

Apatite in Porphyry Systems and its Applications in Mineral Exploration

A thesis submitted for the degree of Doctor of Philosophy

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Emily Brugge
September 2020

Abstract

New techniques in exploration geochemistry are required to reduce the increasing amount of time and resources consumed during exploration of porphyry deposits. This can be achieved through developing our understanding of the processes that result in the formation of mineralised systems, and any associated geochemical signatures which could be recorded in mineral indicators. Apatite chemistry can provide a detailed perspective into porphyry system formation. However, the diversity of apatite occurrence and composition, in addition to its susceptibility to metasomatism, presents added complexity in its application as a mineral indicator.

Here the La Granja Cu-Mo porphyry was used as a case study in which the occurrence and composition of apatite from porphyry systems could be investigated. The composition of hydrothermal apatite varies greatly between those from least fractionated, magmatic-derived fluids and distinct sericitic-associated apatite. Compositions of magmatic apatite closely reflect the magma evolution including melt differentiation and the behaviour of magmatic volatiles.

Apatite inclusions in zircon provide a means to examine the halogen and sulfur content of a melt. At La Granja halogen ratios, together with additional textural and zircon geochemistry evidence, indicate that the late-stage porphyries crystallised rapidly from fractionated, volatile-rich melts, which alludes to the abrupt termination of the system. The highest concentrations of sulfur were observed within apatite inclusions from the mineralised intrusions. The implied increase in sulfur within the melt occurs after the start of porphyry emplacement and may be an important mechanism in the development of mineralisation.

Using the conclusions from this study as a framework it has been possible to develop a series of multivariate discrimination tools effective for exploration. These results demonstrate that studies of apatite chemistry can not only help increase our understanding of porphyry formation, but with careful application can be utilised to aid the exploration of mineralised porphyry systems.

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Abbreviations

Compositions

REE Rare earth elements
LREE Light rare earth elements
MREE Middle rare earth elements
HREE Heavy rare earth elements

Analytical

SEM Scanning electron microscope
EPMA Electron probe micro-analysis
LA-ICP-MS Laser ablation inductively-coupled-plasma mass spectrometry
EDS Energy dispersive spectrum
WDS Wavelength dispersive X-ray spectrometers
BSE Back scatter electron
CL Cathodoluminescence
CT Computed tomography

Dimensions

Ma Million years ago
Myr Million years
μm Microns
apfu. Atoms per formula unit
wt. % Weight percent

ppm Parts per million
kV kilo-volts
nA Nano-amps
Hz Hertz
f.O₂ Oxygen fugacity
QMF Quartz-magnetite-fayalite buffer
J cm⁻² Joules/ cm²
AST Apatite saturation temperature

Mineral abbreviations

Ap Apatite
Fap Fluorapatite
ClAp Chlorapatite
OHAp Hydroxyapatite
Ap_{incl} Apatite inclusions
Ap_{mtrx} Matrix apatite
Ap_{vein} Vein apatite
Qtz Quartz
Bt Biotite
Plg Plagioclase
K-fld K-feldspar
Epi Epidote
Chl Chlorite
Amp Amphibole
Zrc Zircon
Mnz Monazite
Ccl Calcite

Ttn Titanite
Py Pyrite
Bn Bornite
Ccp Chalcopyrite
Cc Chalcocite
Po Pyrrhotite
Rt Rutile

Unit lithologies

AND Andesite
DIO Diorite
GRANO Granodiorite
EQP_{PB} Early quartz porphyry
DP_{PB} Dacite porphyry
EDP_{PB} Early dacite porphyry
DIOP Diorite porphyry
LQP_{PB} Late quartz porphyry
LDP_{PB} Late dacite porphyry
DP_M Dacite porphyry
EQP_M Early quartz porphyry
EDP_M Early dacite porphyry
LQP1_M Late quartz porphyry
LQP2_M Late quartz porphyry
RH Rhyodacite

Chapter 1: Introduction

1.1 Research motivation

Porphyry deposits are large (100 million to 1 billion tonnes), low grade (0.5 – 1.5 % Cu) magmatic-hydrothermal ore deposits. They are classified by the ore-metals they host, but are dominated by Cu $\pm$ Mo $\pm$ Au systems (Sillitoe 2010). Porphyry systems are vital for the future usage of copper and account for the majority of the world's supply (USGS Mineral commodity summary 2020). Current forecasts predict global demand for Cu to almost double by 2050 (Elshkak et al. 2018). This is a result of increased demand from new technologies, especially in the energy and transport sectors (Van de Voet et al. 2018). However, average ore grades of porphyry deposits are declining (Mudd et al. 2009; Crowson 2012; Rötzer & Schmidt 2020), and with 30 % of Cu resources held in 1 % of deposits (USGS report 2014), a drop in ore grade could have a significant output on global supplies. In addition, finding new deposits has evidently become more of a challenge, as exploration expenditure has outstripped new discoveries over the last 10 years (Schodde 2017).

These trends in supply and demand necessitate the development of new methods to aid porphyry exploration. This includes both locating porphyry systems and having the ability to predict the economic validity of projects earlier in the exploration stage in order to save time, energy and resources. Current geochemical techniques are based on research and observations of porphyry systems, and contribute to our current understanding of how a porphyry deposit forms. These include interrogation of bulk rock geochemistry, which can be employed to detect compositions typically associated with porphyry intrusions (i.e. Richards & Kerrich 2007; Loucks 2014; Halley 2020) and therefore identifying potentially mineralised arcs. On a more district scale, vectoring towards the concealed centres of porphyry systems has been achieved using minerals present within the alteration halo that surrounds these centres (Wilkinson et al. 2015; Cooke et al. 2017). More recently, research into the mineral geochemistry of porphyry indicator minerals has highlighted several minerals of interest including zircon, magnetite and apatite (Cooke et al. 2020). Porphyry indicator minerals are species which, either through porphyry-related magmatic or hydrothermal occurrence such as association with mineralisation or alteration, imply the potential for a porphyry system to exist (Cooke 2020; Belousova et al. 2002).

Apatite has been suggested and explored as a porphyry indicator mineral (Mao et al. 2016; Rukhlov et al. 2016; Waychunas 2002; Belousova et al. 2002; Loader 2017a; Cooke et al. 2020). Apatite could be applied as an indicator mineral from samples of stream sediments and whole rock, as its occurrence is widespread, it is relatively resistant to weathering and it is easily identified and processed into grain separates (Bouzari et al. 2016). Apatite, along with titanite, magnetite and zircon, is one of the most common accessory phases within porphyry rocks (Seedorff et al. 2005). It can be magmatic in origin, crystallising in the upper crust, but is also precipitated from hydrothermal fluids within veins or host rocks. This makes apatite more attractive than purely magmatic- or hydrothermal-occurring minerals, as its geochemistry has the capacity to track the multistep and complex formation of porphyry systems. In addition, the wide occurrence of

apatite can inform our understanding on a range of controls on porphyry formation including:

- What are the key differences between porphyry-related and non-porphyry-related arc magmas?
- What are the key processes occurring over the lifespan of porphyry systems; for example what controls the mineralisation of some porphyry units, and what terminates the formation of a porphyry deposits?
- What are the key hydrothermal fluid compositions and which are most commonly associated with mineralisation?

1.2 Literature review: formation of porphyry deposits

Porphyry deposits are magmatic-hydrothermal systems formed from the superposition of multiple intrusions predominantly above subduction zones (Henley et al. 2015; Fig. 1.1). The intrusions, or porphyry stocks, are emplaced within the upper crust and are each mineralised to different degrees (Sillitoe 2010). Mineralisation is present as sulfide and oxide ore minerals and is initially precipitated as hypogene sulfides from exsolved high temperature fluids (Seedorff et al. 2005). Secondary supergene processes can concentrate these minerals and form metal oxides towards the top of the system (Sillitoe 2010; Richards 2013). The hydrothermal portion of the deposit, which transports, concentrates and precipitates the metals is also responsible for the formation of large alteration footprints which are diagnostic to porphyry deposits. These fluids are present in large volumes and interact with the host rock to produce large areas of chemically-altered rocks (Seedorff et al. 2005).

Porphyry magma is typically generated within magmatic arcs (Sillitoe 2010; Fig. 1.1); these may still be active, as in the case of south-east Asia and the west coast of America, or extinct. A number of systems have also formed in post-subduction collisional or extensional regimes (Richards 2009). Within the arc, porphyry deposits cluster regionally over hundreds of kilometres, forming mineralised segments. Their distribution is thought to be controlled by geodynamic stresses lasting between 5 - 20 Myr (Loucks 2014; Sillitoe 2010). Over time these may form linear trends laterally to the arc as a result of a gradually shifting magmatic centre in the overriding plate (Sillitoe 1972; Sillitoe 2010; Richards 2016). Despite these spatial constraints, exploration for new deposits remains a challenge. Large, high-grade porphyry deposits are rare; sub-economic or barren porphyry systems are most common (Richards 2016).

1.2.1 Evolution of magma within the crust

Hydrous, basaltic magma produced in the subduction zone (Fig. 1.1) stalls in the lower crust, forming “MASH” (melting, assimilation, storage, and homogenisation) or deep crustal hot zones (Fig. 1.2). Multiple injections of the mafic melt can provide thermal stability for the magmas in the MASH zone and lead to partial melting of the surrounding lower crust (Annen et al. 2006). Assimilation may also increase the metal content of the melt if the lower crust contains accumulations of earlier metal-rich magmas (Lee et al. 2012; Wilkinson 2013). In addition, the replenishment of the magma enriches it in H₂O and other volatiles, and raises its oxidation state (Annen et al. 2006; Loucks 2014) and the crystallisation of mafic (and especially anhydrous) cumulates can also increase the SiO₂ and water

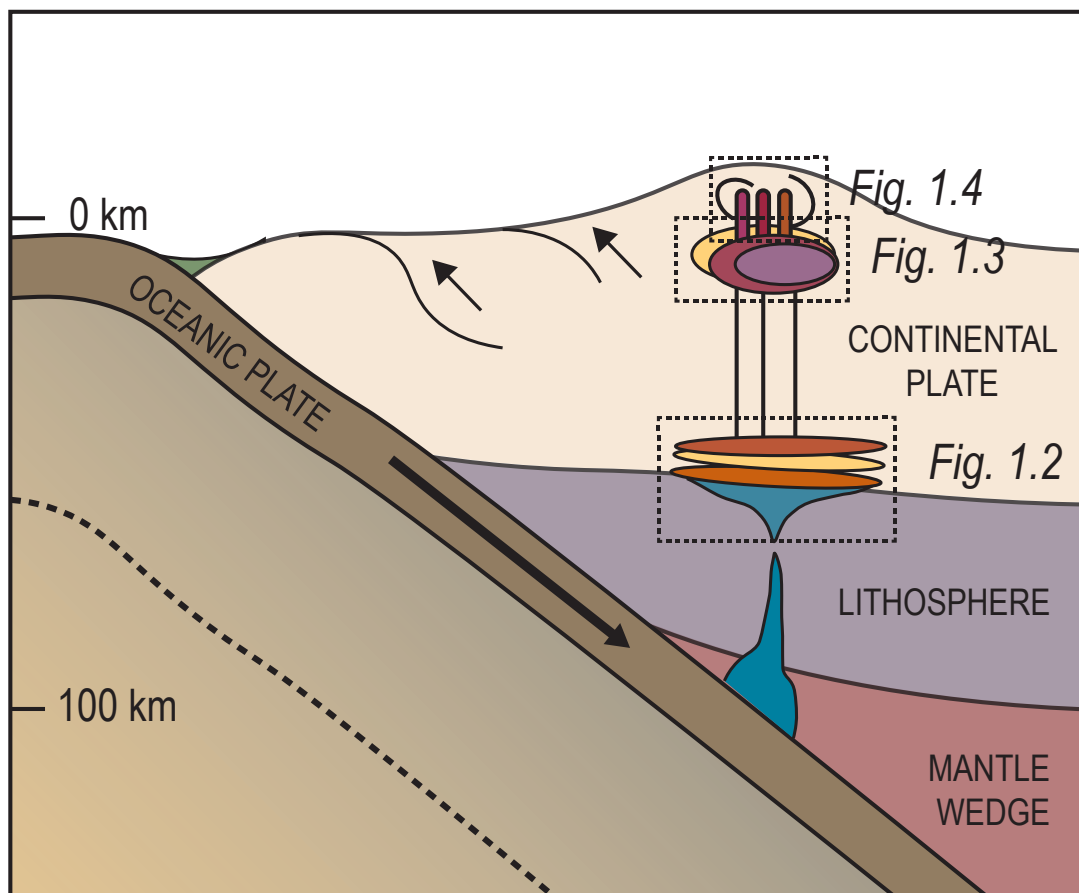


Figure 1.1 The main stages in the evolution of magma leading to the formation of a porphyry deposit. Modified from Winter (2001). Mantle wedge melting is aided by volatiles derived from the subducted plate. This melt travels upwards to the lower crust where it stalls producing sills of magma and a zone of melting, assimilation, storage and homogenisation (MASH; Fig. 1.2). Eventually some melt will reach the upper crust where it is emplaced as plutons (Fig. 1.3). More volatile-rich melts may go on to form porphyry intrusions within magmatic-hydrothermal systems (Fig. 1.4).

content of the residual melt. Some authors believe that, due to differentiation and assimilation of the host rock, the crustal hot zone is where the distinct geochemical signature of porphyry systems originates (e.g. Loucks 2014; Richards & Kerrich 2007; Kay et al. 2005).

The controls on magma ascent are not well understood, but most probably involve the buoyancy of the magma in the dynamic tectonic setting. Once fractionated to a more silicic (and more buoyant) composition, the melt continues to rise. A rapid ascent of the magma may help retain sufficient quantities of metals for porphyry deposit formation (Jenner 2017; Audétat & Simon 2012). The magma ascending from the crustal hot zone begins crystallisation at 7 - 8 km depth following volatile saturation, or 'boiling' of initially CO₂-rich fluids, and pools again between 4 - 10 km depth forming an andesitic-dacitic magma chamber or mush zone which may be compositionally stratified (Richards 2003; Annen et al. 2006; Sillitoe 2010; Audétat & Simon 2012; Wilkinson 2013; Fig. 1.1). Andesitic magmas are the most common arc magma composition observed at the surface, and are often associated with porphyry deposits. These may form in the lower crustal hot zone as described above; however, their formation from magma mixing in upper crustal magma chambers explains the commonly observed disequilibrium mineral assemblages (Audétat & Simon 2012).

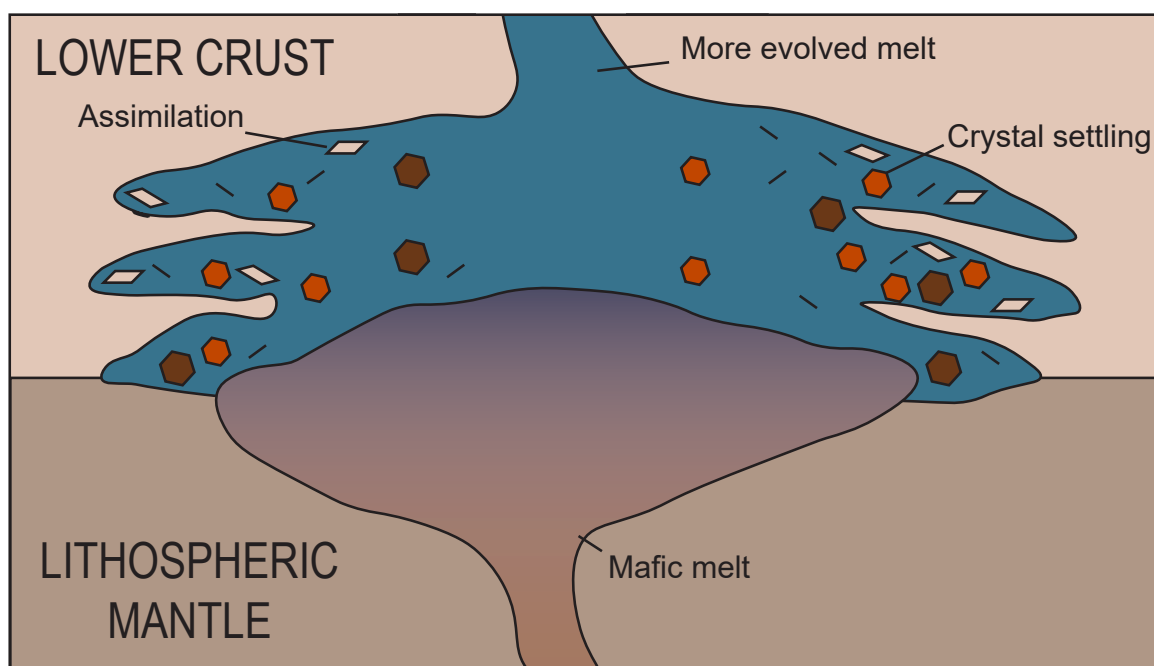


Figure 1.2 Magma stalling in the lithosphere forming MASH (melting, assimilation, storage and homogenisation) zones where it equilibrates to the lower crust. It is thought that the magmatic processes occurring at this point, such as crystal fractionation and assimilation, may be responsible for some of the geochemical characteristics associated with porphyry magmas. Modified from Wilkinson (2013).

1.2.2 Parental magma chamber

Porphyry stocks are emplaced within the shallow crust in short, discrete pulses channelling metal-rich fluids from the underlying magma chamber to the shallow crust (Richards 2016; Sillitoe 1972; Fig. 1.3). The magma bodies below porphyry intrusions assemble over millions of years and are stratified with a typical lifespan of 0.1 - 5 Myr (Wilkinson 2013). Given the size of the magma chambers, their long lifespan suggest that they are episodically replenished with fresh magma (Annen et al. 2006). The range of compositions observed, coupled with evidence of magma mixing, suggest the injected magma is often of a more mafic composition (Audétat & Simon 2012; Rohrlach & Loucks 2005). In addition, high-grade deposits can contain anomalous volumes of sulfur (1 GT; Chambefort et al. 2008) and metals (200 MT Cu, 2.5 MT Mo, 2500 T Au; Cooke & Hollings 2005), with more sulfur in their system than can have originated from the magma chamber (Blundy et al. 2015; Wallace 2005). Therefore it is proposed that an injection of mafic magma into the felsic magma chamber could act as a (secondary) sulfur source as well as contributing to the metal content of the system (Hattori & Keith 2001; Sillitoe 2010). The mixing of silicic and mafic magmas within the porphyry intrusions suggest that injections from an underlying mafic magma chamber may also play a more direct role in porphyry deposit formation (Hattori & Keith 2001; Buret et al. 2016), with the injection of hotter, more volatile rich magma triggering the intrusion of the porphyry dykes (Sillitoe 2010; Buret et al. 2017; Richards 2003 etc.).

1.2.3 Porphyry emplacement

The mineralised stocks are emplaced as pipe-like dykes which are under 1 km in diameter and can extend over 4 km vertically (Sillitoe 2010; Seedorff et al. 2005; Fig. 1.3). They are typically of I-type affinity and range from dioritic to granitic in composition (over 56 wt. % SiO_2). In general,

Mo porphyries are more felsic, and Au porphyries more mafic, than their Cu counterparts (Sillitoe 2010). Porphyry deposits should be regarded as magmatic complexes, as they comprise multiple intrusions that pre- and post-date the mineralised intrusions (Seedorff et al. 2005; Richards 2013; Sillitoe 2010; Fig. 1.2). The mineralised porphyry stocks are believed to be rapidly intruded and volatile-rich, their ascent triggered by destabilising conditions such as the injection of fresh magma or depressurisation of the magma chamber (Richards 2016). Magmatic temperature in excess of 800 °C would cause volatile-rich magma to expand adiabatically forming magmatic vapour plumes or porphyry dykes (Henley & McNabb 1987). The porphyritic texture of the intrusions, together with their aplitic groundmass, suggest that crystallisation commenced within the underlying magma chamber and was shortly followed by rapid crystallisation during forced ascent and pressure-quenching of the magma in the overlying porphyry pipes and dykes (Seedorff et al. 2005). Dating of deposits and SO₂ flux calculations suggest ore formation is a result of one or two events occurring over a 100-100,000 year timescale (Henley et al. 2015; Richards 2016; Mercer et al. 2015; Buret et al. 2016).

1.2.4 Fluid exsolution

The intrusion of a magmatic body carrying volatiles and copper alone will not produce economic concentrations of minerals. Magmatic-derived fluids are crucial in partitioning copper from the melt and concentrating it into sulfides to form ore deposits (Hedenquist & Lowenstern 1994; Sillitoe 2010; Henley et al. 2015; Blundy et al. 2015). Volatile saturation and exsolution are primary controlled by decompression on ascent (Annen et al. 2006). Any fluids exsolved at depth within the crust may lead to metal depletion of the melt unless it is focused and channelled toward a suitable depositional site (Wilkinson 2013). The fluids exsolved at emplacement depth are typically supercritical; however, in shallow parts of the deposit, as the fluid cools and decompresses, it will separate into two phases: a denser, high salinity (35-70 wt. % NaCl) brine enriched in Na, K and Fe; and a less dense, water-rich vapour phase containing SO₂, H₂S, CO₂, HCl and HF (Wilkinson 2013; Sillitoe 2010; Richards 2013).

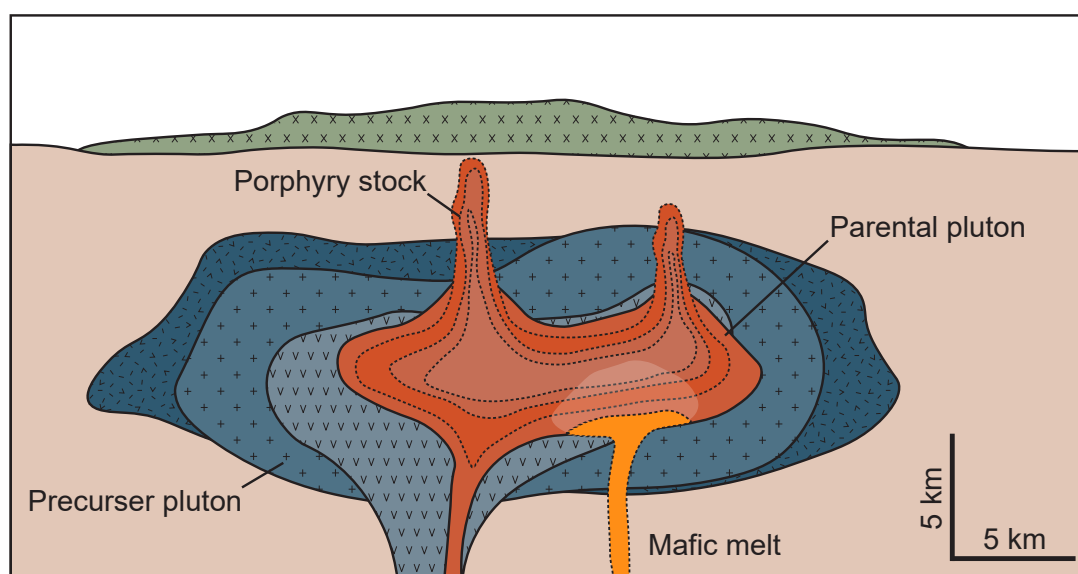


Figure 1.3 Porphyry stocks form from the discrete emplacement of narrow magmatic bodies fed from a larger underlying magma. These parental chambers are thought to be stratified and are also the source of the high temperature fluids. There is textural evidence for mixing with more mafic magma which may provide additional sources of S and metals. Modified from Sillitoe (2010).

Hydrothermal alteration

Porphyry deposits are characterised by the concentric sequence of alteration zones that surround the intrusions (Fig. 1.4), produced by the metasomatic action of magmatic–hydrothermal fluids. Although the intrusive volumes may constitute only about 4 km³, over 10 km³ of host rock may be hydrothermally altered (Seedorff et al. 2005). The overall geometry of a deposit is determined by the number and distribution of the intrusions and the effect of the hydrothermal fluid on the host rock which is controlled by the lithology and presence of structural features (Lowell & Guilbert 1970). The differences between the alteration zones are due to changes in the fluids as they rise and cool through the host rock. High temperature, potassic alteration, dominated by biotite and K-feldspar assemblages (Na, Ca → K) forms proximal to the source of the hydrothermal fluids. With increasing distance from the source, the hydrothermal fluids decrease in temperature and pressure. In addition, there is an increasing amount of rock buffering which, due to acid dissociation, increases the acidity and the intensity of alteration (Sillitoe 2010). Vertically above porphyry systems, low temperature acidic sericitic alteration takes over, comprising chlorite, epidote (in the transitional chlorite-sericite zone), and dominated by muscovite (Ca, Na, SiO₂ → K⁺, H⁺). Overlying this, often outcropping at the surface, is clay-bearing advanced argillic alteration (Ca, Na, K, Mg, Fe → H⁺). The surface expressions of porphyries may be S-rich volcanic fumaroles emitting over 85% H₂O in addition to CO₂, S, SO₂, H₂S and minor HCl (Henley 2013). On the peripherals of porphyry deposits fluids neutralise to low temperature propylitic alteration (Ca, Na → H₂O, CO₂, S, H⁺; Lowell & Guilbert 1970; Seedorff et al. 2005; Barton et al. 1991; Pacey 2016).

Mineralisation

Porphyry copper mineralisation is composed of Cu-Fe sulfides associated with anhydrite within potassically- and sericitically-altered host rock. The host rock is intensity-fractured during magma crystallisation which accommodates the movement of hydrothermal fluids released from the magmas and the formation of mineralised stockwork veins (Seedorff et al. 2005; Henley et al. 2015; Sillitoe 2010). In porphyry models, ore-metals are typically assumed to be transported within the brine phase as they complex with Cl ligands. The melt-fluid partition coefficients for Cu and Au increase with Cl melt content; however, melt-compatible Mo shows little variation in partitioning between melt and fluid as a function of Cl and is instead enriched in more fractionated, granitic rocks. It has also been demonstrated that Cu can also partition, in smaller quantities, into the vapour phase probably via complexing with S-species (Simon et al. 2006; Tattitch et al. 2015; Audétat & Simon 2012; Audétat et al. 2008). The precipitation of Au in porphyry deposits is similar to that of Cu; however, Mo typically precipitates at a greater depth and/or later than Cu-Au mineralisation due to lower solubility in aqueous fluids and potentially progressive increase in the Mo/Cu ratio of late stage melts (Sillitoe 2010).

The sulfides associated with the mineralisation are also zoned around the porphyry system (Fig. 1.4). The early potassic alteration is predominantly associated with Cu-Fe sulfides chalcopyrite and bornite. This transitions out to pyrite-dominated sulfide assemblages in the more distal propylitic alteration. As the temperature of the fluid decreases to between 500-300°C, precipitation of Cu-Fe

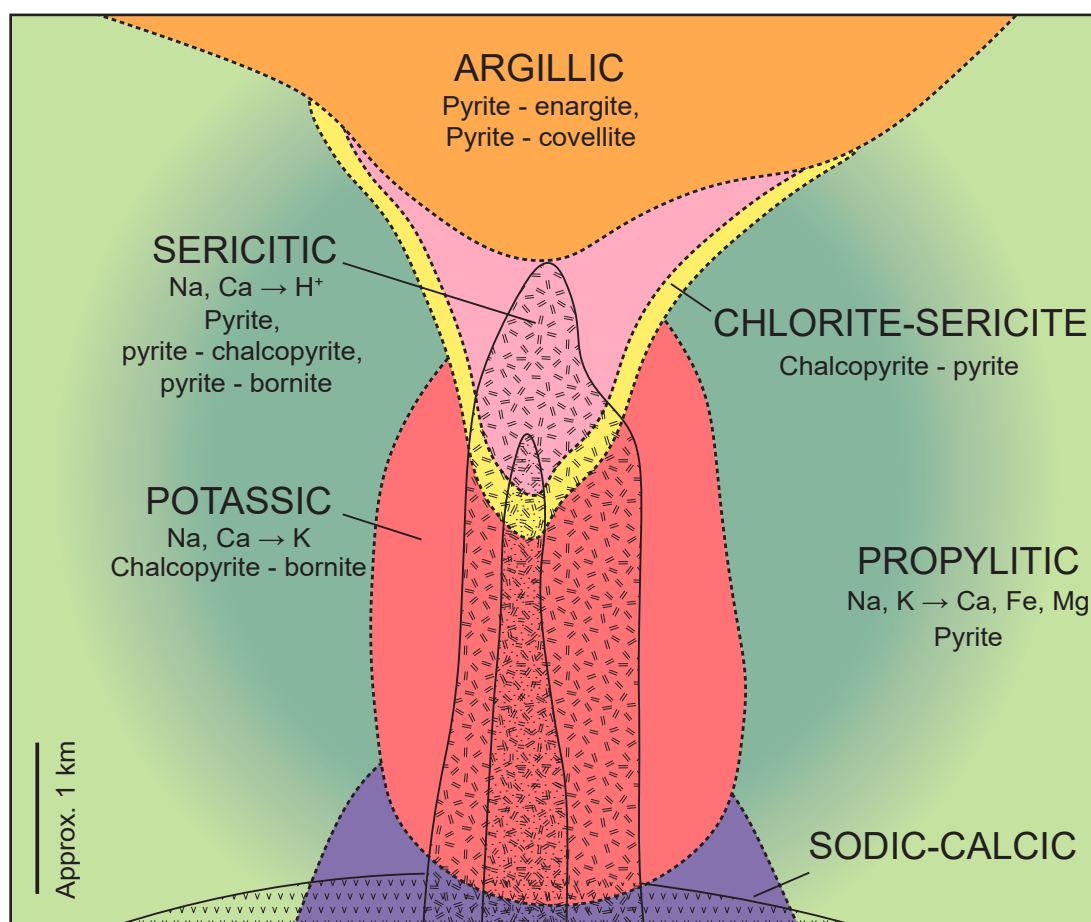


Figure 1.4 Schematic of hydrothermal alteration and mineralisation around a porphyry intrusion. Early sodic-calcic alteration is observed at the base of the porphyry intrusions. This is overprinted by potassic alteration which grades out laterally to propylitic alteration. Sericitic and argillic alteration are observed at the roof of the system, with sericitic alteration overprinting large volumes of potassic alteration. Shallow intrusions may be expressed at the surface by an advanced argillic lithocap or active fumaroles. Modified from Sillitoe (2010).

sulfides occurs as a result of fluid-rock reactions, changes in pH, in addition to a decrease in temperature which lowers metal solubility. The sericitic zone can also contain Cu-Fe sulfide but typically larger quantities of pyrite. The argillic alteration zone contains high sulfidation-state mineralisation assemblages including enargite and covellite (Sillitoe 2010; Seedorff et al. 2005).

Most economic deposits are believed to be formed from multiple events and fluid flows, with mineralisation occurring in rapid, episodic events (Richards 2013; Sillitoe 2010). The formation of sub-economic deposits may be the result of an insufficient volume or duration of arc magmatism, insufficient fluid in dry magmas, or reducing conditions in the mantle source or in evolving magmas leading to sulfide fractionation prior to metal concentration by exsolving fluids. In addition if hydrothermal fluids are not focused upon release, as a result of impermeable or overly-permeable host rock, then sufficient concentrations of precipitated sulfides may not be attained (Richards 2013, 2016).

1.3 Aims, objectives and thesis outline

This study aims to produce a comprehensive study of apatite occurrence and compositional variation within the porphyry environment. In doing so, the potential of apatite as an indicator mineral for use

in porphyry exploration can be assessed, and any conclusions will aid the development of such a tool by statistical learning algorithms. To achieve this, the study is broken down into several objectives which will be addressed in turn within the chapters of this study:

- Develop a methodology for minor and trace-element analysis of apatite with particular focus on collecting large volumes of analyses – *Chapter 3*
- Assess the effects of alteration and diffusion on apatite and suggest a suitable method to account for this in datasets – *Chapter 5*
- Undertake a detailed study of the occurrence of apatite within porphyry systems. Describe occurrence and texture context of apatite and link textural observations to trace-element composition. Then, using knowledge of apatite formation and porphyry condition, suggest what is controlling the compositional variety - *Chapters 6-8*
- Produce a well constrained, large dataset of apatite geochemistry from a global sample set. Then, using this data, build a predictive model using statistical learning techniques. The model should be able to classify apatite composition in a way that would be beneficial to porphyry exploration - *Chapter 9*

In addition, a detailed geology study of the main site used in thesis will be produced in *Chapter 4* on which inferences of the apatite composition will be based.

Chapter 2: Apatite literature review

Apatite, as $\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})$, is a calcium phosphate subgroup of the larger apatite supergroup. It is the tenth most abundant mineral on Earth (Hughes & Rakovan 2015) and is found in most rock types, usually as an accessory mineral (1 vol%; Webster & Piccoli 2015). A large number of elements can be incorporated into the apatite structure to produce a wide variety of chemical compositions. These substitutions are accommodated by the flexibility of the crystal structure which enables ions of different sizes and valence states to be incorporated (Hughes & Rakovan 2015). The effect of the crystallisation conditions on magmatic apatite composition has been well studied and it is possible to infer melt compositions, temperatures, oxidation state and volatile contents of the melt from apatite compositions (Prowatke & Klemme 2006; Harrison & Watson 1984; Konecke et al. 2017; Webster et al. 2019). Less well understood are hydrothermal apatites, although the metasomatism of existing apatite by hydrothermal fluids has been well documented (Bouzari et al. 2016; Harlov 2015; Kusebauch et al. 2015). Apatite's trace-element diversity has made it a mineral of interest in the field of ore deposits, with several studies distinguishing apatite from different rocks and deposit types geochemically (Piccoli & Candela 2002; Mao et al. 2016; Rukhlov et al. 2016).

2.1 Apatite structure and element substitutions

Apatite has the structural formula $\text{M}_5(\text{TO}_4)_3(\text{X})$ and consists of three cation-centred polyhedral (Fig. 2.1): a M^1O_9 trigonal prism, a $\text{M}^2\text{O}_6\text{X}$ irregular polyhedron, and a TO_4 tetrahedron (Hughes & Rakovan 2002; Deer et al. 1966). The X-anions (F, Cl, OH) are arranged in columns at the edge of the unit cell, at the centre of M^2 -cation triangles (Li et al. 2015). Ca is split over the two M-sites and P sits within the T-site (Pasero et al. 2010).

2.1.1 X-site substitutions

X-site substitutions are dominated by F^- , Cl^- , and OH^- which form a ternary solid-solution with endmembers fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$), chlorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{Cl}$), and hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), or FAp, ClAp and OHAp respectively. Fluorapatite is the most abundant apatite endmember followed by OHAp (Deer et al. 1966; Hughes & Rakovan 2002; Zhu & Sverjensky 1991). The large difference in size between F^- , Cl^- , and OH^- affects their positioning within the column, in addition to the nearest neighbours electrostatic attraction and repulsion (Hughes & Rakovan 2015).

Fluorine is the most abundant anion in the F-Cl-OH ternary system. FAp has the simplest crystallographic structure and as a result is used as the framework against which other substitutions and structural variations in apatite are compared. Larger anions are accommodated by incorporating impurities or vacancies into the anion column (Hughes 2015; Hughes & Rakovan 2002). For example, Cl^- are the largest of the endmember anions and in a binary solid solution require column combinations with 0.32-0.72 atoms per formula unit (apfu.) of F^- (Prener 1967), 0.56-0.74 apfu. of OH^- (Ruszala & Kostiner 1975), or 7% vacancies (Prener 1971) to maintain the crystal symmetry of FAp. In addition, M^2 cations also show large shifts in position as a response to different anion combinations, helping to accommodate the size difference (Hughes & Rakovan 2002; Fleet & Pan 1997).

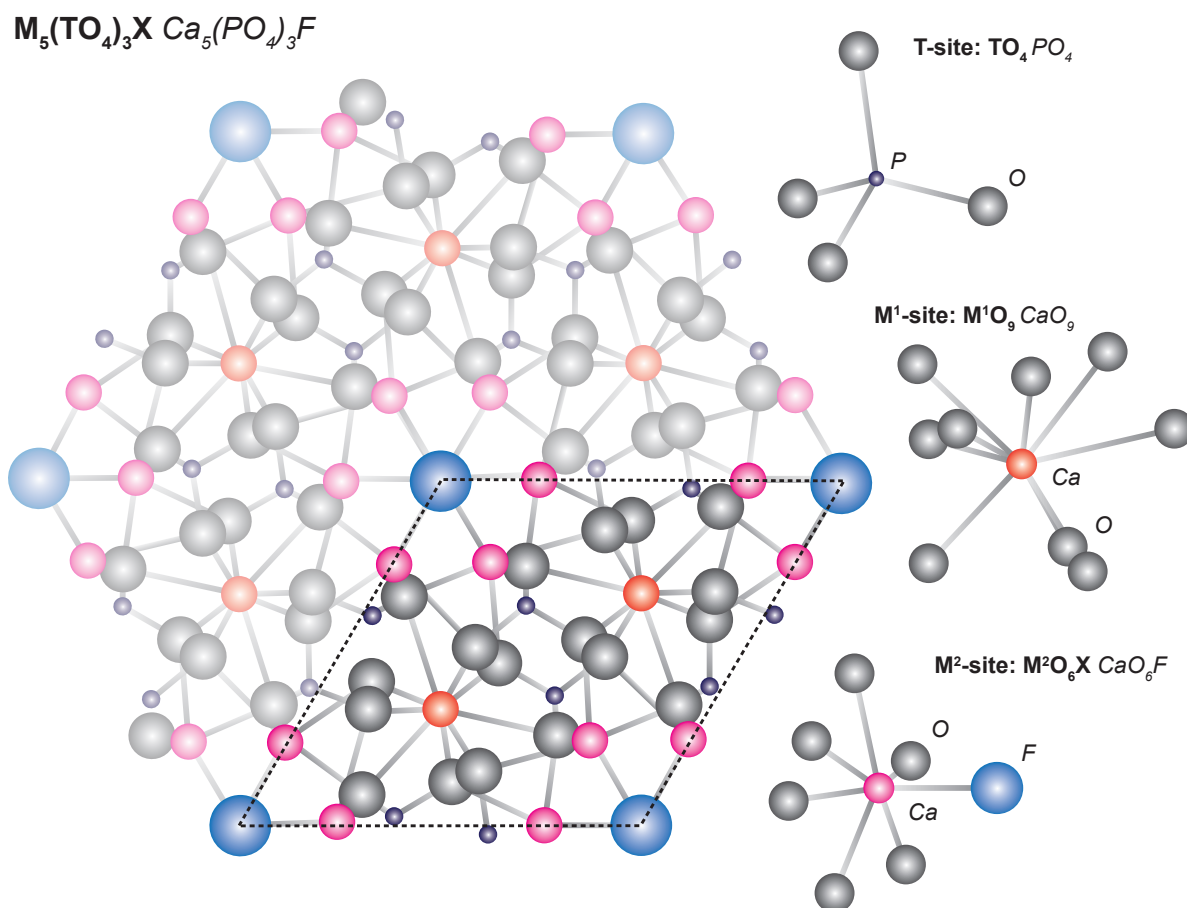
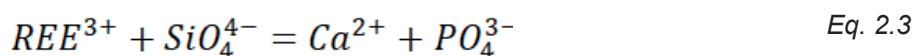
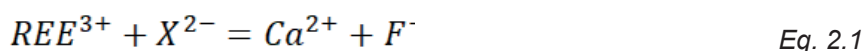


Figure 2.1 The atomic arrangement of apatite ($Ca_5(PO_4)_3F$) projected on [001] which is parallel to the c-axis of the crystal. The unit cell is highlighted. Blue atoms are F, purple are P, red are Ca^1 , pink are Ca^2 and grey are O. On the right are the three cation-centred polyhedral: the T-cation site tetrahedron, the M^1 and M^2 centred polyhedral. The X-anions form part of the M^2 centred polyhedral. Modified from Hughes (2015) and Hughes & Rakavon (2002).

2.1.2 M-site substitutions

Divalent cation substitutions into the M-site are typically straight forward as they share the same charge, and most often are a similar size to Ca. The most common divalent cations observed in natural apatite are Mg^{2+} , Mn^{2+} , Sr^{2+} , Fe^{2+} and Eu^{2+} and can be present in apatite from a few hundred parts per million (ppm) up to a few weight percent (wt. %, Pan & Fleet 2002; Piccoli & Candela 2002; Mao et al. 2016). Sr and Fe typically substitute into the M^2 site and Mg into the M^1 site, although this can change depending on the anion column contents (Pan & Fleet 2002).

The rare earth elements (REE) are trivalent cations that are incorporated into apatite up to several wt. %. There are a number of possible charge balancing substitution reactions including (Pan & Fleet 2002 and references therein):



The X-site was observed to exert a marked control on the REE in apatite (Fleet & Pan 1997; Hughes et al. 1991). Synthesis of FAp illustrates the preferential partitioning of light rare earth

elements (LREE) into its more flexible M² site, heavy rare earth elements (HREE) in FAp are partitioned into M¹, and Nd, or REE of a similar ionic radius, are accommodated in either site (Hughes et al. 1991). It was predicted that ClAp would show a similar, but more enriched pattern to FAp, backed up by analysis from natural and synthetic apatite (Fleet & Pan 1997; Hughes et al. 1991). However, this was contradicted by Fleet et al. (2000) who inferred REE site occupancy ratio was proportional to unit cell volume. They found REE in ClAp prefer M¹, apart from Nd which prefers M². Additionally, the uptake of REE is two orders of magnitude lower in ClAp than in FAp or OHAp. The favoured substitution pair for REE also depends on the X-anion component: Na in ClAp, Na or Si in FAp, and Si in OHAp (Fleet et al. 2000; Pan & Fleet 2002). This change in REE site preference between the apatite species points towards a strong control on the uptake of REE from the anion column. As the M² polyhedral is distorted by the anion column in ClAp, REE are preferentially partitioned into M¹. It is suggested that M-cations are ordered by size and fill up M¹ followed by M² with increasing radius. However, it is stressed that this most likely does not describe REE partitioning (Pasero et al. 2010). More work is needed on the intrinsic controls of REE partitioning.

Sodium is a common monovalent cation, forming a minor component of apatite. It is most often incorporated as part of charge balancing equations with REE³⁺ (Eq. 2.2) into the M¹ site (Pan & Fleet 2002). Tetravalent cations substitutions are less common, but include U⁴⁺ and Th⁴⁺. They do not appear to show any preference for M¹ or M² sites (Luo et al. 2009). They can be accommodated with a vacancy in the M-site (Pan & Fleet 2002):



2.1.3 T-site substitutions

In the apatite sub-group, T-site cations are commonly replaced by other tetrahedral anion groups. The cations involved normally have a valence of +4, +5 or +6, within apatite these most commonly include P⁵⁺, As⁵⁺, V⁵⁺, Si⁴⁺ and S⁶⁺ (Pan & Fleet 2002; Pasero et al. 2010).

2.2 Magmatic apatite

2.2.1 Controls on apatite composition

Apatite-melt partitioning coefficients have been constrained for REE, Y, Sr, S and halogens over a range of magmatic conditions (e.g. Ayers & Watson 1993; Prowatke & Klemme 2006; Parat et al. 2011; Li & Costa 2020). The partitioning of elements between apatite and melt is primarily a function of melt composition and crystallisation conditions such as temperature, pressure and oxidation state (Piccoli & Candela 2002; Jennings et al. 2011; Prowatke & Klemme 2006). As a result, different igneous environments will produce distinct apatite chemistry (Belousova et al. 2002; Piccoli & Candela 2002; Teiber et al. 2015; Mao et al. 2016) and magmatic evolution can be reconstructed from apatite trace element content (Mao et al. 2016; Miles et al. 2014; Scott et al. 2015).

Melt composition

Large variations in magmatic apatite composition within a single rock may be a result of heterogeneity within the magma chamber, such as mineral fractionation or crystallisation from isolated pockets of melt (Belousova et al. 2002). Apatite crystallising from isolated pockets

of melt will exhibit more variable compositions than those crystallising from the main portion of the magma (Scott et al. 2015; Miles et al. 2013). In the case of mineral fractionation, the apatite composition can be used to track melt differentiation (Jennings et al. 2011; Braund et al. 2017; Stock et al. 2018). Concentrations of Mg in apatite have been shown to be proportional to concentrations of Mg in the melt (Prowatke & Klemme 2006) and have been used as a proxy for melt differentiation within apatite compositions (Nathwani et al. 2020).

Apatite-melt partitioning of elements such as REE, Mn and Th increases with polymerisation of the melt (Fleet & Pan 1997; Prowatke & Klemme 2006; Piccoli & Candela 2002). This leads to an increase in the overall REE diversity in apatite with increasing crystallisation of the melt (Prowatke & Klemme 2006). The REE concentrations in apatite are commonly proportional to melt REE composition and several studies have used apatite compositions to infer bulk rock compositions REE from detrital sediments (Belousova et al. 2002; Jennings et al. 2011; Braund et al. 2017). Equivalent apatite REE proportions to bulk rock suggest apatite is often the most dominate and/or earliest-crystallising REE-rich phase (Prowatke & Klemme 2006). By contrast, concentrations of elements such as Sr are routinely lower in concentration in apatite than would be expected given the bulk rock concentrations. Despite Sr apatite-melt partition coefficients being above unity, low Sr in apatite reflects earlier crystallisation of Sr-phases such as plagioclase. Likewise, the amplitude of negative Eu anomalies also increases with fractionation in S- and felsic I-type granites, thought to be a result of feldspar crystallisation reducing Eu content in the melt (Belousova et al. 2002).

Temperature of crystallisation

Apatite is stable over a wide range of temperatures and the apatite saturation temperature (AST) can be estimated, based off the experiments of Harrison and Watson (1984), using the concentration of P_2O_5 and SiO_2 in the melt at the onset of crystallisation. In order to apply this, it is often necessary to assume that bulk rock composition is representative of the melt composition at apatite saturation which may be true for felsic melts. However, in metaluminous magmas the solubility of apatite is higher leading to its later saturation and thus allowing differentiation of the initial melt through crystal fractionation (e.g. feldspar), changing the parent melt composition prior to apatite crystallisation (Piccoli & Candela 1994).

Oxidation state of melt

Apatite can incorporate many elements (such as S, Ce, Eu, Mn, V, and Fe) which have variable oxidation states. As a result, the oxidation state of the melt will affect the composition of apatite because the partition coefficients of these elements differ between valence states (Sha & Chappell 1999). Experimental and natural apatite data indicate that the Ce/Ce* of apatite is consistently small over a range of $f.O_2$ and temperature conditions (Trail et al. 2011; Belousova et al. 2002; Mao et al. 2016). However, the overall abundance of Ce does discriminate between oxidised (Ce >10,000 ppm) and more reduced sources (Ce <2000 ppm; Belousova et al. 2002; Mao et al. 2016; Rukhlov et al. 2016).

Eu/Eu* is usually negative in apatite as Eu is present as both Eu^{2+} and Eu^{3+} in the melt but only Eu^{2+} is incorporated into apatite. Apatite from reduced sources is observed to contain lower

quantities of Eu and a larger negative anomaly (Rukhlov et al. 2016; Mao et al. 2016). However, it is also suggested that the effects of magma oxidation state on Eu in apatite are masked by feldspar crystallisation (Belousova et al. 2002). Eu anomalies are negative in apatite from plagioclase-rich rocks as plagioclase preferentially incorporates Eu (Belousova et al. 2002).

Recently, the valence states of sulfur within igneous apatites were related to the redox conditions of crystallisation suggesting their potential as a redox proxy. Apatites formed in oxidising conditions (FMQ+3) contained predominantly S^{6+} and S^{4+} whereas reduced conditions produced apatites containing predominantly S^{2-} (Konecke et al. 2017). However, it is yet to be understood how redox state and controls on S substitutions relate to the overall S-content in apatite.

2.2.2 Halogens in apatite

The halogen content of apatite can be used to estimate the volatile fugacity (Stock et al. 2016, 2018) and Cl content in the melt (Parat et al. 2011). If the Cl or F content of the melt is known, halogen compositions can also be used to estimate melt water content (Li & Costa 2020). The partitioning of halogens into apatite is complex and cannot be directly linked to melt or fluid composition so halogen ratios are typically used (Webster et al. 2019). Most published partition calculations are thermodynamically constrained and have not been completely verified by experimental studies (Zhu & Sverjensky 1991; Li & Costa 2020).

Variation in halogen ratios between different apatite textures have been used to interpret processes such as magma differentiation and degassing over the crystallisation period. Scott et al. (2015) identified two distinct apatite compositions within erupted volcanics from the Santiaguito volcano, Guatemala. It is suggested that the variation in halogens is a result of changes in the Cl activity from magmatic processes such as degassing or fresh magma injection into the chamber (Boyce & Hervig 2008); however, changes in temperature during apatite crystallisation could also produce such Cl zoning (Scott et al. 2015). Similarly, variations in apatite halogen ratios from the Campi Flegrei volcano were inferred to reflect a fluid under-saturated melt evolving to volatile saturation (Stock et al. 2018). In this case, by modelling how the apatite halogen content would be expected to behave under changing P-T conditions, a magmatic control on the halogen variation could be ruled out.

Alternatively, zonation of halogens in volcanic apatite, rather than multiple generations, can be used to track the evolution of volatile fugacity in the melt. However, halogen zoning is less commonly observed than perhaps would be expected given the exchange substitutions occurring between these major components. This is possibly due to diffusion during periods of protracted cooling (Brenan 1993) which can smooth out earlier compositional variations.

Diffusion in apatite

Apatite is an ionically bonded solid and as a result it's weaker bonded atoms can diffuse faster in comparison to atoms in covalently bonded minerals. As ion diffusion in apatite is fastest when parallel to the C-axis, along which the X-site is aligned, the halogens are more prone to migration and exchange than other elements. Diffusion of Cl, OH and F is five times faster than that of the

REE (Boyce & Hervig 2008; Henderson 2011; Stormer et al. 1993). Of the common cation compositions in apatite, Pb has been observed to diffuse the fastest, followed by Sr and then Mn (Cherniak 2010 and references therein). Diffusion of the divalent cations is typically faster than for tetravalent cations, such as REE. The diffusion of higher charged cations is likely limited by the exchange processes required in their substitutions (Tepper & Keuhner 1999; Cherniak 2000).

2.3 Hydrothermal apatite

In contrast to apatite-melt partitioning, constraints on apatite-fluid element partitioning at upper crustal conditions are rare (Brenan et al. 1995). Available coefficients are limited to halogens (Zhu & Sverjensky 1991), apatite-melt-fluid partitioning (Webster et al. 2009; Doherty et al. 2014), or fluid-equilibration of existing apatite (Brenan 1993; Kusebauch et al. 2015). Descriptions of natural hydrothermal apatite are most common in deposit studies where the halogens, REE and As content are the main areas of interest (Krenta 2017; Frietsch & Perdahl 1995; Li et al. 2015; Liu et al. 2017; Loader 2017a). In these studies hydrothermal apatite shows compositions distinguishable from magmatic apatite consistent with large variations in REE mobility in hydrothermal fluids (Krenta 2017, 2018; Li & Zhou 2015; Raimbault et al. 1993; Migdisov et al. 2016) and the susceptibility of apatite to metasomatism (Bouzari et al. 2016; Harlov 2015; Belousova et al. 2002).

Metasomatism of apatite

Similar to its effects on diffusion, the weakly bonded apatite structure is also susceptible to alteration. Hydrothermal fluids alter apatite chemistry predominantly through the depletion of fluid-mobile elements (Bouzari et al. 2016; Harlov 2015). In the porphyry environment overprinting potassic and sericitic alteration fluids are associated with a decrease in concentrations of Mn, Cl, S, Na, and REE in apatite (Bouzari et al. 2016; Mao et al. 2016; Rukhlov et al. 2016). The remobilised elements can re-precipitate as epitaxial overgrowth (Kusebauch et al. 2015) and the metasomatised portions of the grains can be easily identified as alteration produces predictable textural changes in apatite (Harlov 2015). The removal of Cl ions produces pits aligned with the C-axis; these can subsequently be infilled by monazite formed from the remobilised REE (Fig. 2.2A-B; Harlov 2015; Hansen & Harlov 2007; Harlov et al. 2002). Changes in trace-element concentrations also produce variation in back-

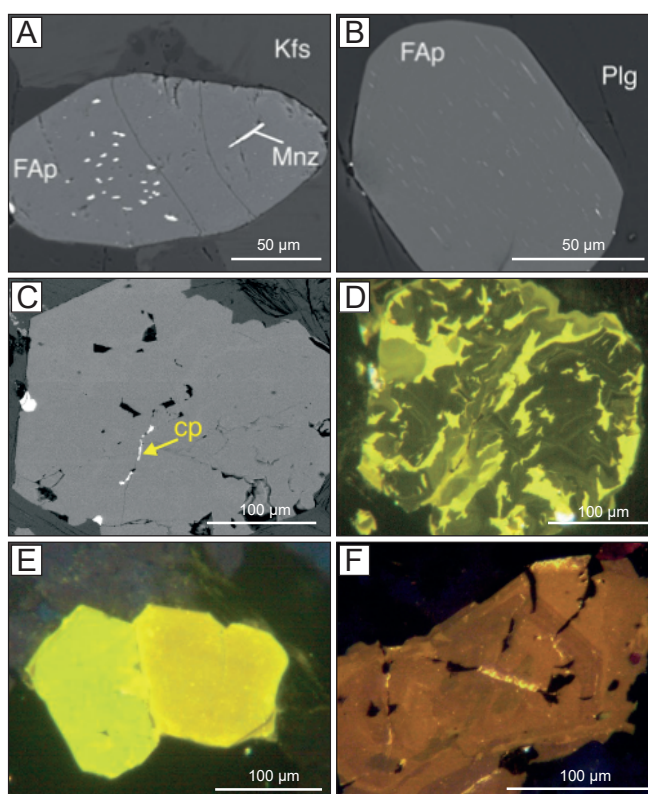


Figure 2.2 Microscopic images of altered apatite imaged by back-scattered electron (A-C) and cathodoluminescence (D-F). A-B) Metasomatically induced monazite (Mnz) in fluorapatite (FAp) showing alignments with the c-axis of the grain. C-D) Cathodoluminescence (CL) imaging reveals more detail than backscattered imaging on the same grain of hydrothermal apatite. Here the darker Cl zones were inferred to be overprinting the brighter yellow phase. E) Apatite from unaltered granodiorite showing yellow F) and zoned brown luminescence. Modified from Harlov (2015) and Bouzari et al. (2016).

scatter electron (BSE) and cathodoluminescence (CL) response. CL imaging of apatite can reveal textural features in grains that otherwise look homogeneous (Fig. 2.2C-D). These include concentric growth zonations and alteration focused along edges and fine fractures (Bouzari et al. 2016).

2.4 Apatite as an indicator mineral

Although apatite has been used to identify sediment provenance (Sha & Chappell 1999) and to distinguish between major igneous rocks types (Piccoli & Candela 2002), few studies have focused on apatite as an indicator mineral specifically for porphyry deposits (Loader 2017a). In one study (Mao et al. 2016), apatite from porphyry deposits was found to be enriched in Mn and contained a more negative Eu anomaly compared to apatites from unmineralised rocks. However, the unmineralised rocks in this study are not arc magma rocks. Thus chemical variation may be more subtle when comparing apatite from mineralised porphyry systems to those from unmineralised arc rocks.

Rukhlov et al. (2016) also highlighted chemical differences between apatites from different porphyry types, in this case Cu-Au and Cu-Mo-Au deposits. The apatites from each deposit, even those of the same system type, have different trace element chemistry as a result of variations in the parent magma composition. In addition, apatite from Cu-Au systems have higher S, V, and lower Mn, Ce contents, possibly as a result of more oxidised magma. However, both studies use analyses of apatite concentrates rather than in-situ apatite and therefore do not distinguish between magmatic and hydrothermal apatite.

In another study, CL imaging of sediments was proposed as an exploration technique for identifying porphyry-related apatites. Unaltered magmatic apatites display a yellow luminescence, with those from alkali magmas being more brown in colour, possibly as a result of elevated Mn content (Bouzari et al. 2016; Williams & Cesbron 1977). Successive stages of hydrothermal alteration in porphyry systems could also be observed, recorded as overprinting of luminescence responds in apatite changing from yellow-brown to green then grey with more intense sericitic alteration (Fig. 2.2E-F; Bouzari et al. 2016).

2.5 Summary: apatite in porphyry systems

Apatite's varied composition and range in environmental stability makes it suitable for use in a broad range of geological studies. It can accommodate a large number of substitutions due to the variety of cation sites in the crystallographic structure. These include elements believed to be important in the formation of porphyry deposits, particularly sulfur and halogens. However, these elements also exhibit high diffusion rates in apatite and therefore current concentrations may no longer be reflective of crystallisation composition in apatite. In addition, metasomatised apatites exhibit systematic changes in composition and cathodoluminescence response. This may be linked to the hydrothermal fluid composition, and is particularly interesting when the fluids are linked to mineralisation events. However, this too means caution must be taken when inferring magmatic conditions from apatite composition.

In porphyry systems, apatite crystallisation can be used to inform on both magmatic and

hydrothermal conditions. As a magmatic accessory mineral, apatite is generally well studied. The controls on REE partitioning between apatite and melt are particularly well reported. In addition there is a good understanding of most substitutions; however any uncertainties surrounding the intrinsic controls on apatite substitution could potentially limit its use as a proxy for the conditions of its crystallisation environment. By contrast, the controls and variation in hydrothermal apatite composition is less well understood for upper crustal P-T conditions. There are also limited descriptions of natural hydrothermal apatite assemblages and compositions.

Apatite has shown potential as an indicator mineral for porphyry exploration. Differences in the trace element composition of apatite have been observed between deposit types (i.e. porphyry Cu-Au, Cu-Mo, Mo) due to slight differences in the magmatic environment. This implies that apatite from barren and fertile arc magmas could also be distinguished. However, although the whole rock composition is often considered when looking at apatite chemistry, few studies take account of the petrographic associations of apatite. Multiple generations of apatite and compositional zoning within crystals add complexity to the interpretation of the crystallization history of a system, but also provide additional information. In order to address the gaps in the published literature this study will provide a detailed textural and compositional study of apatite from multiple porphyry systems. By doing so, this will allow variations in apatite compositions collected as part of a larger global data set to be attributed to magmatic or hydrothermal origins or the effects of metasomatism.

Chapter 3: Method development for EPM and LA-ICP-MS analyses

Apatite hosts a range of elements that vary in concentration over several orders of magnitude and includes several that are difficult to quantify. This variety requires analyses by different instruments to optimise accuracy and precision for each element and may necessitate bespoke method development. In this chapter, the methodology behind the principal quantification techniques used in this thesis is discussed.

3.1 Analytical methods

Apatite can accommodate a wide range of minor and trace elements. The technique by which these elements are best measured depends on their concentration, atomic mass and ionisation efficiency. For example, electron probe microanalysis (EPMA) can be used to determine concentrations as low as 0.01 wt. % but cannot measure light elements, below around 0.05 wt. %. Laser ablation inductively-coupled-plasma mass spectrometry (LA-ICP-MS) can detect elements to below 1 ppm but is not suitable for elements with low ionisation efficiency. A combination of both techniques is required for a full chemical characterisation. Table 3.1 outlines the approximate concentration ranges of key elements in apatite and the most appropriate analytical method required.

3.1.1 Apatite standards

Four natural apatite standards (STD002, STD217, STD0067 and STD262) were analysed for the development of a suitable analytical protocol. These standards include halogen end-member compositions of fluorapatite from Wilberforce, Ontario Canada (STD002) and two pieces of Durango apatite from Cerro de Mercado, an iron deposit in Durango, Mexico (STD0067, STD262) and chlorapatite from Epiwala, Sri Lanka (STD217). Durango is commonly used as a natural apatite standard (Chew et al. 2016; Young et al. 1969) and as a Ca and P standard for microprobe calibration (Streck & Dilles 1998; Mao et al. 2016). Throughout the course of this thesis, analyses of Durango (STD0067 and STD262¹) were run alongside analyses of unknown apatites to monitor instrument drift (see *Appendix A*).

3.2 Electron probe microanalysis methodology

Electron probe microanalysis is a method of quantitative analysis in which a focused electron beam is fired at the polished surface of a sample. The beam interacts with electrons in the atoms, producing a vacancy in that shell that is filled by an electron from a higher energy bound shell. This process ionizes the atom and results in the release of X-rays with frequencies that are characteristic of the parent element as the electron structure of each element is unique. The X-rays of interest are focused on to detectors through wavelength dispersive X-ray spectrometers (WDS) by crystals. The hits on the detectors are converted into an electrical signal, known as counts. The elemental composition of the sample can be quantified by comparing the signal

[1] With further analysis, it has been noted that Durango apatite grain STD262 has minor and trace element heterogeneity within the crystal and is, overall, depleted in trace elements compared to STD0067 and other Durango grains analysed in the literature. As a result, STD0067 is preferentially used over STD262 for all future work.

Table 3.1 Example concentrations of elements in apatite and suggested quantification method.

Element	Concentration in apatite	SEM-EDS	EMPA	LA-ICP-MS
Ca, P	10's wt.%, major element	✓	✓	X
F	0 – 3.76 wt.%, minor to major element	Halogen migration		Poor ionisation
Cl	0 – 5 wt.%, minor to major element			
Na, S	<1 – 2 wt.% trace to major element	Often at or below detection limit	✓	Non-routine
Mn, Fe, Sr, Mg, LREE	<1 wt.%, trace to minor element		✓	✓
HREE, As, Pb, V, Th, U	10 – 100 ppm, trace element	Below detection limit	Below detection limit	✓

intensity, or the number of counts, to the ratio of the known concentration and signal intensity produced from a measured standard. However as the emitted X-rays will interact with the sample a matrix correction must be applied. This correction depends on the composition of the sample and changes for each X-ray of interest as a function of the atomic number, absorption and fluorescence.

EPMA is commonly used as it is a non-destructive method that requires little sample preparation, aside from a high quality polish and a carbon coat to increase the conductivity of the sample. Analyses can be acquired from very small areas ($\sim 1 \mu\text{m}$) and the detection limits are adequate for most minor constituents of minerals. However, as the sample is bombarded with electrons, lighter charged particles in the sample may migrate due to a beam-induced electron field in the sample (Stormer et al. 1993). This means it can be difficult to obtain consistent and accurate volatile and light element concentrations in minerals such as apatite using an electron beam. X-ray counts for F are the most inconsistent (Stormer et al. 1993; Goldoff et al. 2012).

Time-dependent fluctuations in X-ray intensity for F have been observed under EPMA at the NHM (Fig. 3.1), similar to that observed by Stormer et al. (1993). This effect is caused by the migration of ions through an electron field towards the sample surface resulting in erroneously high concentrations of F that exceed stoichiometric values. With time the number of counts decreases to

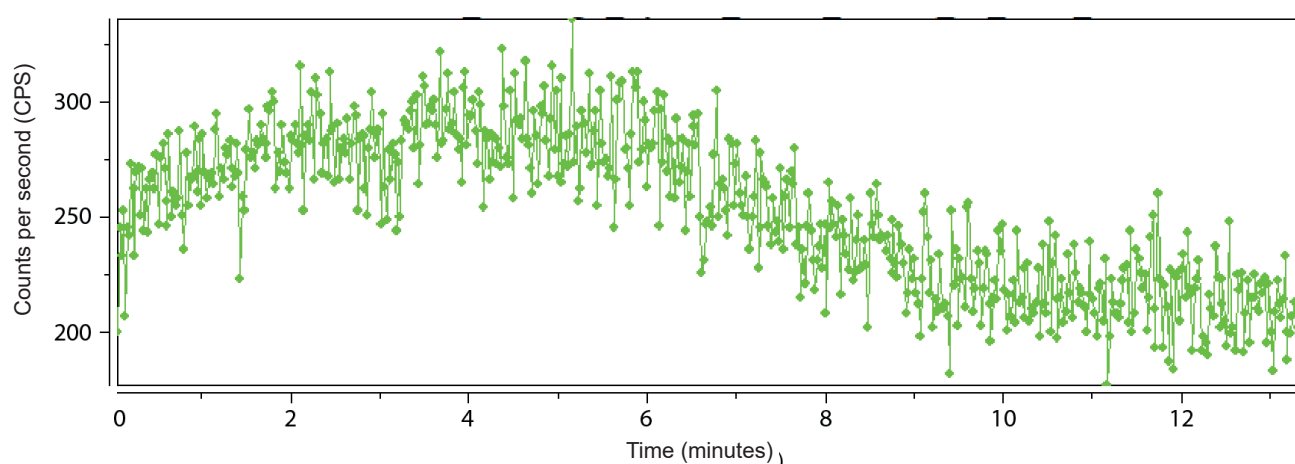


Figure 3.1 Counts per second (cps) on the 40986 keV peak of F in Durango apatite (STD0067) as a function of time. Analysis carried out using the LPCO spectrometer of the Cameca SX100 EPMA at 20kV, 20 nA at the smallest spot size used ($5 \mu\text{m}$). Counts increase to ~ 4 minutes and then decrease to lower than the original values.

below the original values. The F X-ray intensity is not sustained as the low energy X-rays are strongly absorbed by the apatite matrix and therefore the source of these X-rays are limited. In addition beam contamination or carbon coat destruction may lead to a reduced signal. The rate and magnitude of this fluctuation appears to be a function of crystal orientation and operating conditions (Stormer et al. 1993; Goldoff et al. 2012), as well as apatite composition (Henderson 2011; Stock et al. 2015).

The migration of the ions is aided by a thermal gradient and the crystal structure of apatite. It has been suggested that halogens can migrate back over time and at a faster rate by heating (Stock et al. 2015). The halogens move along interstitial C-axis channels, which run the length of the mineral structure. If these channels are orientated perpendicular to the beam, these migration effects are reduced (Stormer et al. 1993).

Because of the analytical difficulties, F concentrations in apatite are often not reported in the literature (e.g. Bouzari et al. 2016). Nonetheless, incorrect analyses are evident throughout the literature. The stoichiometric limit for F in apatite is 3.76 wt. % (equivalent to less than 1 F atom when normalised to 26 cations; Pyle et al. 2002), yet 10% of apatite analyses in the GEOROC4 database have F concentrations in excess of this limit (Webster & Piccoli 2015).

Fortunately, more accurate halogen quantification by EPMA can be achieved using modified EPMA methods (Pyle et al. 2002; Webster et al. 2009; Goldoff et al. 2012; Scott et al. 2015) but each possesses particular properties that make accurate quantitative microanalysis difficult. This chapter provides an overview of the literature concerned with the main problems of electron probe. One approach is to measure X-ray intensity over a longer time period before extrapolating the count back to zero time using time-dependent intensity curves (Adams et al. 2010; Hughes & Rakovan 2015). Alternatively, supercooling the sample (to -80 °C) can remove any thermal gradient (Henderson 2011) helping to reduce ion migration. However, these techniques are time-consuming and impractical for large-scale data collection. It is possible to minimise ion migration effects by using optimal operating conditions: Goldoff et al. (2012) suggested an accelerating voltage of 10 kV, beam current of 4 nA and a beam diameter of 10 µm. This agrees with the conditions proposed by Stock et al. (2015) of < 10-15 kV, < 15 nA and a defocused beam and Henderson (2011) of a beam size > 5 µm.

In this study, the effects of beam diameter and current on EPM apatite analyses were tested on apatite standards with varying halogen concentrations. The effect of accelerating voltage was not tested, as it does not appear to have a significant impact on the maximum-recorded X-ray intensity for F (Stormer et al. 1993). In addition, the analyses were carried out on un-orientated samples, as this variable cannot be controlled in natural, in-situ grains (although the orientation may be inferred in an euhedral crystal). Furthermore, the build-up of surface halogens because of grain orientation is thought to be insignificant compared to the total variation in X-ray flux (Goldoff et al. 2012; Stock et al. 2015). The accuracy, precision

Table 3.2 Peak position, slope background and spectrometer used in EPM set up.

Element peak	Position keV	Background (slope) keV	Spectrometer crystal type
Ca Ka	38386	+500 (1.05)	PET
P Ka	23973	+600 (1.1)	TAP
F Ka	40986	+1000, -1000	LPPO
Cl Ka	54050	+500 (1.05)	PET
Na Ka	46357	+800, -800	TAP
S Ka	61398	+600 (1.05)	LPET
Fe Ka	48090	+950 (1.05)	LLIF
Sr La	78485	+1000 (1.02)	LPET
La La	25108	+350 (1.1)	LPET
Ce La	29305	+600 (1.05)	LPET

and detection limits obtained using each set of conditions were compared to identify those most suited to analysing in-situ apatite with the smallest uncertainties and lowest limits of detection.

3.2.1 Method

Coarse apatite standards (STD0067, STD262, STD217, STD002) were analysed on a Cameca-SX100 electron probe housed in the Imaging and Analysis Centre at the Natural History Museum, London, over a range of beam currents (4 nA, 10 nA, 20 nA) and spot sizes (5 μm , 10 μm and 20 μm) and an acceleration voltage of 20 kV. A higher voltage than those noted in the literature was used, as the accelerating voltage was not found to have a significant impact on F X-ray intensity (Stormer et al. 1993) and so can be increased to raise counts and improve detection limits. The spot locations for each run were positioned close together to minimise the possible effects of compositional zoning.

The elements P, Ca, F, Cl, Na, S, Sr, Fe, La, and Ce were measured with the halogens collected first in the spectrometer sequence. The peak positions and backgrounds for the elements are listed in table 3.2. Peak overlaps were detected for the P peak from Ca, and the F and Nd peaks from Ce. Corrections were applied using the probe software after calibration using wollastonite (for Ca) and Ce glass standards.

3.2.2 Results

Halogens

Effect of apatite composition and beam conditions on halogen composition

All apatite standards show systematic differences in measured F with variations in beam conditions (Fig. 3.2). An increase in beam current and a decrease in spot size both increase

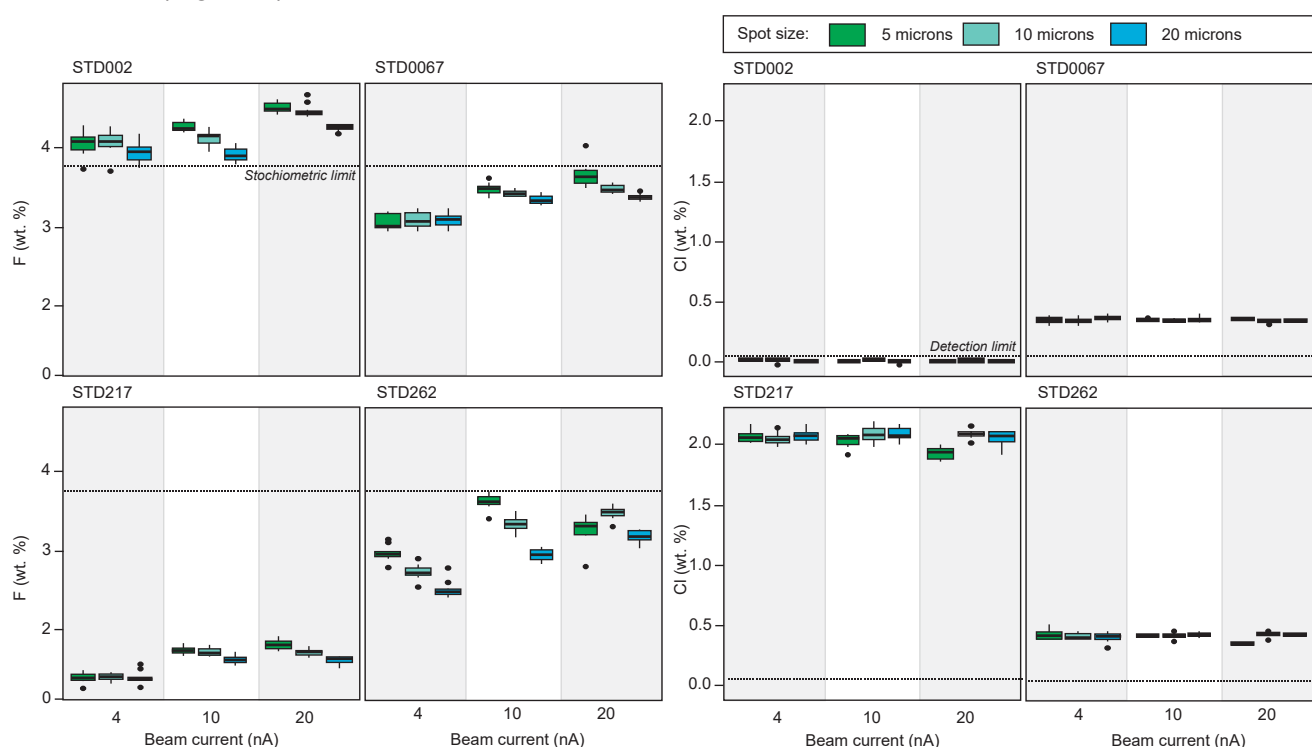


Figure 3.2 Measurements of F and Cl wt. % in apatite standards (STD0067, STD262, STD217, STD002) as a function of beam current and spot size. The stoichiometric limit for F hosted within the X-site of apatite is 3.76 wt. % (Stock et al. 2015), and the average detection limit of Cl for the analysis was 0.04 wt. %.

