse, but calculation of this parameter relies on frequently unjustified assumptions. See 'robust' section                                              |
| Apatite | Sr                                 |  | <b>Moderate.</b> Igneous apatite occasionally preserved in weakly altered rocks, but is largely destroyed in sericitic alteration.<br><br>Frequently replaced by hydrothermal apatite.                                                                                 | <b>Good.</b> Apatite is a common primary phase in igneous rocks over a range of SiO <sub>2</sub> contents and is also frequent in hydrothermal alteration assemblages such as potassic, sodic-calcic, and propylitic (e.g. Seedorff et al., 2005)<br><br>However, it may not be present in rocks which are strongly affected by sericitic or argillic alteration. | <b>Good - Moderate.</b> Apatite may be easily identified using a transmitted light microscope due to its high relief and crystal habit.<br><br>In igneous rocks, apatite is euhedral to subhedral, and is present in characteristic assemblages (inter-grown with magnetite, biotite, hornblende).<br><br>Hydrothermal apatite populations are anhedral, may be harder to identify, and may be missed during analysis. | <b>Good.</b> High Sr contents (>750 ppm) are not observed in apatites from barren rocks, but are frequently observed in igneous and hydrothermal apatites associated with porphyry systems      | <b>Good.</b> Sr straightforward to analyse by LA-ICP-MS. Sr contents may also be sufficiently high to analyse by EPMA.                                                                               |
|         | Mn                                 |  |                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>Excellent.</b> High Mn contents combined with Sr (or Eu/Eu*) may provide a near complete distinction between fertile and barren systems                                                      | <b>Good.</b> Mn straightforward to analyse by LA-ICP-MS. Mn contents may also be sufficiently high to analyse by EPMA.                                                                               |
|         | Fe                                 |  |                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>Good.</b> Notwithstanding analytical difficulties, high Fe contents combined with Sr (or Eu/Eu*) may provide a near complete distinction between fertile and barren systems                  | <b>Poor.</b> Fe analyses by LA-ICP-MS can be inaccurate and imprecise. However, Fe contents may be sufficiently high to analyse by EPMA.                                                             |
|         | Pb                                 |  |                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>Good.</b> High Mn contents combined with Sr (or Eu/Eu*) may provide a near complete distinction between fertile and barren systems                                                           | <b>Good.</b> Pb straightforward to analyse by LA-ICP-MS, although it is typically not present at high enough concentration to analyse by EPMA.                                                       |
|         | Eu/Eu*                             |  |                                                                                                                                                                                                                                                                        |                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                                                                                                                                                                                                                                                                                        | <b>Moderate.</b> Significant overlap exists between igneous apatite from barren and fertile rocks.<br><br>Eu/Eu* is useful in hydrothermal apatites where it coincides with high Mn, Pb, or Fe. | <b>Good.</b> Analysis of REE (including Eu, Sm, and Gd) in apatite is routine by LA-ICP-MS                                                                                                           |

## 7.7 Concluding remarks

Igneous rocks, and the zircon and apatite grains within those rocks, contain chemical signatures which may be useful at various scales and stages of exploration. In this chapter, clear criteria are laid out by which the ore forming potential of a magmatic system may be assessed using the chemistry of these minerals and rocks, and these results are integrated into a scheme which may be used in geochemical exploration. The key results of this chapter are:

- Whole rock signatures ( $\text{Sr/Y}$ ,  $\text{La/Yb}$ ,  $\text{Eu/Eu}^*$ ,  $\text{V/Sc}$ ) mostly form due to mid- to deep crustal, hydrous fractional crystallisation of an assemblage with low (but probably not devoid of) plagioclase, and dominated by garnet and amphibole (e.g. Loucks, 2014).
- Modelling indicates that high  $\text{Sr/Y}$  and  $\text{La/Yb}$  ratios ( $> 20$ ) are best explained by garnet fractionation, as opposed to amphibole.
  - Switches from amphibole to garnet fractionation in strongly mineralised porphyry systems occur rapidly, and broadly coincide with the period of mineralisation.
  - Such switches may be triggered by a rapid and significant increase in  $\text{H}_2\text{O}$  at moderate crustal depths, with no increase in pressure required.  $\text{H}_2\text{O}$  influx could be caused by the subduction of hydrous sea-floor anomalies (e.g. ridges, seamounts).
- Whole rock signatures may be susceptible to hydrothermal alteration.
  - $\text{Sr/Y}$  ratios are most strongly affected by alteration.  $\text{La/Yb}$  and  $\text{Eu/Eu}^*$  values are more robust; the effect of alteration on  $\text{V/Sc}$  ratios remains unclear.
- Zircon  $\text{Eu/Eu}^*$  and  $\text{Ce/Ce}^*$  may be useful for distinguishing magmas with high ore-forming potential on a district or regional scale.

- $\text{Eu}/\text{Eu}^*$  in zircon is mostly inherited from melt Eu anomalies, which are controlled by deep fractionation processes, and shallow crystallisation of REE-rich phases like titanite
- $\text{Ce}/\text{Ce}^*$  is largely controlled by redox processes, and is independent of the crystallisation of REE-rich phases.
- Igneous apatite from porphyry systems (including unmineralised co-magmatic volcanic rocks) contains elevated Sr compared to apatites from barren rocks.
- Hydrothermal apatites from porphyry systems have elevated Mn, Fe, and Pb.
  - These may be distinguished from barren S-type igneous apatite (which also contains high Mn and Fe), because the Sr and  $\text{Eu}/\text{Eu}^*$  values are also high in porphyry apatites, and are characteristically low in S-type apatites.
  - These signatures are observed not only at Resolution and Oyu Tolgoi, but in apatites from porphyry systems around the globe and appear to be unique to hydrothermal apatites from porphyry systems.
- Hydrothermal apatites from high grade systems (and from Cu-rich rocks in low grade systems) consistently have  $\text{Mn} > 2000 \text{ ppm}$ ,  $\text{Fe} > 2000 \text{ ppm}$ , and  $\text{Pb} > 2 \text{ ppm}$ , and these values coincide with high Sr ( $> 300 \text{ ppm}$ ) and  $\text{Eu}/\text{Eu}^* (>0.5)$ .



## Chapter 8: Conclusions and future work

### 8.1 Main conclusions

This study aims to assess the geochemistry of rocks and minerals associated with giant, high-grade porphyry Cu deposits, and draw a comparison with barren and weakly mineralised systems. It aims to identify any signatures which are unique to porphyry deposits, especially giant ones. The final aim is to assess whether these geochemical distinctions may be useful in exploration, and to develop a scheme for their use. To this end, the giant porphyry Cu deposits of Oyu Tolgoi (Mongolia) and Resolution (Arizona, USA) were selected for detailed study, and data from global volcanic arcs were used to represent barren systems. At Oyu Tolgoi, a comparison was drawn between the low-grade, lowtonnage Heruga ore body, and the high-grade, high tonnage Hugo Dummett ore body.

As well as whole rock chemistry from igneous rocks associated with these deposits, a detailed characterisation of both zircon and apatite chemistry was also undertaken. The results of these investigations are presented below.

#### 8.1.1 Whole rock geochemistry

Whole rock signatures of magmatic fertility ( $\text{Sr/Y}$  and  $\text{La/Yb} > 20$ ,  $\text{Eu/Eu}^*$  between 0.8 and 1.2,  $\text{V/Sc} > 12$ ) are observed in pre-, syn- and post-mineralisation intrusions at both Resolution and Oyu Tolgoi.

- $\text{Sr/Y}$ ,  $\text{La/Yb}$ ,  $\text{Eu/Eu}^*$  are all controlled by the crystallisation of an assemblage of amphibole  $\pm$  garnet in the mid-deep crust, under oxidising and hydrous conditions. Plagioclase is also likely to crystallise under such conditions, but the effects of plagioclase crystallisation on these ratios is likely to be overridden by the effects of amphibole and garnet.