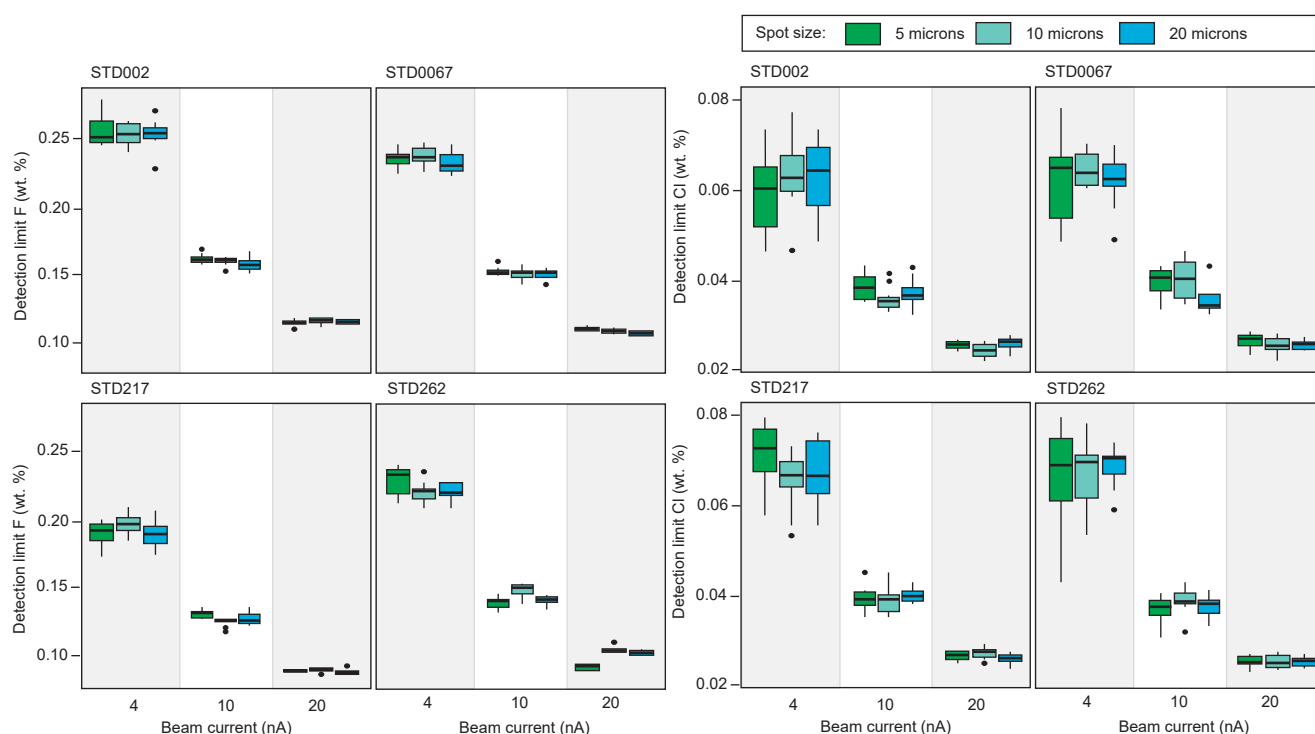


Figure 3.3 Detection limit for F and Cl in apatite standards (STD067, STD262, STD217, STD002) as a function of beam current and spot size.

the measured F concentration. The variation in spot size generally has a greater effect when the beam current is >4 nA and the variation between different beam currents is least for a 20 μm spot. An increase in beam current from 4 nA to 20 nA can increase the measured F within a sample by up to 0.75 wt%. This effect is greater in apatite with higher F contents.

Both Durango samples show comparable F values and, in addition to STD002, are F-rich. The measured F values for STD002 are consistently above the stoichiometric limit of 3.75 wt. % (Stock et al. 2015) but are closest to it for <20 nA current and a 20 μm spot. A higher concentration in F in apatite produces a wider range of results for a given set of beam condition, and a larger change in measured concentrations between different beam conditions. A higher beam current and spot size increases the precision of the analyses. The effect of beam conditions on Cl determination is less prominent, even for more Cl-rich apatites (STD217).

A detection limit for each analysis is calculated as 3σ of the measured background and is the lowest concentration that can be detected with confidence (Fig. 3.3). All halogen analyses, apart from Cl in STD002, were over the detection limit. The detection limit varies the most with changing beam current: and increase from 4 to 20 nA can lower the detection limit to over 0.02 wt. % (Fig. 3.3).

Accuracy of data

Analyses of Durango apatite (STD0067, STD262) from this study are compared to minimum and maximum values reported in the literature (3.23-3.34 wt.% F, 0.37-0.46 wt.% Cl: Marks et al. 2012; Fig. 3.4). These literature values were collected by EPMA (15 kV, 10 nA, 15 μm), however the same study presents a good agreement of these values to those collected by secondary ion mass spectrometry for other natural apatite standards.

STD262 shows large variations in measured F concentrations (2.41 to 3.76 wt.%) with changes

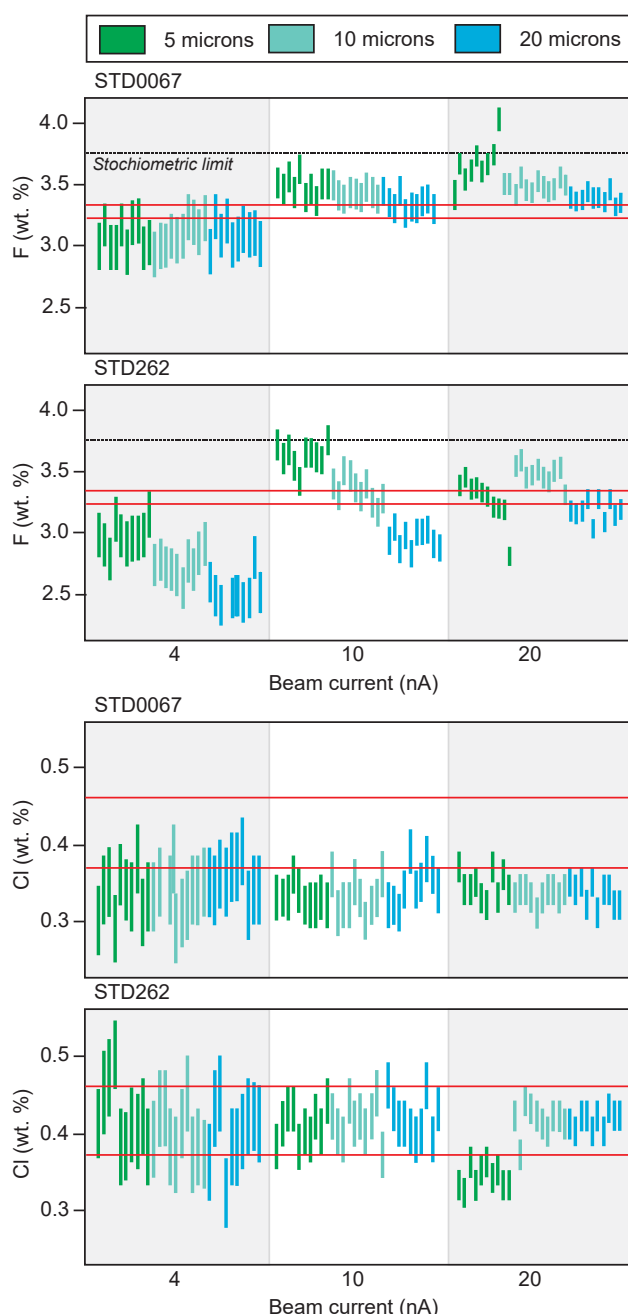


Figure 3.4 Plot of F and Cl wt.% measured on Durango apatite samples (STD262, STD0067). The standard deviation range for each measurement by the EPM software is shown. Concentrations reported in the literature are plotted in red and are taken from Marks et al. (2012) and Chew et al. (2016).

	4 (nA)			10 (nA)			20 (nA)		
	5 (μm)	10 (μm)	20 (μm)	5 (μm)	10 (μm)	20 (μm)	5 (μm)	10 (μm)	20 (μm)
Ca	0.09	0.09	0.09	0.05	0.05	0.04	0.06	0.04	0.04
P	0.06	0.06	0.06	0.04	0.04	0.04	0.04	0.03	0.03
Na	0.11	0.12	0.12	0.07	0.07	0.07	0.08	0.05	0.05
S	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.01	0.01
Mn	0.07	0.07	0.07	0.04	0.04	0.04	0.05	0.03	0.03
Fe	0.07	0.07	0.06	0.04	0.04	0.04	0.04	0.03	0.03
Sr	0.10	0.10	0.10	0.06	0.06	0.06	0.06	0.04	0.04
La	0.06	0.06	0.06	0.04	0.04	0.06	0.04	0.03	0.03
Ce	0.08	0.08	0.08	0.05	0.05	0.05	0.05	0.04	0.03
F	0.24	0.24	0.23	0.16	0.15	0.15	0.11	0.11	0.11
Cl	0.06	0.06	0.06	0.04	0.04	0.04	0.03	0.03	0.03

in beam conditions (Figs. 3.2; 3.4). However, for a given set of beam conditions, analyses are generally within error of each other. Cl-values are relatively consistent over all conditions. Halogen measurements for both Durango standards show the greatest agreement with the literature range at a spot size of 10 μm and a beam current of 10 nA. The error on each analysis is calculated from 2σ of counts for each analysis peak by the EPM software and decreases with a higher beam current. In general, higher concentrations in the sample produce smaller errors for a given set of analytical conditions.

Minor cations (Ca, P, Na, S, Fe, Sr, La, Ce)

Effect on cations by beam conditions

Box plots of analyses of STD262 over the range of beam conditions are shown in figure 3.5. Analyses for Fe and Sr are below the detection limit of the probe, and analyses of the other minor elements are close to detection limits. The measured concentrations of the minor cations show little systematic variation with changes in conditions. However, overall a higher beam current produces a smallest range in results and at a lower beam current, the effect of spot size on the measured value is larger.

The detection limit improves with an increase in current and, by a smaller amount, an increase in spot size (Table 3.3). At 4 nA, the detection limit (wt. %) for many cations is above their average concentration in apatite. However, for analyses of Mn, Fe and Sr a current of at least 10 nA is needed to lower the detection limit below the average concentration in apatite.

Table 3.3 (left) Detection limits calculated by the CAMECA SX100 microprobe software. Values in red are detection limits at or above the average composition in apatite (i.e. the element was rarely quantifiable). Results are shown for currents of 4 nA, 10 nA and 20 nA, and for spot sizes of 5 μm , 10 μm and 20 μm .

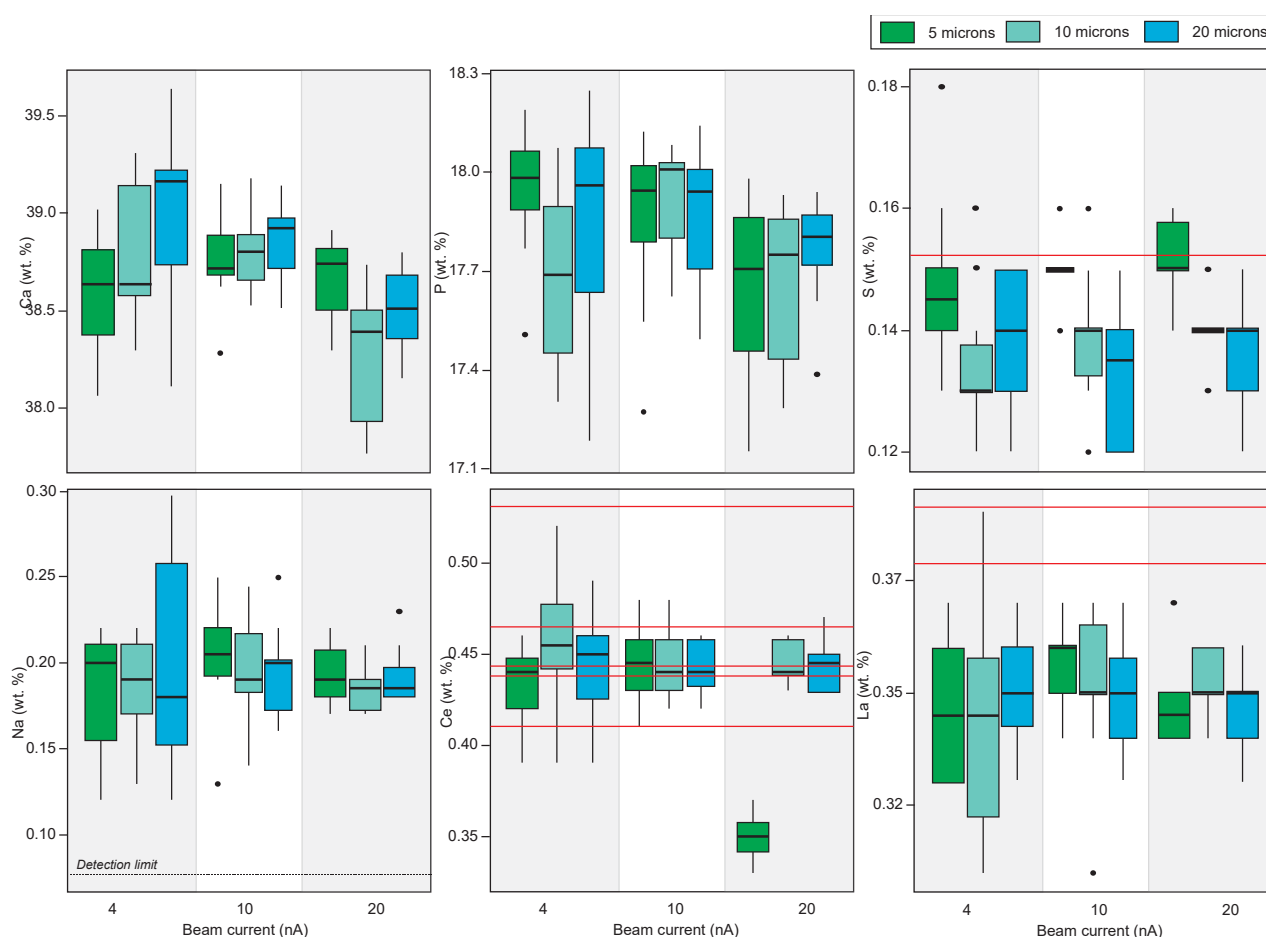


Figure 3.5 Box and whisker plots of measured major and minor cation concentrations in Durango apatite (STD262) as a function of spot size and beam current. Dotted black lines indicate the typical detection limit of the electron probe. Red lines indicate literature values from solution ICP-MS and are taken from Chew et al. (2016), Mao et al. (2016) and Marks et al. (2012).

Accuracy of data

Published analyses of Durango apatite are used to assess the accuracy of the data collected at beam conditions (Fig. 3.5). Literature values for Ce and La were acquired by low-blank solution quadrupole inductively-coupled-plasma mass spectrometry (solution Q-ICP-MS) of Durango apatite (Chew et al. 2016; Mao et al. 2016). Additional values of Ce were collected by EPMA and LA-ICP-MS, and S by EPMA (Marks et al. 2012). Elements that are above detection show good agreement between measured concentrations and literature values. Analyses of Ce overlap with literature. S and La concentrations sit below previously reported values; in the case of La this is ~ 20 % lower. However, the standard deviation on results collected at a set condition is large, resulting in high relative standard deviations especially for Na, Ce and La.

3.2.3 Discussion

From the analyses, it appears that spot size (5 – 20 μm) has a larger influence on the accuracy and precision of a set of analyses than the beam current (4 – 20 nA). Overall, a beam current between 10 and 20 nA and a beam size greater than 4 μm are best to limit variation in results. The lowest detection limits are produced with beam currents greater than 10 μm . For halogen analysis, the concentrations in apatite are well above detection however; the concentrations of other minor cations (e.g. Na, REE, Mn) may be at too low concentrations to measure accurately by EPMA. For

measurements of F, the concentration in the apatite has a large effect on the precision and accuracy and the most accurate concentrations are probably obtained using a larger beam size of 20 μm . However, it is possible that reasonable values can be achieved at spot size of 10 μm and higher beam conditions. This smaller spot size may be more realistic for analyses of natural apatite samples and prevent contamination of the signal from adjacent mineral phases. Therefore, a spot size of 10 μm and a beam current of 10 nA is suggested for most reliable analyses of halogens in in-situ apatite.

The diffusion of ions within the crystal structure requires vacancies, or accompanying diffusion by other ions, to produce a clear path through the structure. The suggestion that F ions diffuse readily along the C-axis is supported by observations that F-rich apatites exhibit higher variations in F migration with changing beam conditions than F-poor, and more Cl-rich apatite (Fig. 3.2). The majority of F ions in the X-site allow for simultaneous diffusion. However these observations counter the assumption of full X-site occupancy that is needed, and used in this study for the calculation of OH endmember proportions in apatite. However in the absence of alternative methods to estimate endmember compositions, this inconsistency will have to remain.

3.3 LA-ICP-MS methodology

3.3.1 Introduction

LA-ICP-MS (laser ablation-inductively coupled-mass spectrometry) analysis can be broken down into three stages: ablation of a solid sample using a laser, aerosol transport and ionization of the ablated material by a plasma, and finally mass spectrometry analysis of the ions produced. First, the sample is ablated on a static spot to produce an aerosol of fine particles. These are carried by He gas to a nebulizer that disperses them evenly into the plasma. The plasma is formed of Ar heated through electromagnetic induction. Here, the sample is atomized further and the large number of free electrons in the plasma ionizes the particles. The ions are focused into a beam and directed into the mass spectrometer where they are separated into pre-selected mass/charge ratios under vacuum. A detector converts the number of ions/second into an electrical signal (counts) that reflects the relative abundance of the isotopes (Longerich 2008). The counts are converted to concentration (i.e. ppm) after calibrating with an external standard and normalizing using an internal standard (element of known concentration). This can be determined by separate electron probe analysis or assumed from stoichiometry (Longerich 2008).

Potential pitfalls during analysis

The interaction of the sample and the laser will differ based on the material and the laser conditions. Apatite and glass standards will ablate differently under a laser and therefore the ablation yields from the two materials (how much material is delivered to the ICP) can vary greatly. However, by calibrating using an internal standard (element) for each unknown, the final concentrations should be relatively unaffected by this process (Sylvester 2008).

Once ablated, the particles can behave differently within the ablation plume. Particles that are more volatile may travel faster. This results in the physical separation of different sized particles either at the site of ablation or during transport and can produce temporal variations

within the ablate which may not be representative of the bulk composition. These processes lead to elemental fractionation and are a function of the sample matrix and the operating conditions. Correcting for elemental fractionation is not easy: different correction factors are required for different elements. It is more effective to use laser conditions that limit this fractionation (Gunther & Koch 2008). For example, a high repetition rate and pulse energy can result in downhole fractionation of elements and fractional evaporation of the lighter elements because of the reduced effects of crater wall melting (Woodhead et al. 2004). A larger spot increases the diameter/depth ratio and can reduce downhole fractionation. However, with a larger diameter beam (> 50 µm), mass-load-induced matrix effects can affect the efficiency of the ionization within the plasma, i.e. there is too much material entering the plasma at once (Liu et al. 2013).

Mass spectrometry and isotope interferences

One of the main sources of error from LA-ICP-MS occurs during mass spectrometry due to isotopic interference and limited peak resolution. This is where the distribution of detected isotopes overlap in terms of mass/charge ratio, thereby producing a spectral interference. Where there is a large difference in isotopic abundance, this can produce a significant overestimation in values (Longerich 2008). Polyatomic interferences occur when the mass numbers of two (or more) combined isotopes sum to the mass number of a measured isotope, for example $^{35}\text{Cl}-^{16}\text{O}$ on ^{51}V and $^{35}\text{Cl}-^{40}\text{Ca}$ on ^{75}As (May et al. 1998). Elements common in apatite, including Na, S, Cl and Ca, can cause polyatomic interferences that affect elements such as Ti, V and Zn. Doubly-charged isotopes cause similar interferences on isotopes of half their mass/charge ratio. This is common in REE, e.g. $^{150}\text{Nd}^{++}$ on ^{75}As . Because only a small fraction of isotopes will become doubly charged in the plasma, the affected element must be at considerably lower concentrations for such interferences to be significant. In general, spectral interferences should be avoided by selecting isotopes based on natural abundance and their potential for interference from other isotopes that may be in significant quantities within the apatite. Where they cannot be avoided, interferences can be corrected for by measuring the contribution of the interfering elements using different isotopes.

Analysis of the external standards is important in calculating accurate concentrations in the unknown samples. An underestimate of elements in unknown sample could be due to spectral interferences within the standard analyses, i.e. concentrations are overestimated in the standards but not the unknowns. Ideally, unknowns and standards should be matrix-matched, with respect to both the physical structure and composition.

Large differences in elemental concentrations between the standard and the unknowns mean that errors are propagated during extrapolation (Longerich 2008; Sylvester 2008).

In this study, analyses of apatite were conducted over a range of laser conditions to determine which were best for quantifying the composition of natural apatite. This

Table 3.4 Specifications and set up for an Agilent 7700 quadrupole ICP-MS with a New Wave ESI 193 µm laser.

<i>Laser parameters</i>	
Laser type	ArF excimer
Laser wavelength	193 nm
Analysis type	Spot
Spot diameter	35 µm
Carrier gas	Helium, (560 ml/min)
<i>Mass spectrometer parameters</i>	
Plasma gas flow	Argon, 1.12 l/min
Forward radio frequency	1350 watts
Dwell time per isotope	10 ms (Li, Co, Cu, As: 20 ms)
Instrument sweep time	0.645 s

considered how well the grain ablated (signal smoothness), degree of fractionation (fractionation index), signal strength (number of counts), instrument sensitivity and limits of detection. In addition, the preferred external standard was considered and the accuracy and precision of the results compared.

3.3.2 Method

Durango apatite (STD262) was analysed on an Agilent 7700 quadrupole ICP-MS using a New Wave ESI 193 μm excimer laser (Table 3.4). Calcium was used as the internal standard with concentration values obtained from EPMA from the same spot. The primary external standard used was NIST612; however, the standards GSD-1G and NIST610 were also analysed for comparison. The measurements were collected within the same session in blocks of 9 standards (3 each of NIST612, GSD-1G, NIST610) followed by 20 unknowns (STD262).

Each analysis started with a 2s pre-ablation to remove any surface contamination and a 15 s washout to clear the tubes. The laser was warmed up for 18 s prior to the main acquisition to ensure its stability. The spot size was fixed at 35 μm , the most commonly used spot size with natural apatite. A dwell time of 10 ms was used for most isotopes, apart from elements close to the detection limit (Li, Sc, Co, Cu, Rb, Nb, Sn and Hf) for which the dwell time was doubled. 52 elements were analysed. Two isotopes of the same element were collected for 10 elements where spectral interference was highlighted as a potential problem. Results were collected at laser repetition rates of 5 and 10 Hz at fluences of 1, 2, 3, 4, 5 and 6 J cm^{-2} , and for 2 and 20 Hz at 2, 3 and 4 J cm^{-2} .

The ablation signals were processed using in-house software ExLAM 2000 (Zacharias & Wilkinson 2007). The signal integration intervals areas for the instrumental gas background and sample ablation were selected manually.

3.3.3 Results

External standards

Apatite and glass standards are not matrix matched. However, although phosphate glass standards have been developed, NIST glasses have been suggested to be more suitable standards for apatite (Jochum et al. 2012). Table 3.5 details the composition of the most common glass standards (GSD-1G, NIST612, NIST610). It is important to note that the concentration of P in all the

Table 3.5 Composition of glass standards GSD-1G, NIST610 and NIST612.

		GSD-1G	NIST610	NIST612
Na	wt. %	2.66	9.92	10.15
Al	wt. %	7.1	1.03	1.07
Ca	wt. %	5.14	8.13	8.49
P	ppm	860	413	46.6
Fe	ppm	10.33 (wt.%)	458	51
Mg	ppm	2.17 (wt.%)	68	432
Mn	ppm	220	444	38.7
Ti	ppm	0.825 (wt.%)	452	44
V	ppm	44	450	38.8
As	ppm	27	325	35.7
Sr	ppm	69.4	515.5	78.4
Y	ppm	42	462	38.3
La	ppm	39.1	440	36
Ce	ppm	41.4	453	38.4
Pr	ppm	45	448	37.9
Nd	ppm	44.7	430	35.5
Sm	ppm	47.8	453	37.7
Eu	ppm	41	447	35.6
Gd	ppm	50.7	449	37.3
Tb	ppm	47	437	37.6
Dy	ppm	51.2	437	35.5
Ho	ppm	49	449	38.3
Er	ppm	40.1	455	38
Tm	ppm	49	435	36.8
Yb	ppm	50.9	450	39.2
Lu	ppm	51.5	439	37
Hf	ppm	39	435	36.7
Ta	ppm	40	446	37.6
Pb	ppm	50	426	38.57
Th	ppm	41	457.2	37.79
U	ppm	41	461.5	37.38

Table 3.6 Durango apatite (STD262) LA-ICP-MS analysis calibrated using GSD-1G and NIST612 external standards compared to solution-ICP-MS analyses (Chew et al 2016). Highlighted values have variation of more than 10 % between results.

	Mean (ppm)	Standard deviation	Mean (ppm)	Standard deviation	1G vs NIST (%)	(Chew et al. 2016) (ppm)
Li	2.24	0.35	2.24	0.35	-0.1	-
Na	1520	141	1551.93	142.93	-1.9	-
Mg	83.28	6.52	107.13	8.36	-22.3	-
P	195020.25	14868.97	191253.48	14849.68	2.0	-
Ca	393572.00	3463.20	393572.00	3463.20	0.0	400000
Ti	0.13	0.03	0.16	0.04	-14.8	-
V	27.87	2.21	28.48	2.22	-2.2	31.87
Mn	81.59	6.46	82.75	6.55	-1.4	95.15
Fe	393.64	25.87	231.87	15.10	69.8	-
As	391.44	39.07	505.23	50.84	-22.5	939.0
Sr	939.36	56.90	520.23	28.14	80.6	501.9
Y	0.80	0.05	869.91	52.55	-99.9	1017
La	4037.05	275.79	3966.30	269.52	1.8	4239
Ce	5283.37	357.29	5334.72	362.23	-1.0	5777
Pr	459.33	30.87	459.59	30.89	-0.1	530.1
Nd	1315.22	85.29	1267.97	82.50	3.7	17729
Sm	187.86	12.15	185.11	11.94	1.5	251.1
Eu	16.62	1.21	16.33	1.19	1.8	20.50
Gd	177.86	11.24	162.56	10.28	9.4	225.9
Tb	21.42	1.36	20.97	1.33	2.1	30.27
Dy	124.42	7.67	118.24	7.29	5.2	167.0
Ho	24.90	1.58	23.99	1.53	3.8	34.78
Er	69.34	4.16	64.75	3.88	7.1	91.94
Tm	8.25	0.52	7.92	0.50	4.2	11.84
Yb	45.12	2.81	43.59	2.71	3.5	60.21
Lu	5.26	0.33	5.01	0.31	5.0	6.60
Pb	0.05	0.01	0.64	0.06	-92.8	0.69
Th	242.21	15.38	237.88	14.59	1.8	358.9
U	11.48	0.92	11.71	0.94	-2.0	18.66

standards and Fe, Mg, Ti in GSD-1G is significantly different to the concentrations typically found in apatite, thereby introducing a possible source of error for these elements.

The effect of the external standard used in LA-ICP-MS analysis of apatite is shown in table 3.6. There are large differences between the Mg, Fe, As, Y and Pb concentrations in apatite calibrated using GSD-1G and NIST612. Comparison with solution ICP-MS data suggests apatite values calibrated using NIST612 are more accurate (Chew et al. 2016).

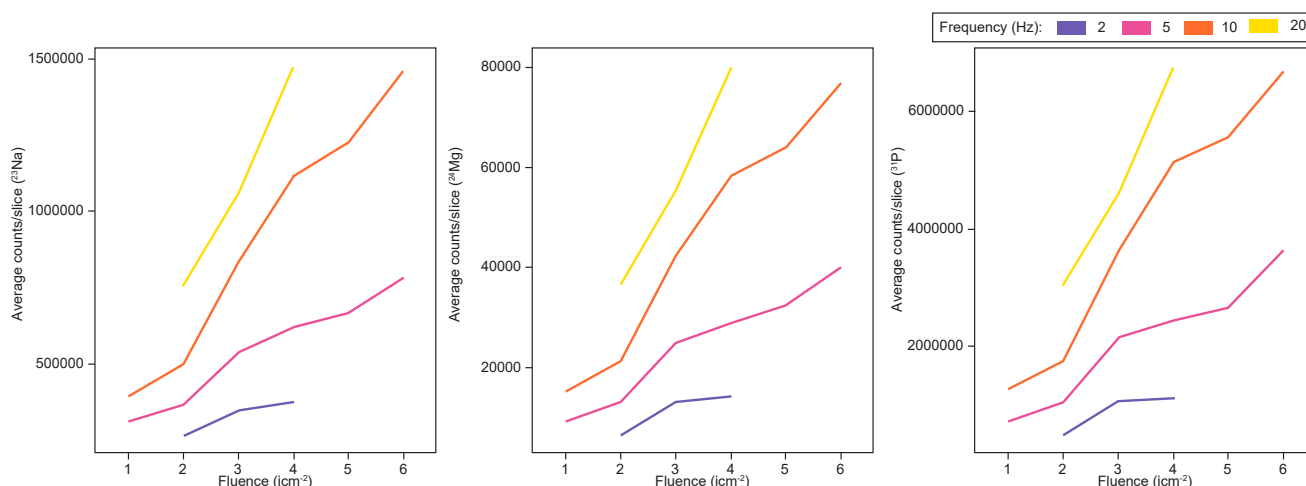
**Figure 3.6** Average counts per second for elements from ablation of Durango apatite over a range of laser operating conditions.

Table 3.7 Relative standard deviation (%) of signals for isotopes measured in Durango apatite (STD262) under different laser operating conditions.

Fluence (J cm ⁻²)	Rep. rate (Hz)	Na23	Mg24	P31	Ca43	Mn55	Fe57	Sr88	Y89	La139	Ce140	Eu151	Lu175	Pb208	U238
1.00	5	0.17	0.43	0.55	0.37	0.41	0.44	0.47	0.34	0.39	0.50	0.50	0.51	0.93	0.44
1.00	10	0.14	0.28	0.39	0.28	0.32	0.34	0.35	0.27	0.22	0.33	0.34	0.36	0.80	0.37
2.00	2	0.11	0.38	0.32	0.35	0.30	0.33	0.29	0.31	0.32	0.39	0.37	0.42	1.09	0.45
2.00	10	0.17	0.24	0.37	0.25	0.25	0.26	0.26	0.18	0.19	0.270	0.24	0.27	0.72	0.30
2.00	20	0.17	0.24	0.31	0.22	0.22	0.27	0.20	0.19	0.20	0.25	0.22	0.25	0.62	0.25
3.00	2	0.33	0.65	0.77	0.61	0.46	0.48	0.58	0.53	0.56	0.62	0.57	0.63	0.95	0.61
3.00	5	0.18	0.26	0.31	0.27	0.25	0.28	0.28	0.26	0.25	0.27	0.29	0.29	0.73	0.28
3.00	10	0.16	0.26	0.27	0.23	0.23	0.25	0.21	0.18	0.20	0.23	0.21	0.22	0.57	0.23
3.00	20	0.34	0.41	0.43	0.37	0.37	0.35	0.39	0.33	0.35	0.38	0.38	0.31	0.62	0.37
4.00	2	0.16	0.31	0.51	0.29	0.22	0.31	0.30	0.26	0.27	0.34	0.30	0.34	0.88	0.41
4.00	5	0.11	0.17	0.30	0.16	0.16	0.22	0.18	0.12	0.14	0.21	0.19	0.20	0.77	0.22
4.00	10	0.16	0.19	0.26	0.20	0.17	0.21	0.18	0.12	0.13	0.19	0.15	0.18	0.50	0.19
4.00	20	0.27	0.32	0.35	0.31	0.30	0.30	0.31	0.28	0.27	0.31	0.28	0.26	0.55	0.31
5.00	5	0.13	0.18	0.21	0.16	0.16	0.23	0.17	0.13	0.11	0.18	0.15	0.20	0.55	0.19
5.00	10	0.10	0.12	0.16	0.12	0.12	0.16	0.10	0.09	0.10	0.09	0.12	0.14	0.51	0.12
6.00	5	0.13	0.19	0.25	0.16	0.14	0.20	0.14	0.12	0.12	0.18	0.14	0.19	0.56	0.20
6.00	10	0.11	0.16	0.19	0.14	0.12	0.15	0.17	0.10	0.10	0.17	0.12	0.15	0.46	0.13

Unknown samples

Raw ablation signal

The raw signal (counts before reduction to a concentration value) can indicate how well a sample is ablating under given laser conditions. The apatite standards generally lack inclusions allowing the signals to be integrated over large intervals. In all tests, apatite was found to ablate effectively suggesting its ablation threshold using the New Wave ESI laser is less than 1 J cm⁻². An increase in laser fluence and repetition rate produce a higher number of counts for each element (Fig. 3.6), which will lead to higher sensitivity and lower limits of detection. The greatest step changes in counts occur at a fluence over 2 J cm⁻² and repetition rates greater than 5 Hz.

Signal smoothness can be linked to the relative standard deviation (RSD) of the multiple measurements (signal slices) made on each isotope in the sample ablation interval; a smoother signal corresponds to a smaller RSD (Table 3.7) and therefore a greater analytical precision. However, a smooth signal that slopes (increasing or decreasing in counts) will also produce a larger RSD. At lower laser frequencies (2-5 Hz), an oscillating signal is produced due to inefficient mixing between the particulates produced by successive laser pulses. These lead to high RSD values because the counts variation is large compared to the total signal. The RSD decreases with an increase in frequency and fluence; the lowest RSD values and therefore the smoothest signals are achieved with ablation at frequencies of 5 or 10 Hz. Frequencies of 20 Hz have an unusually high RSD, a result of the undulation of the signal on a larger scale, probably linked to greater laser penetration depths and consequent more erratic transport of material and/or fractionation.

Downhole fractionation

Fractionation of elements as the laser pit deepens can be tracked by calculating the fractionation index (*FI*) for each isotope:

Chapter 3: Method development for EPM and LA-ICP-MS analyses

Table 3.8 Fractionation index (FI) for Durango apatite analysis with a range of laser operating conditions and for the standards NIST612 and GSD-1G at 10 Hz and 5 J cm⁻². Variations greater than ±5% from a fraction index of 1 are highlighted.

Rep. rate (Hz)	10	10	5	10	10
Fluence (J cm ⁻²)	6	5	3	5	5
Na23	0.96	1.01	0.97	1.00	1.00
Mg24	1.03	1.07	1.01	1.02	1.04
Al27	1.00	1.00	0.85	1.01	0.97
Si29	0.91	1.02	0.87	0.97	0.88
P31	1.10	1.09	0.94	0.76	0.88
V51	1.00	1.01	0.99	1.02	0.98
Mn55	0.99	1.06	1.07	1.02	0.98
Fe57	0.99	1.00	1.10	0.98	1.01
Sr88	1.07	0.98	1.04	1.01	1.02
Y89	0.95	1.00	1.02	1.02	1.00
La139	0.98	1.02	0.97	0.96	0.99
Ce140	1.06	1.02	1.14	1.01	1.03
Pr141	1.07	0.99	1.00	1.03	1.04
Nd145	0.99	1.03	1.03	0.99	1.04
Sm147	0.98	1.06	1.01	1.02	1.03
Eu151	1.00	1.03	1.04	1.03	0.98
Gd157	0.98	1.03	0.98	1.02	0.98
Tb159	0.96	1.02	1.07	1.03	1.03
Dy163	0.96	1.02	1.02	1.08	0.98
Ho165	0.99	1.03	1.07	1.02	0.98
Er167	0.98	1.02	1.00	0.98	1.03
Tm169	1.02	1.03	1.05	1.04	1.02
Yb173	1.01	1.01	0.93	1.00	1.05
Lu175	1.02	1.07	1.05	0.99	1.03
Pb208	0.91	0.85	1.06	0.96	1.12
Th232	0.96	1.01	0.99	1.02	1.00
U238	1.04	1.01	1.00	1.01	1.00

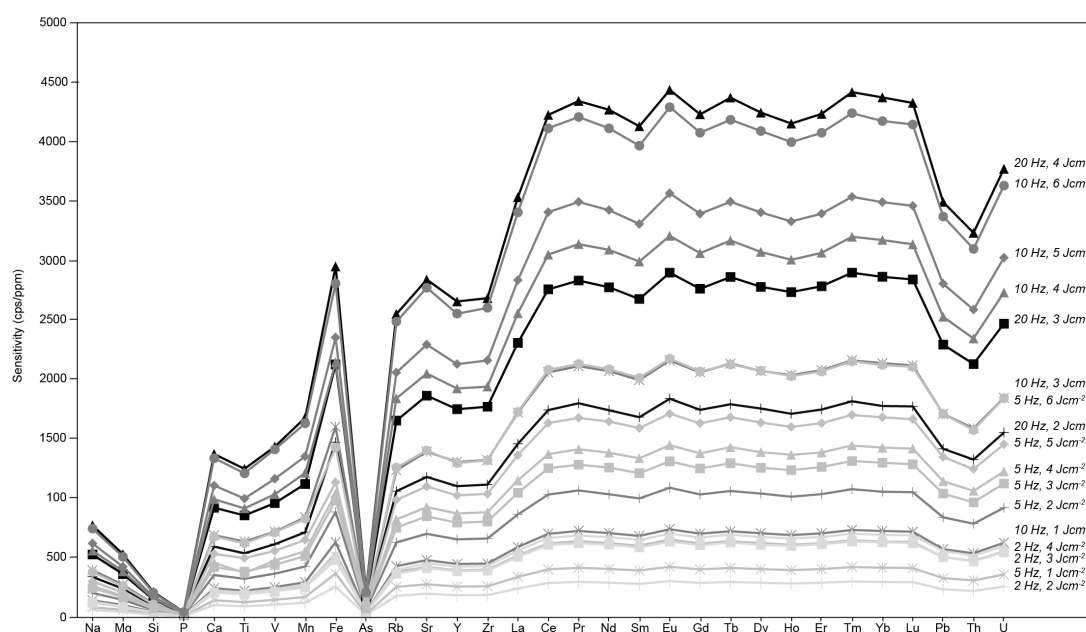


Figure 3.7 Effect of operating conditions on the sensitivity of key isotopes during the analysis of Durango apatite (STD262).

$$FI^i = \frac{cps_{second\ half}^i / cps_{second\ half}^{ns}}{cps_{first\ half}^i / cps_{first\ half}^{ns}} \quad \text{Eq. 3.1}$$

Here cps^i is the net count rate (sample signal – background) of element i and cps^{ns} is the net count rate of the internal standard isotope in the sample (in this case ^{43}Ca). The first half of the ablation signal (taken as measurement slices 60 – 90 s) is compared to the second half (slices 91 – 121 s). No fractionation would produce a FI of 1. Table 3.8 shows the calculated FI for Durango apatite STD262 at laser conditions of 10 Hz and 6 J cm⁻², 10 Hz and 5 J cm⁻², and 5 Hz and 3 J cm⁻². The fractionation index is ~1 for all experiments suggesting that there is little fractionation of elements under these conditions. This suggests conditions up to 6 J cm⁻² and 10 Hz can be used for ablating apatite.

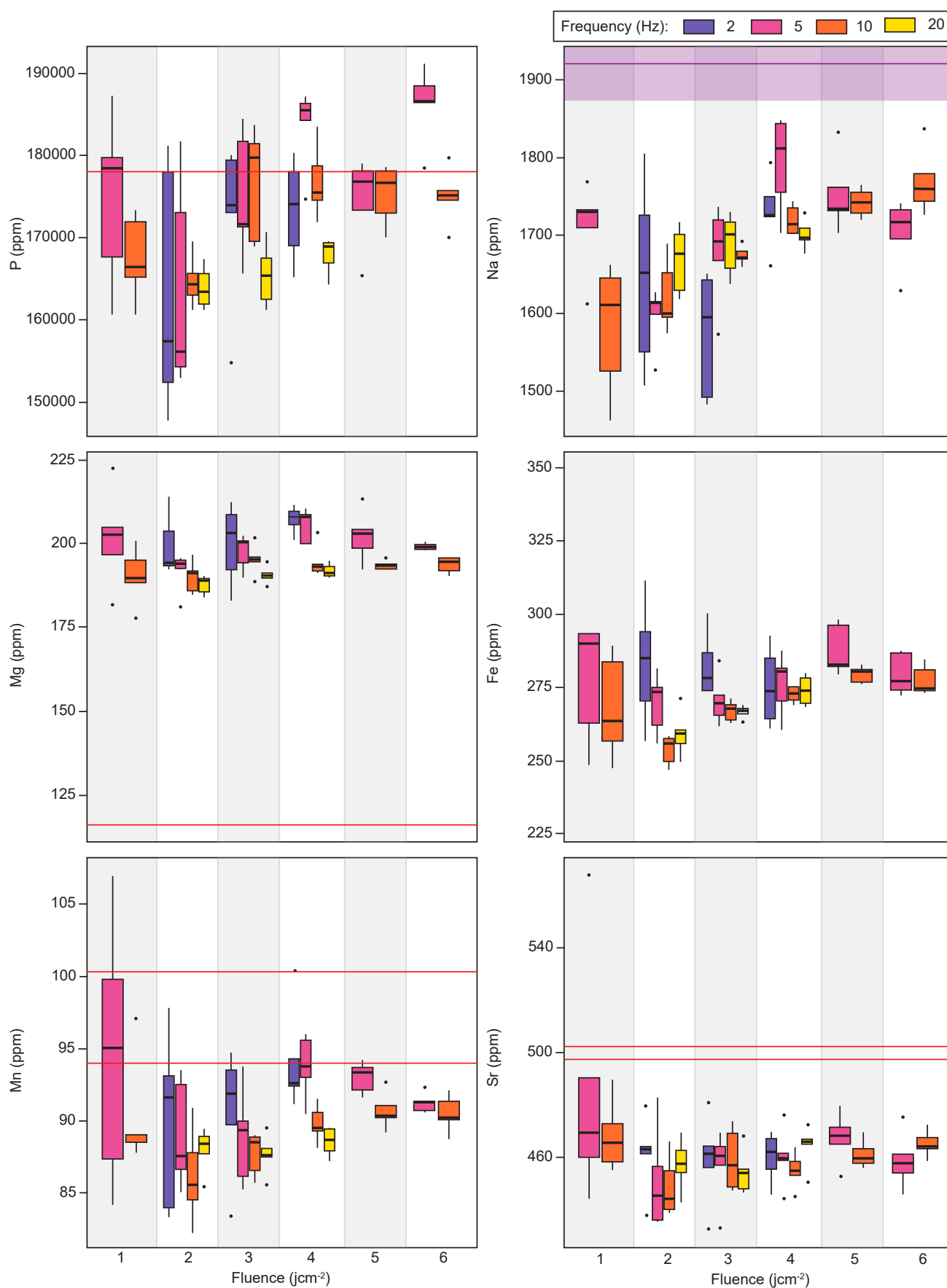
Downhole fractionation within the glass standards was also calculated, in this case for beam conditions of 10 J cm⁻² and 5 Hz (Table 3.8). GSD-1G shows some fractionation of Si and Pb and, for both GSD-1G and NIST612, counts of P/Ca increase with time relative to the other isotope ratios, particularly for the latter standard.

Sensitivity of unknowns

The sensitivity of an instrument can be defined as the smallest observable difference in the results. It is calculated as the ratio of the change in the measured quantity to the change in output. Sensitivity is strongly linked to detection limits and the volume of material being analysed and therefore improves with the laser spot size, the element concentration in the sample and its ability to ionise. The instrumental sensitivity repetition rates of 10 and 20 Hz with fluence having less of an effect on sensitivity (Fig. 3.7). The sensitivity for the REE can be as much as four times higher under these operating conditions.

Table 3.9 Detection limits (ppm) at different laser conditions.

Fluence (J cm ⁻²)	3			4			5		6	
Rep. rate (Hz)	5	10	20	5	10	20	5	10	5	10
Na	17	12	8	15	7	5	12	6	10	5
Mg	0.4	0.2	0.2	0.3	0.2	0.1	0.3	0.1	0.3	0.1
P	35	20	17	34	15	11	28	13	23	11
V	0.08	0.06	0.04	0.08	0.03	0.03	0.07	0.03	0.05	0.03
Mn	0.7	0.4	0.3	0.6	0.3	0.2	0.5	0.2	0.4	0.2
Fe	24	12	10	29	8	7	17	7	13	7
As	1	0.7	0.5	1.2	0.6	0.4	1	0.5	0.8	0.4
Sr	0.01	0.01	0.01	0.01	0.008	0.0076	0.02	0.005	0.007	0.007
Y	0.02	0.007	0.007	0.01	0.006	0.005	0.009	0.004	0.007	0.005
La	0.02	0.007	0.007	0.01	0.006	0.005	0.009	0.004	0.007	0.005
Ce	0.01	0.005	0.005	0.01	0.004	0.003	0.006	0.005	0.007	0.007
Pr	0.01	0.005	0.004	0.006	0.004	0.002	0.006	0.003	0.005	0.002
Nd	0.09	0.06	0.04	0.08	0.04	0.03	0.06	0.05	0.05	0.04
Sm	0.05	0.03	0.03	0.04	0.03	0.01	0.04	0.02	0.03	0.2
Eu	0.02	0.01	0.01	0.01	0.01	0.004	0.01	0.005	0.01	0.005
Gd	0.05	0.03	0.02	0.07	0.03	0.01	0.04	0.02	0.03	0.02
Tb	0.01	0.004	0.003	0.007	0.003	0.002	0.006	0.003	0.005	0.003
Dy	0.03	0.02	0.01	0.03	0.02	0.008	0.02	0.01	0.02	0.008
Ho	0.008	0.004	0.003	0.008	0.003	0.002	0.005	0.003	0.006	0.002
Er	0.04	0.02	0.02	0.03	0.02	0.01	0.02	0.01	0.02	0.01
Tm	0.01	0.005	0.003	0.008	0.003	0.002	0.005	0.003	0.004	0.002
Yb	0.005	0.04	0.02	0.04	0.02	0.01	0.03	0.02	0.03	0.02
Pb	0.01	0.08	0.05	0.1	0.04	0.03	0.01	0.04	0.06	0.03
Th	0.01	0.008	0.005	0.01	0.004	0.004	0.01	0.004	0.007	0.004
U	0.008	0.008	0.006	0.008	0.003	0.002	0.006	0.003	0.007	0.003



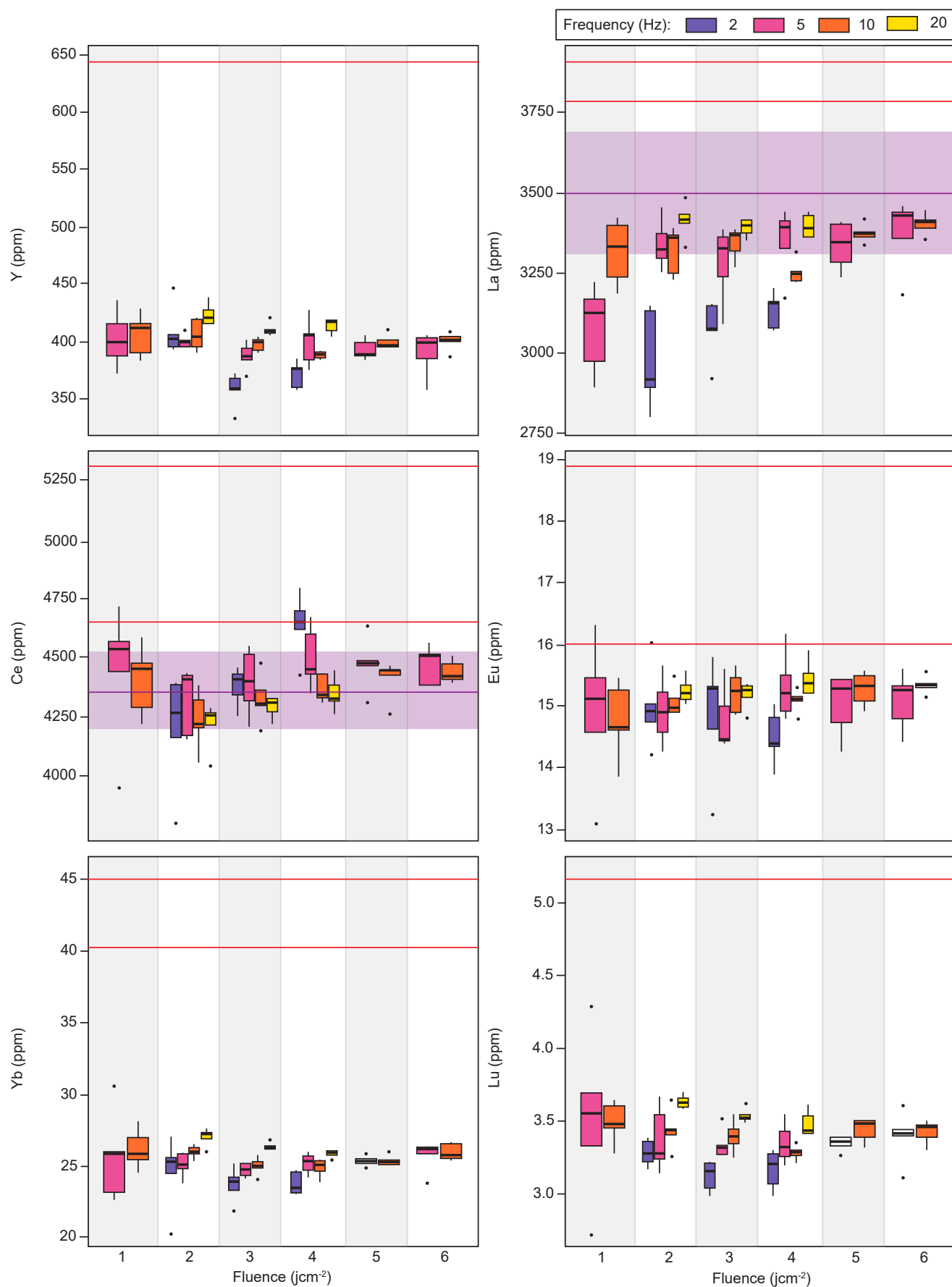


Figure 3.8 Measured element concentrations in Durango apatite (STD 262) at different laser energy pulse and frequency combinations. Mean EPMA values have plotted in purple and red lines indicate values from the literature taken from Chew et al. (2016).

Table 3.10 A comparison of apatite (Durango STD0067) with LA-ICP-MS data with averaged solution ICP-MS data taken from Mao et al. (2016) and Chew et al. (2016).

Durango apatite STD0067		Literature Mean	Natural History Museum Mean RSD (%)		NHM vs Lit. (%)
<i>SEM</i> (wt. %)	Ca	39.63	39.33	0.36	-0.74
	P		17.77	0.18	
	S		0.14	0.04	
<i>EMPA</i> (wt. %)	F*	3.29	3.08	0.09	-6.12
	Cl*	0.42	0.35	0.02	-14.94
<i>LA-ICP-MS</i> (ppm)	Na		0.155	0.014	
	Fe		0.023	0.002	
	Mn	0.010	0.008	0.001	-13.47
	Mg	0.012	0.011	0.001	-8.29
	Sr	0.050	0.052	0.003	3.78
	Y	0.068	0.087	0.005	28.08
	La	0.388	0.397	0.027	2.22
	Ce	0.481	0.533	0.036	10.85
	Pr	0.042	0.046	0.003	8.16
	Sm	0.018	0.019	0.001	2.89
	Eu	0.002	0.002	0.000	-5.37
	Gd	0.016	0.016	0.001	0.79
	Dy	0.013	0.012	0.001	-9.16
	Yb	0.004	0.004	0.000	5.00
	Th	0.026	0.024	0.002	-8.02
	U	0.001	0.001	0.000	2.13

Accuracy and precision of calculated unknowns

The precision of the results varies with the laser operating conditions. The mean values of 10 Durango apatite (STD262) analyses are plotted as a function of laser energies in figure 3.8. The results are calibrated using NIST612 with Ca concentrations of 37.70 wt. % (mean Ca measured by EPMA). The precision of the results increases with higher laser frequencies (markedly above 5 Hz) and fluence (above 2 J cm⁻²). The results are compared to the EPM concentrations and published solution ICP-MS results (Chew et al. 2016). The accuracy of the results does not vary beyond error with changes in operating conditions. For elements determined both by EPMA and by LA-ICP-MS there is good agreement but are overall lower than concentrations reported in the literature.

A detection limit for each analysis is calculated as 3 σ of the measured background. LoDs for the analyses decrease with a higher laser frequencies and a er amount with higher fluence (Table 3.9). However, all reported LoD values fall comfortably below the average apatite concentrations for each respective element.

3.3.4 Discussion

Laser operating conditions

NIST standard glasses provide a closer match in element concentrations to a typical apatite composition than GSD-1G (Table 3.5) and have been demonstrated to be a suitable matrix-match

Table 3.11 Suggested isotopes to be used for analysis of apatite by ICP-MS

Element isotopes

⁷Li, ²³Na, ²⁴Mg, ³¹P, ⁴³Ca, ⁴⁵Sc, ⁴⁹Ti, ⁵¹V, ⁵⁵Mn, ⁵⁷Fe, ⁵⁹Co*, ⁶⁰Ni*, ⁶⁵Cu*, ⁶⁶Zn*, ⁷⁵As, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹³Nb, ⁹⁵Mo, ¹¹¹Cd, ¹¹⁹Sn, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴⁵Pr, ¹⁴⁷Sm, ¹⁵¹Eu, ¹⁵⁷Gd, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁷Er, ¹⁶⁹Tm, ¹⁷³Yb, ¹⁷⁵Lu, ¹⁷⁷Hf, ²⁰⁸Pb, ²⁰⁹Bi, ²³²Th, ²³⁸U

Presence may help detect contaminated analyses

²⁷Al, ²⁹Si, ³⁹K, ⁹⁰Zr

* likely to be absent or in very low concentration

(Jochum et al. 2012). Here, apatite analyses calibrated using NIST612 provide a closer match to average literature data for Durango apatite (Table 3.6). The raw signal from apatite ablation shows no cyclical variation in isotope backgrounds that may induce scatter in the results or reflect fractionation during ablation. Fluences above 3 J cm^{-2} and repetition rates above 5 Hz produce a large increase in counts per second (Fig. 3.6). The sensitivities (Fig. 3.7) are best at repetition rates of 10 or 20 Hz; however, a smoother signal (lower RSD) is produced at repetition rates of 5 and 10 Hz. The accuracy of apatite analyses does not vary significantly with laser fluence but there is a large increase in precision for analyses with fluence greater than 2 J cm^{-2} and repetition rates above 5 Hz.

As a result of these tests, operating conditions of 5 J cm^{-2} and 10 Hz are suggested for apatite analyses using $35 \mu\text{m}$ diameter spots using NIST612 as the external standard and Ca as the internal standard. Results for Durango apatite collected at these conditions are compared to literature values in table 3.10 (Chew et al. 2016; Mao et al. 2016).

Selection of isotopes measured by mass spectrometry

An isotope list for apatite analysis is suggested in table 3.11. These isotopes are the most abundant for each element of interest, avoiding isotopes where they may be an interference from major constituents of the apatite. Additional elements, which are at low concentrations in apatite but are common in other minerals, have been included as a useful test for inclusions or contamination of analyses.

3.4 Final methodology for apatite analyses

The suggested methods of quantification for each element commonly present at detectable levels in apatite are listed in table 3.12. Due to the relatively low concentrations of elements in apatite, most should be measured by LA-ICP-MS. Ca must be analysed by EPMA or SEM-EDS (scanning electron microscope energy dispersive spectroscopy) from the same spot, as it acts as the internal standard for ICP-MS calibration. Using measured Ca values rather than stoichiometric Ca will produce results that are more accurate because of the intrinsic (though limited) natural variability in apatite Ca contents.

The suggested operating conditions for EPMA analysis of apatite are a 10 nA beam current,

Table 3.12 Suggested method of analysis for elements in apatite. The average limit of detection (LoD) and analytical precision (RSD) for analyses collected using the suggested methods are calculated from repeat analyses of Durango (STD 0067).

Element	NHM	LoD (ppm)	Std. Dev (ppm)	RSD (%)
Ca	EMPA	580	1870	0.5
P	EMPA	390	1640	0.9
F	EMPA	1541	980	2.9
Cl	EMPA	430	220	5.4
S	EMPA/SEM	200	100	7.5
Na	LA-ICP-MS	6.0	18.4	1.1
Mg	LA-ICP-MS	0.1	1.4	0.7
V	LA-ICP-MS	0.03	0.27	1.0
Mn	LA-ICP-MS	0.2	1.3	1.4
Fe	LA-ICP-MS	7.0	3.0	1.1
As	LA-ICP-MS	0.5	14.1	1.9
Sr	LA-ICP-MS	0.005	5.5	1.2
Y	LA-ICP-MS	0.004	6.4	1.6
La	LA-ICP-MS	0.004	29.8	0.9
Ce	LA-ICP-MS	0.005	81.7	1.9
Pr	LA-ICP-MS	0.003	6.4	2.0
Nd	LA-ICP-MS	0.05	9.0	0.9
Sm	LA-ICP-MS	0.02	2.2	1.8
Eu	LA-ICP-MS	0.005	0.3	1.8
Gd	LA-ICP-MS	0.02	0.8	0.8
Tb	LA-ICP-MS	0.003	0.1	0.9
Dy	LA-ICP-MS	0.01	0.6	0.9
Ho	LA-ICP-MS	0.003	0.2	1.7
Er	LA-ICP-MS	0.01	0.3	0.9
Tm	LA-ICP-MS	0.003	0.01	1.1
Yb	LA-ICP-MS	0.02	0.4	1.5
Pb	LA-ICP-MS	0.04	0.01	8.6
Th	LA-ICP-MS	0.004	1.6	1.2
U	LA-ICP-MS	0.003	0.1	1.4

Chapter 3: Method development for EPM and LA-ICP-MS analyses

10 kV accelerating voltage and a 10 μm spot size. The peak background positions and the spectrometers used are given in table 3.2. Elements that are most affected by the electron beam (i.e. F, Cl and Na) should be collected first. The samples should be freshly polished and coated, as it is possible that carbon coating degradation can contribute to fluctuation in halogen spot counts (Goldoff et al. 2012; Stormer et al. 1993). It is best to avoid over-exposing samples to the electron beam (such as by extensive sample scanning or collection of CL images) prior to analysis by electron probe. The average detection limits and standards deviation associated with apatite analysis at these conditions are given in table 3.12.

This study shows analyses of apatite from LA-ICP-MS are optimised using laser fluence of 5 J cm^{-2} and repetition rate of 10 Hz. External calibration should be done using NIST612. The average detection limits and standards deviation associated with apatite analysis at these conditions are given in table 3.12. The analytical precision is calculated as the relative standard deviation (RSD) of analyses over the limit of detection. A Durango crystal (STD0067) should be run with every EPMA and LA-ICP-MS analysis to monitor accuracy, precision, drift within run and over the course of a study (see *Appendix A*) The standard should be cleaned and re-polished regularly to mitigate the effects of electron beam exposure.

Chapter 4: The Geology of the La Granja Cu-Mo Porphyry System

This chapter examines the regional and deposit-scale geology of the La Granja porphyry system, Peru. It contains a review of pre-existing work followed by new data including petrographic descriptions, zircon U-Pb ages and zircon trace element analysis and bulk rock geochemistry. Samples used in this study were collected during fieldwork undertaken in November 2017. La Granja is the main case study used in this thesis and this chapter provides the basis on which data from La Granja apatite will be interpreted.

4.1 Literature review

4.1.1 Regional Geology

The La Granja Cu-Mo porphyry deposit (-6.35203°S , $79.127159^{\circ}\text{W}$) lies approximately 40 km north of the city of Chiclayo in Chota province, Peru. It is at an altitude of 2200–3000 m in the Peruvian Andes (Fig. 4.1). It is located within the Peruvian “flat slab segment” of the Andean margin (Fig. 4.2), within the Miocene polymetallic belt that extends NW into Ecuador (Noble & McKee 1990).

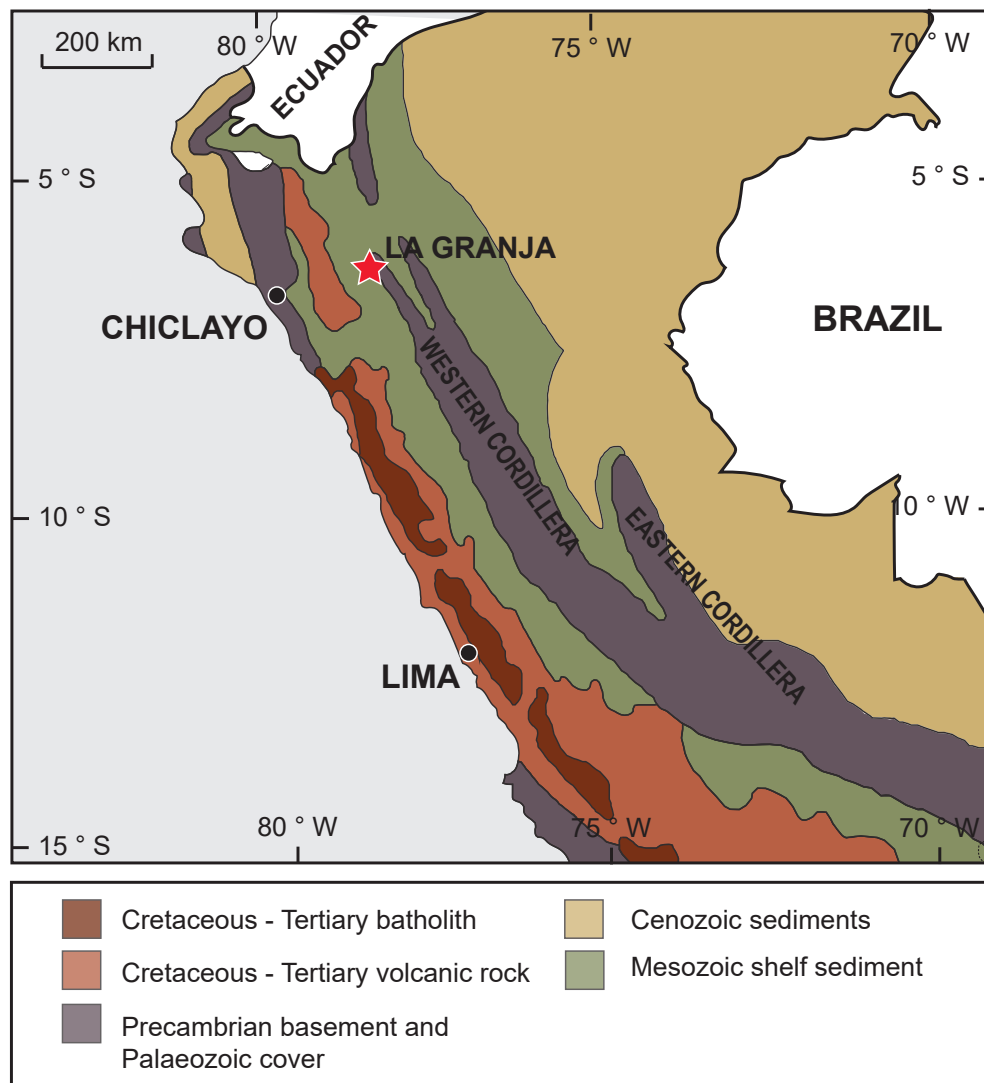


Figure 4.1 The main rock and morpho-structural units of Peru. The La Granja porphyry system is located within the Western Cordillera of the Andes. Modified after Benavides-Cáceres (1999) and Myers (1975).

The Andean Cordillera in Peru is composed of two belts running parallel to the coast (Benavides-Cáceres 1999). The eastern belt is formed of continental-derived Palaeozoic sediments and volcanics metamorphosed to a medium to high grade. The western belt, which hosts La Granja, comprises submarine lava flows and hyaloclastites that formed within horst and graben basins during early Mesozoic extension. These sedimentary and volcanic rocks have been through multiple phases of deformation, the first belonging to the Mochica phase in the mid-Cretaceous which produced folding and thrusting in a NW direction along the present-day coast (Benavides-Cáceres 1999). A second phase of deformation was associated with the Incaic orogeny which occurred in the mid – late Eocene. Deformation at this stage saw the tightening and rotation of fold axes within Cretaceous sedimentary rocks to an E-W trend and was accompanied by igneous activity (Myers 1975; Cobbing 1985; Macfarlane 1989; James 1998).

The Andes is an active orogenic belt running along the western edge of South America formed where the Nazca oceanic plate subducts below the South American continental plate. This subduction generated, and continues to generate, the magmatism responsible for the magmatic arc of the Peruvian Andes and mineral deposits including La Granja. The style of magmatism (plutonism versus volcanism) that has been produced varies greatly with time and along the strike of the Andes, and is a function of the dip of the subducting slab. Presently, there is a gap in active volcanism between 3 and 11 °S, with volcanoes to the north in Ecuador and to the south in central Peru (Fig. 4.2). Between these latitudes the Peruvian flat slab segment occurs in which the subducted Nazca plate is sub-horizontal at depths of around 100 km. Seismic and geochemical data suggest that the “normal” and flat-slab subduction regimes are accommodated through tears in the Nazca plate (Gutscher et al. 1999; Rosenbaum et al. 2005). In the flat-slab region, a hiatus in volcanism occurs as there is a reduced mantle wedge and insufficient melt produced.

The Nazca Plate (which together with the Cocos plate was previously a part of the Farrallon Plate) began subducting around 140 Ma. At ~ 50 – 37 Ma, subduction in the region was linked with a period of mountain building (McQuarrie et al. 2005; Benavides-Cáceres 1999) and, together with the presence of Eocene volcanic and intrusive rocks, suggests that the style of subduction at this time was ‘typical’ Andean – with a moderately steeply-dipping subducting oceanic plate. Slab flattening of the plate in the flat-slab segment has been attributed to subduction of the Nazca Ridge and Inca Plateau (Rosenbaum et al. 2005), although this is likely not the sole driver of slab angle (Lim et al. 2018; Manea et al. 2017; Ma & Clayton 2015). Initial subduction of the Nazca Ridge began around 15 Ma. Since then, around 900 km of plate has been subducted and the ridge has migrated to its current position at 15 °S (Hampel 2002).

Although lacking significant modern volcanism, there are a large number of magmatic-hydrothermal ore deposits along the Peruvian flat slab segment (Noble & McKee 1990). Metallogenic episodes appear to correlate with the onset and migration path of plateau and ridge subduction (Rosenbaum et al. 2005). Reconstruction of the plates during the Miocene period suggests that the formation of La Granja was linked, both spatially and temporally, to the onset of Inca Plateau subduction, and the continued subduction of the Nazca Ridge further south (Fig. 4.2). Tectonic reconstructions also suggest that the Inca Plateau had completely

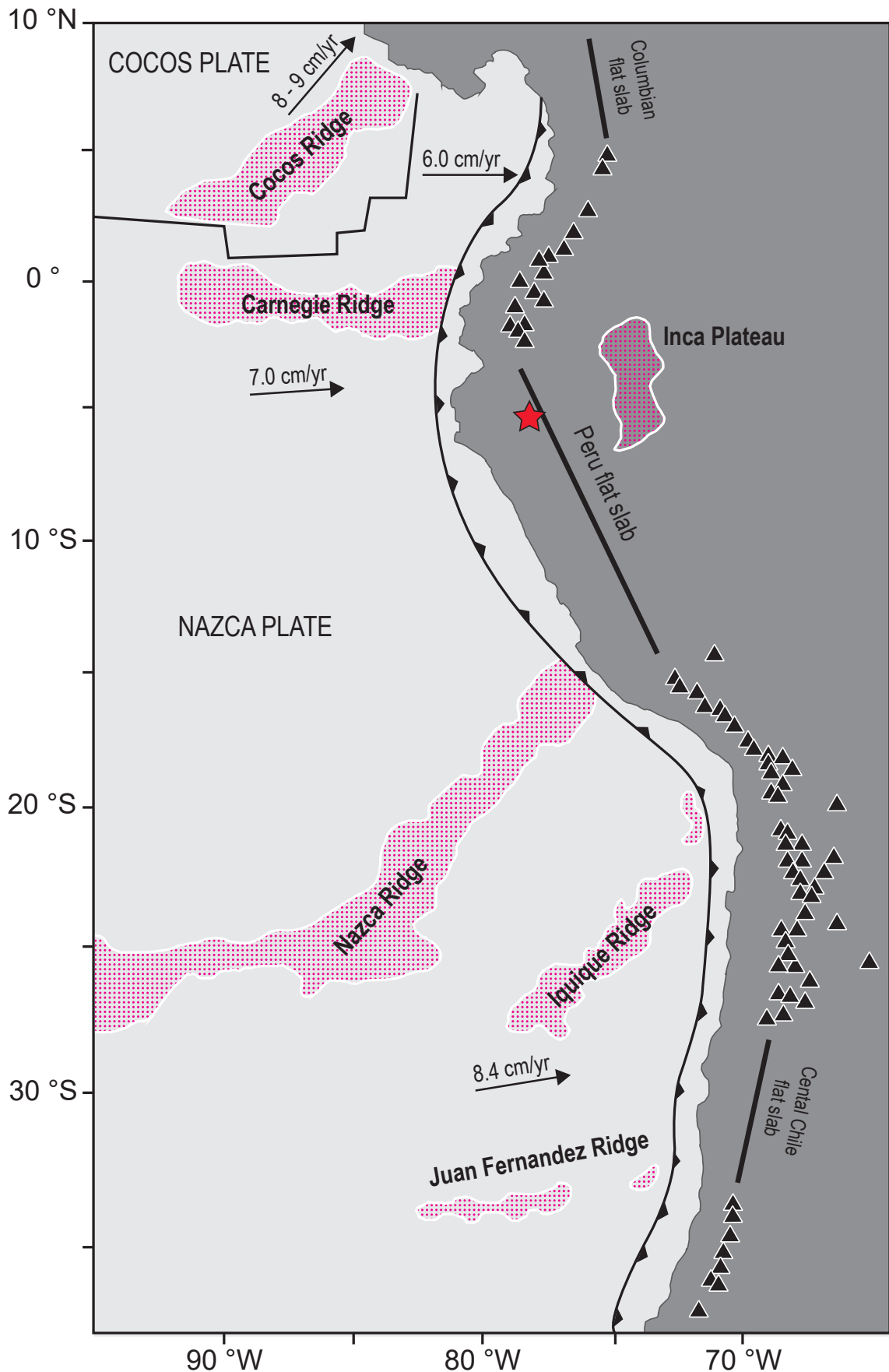


Figure 4.2 Geodynamic elements of the Andean margin showing the location of the present day subduction trench between the Nazca and South American plates, the Nazca Ridge and subducted Inca Plateau. It has been suggested that the subduction of these topographic anomalies may have been responsible for the formation of the Peruvian flat slab segment between approximately 3 – 15 °S. The flat slab is largely free from volcanoes but contains many magmatic-hydrothermal mineral deposits including La Granja, indicated by a star. Modified after Rosenbaum et al. (2005).

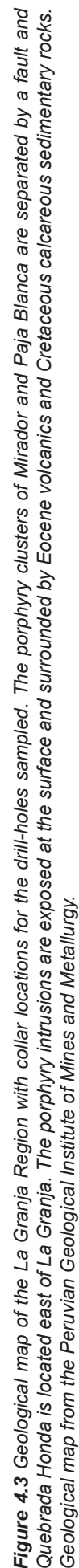
subducted within ~10 Myr and could explain the absence of mineral deposits younger than this in the region (Gutscher et al. 1999). The crustal thickening of the crust brought about by ridge subduction, coupled with the build-up of existing magmatic arcs, is thought to promote compressional regimes which encourage stalling of magma in lower crust or upper mantle where it fractionates (Chiaradia 2009). Deep crustal fractionation is associated with more adakite-like magma (high Sr/Y, La/Yb; Richards & Kerrich 2007, Chiaradia 2015). Additionally, the formation of more hydrous melts produced from interaction of a potentially more serpentanised oceanic ridge may encourage amphibole and/or garnet fractionation. Changes in stresses within the crust may have also triggered ore formation as a consequence of crustal deformation with large faults mobilising magmas from the MASH (melting, assimilation, storage, homogenization) zone, and faults in the upper crust providing fluid pathways (Rosenbaum et al. 2005).

4.1.2 Local geology

The host rocks to La Granja comprise a thick package of mainly Cretaceous marine sedimentary rocks which were later deformed and intruded by a variety of igneous rocks in the middle to late Tertiary period (Davies & Williams 2005). These rocks are unconformably overlain by southeast-dipping Tertiary volcanics; predominantly dacites and andesites (Schwartz, 1982; Davies & Williams 2005). The marine sequence is predominantly composed of sandstones that fine upwards into limestones, marls and shales. The 700 – 800 m thick Goyllarisquisga Group consists of early Cretaceous sandstones interbedded with laminated shales (Macfarlane 1989; Schwartz 1982). These are overlain by the Inca Chuléc Formation of early – mid Albian age. The lower units are composed of 30 m of sandstones, shales, calcareous siltstones and silty limestones (James 1998; McFarlane 1989). The upper portion is a thin unit of graded and laminated limestone with abundant chert nodules (James 1998; Benavides 1956). Lying unconformably above this is dark grey, bituminous limestone interbedded with siltstone belonging to the mid-Cretaceous Pariatambo Formation of Cretaceous age (James 1998).

These units were folded during the Incaic Orogeny, resulting in the development of open, upright folds and imbricate thrust sheets (Davies & Williams 2005). These events are thought to be coeval with the intrusion of voluminous diorite and granodiorite bodies which can be observed around La Granja (Schwartz 1982). During this period (late Mesozoic – early Cenozoic), the marine Cretaceous units were exposed, eroded and subsequently overlain by pyroclastic andesites and rhyolites (Hein et al. 1987). The youngest part of the Llama volcanics has been dated between 54.6 – 42.6 Ma (Atherton et al. 1985; Noble et al. 1990); this is overlain by the Calipuy Formation (dated at 33 – 10 Ma; James 1998). A further orogenic period - the Quechua - took place during the Miocene over three phases (Mégard 1984). The earliest phase occurred between 17 – 15 Ma and is associated with numerous plutons (James 1998), including the porphyry intrusions of La Granja.

In the region around La Granja, faults and ore bodies generally follow a NW strike and there are smaller E-W features. La Granja crops out as an outlier of Miocene intrusions within Eocene intrusive host rocks, bounded by two ENE-WSW faults. A NE-SW striking reverse fault brings older Cretaceous sedimentary rocks in the hanging wall in contact with Cenozoic (Fig. 4.3).