- At Oyu Tolgoi, the switch between amphibole-dominated and garnet-dominated fractionation is preserved in successive intrusions straddling the period of mineralisation. This observation appears to be common to other large porphyry systems (including those in Central and Northern Chile), where switches occur over <2 Myr, and may most easily be accounted for by ephemeral increases in magmatic H<sub>2</sub>O content. Such switches may be triggered by the subduction of hydrous seafloor anomalies (e.g. sea mounts or ridges), which provide the requisite compressive tectonics and increased H<sub>2</sub>O flux over narrow length and timescales.
- V/Sc values are extremely high at both deposits, with the highest values occurring in altered porphyry rocks. Even the lowest values, generally in weakly altered intrusions and nearby volcanics, are exceptionally higher than has previously reported in porphyry systems.
- These signatures are variably susceptible to hydrothermal alteration. Sr/Y values in particular decrease strongly as a function of alteration index (i.e. with increasing feldspar destruction during sericitic alteration). V/Sc values are also higher in sericitically altered rocks at Resolution. La/Yb and Eu/Eu\* are more robust, because REE are hosted in more robust alteration-resistant minerals in granitic rocks.
- Such signatures are not unique to rocks associated with porphyry systems, and have been found associated with ostensibly barren volcanic rocks. There also appears to be no correlation between deposit size or grade and any of these parameters. This highlights the fact that the generation of ‘fertile’ melts is insufficient to generate porphyry mineralisation.
- Given that such signatures are generated by deep crustal processes, and affect a broad area of an arc over a protracted period of time (including rocks with no

mineralisation), and are potentially altered by whole rock geochemistry, these signatures may be used during regional-scale exploration to identify prospective magmatic epochs and arc segments.

#### 8.1.2 Zircon chemistry

Zircons from both Resolution and Oyu Tolgoi contain elevated  $\text{Eu}/\text{Eu}^*$ ,  $\text{Ce}/\text{Ce}^*$  and  $\text{Ce}^{4+}/\text{Ce}^{3+}$  compared to zircons from barren rocks.

- At Resolution, a clear fractionation trend is seen whereby the most primitive zircons (low Hf) have the highest  $\text{Eu}/\text{Eu}^*$ , which then decreases during progressive fractionation. The fractionation ‘trajectory’ of zircons in  $\text{Eu}/\text{Eu}^*$  vs Hf space is different from barren and fertile rocks. Zircon from barren rocks (e.g. the Proterozoic inherited cores) reach low  $\text{Eu}/\text{Eu}^*$  at lower Hf values. Zircons from the Resolution intrusions maintain higher  $\text{Eu}/\text{Eu}^*$  to higher Hf values. This is in accord with observations from other porphyry systems.
- At Oyu Tolgoi, zircon geochemistry is bimodal, with one group containing lower Ta, lower Ta/Nb ratios, and higher  $\text{Eu}/\text{Eu}^*$ ,  $\text{Ce}^{4+}/\text{Ce}^{3+}$ , and Yb/Gd than either the other geochemical group, or other zircons from barren rocks. This ‘low-Ta’ group is typically found in the rims of zircons, and is commonly associated with micro-inclusions of titanite.
  - Modelling results suggest that the divergent geochemistry of these two groups of zircons at Oyu Tolgoi can be replicated by the co-crystallisation of vanishingly small amounts of titanite (~0.3 vol. %).
  - This has the effect of increasing  $\text{Eu}/\text{Eu}^*$  by removing Sm and Gd from the melt at a greater rate than Eu, due to the unequal partitioning of these elements into titanite. Thus,  $\text{Eu}/\text{Eu}^*$  in zircon may be drastically affected by processes

unrelated to changes in oxidation state, and as a result the usefulness of this parameter in determining melt redox is compromised.

- $\text{Ce}^{4+}/\text{Ce}^{3+}$  ratios are similarly strongly affected by the co-crystallisation of titanite, as this parameter is calculated using the assumption that whole rock geochemistry is equivalent to melt chemistry at the time of zircon crystallisation. This assumption is invalid if titanite has crystallised, but not been fractionated. The effects of titanite crystallisation on melt chemistry may be subtle and difficult to identify, especially if titanite has not been removed from the melt.
- $\text{Ce}/\text{Ce}^*$  may represent the most robust proxy for redox conditions in zircon. However, there exist practical problems in determining this parameter, because it relies on knowing the concentration of La and Pr, both of which are often below the limit of detection, and affected by small inclusions of LREE-bearing phases in zircon. Another formulation for  $\text{Ce}/\text{Ce}^*$  is presented which uses Nd and Sm, and which avoids the problems present for La and Pr.
- In spite of these observations, zircon is still considered a useful tool in the assessment of porphyry deposit fertility, because there exists an empirical relationship between fertile systems and high  $\text{Eu}/\text{Eu}^*$  and  $\text{Ce}/\text{Ce}^*$ .
  - It is suggested that two filtering parameters must be applied to zircon data when assessing a magmatic suite for porphyry fertility. First, only zircons with  $\text{Hf} > 10,000$  may be used, to remove the potential for primitive zircons with high  $\text{Eu}/\text{Eu}^*$  to lead to spurious conclusions. Second, only zircons with  $\text{Ta} > 0.2$  may be considered, to remove the potential effects of titanite control.
- In exploration, zircon is useful for highlighting the magmatic epochs and arc segments which are most prospective for porphyry Cu mineralisation. The ability to

accurately date zircon grains is especially useful, and the identification of prospective time periods may feed back into an exploration program to provide additional focus. However, the absence of any difference in zircon chemistry between low-grade/tonnage and high-grade/tonnage deposits (e.g. Heruga and Hugo Dummett) means, as with whole rock geochemistry, that zircon chemistry may only be useful as a blunt tool for exploration, and may lack the sensitivity required of an excellent mineral indicator.

### 8.1.3 Apatite chemistry

Apatite provides the most interesting results for the assessment of porphyry fertility, with hydrothermal apatites from both Oyu Tolgoi, Resolution, and a number of other porphyry systems containing signatures which appear to be unique to porphyry deposits, and may show some sensitivity to rock Cu grade.

- Hydrothermal apatites are recognised in thin section due to their anhedral habits, their close relationship with sulphides, and/or in assemblages replacing mafic phases, and typically have dull cathodoluminescence characteristics. At Oyu Tolgoi, the La/Yb ratio is useful in distinguishing igneous from hydrothermal apatite ( $\text{La/Yb} > 5$  for igneous apatite), whereas the distinction is likely less clear at Resolution.
- Igneous apatites from barren rocks seldom contain Sr values in excess of 750, whereas igneous apatites from Oyu Tolgoi and Resolution (including in associated, unmineralised volcanic rocks) may contain Sr values well in excess of 750 ppm. Similarly, Eu/Eu\* values are typically higher in igneous apatite from porphyry systems ( $> 0.5$ ). Both of these signatures are inherited from the Sr- and Eu-rich melts, which are a key indicator of melt fertility. They are also partly controlled by the suppression of plagioclase crystallisation with respect to apatite crystallisation, due to high magmatic H<sub>2</sub>O content.

- Hydrothermal apatites also show high Sr values, which are inherited from Sr-rich fluids, which themselves generate this character from Sr-rich melts. Hydrothermal apatites frequently show high Sr in conjunction with elevated values for other divalent cations (Mn, Fe, and Pb). Although high Mn, Fe, and Pb may also be observed in igneous apatites from S-type granitoids, they are accompanied by extremely low Sr (<100 ppm). Thus, plots of Mn (or Fe, or Pb) vs. Sr show a near perfect split between barren igneous apatite, and porphyry-related hydrothermal apatite.
  - Intriguingly, hydrothermal apatites from the high-grade Hugo Dummett deposit generally have much higher Mn, Fe, and Pb than the lower grade Hugo Dummett deposit. This is also seen in apatites from rocks with varying Cu content in La Granja porphyry deposit.
  - Given the correlation between Cl and Mn, Fe, and Pb, it is thought that hydrothermal apatite Mn, Fe, and Pb is reflecting elevated concentrations of these elements in highly saline fluids which also contain high Cu. Apatite deposited with Cu sulphides reflect the nature of the fluids which generated mineralisation. Fluids with high Mn, Fe and Cu have been observed in a range of mineralised systems.
- Apatite has great potential as a tool for assessing the fertility of both igneous and hydrothermal systems.