4.1.3 Deposit geology

The La Granja porphyry deposit was discovered following stream sediment surveys for copper anomalies conducted between 1969 and 1971 (Baldock 1977). Drilling began on the prospect in 1979 (Schwartz 1982) which has been owned by Rio Tinto since 2006 (Rio Tinto SEG presentation, 2012). Despite a total resource of 4320 million tonnes of ore at 0.51 % Cu (Rio Tinto Annual Report 2019), there is little published information about the deposit. La Granja has most recently been described as a Miocene porphyry-breccia-skarn system (SEG presentation, 2012). The first published summary of the geology of the deposit (Schwartz 1982) described a mineralised quartz-feldspar porphyry exposed over a 2 by 2.5 km area. The porphyry contains quartz phenocrysts (5 - 15 %), feldspar (20 - 30 %) and a matrix of phyllosilicates and quartz in equal proportions. Its composition grades into a biotite-granodiorite to the west (consisting of 15 - 30% plagioclase, 3 - 15% biotite, 10 - 30 % quartz and K-feldspar) and a hornblende-granodiorite to the southeast (15 - 30 % plagioclase, 15 - 25% quartz and 5-20% hornblende). It was suggested that the hornblende granodiorite may, in fact, be a less-altered version of the quartz-feldspar porphyry. A porphyritic diorite was also identified and was suggested to relate to the Culipuy Formation (Schwartz 1982).

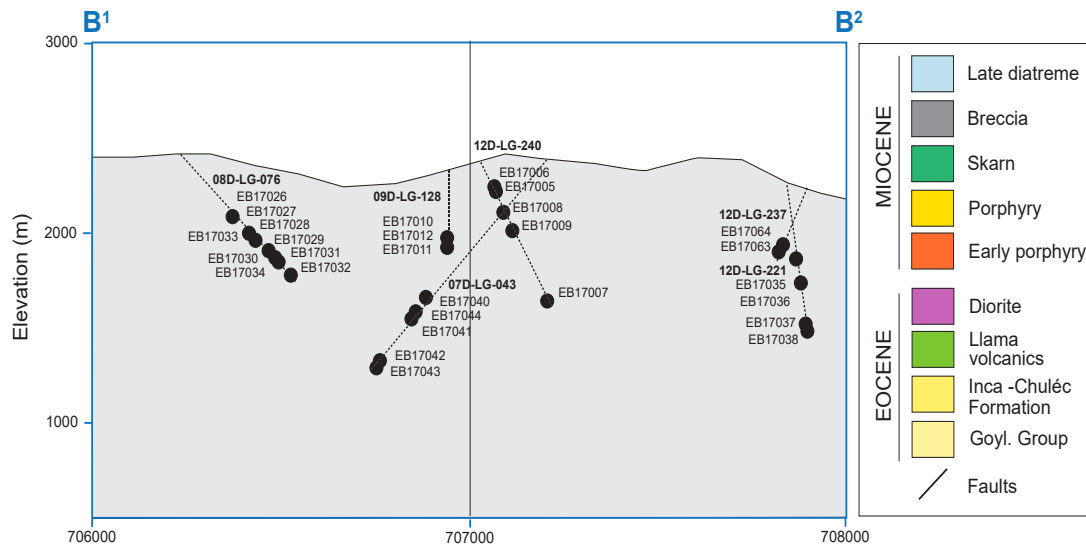
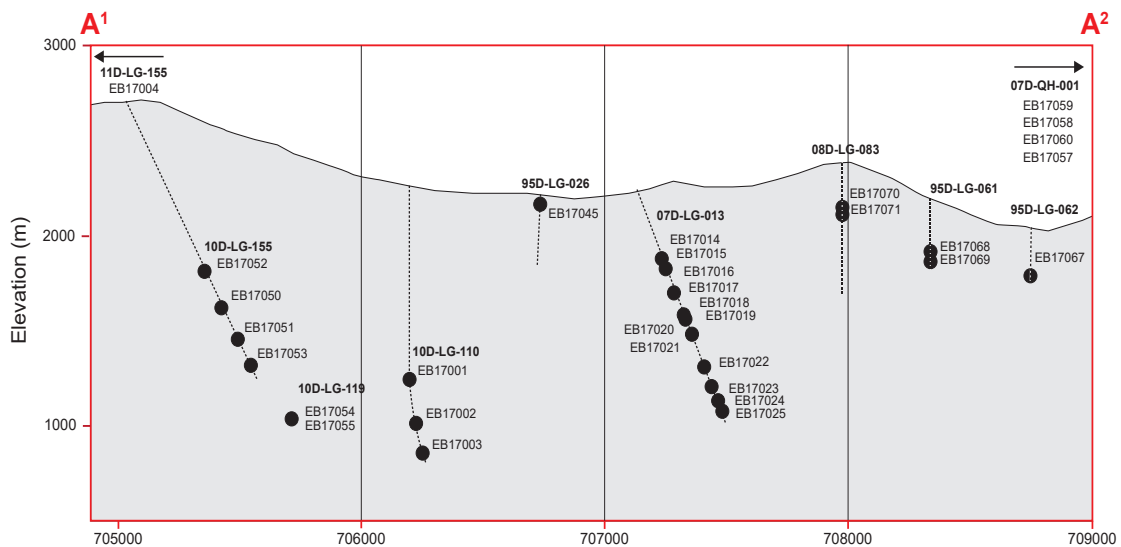
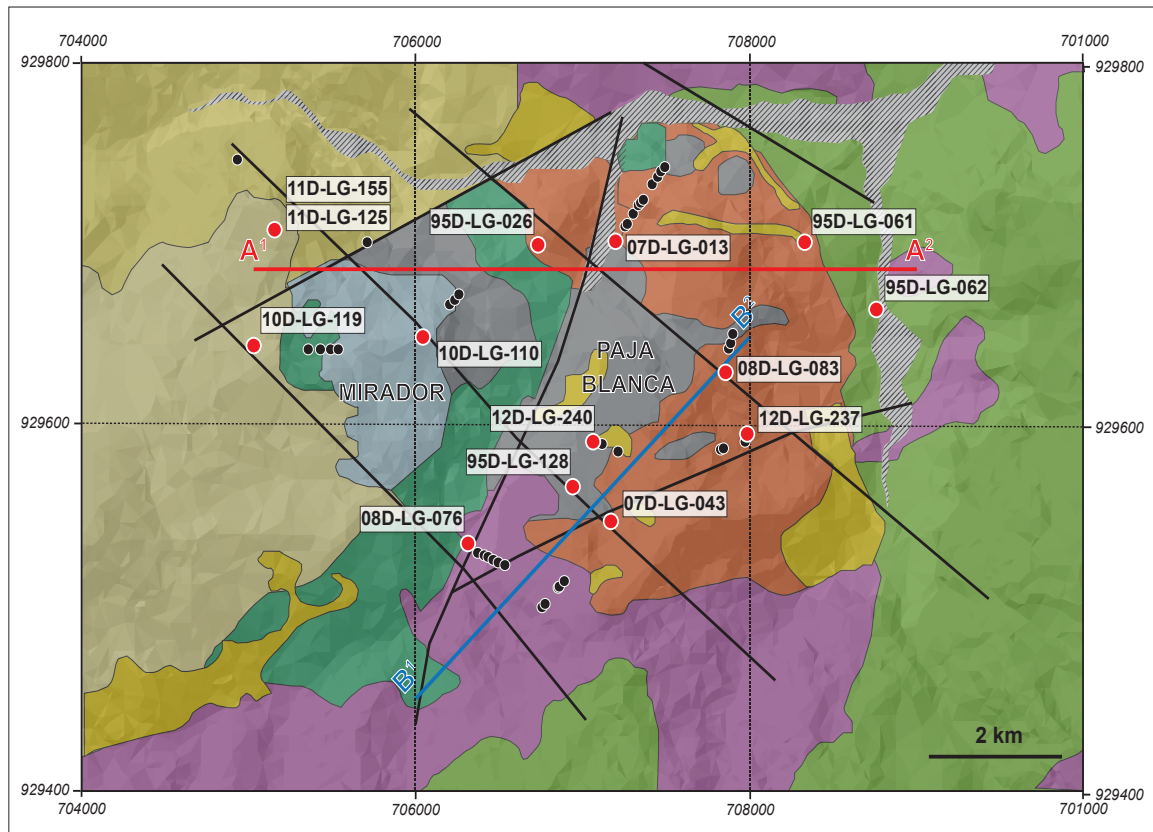
The coordinates of the outcrops described by Schwartz (1982) relate to the position of the Paja Blanca porphyry cluster referred to later in this chapter. A second hypogene resource named Mirador was identified to the northwest of Paja Blanca in 2011 (SEG presentation 2012). Today, La Granja is considered a porphyry district composed of two main porphyry clusters, Paja Blanca and Mirador, which are 1 km apart and separated by a fault. Other porphyries such as Huambrillo in the Paja Blanca cluster and satellite porphyries including Quebrada Honda, ~3 km east of Paja Blanca (Fig. 4.3), Cerro Huambo and El Roble also exist (SEG presentation 2012).

Skarns are present at the contact of the porphyry intrusions with calcareous host rocks (the Chulec, Pariatambo and Pulluicama Formations; Fig. 4.3). Magmatic-hydrothermal breccia is also developed extensively towards the top of the porphyries. A late “diatreme” extends from the deeper hypogene portion of Mirador and links to a rhyodacite dome at the present-day surface (SEG presentation 2012; Fig. 4.4). Intense brecciation and fracturing at the contacts of the porphyry intrusions complicates the distinction of individual intrusive bodies (Schwartz 1982).

Hydrothermal alteration

Hydrothermal alteration at La Granja is described in two published papers covering the alteration types and chemistry of the leached cap above the hypogene resource (Schwartz 1981) and the properties of fluid inclusions (Hein & Tistl 1986) at Paja Blanca. Both described intense alteration and a leached zone focused at the centre of the Cerro Paja porphyry. At depth, potassically altered rocks are overprinted laterally by weak propylitic alteration with assemblages of epidote, chlorite, calcite, clay and quartz. Sericitic alteration (sericite, quartz, clay and chlorite) has been telescoped downwards over the centre of the system and has destroyed most of the primary

Figure 4.4 (Right hand page) Deposit scale map showing the surface topography (Digital elevation model ASTER_S07W090 downloaded from <https://earthexplorer.usgs.gov> on 29/03/2019) and geology (Rio Tinto SEG 2012 presentation). The location of the drill cores (red dots) and relative position of the samples below ground level (black dots) are marked. Cross section lines A (E-W through Mirador and Paja Blanca) and B (NE through Paja Blanca) shows the vertical distribution of samples within the nearby drill core.



textures. This latter alteration is associated with high copper grades (Schwartz 1982; Hein & Tistl 1986). Argillic alteration locally overprints the sericitic zone and is composed of a mixture of andalusite, pyrophyllite, sericite, quartz and diaspore. The grade of the whole system is increased by the presence of a central leached cap (principally containing limonite and clays) underlain by a supergene ore zone containing secondary copper oxides and sulfides (Schwartz 1981).

Mineralisation

Annual reports show total resources of 4320 million tonnes at 0.51% Cu (Rio Tinto Annual Report 2019). Sulfides are described as dominated by pyrite (1 - 12 %) and chalcopyrite with molybdenite and bornite. The hypogene mineralisation is mainly disseminated through the rock but is also hosted in stockwork veins up to 2 cm thick. The sulfosalts enargite and tennantite are also present in veins associated with the sericitic alteration, supergene copper exists mainly in the form of chalcocite and covellite (Schwartz 1981).

4.2 Unit lithologies

The new data in this chapter were generated from 70 samples collected during fieldwork in November 2017 (Table 4.1). All samples were taken from drill core and are chiefly split between the two porphyry clusters - Paja Blanca and Mirador, - with 6 host rocks from the Quebrada Honda region (Figs. 4.3, 4.4). Samples were selected to represent the range of igneous compositions at La Granja and include volcanic and intrusive rocks from below the leached capping and secondary enrichment zone. In addition, 9 samples from skarns and breccias were also selected for comparative purposes. Of the samples, 61 were analysed for whole rock composition (see *section 4.5*; Table 4.1), 31 were made into thin sections and zircon concentrates produced from 15 samples were used to make separates (see *section 4.3*; Table 4.2). Hand sample photographs, plain polarised and reflected light micro-photographs of the thin sections are presented in *Appendix B*.

A comprehensive study by the geologists working at La Granja revealed that there are many more lithologies than described in the literature. Here I include a description of the main igneous units referred to in this study which comprise two main groups: the Eocene igneous host rocks and the Miocene porphyry intrusions. The porphyry intrusions are split between the two main centres of Mirador and Paja Blanca, in which the sequence and petrography of the intrusions are very similar (Fig. 4.5). Cross-cutting relationships are most evident between the host rock and the porphyries where contacts are preserved and the rock compositions are the most distinct. There are a lack of clear contacts between the individual porphyry lithologies which can appear very similar, texturally. Furthermore, distinction of the porphyry units is also hindered by hydrothermal alteration and brecciation. The potential scale of clasts within the breccias means that some of the samples collected from apparently coherent sections of drillcore may actually be from megaclasts within magmatic-hydrothermal breccia (Sillitoe 2010). Where there is evidence to suggest this, it has been noted in table 4.1. Samples are classified into lithologies using mineralogy, texture and the occurrence of veins (types and abundance), supplemented by U-Pb dating and bulk rock geochemistry. The typical vein types observed in these samples are described below in *section 4.2.5*.

Table 4.1 List of samples collected with assigned lithology. GRANO (granodiorite), DIO (diorite), AND (andesite), DIOP (diorite porphyry), DP (dacite porphyry), EQP (early quartz porphyry), DP (dacite porphyry), EDP (early dacite porphyry), LQP (late quartz porphyry), LDP (late dacite porphyry). Samples suspected of being large clasts in a breccia are indicated with an asterisk (*).

Sample	Prospect	Drill core	Sample depth (m)	Lithology	Alteration	Alteration intensity	Data acquired		
							Bulk rock	Thin section	Zircon
EB17001	Mirador	10D-LG-110	1297.0 - 1295.5	EDP _M	Potassic/Sericitic	Moderate	✓	✓	✓
EB17002	Mirador	10D-LG-110	1527.1 - 1525.0	EDP _M	Potassic	Moderate	✓		
EB17003	Mirador	10D-LG-110	1671.2 - 1679.4	EQP _M *	Sericitic	Moderate	✓		✓
EB17004	Mirador	11D-LG-155	792.2 - 790.0	DP _M	Sericitic	Moderate	✓		✓
EB17005	Paja Blanca	12D-LG-240	75.6 - 73.9	LQP _{PB}	Sericitic	Strong	✓		✓
EB17006	Paja Blanca	12D-LG-240	96.2 - 94.6	LDP _{PB}	Propylitic	Strong	✓		✓
EB17007	Paja Blanca	12D-LG-240	102.6 - 100.9	EDP _{PB} *	Propylitic/Sericitic	Moderate	✓		
EB17008	Paja Blanca	12D-LG-240	206.4 - 204.7	GRANO*	Chlorite-sericite	Moderate	✓		
EB17009	Paja Blanca	12D-LG-240	300.9 - 299.1	EDP _{PB}	Sericitic	Strong	✓		
EB17010	Paja Blanca	95D-LG-128	385.5 - 383.9	DIOP	Propylitic	Moderate	✓		✓
EB17011	Paja Blanca	95D-LG-128	439.1 - 438.0	SKARN	-	-	✓	✓	
EB17012	Paja Blanca	95D-LG-128	434.0 - 433.4	DP _{PB}	Potassic/propylitic	Strong	✓	✓	
EB17014	Paja Blanca	07D-LG-013	206.0 - 205.15	DP _{PB}	Chlorite-sericite	Moderate	✓	✓	✓
EB17015	Paja Blanca	07D-LG-013	221.2 - 219.6	DP _{PB}	Chlorite-sericite	Moderate	✓	✓	
EB17016	Paja Blanca	07D-LG-013	257.0 - 255.6	EDP _{PB}	Sericitic	Strong	✓		
EB17017	Paja Blanca	07D-LG-013	394.0 - 392.9	EDP _{PB}	Sericitic	Strong	✓		
EB17018	Paja Blanca	07D-LG-013	524.0 - 523.1	EDP _{PB}	Propylitic/Sericitic	Moderate/Weak	✓	✓	
EB17019	Paja Blanca	07D-LG-013	550.5 - 548.7	EQP _{PB} *	Potassic	Moderate	✓	✓	
EB17020	Paja Blanca	07D-LG-013	623.8 - 621.9	DP _{PB} *	Potassic	Moderate	✓	✓	
EB17021	Paja Blanca	07D-LG-013	627.3 - 626.7	BRECCIA	Potassic	Weak	✓		
EB17022	Paja Blanca	07D-LG-013	838.4 - 836.4	EQP _{PB} *	Sericitic	Moderate	✓	✓	✓
EB17023	Paja Blanca	07D-LG-013	944.7 - 943.3	DIOP	Potassic/chlorite-sericite	Moderate/Weak	✓		
EB17024	Paja Blanca	07D-LG-013	1037.2 - 1036.0	EQP _{PB}	Potassic/chlorite-sericite	Moderate/Weak	✓	✓	
EB17025	Paja Blanca	07D-LG-013	1099.0 - 1097.0	AND	-	-	✓		
EB17026	Paja Blanca	08D-LG-076	153.6 - 151.5	AND	Propylitic	Moderate	✓	✓	
EB17027	Paja Blanca	08D-LG-076	252.7 - 245.6	DIO	Propylitic	Moderate	✓	✓	
EB17028	Paja Blanca	08D-LG-076	295.4 - 293.4	DIOP	Propylitic	Moderate	✓	✓	
EB17029	Paja Blanca	08D-LG-076	368.0 - 366.0	DIOP	Propylitic	Weak	✓		✓
EB17030	Paja Blanca	08D-LG-076	389.6 - 388.3	GRANO	Chlorite-sericite	Moderate	✓	✓	✓
EB17031	Paja Blanca	08D-LG-076	431.8 - 429.8	DIO	Propylitic	Weak	✓		
EB17032	Paja Blanca	08D-LG-076	498.2 - 496.2	DIO	Potassic/propylitic	Weak	✓		
EB17033	Paja	08D-LG-076	255.1 -	DIOP	Potassic/	Weak/ Moderate	✓	✓	

EB17034	Paja Blanca	08D-LG-076	411.2 – 409.4	GRANO	Chlorite - sericite	Strong	✓	✓
EB17035	Paja Blanca	12D-LG-221	574.6 – 572.9	EDP _{PB}	Sericitic	Moderate	✓	
EB17036	Paja Blanca	12D-LG-221	708.0 – 706.0	BRECCIA	-	-	✓	
EB17037	Paja Blanca	12D-LG-221	938.9 – 937.0	EDP _{PB}	Sericitic	Strong	✓	✓ ✓
EB17038	Paja Blanca	12D-LG-221	981.3 – 979.4	EDP _{PB}	Propylitic	Weak	✓	
EB17039	Paja Blanca	07D-LG-043	781.8 – 783.5	DIOP	Propylitic	Weak	✓	✓
EB17040	Paja Blanca	07D-LG-043	891.3 – 890.3	GRANO	Sericitic	Moderate	✓	
EB17041	Paja Blanca	07D-LG-043	1015.7 – 1013.8	GRANO	Propylitic	Weak	✓	✓
EB17042	Paja Blanca	07D-LG-043	1286.3 – 1284.6	DIO	Potassic	Weak	✓	
EB17043	Paja Blanca	07D-LG-043	1313.6 – 1311.6	DIO	Propylitic	Strong	✓	✓
EB17044	Paja Blanca	07D-LG-043	992.5 – 990.6	GRANO	Chlorite-sericite	Strong	✓	✓
EB17045	Paja Blanca	95D-LG-026	49.5 – 32.5	DP _{PB}	Argillic	Strong	✓	
EB17046	Paja Blanca	07D-LG-043	942.0 – 944.1	BRECCIA	-	-		
EB17047	Mirador	10D-LG-119	142.0 – 141.9	LQP1 _M	Sericitic	Moderate		✓
EB17048	Mirador	10D-LG-119	1147.0 – 1146.9	LQP1 _M	Sericitic	Moderate		✓
EB17049	Mirador	10D-LG-119	1355.4 – 1355.3	AND	Sericitic	Moderate		
EB17050	Mirador	10D-LG-119	1157.2 – 1154.4	DP _M	Potassic	Strong	✓	
EB17051	Mirador	10D-LG-119	1334.6 – 1332.6	LQP1 _M	Sericitic	Strong	✓	✓ ✓
EB17052	Mirador	10D-LG-119	946.6 – 944.7	LQP1 _M *	Chlorite-sericite	Weak	✓	✓ ✓
EB17053	Mirador	10D-LG-119	1478.2 – 1476.2	LQP2 _M	Sericitic	Moderate	✓	✓ ✓
EB17054	Mirador	11D-LG-125	1672.8 – 1670.8	DP _M	Sericitic	Weak	✓	
EB17055	Mirador	11D-LG-125	1689.9 – 1687.9	EQP _M	Potassic	Weak	✓	✓ ✓
EB17056	Mirador	11D-LG-127	1786.8 – 1786.7	DIO	Propylitic	Strong		✓
EB17057	Quebrada Honda	07D-QH-001	191.6 – 189.5	AND	Potassic	Weak	✓	
EB17058	Quebrada Honda	07D-QH-001	144.9 – 143.2	AND	Potassic	Strong	✓	✓
EB17059	Quebrada Honda	07D-QH-001	116.6 – 114.9	AND	Propylitic	Strong	✓	
EB17060	Quebrada Honda	07D-QH-001	152.9 – 151.1	AND	Propylitic	Strong	✓	✓
EB17061	Quebrada Honda	07D-QH-001	103.4 – 103.2	AND	Propylitic	Strong		✓
EB17062	Quebrada Honda	07D-QH-001	130.4 – 130.3	AND	Propylitic	Strong		
EB17063	Paja Blanca	12D-LG-237	498.9 – 496.9	SKARN	-	-	✓	
EB17064	Paja Blanca	12D-LG-237	458.8 – 456.8	SKARN	-	-	✓	
EB17065	Paja Blanca	12D-LG-237	431.2 – 431.1	SKARN	-	-		
EB17066	Paja Blanca	12D-LG-237	248.4 – 248.2	SKARN	-	-		
EB17067	Paja Blanca	95D-LG-062	238.4 – 237.5	AND	Propylitic	Strong	✓	
EB17068	Paja	95D-LG-061	216.0 –	SKARN	-	-	✓	

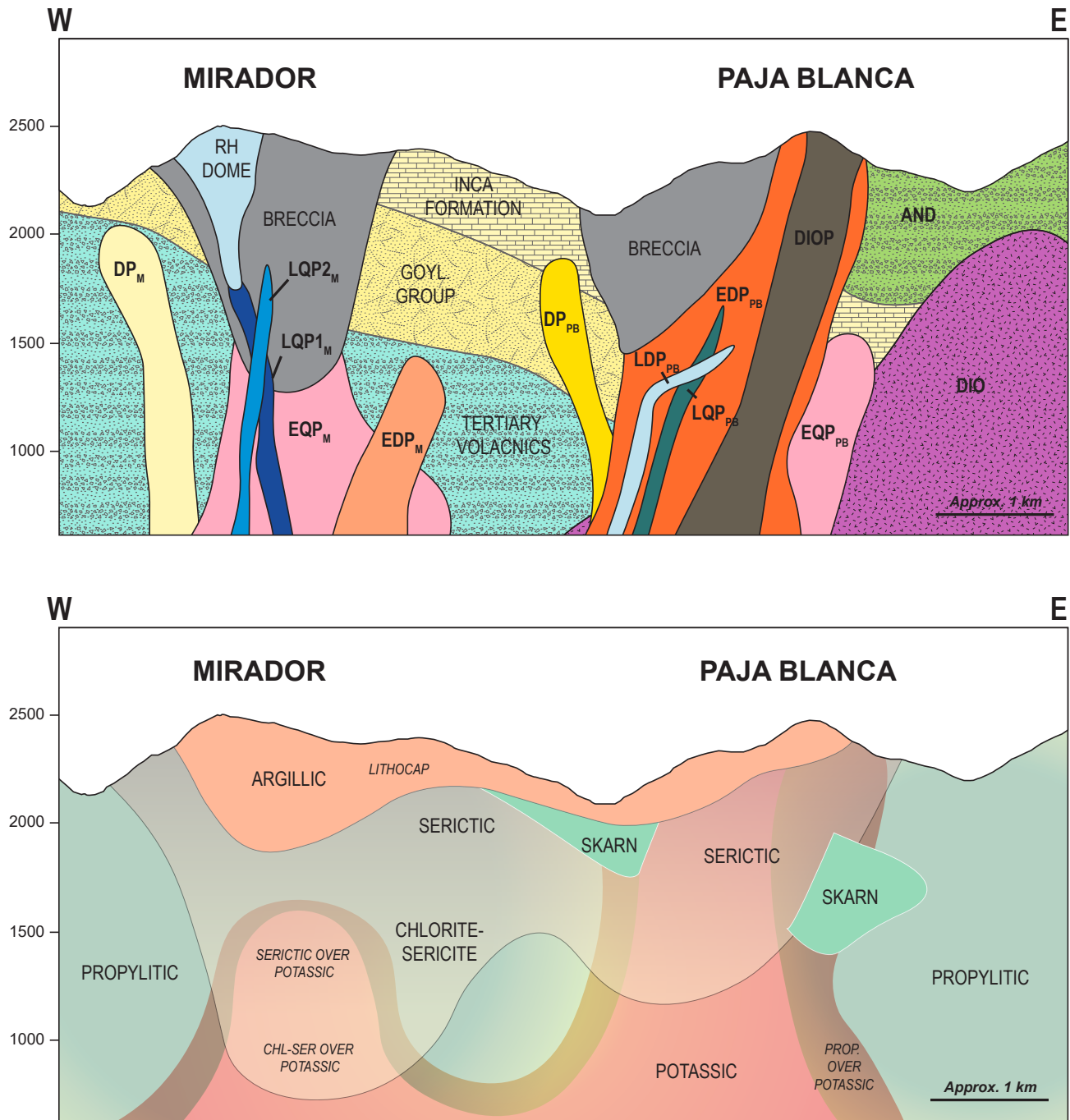


Figure 4.5 Schematic cross sections looking north at La Granja. Top: Schematic of unit lithologies showing relative timing and location of lithologies based on distribution of samples and geochronological relationships inferred from cross-cutting relationship and U-Pb zircon ages of intrusions. Bottom: Distribution of alteration zones. Based on own observations and conclusions of geologists at La Granja (e.g. Rio Tinto SEG presentation 2012).

4.2.1 Host rock units

Granodiorite (GRANO)

Granodiorite samples were collected in the eastern part of the deposit, underlying Paja Blanca (Drill core 08D-LG-076, 07D-LG-043; Fig. 4.4). They contain clasts of volcanic rocks (Figs. 4.6I) and are cut by a diorite porphyry, which exhibits a chilled margin. It is a coarse-grained rock comprising laths of feldspar (> 5 mm, 30 %), with biotite microphenocrysts (1 mm, 10 %), amphibole (5 %) and rare quartz eyes (rounded quartz phenocrysts, < 3 %) in a groundmass of equigranular quartz (30%), feldspar (20 %) and biotite (10 %). Samples contain a moderate number of type A

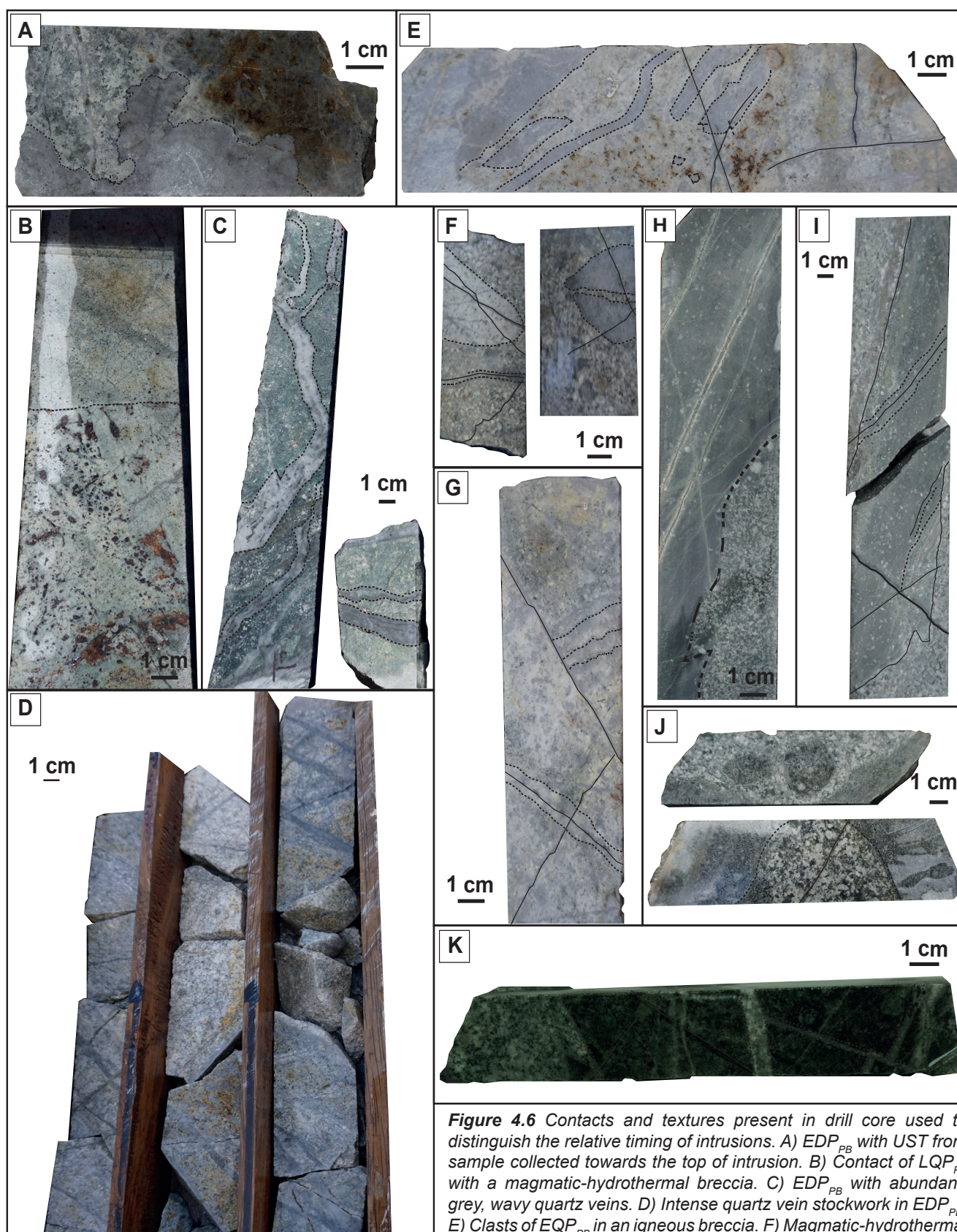


Figure 4.6 Contacts and textures present in drill core used to distinguish the relative timing of intrusions. A) EDP_{PB} with UST from sample collected towards the top of intrusion. B) Contact of LQP_{PB} with a magmatic-hydrothermal breccia. C) EDP_{PB} with abundant, grey, wavy quartz veins. D) Intense quartz vein stockwork in EDP_{PB} . E) Clasts of EQP_{PB} in an igneous breccia. F) Magmatic-hydrothermal breccia with igneous clasts crossed by veins. G) UST developed in EQP_{PB} . H) DIO cutting AND host rock. I) GRANO contact with AND with multiple generations of veins cutting through both units. J) DIO containing clasts of volcanics. K) Clasts of volcanic rock.

and B veins and some D veins containing pyrite. In figure 4.6I the veins cut across both host rock lithologies. Many of the samples show propylitic to chlorite-sericite alteration and, as a result, many of the primary mafic minerals have been replaced by chlorite and plagioclase by sericite.

Andesite (AND)

The andesite forms part of the Llama volcanic series and outcrops to the east of La Granja in the Quebrada Honda district (Fig. 4.3). It is the oldest rock unit sampled and is frequently found as clasts within the granodiorite (Fig. 4.6I) and diorite (Fig. 4.6H). It is composed of coarse quartz phenocrysts (3 - 5 mm) in a fine-grained matrix dominated by biotite and feldspar. The quartz grains vary in abundance and shape between samples; some more rounded, others more euhedral. Samples with a larger abundance of quartz phenocrysts are more dacitic in composition. The rock is cut by many vein types, primarily early quartz veins, A-veins and later D-veins. The samples contain pyrite, which is predominantly located within the veins with some disseminated through the rock. The samples are typically propylitically altered.

Diorite (DIO)

Diorite is a common host rock to the younger porphyries outcropping to the south of La Granja (Fig. 4.4). It displays clear contacts with the more felsic porphyry intrusions and often contains clasts of older volcanics (Figs. 4.6H, J). It is an equigranular, medium-grained rock with feldspar laths (2 mm, 50 %), amphibole (2 mm, 15 %), biotite (<1 mm, 25 %), pyroxene (5 %) and magnetite (5 %). The samples are most commonly propylitically altered, with chlorite and epidote replacing the biotite and amphibole. The diorite hosts many early veins, as well as A-veins and D-veins containing epidote and pyrite.

4.2.2 Mirador porphyry units

Mineralised quartz porphyry (EQP_M)

The EQP_M quartz porphyry has the most felsic composition observed at La Granja and often comprises up to about 50 % quartz by volume. It appears to be associated with mineralisation, containing abundant disseminated Cu-sulfides and mineralised veins. This lithology is the most volumetrically-abundant porphyry at Mirador (Fig. 4.5) and it contains clasts of the host rock sequence, including volcanics and quartzite. It is designated as an early porphyry as it contains early veins. The unit comprises coarse, rounded quartz eyes (3 – 5 mm, 10 %), within a groundmass of quartz grains with biotite (~20 %) and minor feldspar (20 %). It contains a unidirectional solidification texture (UST) which is the mineral alignment of euhedrally-terminated quartz crystals interlayered with feldspar up to 500 µm. This is observed towards the top of the unit.

Dacite porphyry (DP_M)

The dacite porphyry is a small, unmineralised intrusion observed in drill cores 11D-LG-155, 10D-LG-119 and 11D-LG-125 in the west on the district (Fig. 4.4). It is the most mafic of the dacite porphyries at La Granja. It contains laths of feldspars (1 – 2 mm, 20%), biotite microphenocrysts (20 %) and amphibole (5 %) in a fine-grained groundmass of quartz, biotite and feldspar. (~ 50 %) It contains quartz eyes; that are < 1 mm in size and comprise less than 2 % of the rock. There is little veining,

with B-veins the most common however it is also detached from the main porphyry cluster (Fig. 4.5).

Mineralised dacite porphyry (EDP_M)

The mineralised dacite porphyry exhibits a crowded porphyry texture (high proportion of phenocrysts to finer mineral phases) and is composed of predominantly plagioclase (30 %) and alkali feldspar (20 %) laths (1 - 5 mm). Smaller phenocrysts of biotite (15 %) and rare quartz eyes (2 mm, ~ 5 %) are in a groundmass dominated by plagioclase with some quartz (30 %). This unit contains Cu-sulfides that are sometimes disseminated but mainly hosted in quartz veins. At Mirador, EDP_M is topped by a magmatic-hydrothermal breccia (Fig. 4.5).

Late quartz porphyry (LQP1_M, LQP2_M)

The late quartz porphyries are small but texturally distinct intrusions. They contain abundant quartz eyes – some circular in shape while others are more irregular – all with rounded edges (2 – 5 mm, 10 %) and phenocrysts of feldspar (0.5 – 3 mm, 40 %) in a glassy groundmass (47 %). Microphenocrysts of amphibole are euhedral but rare (1 - 2mm, ~3 %). The intrusions are volumetrically small (Fig. 4.5) and LQP2_M cross-cuts LQP1_M in drill core 10D-LG-119.

4.2.3 Paja Blanca porphyry units

Mineralised quartz porphyry (EQP_{PB})

The mineralised quartz porphyry at Paja Blanca is located within drill core 07D-LG-013 as a large clast (Table 4.1) and also occurs as clasts within igneous breccia (Fig. 4.6E). It has a similar composition and texture to the mineralised quartz porphyry at Mirador, including the presence of USTs (Fig. 4.6G). However, it is volumetrically less abundant at Paja Blanca and does not outcrop at the surface. It contains varying amounts of plagioclase phenocrysts (1 – 3 mm, 10 - 25 %) and quartz eyes (2 – 5 mm, ~ 10 - 20 %) plus microphenocrysts of amphibole (2 mm, < 5 %). Its groundmass ranges from fine- to medium-grained and is composed of quartz (250 – 500 µm, 40 %) with fine feldspar and mica (20 %). This intrusion is mineralised and contains disseminated pyrite and chalcopyrite and primarily A-veins.

Dacite porphyry (DP_{PB})

The dacite porphyry at Paja Blanca occurs as a thin stock on the margin of the porphyry cluster. It has a crowded porphyry texture with phenocrysts of feldspar (2 – 3 mm, 50 %), amphibole (2 – 4 mm, 3 %) and biotite (1 mm, 5 %) in a fine-grained quartz and feldspar groundmass (35%). Some samples contain coarse grains of quartz (3 – 5 mm, up to 5 %). Samples contain disseminated pyrite (2 %) and B- and D-veins, but generally this unit contains a significantly lower density of veins than the mineralised dacite porphyries.

Mineralised dacite porphyry (EDP_{PB})

EDP_{PB} is the main mineralised intrusion at Paja Blanca. It comprises coarse feldspar laths (up to 5 mm, 30 %), quartz (2 – 4- mm, 30%) and biotite (1 – 2 mm, 5 %), with feldspar microphenocrysts (1 mm, 10 %). Quartz eyes are less common (1 – 2 mm, 1 - 5 %), but the groundmass (20 %) is quartz-rich. Samples contain disseminated

sulfides and multiple generations of veins, predominantly biotite abundant A-veins (Fig. 4.6D). In addition, coarse, wavy, grey quartz veins are also present (Fig. 4.6C).

Late quartz porphyry (LQP_{PB})

The late quartz porphyry at Paja Blanca contains quartz eyes (2 mm, 15 %) and feldspar phenocrysts (25 %) in a fine-grained matrix (60 %). It is a small intrusion that contains few veins and exhibits is characterised by having a sharp contact with an earlier magmatic-hydrothermal breccia (Fig. 4.6B).

Late dacite porphyry (LDP_{PB})

The late dacite porphyry was only seen in one sample and is similar to the LQP_{PB} except that it does not contain quartz eyes. It occurs as a thin porphyry pipe or dyke that cuts through LQP_{PB} (Fig. 4.5). It is dacitic in composition with a layered texture produced from the alignment of fine feldspar laths.

Diorite porphyry (DIOP)

This is the most mafic of the porphyry units encircling the Paja Blanca cluster (Fig. 4.5). It can be distinguished from the diorite host rock by its porphyritic texture that comprises feldspar laths (2mm, 20 %) in a fine to medium-grained groundmass of feldspar (35 %), mica (20 %), amphibole (15 %) with small amounts of quartz (< 10 %). It contains early quartz veins later D-veins with pyrite.

4.2.4 Hydrothermal alteration

The samples from La Granja exhibit a range of weak, moderate and strong examples of potassic, propylitic, chlorite-sericite, sericitic and argillic hydrothermal alteration. The alteration style within the deposit is dominated by sericitic alteration (Table 4.1; Fig 4.5). Within samples of the host rock propylitic alteration is the most common (Table 4.1) and extends out to Quebrada Honda (Fig. 4.4). No samples are free from alteration. Both prograde and retrograde skarns are also present from the alteration of calcareous wall rock (Inca Formation; Fig. 4.5) and are represented by a limited number of samples (EB17063, EB17064, EB17064, and EB17068). Potassic alteration is most commonly associated with earlier intrusions and is observed overprinted by all other alterations aside from argillic. Sericitic alteration overprints all other alteration styles, again aside from argillic. This is visible at hand-sample scale where multiple generations of veins are present. Sericitic veins produce destructive halos and overprints veins from earlier alteration stages. Argillic alteration is present at the roof of the systems as a lithocap and extends deeper in to the Mirador cluster (Fig. 4.5). As a result, Mirador intrusives are sampled at a greater depth than those from Paja Blanca (Fig. 4.4). A simplified schematic of alteration is presented in figure 4.5 as is sufficient for this study.

4.2.5 Veins

Early veins consist of fine, diffuse, biotite-rich assemblages associated with high temperature alteration. Where the rock has not been overprinted by sericitic alteration, a potassic halo may be visible. In some cases, K-feldspar is present instead of biotite. Early veins are present in the host rocks close to the porphyry centres and cutting early porphyry units and are associated with zones of potassic alteration. A-type veins are also associated with potassic alteration. These are more easily identified as typically thicker (>2 mm); quartz-dominant veins with sharp margins

that often contain sulfides. Frequently, sulfides have been removed by overprinting by acidic alteration. The main sulfides are typically pyrite + chalcopyrite with lesser amounts of bornite. The abundance of A-veins can be used to distinguish the earlier mineralised from the unmineralised (inter-mineral) intrusions because the intensity of veining is much greater in the former (e.g. Fig. 4.6D). B-veins are quartz veins with a centreline of molybdenite. They can display a range of thicknesses from millimetre to centimetre scales. D-veins are those with a texturally-destructive alteration halo and are found in most lithologies. The halo can be many times wider than the vein itself and comprises quartz, sericite and/or chlorite (*Appendix B*). They predominantly contain pyrite, although remnants of Cu-(Fe) sulfide can be present from reopened, earlier A-type veins. The relative timing of veins can be determined through cross-cutting relationships where there are multiple generations present within the same sample. Other common veins include anhydrite and pyrite-bearing veins, which are mainly found in the sericitic alteration zone, together with tennantite and other sulfides in fine veins towards the top of the deposit.

4.3 Zircon geochronology and chemistry

Zircon concentrates from 15 samples were analysed to provide U-Pb ages for crystallisation and zircon trace-element chemistry. The samples are split between porphyries from the Paja Blanca and Mirador clusters and a sample of the host rock (Table 4.2). Zircon (ZrSiO_4) is an abundant accessory mineral in all rock types and is of particular interest in petrogenetic studies due to its robustness. It can contain cation impurities such as REE, Hf, Ti, U and Th at trace to minor element level (Hoskin et al. 2000; Hanchar et al. 2001). These elements have low diffusion rates, meaning that primary zircons retain chemical information despite the existence of later magmatic and hydrothermal events (Cherniak & Watson 2003).

Trace element substitution in zircon, such as of U and Th, produces radiation damage in zircon which can influence the response of the crystal under cathodoluminescence (CL). CL images can therefore reveal internal growth textures within zircon crystals (Harley & Kelly

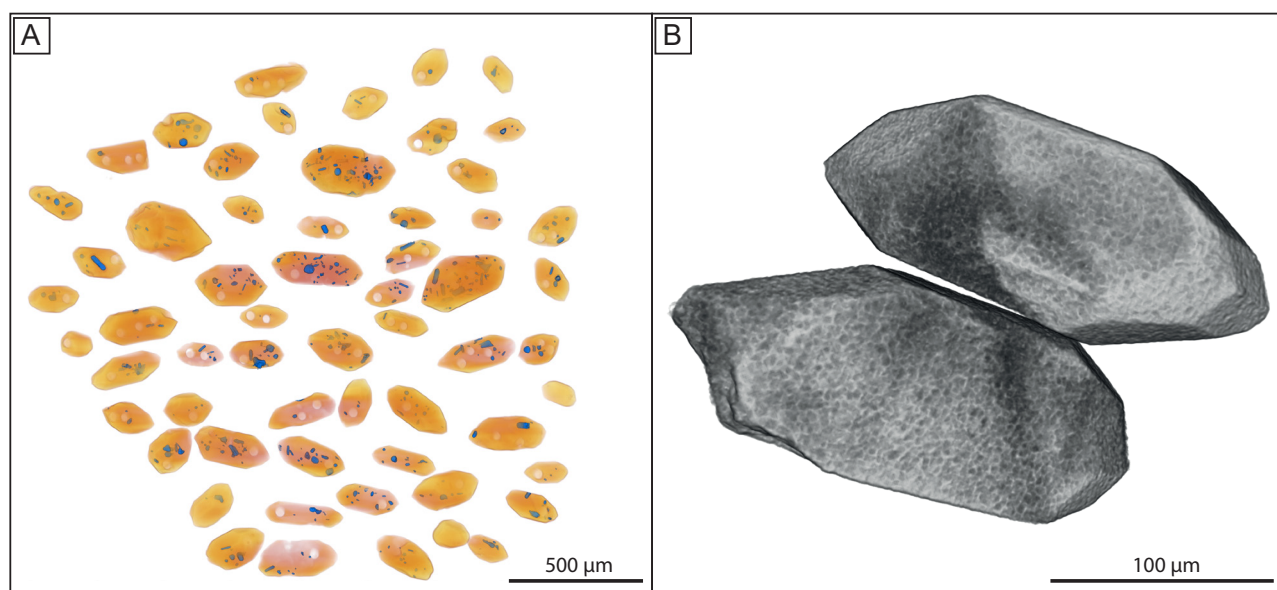


Figure 4.7 Nano-CT images of zircons A) Mounted and polished zircon grains coloured by density. Orange denotes zircon and inclusions are coloured in blue. B) Exterior of unpolished zircons.

Table 4.2 U-Pb zircon ages of lithologies at Paja Blanca and Mirador from core and rim analyses. Single ages are calculated from the weighted mean of multiple core or rim analyses (n). Where ages are inferred to represent an inherited population they are in italics. The mean square weighted deviation (MSWD) is given; where this is higher than the acceptable limit, as defined by Wendt & Carl (1991), these values have been underlined. For explanation of weighted means and MSWD see section 4.3.2.

Sample name	Host Lithology	Core dates Ma (n) [MSWD]	Rim dates Ma (n) [MSWD]
<i>Paja Blanca</i>			
EB17006	LDP _{PB}	14.85±0.38 (7) [1.19]	<u>13.57±0.59 (8)</u> [3.3]
EB17029	DIOP	<u>16±14 (2)</u> [9.8] 33.05±0.43 (4) [0.54]	14.83±0.79 (2) [0.052] 32.51±0.53 (4) [0.63]
EB17005	LQP _{PB}	14.57±0.56 (9) [1.5]	15.09±0.28 (25) [1.3]
EB17010	DIOP	<u>14.69±0.91 (8)</u> [3.7]	15.11±0.50 (8) [0.74]
EB17037	EDP _{PB}	16.41±0.43 (7) [0.5]	15.96±0.27 (38) [1.5]
EB17014	DP _{PB}	17.30±0.76 (9) [1.9]	16.81±0.22 (30) [1.11]
EB17022	EQP _{PB}	17.13±0.74 (3) [0.103] <u>37.2±0.27 (5)</u> [9.8]	16.93±0.87 (6) [0.87] <u>39.9±1.1 (10)</u> [2.4]
EB17030	GRANO	<u>32.8±1.1 (6)</u> [3.2]	34.53±0.78 (8) [0.62]
<i>Mirador</i>			
EB17053	LQP2 _M	<u>14.02±0.35 (17)</u> [2.0]	13.63±0.21 (15) [1.00]
EB17051	LQP2 _M	<u>14.51±0.74 (9)</u> [2.3]	14.24±0.26 (24) [1.4]
EB17052	LQP1 _M	15.22±0.22 (39) [1.9] <u>34.00±21 (2)</u> [14]	<u>14.99±0.25 (39)</u> [2.2]
EB17001	EDP _M	15.13±0.68 (8) [1.4]	<u>15.06±0.26 (41)</u> [1.9]
EB17004	DP _M	16.99±0.39 (10) [0.95]	17.58±0.27 (35) [1.4]
EB17003	EQP _M	32.51±0.44 (9) [1.00]	32.75±0.43 (6) [0.93]
EB17055	EQP _M	32.66±0.80 (4) [0.27]	<u>33.4±1.1 (11)</u> [3.7]

2007). The trace element chemistry of zircon can also be used to infer melt evolution processes and crystallisation conditions. For example, the Ti content of zircon has been calibrated as a geothermometer (Ferry & Watson 2007), the Y and REE contents of zircon can be used to identifying the igneous sources of detrital zircon (Hoskin & Ireland 2000; Belousova et al. 2002; Hanchar & van Westrenen 2007), and the Hf content of as an index of magmatic differentiation at the point that it crystallises (Harley & Kelly 2007). The U content and its subsequent decay to Pb in zircon, along with low diffusivity rates also mean that zircon is suitable for dating.

The crystallisation age of zircon can be calculated through U-Pb dating using the decay series of ^{235}U to ^{207}Pb and ^{238}U to ^{206}Pb where the ratio of U to Pb atoms for the given isotopes reflects the time since crystallisation:

$$\frac{^{206}\text{Pb}^*}{^{238}\text{U}} = e^{\lambda_{238}t-1} \quad \text{Eq. 4.1}$$

Because Pb is not incorporated in zircon above ppb levels, any measured Pb can be assumed to

be a daughter product of the radioactive decay (Pb^*). The ratio of daughter ^{206}Pb atoms to parent ^{238}U atoms is a function of the decay constant (λ) for ^{238}U (1.55125×10^{-10}) and time (t).

The concentrations of the U and Pb isotopes are measured in multiple grains from each sample. The concentration of any non-radiogenic Pb can be checked by measuring the ^{204}Pb content. Low abundances of ^{235}U in zircon do not matter as the modern-day $^{235}U/^{238}U$ ratio is known (1/137.88) and can be used to calculate ^{235}U . The parent/daughter ratios ($^{207}Pb^*/^{235}U$ and $^{206}Pb^*/^{238}U$) from the analyses are then plotted on a Concordia diagram. The axes of a Concordia diagram show the change in the ratios since $t=0$ (at the origin) when $Pb^* = 0$. If the decay system remains closed, i.e. there has been no Pb loss and there is no un-radiogenic Pb present, the points from each analysis should plot along the Concordia line.

Due to the robustness of zircons, inherited (older) zircons are often present in samples and give older formation ages. Such zircons, or zircon cores, may be xenocrystic (incorporated from older host rocks) or antecrystic (representing an earlier stage of zircon crystallisation from the same magmatic system but not the same magma batch). These can easily be identified when plotted on a histogram as multiple peaks will represent different generations of grains.

4.3.1 Samples and methods

Zircon separates were mounted by hand into epoxy resin blocks (Fig. 4.7A). These were then polished to reveal the cores of the zircon grains and then coated with a 10 μm -thick carbon coat. The zircon grains were imaged by CL using a Zeiss EVO 15 LS SEM and by micro-computed tomography (CT) using a Nikon Metrology HMX ST 225, both housed in the Imaging and Analysis Centre (IAC) at the Natural History Museum, London (see *Appendix C* for analytical details). U-Pb isotope and trace element data were collected

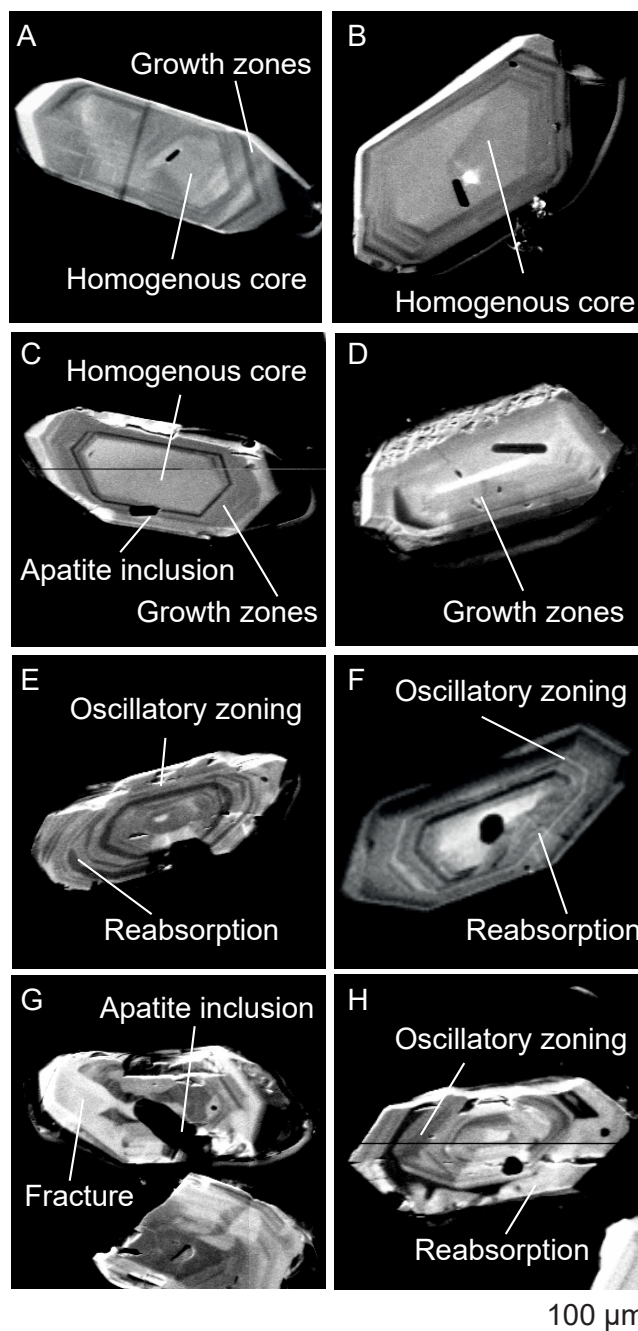


Figure 4.8 Cathodoluminescence scans of zircon grains showing examples of the most common internal textures. A) Elongate zircon with a homogeneous core surrounded by concentric growth zones. B) Stubby zircon with homogeneous core surrounded by concentric growth zones. C) Zircon with apatite inclusion and single dark CL band and later growth zones surrounding a homogeneous core. D) Coarse growth zones and elongate apatite inclusion. E) Oscillatory zoning with reabsorption surface and regrowth. F) Fine oscillatory zoning with reabsorption affecting half of the earlier core. G) Coarse apatite inclusion in complex, sector-zoned grain. H) Dark CL bands of different thicknesses due to reabsorption.

using LA-ICP-MS consisting of an ESI New Wave 193 μm excimer laser coupled to an Agilent 7700 quadrupole ICP-MS system, located in the London Centre for Ore Deposits and Exploration (LODE) Laboratory, IAC. Spots of 35 μm size were used to sample zircon cores and rims with a fluence of 3.5 J cm^{-2} and repetition rate of 5 Hz. The signals were picked from the background and the data were reduced using loLite. In addition to trace-element spot analyses, element maps for 16 grains were produced for U, Hf and Y (2 each from 8 lithological units). These were made using a JEOL JXA-8530F Plus Hyper Probe located in the IAC using an accelerating voltage with a beam of 15 kV, beam current of 200 nA and a spot size of 1 μm . The operating conditions were selected to optimise counts by, for example, raising the dwell times and current. The voltage was set to double the highest energy for the wavelengths being measured, i.e. Yb $L\alpha \sim 7.4$ using a voltage of 15 kV.

4.3.2 Results

The zircon grains in the samples range between 100 – 1000 μm in length, with the majority around 400 μm in length and aspect ratios of 1:2 to 1:4 (Fig. 4.7). The diorite porphyry contained the lowest abundance of zircons of all the lithologies; with low proportions of zircon also observed in the late quartz porphyries and the late dacite porphyry. Silica poor rocks commonly contain lower abundance of zircons. The low abundance in the late porphyries may be due to the reduced grain size of the rocks and therefore reduced recovery of smaller zircon grains. Most zircon grains contain inclusions of other minerals, with apatite the most abundant followed by quartz (Fig. 4.7A). Sulfides (mainly pyrite) were observed in samples EB17003, EB17022 and EB17037. Miocene zircons from the early quartz porphyries contained a very limited number of apatite inclusions.

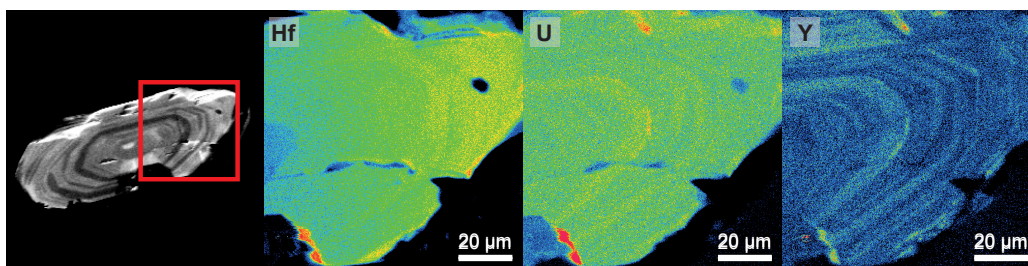
Zircon textures

Zircons display a range of internal textures revealed by CL (Fig. 4.8). Generally, zircons are in a good condition with no re-precipitation textures (Geisler et al. 2007). However, reabsorption surfaces are present in some grains and are most visible where they interrupt zoning (e.g. Fig. 4.8H). The reabsorption may just affect one band or affect a whole section of the zircon. The most common textures within the grains is oscillatory zoning characterised by fine (micron scale), concentric banding of varying CL response (Fig. 4.8B, G, H, J). The bands range in CL intensity from a bright CL response to near black. However, in general, the response is between bright and moderate CL intensity as exemplified by zircons from the LQP1_M and LDP_{PB} which have multiple fine bands (Fig. 4.8E). In addition, zircons from the EQP_{PB} and GRANO contain wider, more diffuse zones (Fig. 4.8A, D). Zircons from the EDP_{PB} and DP_{PB} have fewer bands and are dominated by rare, fine zones with a very dark CL response (Fig. 4.8C).

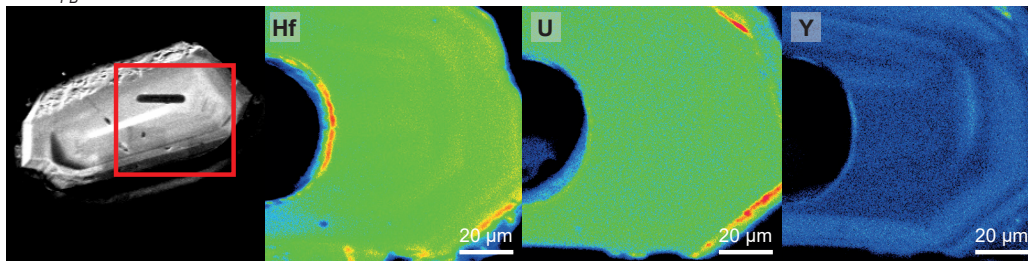
EPM element mapping

Element maps of zircon grains produced by EPM have revealed micron-scale features that are too fine to be detected by LA-ICP-MS spot analysis (i.e they are smaller than 35 μm in size). However, the relative low detection limit of most elements analysed by EPMA restricts the number of elements that can be mapped. Concentrations of Hf and Y show the greatest variations within grain and exhibit fine concentric zonation patterns, with elevated Y and lower Hf correlating with CL-dark zones. The Hf content appears to increase rather systematically towards the rims of the grains, corroborating the

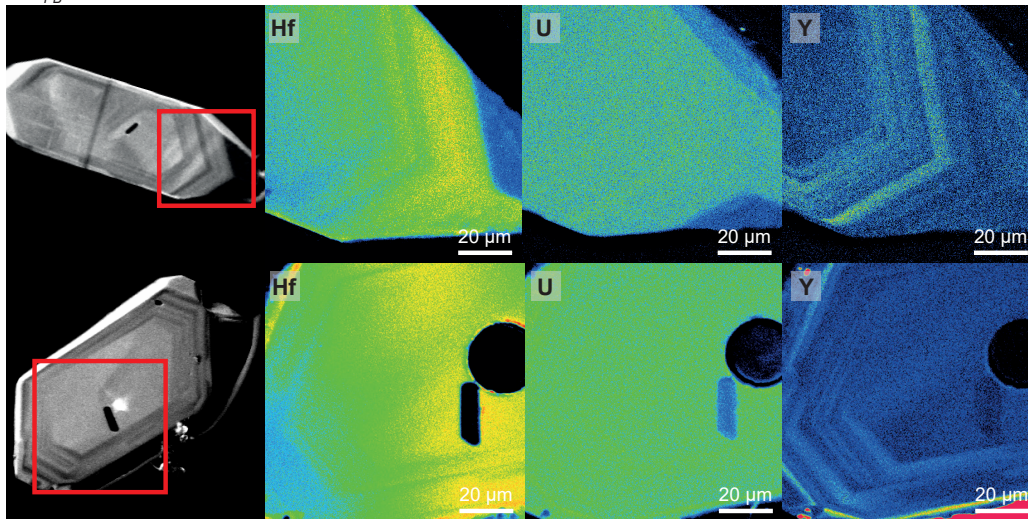
GRANO



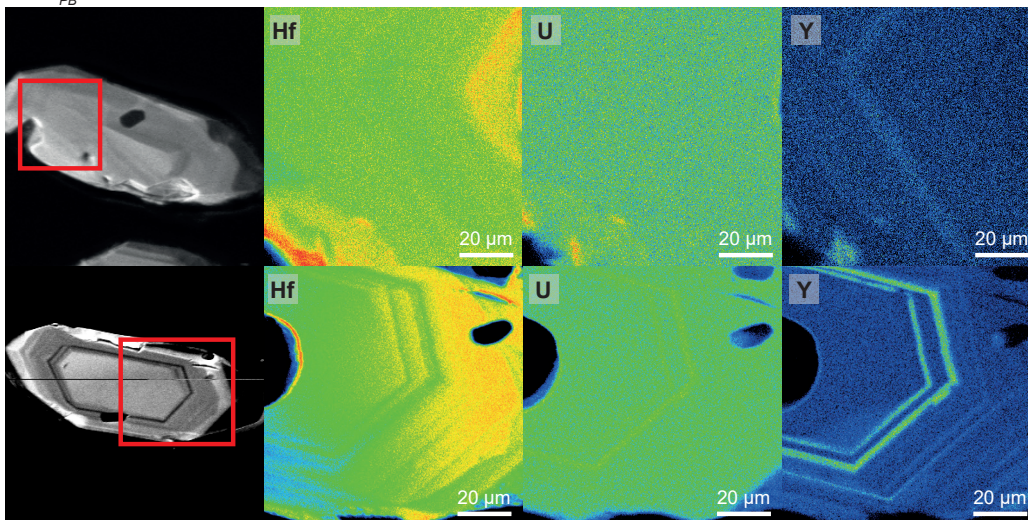
EQP_{PB}



DP_{PB}



EDP_{PB}



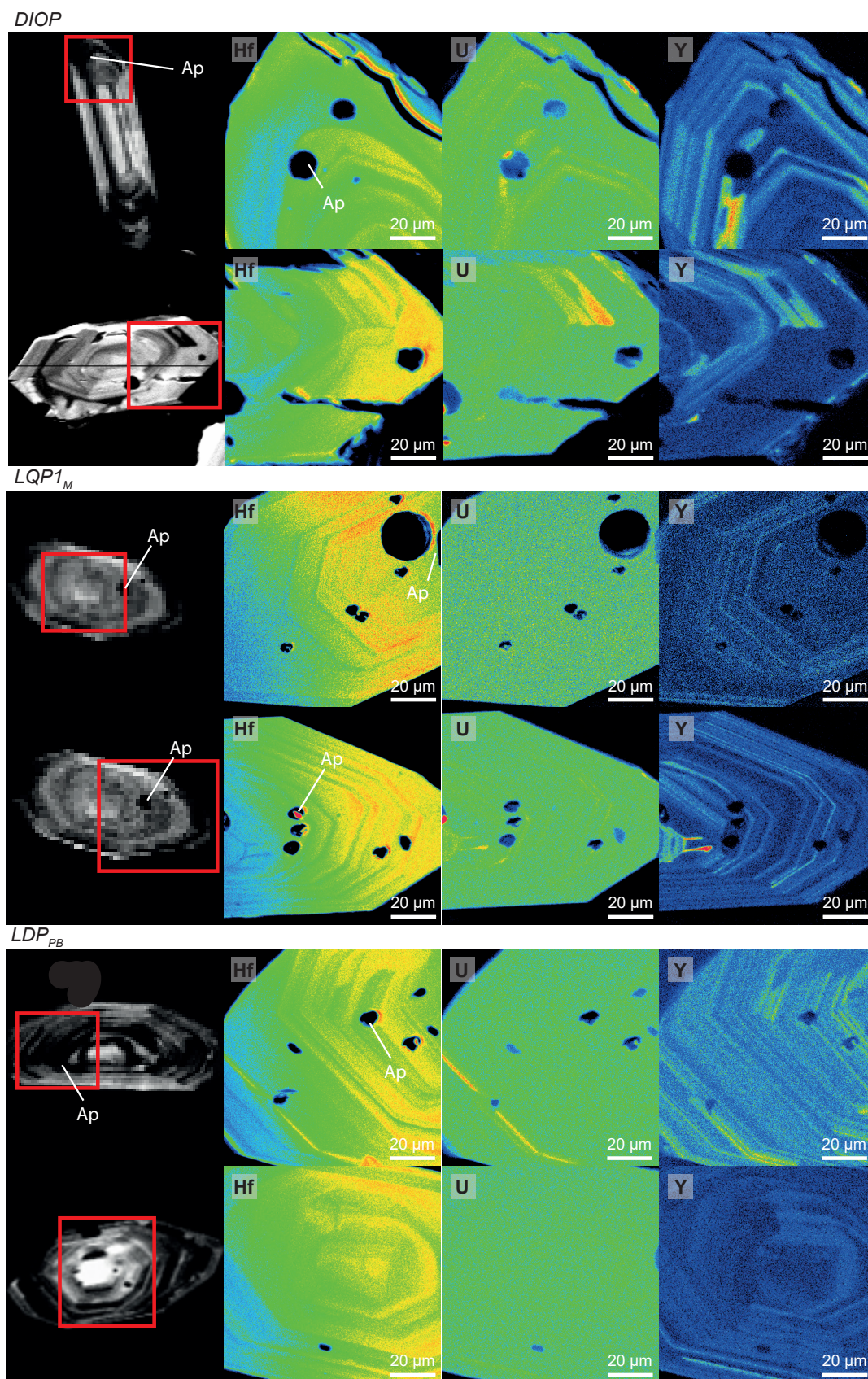


Figure 4.9 Electron microprobe element maps of zircon grains. Element (Hf, Y, U) concentrations are increasing from dark blue – blue – green – yellow – orange with variation mainly limited to concentric bands. Hf and Y concentration correlate to CL images (left hand side). Dark CL bands match higher Y and lower Hf concentrations. U shows little concentration change within grains: this is limited to small variations within DIOP and GRANO.

core-rim LA-ICP-MS trace element analyses. Although variably zoned, there is also a general trend of increasing Y towards grain rims. Variations in U are only visible in certain growth zones; for example, CL-dark zones in the GRANO, EDP_{PB} and DIOP are associated with high U concentrations (Fig. 4.9).

U-Pb zircon ages

The mean weighted U-Pb zircon ages for the cores and rims of each sample are given in table 4.2. In general, rims produce younger ages than crystal cores, or overlap within error. Reporting the age as a weighted mean from a series of individual analyses is considered best practice when using a single isotopic system (Spencer et al. 2016). The weighted mean ($\bar{x}$) produces a 'best fit' age with an uncertainty ($\sigma_{\bar{x}}$), taking into account the uncertainty of each analysis used in the calculation (Spencer et al. 2016):

$$\bar{x} = \frac{\sum_{i=1}^n \left(\frac{x_i}{\sigma_i}\right)^2}{\sum_{i=1}^n \sigma_i^2} \quad \text{Eq. 4.2}$$

$$\sigma_{\bar{x}} = \sqrt{\frac{1}{\sum_{i=1}^n \frac{1}{\sigma_i^2}}} \quad \text{Eq. 4.3}$$

Here x results from a single analysis with uncertainty σ . The mean square weighted deviation (MSWD) is also given in table 4.2 (Wendt & Carl 1991):

$$MSWD = \frac{1}{(n-1)} \sum \frac{(x-\bar{x})^2}{\sigma^2} \quad \text{Eq. 4.4}$$

The MSWD can be used to assess the probability that the samples used to calculate the weighted mean are from the same population and is a function of the number of samples (n) used in the calculation. An acceptable, single-population, MSWD for a given number of samples can be determined from:

$$t = 1 + 2 \sqrt{\frac{2}{(n-1)}} \quad \text{Eq. 4.5}$$

MSWD that are greater than the associated t have only a 5 % probability of belonging to the same population (Wendt & Carl 1991). Results with an MSWD above the threshold, t , have been highlighted in table 4.2. Some of these are from samples with a low number of analyses; these are not regarded as robust tests of single populations.

Density plots of the derived zircon ages reveal two distinct populations (Fig. 4.10), broadly corresponding to the Eocene age of the host rocks and the Miocene age of the porphyry system. Eocene zircons have a larger spread of ages within a single sample. Some samples contain zircons of both ages (e.g. EB17029). In these cases, the older zircons, or zircon cores, are assumed to be inherited. For such samples, the zircons are split into age groups before the mean age is calculated. The inherited zircons are given in italics in table 4.2. In samples where zircons were rare, this has resulted in clearly incorrect ages for some samples (EB17003, EB17005). The inherited zircons commonly have high MSWD values. Within Miocene samples, there are sometimes two age populations corresponding to rim and core crystallisation (Fig. 4.11). Results from these samples (e.g. EB17006, EB17005) are also associated with high MSWD values.

The MSWD of the zircon rim U-Pb ages for the porphyry units range between 17.5 and

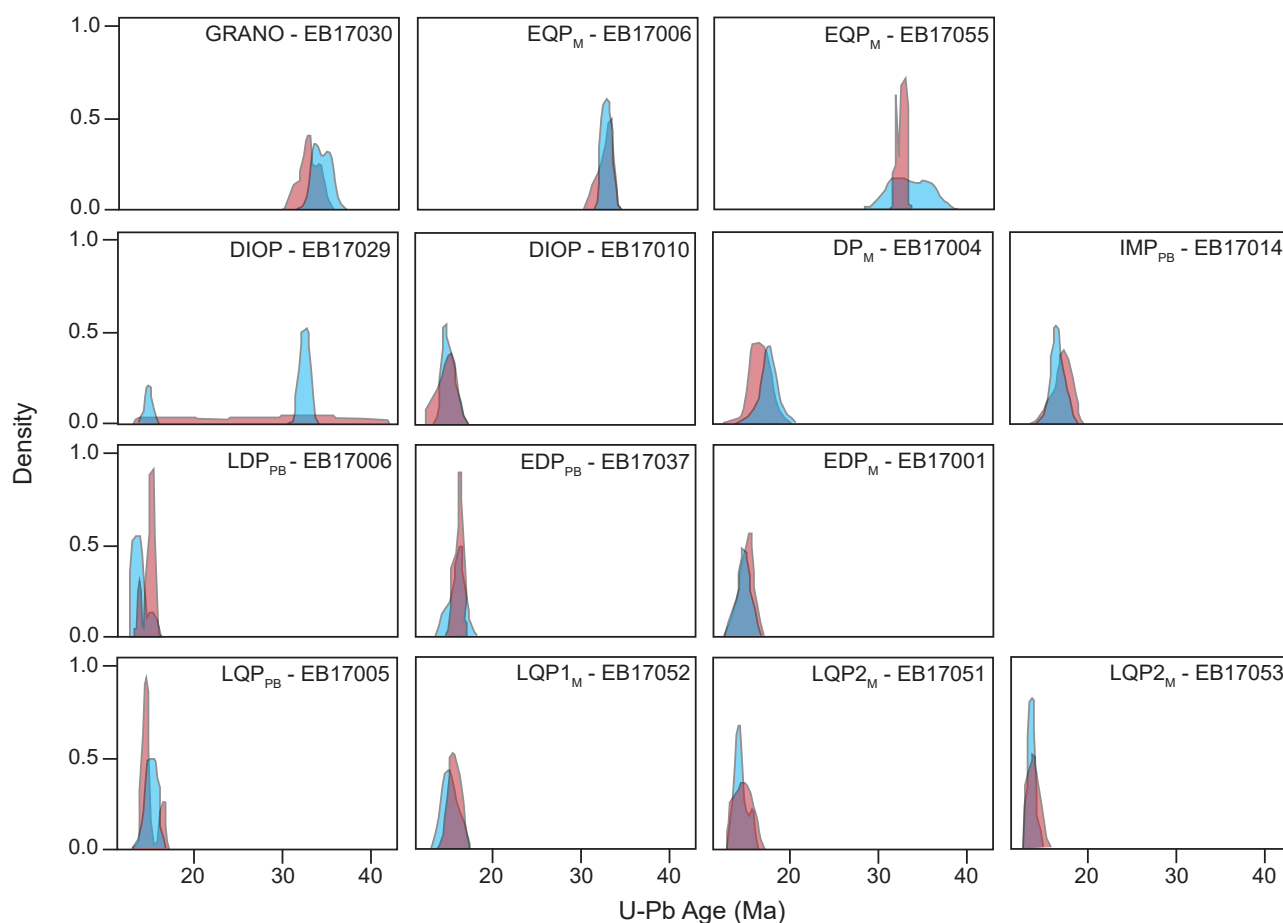


Figure 4.10 Density plots of U-Pb ages of zircon cores (red) and rims (blue). Zircons from the porphyry intrusions produce ages < 20 Ma. Zircons from the host rock are > 30 Ma, as are the zircon cores of some zircons extracted from the porphyry intrusions.

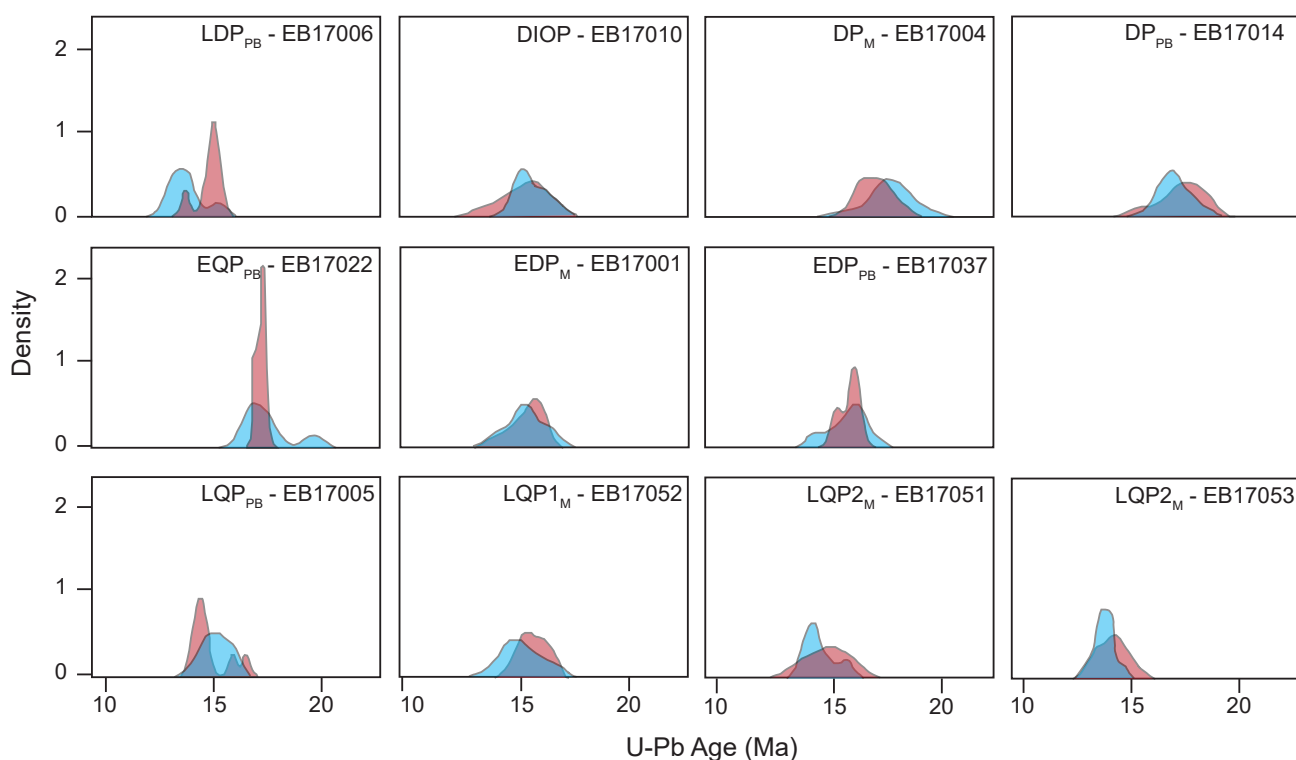


Figure 4.11 Density plot of U-Pb ages of Miocene cores (red) and rims (blue). Within some zircon samples there is a bimodal distribution; however, most ages are within error.

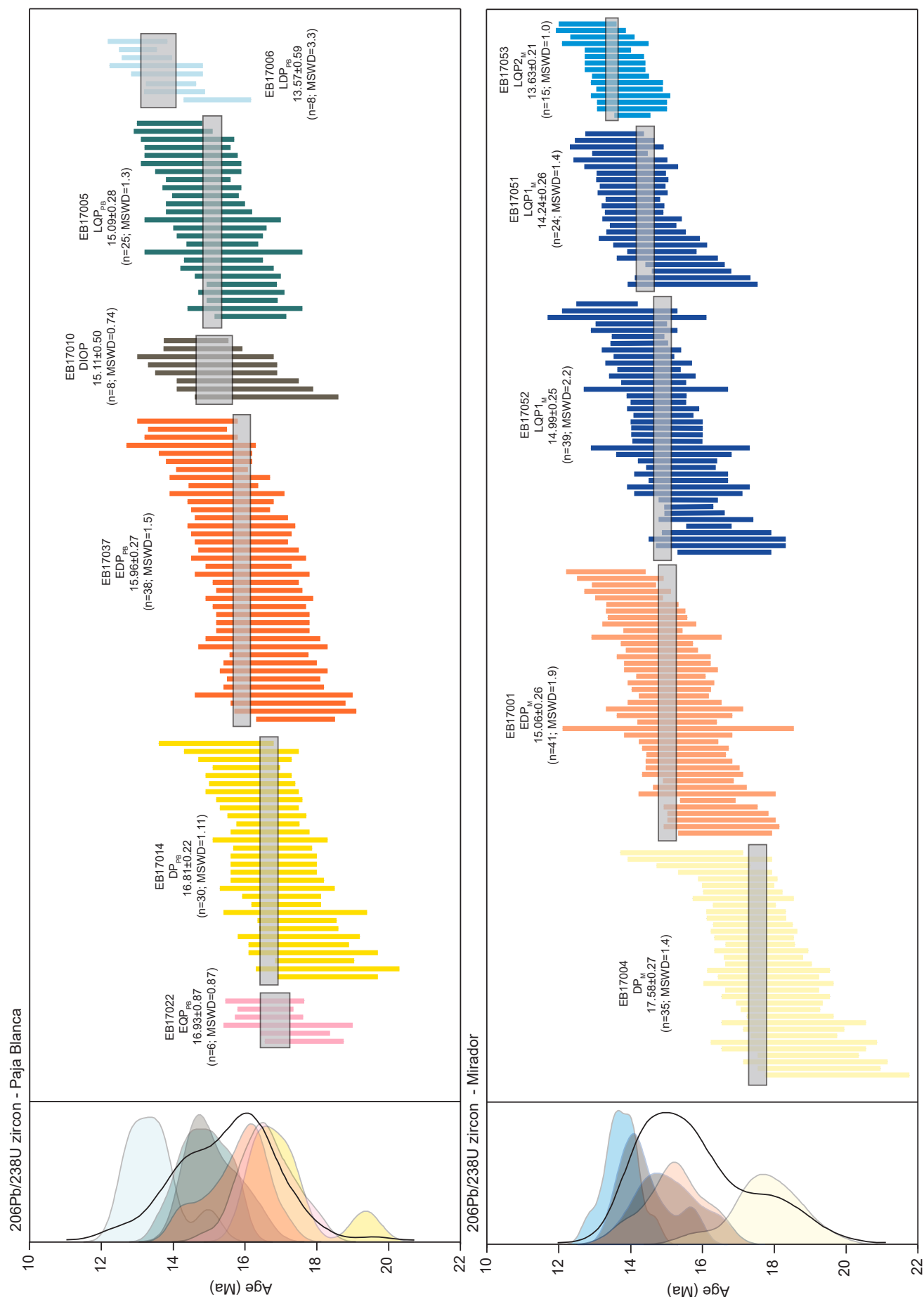


Figure 4.12 (Left hand page) U-Pb zircon ages for Mirador and Paja Blanca porphyry systems. Each vertical bar represents the uncertainty of an individual zircon rim analysis. The weighted mean for each sample is shown by the horizontal bar; its thickness represents 2σ . Density functions of each sample are plotted on the left on an individual sample basis (coloured) and by combining all the data for a given porphyry cluster (black line). The ages group into three main periods of magmatism for each system that are statistically significant.

13.5 Ma (Fig. 4.12). Determining the age intrusions by dating multiple grains within a sample requires the assumption of instantaneous crystallisation whereas porphyry intrusions may take 100's kyr and porphyry systems a few million years to cool. The 2σ error associated with each MSWD represents only two thirds of the probability distribution and as these is greater than the time taken for a porphyry intrusion to cool, the ages determined from U-Pb geochronology should not be over interpreted for exact ages. However, in comparison to the lifespan of the whole system (~ 4.5 Myr) the MSWD and error is small enough for reasonable interpretation of the relative timing of individual emplacement events.

The unit with the oldest MSWD is the unmineralised dacite porphyry (DP_M) at Mirador with a mean rim age of 17.58 ± 0.27 Ma. The oldest units dated within the Paja Blanca cluster are the EQP_{PB} and DP_{PB} . These have overlapping MSWD rim ages of 16.93 ± 0.87 and 16.81 ± 0.22 Ma respectively. At Mirador, the early quartz porphyry is significant both in terms of volume and mineralisation, however, no robust ages from Miocene zircons were measured from EQP_M . EDP_M and EDP_{PB} returned MSWD rim ages of 15.96 ± 0.27 and 15.06 ± 0.26 Ma respectively. The diorite porphyry is slightly younger than dated EDP_{PB} at Paja Blanca with rim ages 15.11 ± 0.50 Ma. Based on field evidence, the final intrusions in both clusters are the late, weakly-mineralised porphyries. Zircon rim ages for the late porphyries (LQP_{PB} , $LQP1_{PB}$, $LQP2_{PB}$, LDP_{PB}) range from 15.09 ± 0.28 to 13.57 ± 0.59 Ma.

Density plots of the zircon ages (Fig. 4.12 - left hand side) form three peaks which suggests that the timing of porphyry emplacement within each deposit may have occurred as three periods of magmatic activity. For each system at least two of these peaks are still visible when the ages are plotted as a single density function (Fig. 4.12 - black line). The significance of these different magmatic events can be tested using a t-test which scores the probability that the results belong to different groups by comparing the mean of the two groups (Kim 2015). The outcome of the test is a p-value which is the probability that the independence of each group occurred by chance. The samples belonging to the earliest and latest peak from each system was compared to those forming the middle peak. An independent t-test for unequal variance was used which requires normally distributed data (Fig. 4.11). These produced p-scores below 0.01 in all instances confirming that the three main pulses present are statistically different. As a further test, the latest peak at Mirador was compared to the latest peak at Paja Blanca, as were the two middle peaks from each system. This t-test from these samples produced a p-score of 0.16 and 0.59 respectively, suggesting that these events can not be statistically separated.

In conclusion magmatism at La Granja occurred between ~ 16 - 13 Ma and comprised three distinct periods of magmatic activity. The final two events at Paja Blanca and Mirador occurred after 16 Ma and may reflect the same events across the two systems with the final magmatic period relating to post-mineralisation intrusions.

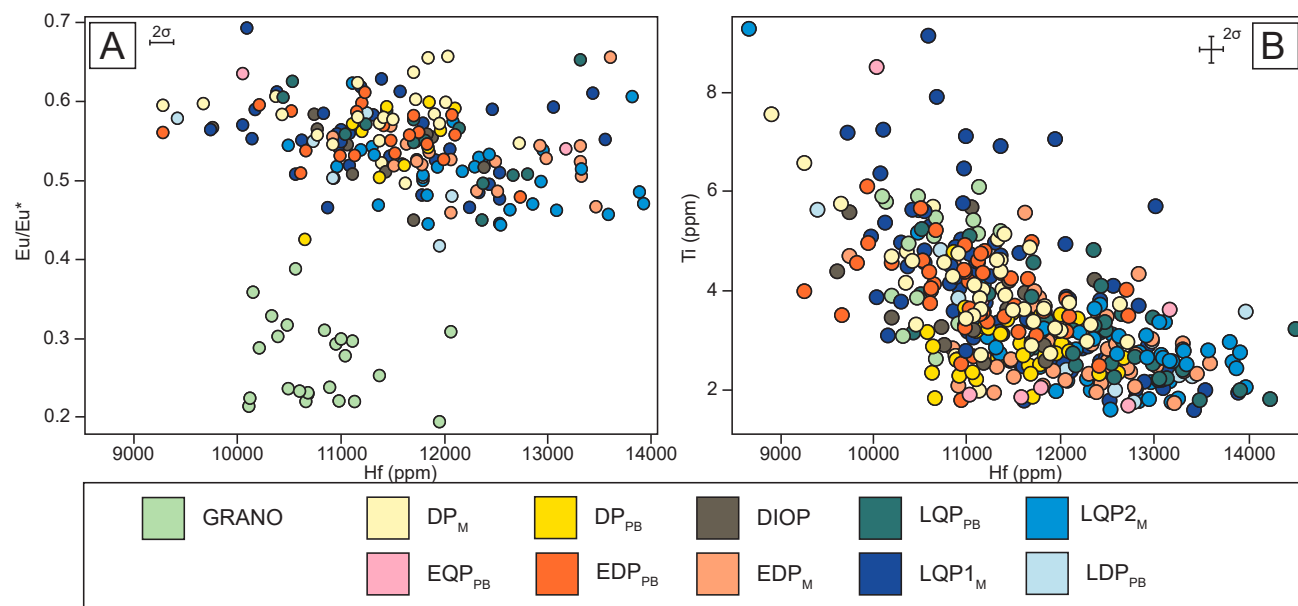


Figure 4.13 Trace element zircon compositions from rim analyses. A) Eu/Eu^* is lower in Eocene zircons and B) Ti concentration decreases with increase in Hf concentration. Analytical precision is given where larger than the symbol size.

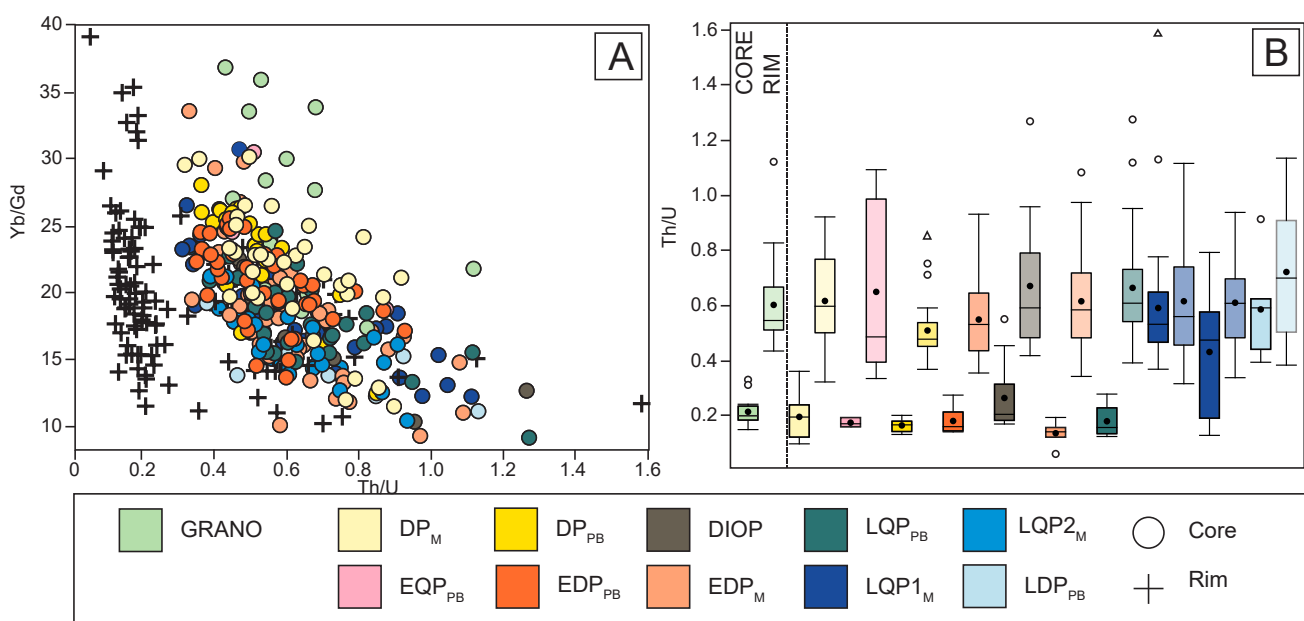


Figure 4.14 Core-rim comparison of trace elements composition of zircon. A) The core of zircons contains lower Th/U ratios than the rim. D) The difference in core – rim composition is less pronounced in zircons from $LQP1_M$, $LQP1_M$ and LDP_{PB} . Analytical error is smaller than the symbols.

Trace element chemistry

The trace element chemistry of the zircons shows systematic changes in REE ratios and trace element substitutions. Concentrations of Hf are lower in zircons with higher Eu/Eu* (Fig. 4.13A) and Ti concentrations (Fig. 4.13B). However, the Eu/Eu* in zircons from GRANO is lower than those from Miocene units. A decrease in Hf concentration within zircon reflects the differentiation of a melt with respect to temperature. The Eu/Eu* of zircon is a function of oxidation state of the melt and co-crystallisation of titanite (Loader et al. 2017b).

There is a statistically significant separation in Th/U, excluding LQP1_M, LQP2_M and LDP_{PB} (Fig. 4.14A-B). This suggests that there is a smaller difference in temperature and melt differentiation between core and rim of these zircon, or more rapid crystallisation. The Th/U of the LQP1_M, LQP2_M and LDP_{PB} matches that of the rim composition of the other porphyry units. The 'main stage' melt composition for these units is similar to the later stages for porphyry melts.

Temperature of zircon crystallisation

If zircon is formed in equilibrium with quartz and rutile, with compositions comparable to those studied here, Ti incorporation in zircon is temperature sensitive (Watson et al. 2006). Ti can therefore be used to estimate the crystallisation temperature of a grain, or part of a grain (Ferry & Watson 2007):

$$\log Ti_{\text{zircon}} = (5.711 \pm 0.072) - \frac{4800 \pm 86}{T} - \log \alpha_{\text{SiO}_2} + \log \alpha_{\text{TiO}_2} \quad \text{Eq. 4.6}$$

Here T is the temperature in Kelvin, Ti_{zircon} is the concentration in ppm, and a_{SiO_2} and a_{TiO_2} are the activities of SiO₂ and TiO₂ within the melt. For this study, silica activity was estimated based on petrological observations and was assumed to range between 0.9 and 1 due to a high contents of quartz. The volume of titanite in the rocks is considerably lower; and as a result, a_{TiO_2} was set between 0.5 and 0.7. Calculated temperatures range between 589 and 916 °C (Table 4.3). Mean temperatures calculated from zircon rims and cores are not significantly different at 694 °C and 700 °C respectively.

Table 4.3 Zircon crystallisation temperatures calculated from centre and rim analyses of zircons from each lithology (Ferry and Watson 2007). A range of activities were used (α_{TiO_2} 0.5 – 0.7, and α_{SiO_2} 0.9 – 1.0) resulting in a range of temperatures for each zircon grain. Here the minimum (Min.), maximum (Max.), mean and standard deviation (2 σ) for each lithology is given.

Ti-in-zircon crystallisation temperature (°C)										
	Core					Rim				
	(n)	Min.	Max.	Mean	2 σ	(n)	Min.	Max.	Mean	2 σ
GRANO	15	624	800	721	23	19	628	843	735	26
DIOP	8	631	767	698	12	8	622	764	688	16
EQP _M	12	622	820	717	28	17	636	889	669	39
EQP _{PB}	13	615	791	722	63	23	636	902	699	63
DP _M	10	604	808	706	33	36	626	822	704	19
DP _{PB}	9	598	737	666	12	30	599	776	684	16
EDP _{PB}	6	602	774	675	28	38	620	800	708	16
EDP _M	8	602	774	675	28	41	577	791	676	22
LQP _{PB}	9	612	785	687	22	25	612	782	689	19
LQP1 _M	24	589	845	684	33	37	595	916	676	35
LQP2 _M	34	617	817	709	22	39	589	794	677	23
LDP _{PB}	7	604	792	689	28	8	595	776	679	26

4.4 Abundance of accessory phases

It is important to know the relative abundance and distribution of accessory minerals within each unit, as these are typically the main hosts for REEs and are therefore important in models of melt evolution. Observations by optical and SEM microscopy can be used to estimate modal abundance for more abundant minerals. However, this is less practical for finer grained, or less common phases. Here, the proportions and associations of accessory mineral phases were determined using automated SEM analysis across a representative selection of samples (Table 4.4). Samples with a similar type and intensity of hydrothermal alteration were used where possible, as this may affect accessory mineral abundance. In this method, a bright-phase scan was used to identify 5 μm pixels containing high BSE grey-scale values, corresponding to oxides, sulfides and accessory minerals. The compositions of these pixels were collected, in addition to adjacent pixels (including other mineral phases) within a 10 μm radius, in order to provide information on mineral associations. Mineral phases were identified by comparing the chemical composition of each pixel comparison to a library of pre-programmed mineral formulae. These analyses were carried out using a Zeiss Sigma 300 analytical scanning electron microscope in the School of Geography, Geology and the Environment at the University of Leicester (see *Appendix D* for the full method).

Bulk mineral abundance

The abundance of bright phases (accessory silicates, phosphates, sulfides and oxides) are listed in table 4.4. Apatite is the most abundant accessory phase (excluding sulfides and oxides) in all samples followed by zircon. Several minerals of potential interest were not recorded above an abundance of 0.005 % but can be found in association with apatite and zircon (Table 4.5). All samples have pyrite as the dominant sulfide, but Cu-(Fe)-sulfides were found in all samples and are highest in concentration within the mineralised quartz and dacite porphyries. As samples with obvious veins were avoided, sulfides are mostly present in disseminated form. Sphalerite was recorded in the LDP_{PB}. The occurrence of rutile and

Table 4.4 Abundance (%) of bright phases relative to whole rock in each sample

	GRANO	DIOP	EQP _{PB}	DP _{PB}	EDP _{PB}	LQP2 _M	LDP _{PB}
	Chl-Ser	Prop	Ser	Chl-Ser	Ser	Chl-Ser	Prop
<i>Bright phases</i>	EB17044	EB17039	EB17022	EB17014	EB17037	EB17052	EB17069
<i>Accessory minerals</i>							
Apatite	0.01	0.02	0.03	0.03	0.18	0.09	0.04
Zircon	0.01	0.01	0.00	0.00	0.00	0.00	0.00
Titanite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Monazite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Allanite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Sulfides</i>							
Cu-(Fe)-sulfides	0.08	0.05	0.99	0.01	0.44	0.02	0.01
Fe-sulfides	0.08	0.52	0.24	2.90	0.59	0.15	0.12
Sphalerite	0.00	0.00	0.00	0.00	0.00	0.02	0.34
<i>Oxides</i>							
Magnetite	0.27	0.73	0.00	0.00	0.00	0.00	0.01
Rutile	0.01	0.04	0.00	0.21	0.23	0.09	0.40
Ilmenite	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<i>Unclassified</i>	0.07	0.25	0.04	0.21	0.16	0.12	0.12

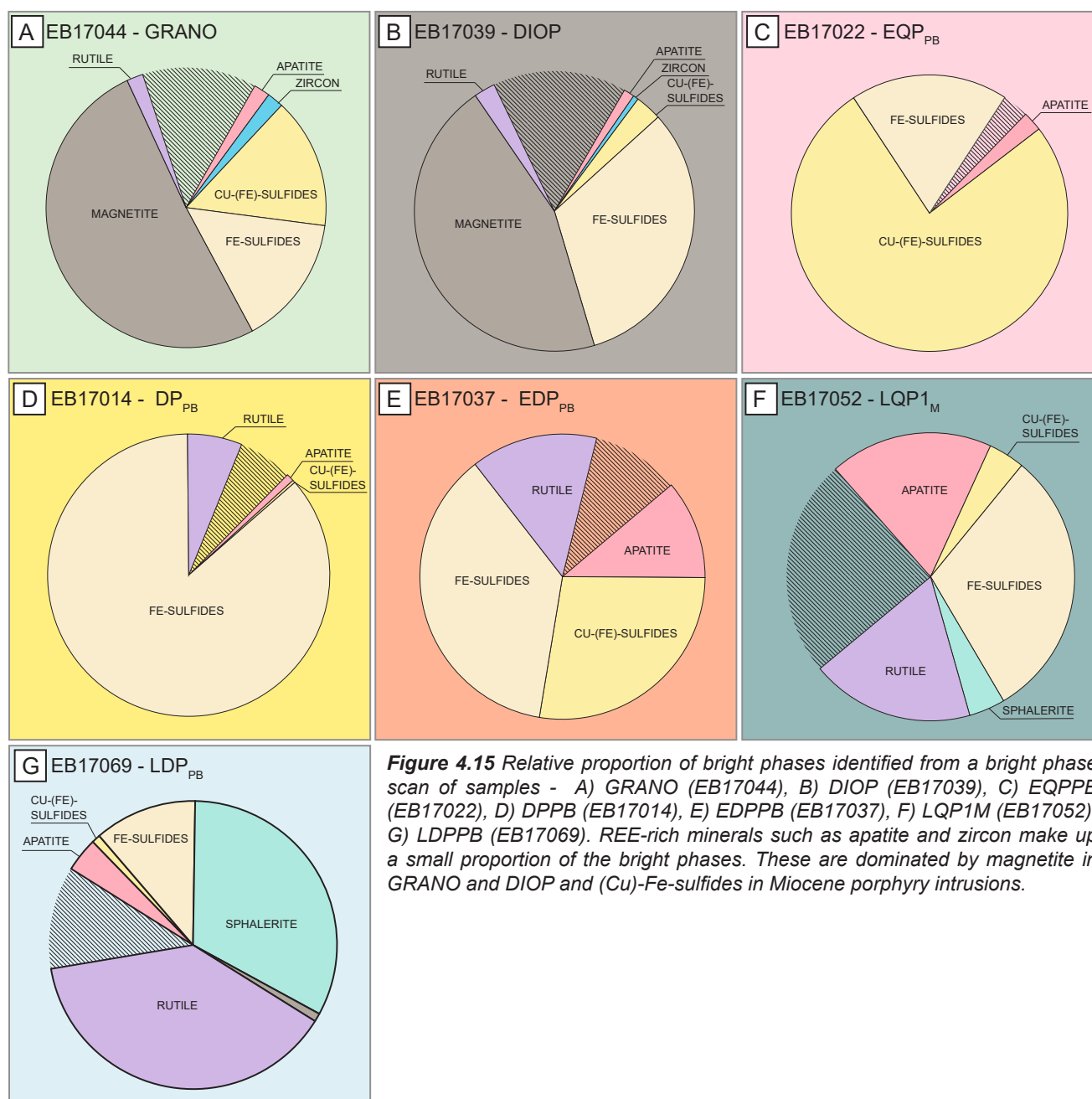


Figure 4.15 Relative proportion of bright phases identified from a bright phase scan of samples - A) GRANO (EB17044), B) DIOP (EB17039), C) EQPPB (EB17022), D) DPPB (EB17014), E) EDPPB (EB17037), F) LQP1M (EB17052), G) LDPPB (EB17069). REE-rich minerals such as apatite and zircon make up a small proportion of the bright phases. These are dominated by magnetite in GRANO and DIOP and (Cu)-Fe-sulfides in Miocene porphyry intrusions.

magnetite varies between lithologies; magnetite is more common in the more mafic intrusions (GRANO and DIOP) and rutile is more common in the porphyry intrusions (Fig. 4.15).

The resolution of the scan limits the minimum size of the grains that can be detected to 5 μm . Samples with the lowest vein abundance were selected so that the values obtained principally reflect the primary igneous mineralogy. However, the presence of alteration minerals of hydrothermal origin are inevitably present as well, potentially including some of the apatite, zircon, magnetite and rutile grains recorded, as well as most of the sulfides. In addition, alteration may affect primary mineral abundance via the dissolution of igneous minerals. Although samples of similar alteration styles were selected, the effects of such processes need to be considered. For example, the sensitivity of titanite to alteration may explain its negligible observed abundance in the main porphyry units.

Association of apatite and zircon

The minerals associated with apatite and zircons were automatically identified from the phases

Table 4.5 Association (%) of total pixels within a 10 µm radius of identified apatite and zircon grains

Accessory/ minerals	GRANO EB17044		DIOP EB17039		EQP _{PB} EB17022		DP _{PB} EB17014		EDP _{PB} EB17037		LQP2 _M EB17052		LDP _{PB} EB17069	
	Apatite	Zircon	Apatite	Zircon	Apatite	Zircon	Apatite	Zircon	Apatite	Zircon	Apatite	Zircon	Apatite	Zircon
Zircon/Apatite	2.03	4.10	1.34	3.82	2.96	2.37	0.12	0.67	0.12	1.85	0.11	1.34	0.01	0.78
Titanite	0.04	0.00	0.90	0.09	0.00	0.00	0.00	0.00	0.01	0.00	0.03	0.00	0.03	0.00
Allanite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Monazite	0.17	0.00	0.00	0.00	5.61	0.74	0.12	0.00	0.31	0.06	0.03	0.00	0.00	0.00
Sulfides														
Fe-Sulfides	2.00	0.14	4.51	0.26	3.62	0.59	14.70	3.54	3.66	2.06	0.44	0.45	2.48	3.14
Cu-sulfides	7.23	0.00	2.40	0.15	37.42	0.15	0.25	0.00	6.17	0.70	0.33	0.03	0.23	0.00
Sphalerite	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.11	0.00	0.25	0.03	0.00	0.00
Oxides														
Magnetite	46.73	0.91	53.06	1.11	0.00	0.00	0.35	0.34	0.07	0.03	0.02	0.00	0.07	0.00
Rutile	4.08	4.66	8.43	4.43	0.61	0.30	5.89	1.77	6.84	3.12	2.84	4.09	7.86	7.06
Ilmenite	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.78
Primary/ Alteration Minerals														
Amphibole	0.10	2.90	0.35	8.48	0.17	9.47	1.49	4.21	0.76	4.78	0.66	3.61	0.89	8.82
Anhydrite	5.98	0.41	0.40	0.00	1.06	0.00	9.81	0.00	0.41	0.00	0.79	0.00	3.02	0.00
Anorthite	0.09	0.00	0.12	0.09	0.00	0.00	1.13	0.00	0.11	0.00	0.26	0.03	0.50	0.00
Biotite	3.04	2.40	0.85	1.02	0.86	0.00	0.12	0.00	0.33	0.42	2.33	3.61	1.08	1.18
Calcite	5.50	1.30	10.16	0.64	18.45	0.74	11.11	0.00	10.12	0.55	17.06	0.70	2.06	0.00
Chlorite	10.17	33.34	10.18	40.15	4.63	12.72	17.32	31.73	11.37	20.11	9.73	27.20	34.56	22.94
Diaspore	0.00	0.00	0.00	0.00	0.00	0.00	1.57	1.52	0.02	0.00	2.58	0.03	0.00	0.00
Epidote	1.94	0.54	0.89	0.58	0.22	0.00	0.43	0.00	0.31	0.00	1.61	0.19	2.66	0.00
K-feldspar	0.92	7.79	0.09	0.38	1.52	8.14	0.00	0.00	0.21	0.24	1.62	1.15	0.28	0.59
Muscovite/Se ricite	1.12	1.12	0.57	3.38	6.54	12.72	0.06	0.00	19.56	17.41	21.13	21.70	12.16	2.55
Plagioclase	6.33	22.57	0.34	2.80	10.16	21.60	0.19	0.00	19.92	19.53	8.86	13.65	7.48	1.37
Pyrophyllite	0.11	1.06	0.08	0.00	0.41	0.44	0.59	0.17	0.16	0.12	0.86	0.22	0.92	0.20
Pyroxene	0.93	8.86	0.28	4.37	2.64	9.47	1.24	1.85	1.29	3.30	1.05	2.14	0.77	5.29
Quartz	1.32	7.79	4.67	27.91	2.83	20.12	15.95	42.17	17.37	25.32	24.22	19.40	16.25	43.14
Topaz/Andal uste/Dickite/ Kaolinite	0.17	0.10	0.29	0.35	0.21	0.44	17.57	12.04	0.76	0.39	3.20	0.42	6.67	2.16

adjacent to each grain (Table 4.5). The frequent spatial association of apatite and zircon with quartz (+ plagioclase and muscovite/sericite), combined with the petrographic descriptions, suggests that these grains are primarily hosted within the groundmass. Apatite has little other association with primary igneous minerals; however, its common occurrence with chlorite, epidote and calcite could indicate a propylitic apatite-bearing assemblage. Similarly, the association of some apatite with muscovite/sericite and clay minerals could indicate an apatite-bearing sericitic alteration assemblage. Unlike apatite, zircon has, after quartz, a strong association with amphibole, biotite, and secondary chlorite formed as a replacement of these mafic minerals, indicating that – as expected – zircon is principally an igneous phase and for some reason tended to crystallise in proximity to the mafic minerals. Monazite is frequently found with apatite but less so with zircon; this is likely because monazite is a common replacement product of apatite (Harlov 2015). As the pixel size is 5 μm , it is unlikely that many inclusions within the finer grained zircon would be captured in these results. Apatite, zircon and titanite are often closely associated with rutile and may be produced from the hydrothermal alteration of titanite, which is only found in association with apatite above 0.01 % in GRANO, DIOP and late quartz and dacite porphyries. Rutile comprises > 4 % of association with apatite in DIOP, GRANO, DP_{PB}, EDP_{PB}, LDP_{PB} and has lower association in LQP2_M (< 3 %) and EQP_{PB} (< 1 %). If the proportions of rutile can be used as a proxy for magmatic titanite than the highest proportion of REE minerals (apatite + zircon + titanite) are present in LDP_P, EDP_{PB} (> 0.44%), EQP_{PB} (0.3 %) DP_{PB} (0.24 %) LQP2_M (0.18 %), GRANO and then DIOP (both < 0.1 %). It is noteworthy that the porphyry units contain lower zircon proportions and the highest titanite proportions (except EQP_{PB}). Apatite is strongly associated with magnetite in GRANO and DIOP comprising > 40 % of associated minerals and is likely to reflect a primary magmatic origin for these grains. Conversely, an association between apatite and sulfides likely indicates a hydrothermal origin, as reported elsewhere in this thesis (Chapter 7).

4.5 Bulk rock geochemistry

Bulk rock analyses were collected externally for all 70 samples by ALS (Australian Laboratory Services). A full description of the method used together with full results table are available in Appendix E.

4.5.1 Mass transfer during hydrothermal alteration

Porphyry ore bodies are hosted within hydrothermally altered rock. The alteration can be divided up into zones of distinct mineralogy and are the result of the interaction of the cooling hydrothermal fluids with the wall rock. However, details of the alteration patterns around different porphyry systems are unique. Telescoping, through cooling and/or uplift, alters the characteristics of the fluid and P-T conditions at a given point in time and space, and multiple magmatic-hydrothermal events lead to the superposition of alteration zones and subsequent deviation from the standard model. Understanding how the compositions of the alteration zones vary within a deposit is important, as the alteration footprint is often used in exploration. Alteration may also affect the composition of primary minerals within each zone, even if they are not destroyed, and the composition of hydrothermal minerals crystallising

from the fluids will vary according to the pathway that they have followed through the system.

The change in bulk rock composition caused by hydrothermal alteration can be calculated from the comparison of whole rock data from different alteration zones. The composition of each zone is a function of the original composition of the rock (or of a previous alteration stage) combined with the changes associated with the addition or removal of mobile elements. Hydrothermal alteration is a metasomatic process involving open system behaviour. Furthermore, element concentrations are measured in relation to a fixed mass of rock (normalised to 100 wt. % or 1,000,000 ppm) and are therefore subject to bulk changes in rock mass due to large-scale hydrothermal mobility. Consequently, net element concentration changes must be considered with respect to the bulk mass loss or gain that a sample may have experienced. In order to address this, Grant (1986) proposed a mass balance equation based on the earlier classic work of Gresens (1967):

$$C_i^A = M^{\frac{O}{A}}(C_i^O + \Delta C_i) \quad \text{Eq. 4.7}$$

where C_i^A and C_i^O are the concentrations of an element (i) in the altered and original rock and ΔC_i is the change in concentration. The mass ratio of altered to the original rock is given by $M^{O/A}$. A $M^{O/A}$ value less than 1 implies that the altered rock has lost mass (bulk mass loss, i.e. net dissolution) relative to the original, unaltered rock, and therefore the measured concentrations of elements would appear higher than in the original rock despite potentially no net metasomatic addition.

To understand the full alteration history, fresh (or least-altered) samples should be used to define values of C_i^O . However, unaltered samples are limited at La Granja, and so in this study C_i^O are derived from weakly- to moderately altered potassic samples. Therefore all ΔC_i calculations are made with respect to a previously potassically altered precursor. This does not matter if one is interested in

Table 4.6 Four different lithologies were used in the mass transfer calculations. The samples used and the type and degree of alteration are listed below. Each lithology has one potassic sample which acts as the baseline to which the altered samples are compared.

Unit	Alteration	Sample	Unaltered lithology
Dacite porphyry (Paja Blanca)	Potassic with strong propylitic	EB17012	Moderate potassic (EB17020)
	Moderate Chl-Ser	EB17014, EB17015	
	Strong argillic	EB17045	
Mineralised dacite porphyry (Paja Blanca)	Weak propylitic	EB17038	Moderate potassic (EB17002)
	Strong propylitic	EB17018	
	Strong sericitic	EB17037	
Late quartz porphyry (Mirador)	Weak chlorite-sericite	EB17052	Moderate potassic (EB17053)
	Strong Sericitic	EB17051	
Andesite (Quebrada Honda)	Strong potassic	EB17058	Weak potassic (EB17057)
	Strong propylitic	EB17060	

the metasomatic modifications that occurred during the later stages of alteration in the system. At La Granja, the grain size of the lithologies is comparatively fine compared to the sample size used for bulk rock analysis and, as such, the samples can be considered homogeneous and representative. Areas with a high concentration of veining were avoided and care was taken when selecting samples from brecciated zones. A summary of the lithologies and alteration types studied is given in table 4.6.

Immobile elements are used to determine $M^{O/A}$ in Eq. 4.7. Immobile elements are assumed to be neither added nor removed during hydrothermal alteration (i.e. $\Delta C_i = 0$) so that Eq. 4.7 defines a straight line through the origin. The HREE and HFSE elements Gd, Dy, Tm, Hf and Zr were selected as immobile elements as the relative concentrations of these elements do not vary between different degrees of alteration of the same protolith. The LREE (La, Ce, Pr, Eu, Nd, and Sm) appear to be slightly more mobile and were therefore not included. A value for $M^{O/A}$ is calculated for each immobile element using Eq. 4.7 where $\Delta C_i = 0$. The uncertainty on $M^{O/A}$ is derived from the analytical error associated with each analysis (σ^{An} : Appendix E) and can be propagated as a relative error:

$$\frac{\sigma_M}{M_i^{O/A}} = \sqrt{\left(\frac{\sigma_i^{an}}{C_i^O}\right)^2 + \left(\frac{\sigma_i^{an}}{C_i^A}\right)^2} \quad \text{Eq. 4.8}$$

A weighted average of $M^{O/A}$ from the immobile elements was then calculated for each alteration domain in each lithology, taking into account the associated error (see Eq. 4.2):

$$M^{O/A} = \frac{\sum_i \frac{M_i^{O/A}}{\sigma_M^2}}{\sum_i \frac{1}{\sigma_M^2}} \quad \text{Eq. 4.9}$$

Results from Eq. 4.9 can then be used in Eq. 4.7 to calculate ΔC_i (the net change in concentration) for each element, in each alteration domain, in each lithology (Table 4.6).

Results

The mass ratio ($M^{O/A}$) is less than 1 for all alteration domains studied; apart from for the chlorite-sericite alteration zone $M^{O/A}$ is within the error limit, suggesting that there is a bulk mass gain in most of the altered samples compared to their potassically altered precursors (Table 4.7). Bulk mass gain can be the result of added minerals, such as through veins, and should correlate to an increase in minerals such as Al and Si. Overall, the mass ratio is lower in later overprinting alterations.

Net changes in element concentrations can be visualised on an isocon diagram which plots the concentration of species in the altered rock against the concentration in the least altered equivalent. The line that passes through the origin defined by the immobile elements (the 'isochron') has a slope of $M^{O/A}$, most REE plot on or near the isochron (Fig. 4.16). Elements that plot above the isocon have an absolute increase in abundance in the altered sample. Relative concentrations of Na_2O , CaO are depleted in altered samples relative to the potassically altered precursors. The REE, HFSE and Al_2O_3 typically plot on or near the isochron suggesting relative immobility. However, the LREE (i.e. La) and Ce do show greater variation between the different alteration styles.

A comparison of the changes in element concentrations with alteration across all lithologies is shown in figure 4.17. Overall, the alteration of different lithologies produces similar variations

Table 4.7 The mass ratio (MO/A) calculated for each sample and the calculated change in element concentrations from potassic alteration.

	POT	POT/PROP	PROP			CHL-SER			SER		ARG
	Strong	Strong	Weak	Moderate	Strong	Weak	Moderate	Moderate	Strong	Strong	Strong
	AND	DP _{PB}	EDP _{PB}	EDP _{PB}	AND	LQP2 _M	DP _{PB}	DP _{PB}	EDP _{PB}	LQP2 _M	DP _{PB}
M ^{O/A}	0.71	0.68	0.73	0.90	0.92	1.02	0.91	0.90	0.85	0.90	0.91
wt. %											
SiO ₂	15.85	21.29	17.91	7.99	1.71	-2.54	8.67	9.04	13.87	6.95	12.27
Al ₂ O ₃	4.12	5.93	5.75	2.29	1.21	-0.54	2.50	2.32	2.71	1.29	2.75
Fe ₂ O ₃	2.41	2.12	2.83	1.98	1.90	0.00	5.05	5.41	0.97	0.71	1.29
CaO	2.28	-0.38	2.00	-0.84	2.88	2.61	-3.52	-3.47	-1.20	0.05	-3.51
MgO	0.96	1.01	1.02	0.46	1.64	0.07	-0.95	-0.93	0.78	0.13	-0.70
Na ₂ O	0.77	-1.22	2.69	-0.32	-0.02	1.75	-3.67	-3.61	1.18	-0.01	-3.66
K ₂ O	0.70	1.53	-1.60	0.25	0.25	-1.60	-1.93	-1.89	-1.43	0.59	0.59
TiO ₂	0.23	0.11	0.36	0.22	-0.07	-0.02	0.08	0.08	0.19	0.03	0.38
MnO	0.02	0.10	-0.01	0.02	0.03	0.12	-0.02	-0.02	-0.01	-0.01	-0.02
P ₂ O ₅	0.06	0.09	0.09	0.07	-0.05	-0.03	0.01	0.06	0.05	0.00	0.06
ppm											
S	-0.47	-0.45	-0.08	-0.86	-0.44	-0.41	3.70	3.89	-1.00	0.56	-1.76
As	0.78	5.85	-50.67	-2.55	0.31	-17.24	15.03	12.64	-14.32	-5.94	217.73
V	60.58	37.84	52.17	17.88	10.49	-2.65	25.00	23.63	24.34	4.17	52.01
Sr	86.23	-222.91	456.81	-168.31	9.92	266.25	-142.70	-64.91	19.46	-14.09	-84.66
Y	9.78	2.99	3.25	3.57	2.44	0.95	0.65	1.30	2.08	1.03	0.25
La	12.66	-0.10	6.53	3.87	4.66	-0.12	3.04	2.77	4.37	0.51	2.64
Ce	27.66	1.66	14.09	9.90	10.28	-0.65	6.96	6.62	9.51	1.20	5.77
Pr	3.54	0.92	1.87	1.37	1.35	-0.01	0.90	0.80	1.09	0.20	0.69
Nd	14.83	6.91	8.20	5.74	5.63	-0.31	4.63	4.04	4.62	0.92	3.63
Sm	2.86	1.81	1.58	1.01	1.22	0.04	0.67	0.42	0.79	0.32	0.30
Eu	0.97	0.42	0.51	0.27	0.29	-0.05	0.06	0.07	0.26	-0.06	-0.04
Gd	2.38	1.37	1.16	0.87	0.62	-0.04	0.47	0.52	0.58	0.19	0.34
Tb	0.37	0.15	0.17	0.10	0.12	0.02	0.06	0.06	0.09	0.02	0.02
Dy	2.18	0.53	0.72	0.71	0.55	0.08	0.17	0.10	0.40	0.19	0.03
Ho	0.42	0.08	0.13	0.10	0.05	0.04	0.02	0.02	0.08	0.04	-0.02
Er	1.06	0.18	0.33	0.20	0.36	-0.02	-0.02	0.08	0.16	0.09	-0.06
Tm	0.13	0.04	0.03	0.01	0.04	0.00	0.01	0.01	0.03	0.00	0.00
Yb	0.88	0.20	0.33	0.04	0.24	0.01	0.06	0.00	0.22	0.10	0.01
Lu	0.11	0.03	0.05	0.05	0.06	0.00	-0.01	-0.01	0.03	0.00	0.01
Pb	1.17	8.80	15.38	11.01	-2.54	-80.54	20.96	9.01	-35.05	-18.86	12.06
Th	1.53	0.72	1.35	0.19	-1.14	-0.25	1.32	1.07	0.98	0.12	-0.46
U	0.36	0.56	-0.14	0.70	-0.31	-0.61	-0.03	-0.03	-0.34	0.06	0.06

in element abundance, with the strength of the alteration also affecting the net concentration change in elements, compared to weakly potassically altered samples. Strong potassically and propylitically altered samples have higher MgO, Na₂O, Fe₂O₃, CaO and lower K₂O abundance relative to the potassically altered sample. The propylitic samples are examples proximal alteration and therefore do not show the wide compositional range of the propylitic zone presented in the literature. Chlorite-sericite and sericitic altered samples have all undergone significant loss of CaO and K₂O compared to the potassic altered sample. Chlorite-sericite alteration shows a strong increase in Fe₂O₃ and Al₂O₃. This increase in FeO₃ may reflect the presence of pyrite within these samples as these samples also show a net gain in S (Table 4.7). In general, the change in REE abundance compared to potassic samples is similar across the alterations although the LREE show more variation. Sr shows some of the greatest changes in abundance however this occurs in the

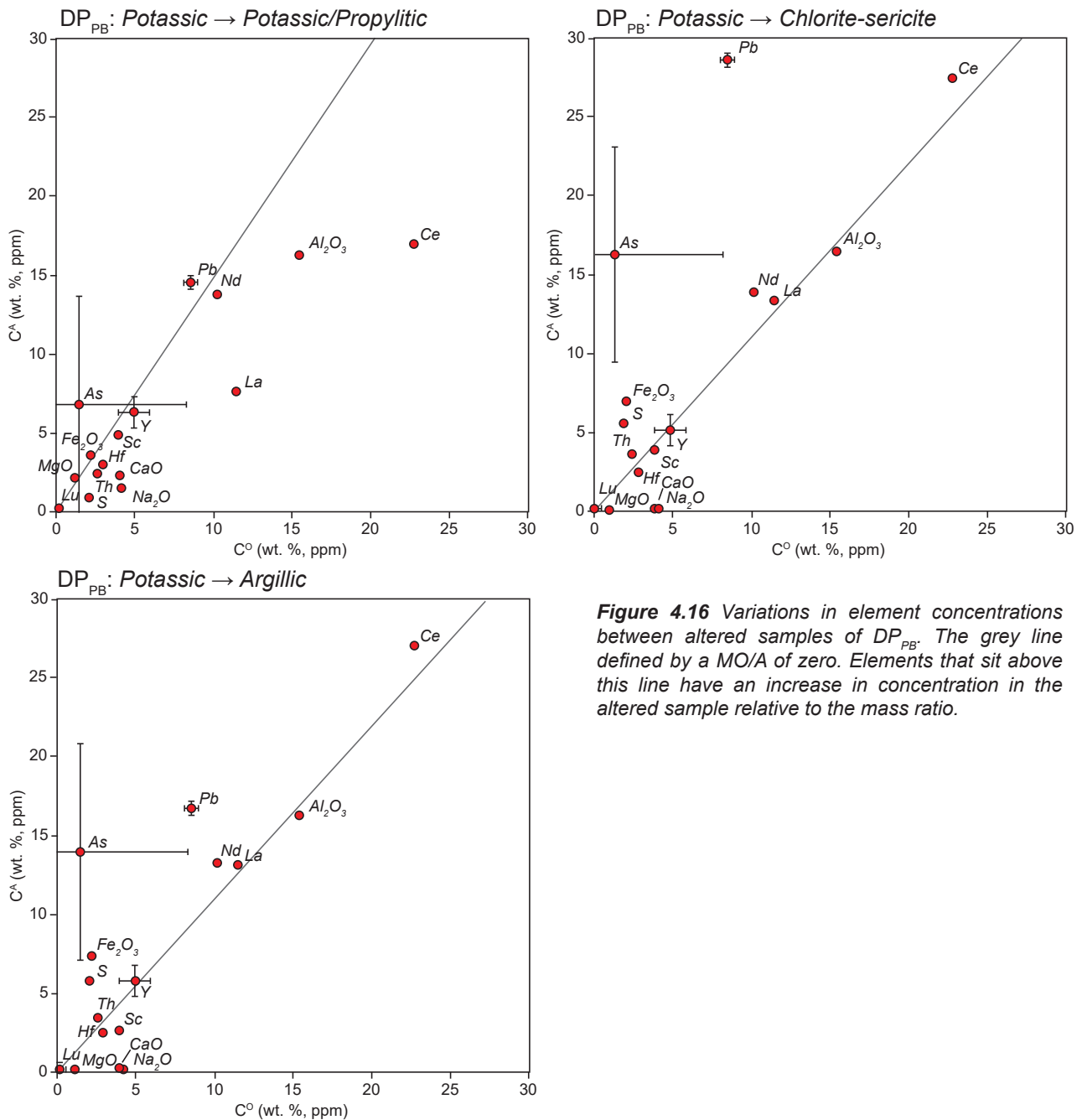
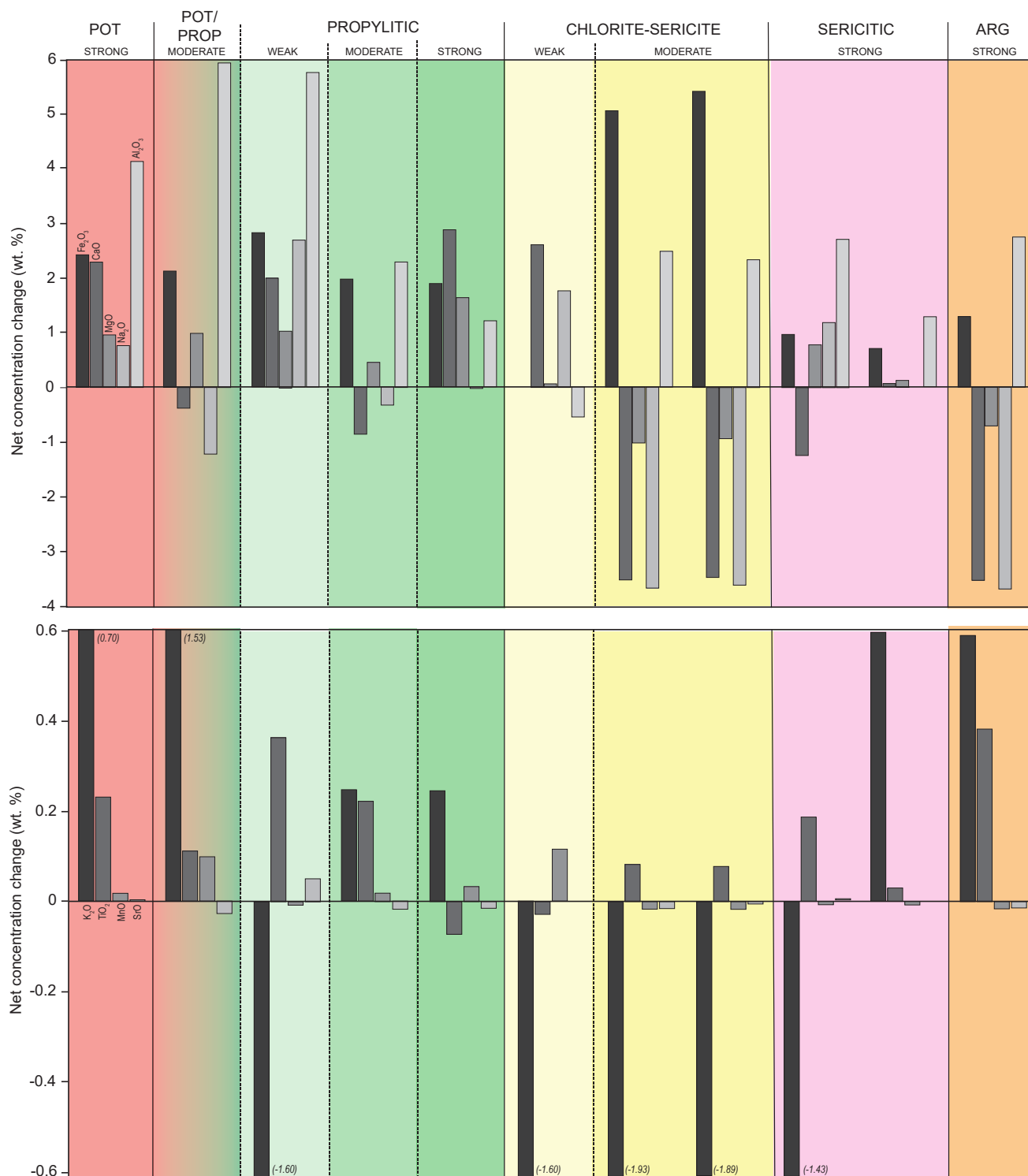


Figure 4.16 Variations in element concentrations between altered samples of DP_{PB}. The grey line defined by a MO/A of zero. Elements that sit above this line have an increase in concentration in the altered sample relative to the mass ratio.

plagioclase-rich lithologies (EDP_{PB}, DP_{PB} etc.) reflecting the susceptibility of this mineral to alteration.

4.5.2 Whole rock geochemistry at La Granja

Igneous rocks can be classified using whole rock chemistry and this approach is often based on the major element oxide components. However, because most samples have undergone hydrothermal alteration and this can result in significant modification of these components, major element plots must be used with caution. The weak correlations present between bulk rock SiO₂ and major oxide concentrations (except for MgO where R² = 0.80; Fig. 4.18) are evidence to this. Plots of K₂O show a broader spread in the data (Fig. 4.18B), most samples fall with the medium K range with samples within the high-K field associated with sericitic and potassic alteration. There is a large spread in data with Na₂O showing how susceptible it is in potassic and sericitic alteration. As a result, the aluminium saturation index (ASI: molar ratio of Al₂O₃/CaO + K₂O + Na₂O) are



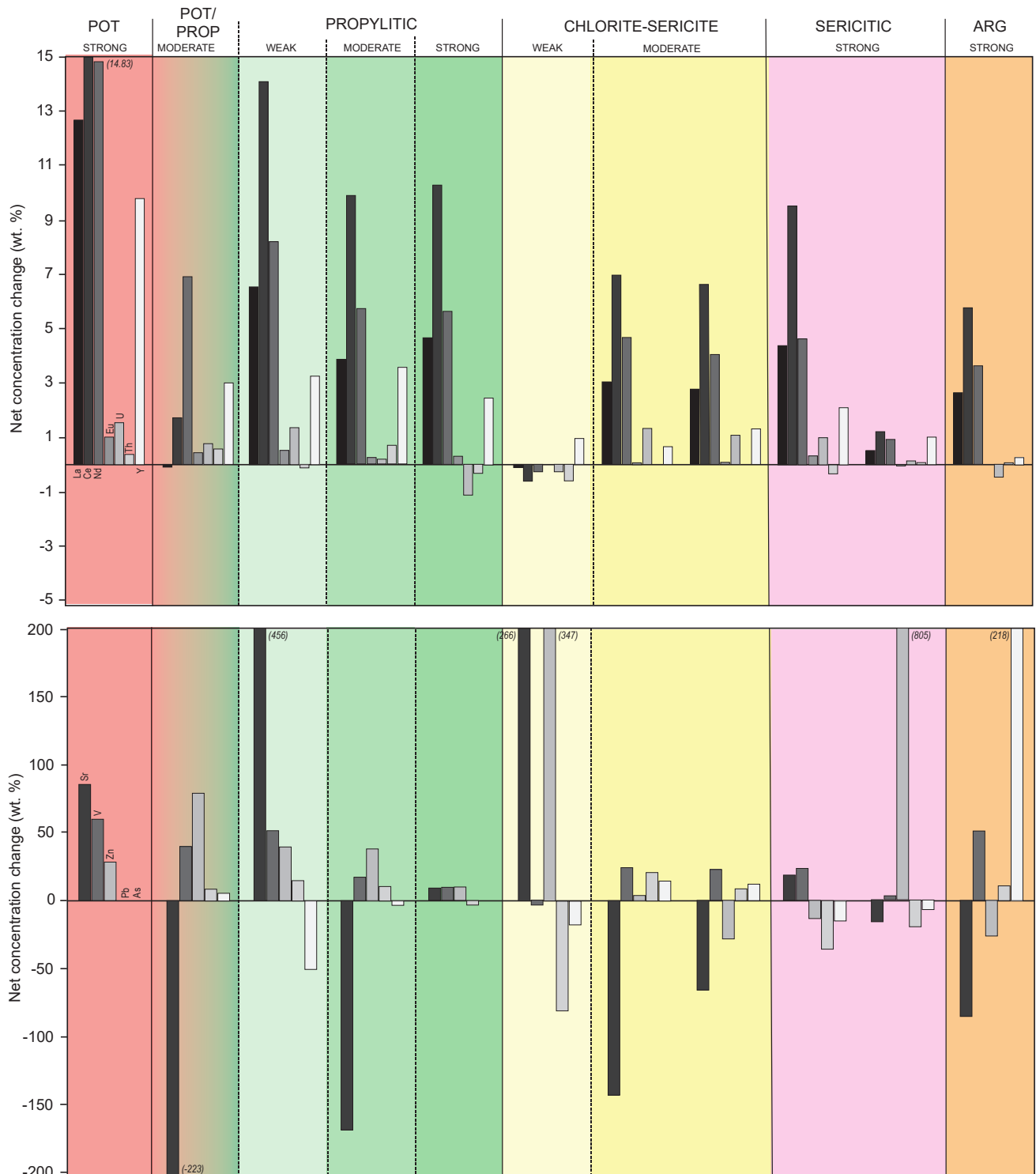


Figure 4.17 Net changes in element concentration between samples grouped by alteration style and intensity.

overestimated in more altered samples, mean ASI is 2.4, suggesting these are peraluminous rocks.

Plots of Zr/Ti against Nb/Y can be used as an immobile element version of the TAS classification, where Nb/Y is a proxy for alkalinity ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) and Zr/TiO_2 for degree of differentiation (cf. silica content; Pearce 1996). A Th-Co plot was more recently suggested as an alternative to $\text{K}_2\text{O}-\text{SiO}_2$ (Hastie et al. 2007). Both these diagrams suggest that the Eocene and Miocene units are calc-alkaline, ranging from andesite to dacite in composition (Fig. 4.19A-D). The implied composition from the Zr/Ti vs. Nb/Y plot are slightly more mafic ranging from basalt to andesite for the Eocene rocks and andesite to dacite for the Miocene rocks (Fig. 4.19C-D). In Th-Co space the Miocene lithologies plot in two groups, DP_{PB} with DIOP, where as in Zr/Ti – Nb/Y bulk rock analyses of DP_{PB} have a more evolved composition (Fig. 4.19). In general the immobile element plots show an evolving composition of the porphyry units with later intrusions with DIOP, EQP_{M} and EQP_{PB} fitting within a different trend of increasing Th (Fig. 4.19B).

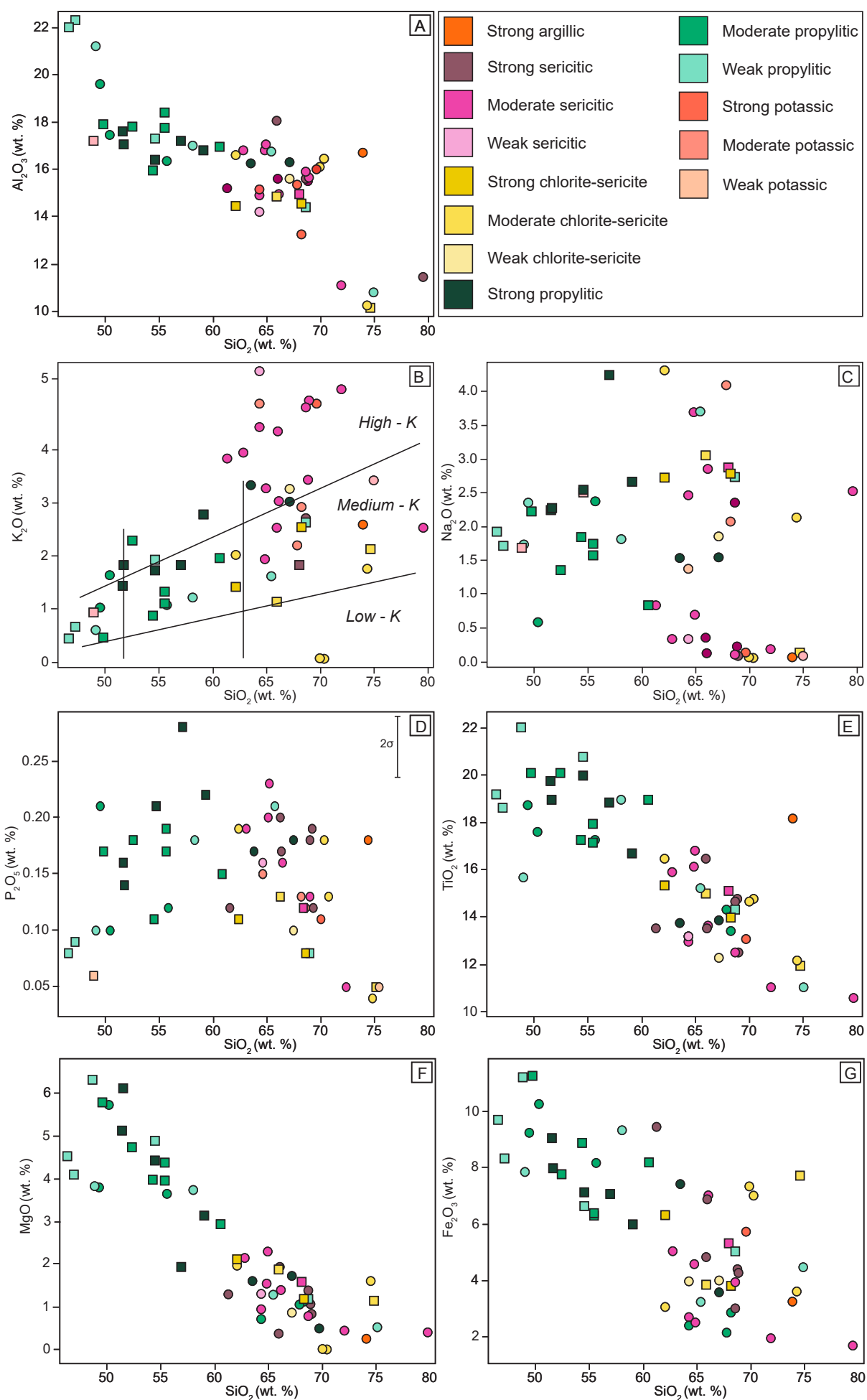
REE patterns

Chondrite-normalised REE plots (Sun & McDonough 1989) are typical of those of I-type granites and are enriched in LREE (Fig. 4.20). The REE profiles are flatter (more HREE enriched) for the Eocene igneous rocks (AND, GRANO, DIO; La/Yb: 6.8) and for the diorite porphyry (La/Yb: 6.9) than the Miocene porphyries (La/Yb: 20.8). Most samples display negative Eu anomalies. The Miocene porphyry suite display much steeper LREE-MREE slopes, lack Eu anomalies, and have very depleted HREE, with a near flat or slightly rising HREE trend. The mineralised quartz porphyries (EQP_{PB} , EQP_{M}) are notable in being less HREE depleted than the other intrusions; conversely, the late quartz porphyries are the most strongly MREE and HREE depleted.

Harker plots

Harker diagrams reveal variations in element concentrations with melt evolution. Despite alteration, which produces scatter in the data, there are still some weak correlations present for the La Granja samples. Compatible Al_2O_3 , TiO_2 , MgO and Fe_2O_3 decrease with increasing SiO_2 (R^2 values of 0.62, 0.67, 0.80 and 0.55 respectively; Fig. 4.18). This is consistent with derivation from a source undergoing fractional crystallisation. P_2O_5 increases with SiO_2 until ~ 60 wt. % and then decreases, this is inferred to reflect crystallisation of apatite although this too shows spread in the data (Fig. 4.18D). The REE concentrations increase with bulk rock SiO_2 until around 60 wt. %, upon which point the decrease coinciding with the saturation of apatite and later titanite (Fig. 4.18). The LREE show a greater spread, especially in the porphyry units, reflecting their greater mobility compared to other REE (Fig. 4.21A). The concentration of HREE increase in Eocene lithologies, even in more evolved GRANO which sees a decrease in MREE (Fig. 4.21B). However, HREE are depleted in most felsic porphyry units (Fig. 4.21C).

Figure 4.18 (Right hand page) Harker diagrams of bulk rock major oxides against SiO_2 wt. % for igneous units. Squares denote Eocene lithologies and circles Miocene lithologies. Points are coloured by degree and type of alteration. A) Bulk rock Al_2O_3 decreases with SiO_2 and shows little spread with alteration. B) Most units plot in the mid-K range, sericitic and potassic altered samples plot in the high-K fields. (Rickook 1989). C) Bulk rock Na_2O are largely affected by alteration. D) An inflection in the P_2O_5 concentration around 58 – 62 wt. % SiO_2 could be inferred to reflect the saturation point of apatite and its fractionation from the melt. E) TiO_2 show decreasing concentrations in more evolved melts and a small spread from alteration as do F) MgO and G) FeO. Analytical precision is given where larger than the symbol size.



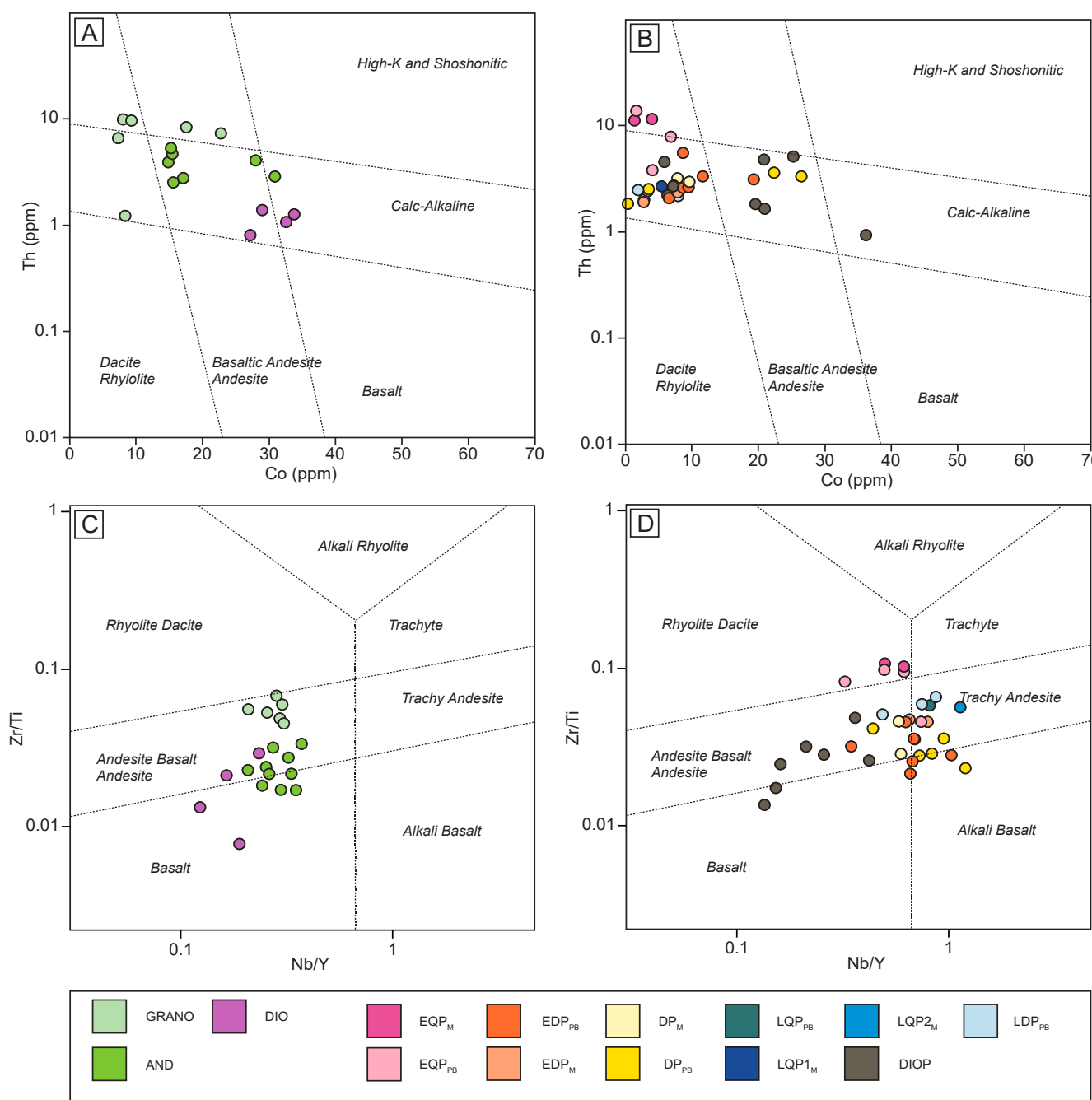


Figure 4.19 Bulk rock geochemistry for magmatic lithologies at La Granja. Trace element proxies were used in place of more traditional silica-alkalinity plots as hydrothermal alteration will have affected the composition. A) Eocene host rocks are classified as calc-alkaline to high-K calc-alkaline and range in composition from basaltic andesite to dacite. B) Porphyry-related samples are calc-alkaline apart from the EQP samples that trend into the high-K calc-alkaline domain. EQP lie on a different trend to DP and EDP porphyries. C, D) Zr/Ti – Nb/Y plots suggest samples are less felsic than the Th-Co plots and data straddle the calc-alkaline/high K calc-alkaline boundary. Most porphyry intrusions cluster together, apart from the diorite porphyry which exhibits a more primitive composition and the EQP samples that appear to be slightly more evolved. Analytical error is smaller than the symbols.

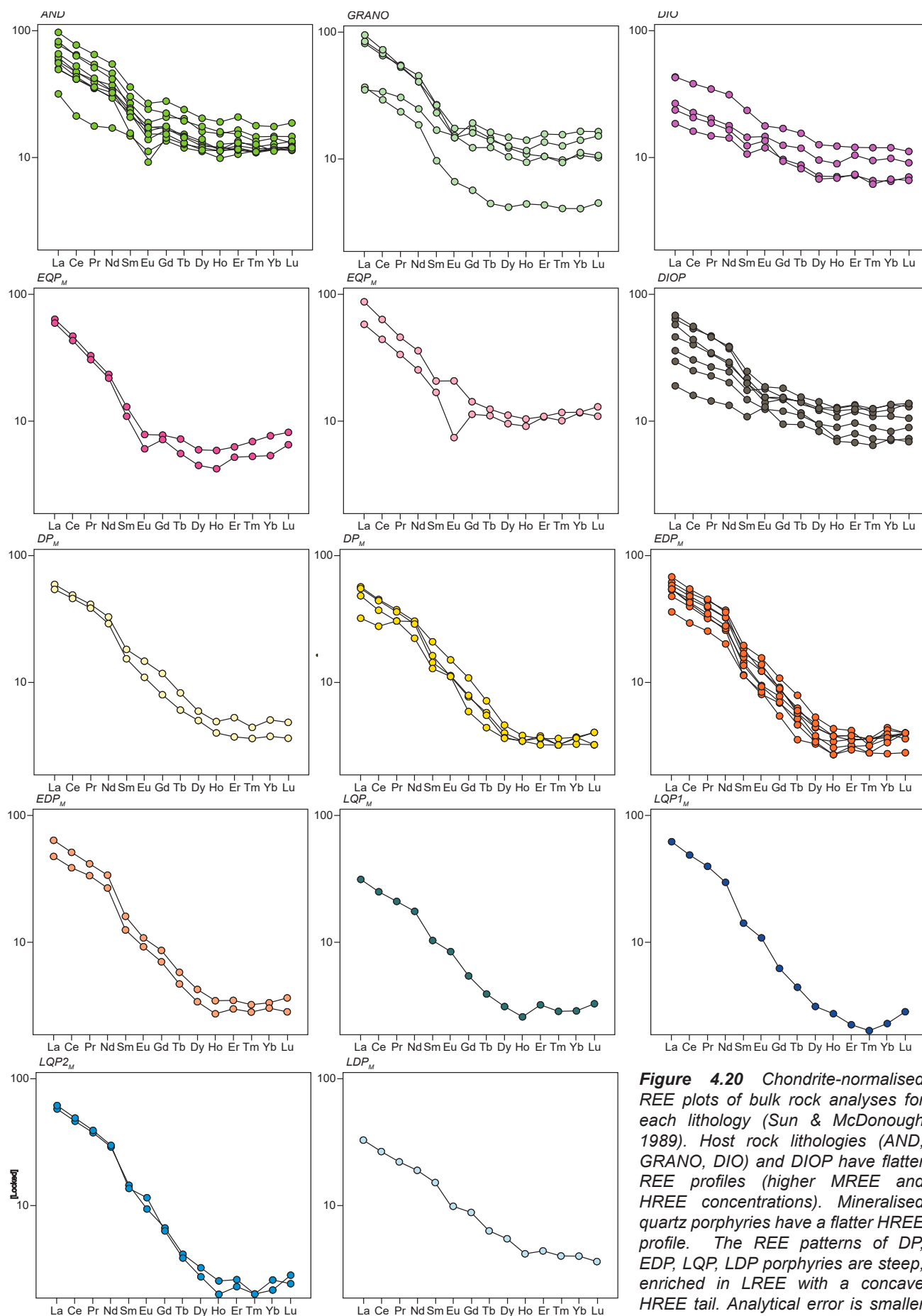


Figure 4.20 Chondrite-normalised REE plots of bulk rock analyses for each lithology (Sun & McDonough 1989). Host rock lithologies (AND, GRANO, DIU) and DIOP have flatter REE profiles (higher MREE and HREE concentrations). Mineralised quartz porphyries have a flatter HREE profile. The REE patterns of DP, EDP, LQP, LDP porphyries are steep, enriched in LREE with a concave HREE tail. Analytical error is smaller than the symbols.

4.6 Comparison of Eocene and Miocene magmatism

4.6.1 Eocene magmatism

Three igneous host rocks are identified in this study: granodiorite, diorite and andesite. They are inferred to be Eocene in age (Schwartz 1982); the granodiorite has been dated here as Eocene (34.53 ± 0.78 Ma) and the andesite have been mapped by as part of the Llama Formation (Fig. 4.3, Peruvian Geological Institute of Mines and Metallurgy), the lower part of which has been dated between 54.6 and 42.6 Ma (Atherton et al. 1985; Noble et al. 1990). This, together with textural relationships observed in the drill core (Fig. 4.6H-I), suggests that the andesitic volcanics are the oldest sampled unit.