## **8.2 Recommendations for future work**

### **8.2.1 The role of Mn, Fe (and Cu) rich fluids in porphyry formation**

The identification of Mn-rich fluids associated with large, high grade porphyry systems has implications for exploration that extend beyond the scope of this study. If fluids associated with high grade mineralisation are especially enriched in Mn, Fe, and Pb, and the effect of this is seen in hydrothermal apatite from the potassic core of porphyry systems, how

might this affect the chemistry of hydrothermal minerals in more distal alteration zones? Mn-, Fe-, and Pb-rich fluids may advect these metals away from the core of the system, and deposit them upon interaction with wall rocks and meteoric fluids in the propylitic halo at some distance from the ore body. A particularly receptive mineral for this would be chlorite, which readily incorporates Mn into its structure (Deer et al., 1992). Epidote also readily accepts Mn into its structure. The question may be posed - are chlorite and epidote from the propylitic halo of Hugo Dummett more enriched in Mn (Fe, Pb) than chlorite from the propylitic halo of Heruga? Furthermore, does this apply to other high- and low grade systems? Wilkinson et al. (2015) briefly note the preliminary results of such an investigation, which suggest that Mn concentration in chlorite from the propylitic halo may indeed reflect the metal budget of the systems with which they are associated. Apatite is also a common phase in the propylitic environment, and its chemistry may reflect the chemistry of fluids distal to large porphyry ore bodies. More work is required to further constrain the sources and sinks of Mn in the hydrothermal alteration assemblages of high grade porphyry systems.

#### 8.2.2 Apatite as a measure of redox

To what extent does the Mn content of hydrothermal apatite reflect the oxidation state of the fluids with which it is in equilibrium? How sensitive is Eu/Eu\* or Ce/Ce\* in apatite to redox conditions?

#### 8.2.3 False positives in whole rock geochemistry fertility indicators

Several examples have been highlighted in this study of ostensibly barren systems with elevated whole rock fertility indicators. For example, the Quaternary volcanic rocks of central Chile (e.g. Cerro Llullaillaco, Cerro Abra Grande). Another example is the Sr-Ba rich granites of northwest Scotland (e.g. the Strontian Granite). These barren systems require further investigation, to assess the following questions.

- Are these systems truly barren? Or is mineralisation actually associated with these deposits, but remains undiscovered?
- How are the signatures of fertility generated in these rocks? Are these signatures generated in a different way to how these signatures are generated in porphyry systems?
- Are there any other geochemical criteria by which these (ostensibly) barren systems may be distinguished from fertile systems with the same signatures of fertility?
- To what extent are the whole rock signatures of fertility in these rocks reflected in the mineral chemistry (e.g. apatite and zircon chemistry)?

#### 8.2.4 The generation of garnet signatures in arc rocks

Given the importance of the crystallisation of (or equilibration with) garnet during the formation of fertile magmas, the mechanisms by which garnet signatures may be generated should receive further investigation. Specifically, is it possible to distinguish the signatures of igneous garnet fractionation from equilibration with (or partial melting of) garnetiferous lower crust?

One possible way to test this is to look at igneous rocks which contain garnet as a phenocryst. These are extremely rare, and are commonly associated with melts with unusual chemistry (e.g. elevated Mn or Al). Examples of typical calc-alkaline volcanic rocks with garnet phenocrysts may provide a means with which to investigate deep crustal fractionation.



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