The Eocene rocks have a flatter chondrite-normalised REE patterns leading to lower La/Yb (mean: 6.8) ratios compared to the Miocene porphyry intrusions (Fig. 4.20). Differences are also observed in the zircon trace element chemistry where Eocene zircons have generally lower Hf, and much lower Eu/Eu* ratios (Fig. 4.20).

Source and evolution of Eocene magmas

These three units represent a period of arc construction in the Eocene, the Incaic Orogeny, prior to the formation of the mineralised belt (McQuarrie et al. 2005; Silver et al. 1998). A study of the bulk rock geochemistry of igneous suites in the Cajamarca district, northern Peru, concluded that early Eocene lithologies reflect generation within an immature magmatic arc and reflect the residue from the fractionation of anhydrous minerals (i.e. pyroxene and olivine; Davies 2002). This could explain the lower bulk rock La/Yb ratios observed in these samples. The lower water content of the melts was proposed as a contributing factor towards the lack of Eocene age mineralisation. In addition, the low Eu/Eu* observed within the zircon in this study may also reflect a more reduced melt that could also hinder the formation of porphyry-style mineralisation.

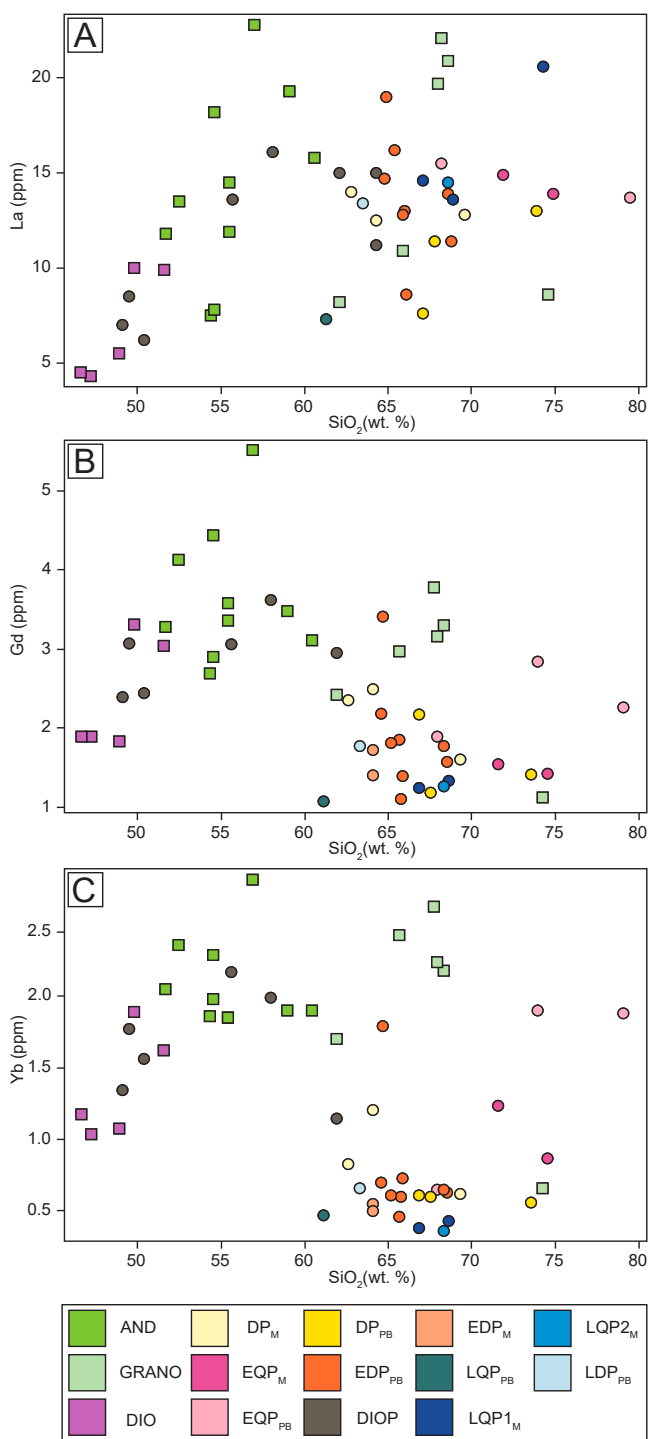


Figure 4.21 Fractionation trends of light, middle and heavy REE's with bulk rock SiO₂. A) LREE (La) increase with SiO₂ until about 60 wt. % SiO₂. B) MREE (Gd) increase with SiO₂ up to 60 wt. % SiO₂ then decrease. C) HREE (Yb) increase with SiO₂ and are depleted in porphyry units with SiO₂ > 60 wt. %. Analytical error is smaller than the symbols.

4.6.2 Miocene magmatism

The U-Pb ages of individual zircons span ~4 Myr from approximately 18 – 14 Ma. This time period corresponds to the first phase of the Quechua Orogeny (Mégard 1984). At this time, structures in the Western Cordillera formed during the previous Incaic Orogeny (~59-22 Ma) were re-activated (Farías et al. 2008). These structures could have acted as magma and fluid pathways and may explain the close spatial association of the Eocene intrusions with the Miocene porphyries.

Porphyry deposits are commonly formed of multiple intrusions that are superimposed on each other in which an initial mineralisation event is followed by a succession of intrusions that become less mineralised and altered with time (Sillitoe 2010). At La Granja, 10 different units have been identified in this study, four of which are associated with the majority of mineralisation across the two porphyry centres. The two porphyry clusters at La Granja are defined by the mineralised intrusion. At Mirador EQP_M is dominant and the EDP_{PB} at Paja Blanca. The porphyry intrusions are calc-alkaline and predominately intermediate to felsic in compositions (DIOP excluded).

DP_M is a pre-mineral porphyry observed to the edge of the Mirador cluster. Early quartz porphyries (EQP_M and EQP_{PB}) are the oldest mineralised porphyries sampled. At Paja Blanca an inter-mineral dacite porphyry (DP_{PB}) is observed. A second mineralised porphyry stage, represented by EDP_{PB} and EDP_M, is then followed by DIOP at Paja Blanca and late-/post mineralisation intrusions (LQP_{PB}, LDP_{PB}, LQP1_M, LQP2_M) at both clusters. The latter appear to be associated with a rhyodacite dome at Mirador. A previous age of 13.8 Ma from K-Ar dating of hydrothermal muscovite (Noble & McKee 1990) suggests that sericitic alteration (or cooling of the system post-sericitic alteration) coincides with the late porphyries. These intrusions can be grouped into three main periods of magmatic activity (Fig. 4.12). However, the absolute timing of the early quartz porphyries and the diorite porphyries are not well constrained.

Source and evolution of La Granja magmas

Porphyry intrusions are thin stocks or dykes that crystallise relatively quickly in around 0.1 Myr (Braxton et al. 2012). These dykes are shallow crustal expressions of a larger, deeper body of magma. Therefore, each porphyry intrusion represents a snapshot of the magmatic evolution of a system which may have a lifespan of a few million years (Ballard et al. 2001; Chiaradia et al. 2009; Sillitoe 2010; Chiaradia & Caricchi 2017). The duration of the system at La Granja of ~4 My is at the upper end of those for porphyry systems. The lifespan of a single porphyry system can be increased with a larger, hotter magma source, or one that is repeatedly replenished (Chelle-Michou et al. 2014).

The close spatial and temporal evolution of the La Granja porphyry clusters, as well as the extended lifespan of the system, suggests that they have originated from a single, larger, parental source. This is supported by the comparable whole rock and zircon geochemistry. Bulk rock compositions generally increase in silica and alkalinity with decreasing age (Fig. 4.19) and zircon compositions trend towards lower Yb/Gd, Th/U and Ti concentrations and higher Hf concentrations in younger intrusions (Figs. 4.13, 4.14), consistent with growth within a cooling and fractionating melt (Buret et al. 2016). Despite the similarity of EDP_M and EQP_{PB} geochemically, given petrological observations, spatial distributions and U-Pb crystallisation ages these are unlikely to be the same

lithology. By contrast, EQP and DIOP lithologies lie off the main trend lines observed in the other porphyry intrusions and are distinct petrologically and compositionally through bulk rock and zircon geochemistry (i.e. Figs. 4.22B, 4.23). The late porphyry intrusions (LQP1_M, LQP2_M, LDP_{PB}) have depleted bulk rock HREE concentrations (Fig. 4.20) reflecting crystallisation from a more fractionated melt. In addition, Th/U ratios in zircon are higher and core-rim composition show little difference (Fig. 4.14) suggesting a more rapid crystallisation of these lithologies. This supported by their finer groundmass texture.

4.6.3 Source of Eocene magma versus porphyry magma

Although there is a close spatial relationship between the Eocene intrusions and the Miocene porphyry units, they are compositionally distinct. These differences reflect the divergent evolutionary paths of the Eocene arc magmas and the Miocene arc magmas that went on to form porphyry deposits. One of the most notable differences is the higher La/Yb ratios in the porphyry related lithologies (Fig. 4.20). High La/Yb (low HREE) is derived from lower crustal differentiation and the fractionation of amphibole and/or garnet and is observed in porphyry magma. High Sr/Y ratios also form the 'adakite-like' signature observed in porphyry intrusions. Bulk rock Sr concentration is linked to plagioclase fractionation and Y to amphibole. The timing of plagioclase crystallisation is affected by P and T but also varies greatly as a function of water content (Blatter & Carmichael 1998). High Sr/Y values can be achieved by a high water content suppressing plagioclase crystallisation to the point that amphibole fractionates earlier (Loucks 2014). In addition, high Sr/Y within magmatic arcs has been correlated with slab thickness (Chiaradia 2015). Therefore, both high La/Yb and Sr/Y can be produced from fractionation of H₂O-rich melt (stabilising garnet and suppressing plagioclase) at high pressures (stabilising amphibole).

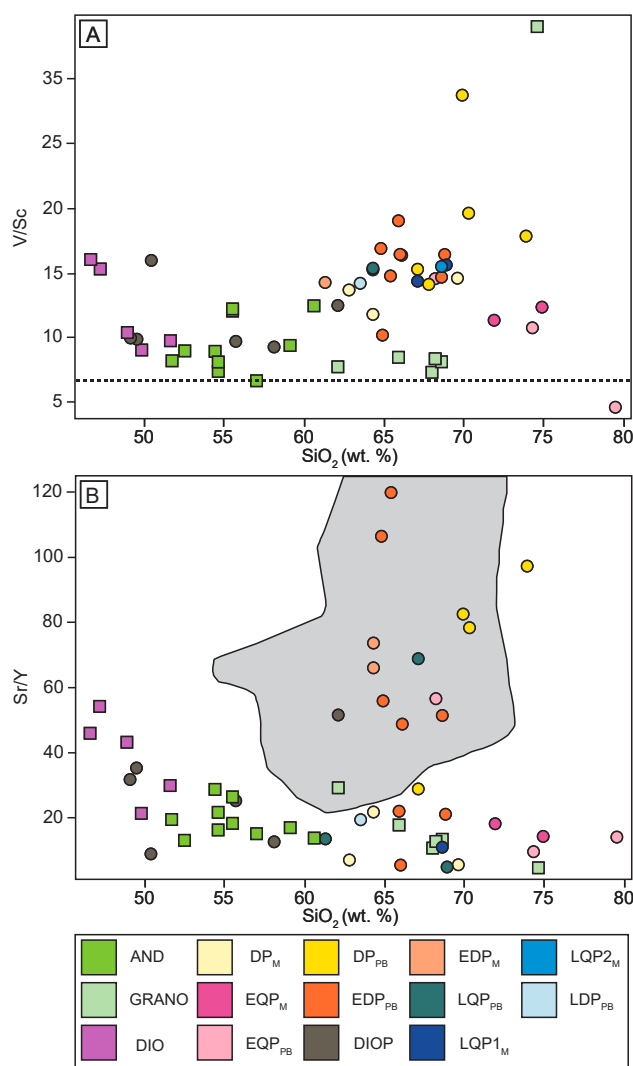


Figure 4.22 Plots for bulk rock fractionation of minerals coloured by unit lithology. Squares denote Eocene lithologies, circles Miocene lithologies. A) V/Sc ratio in oxidised rocks plots fractionation of magnetite, which preferentially take in V, and mafic silicates such as amphibole, pyroxene and biotite which incorporate Sc. In reduced melts V, as V3+, is fractionated at the same rate as Sc. V:Sc ratios stay around 7:1 over a range of melt silica contents (Halley 2020). Porphyry units have increasing V/Sc with bulk rock SiO₂. In more oxidised melts V is incorporated exclusively as V4+ into magnetite. In more water rich melts amphibole fractionation occurs before magnetite, raising V/Sc in melt. B) In non-porphphyry related melts Sr/Y ratios decrease with SiO₂ as a result of plagioclase fractionation. Porphyry rocks typically have higher Sr/Y ratios associated with adakite-like melts (grey field; Loucks 2014). Analytical error is smaller than the symbols..

Bulk rock analyses of the dacite porphyries at La Granja contain high Sr/Y values

relative to SiO_2 (Fig. 4.22). This combines with high La/Yb ratios differentiated the bulk rock from the Eocene intrusions and reflects a regime promoting the stalling of melt in the lower crust where it can equilibrate. The Quescha pulse during the Miocene is associated with a period of intense crustal thickening brought on by an increased divergence rate (Davies 2002) and an intense magmatism (Kano et al. 1996). Melts with higher water contents may have also been produced during the Miocene following the subduction of the potentially more serpentanised Inca plateau and Nazca ridge (Rosenbaum et al. 2005).

The Eocene arc magmas may have also been more reduced compared to the Miocene porphyry related melts. Eocene units contain lower zircon Eu/Eu^* which may be attributed to a more reduced oxidation state (Loader et al. 2017b). However the fractionation of V relative to Sc may suggest a more likely explanation. In reduced melts V^{3+} will partition to the same degree as Sc into amphibole, pyroxene and biotite. The ratio V:Sc will remain proportional (7:1, Halley 2020) over a range of bulk rock silica contents. However, in more oxidised melts V is incorporated exclusively as V^{4+} into magnetite. Bulk rock V/Sc ratios of Eocene rocks are comparable however, V/Sc ratios in porphyry related rock increase with SiO_2 (Fig. 4.22A). In more water-rich, oxidised melts amphibole fractionation occurs before magnetite raising V/Sc in the residual melts.

4.6 Conclusions

- La Granja is a cluster of porphyries, the two main centres being Paja Blanca and Mirador
- In this study the sampled porphyry intrusions cover pre-, early, syn- and late-mineralisation.
- The porphyries were emplaced during the Miocene period and samples record about 4Myr of magmatic activity.
- Zircon and bulk rock chemistry from the porphyry samples reflect normal magmatic differentiation for most units.
- The porphyries can be distinguished compositionally from the porphyry units.
- The samples are extensively altered. Sericitic alteration is the most common overprint.
- Apatite is found within all porphyry lithologies in addition to lesser amounts of zircon and titanite.

Chapter 5: Metasomatism and diffusional re-equilibration of apatite in porphyry systems

5.1 Introduction

Apatite has special utility in studies of the formation of porphyry-type ore deposits because of its incorporation of the essential volatile species Cl, F and S, which play a key role in the transport and deposition of metals. Unfortunately, apatite is prone to alteration in the presence of hydrothermal fluids, and these elements in particular are susceptible. The metasomatism of apatite has been well studied in natural samples from the porphyry (Bouzari et al. 2016; Loader 2017a; Belousova et al. 2001) and non-porphyry environment (Krneta et al. 2018; Li & Zhou 2015) and experimentally (Kusebauch et al. 2015; Harlov et al. 2002, 2015).

Although strong alteration can be recognised through predictable changes in cathodoluminescence response and textural modification (Harlov 2015; Bouzari et al. 2016), the re-equilibration of elements in apatite by diffusional processes may not leave an obvious textural trace, and is often not considered. The diffusion rate of Cl in apatite is very high ($4.2 \times 10^{-16} \text{ m}^2/\text{s}$ at 800 °C and 1 GPa; Brenan 1994) and so primary Cl contents are generally only preserved in volcanic apatites that crystallized less than a few years before their eruption (Piccoli & Candela 1994). The diffusion rates of other cations in apatite are also high: for example, Sr diffuses at up to $2.4 \times 10^{-7} \text{ m}^2/\text{s}$ above 700 °C (Cherniak & Ryerson 1993; Watson et al. 1985) and Mn at up to $5.4 \times 10^{-7} \text{ m}^2/\text{s}$ above 650 °C (Cherniak & Ryerson 1993). Therefore diffusional re-equilibration is likely to pose a significant problem in porphyry systems due to their formation in a hypabyssal setting associated with the emplacement of multiphase igneous intrusions over time-scales of up to several Myr, coupled with pervasive, post-magmatic fluid flow.

In this chapter first the effects of metasomatism (which is compositional alteration associated with visible textural changes), and then diffusion will be investigated on magmatic apatites from La Granja. The results of this study will have implications for future apatite analyses and interpretation of their compositions.

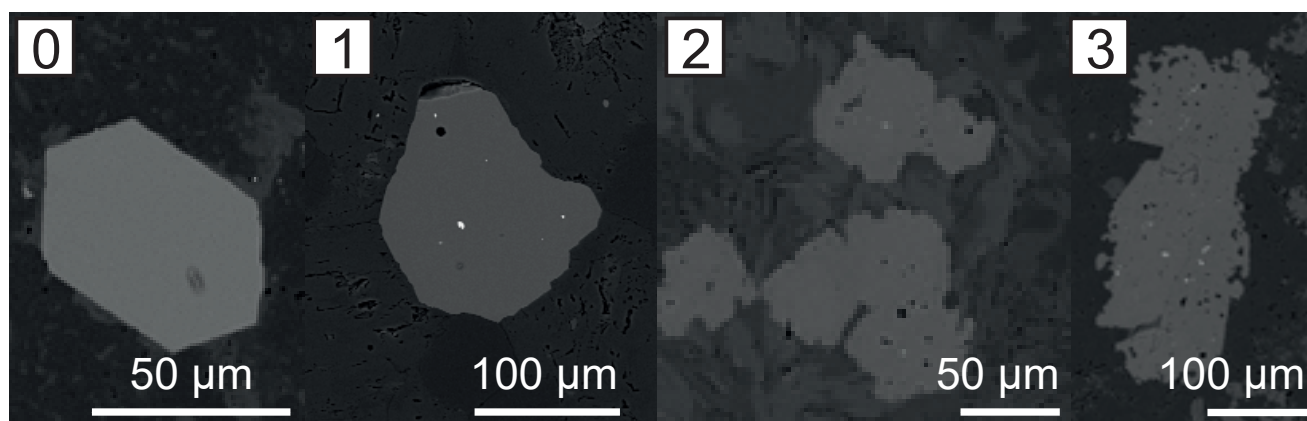


Figure 5.1 Alteration classifications of visibly metasomatised apatites. As visible in the BSE images, a score of 0 denotes apparently fresh apatite, 1 a slightly pitted surface or presence of monazite inclusions, 2 pitted surfaces and an uneven grain boundary. An increase in alteration score correlated with changes in apatite composition.

5.2 Effects of metasomatism on apatite

5.2.1 Samples

Magmatic microphenocrysts of apatite from host rock AND, GRANO, DIO and porphyry units EQP_{PB}, DP_{PB}, EDP_{PB}, EDP_M, DIOP, LQP1_M, LQP2_M where analysed by EPM and LA-ICP-MS methods described in *Chapter 3*. Each grain was observed in detail using back-scatter electron (BSE) imaging by SEM. Textural observations of features associated with metasomatism (ragged grain boundaries, reaction rims, pitted surface and inclusions of monazite, as in Harlov 2015; Bouzari et al. 2016) were recorded for each grain.

5.2.2 Textures in metasomatised apatite

All apatites show varying textures that are inferred to be a result of alteration and are subsequently used as a proxy metasomatism. The degree of alteration has been classified for each apatite grain

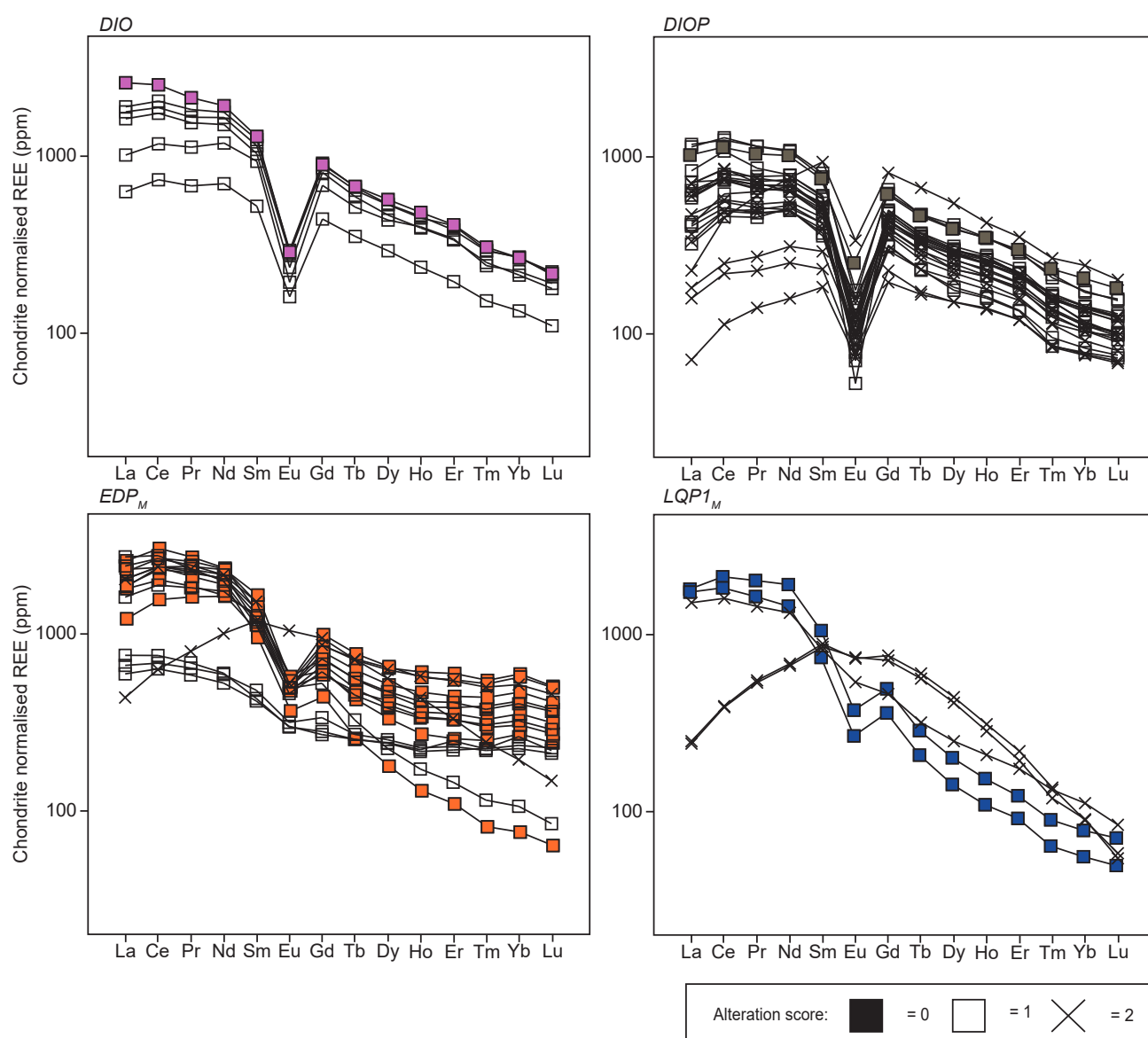


Figure 5.2 Effect of metasomatism on REE concentrations in apatite represented by alteration score (filled coloured squares = 0, empty squares = 1, crosses = 2). LREE are removed preferentially compared to HREE elements. In more altered apatite (alteration score > 1) MREE are enriched and Eu anomaly becomes more positive. The relative standard deviation of each analyses is less than 2 % and therefore smaller than the symbol size.

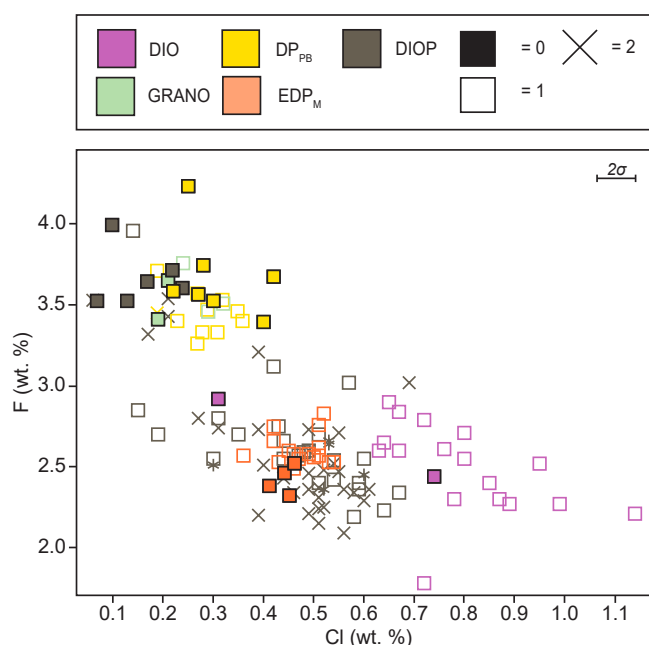


Figure 5.3 Changes in Cl and F concentration in magmatic apatite with degree of metasomatism (alteration score: filled squares = 0, empty squares = 1, crosses = 2. Average analytical error for Cl is shown; error for F is smaller than symbol size.

on a scale from 0 – 3, where a score of 0 indicates an apparently unaltered grain and a score of 3 indicates extensive alteration (Fig. 5.1). Most metasomatised apatites show only light alteration textures, 34 % of magmatic apatites have an alteration score of 1. There are no results for apatites with an alteration score above 2; the high volume of inclusions in these grains likely prevented a good analysis of the apatite. The amount of altered apatites varies between samples. Host rocks contain fewer analyses of altered apatite, whereas early or intermineral intrusions contain the most.

5.2.3 Changes in composition with metasomatism

Textural changes observed in BSE imaging can be linked to compositional changes in apatite. Total REE concentrations (Σ REE - sum of the REE concentrations) decrease with increasing alteration score (Fig. 5.2). LREE are removed preferentially over HREE, and in more altered apatites (alteration score > 1) concentrations of MREE and HREE may also increase. In addition the Cl content of apatite is typically lower in more altered grains from the same sample (Fig. 5.3). Elements Pb, Na and As show the greatest variation in concentration between least-altered and altered apatite (Fig. 5.4). Concentrations of As increase, and Na decrease in more altered apatite. Concentrations of Mg, Sr, Fe and Mn have a larger range in more altered grains; however whether the concentrations increase or decrease with alteration is not consistent between samples (Fig. 5.4).

5.2.4 Discussion: quantifying metasomatism

As expected, more fluid mobile elements (see section 4.5.1) show the greatest variation in concentration in least-altered and altered apatite. However there are no systematic changes in element concentrations which can be used to back calculate an unaltered magmatic composition. The degree of change in element concentration will depend of the altering fluid's composition and the intensity on the alteration which can vary within a sample.

The formation of pits on grain surfaces is a result of the removal of Cl ions from the crystal structure. Removal of Cl produces porosity in the apatite structure from a change in molar volume (Yanagisawa et al. 1999). Replacement experiments on Cl-rich apatite show that around 2.9 % porosity can be produced (Kusebauch et al. 2015). The re-precipitation of mobilised REE within these spaces can lead to the formation of monazite inclusions (Harlov 2015; Fig. 5.1). It has been suggested that crystallisation of monazite may produce negative Nd anomalies (Nd/Nd^*) in co-existing REE-phases (Chu et al. 2009, Miles et al. 2013).

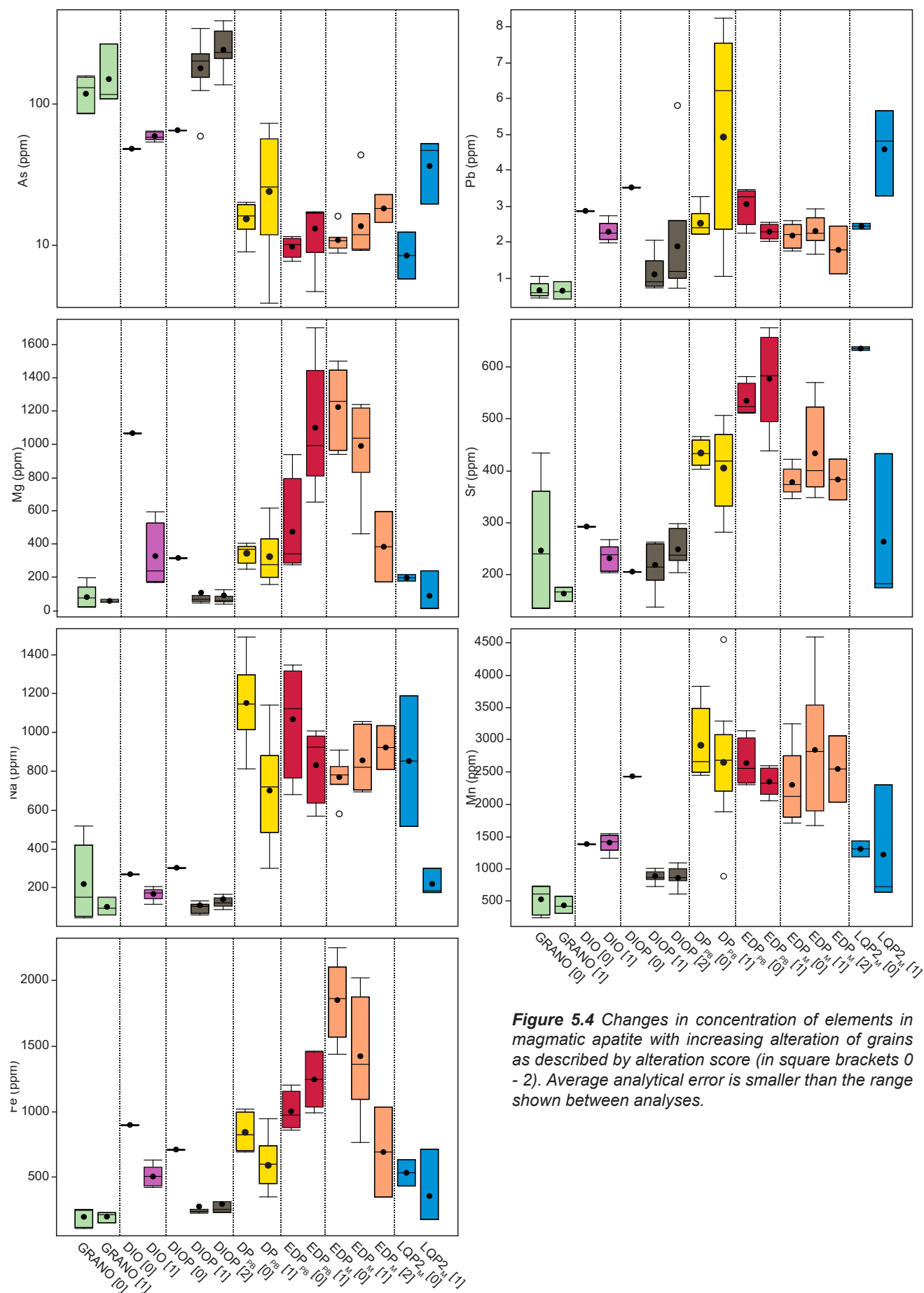


Figure 5.4 Changes in concentration of elements in magmatic apatite with increasing alteration of grains as described by alteration score (in square brackets 0 - 2). Average analytical error is smaller than the range shown between analyses.

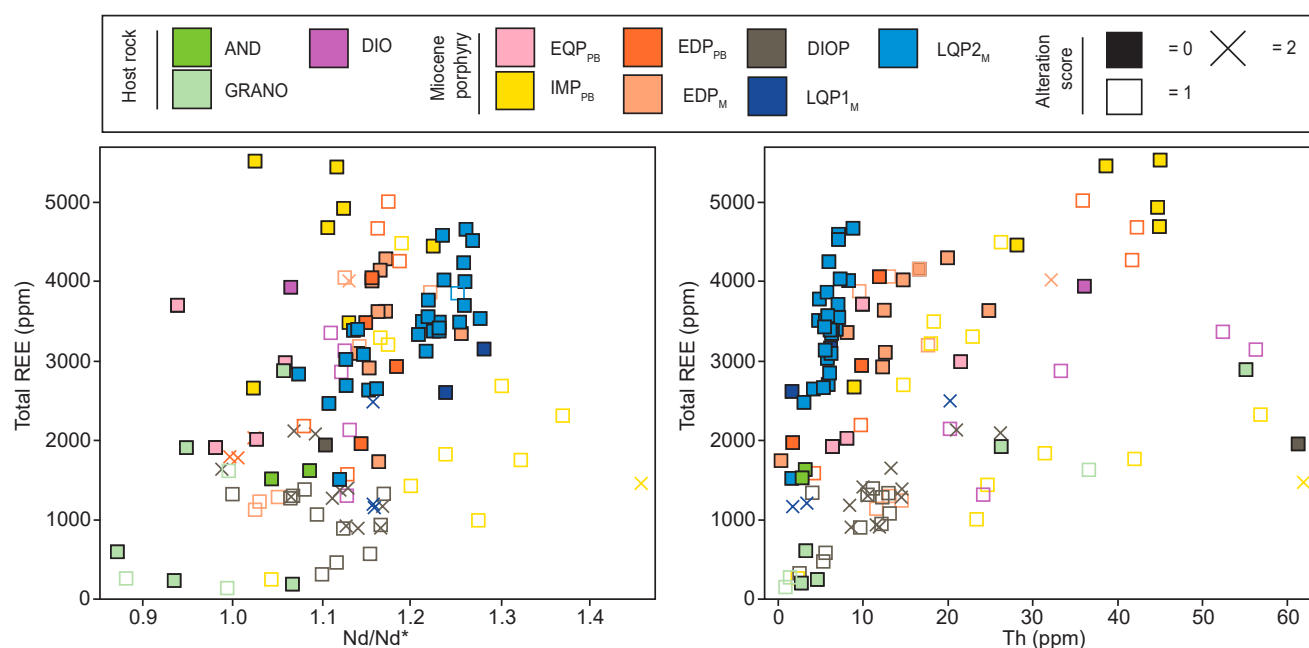


Figure 5.5 Changes in apatite composition with alteration score inferred to reflect the re-precipitation of monazite. Apatites from early and inter-mineral porphyries contain a higher number of altered apatite analyses. A) Metasomatised apatites typically have lower Nd/Nd* and B) Th concentrations with respect to total REE. Analytical error on analyses is smaller than the symbol size.

$$\frac{Nd}{Nd^*} = \frac{Nd_{CN}}{\sqrt{Ce_{CN} \cdot Sm_{CN}}} \quad \text{Eq. 5.1}$$

In addition monazite contains higher concentrations of Th than apatite. Changes in Nd/Nd*, Th and REE concentrations in apatite could be used as a proxy for the formation of monazite to quantify degree of metasomatism of apatite. Apatites with a higher alteration score contain lower Th concentrations, with respect to total REE concentrations consistent with the re-precipitation of monazite (Fig. 5.5). However only the most altered apatite grains (alteration score > 1) contain lower Nd anomalies. Classification of alteration by grain textures remains the best way to ensure least altered apatite composition.

These findings affect how magmatic apatite analyses will be interpreted in this study, with the understanding that the composition may no longer represent equilibrium composition within the melt at the time of its crystallisation, but lie along a mixing model with a hydrothermal endmember. Because of the variable effects of alteration on magmatic apatite compositions, from this point only magmatic apatites (microphenocrysts) with an alteration score of zero will be inferred to represent least-altered magmatic apatite. However caution must still be taken with As, Na, Pb, the most mobile of the elements, REE ratios may prove more reliable than individual concentration. Apatite is initially altered from the grain boundary with phases re-precipitated as overgrowths around apatite. This new growth, similar to the altered apatite, is pitted (Putnis 2009; Kusebauch et al. 2015). By analysing the apatite at the centre of the grain, and avoiding the most pitted areas, the most extreme changes in composition can be avoided.

5.3 Diffusion in apatite

Unlike metasomatism in apatite in which the compositional effects of are well studied, the

diffusion of elements in apatite in the porphyry environment is less well understood. In addition, whilst metasomatism can be easily accounted for when compared to textural changes in apatite, diffusion of elements may occur in apatites that are apparently unaltered apatite. In order to access the potential for post-crystallization changes in apatite, zircon-hosted apatite (Ap_{incl}) can be compared to apparently unaltered igneous apatite (Ap_{mtrx}). The premise being that the zircon host armours the apatite inclusions, preventing post-crystallization re-equilibration. Ap_{incl} and Ap_{mtrx} have been compared before in *unmineralised* plutonic rocks exhibiting a range of silica contents (Jennings et al. 2011; Braund et al. 2016). In these cases, the concentrations of Sr, Y and Ce were found to be equivalent in both types, suggesting that diffusional re-equilibration does not occur for these elements in systems with limited, super- or sub-solidus water flux.

5.3.1 Samples

In this study the trace element contents of in-situ microphenocrysts of apatite (Ap_{mtrx}) and apatite inclusions in zircon concentrates (Ap_{incl}) were analysed from four porphyry intrusions at La Granja. The porphyry intrusions were emplaced over a period of ~3.5 Myr and include DP_{PB} (17.58 ± 0.27 Ma), EDP_{PB} (15.06 ± 0.26 Ma), EDP_M (15.96 ± 0.27 Ma) and $LQP2_M$ (14.01 ± 0.20 Ma). At Mirador the late quartz porphyry is believed to be connected via a diatreme to a rhyodacite dome and is inferred to be one of the final intrusions at La Granja. The samples show moderate degrees of overprinting sericitic alteration, with sericitization of the plagioclase phenocrysts and replacement of primary amphibole by secondary biotite and subsequently chlorite (see Chapter 4 for more information).

5.3.2 Methods

All imaging and analyses were carried out in the Imaging and Analysis Centre at the Natural History Museum, London, UK. Ap_{incl} were analysed in resin-mounted zircon blocks and Ap_{mtrx} in polished thin sections. Both apatite types were identified using back-scattered electron imaging; apparently unaltered (alteration score < 1) igneous Ap_{mtrx} grains were selected based on observations of apatite texture and mineral

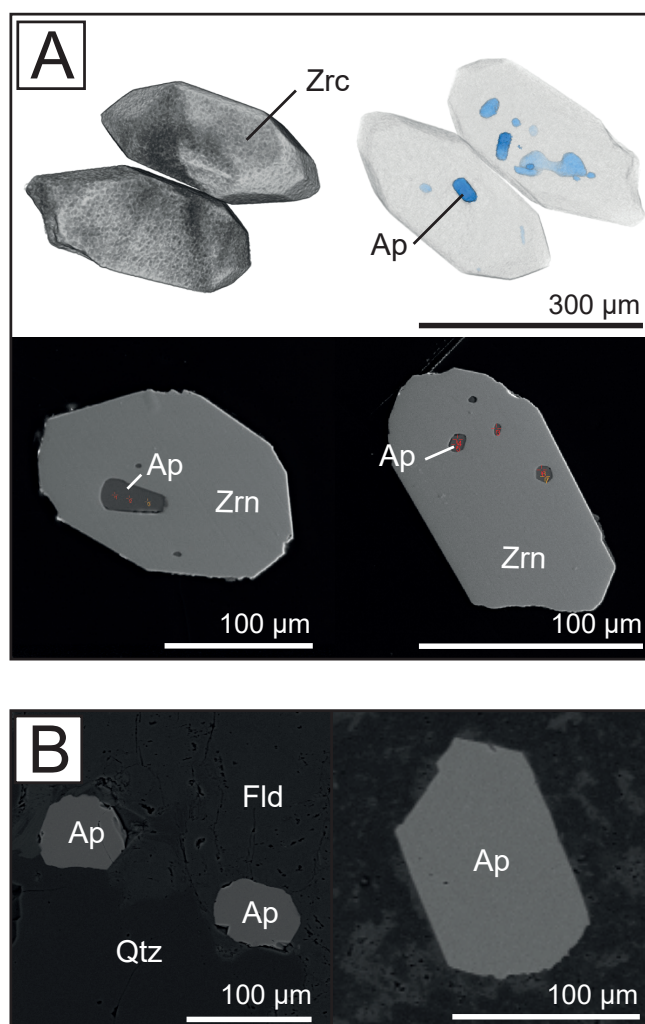


Figure 5.6 Textural comparison of A) zircon-hosted apatite inclusions (Ap_{incl}) and B) apatite microphenocrysts within the groundmass (Ap_{mtrx}). A) Nano CT image of zircon (left) showing inclusion phases within (right). Bottom: SEM-BSE images of mounted and polished zircon with Ap_{incl} . The apatite is typically elongate in shape pointing towards the centre of the zircon. B) SEM-BSE images of apatite microphenocrysts within the groundmass. Within Ap_{mtrx} are typically more equant in habit, subhedral to euhedral in shape. They show no obvious alteration features.

Table 5.1 Average composition of Durango apatite, data collected using a diffused beam (10µm). The results are compared to literature EPMA (Young et al. 1969; Marks et al. 2012). Elements whose EPMA results are used are indicated. The other elements are taken from LA-ICP-MS results.

Literature data*				This study			
				10 µm		1 µm	
Avg.	STD	Min	Max	Avg. (31)	STD	Avg. (13)	STD
P**		17.91	0.15			17.99	0.21
Na**		0.46	0.40			0.16	0.03
Si		0.14	0.03			0.10	0.08
Al		0.37	-			0.05	0.09
K		0.01	-			0.00	0.01
S**		0.15	0.06	0.1	0.21	0.14	0.02
Ca**		38.67	0.09			38.10	0.28
Mn		0.01	-			0.01	0.01
Fe**		0.05	0.00			0.04	0.01
Sr		0.055	0.01			0.09	0.11
La		-	-			0.36	0.10
Ce		-	-			0.49	0.12
Pr		-	-			0.03	0.02
Nd		-	-			0.10	0.03
F**		3.34	0.11	3.23	3.45	3.01	0.63
Cl**		0.46	0.08	0.39	0.51	0.52	0.58
Mg		0.01	-			0.01	0.04

*Literature data from Marks et al. (2012) for S, F, Cl, and Marks et al. (2012) and Young et al. (1969) for remaining elements.

** Element concentrations reported in this study are collected by EMPA.

Table 5.2 Trace element (ppm) analyses of Durango fluorapatite collected during Ap_{incl} and Ap_{mtr} analyses using the modified LA-ICP-MS operating conditions. Results are compared to solution ICP-MS literature data for Durango (Chew et al. 2016; Mao et al. 2016). Ca was used as the internal standard which was kept constant for both literature analyses (40 wt. %) and this study (37.12 wt. %; taken from average of EPMA of the same grain).

Durango STD0067							
	Mean of literature data (4)	2σ	LA-ICP-MS (12)	2σ	RSD	Min	Max
Mg	117	12	94	10	11	76	108
Mn	95	3	83	10	12	64	101
Sr	501	16	516	6	12	437	640
Y	746	164	851	112	13	752	1100
La	3952	197	3530	245	7	3084	4024
Ce	5007	529	4634	318	7	4002	5152
Pr	446	56	413	30	7	378	459
Nd	1631	137	1488	145	10	1317	1776
Sm	194	38	199	16	8	185	233
Eu	18	2	18	2	8	16	21
Gd	175	32	201	39	19	171	284
Tb	27	4	23	2	9	21	28
Dy	148	26	138	16	12	122	171
Ho	31	6	28	4	15	25	37
Er	80	16	78	11	14	66	98
Tm	10	2	9	1	13	8	12
Yb	45	9	50	8	16	40	66
Lu	6	1	6	1	18	5	8

association. Additional images of Ap_{incl} were collected by Nano computed tomography (CT) on an Xradia 520 Versa (90 kV, 8 W, 40 mm distance between sample and source).

The chemical composition of the apatite was acquired first using an electron microprobe (EPM) for major and minor elements (Ca, P, F, Cl, S, Na, Fe) followed by LA-ICP-MS for trace element concentrations (e.g. REE, Mg, Mn, Sr, Y). Due to the small size of Ap_{incl} (Fig. 5.6), modified EPMA (Cameca SX100, accelerating voltage 10 kV, beam current 10 nA, beam size 1 μ m) and LA-ICP-MS methods (3.5 J cm^{-2} , 10 Hz, 5 μ m spot size, external standard NIST610) for apatite analyses were adopted. The accuracy and precision of the data were monitored by regular analysis of Durango apatite (Young et al. 1969). To allow for direct comparison, the same analytical method was used for Ap_{mtrx} and Ap_{incl} .

The modified EPMA method is non-ideal for apatite analysis because a focused electron beam has been found to contribute towards artificially elevated F values (Stormer et al. 1993; Stock et al. 2016). The influence of this was monitored throughout data collection from the analysis of Durango apatite at both 1 μ m and a diffused 10 μ m spot size with reference to published Durango data (Marks et al. 2012; Table 5.1). In general, a diffused electron beam does result in lower halogen values but with lower precision of the results. Nonetheless, data collected using a 1 μ m spot were within error of the literature data, with the observed range being attributed largely to the heterogeneity of the apatite standard (Marks et al. 2012).

The reduced spot size of the laser limited the number of isotopes that could be measured accurately by mass spectrometry due to low counts. Measurements of Durango apatite collected during LA-ICP-MS analyses are compared to solution ICP-MS data on Durango (Chew et al. 2016; Mao et al. 2016). The results in the study were normalised to 37.12 wt. % Ca based of average EPMA on the same grain whilst the published analyses are normalised to 40 and 39.5 wt. % Ca based on stoichiometry. Despite this, overall the analyses collected using the modified laser operating conditions match results from the literature within error (Table 5.2). Marks et al. (2012) found that there could be significant heterogeneity in element concentration, particularly REE, within a single Durango grain (2σ of La: 23%, Y: 30%, Th: 24%, Sr: 770 μ g/g) which is consistent with the larger variations present in measured elements in this sample.

The detection limits and analytical precision for each element as measured by EPMA and

Table 5.3 Detection limit and analytical precision for modified EPMA and LA-ICP-MS methodology for Ap_{incl} analyses. The detection limits are calculated as 3σ of the measured background, an asterisk indicates that the detection limit falls below some measured values. The analytical precision, given to two standard deviations, is calculated as the mean of the standard deviations that are above detection limits.

	Detection limit	Analytical precision ($2\sigma^{an}$)
<i>EMPA (wt. %)</i>		
<i>P</i>	0.03	0.18
<i>Ca</i>	0.05	0.65
<i>Na</i>	0.08*	0.05
<i>Fe</i>	0.03*	0.02
<i>S</i>	0.02	0.02
<i>F</i>	0.16	0.18
<i>Cl</i>	0.05	0.06
<i>LA-ICP-MS (ppm)</i>		
<i>Na</i>	52*	422.7
<i>Mg</i>	33	44.8
<i>Mn</i>	30	162.3
<i>Fe</i>	390	864.7
<i>Sr</i>	2.1	76.1
<i>Y</i>	1.1	39.5
<i>La</i>	0.75	106.5
<i>Ce</i>	0.58	196.3
<i>Pr</i>	0.93	21.3
<i>Nd</i>	0.89	120.8
<i>Sm</i>	9.8	18.8
<i>Eu</i>	1.8	3.4
<i>Gd</i>	7	13.2
<i>Tb</i>	0.62	1.9
<i>Dy</i>	2.4	12.3
<i>Ho</i>	0.76	2.3
<i>Er</i>	8.1	8.3
<i>Tm</i>	0.71	1.4
<i>Yb</i>	3.8	11.1
<i>Lu</i>	2.2	2.0

LA-ICP-MS is given in table 5.3. The detection limit is 3σ of the measured background. The analytical precision is calculated as the mean of the standard deviation for each analysis above detection. Quantification of Na and Fe produce relatively large errors when analysed by LA-ICP-MS and concentrations in apatite lie close to detection limits for both methods.

5.3.3 Ap_{mtrx} and Ap_{incl} textures

Apatite is the most abundant inclusion type observed within the zircon grains. Nano-CT imaging demonstrates that Ap_{incl} typically occur as acicular or prismatic crystals $<10\ \mu m$ in diameter (Fig. 5.6A), but can occur as more equant crystals, up to $30\ \mu m$ in maximum dimension. U-Pb ages for the centre and rim of each zircon were determined and compared to ensure that no xenocrystic or antecrystic grains were used in the study. This ensures that all zircons, and therefore the included apatites, can be directly related to the host igneous rock.

Seemingly unaltered Ap_{mtrx} grains were selected from the groundmass of all samples.

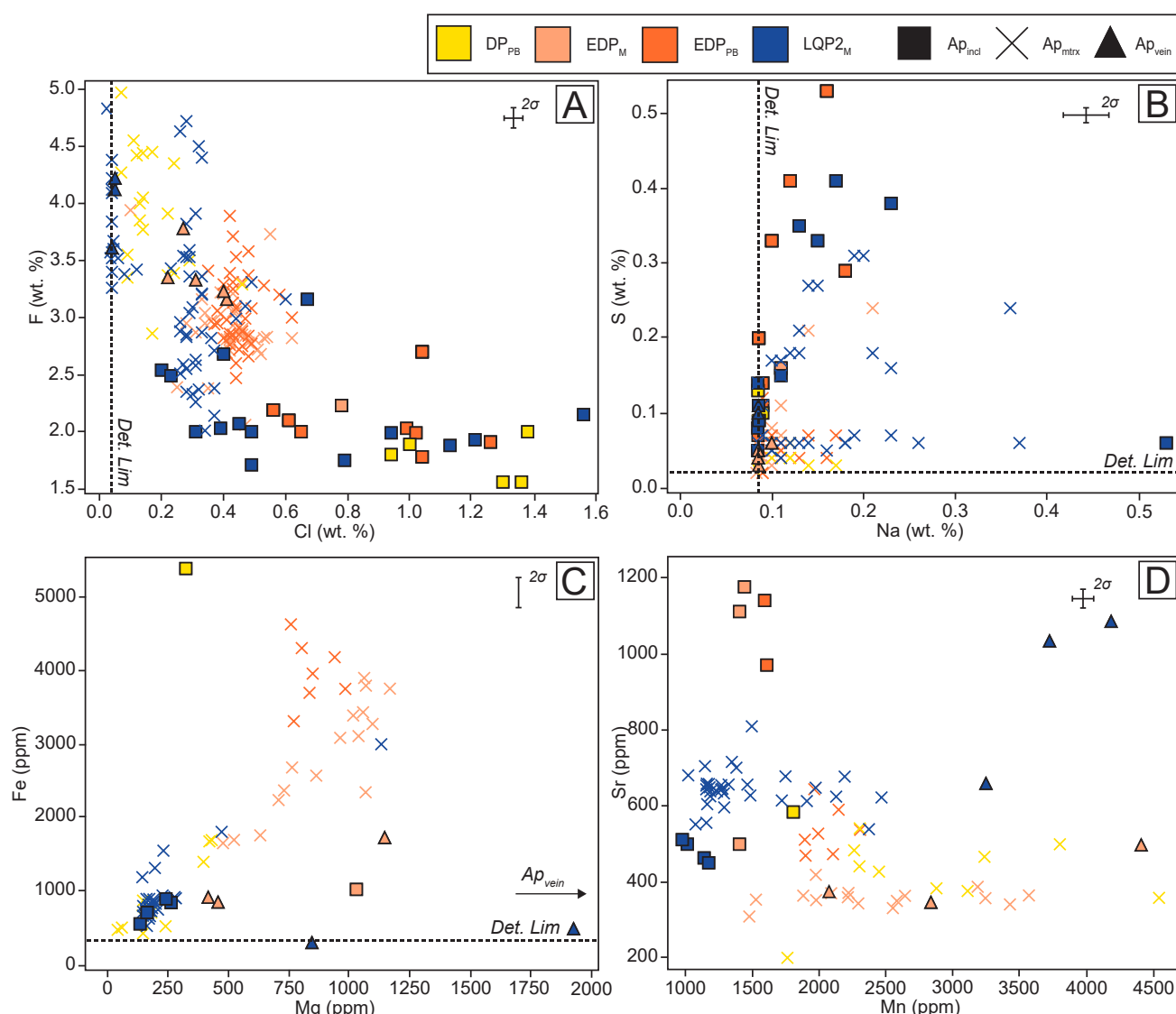


Figure 5.7 Comparison of Ap_{incl} (squares), Ap_{mtrx} (crosses) and Ap_{vein} (triangles) compositions by lithology. Average analytical error is given as two standard deviations where larger than the symbols. A) EPMA give lower Cl concentrations and B) lower S concentrations for Ap_{mtrx} compared to Ap_{incl} and correspond with Ap_{vein} . C) LA-ICP-MS analyses of Fe and Mg show positive correlation for Ap_{incl} and Ap_{mtrx} whilst Ap_{vein} lie off to the right side of the plot. D) Mn and Sr concentrations in Ap_{mtrx} trend towards Ap_{vein} compositions for the same samples.

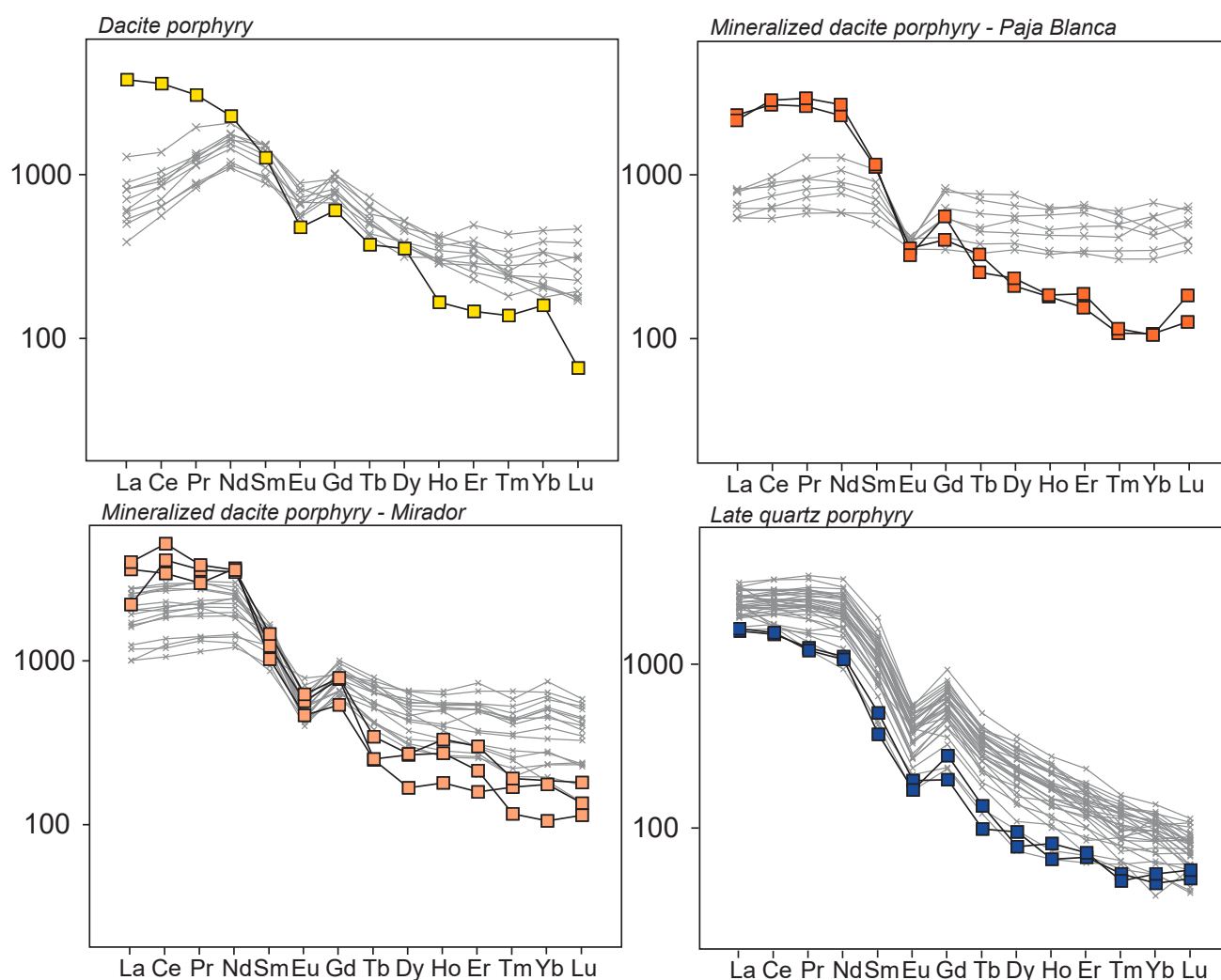


Figure 5.8 Chondrite normalised rare earth element pattern for Ap_{incl} (squares) and Ap_{mtrx} (crosses) by lithology (Sun & McDonough 1989). Analytical error on analyses is smaller than the symbol size.

Ap_{mtrx} range in size from 30 – 50 μm , are generally subhedral to euhedral, and present as micro-phenocrysts within the predominantly quartz-feldspar groundmass (Fig. 5.6B). Evidence for a lack of visible alteration includes homogeneous SEM backscattered electron images and homogeneous, high total REE content (Bouzari et al. 2016).

5.3.4 Results

Representative compositions are displayed in table 5.4. The magnitude of the relative enrichment/depletion of elements between Ap_{incl} and Ap_{mtrx} varies for each element and between lithologies. Both Ap_{incl} and Ap_{mtrx} from the porphyry intrusions are fluorapatite endmembers; Cl contents range from below the detection limit (0.03 wt. %) to 1.56 wt. % (Fig. 5.7A). Due to the small EPMA beam size required, over 10 % of analyses resulted in F values above the stoichiometric limit (3.76 wt. %), an unavoidable problem when carrying out in-situ analysis of F-rich apatite with a fine electron beam (Pyle et al. 2002). Both Cl and S concentrations in Ap_{incl} are generally elevated relative to Ap_{mtrx} (Fig. 5.7B), which cannot be attributed to beam-induced migration. The difference between Ap_{incl} and Ap_{mtrx} in terms of Cl and S concentrations is more distinct in the dacite porphyry and mineralised dacite porphyries in comparison to Ap_{incl} and Ap_{mtrx} from the late quartz porphyry. Concentrations of Na are comparable between

Table 5.4 Representative results for Ap_{incl} and Ap_{mtrx} analyses from EPMA and LA-ICP-MS analysis. Values in *italics* are below the limit of detection. Mole fractions of halogen calculated as $XF = F/3.767$, $XCl = Cl/6.809$, $XOH = 1 - XF - XCl$ (Piccoli and Candela 2002).

	Dacite porphyry (Paja Blanca)								Mineralised dacite porphyry (Mirador)							
	Ap(incl)				Ap(mtrx)				Ap(incl)				Ap(mtrx)			
	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev
wt. %	n=5				n=19				n=2				n=35			
P	17.67	18.07	17.84	0.17	16.24	18.7	17.84	0.84	18.07	18.07	18.07	0	17.24	18.83	18.54	0.28
Ca	36.71	37.56	37.25	0.36	35.06	38.78	37.39	1.17	37.67	37.67	37.67	0	37.38	38.91	38.49	0.38
Na	0.01	0.09	0.05	0.04	0	0.17	0.08	0.04	0.11	0.11	0.11	0	0.03	0.21	0.08	0.03
Fe	0.07	0.23	0.12	0.06	0.03	1.19	0.24	0.34	0.08	0.08	0.08	0	0.15	0.48	0.33	0.09
S	0.09	0.13	0.1	0.02	0	0.09	0.04	0.02	0.16	0.16	0.16	0	0.01	0.24	0.06	0.05
F	1.56	2	1.76	0.2	2.86	4.97	3.91	0.55	2.23	2.23	2.23	0	2.06	3.94	2.93	0.34
Cl	0.94	1.38	1.2	0.21	0.07	0.46	0.17	0.09	0.78	0.78	0.78	0	0.1	0.62	0.42	0.1
XF	0	0.53	0.39	0.2	0	1.32	0.68	0.52	0	0.59	0.3	0.34	0	1.05	0.51	0.38
XCl	0	0.2	0.15	0.08	0	0.07	0.02	0.02	0	0.11	0.06	0.07	0	0.09	0.04	0.03
XOH	0.27	1	0.46	0.27	-0.33	1	0.3	0.53	0.29	1	0.65	0.41	-0.07	1	0.45	0.41
ppm	n=1				n=10				n=2				n=18			
Mg	323	323	323	0	41	430	220	146	75	1028	552	674	477	1166	888	221
Mn	1808	1808	1808	0	1764	4544	2866	835	1405	1405	1405	0	1479	3571	2430	646
Sr	584	584	584	0	200	541	417	96	499	1112	806	433	309	418	358	24
Y	290	290	290	0	425	727	537	98	272	342	307	50	349	996	665	190
La	921	921	921	0	92	302	168	60	523	856	690	236	239	658	460	144
Ce	2254	2254	2254	0	342	833	521	146	2093	2522	2308	303	651	1819	1273	385
Pr	291	291	291	0	77	179	110	30	277	334	305	40	106	285	201	59
Nd	1066	1066	1066	0	499	937	695	142	1589	1677	1633	62	555	1375	967	258
Sm	192	192	192	0	130	224	182	36	152	183	167	22	129	248	195	34
Eu	28	28	28	0	31	50	39	7	26	32	29	4	23	40	29	5
Gd	124	124	124	0	133	201	166	24	108	154	131	33	119	201	154	26
Tb	14	14	14	0	15	26	20	3	9	9	9	0	14	29	21	5
Dy	90	90	90	0	77	128	102	17	42	66	54	17	71	163	118	32
Ho	9	9	9	0	16	23	19	3	10	15	12	4	12	36	25	7
Er	24	24	24	0	37	78	53	12	26	34	30	6	32	118	71	24
Tm	3	3	3	0	5	12	7	2	3	4	4	1	3	16	10	4
Yb	26	26	26	0	29	73	46	15	17	28	23	8	27	121	70	27
Lu	1.7	1.7	1.7	0	4.2	11.4	6.6	2.4	2.8	3.3	3.1	0.4	3.3	14.5	9.3	3.3
Ce/Ce*	0.7	0.7	0.7	0	0.6	0.7	0.6	0.04	0.2	0.4	0.3	0.1	0.4	0.6	0.5	0.1
Eu/Eu*	0.5	0.5	0.5	0	0.5	0.9	0.7	0.1	0.6	0.6	0.6	0.03	0.5	0.9	0.7	0.1
La/Yb	35	35	35	0	2	6	4	1	30	31	30	0.4	2	22	8	6
Sr/Y	2	2	2	0	0.3	1.3	0.8	0.3	1.8	3.3	2.5	1	0.3	1	0.6	0.2

Chapter 5: Metasomatism and diffusional re-equilibration of apatite in porphyry systems

	Mineralised dacite porphyry (Paja Blanca)								Late quartz porphyry							
	Ap(incl)				Ap(mtrx)				Ap(incl)				Ap(mtrx)			
	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev	Min	Max	Mean	Stdev
wt. %	n=16				n=37				n=6				n=56			
P	17.63	18.2	17.87	0.18	17.15	18.74	18.42	0.39	17.44	18.45	17.99	0.35	16.54	18.82	18.02	0.51
Ca	36.46	37.73	36.99	0.34	35.92	39.15	38.67	0.55	37.45	38.87	37.99	0.64	35.65	39.3	38.04	0.97
Na	0.04	0.18	0.11	0.05	0.01	0.17	0.07	0.04	0.01	0.15	0.05	0.05	0.01	0.37	0.11	0.08
Fe	0.09	0.46	0.2	0.13	0.28	0.6	0.35	0.06	0.06	0.21	0.12	0.07	0.02	0.83	0.12	0.11
S	0.07	0.53	0.28	0.14	0	0.12	0.04	0.03	0	0.33	0.11	0.11	0.02	0.31	0.09	0.07
F	1.78	2.7	2.14	0.3	2.47	3.89	3.05	0.32	1.93	3.16	2.49	0.43	2.01	4.83	3.29	0.69
Cl	0.56	1.26	0.87	0.26	0.35	0.62	0.45	0.05	0.2	1.56	0.71	0.56	0	0.6	0.24	0.14
XF	0	0.72	0.48	0.23	0	1.03	0.68	0.31	0	0.84	0.5	0.32	0	1.28	0.56	0.45
XCl	0	0.19	0.11	0.06	0	0.09	0.06	0.03	0	0.23	0.08	0.08	0	0.09	0.02	0.02
XOH	0.13	1	0.41	0.27	-0.09	1	0.27	0.33	0.06	1	0.43	0.36	-0.29	1	0.42	0.46
ppm	n=3				n=7				n=2				n=32			
Mg	188	569	425	206	757	982	847	85	134	163	148	21	143	1131	221	177
Mn	1443	1611	1549	92	1894	2308	2045	151	978	1016	997	27	1022	2468	1451	399
Sr	971	1177	1096	110	469	644	536	63	499	511	505	8	539	810	644	50
Y	287	381	326	49	430	884	643	166	122	129	125	5	110	383	235	65
La	523	949	678	236	130	194	162	28	376	389	383	9	377	733	554	88
Ce	1685	3177	2219	831	333	594	461	97	928	951	940	16	989	1981	1416	254
Pr	250	356	295	55	54	118	78	22	112	116	114	3	112	317	211	48
Nd	1079	1638	1324	285	269	582	395	113	487	507	497	14	420	1482	948	245
Sm	170	216	187	25	75	159	111	30	55	74	65	14	62	280	162	48
Eu	19	35	25	9	20	24	22	1	10	11	10	1	9	32	22	6
Gd	82	157	118	37	70	165	117	35	39	55	47	11	45	181	10	31
Tb	9	12	11	2	12	28	19	6	4	5	4	1	4	18	11	3
Dy	53	67	60	7	86	186	129	36	19	23	21	3	18	88	54	17
Ho	10	18	13	5	18	35	26	7	3	4	4	1	3	15	9	3
Er	26	48	35	12	53	105	79	21	11	11	11	1	10	36	21	6
Tm	3	5	3	1	8	15	11	3	1	1	1	1	1	4	3	1
Yb	18	18	18	1	50	109	77	21	7	8	8	1	6	22	15	4
Lu	3	5	4	1	9	16	12	3	1	1	1	1	1	3	2	1
Ce/Ce*	0.4	0.6	0.5	0.1	0.7	1.1	0.9	0.1	0.4	0.5	0.5	0.1	0.5	0.7	0.6	0.1
Eu/Eu*	0.4	0.6	0.5	0.1	0.4	0.8	0.6	0.2	0.5	0.6	0.6	0.1	0.4	0.8	0.5	0.1
La/Yb	30	32	31	1	1	3	2	1	46	51	48	3	23	77	40	12
Sr/Y	3.1	3.7	3.4	0.3	0.6	1.2	0.9	0.3	3.9	4.2	4	0.2	1.7	5.1	3	0.9

Ap_{incl} and Ap_{mtrx} of all lithologies however many analyses are below detection limit (Fig. 5.7B).

The Mg content of apatite varies between lithologies and increases with Fe concentrations in apatite ($R^2 = 0.81$ for Ap_{mtrx}). Mg concentrations are comparable between Ap_{incl} and Ap_{mtrx} from the same host rock where as concentrations of Fe are typically higher in Ap_{mtrx} (Fig. 5.7C). Concentrations of Mn are generally lower in Ap_{incl} relative to Ap_{mtrx} . Conversely, concentrations of Sr are higher in Ap_{incl} than in Ap_{mtrx} (Fig. 5.6D). These differences are again less marked between Ap_{incl} and Ap_{mtrx} in the late quartz porphyry.

Chondrite-normalized REE patterns (Sun & McDonough 1989) show typical I-type magmatic features for both Ap_{incl} and Ap_{mtrx} (Fig. 5.8), with enrichment in LREE relative to HREE and negative Eu anomalies. Ap_{incl} from the mineralised dacite porphyries are significantly more enriched in LREE and depleted in HREE compared with Ap_{mtrx} from the same samples which have a flatter REE profile (mean La/Yb of 30 compared to 2 and 8). By contrast, Ap_{incl} from the late quartz porphyry display similar REE patterns to Ap_{mtrx} (e.g., mean La/Yb of 48 and 40 respectively; Table 5.4).

5.3.5 Evidence for diffusional re-equilibration

The data show distinct differences in composition between Ap_{incl} and Ap_{mtrx} for Cl, S, Mn, Sr, Fe and REE (Table 5.4). Cl, Mn, Sr and REE are known to be mobile in apatite during hydrothermal alteration (Harlov 2015; Bouzari et al. 2016; Kusebauch et al. 2015) and have comparatively high diffusion rates (Cherniak 2010). Given this, and the similarity of Ap_{mtrx} and Ap_{incl} compositions in the less-altered, post-mineralisation, late quartz porphyry, the difference in some elements could be the result of re-equilibration occurring in response to exposure to super- or subsolidus hydrothermal fluids. Alternatively differences may be the result of melt differentiation between Ap_{incl} and Ap_{mtrx} . This hypothesis can be tested by comparing

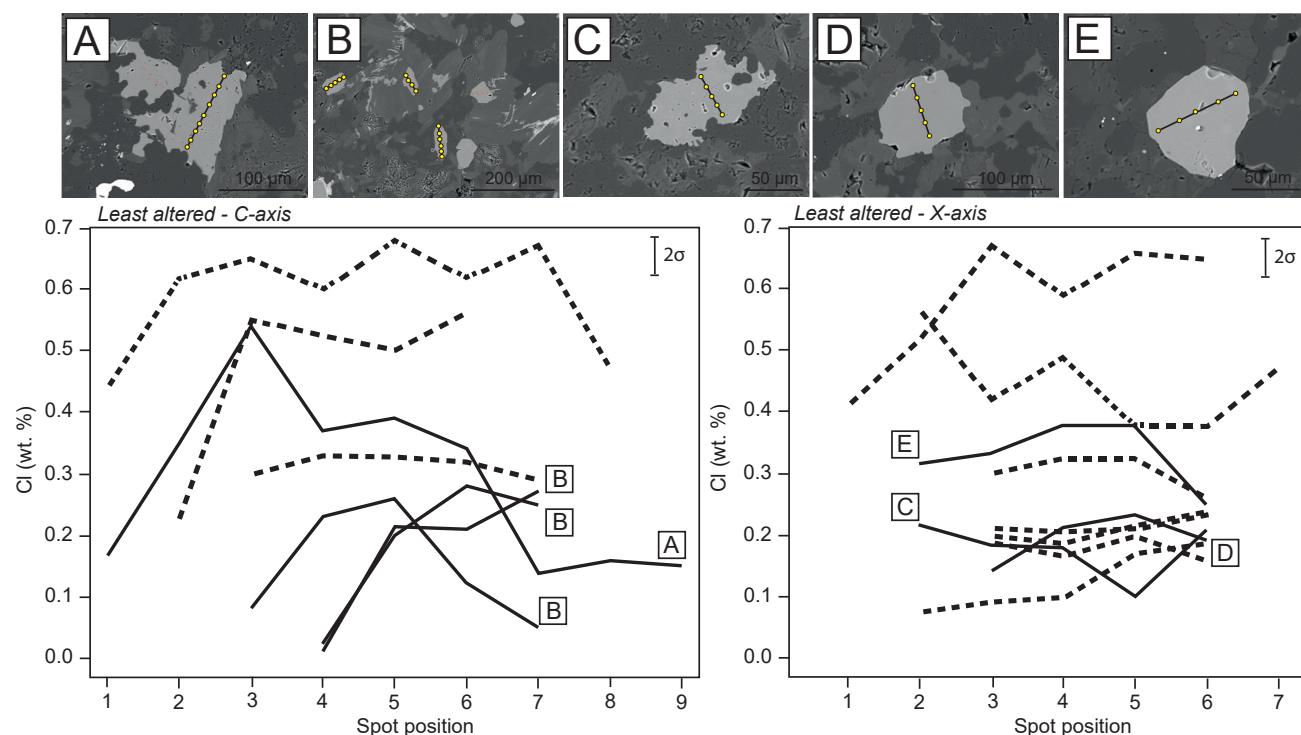


Figure 5.9 Diffusion profiles of Cl in least altered Ap_{mtrx} . A) Traverses parallel to the c-axis show low Cl rims. B) Traverses in other directions show no consistent decrease in Cl concentration.

the compositions of Ap_{mtrx} with demonstrably hydrothermal apatites (Ap_{vein}), evidenced by their intergrowth with hydrothermal phases in ore-stage veins, present in EDP_M and $LQP2_M$.

Ap_{mtrx} compositions for Cl, S, Sr and Mn spread between Ap_{incl} and Ap_{vein} and support hydrothermal modification (Fig. 5.7). S and Cl concentration in apatites from the porphyritic matrix of the same samples have been compositionally modified during post-crystallisation diffusional re-equilibration with later hydrothermal fluids. This process does not necessarily leave a distinct textural record in apatite morphology or SEM backscattered electron response. Additionally lower Cl concentrations in the rim of Ap_{mtrx} parallel to the C-axis support diffusion rather than original compositional zoning. Cl can diffuse up to 3 orders of magnitudes faster parallel to the C-axis in apatite compared to other orientations (Cherniak 2010). Unaltered Ap_{mtrx} show a drop in Cl concentrations across traverses of the grains parallel to the C-axis, but no apparent change in other orientations (Fig. 5.9). The diffusion of cations in apatite do not share the same crystallographic controls (Cherniak 2010).

Strontium is the fastest diffusion cation in apatite after Pb. The change in Sr concentration Ap_{mtrx} and Ap_{incl} is not consistent with melt evolution; the direction of change is not consistent between lithologies. However the trajectory of Ap_{mtrx} trends towards that of Ap_{vein} of the same sample consistent with variable degrees of re-equilibration with different fluid compositions (Fig. 5.7D). However concentrations of Fe in Ap_{mtrx} and Ap_{incl} lie along a trend with Mg independent from Ap_{vein} . Differences in REE between Ap_{mtrx} and Ap_{incl} also do not correspond with fluid re-equilibration were a decrease in total REE would be expected (Fig. 5.2). As REE are tetravalent cations, diffusion is restricted by the available exchange reactions (Hughes et al. 1991) In addition for diffusion rates approaching that of Sr temperatures in excess of those prevalent under hydrothermal conditions (Cherniak 2000). Instead the similarity of REE profile between Ap_{mtrx} of the same lithology suggests a melt control which relative HREE depletion and LREE enrichment the result of co-crystallising HREE-phases.

5.4 Conclusions

- Apatite inclusions in zircon preserve primary records of magmatic evolution in porphyry systems where as Ap_{mtrx} are susceptible to metasomatism and diffusion of elements.
- Metasomatism of apatite can produce changes in both texture and composition with a higher degree of alteration produces larger response in both.
- Concentrations of Cl, Na, Pb, As and REE show the largest change with metasomatism and are typically depleted with alteration, apart from As. The LREE are more mobile than HREE in apatite. Variation in other cations such as Mn, Sr, Fe are less consistent and we proposed depend on the alerting fluid composition.
- Concentrations of Cl and S in Ap_{mtrx} should not be assumed to reflect crystallisation compositions. Concentrations of Sr and Mn may also be prone to lesser amounts of diffusion and should also be used with caution when inferring magmatic compositions in least altered Ap_{mtrx} .
- Analyses of Ap_{incl} using a modified analytical methodology provide a useful way of accurately determining preserved S and Cl concentrations in magmatic apatite.

Chapter 6: Magmatic apatite at La Granja

6.1 Introduction

In this chapter the textural occurrence and composition of magmatic apatite from the porphyry units and igneous host rocks at La Granja are described. The composition of magmatic apatite is a function of the melt from which it crystallised and the apatite-melt partitioning coefficients. The partitioning behaviour of elements into apatite varies with the magmatic conditions (e.g. pressure, temperature, oxygen fugacity) and the melt composition (Pan & Fleet 2002). As a result magmatic apatite composition can capture upper crustal conditions and magmatic processes, but may also retain geochemical signatures in the melt that are inherited from deeper crustal processes. Therefore differences between apatite from the unmineralised Eocene host rocks and the porphyry units may reflect melt conditions that control arc segment fertility. Changes in apatite composition within units can be used to track individual melt evolution and the differences between subsequent porphyry intrusions can be related to the broader development of the deposit. In particular, the differences between more and less mineralised intrusions and the causes of the end of porphyry systems will be investigated. Further to contributing to the wider understanding of fertile arc and porphyry deposit formation, results from this chapter will be used to develop magmatic discrimination tools for porphyry exploration in *Chapter 9*.

6.2 Magmatic apatite textures, occurrence and classification

Magmatic grains are typically more euhedral in shape and larger than hydrothermal apatite. The size of the magmatic grains varies with the grain size of the host rock, but the maximum dimension is typically >50 μm for micro-phenocrysts. When present as inclusions within other phases, apatite grains can be <5 μm in diameter. As the grains for analysis were selected by eye, there could be a selection bias in this study towards coarser micro-phenocrysts, limiting the number of analyses on smaller, late-crystallising apatite.

Based on the conclusions of *Chapter 5*, only least-altered magmatic apatites (alteration score <1) were selected to remove the effects of metasomatism on composition. Just over 50 % of magmatic apatites identified in these samples were classed as unaltered. However, an alteration score of 0 does not mean that the apatite has necessarily retained its original magmatic composition. Therefore, in addition apatite inclusions in zircons are also used in this study.

Apatite within the groundmass (Ap_{mtrx})

Apatites within the groundmass of the samples, or Ap_{mtrx} , are the most abundant and are observed in all lithologies. They are most commonly present as micro-phenocrysts and grains are typically subhedral or euhedral and range from 15 – 250 μm in length (Fig. 6.1A-C). As they are found within the groundmass they are most commonly associated with quartz, feldspar and biotite. Inclusions of quartz, feldspar and biotite can be present however are not common (Fig. 6.1C). Euhedral grains are less common in lithologies with a fine groundmass such as LQP and LDP, although this may perhaps be due to size bias. Here grains are more

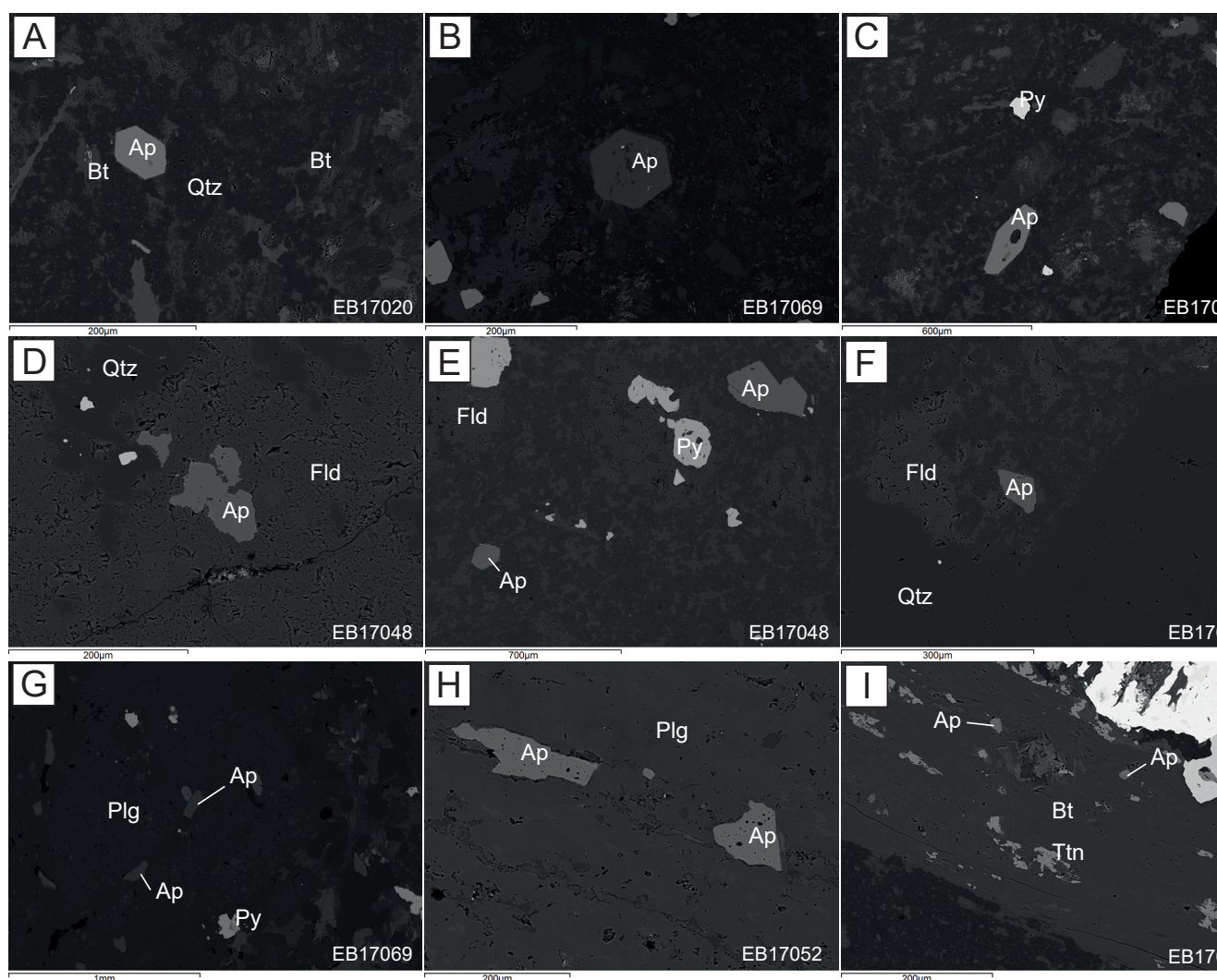


Figure 6.1 Scanning electron microscope backscattered electron (BSE) images of igneous apatite at La Granja. A) Euhedral apatite (Ap) micro-phenocryst in quartz (Qtz), feldspar and biotite (Bt) groundmass. B) micro-phenocryst of apatite with inclusions of quartz. C) Apatite in groundmass with inclusions of quartz. D) Fine irregular apatite inter-grown with the groundmass. E-F) Subhedral apatite in a fine matrix. G) Fine apatite within plagioclase (Plg); grains are irregular in size and orientated with growth directions. H) Irregular apatite inclusions within plagioclase. I) Apatite inclusions within biotite associated with titanite (Ttn) and pyrite (Py).

irregular shape, finer and often closely interlocked with the groundmass material (Fig. 6.1E-F).

Apatite inclusions in plagioclase

Plagioclase is abundant in all samples; however, the majority of plagioclase phenocrysts are altered so, like apatite inclusions in biotite, potentially analysable inclusions in plagioclase are limited to less-altered samples. The apatite forms fine grains that are more irregular in shape than the other magmatic apatites (Fig. 6.1G-H). The grains tend to be slightly rounded and are aligned within concentric zones in the plagioclase. Again, these grains were commonly too small to be analysed, at least by LA-ICP-MS.

Apatite inclusions in biotite

Apatite inclusions within phenocrysts of primary biotite are not very abundant. Furthermore, it is uncommon for primary biotite to survive alteration and, therefore, these apatites are only present in less-altered samples. The grains are small, frequently < 20 µm, and occur as short laths or more elongate crystals (Fig. 6.1I). The long axes of the grains are aligned with the biotite cleavage

and the short edge is often ragged. The small size of these grains means that they frequently impossible to analyse.

Apatite inclusions in zircon (Ap_{incl})

Apatite inclusions in zircon (Ap_{incl} ; Fig. 6.2) are described in section 5.2.2. These were analysed from zircon concentrates mounted in resin blocks. Each zircon may contain 1 - 2 grains of apatite and the zircon host was polished to the right depth in order to expose the inclusion. Due to the extra analytical steps involved, there are limited numbers of analyses for these apatites. However, these inclusions

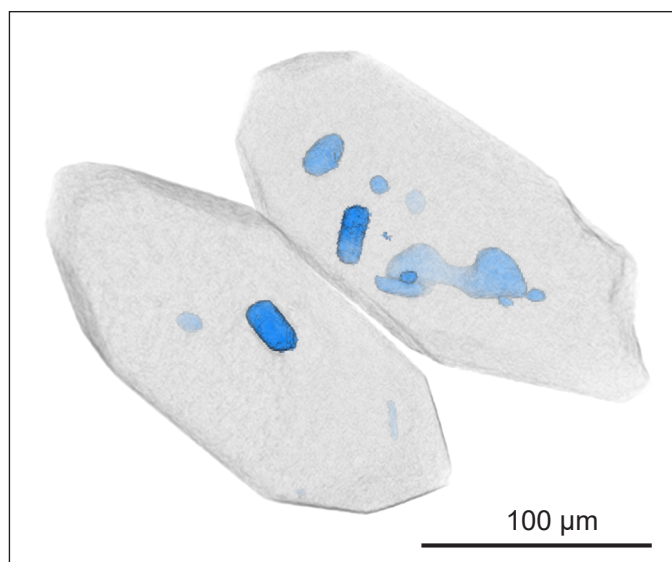


Figure 6.2 Nano CT scan of zircon grains. Inclusions are highlighted in blue. Spherical and lobate inclusions are likely to be melt inclusions, and the more elongated crystals are apatite.

are particularly useful they are inferred to be free from the effects of overprinting by later fluids (see Chapter 5). Ap_{incl} from the porphyry units EDP_M , EDP_{PB} , DP_M , $LQP2_M$ and LDP_{PB} were analysed by electron probe for halogen and S concentrations. Ap_{incl} from the EQP_{PB} , EDP_{PB} , EDP_M , DP_{PB} , LQP_{PB} , $LQP1_M$, $LQP2_M$, LDP_{PB} units were analysed by LA-ICP-MS for REE and other trace elements. In addition, Ap_{incl} from the Eocene GRANO and DIO host rocks were also analysed.

6.3 Magmatic apatite composition

Major and trace-element compositions of Ap_{incl} were analysed according to the method described in Chapter 5. The other apatite types were analysed by the electron probe and LA-ICP-MS as described in Chapter 3. Due to the low numbers of apatite inclusions in biotite and plagioclase, these data are combined with those from the apatite micro-phenocrysts for the purposes of reporting (Ap_{mtrx}). A table of results by sample are included in the *digital appendices*.

6.3.1 Least altered apatite microphenocrysts

Representative compositions of least altered magmatic apatites by lithology are given in tables 6.1 and 6.2. Analyses of Cl and S should not be inferred to represent original magmatic compositions as they have been shown to decrease during re-equilibration, while analyses of Sr and Mn should be used with caution (see Chapter 5).

F-Cl-OH endmembers

X_F , X_{Cl} and X_{OH} are used to describe the mole fractions of fluorapatite, chlorapatite and hydroxyapatite end-members of the analysed apatites. The relative proportions of these components were calculated from F and Cl concentrations determined by EPMA using the method suggested by Piccoli & Candela (2002):

$$X_F^{Ap} = C_F^{Ap} / 3.767 \quad \text{Eq. 6.1}$$

$$X_{Cl}^{Ap} = C_{Cl}^{Ap} / 6.809 \quad \text{Eq. 6.2}$$

Here C_i^{AP} is the concentration of i in apatite. As OH was not obtained from probe analysis, XOH can only be estimated assuming total occupancy of the halogen site by F, Cl and OH.

$$X_{OH}^{Ap} = 1 - X_F^{Ap} - X_{Cl}^{Ap} \quad \text{Eq. 6.3}$$

This assumption contradicts observations of fluorine migration and diffusion in Chapter 3, which demonstrate the presence of vacancies. These calculations will also result in high XF/XOH and XF/XCl ratios for F-rich apatites where F is measured over the stoichiometric limit. The effect of these assumptions will be considered in later sections.

Almost all apatites in this study are fluorapatite, $XF > 0.5$. Measured concentrations of F approach, and in some cases exceed, the stoichiometric limit in apatite (3.76 wt. %; Pyle et al. 2002). Generally, apatites from the host rock units have higher Cl compared to magmatic apatite from porphyry-related intrusions (Table 6.1). However due to the effects of diffusion, the Cl concentrations of apatite may have decreased from the time of crystallisation.

Sulfur

The range of sulfur concentrations in magmatic apatite is small (< 0.2 wt. %) and many analyses are below the detection limit (~ 0.02 wt. %). Host rock apatites tend to contain less S than apatites from the Miocene lithologies with the exception of those from the DIOP and EQP_{PB} which also exhibit low S. As with halogen concentrations, S in apatite microphenocrysts is prone to diffusion and should not be used to infer melt compositions.

Iron and magnesium

Iron and magnesium concentrations determined by EPMA are close to detection limits (Table 6.1). Analyses by LA-ICP-MS reveal an increase in both elements with time in porphyry-related intrusions up to the late porphyries at which point both decrease in concentration, Fe markedly so (Fig. 6.3).

Sodium and manganese

Sodium concentrations are mostly below EPMA detection limits so were also collected by LA-ICP-MS. Host rock and DIOP apatites display the lowest concentrations of Na and Mn (Fig. 6.3). Both are significantly elevated in the earlier porphyry intrusions relative to the Eocene units and decrease in apatites from later porphyry intrusions.

Strontium and yttrium

Strontium and yttrium are both low in apatite from the host rock and DIOP. The porphyry-related apatites are significantly enriched in Sr with the exception of the EQP_{PB}, and Sr broadly increases through the emplacement sequence. By contrast, Y is highest in apatites from EQP_{PB} and decreases in concentration in apatites from the later intrusions (Fig. 6.3)

Lead and uranium

Concentrations of Pb and U are all present at relatively low concentrations (mostly < 50 ppm). Uranium concentration is low in the host rock samples, the DIOP and the late quartz porphyries but is significantly elevated in the other porphyry units (Fig. 6.3).

Table 6.1 Representative composition of least altered (alteration score < 1) magmatic apatite from EMP analyses by lithology for number of analyses (n). The minimum (Min.), maximum (Max.) of results for each lithology is given as well as the calculated mean and associated standard deviation (Sd.) of results for each lithology are given. Calculations of mole fractions of halogens are described in the text (Piccoli & Candela 2002). Values in *italics* are below detection limits (see Chapter 3).

	AND (n = 15)				DIO (n = 21)				GRANO (n = 7)				EQP _M (n = 18)				DP _{PB} (n = 15)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
<i>wt. %</i>																				
Ca	38.42	39.83	39.13	0.58	37.75	39.49	38.45	0.36	37.69	39.26	38.58	0.53	38.45	39.35	38.98	0.20	38.60	39.43	38.90	0.26
P	18.18	18.65	18.45	0.11	18.29	18.98	18.69	0.18	18.55	19.09	18.87	0.19	18.66	19.03	18.84	0.10	18.85	19.21	19.01	0.12
Fe	0.07	0.31	0.13	0.07	0.06	0.32	0.17	0.07	0.07	0.80	0.35	0.24	0.05	0.21	0.13	0.05	0.07	0.32	0.16	0.07
Mg	0.01	0.24	0.04	0.07	0.01	0.23	0.05	0.08	0.01	0.30	0.06	0.11	0.01	0.03	0.02	0.01	0.01	0.06	0.02	0.01
Mn	0.02	0.12	0.05	0.03	0.12	0.21	0.15	0.02	0.03	0.32	0.20	0.11	0.24	0.55	0.35	0.10	0.18	0.37	0.28	0.06
Na	0.01	0.06	0.03	0.02	0.01	0.04	0.02	0.01	0.01	0.03	0.02	0.01	0.03	0.12	0.07	0.03	0.01	0.17	0.09	0.04
Al	0.01	0.19	0.04	0.06	0.01	0.13	0.04	0.05	0.01	0.28	0.06	0.11	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00
S	0.01	0.03	0.02	0.01	0.01	0.01	0.01	0.00	0.01	0.03	0.02	0.01	0.01	0.04	0.02	0.01	0.01	0.07	0.04	0.02
Si	0.01	0.42	0.10	0.11	0.02	0.38	0.11	0.10	0.02	0.49	0.10	0.17	0.01	0.09	0.04	0.02	0.01	0.08	0.03	0.02
Sr	0.01	0.05	0.02	0.01	0.01	0.05	0.03	0.01	0.01	0.04	0.02	0.02	0.01	0.05	0.02	0.01	0.01	0.07	0.05	0.02
Y	0.01	0.11	0.08	0.03	0.01	0.10	0.05	0.02	0.02	0.11	0.06	0.03	0.09	0.23	0.14	0.04	0.06	0.12	0.08	0.02
F	1.77	3.32	2.47	0.52	1.78	3.40	2.54	0.33	3.21	3.76	3.52	0.19	3.12	3.58	3.38	0.15	3.26	4.00	3.51	0.20
Cl	0.18	1.33	0.78	0.26	0.30	1.14	0.76	0.17	0.16	0.32	0.23	0.06	0.17	0.39	0.26	0.07	0.19	0.40	0.28	0.06
O	39.19	40.11	39.71	0.31	39.31	40.13	39.80	0.23	40.01	40.34	40.16	0.13	39.96	40.37	40.20	0.14	40.21	40.67	40.41	0.15
Total	100.16	101.61	101.05	0.48	100.27	101.71	101.01	0.43	101.96	102.44	102.25	0.17	102.01	103.11	102.58	0.32	102.35	103.64	103.07	0.35
O=F	0.03	0.13	0.05	0.03	0.03	0.13	0.07	0.03	0.03	0.34	0.15	0.10	0.02	0.09	0.06	0.02	0.03	0.13	0.07	0.03
O=Cl	0.04	0.29	0.17	0.06	0.07	0.25	0.17	0.04	0.04	0.07	0.05	0.01	0.04	0.09	0.06	0.01	0.04	0.09	0.06	0.01
Corrected total	100.09	101.19	100.82	0.39	100.18	101.32	100.77	0.36	101.90	102.03	102.05	0.06	101.95	102.94	102.46	0.28	102.28	103.42	102.94	0.31
XF	0.47	0.88	0.66	0.14	0.47	0.90	0.68	0.09	0.85	1.00	0.94	0.05	0.83	0.95	0.90	0.04	0.87	1.06	0.93	0.05
XCl	0.03	0.20	0.12	0.04	0.04	0.17	0.11	0.03	0.02	0.05	0.03	0.01	0.02	0.06	0.04	0.01	0.03	0.06	0.04	0.01
XOH	0.04	0.38	0.23	0.13	0.05	0.42	0.21	0.07	0.00	0.12	0.03	0.05	0.00	0.12	0.06	0.04	0.00	0.09	0.03	0.05

Table 6.1 (cont.)

	EDP _M (n = 18)				EDP _{Fe} (n = 18)				DIOP (n = 58)				LQP1 _M (n = 11)				LQP2 _M (n = 33)				LDP (n = 16)			
	Min	Max	Mean	Sd	Min	Max	Mean	Sd	Min	Max	Mean	Sd	Min	Max	Mean	Sd	Min	Max	Mean	Sd	Min	Max	Mean	Sd
wt. %																								
Ca	38.55	39.41	39.03	0.22	38.02	38.73	38.37	0.22	38.67	39.91	39.38	0.33	37.77	39.08	38.60	0.38	38.23	39.34	38.79	0.23	38.30	39.56	39.19	0.34
P	18.14	18.72	18.45	0.20	18.68	18.91	18.81	0.06	18.05	19.17	18.65	0.23	18.63	19.21	18.96	0.18	18.08	19.05	18.60	0.24	18.65	19.17	18.93	0.15
Fe	0.23	0.46	0.35	0.05	0.14	0.46	0.31	0.11	0.03	0.30	0.10	0.06	0.01	0.15	0.07	0.04	0.06	0.30	0.10	0.05	0.07	0.98	0.29	0.23
Mg	0.06	0.12	0.08	0.01	0.03	0.16	0.10	0.04	0.01	0.20	0.02	0.03	0.01	0.02	0.01	0.01	0.01	0.07	0.02	0.01	0.01	0.34	0.05	0.08
Mn	0.15	0.28	0.22	0.03	0.18	0.47	0.29	0.10	0.04	0.18	0.10	0.03	0.04	0.43	0.13	0.11	0.10	0.42	0.19	0.11	0.07	0.13	0.10	0.02
Na	0.03	0.15	0.07	0.03	0.03	0.12	0.07	0.02	0.01	0.12	0.02	0.02	0.01	0.13	0.05	0.04	0.01	0.12	0.05	0.03	0.01	0.10	0.05	0.03
Al	0.01	0.04	0.01	0.01	0.01	0.16	0.02	0.04	0.01	0.75	0.09	0.17	0.01	0.23	0.05	0.09	0.01	0.28	0.02	0.05	0.01	0.33	0.05	0.11
S	0.01	0.07	0.03	0.02	0.02	0.12	0.06	0.03	0.01	0.02	0.01	0.00	0.01	0.19	0.07	0.06	0.03	0.15	0.06	0.03	0.01	0.14	0.06	0.04
Si	0.01	0.08	0.04	0.02	0.01	0.24	0.06	0.06	0.01	0.41	0.07	0.07	0.01	0.26	0.07	0.08	0.03	0.46	0.09	0.08	0.02	0.37	0.08	0.08
Sr	0.02	0.07	0.04	0.01	0.02	0.09	0.05	0.02	0.01	0.05	0.02	0.01	0.01	0.10	0.04	0.03	0.03	0.14	0.07	0.02	0.01	0.13	0.05	0.03
Y	0.03	0.15	0.08	0.03	0.02	0.09	0.05	0.02	0.01	0.07	0.03	0.02	0.01	0.04	0.03	0.01	0.01	0.04	0.02	0.01	0.01	0.29	0.06	0.07
F	2.38	2.83	2.61	0.11	2.98	3.84	3.32	0.23	2.09	3.99	2.67	0.46	2.73	4.57	3.92	0.65	2.39	3.85	2.90	0.36	3.73	4.55	4.16	0.27
Cl	0.22	0.54	0.47	0.07	0.18	0.64	0.43	0.15	0.06	0.69	0.44	0.15	0.01	0.49	0.16	0.18	0.27	0.59	0.37	0.08	0.02	0.22	0.08	0.06
O	39.34	40.19	39.80	0.25	39.86	40.36	40.08	0.13	39.26	40.55	40.02	0.25	39.91	40.41	40.18	0.15	39.18	40.36	39.89	0.32	40.17	40.77	40.50	0.17
Total	100.79	102.07	101.45	0.45	101.83	102.83	102.20	0.29	99.72	103.12	101.59	0.67	100.79	103.30	102.35	0.79	99.65	102.94	101.41	0.80	103.17	104.44	103.74	0.31
O=F	0.10	0.19	0.15	0.02	0.06	0.19	0.13	0.05	0.01	0.13	0.04	0.03	0.00	0.06	0.03	0.02	0.03	0.13	0.04	0.02	0.03	0.41	0.12	0.10
O=Cl	0.05	0.12	0.10	0.02	0.04	0.14	0.09	0.03	0.01	0.15	0.10	0.03	0.00	0.11	0.04	0.04	0.06	0.13	0.08	0.02	0.00	0.05	0.02	0.01
Corrected total	100.64	101.76	101.20	0.41	101.73	102.50	101.98	0.22	99.69	102.84	101.45	0.61	100.78	103.13	102.29	0.73	99.57	102.88	101.29	0.76	103.14	103.98	103.60	0.20
XF	0.63	0.75	0.69	0.03	0.79	1.02	0.88	0.06	0.55	1.06	0.71	0.12	0.72	1.21	1.01	0.18	0.63	1.02	0.77	0.09	0.99	1.21	1.10	0.07
XCl	0.03	0.08	0.07	0.01	0.03	0.09	0.06	0.02	0.01	0.10	0.06	0.02	0.00	0.07	0.02	0.03	0.04	0.09	0.05	0.01	0.00	0.03	0.01	0.01
XOH	0.17	0.31	0.24	0.03	0.00	0.12	0.06	0.05	0.00	0.36	0.23	0.11	0.00	0.23	-0.03	0.16	0.00	0.32	0.18	0.10	0.00	0.00	-0.12	0.07

Table 6.2 Representative compositions of least altered (alteration score < 1) magmatic apatite from LA-ICP-MS analyses by lithology for number of analyses (n). The minimum (Min.) and maximum (Max.) of results for each lithology is given as well as the calculated mean and associated standard deviation (Sd.). Values in italics are below detection limits (see Chapter 3).

(ppm)	AND (n = 9)				DIO (n = 5)				GRANO (n = 6)				DP _{PB} (n = 7)				EQP _{PB} (n = 7)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Na	264.2	4522.4	1566.7	1379.0	22.4	507.3	230.8	180.3	44.8	518.2	195.1	188.2	812.8	1491.9	1181.2	215.0	546.3	1061.0	940.5	182.8
Mg	121.5	5946.1	1547.1	1991.0	521.5	4740.5	2861.0	1923.3	19.8	197.3	71.5	68.0	249.1	405.0	334.5	60.3	106.4	329.1	188.5	96.8
V	4.1	39.5	17.1	12.0	1.7	55.5	24.1	20.3	5.2	59.0	24.4	24.7	4.4	7.6	6.1	1.1	1.5	2.2	2.0	0.2
Mn	329.1	1165.1	603.3	344.8	1374.8	2691.7	1679.6	568.9	217.8	736.9	478.5	240.5	2450.2	3825.5	2906.8	512.1	1865.2	4873.1	3280.1	1353.4
Fe	335.8	6147.4	1834.5	1961.7	492.7	2775.1	1742.8	994.6	113.0	259.2	187.8	74.5	695.5	1022.2	826.9	135.1	435.1	867.5	601.2	185.8
Sr	94.5	224.9	178.7	37.9	58.1	291.9	211.2	90.8	102.4	434.0	221.8	125.7	402.6	465.8	433.7	23.2	109.2	195.3	158.0	29.9
Y	150.4	663.8	378.3	207.7	120.1	669.7	522.2	229.4	62.6	830.7	273.1	302.7	671.3	1091.6	874.3	136.3	882.3	2081.3	1444.1	511.9
La	84.3	186.8	154.3	29.0	88.2	614.4	412.5	208.7	34.5	371.2	154.6	152.1	248.2	919.5	592.3	210.3	112.3	347.2	196.7	106.3
Ce	191.7	489.2	387.2	87.0	183.3	1547.2	1052.0	540.5	73.5	1046.7	390.1	430.9	994.0	2852.5	1914.7	597.7	432.9	1000.0	687.7	242.9
Pr	25.6	71.7	55.4	16.3	26.8	198.2	137.9	68.3	8.9	138.7	46.8	54.7	145.3	422.9	283.7	84.3	78.1	142.6	110.1	28.2
Nd	126.2	381.5	279.6	100.0	131.2	879.2	627.9	297.4	40.5	629.7	203.2	242.7	586.2	1747.4	1210.6	338.9	401.2	698.1	564.0	139.5
Sm	45.6	127.8	86.7	33.4	32.6	191.3	141.4	64.0	8.5	147.3	46.5	55.7	143.5	313.1	263.8	58.3	159.9	240.6	205.1	37.6
Eu	6.9	11.7	9.4	1.6	10.6	16.3	13.6	2.1	1.3	13.2	5.4	4.9	25.0	34.4	30.4	3.1	36.6	43.9	41.0	3.1
Gd	52.6	157.6	103.8	42.3	35.1	178.2	138.9	59.2	11.5	155.9	51.2	58.0	127.7	241.1	204.3	36.5	175.6	310.5	252.1	52.6
Tb	7.2	23.4	15.2	6.6	4.5	24.4	19.0	8.2	1.5	23.3	7.5	8.6	22.4	35.9	29.6	4.1	29.3	57.8	45.8	11.2
Dy	40.9	133.2	83.9	38.2	23.7	140.2	106.5	47.4	9.3	148.4	45.9	54.6	144.4	207.2	171.4	21.5	198.7	370.6	288.0	73.8
Ho	6.9	25.3	15.2	7.5	4.0	26.3	19.9	9.0	2.2	31.0	9.7	11.3	27.9	39.3	33.7	4.3	38.0	76.1	55.7	17.4
Er	15.4	64.2	36.7	19.5	8.1	65.7	49.4	23.5	6.8	87.8	27.8	31.5	76.2	110.2	92.9	12.3	94.0	202.5	148.3	49.0
Tm	1.8	7.7	4.3	2.3	0.8	7.8	5.8	2.9	0.9	11.5	3.5	4.1	12.4	15.1	13.5	1.1	12.4	27.5	19.8	6.9
Yb	9.8	42.0	24.2	12.3	3.5	45.0	33.5	17.1	5.5	73.0	22.5	25.9	80.6	103.2	93.2	8.1	70.6	173.8	123.0	47.5
Lu	1.3	5.2	3.0	1.5	0.4	5.7	4.2	2.2	1.0	10.7	3.4	3.7	11.1	15.5	13.2	1.7	8.1	22.6	15.5	6.5
Pb	0.3	1.6	0.8	0.5	0.4	2.9	1.9	1.0	0.4	1.0	0.6	0.2	2.2	3.3	2.5	0.4	1.3	2.4	1.8	0.5
Th	2.5	7.9	4.2	1.8	0.3	46.5	30.7	17.9	2.6	55.2	15.8	21.4	8.9	45.1	33.3	14.0	6.4	21.5	12.0	6.7
U	1.3	4.0	2.6	0.7	0.1	12.2	7.7	4.7	0.2	11.5	2.8	4.5	17.7	31.8	25.7	4.4	21.3	50.7	40.6	11.4
La/Sm	1.2	3.4	2.0	0.8	2.4	3.2	2.9	0.3	2.5	4.6	3.9	0.7	1.2	2.9	2.2	0.5	0.7	1.4	0.9	0.4
Gd/Yb	3.8	6.1	4.5	0.7	3.8	10.1	5.2	2.7	1.6	3.1	2.2	0.5	1.3	2.8	2.2	0.5	1.8	3.0	2.2	0.6
La/Yb	3.8	12.7	7.9	3.6	8.8	25.4	14.6	6.4	4.1	11.8	7.1	2.9	2.5	11.4	6.5	2.8	1.2	2.0	1.6	0.3
Ce/Ce*	0.8	1.3	1.0	0.2	0.8	0.9	0.9	0.0	0.9	1.3	1.1	0.2	0.7	1.0	0.8	0.1	0.9	1.1	1.0	0.1
Eu/Eu*	0.2	0.4	0.3	0.1	0.2	1.0	0.4	0.3	0.3	0.9	0.4	0.2	0.3	0.7	0.4	0.1	0.5	0.8	0.6	0.1
ΣREE	629.6	1657.9	1258.9	365.4	552.8	3937.3	2762.7	1342.4	206.0	2888.3	1018.2	1126.7	2669.9	6921.1	4947.5	1289.5	1922.2	3711.8	2752.9	801.9

Table 6.2 (cont.)

(ppm)	EDP _{Pb} (n = 5)				EDP _M (n = 8)				DIOP (n = 3)				LQP1 _M (n = 2)				LQP2 _M (n = 28)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Na	680.3	1576.3	1170.0	339.7	580.6	909.4	770.2	94.9	302.8	335.1	319.0	22.8	516.3	1189.3	852.8	475.9	392.9	1570.7	646.8	243.6
Mg	275.6	938.0	547.0	315.3	939.2	1500.1	1223.7	229.3	172.6	316.7	244.6	101.9	177.7	216.8	197.2	27.7	165.0	254.4	210.5	18.1
V	0.9	36.8	8.5	15.8	2.6	8.4	5.8	2.3	5.5	7.5	6.5	1.4	8.6	23.7	16.1	10.7	3.8	34.3	11.7	7.1
Mn	2303.5	3138.5	2636.1	322.3	1710.6	3245.7	2302.2	549.3	1897.6	2434.7	2166.2	379.8	1188.7	1433.2	1311.0	172.8	1150.6	2974.1	1639.9	486.9
Fe	862.4	2010.8	1206.4	467.5	1440.2	2251.2	1852.2	282.8	714.3	1113.8	914.0	282.5	436.8	637.4	537.1	141.8	380.9	649.9	529.7	57.9
Sr	483.5	581.5	524.6	36.1	345.9	421.9	377.7	26.2	204.9	273.3	239.1	48.3	632.4	639.2	635.8	4.8	565.6	756.3	662.9	37.6
Y	707.4	835.3	773.6	53.3	194.3	869.0	601.4	223.2	514.1	669.4	591.7	109.8	170.5	228.0	199.3	40.7	73.3	305.5	212.9	52.8
La	155.8	423.7	318.5	118.1	284.5	604.6	465.7	96.7	219.1	240.5	229.8	15.1	410.3	427.0	418.6	11.8	301.8	770.0	551.4	89.1
Ce	554.9	1378.2	1031.2	321.9	944.1	1833.1	1415.3	261.1	630.0	687.6	658.8	40.7	1121.6	1294.6	1208.1	122.4	733.4	1994.6	1469.3	270.6
Pr	94.4	220.0	164.7	46.1	148.0	247.5	202.2	32.6	95.6	104.4	100.0	6.2	151.7	186.8	169.2	24.8	80.5	285.6	194.9	45.6
Nd	479.3	1082.2	824.3	219.1	734.9	1056.2	913.2	129.8	461.7	512.0	486.9	35.6	659.4	872.7	766.1	150.8	300.8	1220.8	843.9	222.3
Sm	137.4	276.2	216.1	50.2	139.5	241.6	188.6	32.8	110.5	160.1	135.3	35.1	109.8	155.6	132.7	32.4	42.7	205.3	144.7	41.0
Eu	23.6	39.4	35.1	6.5	20.4	31.9	28.1	3.6	14.1	34.6	24.4	14.5	15.1	21.1	18.1	4.2	8.3	28.1	19.4	4.9
Gd	131.5	219.8	181.9	32.4	87.0	194.4	139.3	33.3	121.7	172.0	146.8	35.6	71.9	98.3	85.1	18.7	25.4	130.6	93.2	26.2
Tb	22.4	29.9	26.4	2.8	9.2	27.5	19.2	5.9	16.7	26.8	21.8	7.2	7.5	10.4	9.0	2.0	2.8	14.2	9.9	2.8
Dy	142.9	167.3	152.1	10.2	43.6	158.8	109.1	38.2	95.9	154.9	125.4	41.8	35.1	49.7	42.4	10.3	13.4	66.8	46.2	12.6
Ho	28.4	32.0	29.9	1.5	7.0	32.8	21.1	8.4	19.0	28.1	23.6	6.5	6.0	8.4	7.2	1.7	2.4	11.5	7.9	2.1
Er	78.5	87.2	83.4	4.0	17.4	94.4	59.8	24.8	47.7	70.9	59.3	16.4	14.7	19.7	17.2	3.6	5.8	26.7	18.5	4.8
Tm	10.6	12.8	11.6	0.9	2.0	13.3	8.7	3.7	5.7	10.3	8.0	3.2	1.6	2.2	1.9	0.5	0.7	3.1	2.1	0.5
Yb	72.8	89.2	79.5	6.4	12.1	94.4	60.9	27.0	33.0	68.7	50.9	25.2	9.0	12.7	10.8	2.6	4.4	17.2	12.0	2.6
Lu	9.9	12.0	11.0	0.8	1.6	12.3	8.1	3.5	4.4	9.7	7.1	3.7	1.2	1.8	1.5	0.4	0.7	2.1	1.6	0.3
Pb	2.2	3.9	3.2	0.6	1.8	2.6	2.2	0.3	1.7	3.5	2.6	1.3	2.4	2.5	2.4	0.1	2.0	2.7	2.3	0.2
Th	1.7	11.9	7.9	4.0	8.1	24.8	15.2	5.2	12.9	61.3	37.1	34.2	1.6	6.2	3.9	3.2	1.6	8.8	6.0	1.4
U	10.8	33.6	25.4	8.9	14.1	37.3	30.2	7.6	12.8	13.2	13.0	0.3	0.9	2.5	1.7	1.1	1.1	3.9	2.7	0.5
La/Sm	1.0	1.8	1.5	0.4	1.5	3.9	2.5	0.7	1.4	2.2	1.8	0.6	2.7	3.7	3.2	0.7	2.5	7.2	4.1	1.2
Gd/Yb	1.5	2.7	2.3	0.5	1.8	7.2	2.9	1.8	2.5	3.7	3.1	0.8	7.8	8.0	7.9	0.2	5.5	9.0	7.6	0.9
La/Yb	1.7	5.3	4.1	1.7	3.0	44.5	12.1	13.5	3.2	7.3	5.2	2.9	33.7	45.6	39.6	8.4	29.4	75.5	47.5	10.1
Ce/Ce*	0.7	0.8	0.8	0.0	0.6	0.8	0.7	0.0	0.8	0.9	0.9	0.0	0.6	0.7	0.6	0.0	0.6	0.9	0.7	0.1
Eu/Eu*	0.5	0.6	0.5	0.1	0.4	0.6	0.5	0.1	0.4	0.6	0.5	0.2	0.5	0.5	0.5	0.0	0.5	0.8	0.5	0.1
ΣREE	1971.3	4055.9	3165.6	777.4	2922.7	4293.9	3639.4	494.5	1954.3	2201.8	2078.0	175.0	2614.9	3160.9	2887.9	386.1	1523.0	4665.9	3415.2	684.7

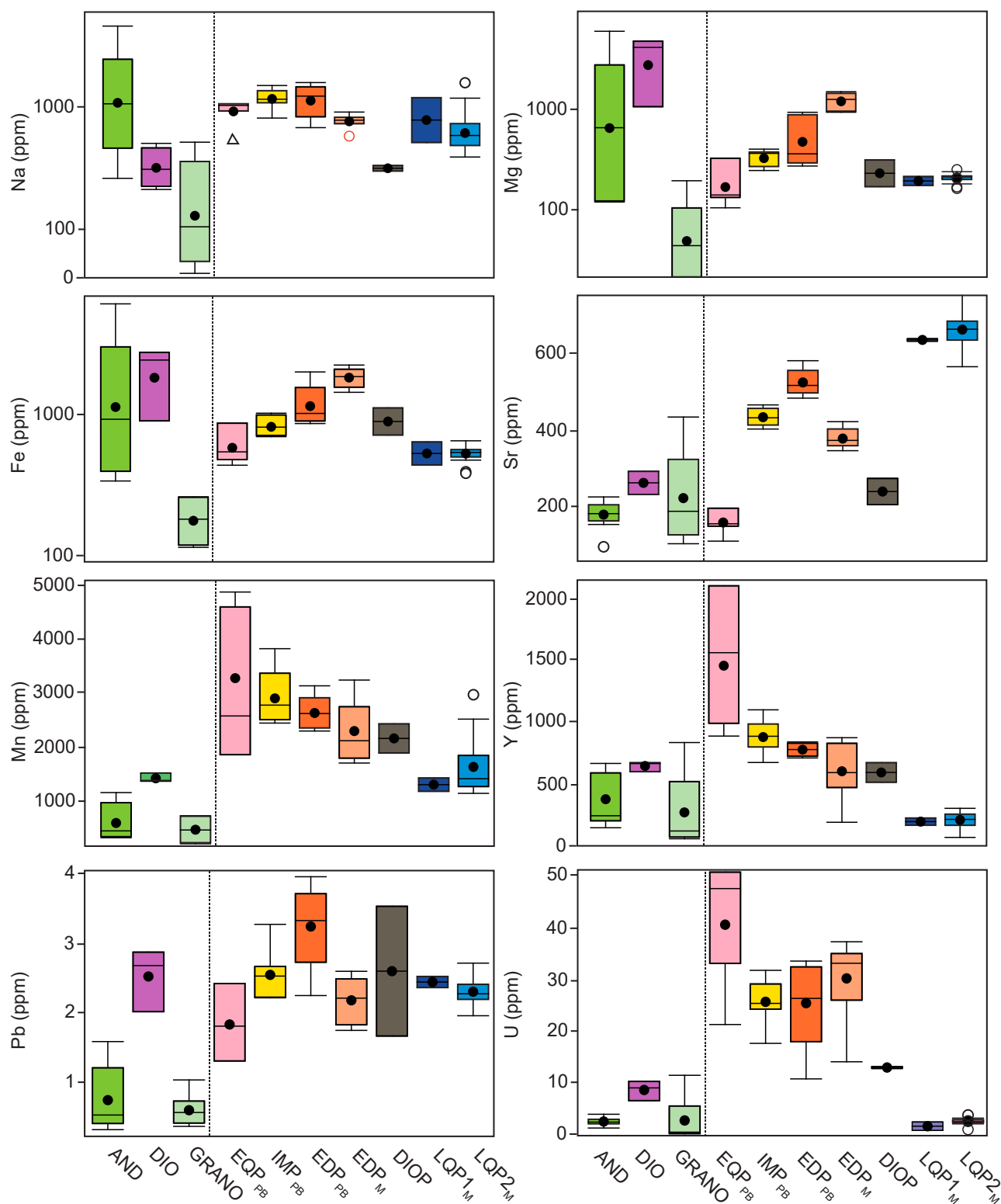


Figure 6.3 Box plot of trace elements compositions collected by LAICPMS from least altered Ap_{mtrx} . Analytical error is smaller than the range in results.

Rare earth elements

The chondrite-normalised REE patterns (Sun & McDonough 1989) of apatites show relative enrichment in LREEs, with slight positive Ce and marked negative Eu anomalies (Fig. 6.4). There is significant variation in REE concentrations of different apatites from the same units with the flattest REE profiles (i.e. lowest La/Yb) which are also those with the lowest total concentration of REE. The shape of the REE pattern can be described quantitatively through ratios of LREE, MREE and HREE (i.e. La/Sm, Gd/Yb).

There are significant differences in apatite REE pattern between the units (Fig. 6.5). Apatites from non-porphyry related intrusions have the least HREE-depleted compositions (lower La/Yb) and have larger negative Eu anomalies (lower Eu/Eu*). Granodiorite-hosted

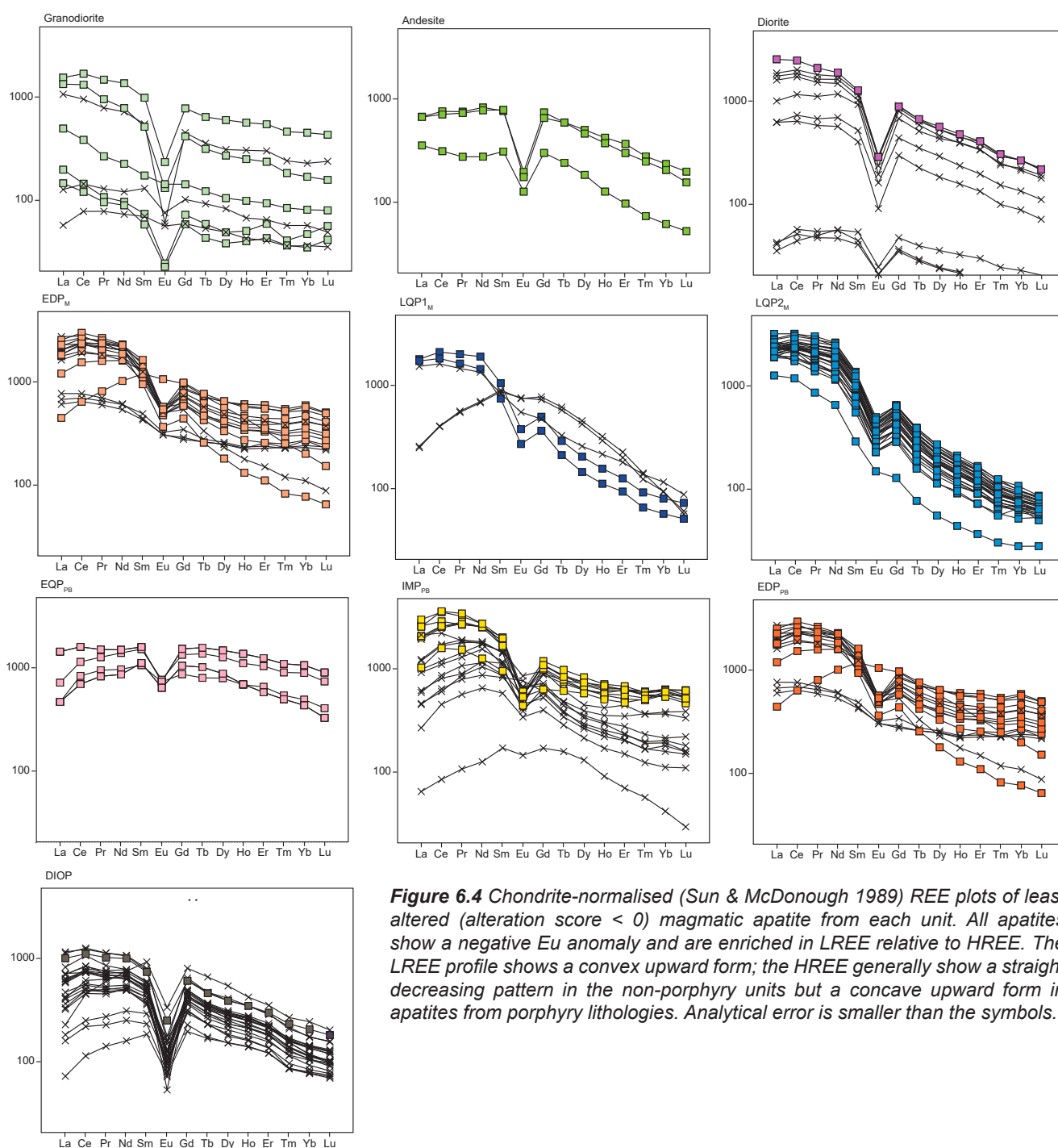


Figure 6.4 Chondrite-normalised (Sun & McDonough 1989) REE plots of least altered (alteration score < 0) magmatic apatite from each unit. All apatites show a negative Eu anomaly and are enriched in LREE relative to HREE. The LREE profile shows a convex upward form; the HREE generally show a straight decreasing pattern in the non-porphyry units but a concave upward form in apatites from porphyry lithologies. Analytical error is smaller than the symbols.

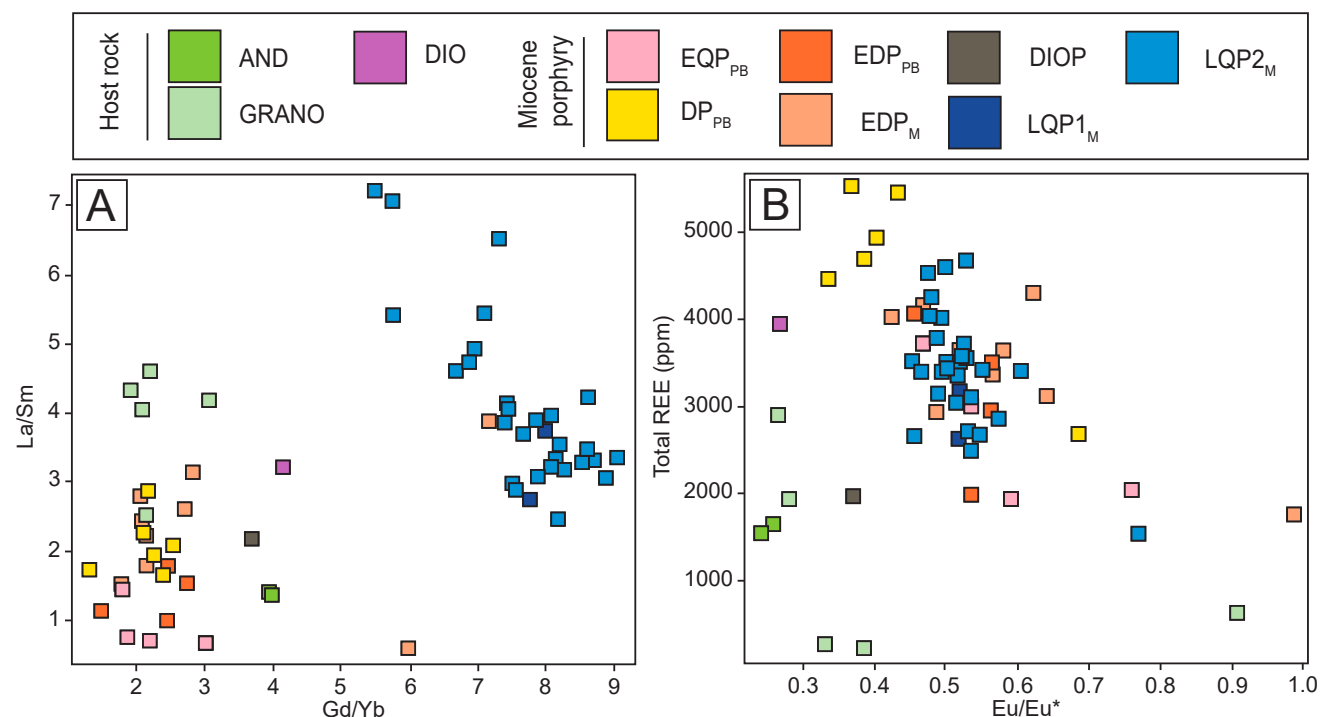


Figure 6.5 REE ratios of REE plots of least altered (alteration score < 0) magmatic apatite by unit. A) apatite from late porphyries typically have higher Gd/Yb and La/Sm than apatite from earlier porphyry units and host rock. B) All apatites show a negative Eu anomaly. Apatite from host units have a much larger Eu anomaly relative to total REE. Analytical error is smaller than the symbols.

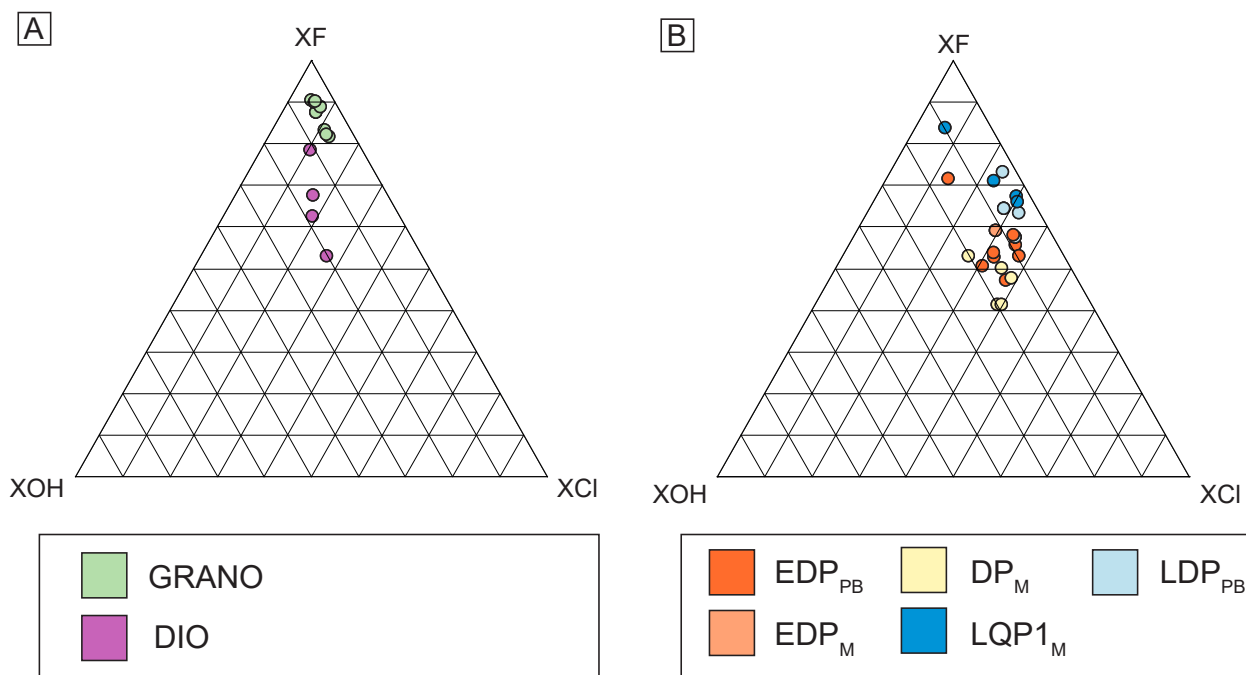


Figure 6.6 XF-XCI-XOH plot of Ap_{incl} in A) the host rock lithologies, B) Porphyry intrusions. Calculations of mole fractions of halogens assume full X-site occupancy and are described in the text (Piccoli & Candela 2002).

apatites have the flattest REE slopes and also generally the lowest total REE. Apart from the Eu anomaly, the LREE-MREE pattern is similar to apatites from the main porphyry units but they tend towards higher La/Sm, and apatites from the late porphyries (LQP1_M, LQP2_M) are more HREE-depleted with the highest La/Sm, La/Yb and Gd/Yb ratios (Table 6.2; Fig. 6.5).

6.3.2 Apatite inclusions in zircon

Representative compositions of Ap_{incl} are given in tables 6.3 and 6.4. Due to the modified method required for analysis of fine Ap_{incl}, measurement of Mg, Na and Fe have high detection limits and/or analytical error. The standard deviations and limits of detection associated with these analyses are available in Chapter 5.

F-Cl-OH endmembers

As with the apatite phenocrysts, all Ap_{incl} are fluorapatite ($X_F = 0.5 - 1$; Fig. 6.6). The concentrations of F and Cl are inversely correlated (Fig. 6.7A). The proportions of X_F and X_{Cl} overlap between

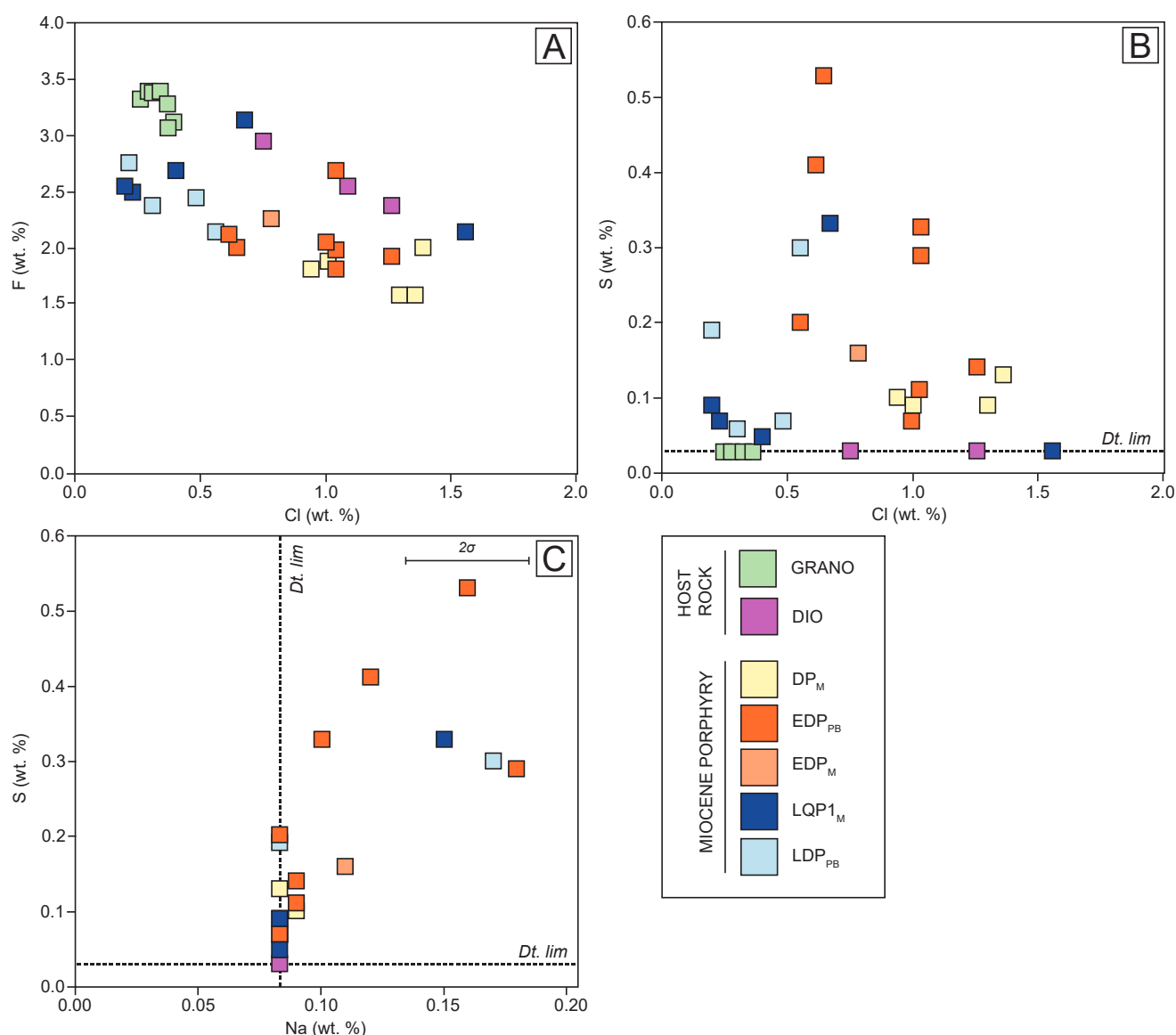


Figure 6.7 EMP analyses of Ap_{incl}. Average error is given as two standard deviations where larger than symbols. A) F and Cl concentration show a negative correlation. B) Host rocks contain S concentrations at or near detection limit. C) Analyses of Na and S by EMP are near detection limit and have large associated analytical error.

Table 6.3 Representative composition of Ap_{incl} EMP analyses for number of analyses (n). The minimum (Min.), maximum (Max.) of results for each lithology is given as well as the calculated mean and associated standard deviation (Sd.) of results for each lithology are given. Values in *italics* are below detection limits (see Chapter 5).

	GRANO (n = 9)				DIO (n = 4)				IMP _M (n = 5)				EDP _{PB} (n = 8)			
	Min	Max	Mean	Sd.	Min	Max	Mean	Sd.	Min	Max	Mean	Sd.	Min	Max	Mean	Sd.
wt. %																
Ca	38.49	38.73	38.61	0.08	36.41	37.76	36.97	0.59	36.71	37.56	37.25	0.36	36.46	37.73	37.06	0.40
P	18.29	18.63	18.46	0.13	17.58	18.19	17.89	0.30	17.67	18.07	17.84	0.17	17.63	18.20	17.88	0.20
Fe	0.01	0.04	0.02	0.01	0.16	0.46	0.26	0.14	0.07	0.23	0.12	0.06	0.09	0.46	0.18	0.12
Mg	0.03	0.03	0.01	0.02	0.00	0.11	0.04	0.05	0.01	0.03	0.02	0.01	0.02	0.06	0.04	0.01
Mn	0.02	0.11	0.06	0.04	0.09	0.35	0.16	0.13	0.09	0.17	0.14	0.03	0.11	0.20	0.14	0.03
Na	0.01	0.01	0.01	0.00	0.01	0.06	0.03	0.03	0.01	0.09	0.05	0.04	0.04	0.18	0.11	0.04
Al	0.03	0.20	0.06	0.05	0.15	0.52	0.31	0.16	0.09	0.67	0.34	0.23	0.07	0.89	0.31	0.26
S	0.01	0.03	0.02	0.01	0.00	0.01	0.01	0.01	0.09	0.13	0.10	0.02	0.07	0.53	0.26	0.16
Si	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.02	0.00	0.01	0.01	0.06	0.00	0.02
Sr	0.01	0.03	0.02	0.01	0.01	0.06	0.03	0.02	0.03	0.07	0.05	0.02	0.04	0.09	0.07	0.02
Fe	3.08	3.41	3.27	0.13	2.00	2.96	2.47	0.40	1.56	2.00	1.76	0.20	1.78	2.70	2.09	0.28
Cl	0.25	0.39	0.34	0.05	0.75	1.38	1.12	0.27	0.94	1.38	1.20	0.21	0.56	1.26	0.90	0.25
O	39.08	39.56	39.35	0.20	38.13	38.92	38.48	0.36	38.24	39.31	38.62	0.42	38.30	39.20	38.85	0.29
Total	99.70	100.58	100.24	0.38	97.38	99.53	98.32	1.01	97.21	99.06	97.90	0.71	97.43	99.22	98.21	0.57
O=F	1.30	1.44	1.38	0.06	0.84	1.25	1.04	0.17	0.66	0.84	0.74	0.08	0.75	1.14	0.88	0.12
O=Cl	0.06	0.09	0.07	0.01	0.17	0.30	0.25	0.06	0.21	0.30	0.26	0.05	0.12	0.28	0.20	0.06
Corr. Total	98.35	99.06	98.79	0.32	96.37	97.98	97.03	0.78	96.35	97.91	96.89	0.58	96.56	97.81	97.13	0.40
XF	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
XCl	0.04	0.06	0.05	0.01	0.11	0.20	0.16	0.04	0.14	0.20	0.18	0.03	0.08	0.19	0.13	0.04
XOH	0.96	0.94	0.95	0.99	0.89	0.80	0.84	0.96	0.86	0.80	0.82	0.97	0.92	0.81	0.87	0.96
	EDP _M (n = 2)				LQP1 _M (n = 4)				LDP _{PB} (n = 6)							
	Min	Max	Mean	Sd.	Min	Max	Mean	Sd.	Min	Max	Mean	Sd.				
wt. %																
Ca	37.67	37.67	37.67	-	37.67	38.87	38.25	0.65	37.66	38.74	38.22	0.36				
P	18.07	18.07	18.07	-	17.90	18.45	18.13	0.28	18.09	18.39	18.21	0.12				
Fe	0.08	0.08	0.08	-	0.06	0.11	0.08	0.02	0.05	0.08	0.06	0.01				
Mg	0.03	0.03	0.03	-	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.00				
Mn	0.12	0.12	0.12	-	0.08	0.15	0.11	0.03	0.09	0.12	0.11	0.01				
Na	0.11	0.11	0.11	-	0.01	0.15	0.05	0.07	0.03	0.17	0.09	0.07				
Al	0.15	0.15	0.15	-	0.01	0.23	0.11	0.13	0.01	0.01	0.01	0.00				
S	0.16	0.16	0.16	-	0.05	0.33	0.14	0.13	0.06	0.30	0.17	0.12				
Si	0.01	0.01	0.01	-	0.01	0.09	0.03	0.05	0.07	0.21	0.13	0.06				
Sr	0.10	0.10	0.10	-	0.07	0.11	0.08	0.02	0.02	0.06	0.04	0.02				
Fe	2.23	2.23	2.23	-	2.49	3.16	2.72	0.31	2.17	2.76	2.39	0.22				
Cl	0.78	0.78	0.78	-	0.20	0.67	0.38	0.22	0.20	0.55	0.43	0.14				
O	38.93	38.93	38.93	-	38.58	39.63	39.18	0.46	39.06	39.49	39.31	0.16				
Total	98.73	98.73	98.73	-	98.00	100.35	99.51	1.04	98.59	99.87	99.49	0.46				
O=F	0.94	0.94	0.94	-	1.05	1.33	1.14	0.13	0.91	1.16	1.01	0.09				
O=Cl	0.17	0.17	0.17	-	0.04	0.15	0.08	0.05	0.04	0.12	0.09	0.03				
Corr. Total	97.62	97.62	97.62	-	96.91	98.87	98.29	0.86	97.63	98.59	98.39	0.34				
XF	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00				
XCl	0.11	0.11	0.11	-	0.03	0.10	0.06	0.03	0.03	0.08	0.06	0.02				
XOH	0.88	0.88	0.88	-	0.97	0.90	0.94	0.97	0.97	0.92	0.94	0.98				

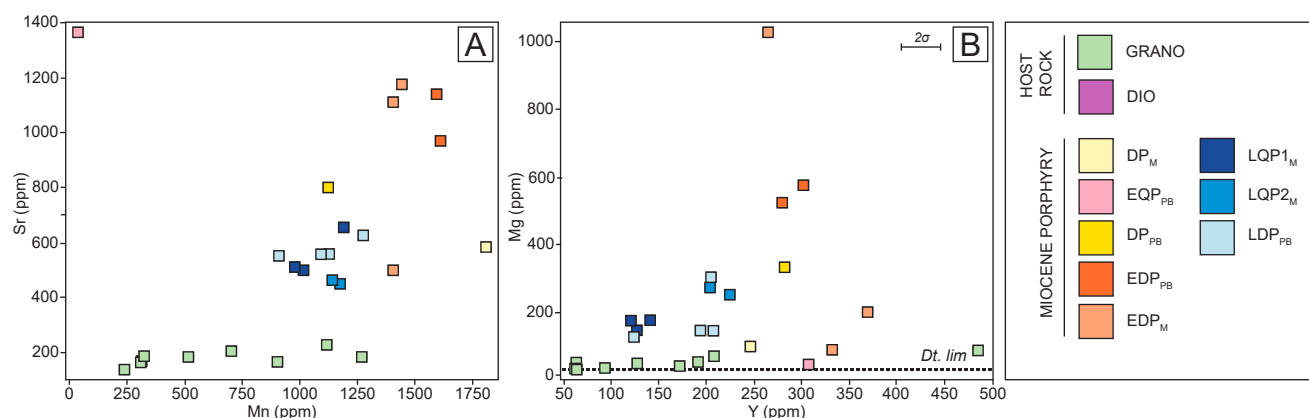


Figure 6.8 LA-ICP-MS analyses of Ap_{incl} . Average error is given as two standard deviations where greater than the symbol size. A) Mn and Sr concentrations can separate apatite from mineralised, less mineralised and host rock. B) Mg and Y are highest in mineralised intrusions.

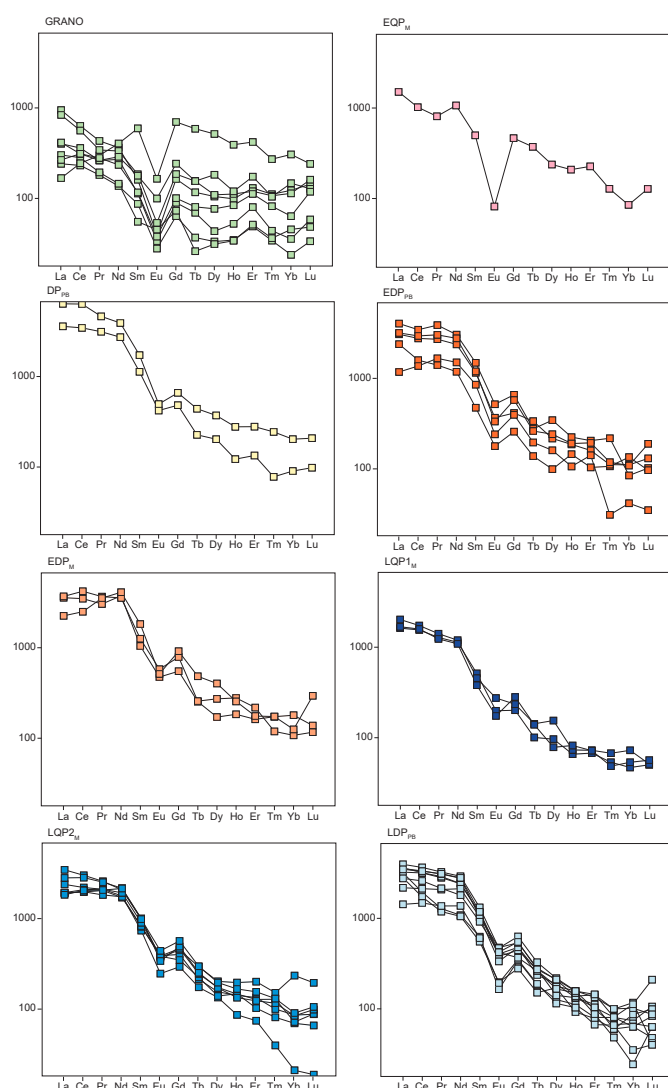


Figure 6.9 Chondrite-normalised (Sun & McDonough 1989) REE plots of Ap_{incl} data. All apatites show a negative Eu anomaly and are enriched in LREE relative to HREE. Apatites from the Eocene intrusions have flatter REE slopes and larger negative Eu anomalies. Analytical error is smaller than the symbol size.

apatites from different lithologies and there is little systematic difference. However Eocene apatites typically have lower X_{Cl} and X_{Cl}/X_{OH} ratios (Fig. 6.6).

Sulfur

Ap_{incl} from Eocene intrusive rocks have low S (mean value below the limit of detection) relative to Ap_{incl} from the porphyry intrusions, which have S concentrations of ~0.05 – 0.5 wt. % (Table 6.3). Many analyses fall below detection limits (Fig. 6.7).

Iron, magnesium, sodium, manganese, strontium and yttrium

Concentrations of Mg, Mn, Fe and Sr are lowest in apatites from the host rock (GRANO). Maximum concentrations of Mg, Mn, Sr and Y in Ap_{incl} are observed in the mineralised porphyry units and are lower in the less mineralised/late porphyry intrusions (Fig. 6.8).

Rare earth elements

There are less differences between the REE profiles of different lithologies for Ap_{incl} than Ap_{mtrx} (Fig. 6.9) Ap_{incl} from GRANO can be distinguished from those in the Miocene

porphyries by lower La/Yb ratios (means of 10 and 43 respectively) and lower Eu/Eu*. However, Ap_{incl} from the porphyry units show comparable La/Sm, Gd/Yb and Eu/Eu* ratios (Table 6.4).

Chapter 6: Magmatic apatite at La Granja

Table 6.4 Representative composition of Ap_{incl} from LA-ICP-MS analysis by lithology for number of analyses (n). The minimum (Min.), maximum (Max.) of results for each lithology is given as well as the calculated mean and associated standard deviation (Sd.) of results for each lithology are given. Values in italics are below detection limits (see Chapter 5).

ppm	GRANO ($n = 9$)				DP _{tr} ($n = 1$)				DP _{ps} ($n = 1$)				EQP _{ps} ($n = 1$)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Na	188.5	188.5	188.5	0	-	-	-	-	854.2	854.2	854.2	-	188.5	188.5	188.5	-
Mg	15.7	73.2	35.5	18.8	322.7	322.7	322.7	-	85.1	85.1	85.1	-	31.1	31.1	31.1	-
Mn	237.9	1268.4	632	385.4	1808	1808	1808	-	1123.1	1123.1	1123.1	-	36	36	36	-
Fe	90.5	318.2	156.2	100.9	5387.9	5387.9	5387.9	-	460.4	460.4	460.4	-	90.5	90.5	90.5	-
Sr	137.5	228	180.2	26	583.9	583.9	583.9	-	801	801	801	-	1366.5	1366.5	1366.5	-
Y	60.9	501.3	166	139	289.9	289.9	289.9	-	252.6	252.6	252.6	-	316.1	316.1	316.1	-
La	39.3	221.4	99	65.2	920.9	920.9	920.9	-	846.7	846.7	846.7	-	351.2	351.2	351.2	-
Ce	127.7	383.5	212	90.2	2254.4	2254.4	2254.4	-	2107	2107	2107	-	615.9	615.9	615.9	-
Pr	16.7	39.7	24.9	7.5	291	291	291	-	289.2	289.2	289.2	-	74	74	74	-
Nd	62	182.7	117.4	44.4	1065.5	1065.5	1065.5	-	1239	1239	1239	-	480.1	480.1	480.1	-
Sm	8.1	86.9	25.5	24	192.4	192.4	192.4	-	166.8	166.8	166.8	-	72.8	72.8	72.8	-
Eu	1.6	9.2	3.5	2.6	27.6	27.6	27.6	-	23.7	23.7	23.7	-	4.5	4.5	4.5	-
Gd	12.6	137.4	37.2	39.4	123.7	123.7	123.7	-	95.9	95.9	95.9	-	91.1	91.1	91.1	-
Tb	0.9	21	5.1	6.2	13.9	13.9	13.9	-	8.2	8.2	8.2	-	13.3	13.3	13.3	-
Dy	7.6	125.4	30.7	37.5	89.5	89.5	89.5	-	50	50	50	-	57.7	57.7	57.7	-
Ho	1.8	21.2	5.9	6	9.4	9.4	9.4	-	6.7	6.7	6.7	-	11.3	11.3	11.3	-
Er	5.5	66.4	20.6	18.6	24.1	24.1	24.1	-	21.5	21.5	21.5	-	35.8	35.8	35.8	-
Tm	0.6	6.6	2.2	1.9	3.5	3.5	3.5	-	1.9	1.9	1.9	-	3.1	3.1	3.1	-
Yb	3.8	48.7	16	14.1	26.4	26.4	26.4	-	14.6	14.6	14.6	-	13.5	13.5	13.5	-
Pb	0.4	12.6	2.9	4.3	-	-	-	-	0.4	0.4	0.4	-	0.4	0.4	0.4	-
Th	0.6	7.8	4	2.6	16.8	16.8	16.8	-	8	8	8	-	2.3	2.3	2.3	-
U	0.1	1.4	0.5	0.4	4.1	4.1	4.1	-	3	3	3	-	0.1	0.1	0.1	-
La/Sm	0.5	9.4	5.3	2.8	4.8	4.8	4.8	-	5.1	5.1	5.1	-	4.8	4.8	4.8	-
Gd/Yb	1.6	3.3	2.4	0.6	4.7	4.7	4.7	-	6.6	6.6	6.6	-	6.7	6.7	6.7	-
La/Yb	0.8	16.5	9.1	5	34.8	34.8	34.8	-	58.1	58.1	58.1	-	25.9	25.9	25.9	-
Ce/Ce*	0.6	1.1	0.8	0.2	0.9	0.9	0.9	-	0.5	0.5	0.5	-	0.4	0.4	0.4	-
Eu/Eu*	0.2	0.7	0.4	0.2	0.5	0.5	0.5	-	0.6	0.6	0.6	-	0.2	0.2	0.2	-
ΣREE	327.3	948.8	636.9	248.5	5044	5044	5044	-	4873.8	4873.8	4873.8	-	1827.5	1827.5	1827.5	-

ppm	EDPPB ($n = 2$)				EDP _{tr} ($n = 3$)				LQP1 _{tr} ($n = 3$)				LQP2 _{tr} ($n = 2$)				LDP _{tr} ($n = 4$)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Na	188.5	188.5	188.5	0	188.5	2740.4	1039.1	1473.3	437.5	580.8	526.4	77.6	759.2	994.8	877	166.6	688.4	972.3	798.5	122.6
Mg	516.7	568.8	542.7	36.8	75.3	1027.9	430.4	520.5	133.6	163.7	153.3	17.1	240.6	262	251.3	15.1	113.4	292.8	167.9	83.8
Mn	1593.5	1610.5	1602	12	1405.3	1442.7	1417.8	21.5	977.6	1190	1061.1	113.3	1140.9	1175	1157.9	24.1	908.6	1275.2	1100.7	150.7
Fe	-	-	-	-	90.5	1022.7	556.6	659.2	552.9	708.3	623.9	78.6	842	893.4	867.7	36.3	522.3	1828.9	881.5	633.3
Sr	970.9	1140.8	1055.9	120.2	499.2	1176.8	929.3	373.9	499.2	655.5	555.3	87	450.2	463.1	456.6	9.1	552.2	626.5	573.7	35.3
Y	287.4	310.5	298.9	16.3	271.9	380.6	331.5	55.1	122.1	143.2	131.3	10.8	208.5	230	219.3	15.2	125.3	212.2	186.2	41.1
La	722.9	748.3	735.6	18	827.7	1136.5	940.2	170.6	376.2	468.2	411.1	49.8	454.1	456.9	455.5	2	333.7	828.2	606.6	227.7
Ce	1685	1794.4	1739.7	77.4	2093.1	3176.7	2597.2	545.7	928.5	1039	973	58.3	1200.9	1273.9	1237.4	51.6	893.3	2015.7	1527.3	532.4
Pr	249.8	279.1	264.4	20.7	278.6	356.2	322.1	41	112.1	127.9	118.7	8.2	189.1	195	192	4.2	125.4	281.9	213.7	70.4
Nd	1079.4	1258	1168.7	126.3	1589.1	1677.1	1634.6	44.1	486.7	533.6	509	23.5	777.4	875.4	826.4	69.2	619.2	1248.9	977.6	267.2
Sm	170	175.9	172.9	4.2	151.8	216	183.5	32.1	55.1	74.4	65.2	9.7	120.1	132.9	126.5	9	88.4	168.4	139.6	35.1
Eu	18.8	20.7	19.7	1.3	26.3	35.3	31.2	4.6	9.6	15.1	11.9	2.9	21.7	21.9	21.8	0.2	10.7	26.5	19.6	6.7
Gd	82.2	114.2	98.2	22.7	107.5	156.8	139.5	27.7	39.3	55	46.7	7.9	79.7	92.6	86.2	9.1	69	105.5	90.7	15.4
Tb	9.4	12.1	10.8	1.9	9	12.5	10.2	2	3.6	5	4.5	0.8	7.7	8.8	8.3	0.8	6.7	10.1	8.7	1.5
Dy	53.2	59.3	56.3	4.3	41.5	66.8	58.1	14.4	19	37.3	26.5	9.6	38.2	42.7	40.4	3.2	27.9	50.9	42	9.9
Ho	10.2	10.4	10.3	0.2	9.9	18.2	14.3	4.2	3.5	4.4	4	0.4	7.8	8	7.9	0.2	5.6	8.5	7.2	1.2
Er	25.6	31	28.3	3.8	25.5	48.3	36.1	11.5	10.6	11.4	11.1	0.4	20.5	21.4	21	0.7	10.6	22.7	16.3	4.9
Tm	2.8	2.9	2.8	0.1	2.9	4.7	4	1	1.2	1.6	1.4	0.2	2.5	3.2	2.8	0.5	1.6	2.4	1.9	0.4
Yb	17.5	17.8	17.7	0.2	17.1	28.5	22.8	8.1	7.4	11.5	9.1	2.1	11.6	13.9	12.8	1.6	5.6	18.7	11.4	5.4
Pb	3	6.8	4.9	2.7	0.4	8.3	4.1	4	0.3	2.5	1.6	1.2	2.1	2.3	2.2	0.2	1.8	10.4	4.7	3.9
Th	13.8	18.7	16.2	3.4	11.4	20.5	17.2	5	5.1	7.6	6.2	1.3	8.1	10.7	9.4	1.8	2.2	6.1	4.5	1.7
U	3.1	3.4	3.2	0.2	1.3	15.1	7.7	6.9	2.2	3.5	2.8	0.6	2.5	3.1	2.8	0.5	0.7	2.5	1.8	0.8
La/Sm	4.3	4.3	4.3	0	4.7	5.5	5.1	0.5	5.1	7.1	6.4	1.2	3.4	3.8	3.6	0.2	3.4	5.5	4.3	0.9
Gd/Yb	4.6	6.5	5.6	1.3	3.8	9	6.4	3.7	4	6.5	5.3	1.3	5.7	8	6.9	1.6	5.6	12.3	8.9	2.7
La/Yb	40.6	42.7	41.6	1.5	29	50.1	39.6	14.9	40.7	50.7	45.8	5	32.7	39.3	36	4.7	44.3	68.7	55.7	10.7
Ce/Ce*	0.5	0.6	0.5	0.1	0.3	0.4	0.3	0.1	0.5	0.6	0.6	0.1	0.5	0.5	0.5	0	0.4	0.6	0.5	0.1
Eu/Eu*	0.4	0.5	0.5	0.1	0.6	0.6	0.6	0	0.5	0.8	0.7	0.2	0.6	0.7	0.6	0.1	0.4	0.6	0.5	0.1
ΣREE	4134.8	4523.9	4329.4	275.2	5282.2	5817.2	5549.7	378.3	2103.4	2367.6	2193.5	150.8	2937	3145.3	3041.1	147.3	2198.8	4770.4	3663.9	1159.6

6.4 Apatite crystallisation relative to melt evolution

6.4.1 Timing of apatite crystallisation

Various studies have observed apatites as inclusions in clinopyroxene, amphibole, biotite, plagioclase and zircon (Stock et al. 2018; Jennings et al. 2011; Bruand et al. 2014) as well as forming micro-phenocrysts and as part of the groundmass of igneous rocks. There can be an assortment of these different texturally associated apatites, or multiple generations of apatite within a single rock. This suggests apatite can crystallise over an extended period during magma differentiation. The difference in Ap_{mtr} and Ap_{incl} composition, for elements with low diffusion rates, may reflect crystallisation from different melt compositions. In order to understand how the melt composition is evolving for each lithology, it is important to establish an order of crystallisation.

Temperature of crystallisation

Harker diagrams of bulk rock composition (Fig. 4.22D) show an inflection in the trend

of P_2O_5 against SiO_2 occurring between 58 – 65 wt. % SiO_2 . As apatite is the dominant phosphorus sink in most igneous rocks, this switch to P_2O_5 decreasing with increasing SiO_2 is inferred to represent an onset of apatite fractionation in the magmatic systems supplying the Eocene and Miocene intrusions. This would suggest that for most porphyry units (except perhaps DIOP) apatite is close to saturation or already saturated.

The temperature of apatite saturation in a melt is a function of melt composition (particularly SiO_2 and P_2O_5), H_2O content, pressure and temperature (Harrison & Watson 1984; Piccoli & Candela 2002). The temperature of apatite saturation (AST) for a given melt composition can be calculated using the equation from Harrison & Watson (1984):

$$\ln(D_p) = \frac{8400 + 26400(SiO_2 - 0.5)}{AST} - 3.1 - 12.4(SiO_2 - 0.5) \quad \text{Eq. 6.4}$$

$$P_2O_5 = \frac{42}{D_p} \quad \text{Eq. 6.5}$$

Here AST is in Kelvin, D_p is the P_2O_5 distribution coefficient for apatite-melt and SiO_2 is the weight fraction of silica in the melt. The effects of P_{melt} and water content have been shown to have a smaller, non-independent degree of control and are therefore not accounted for in this equation (Harrison & Watson 1984). However, it is important to recognise that the Eocene intrusions (GRANO and DIO) probably crystallised at higher pressures, and are now at the same level as the Miocene porphyry intrusions that were emplaced ~20 Myr later. Uplift in the central Andes during the early Miocene is estimated at a maximum of 0.02 mm/yr (Gregory-Wodzicki 2000), and resulted in about 4 km of uplift over this time period represented by these intrusions. Assuming that porphyries were intruded at around 3 km depth (~80 MPa; Sillitoe 2010), then the juxtaposition of the older and younger intrusives suggests that Eocene intrusions were emplaced at a depth of around ~7 km (~1 GPa). Calculations of AST assume that the melt of interest has a composition equivalent to the current bulk rock, an assumption that is only correct where apatite crystallises early before significant differentiation of the melt. Apatite solubility is higher in more primitive melts so that in the more mafic lithologies (< 58 wt. % SiO_2 , e.g. DIO and DIOP) it is inferred that apatite did not saturate early (as a liquidus phase) and only started to crystallise after more advanced differentiation of the melt. In addition, apatite saturation is delayed relative to melt evolution in more peraluminous melts (i.e. $ASI = Al_2O_3 / (CaO + Na_2O + K_2O) > 1$) due to either low P/Ca ratios or decreased Ca activity (Bea et al. 1992). In these cases a higher degree of fractionation would occur prior to apatite saturation causing the melt composition to significantly differ from the starting bulk rock composition. Therefore, this equation for ASI is only valid for metaluminous melts with 45 – 75 wt. % SiO_2 . The effects of the higher aluminosity on the AST equation of Harrison & Watson (1984) can be corrected using an equation from Bea et al. (1992). However, due to the altered nature of the rocks, the calculated ASI is imprecise and the apatite saturation temperatures derived here will to be overestimated as a result.

The mean AST s for the units range between 644 – 973 °C (Table 6.5; Fig. 6.10). Temperatures below 850 °C are outside the limits set by the equation (850 – 1000 °C, 0 – 10 wt. % H_2O) and are a result of low SiO_2 . The concentration of SiO_2 in the melt has the strongest control on AST (Fig. 6.10A; $R^2 = 0.78$). Apatite is more soluble in mafic melts and it has been estimated that up to one-third

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of such melts may have crystallised before apatite saturates (Piccoli & Candela 2002). As these values are saturation temperatures, it is possible that apatite continued to crystallise at temperatures below this. However, it is thought that the majority of apatite in felsic rocks will crystallise within 60 – 100 °C of the saturation temperature (Piccoli & Candela 1994).

Zircon saturation is controlled by temperature, alkalinity and the melt Si and Al contents (Watson & Harrison 1983). As a result zircon crystallisation favours more evolved melt with multiple studies suggesting that crystallisation occurs after 65 wt. % SiO₂ (e.g. Hoskin

et al. 2000). Calculated saturation temperatures for apatite are between 100 - 200 °C higher than the calculated zircon crystallisation temperatures for the porphyry units (Table 6.5; see section 4.3). Although the saturation temperatures are probably overestimates, it is still thought probable that the majority of the magmatic apatite crystallised before the zircon. In this study the timing of Ap_{incl} crystallisation is inferred to be comparable to the zircon host suggesting that the apatite micro-phenocrysts formed before Ap_{incl}. This is like work by Hoskin et al. (2000) who applied an integrated approach to unravelling accessory mineral saturation: apatite was found to saturate earliest in most phases, with zircon constrained to more felsic zones of the pluton.

Mineral textures

Temperature estimates for the relative timing of apatite and zircon saturation are supported by textural evidence. Zircons lack inherited cores when observed by CL imaging, electron probe mapping and in comparison of U-Pb ages (see section 4.3), which implies that the porphyry melts were initially under-saturated in zircon. Zircon has a strong affinity to quartz suggesting a dominant occurrence within the later groundmass (see section 4.4). Apatite has more varied mineral associations and is a common inclusion in coarse euhedral phenocrysts of plagioclase, indicating a relatively early crystallisation. Within the majority of the porphyry units, micro-phenocrysts of apatite are generally equant crystals within a finer groundmass (Fig. 6.1A-C). In the late porphyry units (i.e. LQP_M, LDP_{PB}) magmatic apatite is finer grained, more irregular in shape and forming part of the groundmass (Fig. 6.1D-F).

Apatite inclusions within zircon are common; conversely, inclusions within apatite mainly consist of the major rock forming minerals (plagioclase, biotite, quartz) and only contain zircon in the late quartz porphyries. Inclusions of apatite in zircon have been identified in several studies (Jennings et al. 2011; Bruand et al. 2014) and have been used to infer some degree of overlap with apatite and zircon crystallisation; with the acknowledgement that apatite was likely slightly earlier. This

Table 6.5 Apatite saturation temperatures (Harrison & Watson 1984) and zircon crystallisation temperatures (Ferry & Watson 2007) calculated for each lithology. Results in italics are outside limit of equation.

Lithology	AST (°C)	Ti-in-zircon temperature (°C)	Temperature difference (°C)
AND	774	-	
GRANO	830	735	95
DIO	644	-	
EQP _M	871	669	202
EQP _{PB}	882	699	183
DP _M	902	704	198
DP _{PB}	936	684	252
EDP _{PB}	943	708	235
EDP _M	886	676	119
DIOP	745	688	57
LQP _{PB}	826	689	-
LQP1 _M	914	676	238
LQP2 _M	973	677	-
LDP _{PB}	837	679	-

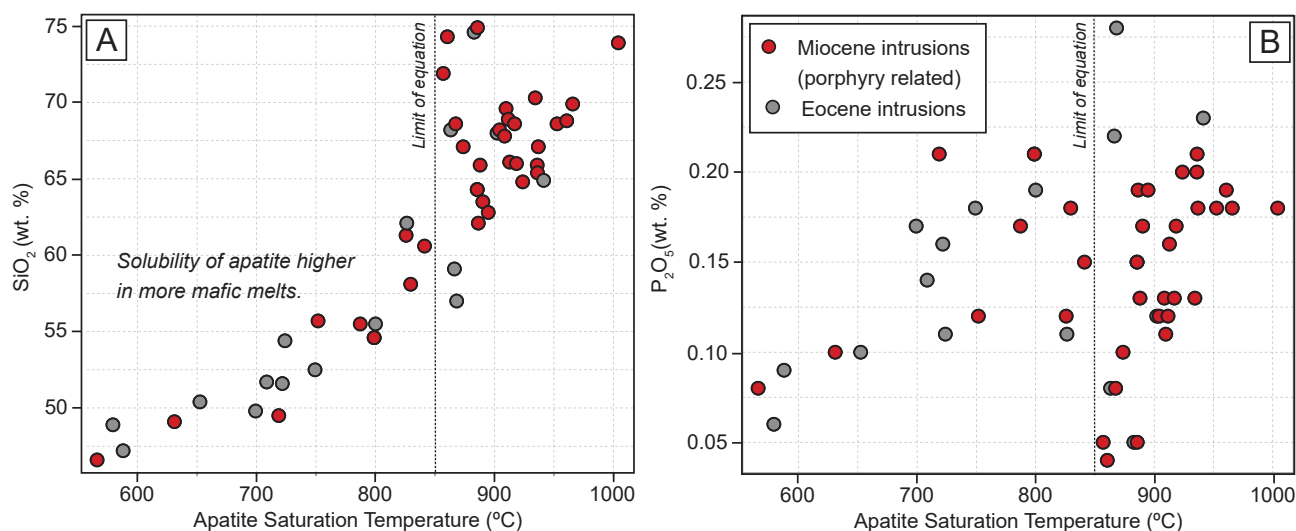


Figure 6.10 Temperature of apatite saturation (AST) calculated from bulk rock (Harrison & Watson 1984) as a function of A) SiO_2 and B) P_2O_5 . AST is closely linked to silica content ($R^2 = 0.78$) and apatite solubility is higher in more mafic melts. P_2O_5 correlates with AST at lower temperatures.

textural evidence suggests that the relative timing of accessory phases varies between the units.

6.4.2 Apatite composition during magma differentiation

The Mg content of apatite has been shown, via experimental (Prowatke & Klemme 2006) and empirical (Nathwani et al. 2020) work, to be proportional to Mg_{melt} and consequently it can be used to track relative timing of apatite crystallisation during differentiation magmas. The substitution of Mg for Ca in apatite does not require a charge balance and Mg concentration is not intrinsically linked to other substituting elements (Piccoli & Candela 2002) and therefore compositions should reflect equilibrium conditions. At La Granja, Harker plots of bulk rock compositions show a steady decrease in MgO with increasing silica content (Fig. 5.20) and mass transfer calculations (see section 4.5.2) suggests that any net gain/loss of Mg in these samples as a result of hydrothermal alteration is small (< 1 wt. % change). Therefore, Mg concentrations in apatite can be used as a proxy for melt differentiation; apatite with higher Mg concentrations indicates earlier crystallisation from a less differentiated melt.

Concentrations in Mg decrease from Ap_{mtrx} to Ap_{incl} in all lithologies concurring with the suggested order of crystallisation (Fig. 6.11). However, Ap_{mtrx} and Ap_{incl} from the late porphyries (LQP1_M , LQP2_M , LDP_{PB}) and GRANO show more overlap in composition consistent with a more coeval timing of crystallisation in these units. The Mg concentration in the magmatic apatites from La Granja varies between 10 and ~6000 ppm. This variation in concentration can be captured within a single unit or be as little as ~80 ppm (LQP1_M). Changes in Mg apatite could be the result of crystallisation of an Mg-rich phase or other temporal variations in melt (such as magma mixing). A small range in Mg concentrations within a unit suggests there was a lack of Mg-rich phases co-crystallising with apatite. The $\text{Mg}_{\text{Ap}}/\text{Mg}_{\text{bulk rock}}$ ratio of Ap_{mtrx} from all samples ranges over an order of magnitude from a mean of around 0.1 in DIO, EDP_{PB} , EDP_M , to a mean of around 0.01 in EQP_{PB} , GRANO, DIOP. Partition coefficients for Mg can be approximated to 0.1 (Richter et al. 2016) which suggest that Ap_{mtrx} from DIO, EDP_{PB} , EDP_M crystallised early in the melt evolution when the melt composition was equivalent to bulk rock.

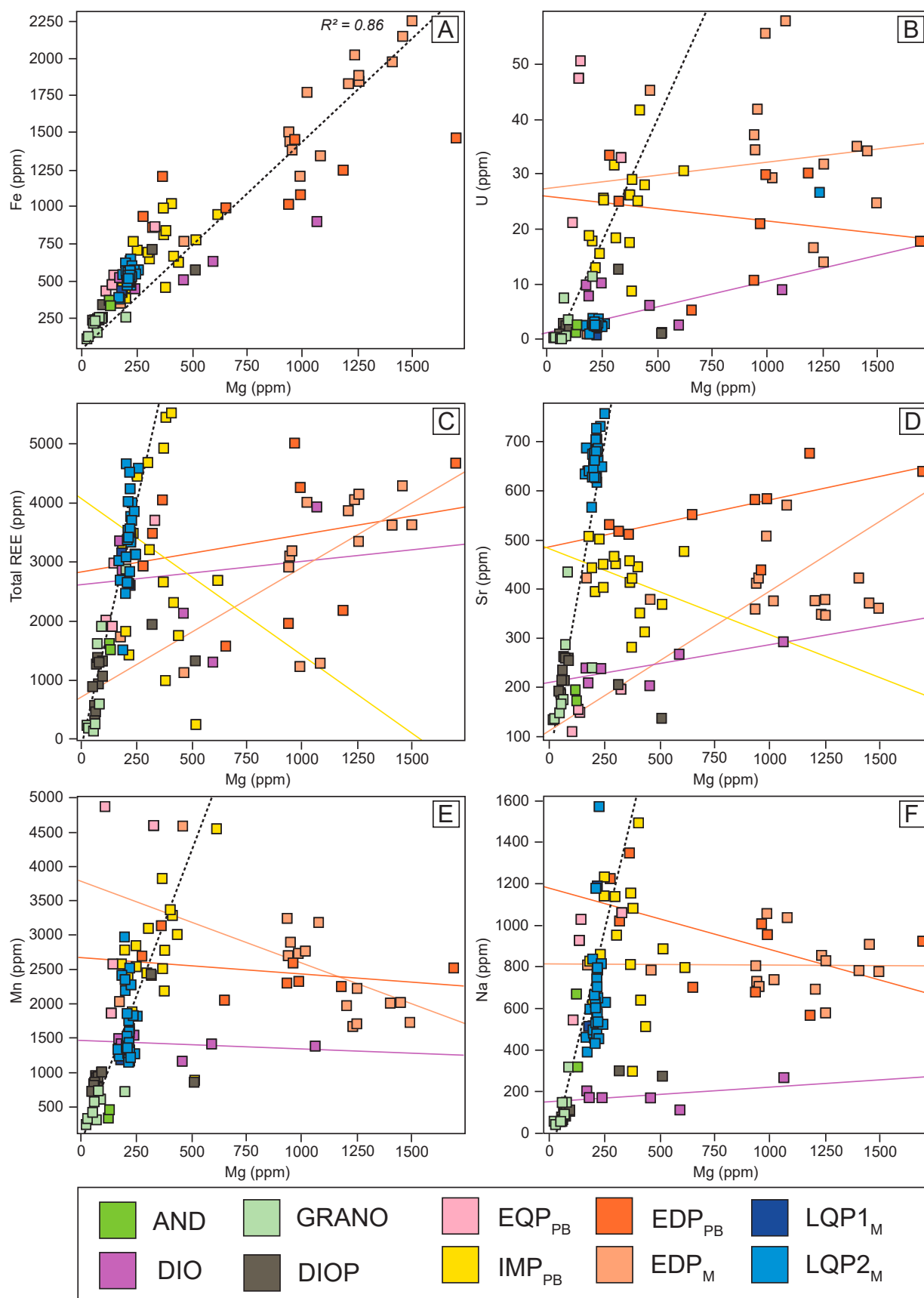


Figure 6.11 Comparison of least altered Ap_{mix} compositions plotted against Mg concentrations in apatite which is proportional to melt Mg. Analytical error is smaller than the symbol size. Ordinary least square regressions are plotted for individual units (coloured) or grouped units (black dashed line). A) Concentrations of Fe have a strong negative correlation with Mg, R^2 values of 0.86. B-E) Concentrations of U, total REE, Sr, Mn and Na have a weaker correlation ($R^2 < 0.40$). Apatites from EDP_M, EDP_{PB}, DIO and IMP_{PB} have high Mg concentrations that have a weaker correlation to Mg ($R^2 < 0.1$).

Several studies have demonstrated the sensitivity of apatite composition to magma evolution and petrogenetic processes. The changes in the minor element concentration in apatite have been linked to magma differentiation and are inferred to be controlled by crystallisation of other phases (Hsieh et al. 2008; Chu et al. 2009; Cao et al. 2012; Broska et al. 2004). In this study Fe has a strong negative correlation with Mg concentration in apatite ($R^2 = 0.86$; Fig. 6.11A). This is inferred to reflect differentiation of ferro-magnesium minerals during apatite crystallisation. Phenocrysts of amphibole and biotite with inclusions of apatite are common in the samples, albeit now pseudomorphed. As a result, higher Fe concentrations in apatite within a unit are produced from earlier crystallisation within the melt.

By comparison, correlations of other cations with Mg in apatite are not as robust (R^2 is low, typically < 0.4); in particular apatite from DP_{PB} , EDP_M , and $DIOP$ show varying slope gradients with low R^2 values, this is a result of high Mg concentrations (Fig. 6.11B-E). The more Mg-rich apatites show no significant change in concentrations of elements such as Mn, Sr and total REE with decrease in Mg. This suggests that early apatites in these units crystallised before significant differentiation of phases rich in these elements, but during crystallisation of Mg-rich phases. Despite the weaker trends, most elements, such as Mn (Fig. 6.11B) show negative correlations with Mg. Apatites from late porphyries have a large range in Mn concentration with little change in Mg. These trends are visible within Ap_{incl} and Ap_{mtrx} ; however, comparisons between Ap_{mtrx} and Ap_{incl} should be made with care due to the potential for diffusion in Ap_{mtrx} (see Chapter 5). Other elements, such as Sr show little correlation with Mg concentrations (Fig. 6.11C). Concentrations of ΣREE decrease in apatite with lower Mg concentrations (Fig. 6.11D); however, the trajectories of the REE ratios with Mg concentrations vary between units (Fig. 6.11E). This suggests that the crystallisation of REE-phases are driving melt evolution but that the assemblages differ between units.

6.5 Effect of plagioclase crystallisation on apatite composition

Concentrations of Sr in apatite show little change with melt differentiation (Fig. 6.11A). In addition, Sr in Ap_{incl} produces a clear separation between mineralised, less mineralised and host rock units (Fig. 6.8A). Plagioclase is one of the main hosts from Sr and its crystallisation can significantly deplete the residual melt of Sr (Chiaradia 2015; Belousova et al. 2002). Therefore, the timing of plagioclase crystallisation relative to apatite could explain some of the patterns in Sr concentrations observed. However,

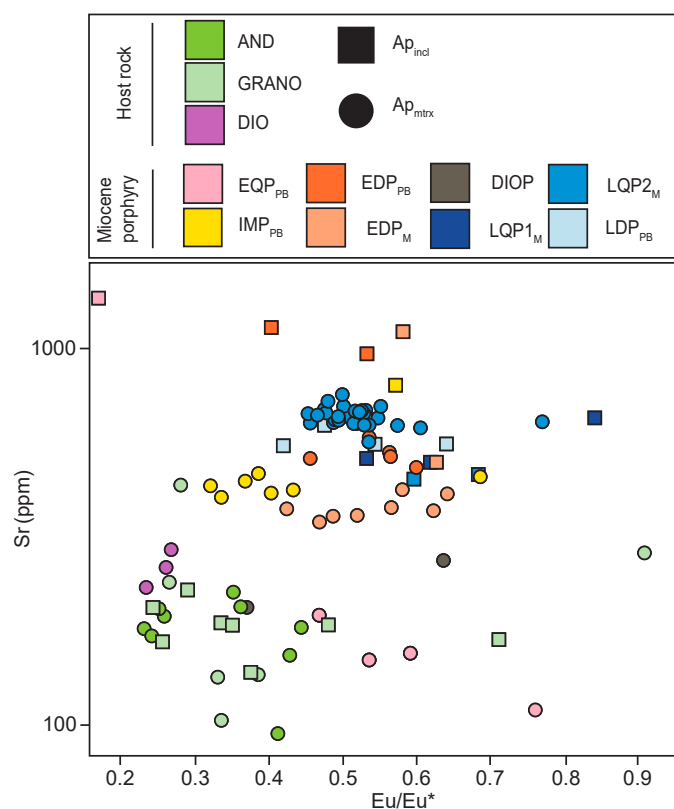


Figure 6.12 Sr concentrations against Eu/Eu^* in Ap_{mtrx} and Ap_{incl} show little correlation. Analytical error is smaller than symbol size.

modelling Sr behaviour in the melt is problematic as it is mobilised in the bulk rock from alteration (Table 4.7) and plagioclase crystals, the composition of which are needed to determine accurate Sr partitioning coefficients (Blundy & Wood 1991), have all been significantly altered. In place of Sr in apatite, Eu/Eu* which is less mobile in both bulk rock and apatite (see *Chapters 4 and 5*) can be used to model the effect of plagioclase crystallisation on apatite and to determine the relative timing of each. Concentrations of Sr varies significantly between units for a given Eu/Eu* (Fig. 6.12).

6.5.1 Effect of oxidation state and plagioclase crystallisation on Eu/Eu*

Eu partitioning between apatite, melt and plagioclase

The partitioning of Eu into apatite does not correspond to the partitioning of other REE because although Eu²⁺ is preferentially incorporated in the apatite structure, Eu is present as both trivalent and divalent cations in the melt. Therefore, the Eu content of apatite is a function of Eu³⁺/ΣEu. This ratio can be described as a function of temperature and oxygen fugacity at a fixed pressure (Burnham et al. 2015) as:

$$\frac{Eu^{3+}}{\Sigma Eu}^{melt} = \frac{1}{1 + 10^{-0.2510g_2 - \frac{6410}{T} - 14.2\Delta + 10.1}} \quad \text{Eq. 6.6}$$

The melt parameters can be expressed as the optical basicity (Δ; Duffy 1993). This cannot be calculated accurately from altered rocks so an average value from previous studies of similar rock compositions was used (Δ = 0.6). A temperature (T, in Kelvins) of 900 °C was used although in this relationship temperature has a negligible effect compared to oxygen fugacity. In addition, through comparison to Ce, another multivalent REE, pressure is hypothesized to also not have a significant effect at crustal pressures (Burnham & Berry 2012). According to Eq. 6.6 the proportion of Eu³⁺ in a melt increases with oxidation and with a decrease in temperature and melt polymerisation. Lower Eu³⁺/ΣEu in the melt will produce a more negative Eu anomaly or smaller Eu/Eu*.

Furthermore, the negative Eu anomalies can be produced by plagioclase crystallisation. Although the partitioning of Eu into plagioclase is much lower than for apatite (Table 6.6), plagioclase will crystallise in much higher abundance depleting ΣEu and therefore lowering Eu²⁺. As D^{Eu²⁺} for plagioclase is typically higher than D^{Eu³⁺}, the effect of plagioclase crystallisation on Eu/Eu* in apatite is lesser at more reduced melt conditions. The partition coefficient for an element (i) between a mineral and melt phase is the ratio of its concentration in the two:

$$D_i = \frac{C_i^{mineral}}{C_i^{melt}} \quad \text{Eq. 6.7}$$

Mineral-melt partition coefficients for Eu can be calculated from:

$$D_{Eu} = \frac{D_{Eu^{3+}} + \left(\frac{Eu^{2+}}{Eu^{3+}}\right)_{melt} D_{Eu^{2+}}}{\left(\frac{Eu^{2+}}{Eu^{3+}}\right)_{melt} + 1} \quad \text{Eq. 6.8}$$

here Eu²⁺/Eu³⁺_{melt} is the ratio of Eu valence states in the melt and D_{Eu}²⁺ and D_{Eu}³⁺ are the partition coefficients of Eu²⁺ and Eu³⁺. The similar ionic radii of Eu²⁺ and Sr²⁺ means that D_{Eu}²⁺ can be assumed to be the same as D_{Sr} (Table 6.6; Prowatke & Klemme 2006; Nielsen et al. 2017) and D_{Eu³⁺} can be estimated by interpolation from its neighbouring trivalent REE ((D_{Sm} * D_{Gd})^{0.5}).

The effect of the crystallisation of minerals on melt composition is comparable

to fractional crystallisation. Although these minerals may not be removed physically from the melt (so not impacting bulk magma composition), they can be considered to be no longer interacting with the melt. Thus, for elements where the bulk D is not equal to 1, crystallisation produces an exponential change in the residual melt composition over time as described by the Rayleigh fractionation equation:

$$C_l = C_o F^{D-1} \quad \text{Eq. 6.9}$$

Here D is the partition coefficient, F is the fraction of melt remaining, C_o is the concentration of an element in the initial melt, C_l is the concentration in the final melt. The partition coefficient, describes how an element behaves during equilibrium between two phases. Equilibrium between apatite, plagioclase and the melt is assumed as there is no evidence to the contrary.

Based on this approach, the effects of plagioclase crystallisation on coeval apatite composition were modelled over a range of oxidation states (FMQ+2, FMQ+1, FMQ, and FMQ-1) using the Rayleigh fractionation equation (Eq. 6.9). The amount of plagioclase crystallisation was modelled between 0 and 50 % based on sample petrography (see section 4.2). As plagioclase crystallises earlier than most REE-phases within melt, Eu_{met} was assumed as bulk rock Eu . The details of the model are provided in *Appendix F*.

Results

The calculated Eu anomaly for each lithology and modelled condition is given in Fig 6.13. As predicted, an increase in plagioclase crystallisation produces a lower Eu/Eu^* in co-crystallising apatite and an increase in oxidation state results in a higher Eu/Eu^* . Modelled Eu/Eu^* is compared to Ap_{mtx} and Ap_{incl} . Apatites from DIO, DIOP and AND have the lowest Eu/Eu^* values, which can only be reproduced with low to moderate degrees of plagioclase crystallisation from relatively reduced melts (most scenarios <FMQ). Apatites from GRANO have a wide range in Eu/Eu^* values which could reflect apatite crystallisation over a long period of continued plagioclase crystallisation.

Table 6.6 Mineral-melt partition coefficients for REE and Sr at upper crustal P - T conditions.

	Apatite		Zircon	Titanite	Hornblende	Plagioclase	
	Sano et al. 2002	Prowatke & Klemme (2006)	Sano et al. 2002	Bachman et al. 2005	Klein et al. 1997	Dunn & Senn (1994)	Nielsen et al. (2017)
	Dacite	Andesite	Dacite	Rhyolite	Andesite	Basaltic Andesite	Basalt
La	36	16.6	0.00046	113	0.37		
Ce	48	18.1	0.36	223	0.73		
Pr	64	20.6	0.0172	377*	0.73*		
Nd	77	23.0*	0.077	639	0.73		
Sm	93	25.7	0.8	930	2.01	0.038	
Eu	Eq. 6.8		1.22	661	1.33	Eq. 6.8	
Gd	127	21.5	8	855	2.3	0.067	
Tb	102		20.7	894*	2.49*		
Dy	76		45.9	935	2.68		
Ho	62		80	771*	2.58*		
Er	57		136	636	2.47		
Tm	53		197	500*	2.29*		
Yb	48		277	393	2.1		
Lu	33	3.01	325	300	1.7*		
Sr		1.37					1.38

*For elements missing from the literature, values have been interpolated from the neighbouring coefficients.

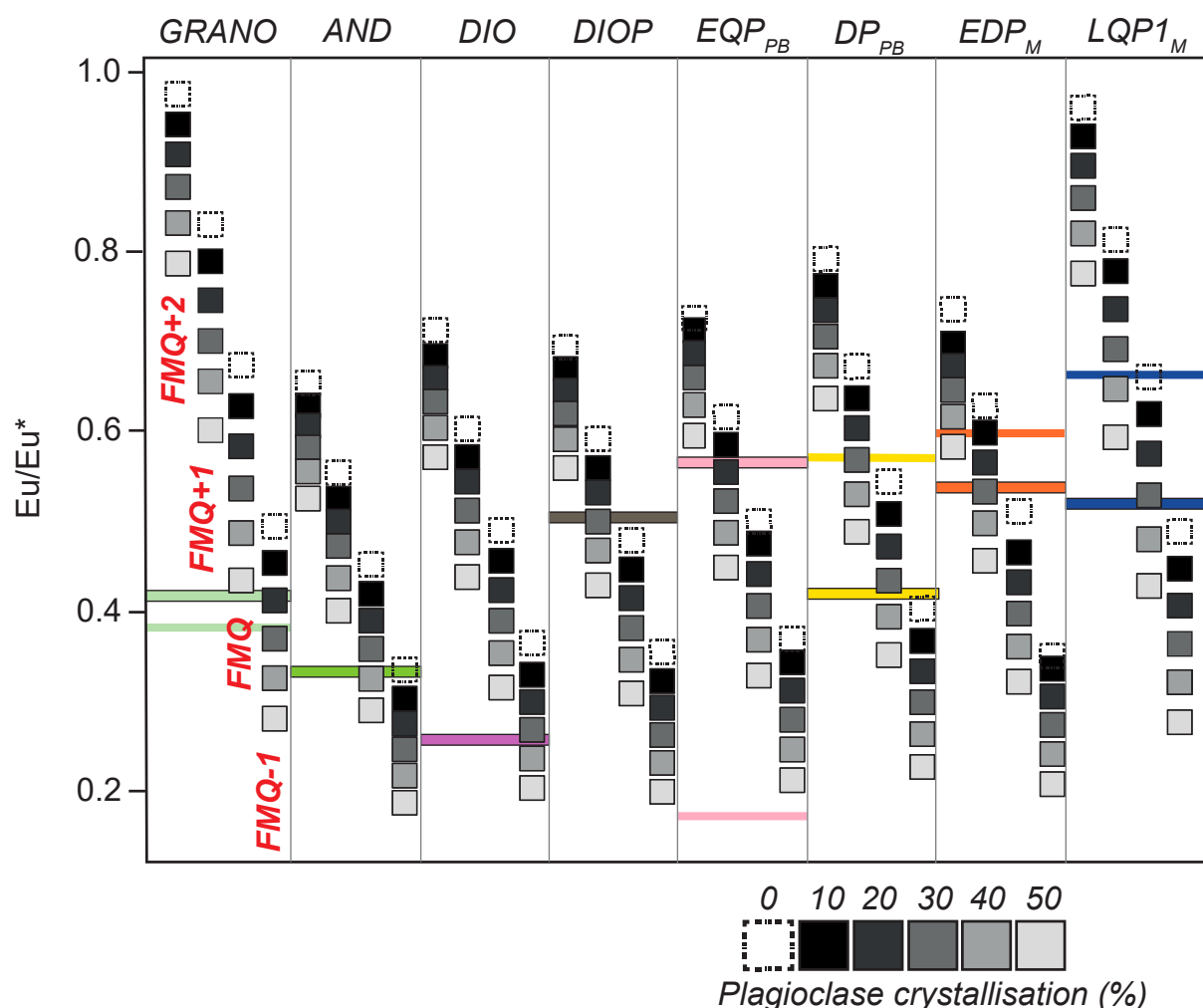


Figure 6.13 Modelled Eu/Eu^* in apatite as a function of variable degrees of plagioclase crystallisation (0 – 50 %) and oxidation state (FMQ+2, FMQ+1, FMQ, FMQ-1). Bulk rock Eu/Eu^* is used as the starting melt. $\text{Eu}^{3+}/\Sigma\text{Eu}$ and Eu mineral-melt partition coefficients are calculated from Burnham et al. (2015) using values from Prowatke & Klemme (2006), Dunn & Senn (1994) and Nielsen et al. (2017). Coloured boxes reflect mean Eu/Eu^* of apatites (Black outline – Ap_{mtr} , no outline – Ap_{inc}).

Modelled Eu/Eu^* values for porphyry units (apart from DIOP) are consistent with melt $f.\text{O}_2$ of between FMQ and FMQ+2 with the higher $f.\text{O}_2$ values requiring greater degrees of plagioclase crystallisation.

The range in oxygen fugacity predicted by the models spans the range expected from a typical oxidised porphyry to a mildly reduced melt. If melt $f.\text{O}_2$ is between FMQ+1 to FMQ+2, as comparable to other porphyry systems (Audétat & Simon 2012; Sillitoe 2010; Richards 2003), then the high abundance of plagioclase observed in the porphyry units (~40 % in dacite porphyries) appears to have formed mostly prior to or during apatite crystallisation. This is consistent with plagioclase occurring predominantly as coarse phenocrysts (see section 4.2). However, the host rocks require a more reduced melt ($f.\text{O}_2$ between FMQ to FMQ-1) to produce the lower Eu/Eu^* with the abundance of observed plagioclase. This is towards the lower end of reported $f.\text{O}_2$ for arc magmas; the mantle wedge source has an oxidation state of FMQ+1 $\pm$ 1 (Richards 2015). However, for DIO and AND where Eu/Eu^* is lowest, a more mafic, less polymerised melt would also increase $\text{Eu}^{2+}/\text{Eu}^{3+}_{\text{melt}}$, aiding production of a lower Eu/Eu^* in apatite (Burnham et al. 2015).

6.5.2 Strontium concentrations in apatite

The timing of apatite saturation relative to plagioclase is primarily controlled by the aluminosity of

a melt. The solubility of apatite is higher in peraluminous melts compared to metaluminous melts (Harrison & Watson 1984; Bea et al. 1992). Typically, apatite is under-saturated in a melt, and plagioclase will crystallise first, raising P/Ca of the residual melt (London 1997; Piccoli & Candela 2002) to the point at which apatite begins to crystallise. Despite the issues surrounding the use of bulk rock analyses in altered porphyry rocks, Eu/Eu^* in Ap_{mtrx} produces a weak negative correlation with $\text{CaO}_{\text{bulk rock}}$ (slope of -0.16 with R^2 of 0.51) and a weaker positive trend with $\text{SiO}_{2\text{bulk rock}}$ (Fig. 6.14A-B). The trend between Ap_{mtrx} of the host rock and porphyry units differ slightly reflecting the influence of melt $f\text{O}_2$. This suggests that, assuming comparable $f\text{O}_2$ and melt Eu/Eu^* , such as is the case between EQP_{PB} and EDP_{PB} , Ap_{mtrx} from EQP_{PB} crystallised following lower amounts of plagioclase crystallisation Ap_{mtrx} from EDP . This is largely a result of low melt CaO and high SiO_2 , encouraging early crystallisation of apatite relative to plagioclase and resulting in higher Eu/Eu^* . This matches petrological observations of low proportions of plagioclase phenocrysts in EQP_{PB} .

Strontium in apatite produces comparable results: Sr concentrations in apatite produce a negative correlation with $\text{CaO}_{\text{bulk rock}}$ (slope of -80.15; Fig. 6.14C). An opposite correlation is present between Sr_{Ap} and $\text{SiO}_{2\text{bulk rock}}$ (slope of 4.36; Fig. 6.14D) as implied by the controls on apatite saturation (Eq. 6.4). The partitioning of Sr into plagioclase is strongly dependant on its endmember composition, with Ca-rich anorthite incorporating less Sr into its crystal structure than albite (Blundy & Wood 1991). The determination of the crystallising plagioclase phase is linked to many factors including CaO, Al_2O_3 and H_2O of the melt (Panjasawatwong et al. 1995). This makes it difficult to compare Sr in apatite between the altered intrusions without prior knowledge of the plagioclase composition. However, Ap_{mtrx} from EQP_{PB} , DIOP and GRANO fall below the Sr_{Ap} -CaO trend. Given the previous inferences about plagioclase crystallisation in EQP_{PB} , one solution could be a higher D^{Sr} for plagioclase. This can be the result of a more Na-rich composition or an increase in temperature (Blundy & Wood 1991). Albite plagioclase is favoured by lower melt CaO and Al_2O_3 (Panjasawatwong et al. 1995) which are both observed in bulk rock (see section 4.5).

In most lithologies, Sr concentrations are comparable between Ap_{mtrx} and Ap_{incl} ; however, there is an increase in concentrations in apatites from EDP lithologies, especially from earlier (Mg-rich) Ap_{mtrx} (Fig. 6.11C). Although care must be taken when interpreting changes in Sr concentrations between Ap_{mtrx} and Ap_{incl} (as discussed in Chapter 5), this observation is also supported by comparable Eu/Eu^* of Ap_{mtrx} and Ap_{incl} (Fig. 6.12). Together these imply there was limited plagioclase crystallisation between Ap_{mtrx} and Ap_{incl} . A hiatus in plagioclase crystallisation could be responsible for an increase in Sr with melt differentiation. Where Ap_{mtrx} and Ap_{incl} crystallise coevally, such as in GRANO or late porphyries, Sr concentrations are of similar concentrations (Figs. 6.11C; Fig. 6.12). In another study by Cao et al. (2012), higher Sr contents are reported in apatite present as finer crystals within the groundmass of porphyries compared to apatite present as microphenocrysts as in early inclusions of biotite and hornblende. This trend also goes against that expected by normal fractionation and is comparable to the observations made in this study. The crystallisation of early apatite in EDP_{PB} and EDP_{M} ($\text{Mg}_{\text{Apatite}}/\text{Mg}_{\text{bulk rock}} \sim 0.1$) suggest that initial melt composition has a sufficiently low P/Ca ratio and aluminosity for plagioclase and then apatite to crystallise before significant melt differentiation.

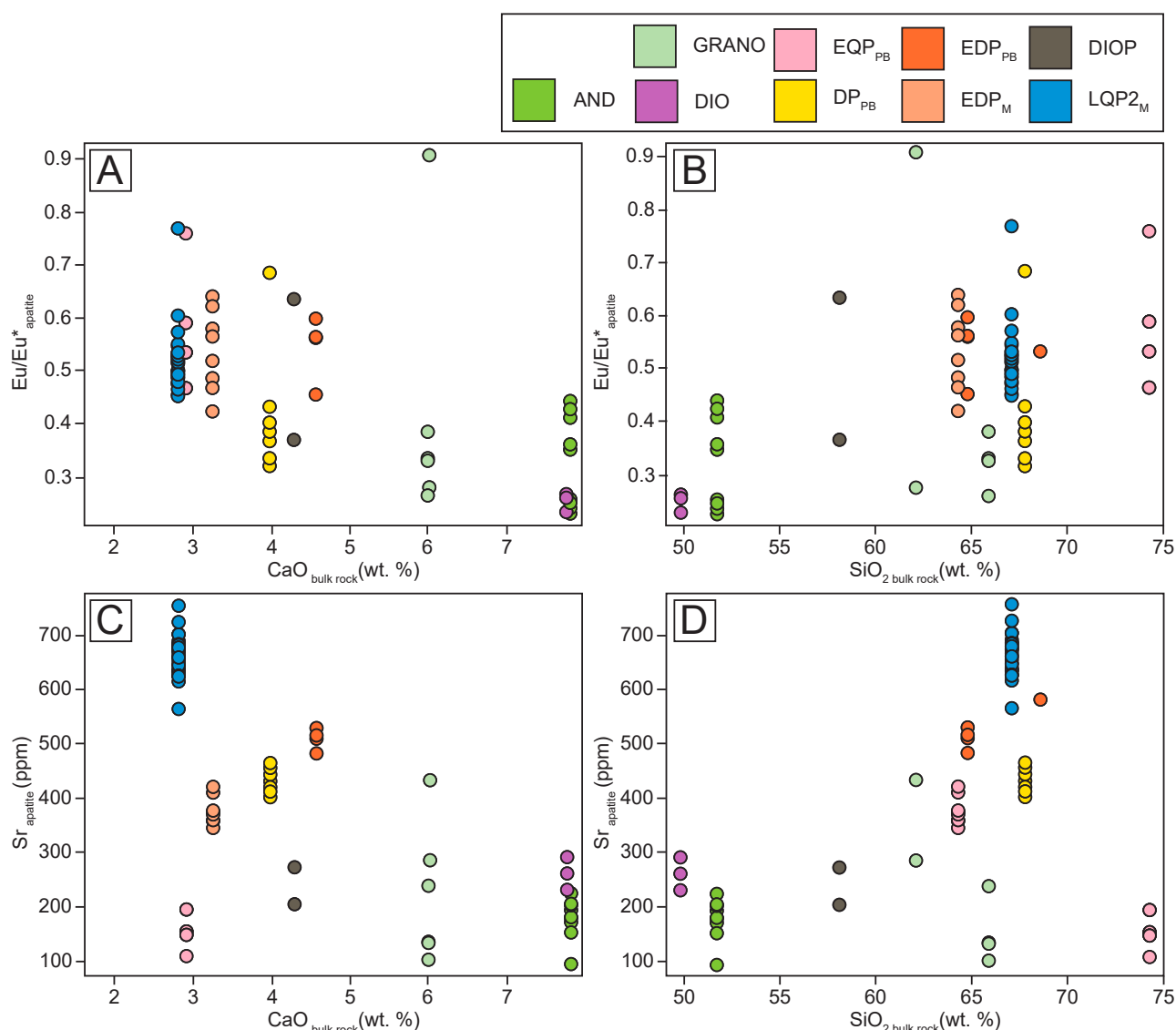


Figure 6.14 Eu/Eu^* in Ap_{mtx} A) with bulk rock CaO and B) bulk rock SiO_2 ; C-D) Sr concentration in apatite with bulk rock CaO and SiO_2 ; however, apatite from EQP_{PB} and $DIOP$ have lower Sr concentrations. Analytical error is smaller than symbol size.

6.6 Effects of co-crystallising REE-phases on apatite composition.

Rare earth element rich accessory phases, such as zircon and titanite, compete for REE and therefore influence the uptake of REE in apatite by modifying the local melt composition, especially with respect to the HREE in which apatite is not as strongly enriched. Through modelling the effect of this competition, the differences in REE trends between lithologies with magma differentiation could be explained (Fig. 6.11E).

6.6.1 Method

Titanite preferentially incorporates LREE into its structure and is more REE-enriched than apatite by up to an order of magnitude. Conversely, zircon is HREE-enriched and is typically more enriched than apatite in these elements. Apatite crystallisation itself will progressively modify the local melt so that later apatite growth stages may be relatively LREE-depleted (Fig. 6.15). The effect of the crystallisation of these phases on the melt composition can be described using *Eq. 6.9*; however, when modelling mineral assemblages a bulk distribution coefficient ($\bar{D}$) must be used in place of D . The bulk distribution coefficient describes the overall behaviour of an element within an assemblage

and is the sum of the product of the phase abundance (X) and partition coefficient:

$$\bar{D} = \sum(X_i \cdot D_i^{\frac{X_i}{\sum X_i}}). \quad \text{Eq. 6.10}$$

Therefore, although titanite has higher bulk partition coefficients, it is observed in lower final abundance than apatite (see section 4.4) so may have a smaller effective $\bar{D}$ than greater amounts of apatite. Likewise, hornblende, although not a REE-rich phase (Table 6.6), will crystallise in significant quantities as to influence HREE concentrations in the residual melt.

The largest source of uncertainty in partitioning models comes from the selection of partition coefficients (Table 6.6). For REE in apatite these vary with P, T, oxygen fugacity, melt and mineral composition. The partitioning of REE into apatite has been shown to increase with a decrease in temperature (Watson & Green 1981; Khudolozhkin et al. 1973; Shironosova & Kolonin 2012). Higher partition coefficients were derived from analyses of natural dacite samples (Sano et al. 2002) than from experimentally-derived coefficients using andesite melt at 1250 °C and 100 MPa (Prowatke & Klemme 2006; Table 6.6) which could be due to any of these controls. However, ratios of the partition coefficients are comparable between the two datasets and produce similar model outcomes at degrees of crystallisation comparable to abundances observed in the samples (Table 6.7) so ratios of the partition coefficient can be considered to be more reliable.

6.6.2 Results

La/Yb – Gd/Yb ratios in least altered magmatic apatites, apatite inclusions in zircon for host rock (GRANO), inter-mineralisation (DP_{PB}), mineralised porphyry unit (EQP_{PB} , EDP_M , EDP_{PB}) and late porphyries ($LQP1_M$, $LQP2_M$) are compared in figure 6.16. In addition, apatite-equivalent zircon compositions have been calculated as apatite in equilibrium with a calculated melt in equilibrium with zircon, using partition coefficients in table 6.6 (Zircon data provided in *Appendix C*).

La/Yb and Gd/Yb vectors were modelled for apatite, zircon, and titanite crystallisation. By plotting ratios with the same denominator on a logarithmic scale, fractionation vectors which do not depend on the starting position can be compared to trajectories present in the mineral compositions. All trajectories present within apatite appear to suggest crystallisation within a melt with differentiation dominated by apatite with minor zircon (Fig. 6.16). Compositions of Ap_{mtx} and Ap_{incl} in GRANO and late porphyries are comparable and do not show strong differentiation trends. By contrast, Ap_{mtx} and Ap_{incl} compositions within inter-mineralisation and mineralised porphyries appear to follow two different evolution trends. The fractionation vectors imply an initially apatite-dominated assemblage with zircon, followed by a hiatus in recorded apatite crystallisation before Ap_{incl} crystallisation. The apatite equivalent zircon compositions sit between La/Yb and Gd/Yb ratios for Ap_{mtx} and Ap_{incl} .

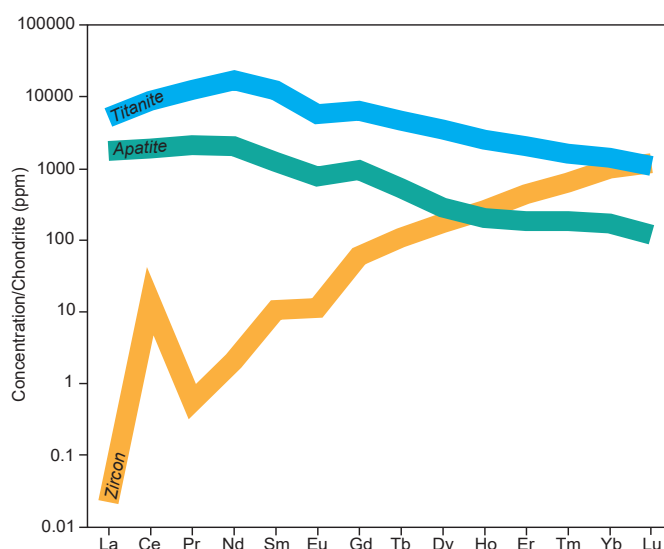


Figure 6.15 Typical chondrite-normalised REE patterns of apatite, zircon and titanite.

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Table 6.7 Modelled La/Sm apatite compositions calculated using apatite-melt partition coefficients from Sano et al. (2002) and Prowatke & Klemme (2006) over a range of apatite crystallisation (0.02 – 0.1 %). Starting melt composition based on average least altered bulk rock compositions.

Ap. crystallisation (%)	Sano 2002					Prowatke & Klemme 2006				
	0.02	0.04	0.06	0.08	0.1	0.02	0.04	0.06	0.08	0.1
GRANO	1.3	1.5	1.7	1.9	2.1	2.0	2.0	2.1	2.1	2.2
AND	1.8	2.0	2.2	2.5	2.8	2.7	2.7	2.8	2.8	2.9
DIO	2.0	2.2	2.5	2.8	3.1	3.0	3.0	3.1	3.2	3.2
DIOP	1.9	2.1	2.4	2.7	3.0	2.9	2.9	3.0	3.1	3.1
EDP _{PB}	2.0	2.2	2.5	2.8	3.2	3.0	3.1	3.1	3.2	3.3
EQP _{PB}	2.5	2.8	3.1	3.5	3.9	3.7	3.8	3.9	3.9	4.0

The effect of co-crystallisation phases can be quantified by modelling best-fit fractionation assemblages for each unit. In each case the most Mg-rich apatite was used as the starting melt composition as bulk rock cannot be assumed equivalent to melt composition for apatites from all units. The results of these models are provided in *Appendix F* and selective trends are shown in figure 6.17. Apatite from porphyry units EDP_{PB}, EDP_M, DP_{PB} typically match modelled apatite dominated fractionation trends (Fig. 6.17 - yellow line) with most Ap_{mtx} compositions explained by up to 1 % crystallisation of apatite. Ap_{mtx} from EQP_{PB} are best explained by co-crystallisation of apatite and zircon (Fig. 6.17 - pink line). Ap_{mtx} compositions match 0.7 % apatite crystallisation and 0.3 % zircon crystallisation from the melt. Apatite evolution from the late porphyries match modelled apatite-dominated crystallisation with minor zircon (~0.05 – 0.1 % crystallisation; Fig. 6.17 - blue line). Crystallisation of titanite is not required to explain the trends observed; however, some minor (~ 0.5 %) crystallisation can be incorporated into models for EQP_{PB} to explain the low Σ REE. In addition, the low Σ REE observed in apatite from GRANO (Fig. 6.9) may be explained by titanite crystallisation.

Ap_{incl} and Ap_{mtx} from late porphyries lie on the same fractionation trend supporting the hypothesis of overlapping periods of crystallisation. Ap_{incl} from EQP_{PB} can be explained by further melt differentiation, but lies along the same differentiation trend. Ap_{incl} from EDP_{PB}, EDP_M and DP_{PB} lie on a more HREE-depleted trend. Crystallisation of ~0.3 % zircon is required to increase Dy/Yb ratios without depleting Σ REE. In fact, an increase in Σ REE is observed with magma differentiation for most Ap_{incl} (Fig. 6.11D). An increase in REE concentration in the melt could be produced by a hiatus in the crystallisation of REE-rich phases. Assuming Ap_{incl} directly follows Ap_{mtx} crystallisation, around half the residual melt would need to be crystallised to increase REE concentrations in apatite from approximately 300 ppm to a maximum of 6000 ppm. Alternatively, or additionally, REE partitioning coefficients could be increased from polymerisation of the melt and a decrease in temperature (Watson & Green 1981; Prowatke & Klemme 2006). Changes in temperature between Ap_{mtx} and Ap_{incl} crystallisation are limited given AST and Ti-in-zircon calculations (Table 6.5). However, assuming partitioning of REE into apatite increases uniformly with SiO₂ of the melt, partitioning of REE into apatite could be doubled with just over a 5 wt. % increase in SiO₂ for comparable bulk rock compositions (Watson & Green 1981; Prowatke & Klemme 2006). Complex modelling to account for possible changes in partition coefficients with magma differentiation is beyond the scope of this study. Ultimately these results supports the interpretation that Ap_{mtx} and Ap_{incl} during different periods in the melt evolution but that these were much more similar for apatites crystallising within GRANO and late porphyries

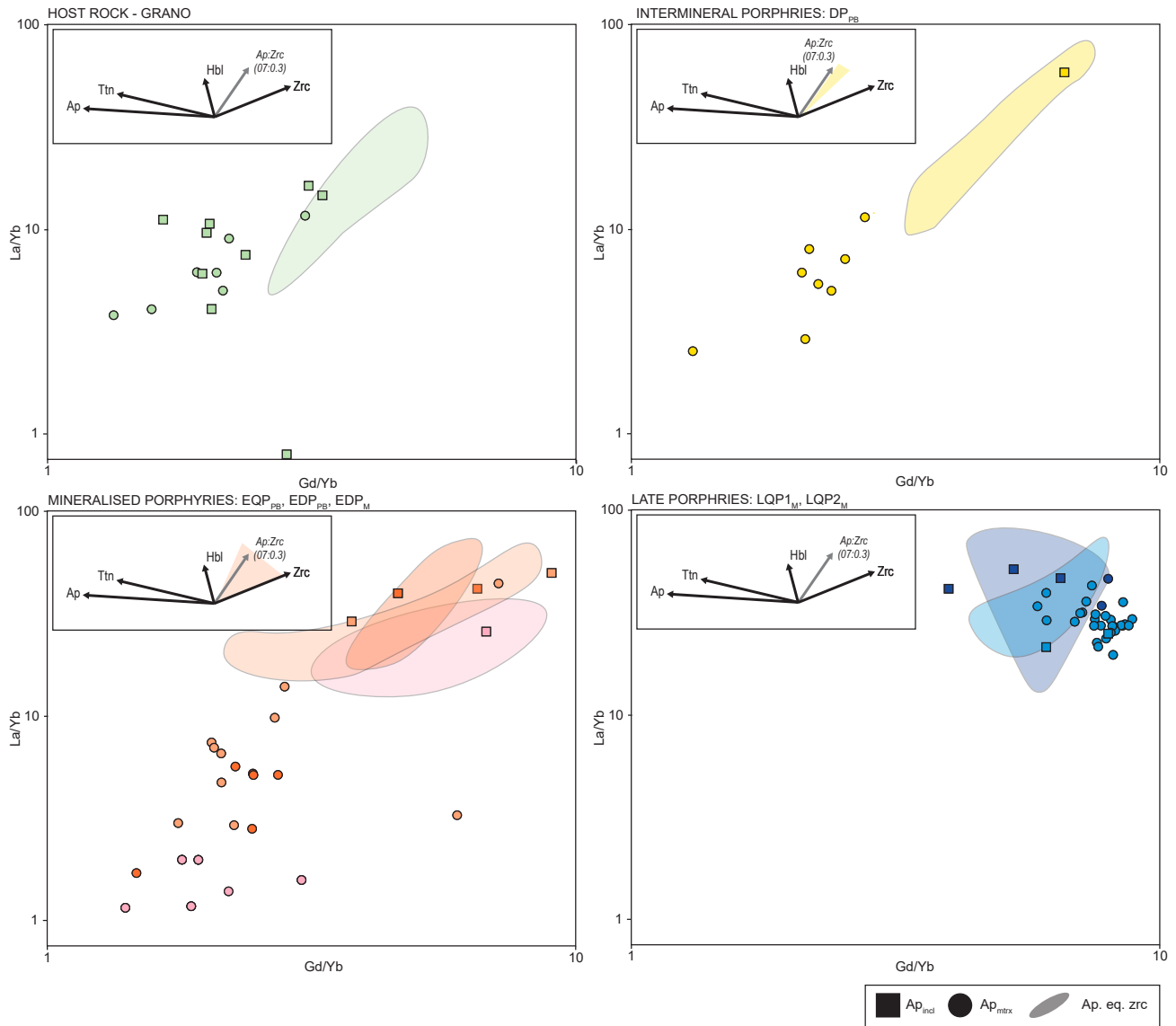


Figure 6.16 La/Yb – Gd/Yb compositions of Ap_{mtr} (squares), Ap_{incl} (circles), and apatite equivalent zircon compositions (shaded area) or different intrusive phases at La Granja. The fractionation trend produced from crystallisation and apatite, zircon, hornblende and titanite and an apatite-zircon assemblage (0.7:0.3) are shown. In addition, where analyses form a clear trend (intermineral and mineralised porphyries), the vector is also described. Partition coefficients from Sano (2002), Bachman et al. (2005) and Klein et al. (1997).

The effect of allanite and monazite, which are LREE-rich, and xenotime which is HREE-rich, were not modelled as they were not observed in petrographic studies and SEM bright scans as a magmatic phase (see section 4.4). Monazite is observed with apatite; however, this is interpreted to be part of an alteration assemblage. Xenotime fractionation would have a similar compositional effect as zircon; however, its presence in much smaller concentrations would result in any changes being negligible in comparison. In addition, the crystallisation of allanite in other porphyry systems has been attributed to upwards convex LREE curves in apatite similar to those seen in DP_{PB} , EDP_{PB} , EDP_M , $LQP1_M$, $LQP2_M$ (Fig. 6.5: Cao et al. 2012). As a corresponding La depletion is not observed in the bulk rock, allanite may also be present in these samples.

6.7 Inferring melt composition from apatite chemistry

Reliable estimation of melt compositions from magmatic apatite in this study is hindered for many elements by metasomatism of the microphenocrystic apatite grains (Fig. 6.9). In Chapter 5 it is

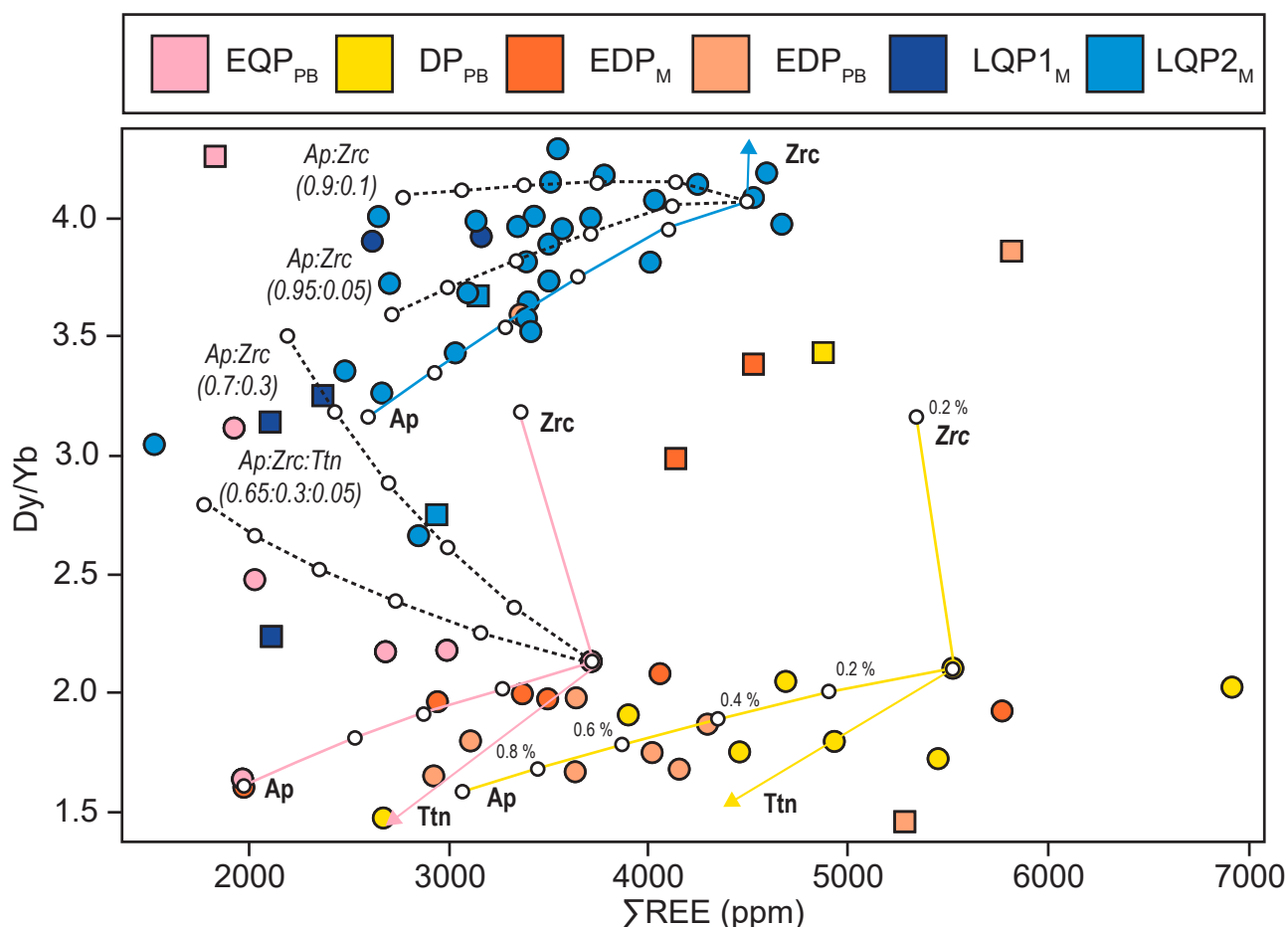


Figure 6.17 Modelled fractionation trends for apatite crystallisation using partition coefficients from Sano (2002) and Bachman et al. (2005). Fractionation was modelled from most Mg-rich apatite composition in each case. REE evolution of Apmtrx from EDP_{PB} , EDP_M and DP_{PB} can be explained melt differentiation dominated by apatite crystallisation. Apmtrx and Ap_{incl} compositions from EQP_{PB} are best fit by models of co-crystallising apatite with zircon. Both Apmtrx and Ap_{incl} from $LQP1_M$ and $LQP2_M$ are explained by apatite crystallising with minor amounts of zircon

shown that post crystallisation re-equilibration of Cl and S can occur in magmatic apatite grains, even those that otherwise appear unaltered (alteration score of 0). Thus, only elements resistant to diffusional modification can be considered with respect to microphenocryst data, or those elements that can be reliably determined in the small, zircon-hosted apatite inclusions (Ap_{incl}).

6.7.1 Sulfur content of the melt

The low S content of Ap_{incl} from Eocene rocks (Fig. 6.7B; Table 6.3) may simply reflect low S_{melt} in these magmas at the time of zircon (and apatite) crystallization. However, the S_{Ap}/S_{WR} ratio is also very low – at least relative to the porphyry rocks (0.003 and 0.03 respectively), despite the effect of hydrothermal addition of sulfide to the porphyry rocks which would serve to artificially lower their bulk rock S_{Ap}/S_{WR} ratios. Thus, it is possible that the partition coefficient D_{Ap}^S was lower in the older magmas. Given the role of sulfur speciation in apatite-melt partitioning (S^{6+} partitions more freely into the apatite structure; Konecke et al. 2017), it is suggested that there could have been a higher S^{2-}/S^{6+} ratio in the Eocene melts. Because magma oxidation state exerts a strong control on S valence states (between FMQ and FMQ+2 the proportion of S^{2-} to S^{6+} changes rapidly; Botcharnikov et al. 2010; Jugo et al. 2010), the Ap_{incl} data can be explained by more reduced magmas in the Eocene (~FMQ, where less than 5 % of total S is silicate; Jugo 2009) and more oxidized magmas (~FMQ

+2), where the majority of sulfur is present as S^{6+} , for the Miocene mineralised intrusions. These suggested differences magma redox states are consistent with the Eu partitioning models presented above, which propose a more oxidised mineralised porphyry magmas (FQM to FQM+2) and more reduced Eocene and DIOP magmas ($\leq$ FMQ; Fig. 6.13). Despite this, it is important to note that the effects of variable S_{melt} and melt $f.O_2$ are difficult to deconvolve using apatite chemistry alone.

The partitioning of S between an oxidised melt and apatite increases with decreasing temperature and is independent of pressure (Peng et al. 1997). S_{melt} in equilibrium with apatite can be estimated using a non-Henrian partitioning relationship defined in Parat et al. (2011) that uses natural and experimental data from Baker & Rutherford (1996), Parat & Holtz (2004, 2005), and Parat et al. (2011):

$$S_{apatite}(wt. \%) = 0.0629 \cdot \ln S_{melt}(wt. \%) + 0.4513 \quad \text{Eq. 6.11}$$

here the uncertainty (σ_s^{melt}) is propagated from analytical error (σ_s^{Ap}) derived from EPMA software (see Chapter 3):

$$\sigma_s^{melt} = 0.0629 \cdot \frac{\sigma_s^{Ap}}{S_{melt}} \quad \text{Eq. 6.12}$$

This relationship assumes all S is present as S^{6+} which is the principal form substituted into apatite; underestimation of S_{melt} will occur in the case of more reduced magmas where significant S^{2-} is present. As a result, S_{melt} calculations are only applied to porphyry-related apatite and $f.O_2$ was assumed to remain approximately constant for these magmas. The temperature conditions of the experimental dataset overlap with the temperature range inferred for La Granja (Table 6.5).

Calculated values of S_{melt} from Ap_{incl} are given in table 6.8 and range from 10's to 10000's ppm. S_{melt} greater than 0.1 wt. % are outside the recommended application range of Eq. 6.11 and are highlighted. S_{melt} concentrations overlap between intrusions but are highest and most variable in the mineralised EDP at Paja Blanca (Fig. 6.18). The large range in calculated S_{melt} could reflect temporal variations in the melt, such as localised crystallisation of phases, or variation in S_{melt} with time. Unfortunately, Ap_{incl} are too small for core-rim comparison, and there are limited occurrences of multiple apatite inclusions within a zircon. Instead, apatite composition can be plotted against tracers of melt differentiation, as Mg is often below detection limits in EPMA, concentrations of Fe are used instead. Fe in apatite analysed by LA-ICP-MS shows strong correlations to Mg over wide range of concentrations (Fig. 6.11A).

In LQP1_M and LDP_{PB} the earliest apatite analysed (as inferred by highest Fe contents) has the highest S concentrations, which then decreases with melt differentiation (Fig. 6.19). Within EDP_{PB} high S concentrations do correlated with Fe; however, there is a significant span of S concentrations within set period of melt evolution. In addition, there is a single, high Fe analysis from EDP_{PB} with slightly lower S concentrations. Of note are the low concentrations of S in DP_M which do not show a strong positive correlation between S and Fe concentrations.

Sulfur source and evolution within porphyry units

The low S concentrations in DP_M (the earliest porphyry studied at La Granja; Fig. 4.5) compared to relative high S concentration in the late porphyries suggest that there was a

Chapter 6: Magmatic apatite at La Granja

Table 6.8 Calculated S_{melt} and Cl_{melt} from EMP analysis of Apin_{cl}. U-Pb ages are mean weighted averages from rim analyses of zircons (see 4.3 Zircon geochemistry). S_{melt} calculated using Parat et al. (2011), values underlined indicate S concentrations outside the limit constrained by the equation ($S_{\text{melt}} > 0.1$ wt. %). Cl_{melt} calculated using Li and Hermann (2017) using Ti-in-zircon temperatures of individual grains (Ferry and Watson 2007) or apatite saturation temperatures (AST) calculated from bulk rock geochemistry (Harrison and Watson 1984). Minimum (Min.) and Maximum (Max.) values are calculated using αXCl and αXOH . Cl_{melt} concentrations calculated using XOH-XCl partition coefficients from Li & Costa (2020) are also provided for comparison.

Sample	Lithology	U-Pb age (Ma)	$\sigma^{\text{U-Pb}}$	S_{melt} (ppm)	$\sigma^{S(\text{melt})}$	Cl_{melt} (Li and Hermann 2017)			Cl_{melt} (Li and Costa 2020)	
						Ti-in-zircon			AST	
						Cl_{melt} (wt. %)	Cl_{melt} Min. (wt. %)	Cl_{melt} Max. (wt. %)	Cl_{melt} (wt. %)	Cl_{melt} (wt. %)
EB17041	DIO	34.7	0.49	-	-	0.35	0.19	0.62	0.64	0.45
EB17041	DIO	34.7	0.49	-	-	0.44	0.23	0.84	0.74	0.61
EB17041	DIO	34.7	0.49	-	-	0.42	0.21	0.85	0.77	0.72
EB17041	DIO	34.7	0.49	-	-	0.53	0.23	1.34	0.74	0.67
EB17030	GRANO	34.5	0.78	-	-	0.23	0.10	0.56	0.40	0.36
EB17030	GRANO	34.5	0.78	-	-	0.25	0.11	0.67	0.42	0.39
EB17030	GRANO	34.5	0.78	-	-	0.20	0.09	0.48	0.38	0.37
EB17030	GRANO	34.5	0.78	-	-	0.38	0.14	1.63	0.66	0.83
EB17030	GRANO	34.5	0.78	-	-	0.52	0.16		0.74	0.73
EB17030	GRANO	34.5	0.78	-	-	0.32	0.10	2.83	0.69	0.88
EB17030	GRANO	34.5	0.78	-	-	0.36	0.11	3.03	0.64	0.82
EB17030	GRANO	34.5	0.78	-	-	0.26	0.09	1.05	0.40	0.41
EB17004	DP _M	17.58	0.27			0.35	0.16	0.73	0.64	0.45
EB17004	DP _M	17.58	0.27	60	19	0.31	0.16	0.59	0.54	0.29
EB17004	DP _M	17.58	0.27	32	10	0.30	0.15	0.59	0.52	0.27
EB17004	DP _M	17.58	0.27	32	15	0.32	0.16	0.61	0.43	0.23
EB17004	DP _M	17.58	0.27	38	12	0.29	0.14	0.54	0.47	0.32
EB17037	EDP _{PB}	15.96	0.27	71	23	0.35	0.20	0.58	0.56	0.36
EB17037	EDP _{PB}	15.96	0.27	770	367	0.50	0.23	1.10	0.84	0.78
EB17037	EDP _{PB}	15.96	0.27	<u>1454</u>	693	0.27	0.16	0.43	0.45	0.25
EB17037	EDP _{PB}	15.96	0.27	44	14	0.30	0.17	0.50	0.47	0.29
EB17037	EDP _{PB}	15.96	0.27	23	7	0.28	0.16	0.47	0.47	0.29
EB17037	EDP _{PB}	15.96	0.27	<u>34945</u>	16667	0.21	0.12	0.33	0.33	0.20
EB17037	EDP _{PB}	15.96	0.27	<u>5186</u>	2474	0.19	0.11	0.31	0.30	0.18
EB17037	EDP _{PB}	15.96	0.27	184	59	0.19	0.11	0.31	0.29	0.17
EB17001	EDP _M	15.06	0.26	97	31	0.25	0.12	0.51	0.45	0.37
EB17051	LQP1 _M	14.25	0.26	8	2	0.43	0.22	0.81	0.81	0.79
EB17051	LQP1 _M	14.25	0.26	<u>1454</u>	462	0.64	0.24	2.72	1.17	1.37
EB17051	LQP1 _M	14.25	0.26	17	8	0.16	0.08	0.30	0.29	0.27
EB17053	LQP1 _M	13.63	0.21	23	7	0.10	0.04	0.21	0.14	0.08
EB17053	LQP1 _M	13.63	0.21	32	10	0.09	0.03	0.20	0.12	0.08
EB17006	LDP _{PB}	13.57	0.59	902	287	0.18	0.08	0.35	0.00	0.16
EB17006	LDP _{PB}	13.57	0.59	23	7	0.15	0.06	0.34	0.27	0.17
EB17006	LDP _{PB}	13.57	0.59	20	6	0.12	0.06	0.21	0.19	0.14
EB17006	LDP _{PB}	13.57	0.59	157	50	0.08	0.02	0.22	0.15	0.13

change in S_{melt} over the course of deposit formation. In LQP1_M, LDP_{PB} and DP_M the S highest in apatite is from least differentiation melt suggesting S_{melt} , as recorded by apatite, was already at its peak around the time Ap_{incl} crystallised. Within EDP_{PB} there is a considerable range in S at a set stage in melt evolution (Fig. 6.19). As EDP_{PB} also contains the highest S concentrations, and it is one of the main mineralised intrusions, this heterogeneity could reflect an increase in SO₃ volatile flux to the porphyry melt linked to onset of mineralisation.

In intermediate to felsic volcanic systems, rapid changes in S content are thought to be related to an external, normally more mafic, magma. Volcanic eruptions triggered by mixing of felsic and mafic melt have been observed at Merapi volcano, Indonesia (Nadeau 2015) and Mount Pinatubo, Philippines (Hattori 1993; De Hoog et al. 2004), and the emplacement of porphyry intrusions has been linked to an influx of mafic melt into a more silicic magma reservoir (Sillitoe 1997; Halter et al. 2005). Such interactions with more mafic magmas may be critical for facilitating the introduction of additional volatiles and sulfur and, if the timescale for change in flux are comparatively short, this may cause the heterogeneity seen within a single unit. Elsewhere, high S cores of apatite have been inferred to be inherited (Economos et al. 2017) which would also suggest a deeper S-rich, oxidised magma source. Alternatively, an increase in S_{melt} could be the result of ‘melting’ of sulfide phases

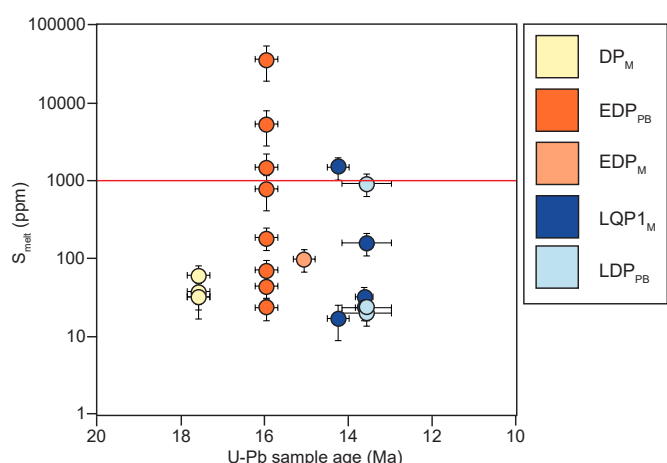


Figure 6.18 Calculated S_{melt} from Ap_{incl} based on Parat et al. (2011). Red line indicates limit of equation. Error bars (2σ) for S_{melt} are propagated from the analytical error derived from EMPA. Horizontal error bars (2σ) are MSWD for each sample (see Chapter 4). S_{melt} is highest in the mineralised intrusions but shows significant variation within individual lithologies.

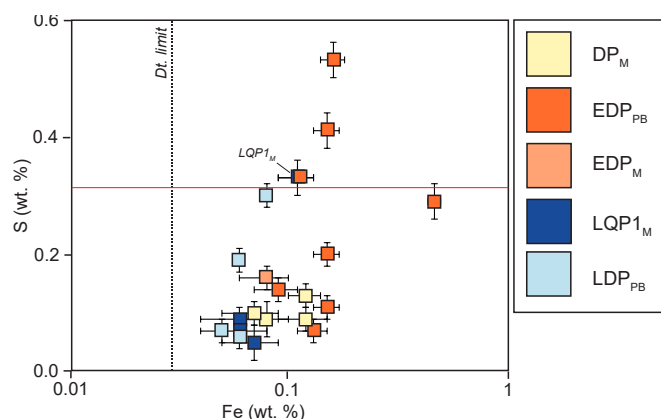


Figure 6.19 S concentration in apatite plotted against Fe which is used as a proxy for melt differentiation. Red line indicates limit of equation. Error bars (2σ) are analytical error derived from EMPA. For all units, S concentrations decrease with melt differentiation from early to late porphyry units.

from the addition of a hot, oxidised fluid ($f.O_2 > \text{FMQ}$; Jugo et al. 2010). This process could account for the lack of magma mixing visible at La Granja, which is evident elsewhere where mafic mixing has been inferred (Maughan et al. 2002). However, the S content of Ap_{incl} bears little correlation to temperature (Fig. 6.20).

This decrease in S_{melt} with melt evolution across the porphyry units (Fig. 6.19) may reflect a decrease in S solubility, which decreases with P, T, $f.O_2$ and FeO_{melt} , or preferential partitioning into another phase such as via the formation of magmatic sulfides or volatile degassing. In an oxidised dacite melt (100 – 300 MPa, 1000 °C, 2 – 5 wt. % FeO) S saturation occurs between 1500 – 3000 ppm (Carroll & Rutherford 1985; Fig. 6.19 - red line). These temperatures are higher than those calculated for these units (676 – 708 °C; Table 6.5) and as solubility increases with temperature, this suggests that at times, the melt is near or at sulfide saturation in the mineralised intrusions. This suggests that the maximum S concentration in Ap_{incl} could be a result of melt solubility. In addition, solubility increases with FeO content of the melt, matching increase in S with Fe concentration of apatite (Fig. 6.19).

Alternatively, the crystallisation of phases such as sulfides or anhydrite could cause a decrease in S_{melt} . Anhydrite is stabilised from 1025 °C in oxidised melts (100 – 300 MPa; Carroll & Rutherford 1985). Although there is little evidence for magmatic anhydrite within the samples, it is readily removed upon hydrothermal alteration and it has been readily observed within other porphyry systems (Sillitoe 2010). By contrast, disseminated sulfides are present within all the porphyry units. Bright phase analyses (avoiding veins which reflect a hydrothermal overprint) suggest late porphyry units have lower amounts of sulfides compared to mineralised porphyries (0.47-0.19 % and 1.23 – 1.03 % respectively; Table 4.4). Therefore, sulfide saturation is more likely the cause for decrease in S_{melt} for mineralised porphyries but not for late porphyries, and would also indicate $f.O_2$ towards the lower end of previous estimates where there is sufficient S^{2-} . Finally, a transition from a melt to gas phase could decrease S_{melt} , especially when coupled to volatile exsolution. Fluids overprinting late stage porphyries are Cu-(Fe)-sulfide-rich so could be responsible for the lower S_{melt} calculated for these units.

Other studies have used magmatic apatite to track changes in melt using S isotopes. Apatites from the Cadiz Valley Batholith contain variations in S concentrations within grains and within samples of a similar range to those observed in this study. The changes in S concentrations and isotopic compositions are inferred to reflect a combination of magma mixing and degassing (Economos et al. 2017). However, it should be noted that whilst this study uses Ap_{incl} , most other studies use apatite micro-phenocrysts. In the porphyry units, Ap_{incl} represent relatively late crystallisation and therefore may not capture earlier key changes in S behaviour.

In addition, here S^{6+} is interpreted as S_{melt} which may oversimplify the multi-phase and multi-variant nature of S and total S_{melt} is likely to be much higher. Of note are the low S concentrations in DP_M which may have remained below S-saturation, or lost S_{melt} removed prior to apatite crystallisation, and could be key in explaining onset of mineralisation within a porphyry system.

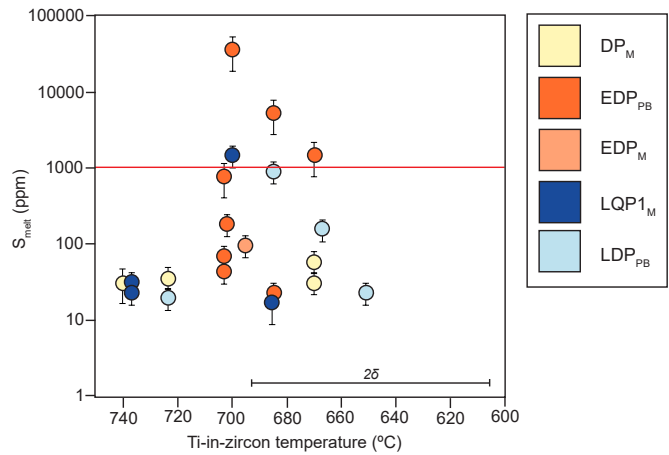


Figure 6.20 Smelt from Ap_{incl} based on Parat et al. (2011) against temperatures calculated by Ti-in-zircon geothermometry (Ferry & Watson 2007). Red line indicates limit of equation. Vertical error bars (2σ) for Smelt are propagated from the analytical error derived from EMPA. Horizontal error bars are standard deviation of individual analyses from Ti-in-zircon geothermometry calculation.

6.7.2 Volatile species behaviour in apatite and melt

The concentrations of F, Cl and OH are intrinsically linked in apatite as they occupy the same site (Piccoli & Candela 2002; i.e. Fig. 6.7A). The substitution of these species in magmatic apatite is related to the melt composition by partition coefficients, K , that are a function of pressure and temperature such as:

$$K_{(P-T)} = \frac{f_{H_2O}^l \cdot X_F^{Ap}}{f_{HF}^l \cdot X_{OH}^{Ap}} \quad \text{Eq. 6.13}$$

Therefore the mole fractions of halogens and OH in apatite can be used to infer the relative ratios in the melt (where X_F^{Ap} is related to the fugacity of HF, X_{Cl}^{Ap} to HCl and X_{OH}^{Ap} to H_2O ; Stock et al. 2016). If Cl, F and OH all behave incompatibly, the ratios of F, Cl and OH in crystallising apatite will be constant for a set range of P-T conditions (Candela 1986; Piccoli & Candela 2002). If the conditions within the melt change, then the ratios of F, Cl and OH in the apatite will also change (Piccoli & Candela 1994). Volatile exsolution from a melt would result in strong partitioning of these species out of the melt into the aqueous phase but in different proportions leading to an increase in F/OH and F/Cl in the melt but a decrease in Cl/OH. Piccoli & Candela (2002) concluded that a decrease in Cl/OH in magmatic apatite is probably the best indicator of volatile saturation in the melt and Coulson et al. (2001) concluded that a decrease in apatite (and biotite) Cl/F during differentiation tracked decreasing HCl/HF in the melt, possibly reflecting preferential loss of Cl to a separating magmatic volatile phase.

Stock et al. (2016, 2018) compared changes in X_F^{Ap} , X_{Cl}^{Ap} and X_{OH}^{Ap} ratios in volcanic apatite to corresponding melt inclusions hosted within different phases of a single melt. To rule out cooling

and decompression of the melt as a dominant control of the changing ratios, Stock et al. (2016, 2018) modelled the trajectory of these ratios in apatite for such conditions using Piccoli & Candela (2002, 2004) and data from Zhu & Sverjensky (1992). At isobaric conditions between 300 – 50 MPa, a decrease in temperature from 1200 – 700 °C (at FQM + 1 and 2 -3 wt. % H₂O) produces an increase in $X_{F/Cl}^{Ap}$ and $X_{F/OH}^{Ap}$ in the melt, but a smaller increase in $X_{Cl/OH}^{Ap}$ in crystallising apatite. As XOH is calculated from F and Cl concentrations in apatite (Eq. 6.1, 6.2 and 6.3) the results are based on assumptions of full X-site occupancy and are also not independent variables. However as all analyses have a small range in F concentrations (0.5 > F wt.% < 1), the difference in the proportion of vacancies between the grains is assumed to be minimal and that ratios of endmember mole fractions are the best way to compare the non-ideal halogen solid solution

Chlorine content of melt

Calculating Cl content of melt from apatite is complex, as Cl partitioning between apatite-melt is non-Nernstian, it being a function of P-T, melt and apatite composition (Webster et al. 2019). Cl_{melt} can be estimated from apatite using an equation proposed by Li & Hermann (2017) based on experiments run at conditions of 200 MPa and 900 °C (Webster et al. 2009):

$$Cl_{melt} \text{ (wt. \%)} = \frac{X_{Cl}^{ap}}{X_{OH}^{ap}} \frac{1}{Kd_{Cl-OH}^{ap-melt}} * 10.79 \quad \text{Eq. 6.14}$$

$$Kd_{Cl-OH}^{ap-melt} = e^{(25.81 + (X_{Cl}^{ap} - X_{OH}^{ap}) * 17.33) * \frac{10^3}{8.314 * T}} \quad \text{Eq. 6.15}$$

X_{Cl}^{Ap} and X_{OH}^{Ap} are the mole fractions of Cl and OH in apatite and T is the temperature in Kelvin.

Results for La Granja Ap_{incl} data are presented in table 6.8. Both Ti-in-zircon temperatures calculated individually for each zircon grain and AST based on bulk rock compositions are used for comparison. Minimum and maximum values from Cl_{melt} are calculated based on the error associated with X_{Cl}^{Ap} and X_{OH}^{Ap} from σ_{Cl}^{An} and σ_F^{An} . As the equation from Li & Hermann (2017) assumes a

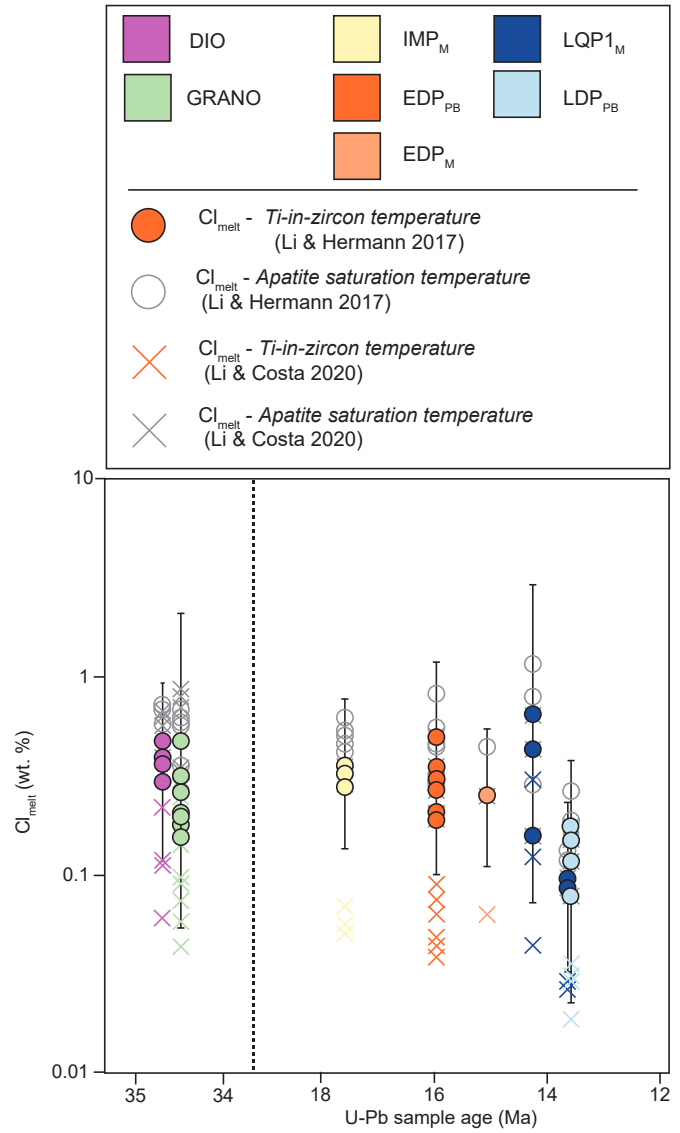


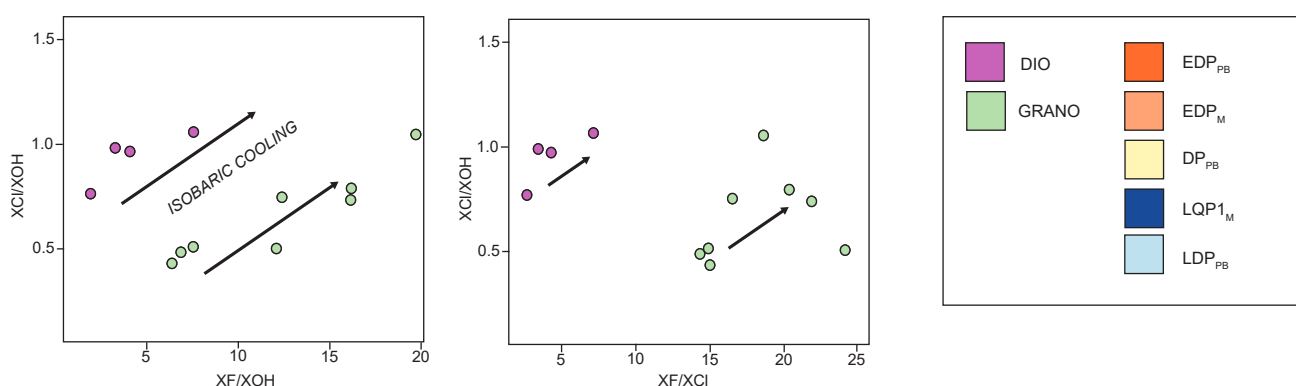
Figure 6.21 Calculated Cl_{melt} is similar for Ap_{incl} from Eocene intrusions and porphyry-related rocks and decreases in later porphyry intrusions. Calculated using Cl-OH partition coefficients from Li & Hermann (2017) produce similar results when calculated using AST and Ti-in-zircon temperatures. Cl-OH partitioning using thermodynamic equation of Li & Costa (2020) produce lower values where AST is used. Vertical error bars (2σ) for $Smelt$ are propagated from the analytical error derived from EMPA. Horizontal error bars (2σ) are MSWD for each sample (see Chapter 4).

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ideal solid solution, Cl_{melt} was also calculated using values Kd_{OH-Cl} from the thermodynamically constrained partition coefficients of Li & Costa (2020) which assumes a non-ideal solid solution.

The calculated Cl_{melt} concentrations from partition coefficients of Li & Hermann (2017) using both zircon crystallisation temperatures and the higher apatite saturation temperatures sit within the uncertainty related to analytical data derived from σ_{XCl} and σ_{XOH} (Fig. 6.21). Cl_{melt} calculated using partition coefficients from Li & Hermann (2017) and AST also sit within the uncertainty; however, those calculated focusing on zircon crystallisation temperatures produce lower Cl_{melt} concentrations. The calculated Cl_{melt} derived from the Eocene host rocks is broadly comparable to that from the porphyry with overlapping units. However, pressure at the time of GRANO and DIO crystallisation is considerably higher than the data used to calibrate the equation.

Non-porphyry related intrusions



Porphyry related intrusions

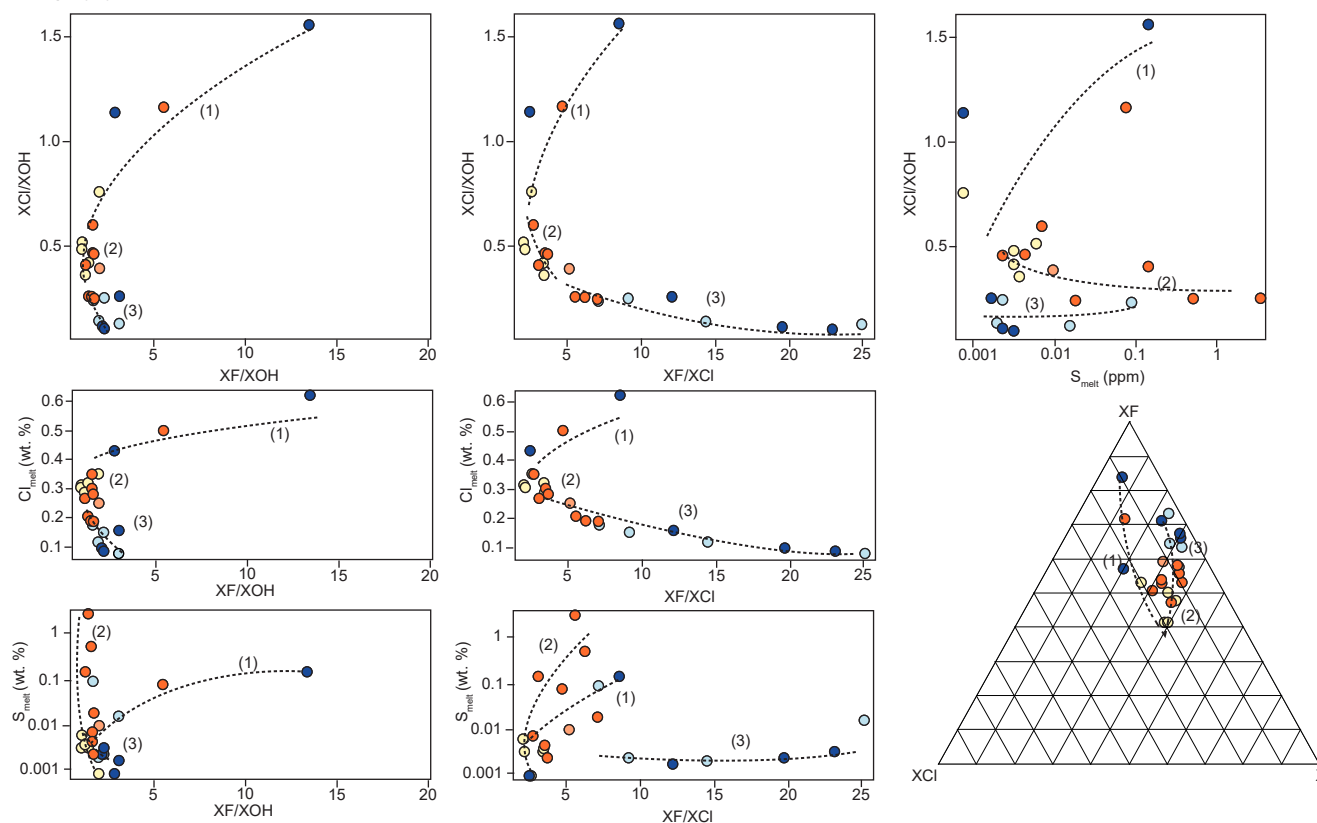


Figure 6.22 Volatile ratios in apatite inclusions from porphyry related intrusions (~ 80 MPa) and Eocene intrusions (~ 1.9 GPa). Models of apatite composition evolution as a result of isobaric cooling from Stock et al. (2016).

Although there is quite a lot of uncertainty in the absolute values, a temporal trend of decreasing Cl_{melt} with time is observed, particularly where the – arguably more appropriate – zircon grain crystallisation temperatures are used. The behaviour of Cl in porphyry melts is important as it is a key ligand enabling efficient extraction of Cu from the melt and onward fluid transport. Given the generally high incompatibility of Cl so that it tends to become enriched in late-stage melts but the strong preference for an aqueous phase if present, a marked decrease in Cl_{melt} is most likely to reflect progressive exsolution of a magmatic volatile phase. This can be explored further through changes in ratios of halogen mole fractions.

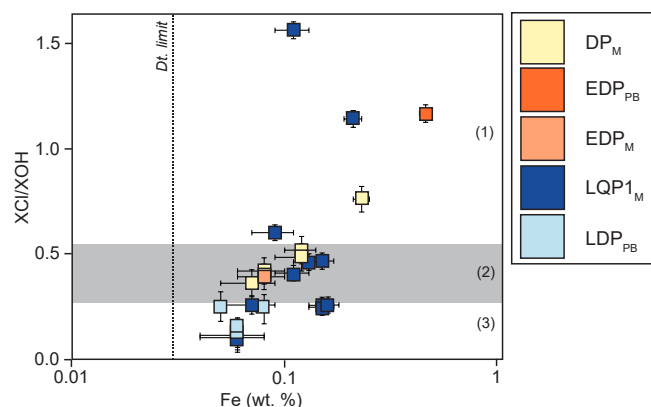


Figure 6.23 Halogen ratio $X_{Cl/OH}^{Ap}$ decreases with Fe concentration in Ap_{incl} (slope of 2.25). Analytical error is shown as 2 σ .

Evolution of volatile phases in porphyry melts and Eocene host rocks

At La Granja, a cooling/decompression trajectory consistent with that described in Stock et al. (2016, 2018) can be used to explain increasing $X_{Cl/OH}^{Ap}$, $X_{F/OH}^{Ap}$ and $X_{F/Cl}^{Ap}$ ratios of Ap_{incl} observed in the Eocene GRANO and DIO lithologies (Fig. 6.22). The Ap_{incl} data from the Miocene porphyries (Fig. 6.22) show considerable variation within each lithology but appear to define systematic trends and are split into three distinct paths. The direction of change in the ratios can be inferred by comparing to Fe composition in the apatites. In general, Ap_{incl} from the porphyry intrusions show a decrease in $X_{Cl/OH}^{Ap}$ with Fe concentration across paths 1 to 3 (Fig. 6.23).

Path 1 comprises apatites from different lithologies and as such it is not possible to infer changes in the magmatic volatiles behaviour for each magma. However, the similarity of the trends could suggest they may have been inherited from the same source, such as DIO which has overlapping halogen ratios. Alternatively, as they are all the most Fe-rich Ap_{incl} from each unit, they may represent earlier portions of the porphyry intrusions. This would suggest that each intrusion (apart from LDP) followed a similar evolution of volatiles at depth. Within each unit the Fe concentrations of Ap_{incl} are comparable to Ap_{mtrx} and so may reflect this period in melt differentiation. Together a decrease in $X_{F/OH}^{Ap}$ and $X_{Cl/OH}^{Ap}$ coupled with a decreasing $X_{F/Cl}^{Ap}$ is consistent with progressive crystallisation and increasing H_2O_{melt} in a water-undersaturated magma at approximately constant P-T. The halogens behave incompatibly in the melt (Stock et al. 2016), with F partitioning preferentially over Cl in apatite. The OH concentration in apatite is controlled by the availability of OH until the melt is water-saturated, at which point the OH content of apatite is buffered. The composition of the Ap_{incl} and the zircon host provide no definitive evidence for either theory, and therefore the Ap_{incl} in path 1 have been underlined in table 6.8.

Path 2, represented by Ap_{incl} data from the porphyry units (EDP, DP_M), exhibits a decrease in $X_{Cl/OH}^{Ap}$ and Cl_{melt} coupled with a slight increase in $X_{F/Cl}^{Ap}$ and little change in $X_{F/OH}^{Ap}$. This can be explained by continued crystallisation in a fluid under-saturated state, and perhaps reaching the

point of volatile exsolution accounting for decreasing X_{Cl} as it preferentially partitions into the volatile phase. Alternatively, a decrease in $X_{\text{Cl/OH}}^{\text{Ap}}$ and increase in $X_{\text{F/Cl}}^{\text{Ap}}$ under volatile-undersaturated conditions could occur in response to a decrease in pressure (Zhu & Sverjensky (1991). In this stage, the mineralised EDP is only differentiated from DP_M by the much higher S_{melt} concentrations.

In path 3, a sharp increase in $X_{\text{F/Cl}}^{\text{Ap}}$ but only a small increase in $X_{\text{F/OH}}^{\text{Ap}}$ and further decrease in $X_{\text{Cl/OH}}^{\text{Ap}}$ and Cl_{melt} in Ap_{incl} is observed, only in samples from the late porphyries. This is most likely to be a result of increased Cl partitioning into a magmatic volatile phase associated with more volumetric fluid-saturation (Stock et al. 2018) although it should be noted that decreasing temperature could also cause this effect (Piccoli & Candela 2002). The absence of Ap_{incl} with these compositions in the earlier mineralised porphyries is significant and may indicate that the late porphyries were emplaced after extensive prior volatile loss and carried late-formed apatites from depth that had recorded this process. LDP_{PB} and LQP1_M have a very fine-grained matrix and the majority of magmatic apatite is present as subhedral – euhedral micro-phenocrysts. Calculated S_{melt} is low at this stage, suggesting that S had also been depleted prior to formation of these apatites and emplacement of the LDP and LQP.

6.8 Magmatic evolution of the units as inferred from apatite

6.8.1 Eocene host rock versus Miocene porphyry units

Variations in the halogen composition of Ap_{incl} within GRANO are consistent with isobaric cooling (Fig. 6.22). Slow cooling of the large intrusions DIO and GRANO resulting in high degrees of melt differentiation could explain the large range in element concentrations observed within the apatite (Fig. 6.3). This crystallisation history is supported by the coarser grain size and more equigranular texture of DIO and GRANO. By contrast the smaller range of compositions observed in apatite from the porphyry intrusions may reflect a more rapid timescale of crystallisation (Fig. 6.3). This is inferred from the smaller volume of the intrusions, shallower emplacement depth and the phenocrystic texture.

The crystallisation history of Ap_{mtrx} and Ap_{incl} differs between GRANO and the main porphyry units (EQP_{PB}, EDP, DP_{PB}). Ap_{mtrx} from the porphyry units were the earliest textural associations studied. Calculated AST for EDP_{PB} (Table 6.6) is comparable to the liquidus of dacite (950 °C, 200 MPa, 5 wt. % H₂O; Costa et al. 2004). Zircon crystallisation temperatures which are used to infer Ap_{incl} crystallisation are 100 – 200 °C lower (Table 6.5) and therefore preserve melt compositions from later in the melts' evolutions. This evolution of composition over different textural associations of apatite is more consistent with apatite within volcanic systems and the observations of Stock et al. (2016; 2018) who reconstructed magma evolution using inclusions of apatite in pyroxene and biotite followed by apatite microphenocrysts.

By contrast, AST in GRANO falls outside the lower limits for the equation, which together with low $\text{Mg}_{\text{Ap}}/\text{Mg}_{\text{bulk rock}}$ suggests it was not saturated at the liquidus. However, zircon crystallisation temperatures remain similar to those of the porphyries. This matches previous studies of apatite inclusions in zircon from unmineralised plutons (Bruand et al. 2016; Jennings et al. 2011) in which

the REE contents of Ap_{incl} are equivalent to bulk rock, implying early crystallisation relative to REE fractionation. Although pressure is said not have much of an effect on apatite saturation (Harrison & Watson 1984), higher pressures lower the temperatures for the stability fields for most igneous phases including plagioclase (Loucks 2014). This may delay onset of apatite crystallisation to closer to zircon saturation temperatures so that Ap_{mtrx} and Ap_{incl} compositions are more comparable.

The trace element compositions of Ap_{mtrx} and Ap_{incl} (from all but the mineralised porphyries) sit within the granitoid field of larger apatite petrogenetic studies (Belousova et al. 2002). Ap_{mtrx} from Eocene units contain lower Mn, Sr, Y and U concentrations and lower Eu/Eu* and Gd/Yb than those from porphyry units. Lower U concentrations are not observed in Ap_{incl} and therefore differences in concentration may be a result of diffusion (see Chapter 5; Chernaik 2010). One common variable in mineral-melt partition coefficients is a variation in response to melt SiO_2 , a control attributed to melt polymerisation (Mahood & Stimac 1990; Blundy & Wood 2003; Schmidt et al. 2006). Polymerisation increases mineral partitioning as a more linked melt structure has a reduced ability to incorporate other elements (Stokes et al. 2019). Increasing apatite-melt partitioning has been observed for REE (+Y) and Mn (Prowatke & Klemme 2006; Stokes et al. 2019) as a function of increasing SiO_2 , with the opposite effect for Na due to its low ionic charge/radius (Ryerson & Hess 1978). Similar relationships can be observed between Ap_{mtrx} and bulk rock from this study (Fig. 6.24). These results appear to suggest that for given P-T, differences in Mn and total REE between the units are strongly influenced by melt polymerisation. The higher pressures of GRANO and DIO may suppressing mineral-melt partition, resulting in lower Mn and REE concentration (Prowatke & Klemme 2006).

REE ratios are more consistent with changing partitioning coefficients (e.g. Table 6.7) and, as apatite is commonly the earliest, or most significant REE phase to crystallise, the REE ratios in Ap_{mtrx} correspond to bulk rock. The relationship between the REE profile of magmatic apatite and magma petrogenesis has been noted several times (Piccoli & Cannadela 2002; Belousova et al. 2002; Mao et al. 2016). As a result, apatite can preserve high La/Yb ratios linked to more fertile arc magmas (see Chapter 4).

Porphyry deposits require oxidised, water-, Cl- and S-rich magmas and fluids to form. Both Eu/

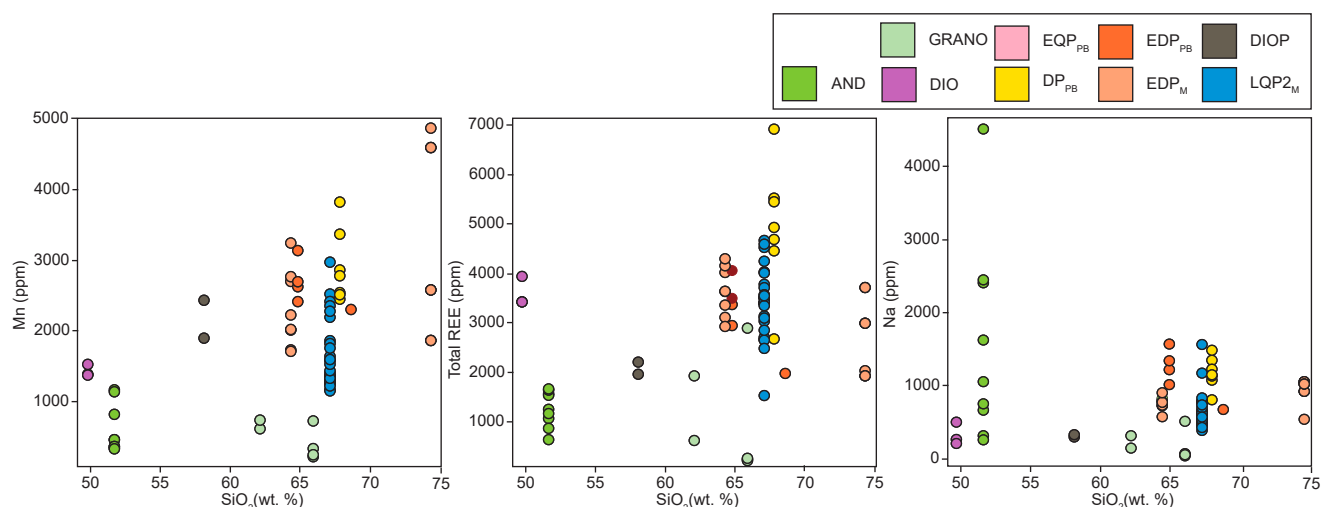


Figure 6.24 Changes in Ap_{mtrx} concentration with bulk rock SiO_2 . A-B) Concentration in Mn and total REE are typically higher in more SiO_2 -rich bulk rock; however, apatites from GRANO and DIO are not. C) Na shows no correlation with bulk rock SiO_2 . Analytical error is smaller than the symbol size.

Eu* modelling and inferences from S concentration in apatite suggest that the Eocene magmas were more reduced ($\leq$ FMQ) whereas the porphyry units were more oxidised ($\geq$ FMQ +1). The high oxidation state of arc magmas (with oxygen fugacity between Δ FQM +1 and Δ FQM +3) suppresses sulfide formation with sulfur occurring as $S^{4+}O_2$ in the fluid and prevents the chalcophile metals from being scavenged out of the magma (Audétat & Simon 2012; Sillitoe 2010; Richards 2003). In addition, more oxidised melts have higher sulfur content at sulfide saturation (Jugo 2009; Carroll & Rutherford 1985). More oxidised arc magmas are thought to be the result of subduction of an altered oceanic crust gradually elevating the oxidation state in the mantle wedge (Richards 2015). The Eocene magmas are inferred to be from an immature arc, whereas the magma forming the porphyry intrusions were generated from a more mature arc following subduction of ridge (Rosenbaum et al. 2005; Davies 2002; see *Chapter 4*). Alternatively, a more reduced melt could be the result of more shallow processes. Samples of GRANO, DIO contain abundant magnetite (Fig. 4.19), the crystallisation of which may be sufficient to convert sulfate to sulfide (Jenner et al. 2010). A more reduced magma may explain the lack of magmatic sulfides in Eocene host rocks (Fig. 4.9). In the porphyry units, the presence of sulfide inclusions within the zircons hosting Ap_{incl} (see *section 4.3*) suggest that the oxidation state is closer to FMQ in order to facilitate multiphase S and its precipitation as sulfides (Jugo 2009).

A high water content of the magma means that a large volume of fluid can be exsolved, capable of partitioning and transporting significant quantities of metals through coupling with Cl ligands (Candela & Holland 1984; Tatitch & Blundy 2017). Ap_{incl} in Eocene units do not record melt reaching fluid saturation; in the porphyry units this happens over subsequent intrusions (see *section 6.7.2*). In addition these are large areas of UST at La Granja (Fig 4.7A; Appendix B) which is further evidence for volatile-rich magma and the magmatic-hydrothermal nature of the porphyry intrusions. Calculated Cl_{melt} in porphyry units are comparable to those in the literature magmas (0.3 wt. %; Chelle-Michou & Chiradia 2017). However, the range available for non-mineralised arc magmas is much larger (average 0.6 wt. %; 0.01 – 0.85 wt. %: Chelle-Michou & Chiradia 2017; Aiuppa et al. 2009; Hattori & Keith 2001; Wallace 2005; Blundy et al. 2008) and due to the differences in pressure Cl_{melt} cannot be properly estimated for Ap_{incl} from Eocene porphyries. Estimates of S_{melt} for Eocene magmas are also not possible due to the lower inferred oxidation state. Melt inclusions from arc dacite indicate S_{melt} typically < 200 ppm (Hattori & Keith 2001; Wallace 2005; Blundy et al. 2008). S_{melt} porphyry intrusions span this value, with earlier Ap_{incl} producing considerably higher estimates.

6.8.2 Differences between porphyry units

Mineralised porphyry units

Akin to the bulk rock compositions and zircon chemistry (see *Chapter 4*); apatites from EDP and DP units have similar trace element concentrations. In addition, P-T and $f.O_2$ conditions are inferred, or calculated, to be similar. Any compositional differences that do exist can be explained through changes in bulk rock and/or partition coefficients. Further, calculated Cl_{melt} from DP_M , EDP_{PB} and EDP_M are comparable - suggesting that this was not a limiting factor in the mineralisation of EDP. The main difference evident between the pre-mineral and mineralised

intrusions is the S content. The sulfur content of the melt has previously been identified as a limiting factor in copper mineralisation. Residual oxidised felsic melts may hold sufficient copper to form deposits; however, a low sulfur solubility from the strong fractionation of sulfur from chlorine means that even very large magma chambers are unable to provide enough sulfur to precipitate the quantities of sulfides observed (Lee et al. 2012; Hattori & Keith 2001; Cline & Bodnar 1991).

Calculated S_{melt} for DP_M are comparable to that of arc dacite and remain consistent over melt differentiation (Hattori & Keith 2001; Wallace 2005; Blundy et al. 2008). The high concentrations and heterogeneity of S_{melt} in EDP_{PB} could be explained by an external input. Sulfides present within the glass groundmass of felsic porphyry intrusions at Bingham Canyon, Utah, indicate the late saturation of sulfides. In addition, textural evidence indicates that mixing with mafic magma occurred at the time of porphyry mineralisation and intrusion of the felsic stocks (Maughan et al. 2002). Mount Pinatubo, which is spatially associated with several porphyry deposits, also shows evidence for mafic magma mixing, and has evidence of magma ascent from the release of SO_2 and deep (>35 km) seismic activity prior to eruption (Hattori & Keith 2001; Hattori 1993). From experimental evidence Mungall et al. (2015) produced a model to explain the mixing of hotter, dense mafic melt at the top of the magma chamber. Mafic melt droplets can attach to vapour bubbles rising through the chamber enriching metals and sulfur in the volatile phase. Alternatively, it has been suggested that the excess sulfur in porphyry deposits may be derived from degassing of mafic magma at the bottom of the magma chamber (Nadeau 2015). A degassing of hotter, mafic magma as opposed to direct magma mixing would correspond to the lack of such visible textures or changes in bulk rock, zircon (*Chapter 4*) or apatite chemistry visible within the porphyry units at La Granja. The presence of DIOP is testament to the presence of a less evolved magma coeval with the formation of La Granja. Alternative evidence for late magma mixing comes from the dark CL bands in the zircons identified in *Chapter 4*. These are most prominent on zircons from EDP_{PB} , are U- and Y-rich and Hf-poor and *may* reflect abrupt and short-lived changes in melt chemistry. Similar features have been interpreted from other deposits to reflect rapid zircon growth following a CO_2 rich injection of mafic magma (Buret et al. 2016). These findings support existing thinking (e.g. Seo et al. 2009; Wilkinson 2013) that the S_{melt} content is important in the development of mineralised systems. Therefore the size and timing of the S addition as recorded in Ap_{incl} would therefore be a key control on the degree to which a system is mineralised. The S concentration in Ap_{incl} decreases over subsequent intrusions, this depletion in S_{melt} may contribute to the lower degrees of mineralisation present later in the system.

Late porphyry intrusions

The final porphyry intrusions may give clues to the conclusion of a porphyry system. At La Granja the composition of Ap_{incl} and Ap_{mtrx} from the late porphyries ($LQP1_M$, $LQP2_M$, LDP_{PB}) overlap. This, together with the similar zircon core and rim compositions (see *section 4.3*), suggests that the REE-phases crystallised more rapidly or were accompanied by less melt differentiation (apatite from late porphyries contain a small range in Mg concentrations). This is easiest explained when compared to the magmatic volatile ratios which suggest that the late porphyries were emplaced after extensive volatile loss. Together with the decrease in Cl_{melt} , Ap_{incl} show a sharp drop in Mn concentration, which is thought to couple strongly with Cl-rich phases (Audétat et al. 2008), and

decrease in S_{melt} which will also follow the a fluid phase as gas loss proceeds. The composition of apatite from the late porphyries matches that of Ap_{incl} from the main porphyry intrusions. This, together with changes in bulk rock compositions (see *section 4.5*) is consistent with the melt of the late porphyries reflecting fractionated porphyry magma. Temperature estimates (AST and Ti-in-zircon; Table 6.5) do not suggest that apatite did not crystallise at significantly cooler conditions. However, the finer groundmass and fine oscillatory zoning present in zircons are similar to that of volcanic rocks (Fig. 4.12) and could be a relatively unique to magmatic-hydrothermal systems. At La Granja, the surface expression of this event is the Rhyodacite dome present at Mirador. Other studies have placed close temporal links between volcanism and porphyry intrusions (e.g. Longo & Teal, 2005). At Baja de la Alumbrera, Argentina, only 20 Kyr was placed between porphyry mineralisation and overlying ignimbrite (Buret et al. 2017).

Another key difference of apatite from late porphyries is that the relative timing of Ap_{mtrx} crystallisation appears to be delayed compared to earlier porphyry intrusions. Within late porphyries Ap_{mtrx} have low Mg concentrations, similar compositions to late crystallising Ap_{incl} , and are present as fine crystals in the groundmass. The timing of apatite saturation is strongly linked to the melt P/CA ratio (see *section 6.4*) which is also affected by plagioclase crystallisation (see *section 6.5*). Modelling of Eu/Eu* indicates that the amount of plagioclase crystallisation prior to Ap_{mtrx} from late porphyries is similar to that of the earlier intrusions (Fig. 6.13). In early porphyries initial melt P/Ca is high enough for early crystallisation of plagioclase then apatite. However if plagioclase crystallisation is suppressed, which could occur from a higher water content of the melt, it may mean that magmas evolve with a relatively flat P/Ca trend. This may mean that the more evolved magmas on such trends, like the later intrusions, may reach apatite saturation later.

6.9 Conclusions

- Much of composition of Ap_{mtrx} is derived from melt composition and therefore could prove useful when discriminating magmas associated with porphyry systems. Fertility signature such as La/Yb and Eu/Eu* are preserved in apatite even at different P-T conditions. However Sr/Y ratios can be masked by plagioclase crystallisation.
- The persistence of apatite crystallisation over melt differentiation and its occurrence within distinct textural association (Ap_{mtrx} , Ap_{incl}) provides the opportunity to track magma evolution in porphyry units. However the relative timing of Ap_{mtrx} differs between porphyry intrusions.
- The behaviour of magmatic volatiles in Eocene apatite is consistent with isobaric cooling. However, apatite from porphyry intrusions record at least three stages of evolution. Earlier Mg-rich Ap_{mtrx} crystallise as microphenocrysts in the main porphyry units, followed by Ap_{incl} which indicate increasing fluid-saturated conditions and crystallise at similar times relative to melt evolution across intrusions. These are more comparable to the composition of Ap_{mtrx} from the late porphyry intrusions. Finally, apatite from the late porphyries crystallises rapidly following fluid-saturation.
- S_{melt} as recorded by Ap_{incl} appears to be a key difference between pre-mineral and mineralised

intrusions. Large variations in the S content of Ap_{incl} suggest that S may be added relatively late in the magmas evolution coinciding with the most mineralised phase.

Chapter 7: Hydrothermal apatite at La Granja

7.1 Introduction

This chapter describes the occurrence and composition of hydrothermal apatite at La Granja. Hydrothermal apatites are grains which have crystallised as a result of, and in the presence of, hydrothermal fluids. They can be identified as such through their textures and association with other hydrothermal minerals. Apatite-bearing hydrothermal assemblages are more varied than apatite-bearing magmatic assemblages. These assemblages reflect varying degrees of interaction between hydrothermal fluids and the host rock and the associated apatites can be separated into three subgroups: 1) **replacement**; 2) **vug** and 3) **vein apatite**. Replacement apatites form part of alteration assemblages and are the result of a hydrothermal fluid interacting with a pre-existing mineral phase. Vug apatites are also present in alteration assemblages; however these show no obvious replacement textures and are often observed together with sulfides within vugs. They are the most common in areas of more destructive alteration. Vein apatites are those that occur within clearly-defined veins and which precipitated directly from a fluid. In addition, as evidenced in *Chapter 5*, metasomatised magmatic apatite also exhibits compositional characteristics as a result of partial equilibration to a hydrothermal fluid.

Hydrothermal apatites from 17 samples and 11 units at La Granja were analysed with careful attention paid to associated minerals. Based on the alteration assemblages, hydrothermal apatite can be linked to three main alteration stages in the deposit: potassic, propylitic and sericitic (Fig. 4.5). In this chapter the relationship between the apatite composition and the evolution of the hydrothermal environment is explored. In addition, as hydrothermal fluids are responsible for the transportation and deposition of sulfides, the relationship between hydrothermal apatite types and mineralisation is also examined.

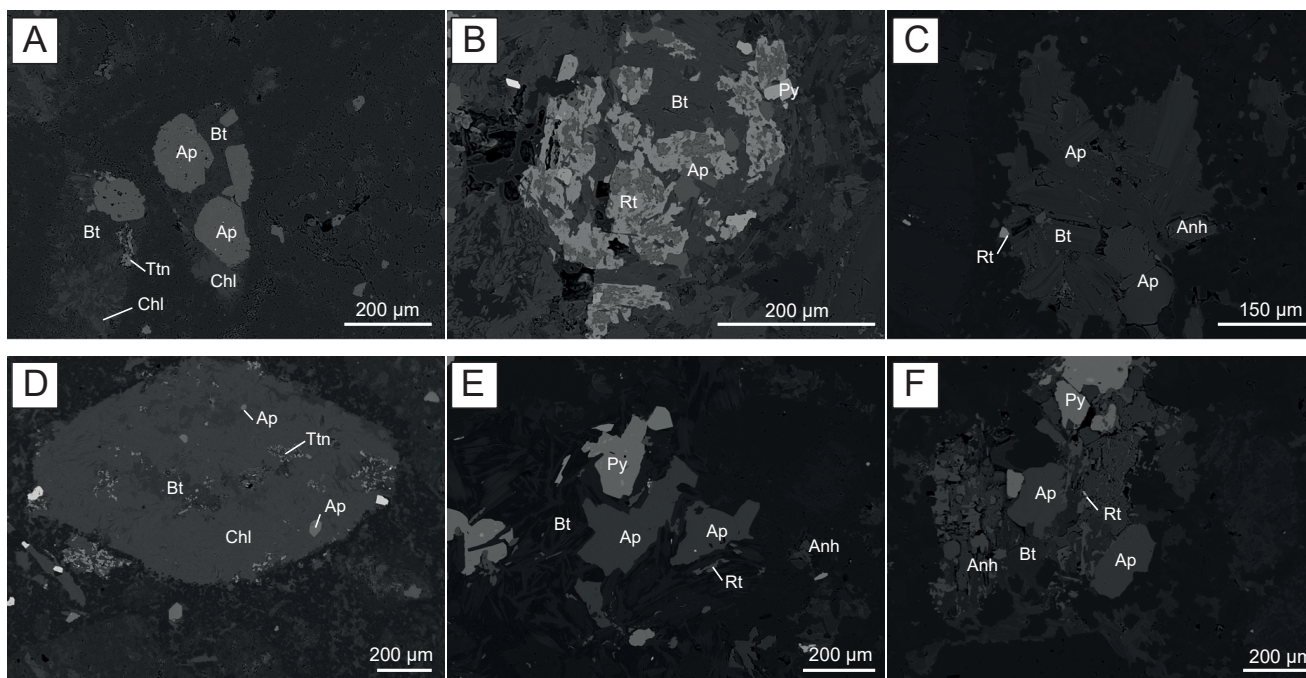
7.2 Apatite textures, occurrence and classification

Textural information - including grain appearance and associations with other minerals - was examined for hydrothermal apatites using SEM-BSE imaging. In general, hydrothermal apatite has a more irregular shape than magmatic apatite and is often intergrown with the other hydrothermal phases. It is abundant in the rocks at La Granja and accounts for about 60 % of the apatite analyses conducted in this study.

Replacement apatite

Apatite present within assemblages of secondary minerals that replace earlier phases through metasomatic processes is classed as replacement apatite (Fig. 7.1). At La Granja, this type of apatite is only observed in potassic and propylitic assemblages. There is a possibility that some apatite found within replacement assemblages may be a remnant from an earlier, magmatic assemblage. A number of previous studies have observed magmatic apatite as inclusions in phenocrystic biotite, feldspar and amphibole in other magmatic settings (Jennings et al. 2011; Stock et al. 2018). In a porphyry setting, these host phases are commonly pseudomorphed

POTASSIC



PROPYLITIC

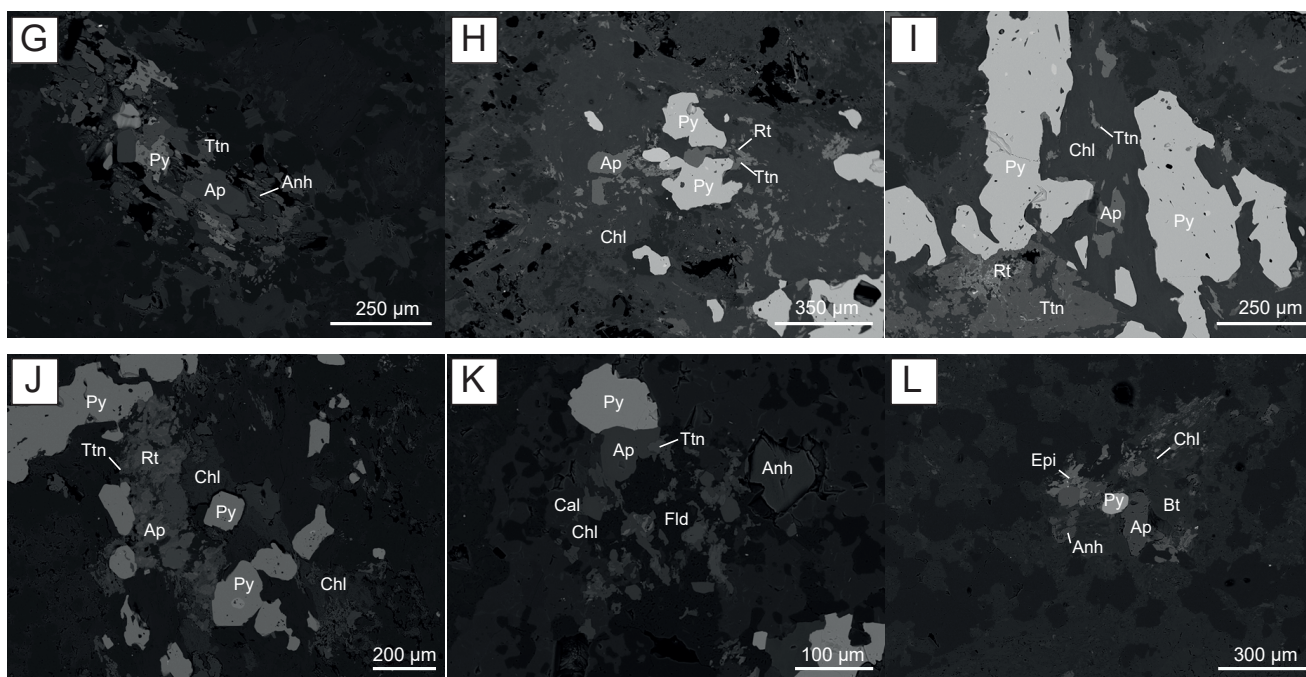


Figure 7.1 SEM backscattered electron images of replacement apatite. Potassic assemblages: A) Biotite (bt) and apatite (ap) that has replaced primary pyroxene; there is slight alteration of the secondary biotite to chlorite (chl) and titanite (ttn). B) Biotite, rutile (rt) and apatite that has replaced coarse amphibole (amp) a crystal in diorite. The rutile has an exsolution texture of $\text{TiO} - \text{Fe(Mn)O}$. C) Clot of secondary biotite with small amount of rutile. D) Partial replacement of amphibole by biotite, titanite and apatite with rare pyrite (py). Secondary biotite has been almost completely replaced by chlorite. E) Biotite, apatite and anhydrite (anh) assemblage replacing amphibole. F) Biotite, anhydrite, rutile, pyrite and apatite assemblage in dacite porphyry. Propylitic assemblages: G) Chlorite, anhydrite, titanite, pyrite and apatite in dacite porphyry after biotite. H-I) Chlorite, rutile, titanite, pyrite and apatite in diorite, possibly after amphibole. J) Chlorite, pyrite, rutile, titanite and apatite replacement of amphibole or pyroxene. K) Replacement of feldspar by chlorite, calcite (Cal), pyrite, anhydrite and apatite; L) Epidote (epi) chlorite, anhydrite, pyrite and apatite that has partially replaced biotite.

during alteration. However, in most cases, this can be discounted because within hydrothermal assemblages, apatite is present in relatively high concentrations (higher than is observed in magmatic phases), typically has an irregular shape, and is intimately intergrown with the hydrothermal minerals. A second complication is where propylitic minerals have replaced an earlier potassic assemblage (e.g. chlorite for biotite), it may be unclear to which stage the apatite belongs. In such instances it is considered likely that any remaining potassic apatite (if it existed) would have equilibrated with the propylitic fluid and would exhibit textural evidence for metasomatism. However, these two complications are considered unlikely to present classification difficulties.

In the potassic zone, replacement apatite is typically present with secondary biotite pseudomorphing mafic minerals, often accompanied by rutile, ilmenite, anhydrite, pyrite and, less commonly, chalcopyrite (Fig. 7.1A-F). Minor amounts of chlorite and titanite are also present where the potassic zone is moderately overprinted by propylitic alteration (Fig. 7.1A, D). Assemblages may appear as knitted mats of fine biotite with pyrite, anhydrite and small amounts of rutile for which any precursor primary minerals are unclear. In these assemblages the apatite is usually irregular in shape and up to 300 µm in size (Fig. 7.1E). Alternatively, potassic assemblages may have more obviously pseudomorphed primary amphibole and/or pyroxene (Fig. 7.1B, D). These assemblages generally contain lower proportions of sulfides and rutile-ilmenite. Here, the apatite occurs as rounded crystals up to 400 µm in maximum dimension.

Propylitic replacement assemblages containing apatite are dominated by chlorite, epidote and pyrite, and can also contain calcite, titanite, rutile and anhydrite (Fig. 7.1G-L). They most commonly form from the replacement of primary or secondary biotite (Fig. 7.1G). Feldspar is also replaced; here, calcite (+chlorite) is the dominant assemblage (Fig. 7.1K).

Table 7.1 Summary of vein apatite analysed at La Granja.

Sample	Unit	Vein(let) thickness	Assemblage	Alteration	EMPA (n)	LA-ICP-MS (n)	Reference
EB17001	EDP _M	50 µm	Ap	-	2	1	Fig. 7.2A
EB17001	EDP _M	0.25 mm	Anh (Py)	Potassic	3	2	Fig. 7.2B-C
EB17001	EDP _M	0.25 mm	Bt + Anh + Py + Ccp	Potassic	4	-	Fig. 7.2H
EB17020	IMP _{PB}	500 µm	Anh + Ccp	Potassic	4	3	Fig. 7.2D
EB17027	DIO	150 µm	Epi + Chl + Qtz	Propylitic	1	1	Fig. 7.2I
EB17028	DIOP	200 µm	Chl + Anh + Ccp	Propylitic	1	2	Fig. 7.2J
EB17047	LQP1 _M	> 8mm	Qtz + Py + Ccp (Te-S)	Sericitic	48	44	Figs. 7.2M-M
EB17048	LQP1 _M	1 cm	Qtz + Ser+ Py + Ccp	Sericitic	45	56	Figs. 7.2O-P
EB17053	LQP1 _M	200 µm	Qtz + Ser + Rt (Py)	Sericitic	5	7	Fig. 7.2Q
EB17058	AND	150 µm	Qtz + Kfs+ Py	Potassic	9	3	Fig. 7.2E
EB17060	AND	300 µm	Bt + Kfs + Py	Potassic	3	3	Fig. 7.2F
EB17060	AND	600 µm	Qtz + Chl + Py	Propylitic	8	8	Fig. 7.2K
EB17069	AND	100 µm	Chl + Py	Propylitic	10	14	Fig. 7.2L
EB17069	AND	< 100 µm	Bt + Rt	Potassic	3	6	Fig. 7.2G
EB17056	DIO	2 cm	Qtz + Py + Mo + Cc	Potassic	-	-	-
EB17056	DIO	500 µm	Ser + Chl + Cpy + Cc	Sericitic	1	1	-

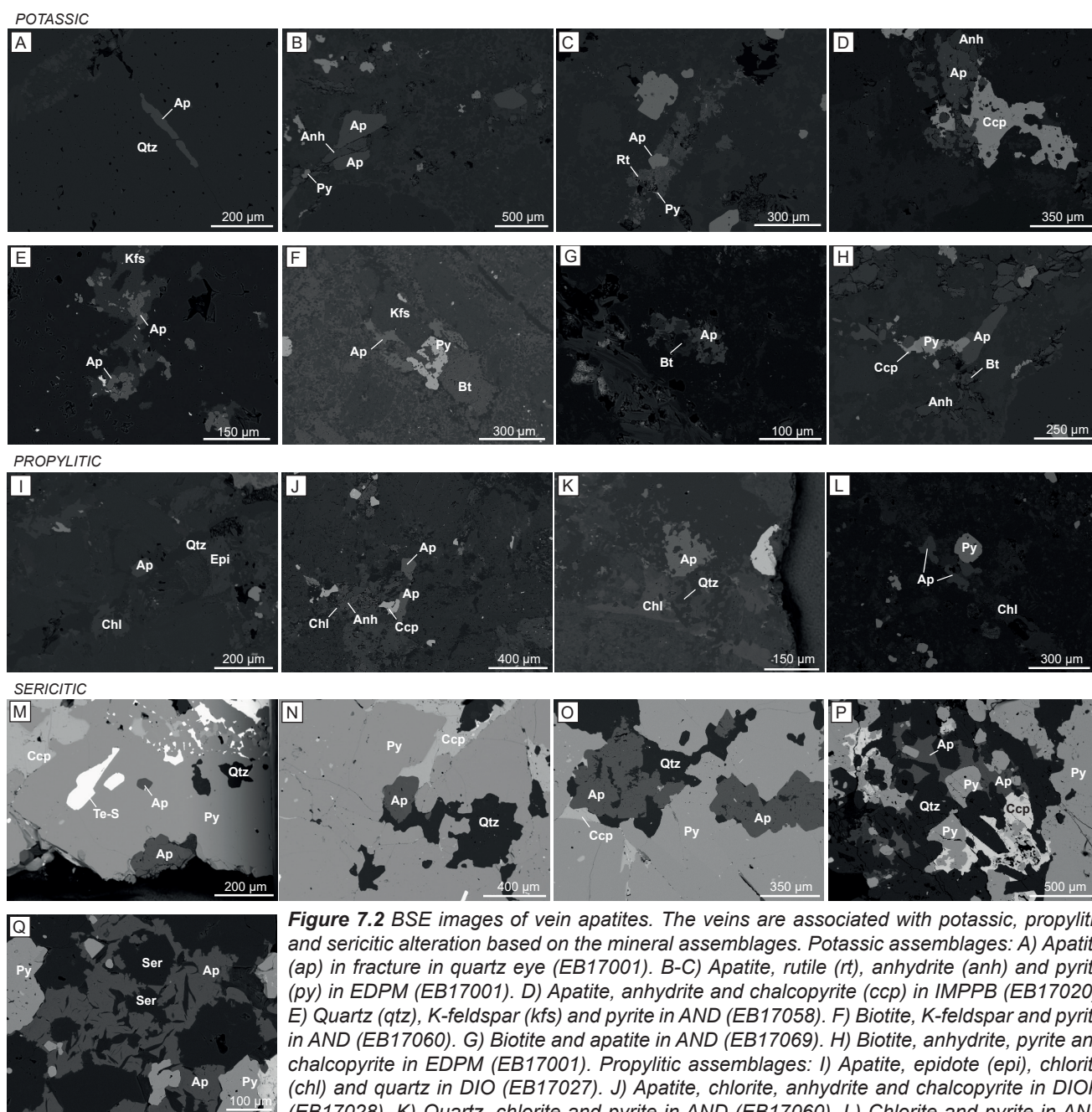


Figure 7.2 BSE images of vein apatites. The veins are associated with potassic, propylitic and sericitic alteration based on the mineral assemblages. Potassic assemblages: A) Apatite (ap) in fracture in quartz eye (EB17001). B-C) Apatite, rutile (rt), anhydrite (anh) and pyrite (py) in EDPM (EB17001). D) Apatite, anhydrite and chalcopyrite (ccp) in IMPPB (EB17020). E) Quartz (qtz), K-feldspar (kfs) and pyrite in AND (EB17058). F) Biotite, K-feldspar and pyrite in AND (EB17060). G) Biotite and apatite in AND (EB17069). H) Biotite, anhydrite, pyrite and chalcopyrite in EDPM (EB17001). Propylitic assemblages: I) Apatite, epidote (epi), chlorite (chl) and quartz in DIO (EB17027). J) Apatite, chlorite, anhydrite and chalcopyrite in DIOP (EB17028). K) Quartz, chlorite and pyrite in AND (EB17060). L) Chlorite and pyrite in AND (EB17069). Sericitic assemblages: M-N) Quartz, pyrite, chalcopyrite and Te-S in LQP1M (EB17047). O-P) Quartz, sericite (ser), pyrite and chalcopyrite in LQP1M (EB17048). Q) Quartz, sericite, rutile and pyrite in LQP1M (EB17053).

Vein apatite

Apatite is observed in veinlets and veins ranging from unmineralised, thin (100 micron scale) fractures to coarser (centimetre scale) mineralised veins (Table 7.1). In the smaller veins, apatite forms an elongate shape and fills the vein cavity (Fig. 7.2A). Potassic veins containing apatite are generally narrow < 500 μ m wide and largely unmineralised. Vein assemblages include biotite or K-feldspar with pyrite and occasionally anhydrite and chalcopyrite. The apatite is intergrown with these minerals (Fig. 7.2B-H). Thin (< 200 μ m) propylitic veins containing apatite are rarely mineralised with a typical assemblage of chlorite, quartz and pyrite, with epidote and/or anhydrite and sometimes chalcopyrite and are typically < 200 μ m wide. These veins have less well-defined edges than potassic or sericitic veins (Fig. 7.2I-

Table 7.2 Summary of vug apatite analysed at La Granja.

Sample	Unit	Size	Assemblage	Alteration	EMPA (n)	LA-ICP-MS (n)	Reference
EB17037	EDP _{PB}	1 mm	Py + Ccp + Bn + Rt	Potassic	45	17	Fig. 7.3.A, C
EB17039	DIOP	300 µm	Py + Rt + Ccp	Potassic	6	7	Fig. 7.3.B
EB17051	LQP2 _M	1 mm	Py + Ccp + Rt + Ser	Sericitic		23	Fig. 7.3.D, E
EB17053	LQP2 _M	500 µm	Rt + Ccp + Ser	Sericitic	4	-	Fig. 7.2.F, G
EB17051	LQP2 _M	2 mm	Py (+Po) + Ser (+Zrc)	Sericitic	15	3	Fig. 7.2.H
EB17053	LQP2 _M	1 mm	Py + Ccp + Rt + Ser	Sericitic	50	36	Fig. 7.2.I

L). Sericitic veins containing apatite are strongly mineralised. These form coarse veins (≥ 1 cm) typically containing quartz, sericitic, pyrite, chalcopyrite and sometime chalcocite and pyrrhotite. Apatite can be found at the edges of the veins intergrown with the gangue minerals (Fig. 7.2P) or precipitated with sulfides in the centre of the veins (Fig. 7.2M-O). Alternatively, they may form larger masses ($> 500 \mu\text{m}$) of irregular crystals within vein selvages (Fig. 7.2Q).

Vug apatite

Vug apatite is neither confined to pseudomorphed minerals nor vein boundaries but is present within vugs or large areas of secondary porosity. It is usually associated with sericitic alteration where vugs are produced as a result of fluid-rock reactions (Table 7.2; Fig. 7.3). The precipitated minerals which infill the porosity show evidence for inwards growth from the margins where the minerals are platy (Fig. 7.2D-E, H), or mineral zoning from towards the centre of the vug (Fig. 7.2D-E). Potassic assemblages with vug apatite are characterised by rutile, pyrite, chalcopyrite and sometime biotite and bornite. Sulfides are the dominate phase with apatite closely associated with rutile towards the edges of the polyminerale clots (Fig. 7.3A-C). Sericitic vug apatite occurs in similar assemblages (rutile + pyrite + chalcopyrite) but these are associated with large mats of fine-grained sericite. Again, the apatite is positioned at the edges of the vugs or around the outside of the sulfides intergrown with rutile and sericite (Fig. 7.3D-I). Some pyrite contains inclusions of anhydrite, which could be a relic from an earlier, potassic, assemblage (Fig. 7.3H). These vug apatites are all very irregular in shape and contain inclusions of other minerals.

Metasomatised apatite

In *Chapter 5*, it was suggested that apatite grains interpreted to be of magmatic origin but with alteration scores ≥ 1 had been overprinted by hydrothermal fluids. As these grains are clearly texturally and likely chemically, modified, they were not included in the magmatic comparison. Such altered apatites are present in nearly all samples from La Granja and should not be ignored as they form a substantial part of the apatite within a porphyry system. They also record part of the magmatic-hydrothermal evolution and so will be compared with other hydrothermal apatite types in this chapter in order to decipher how their composition can be used to infer fluid evolution paths, and potentially used for the development of discrimination tools.

It should also be noted that hydrothermal apatite can also exhibit textural evidence of metasomatism. Inclusions of monazite are predominantly restricted to hydrothermal apatite within potassic assemblages (Fig. 7.1A). Admittedly metasomatised hydrothermal

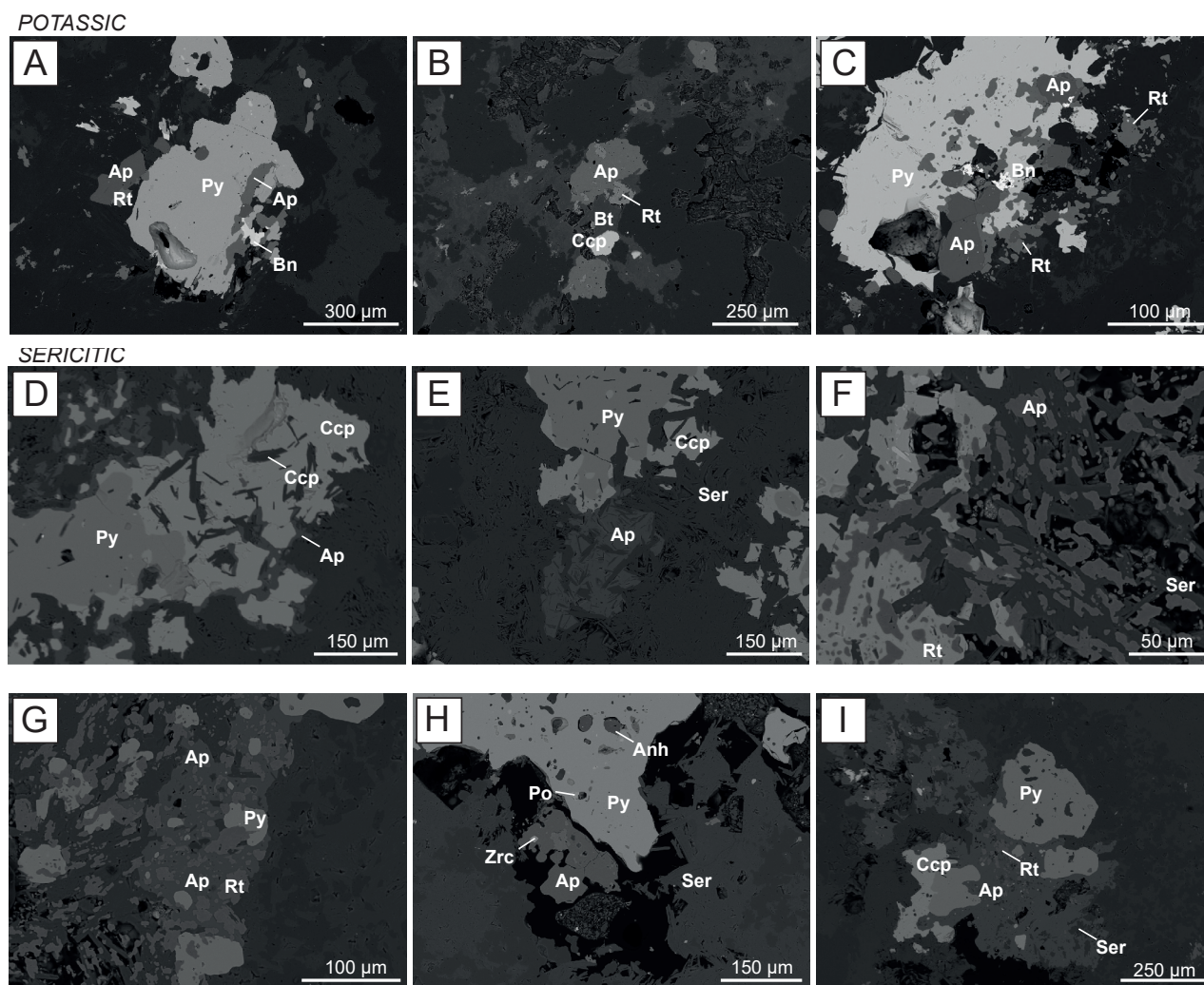


Figure 7.3 BSE images of vug apatite at La Granja. Here the apatite forms part of a hydrothermal assemblage with sulfides or oxides that is not confined to a fracture or vein but infill large vugs. Potassic assemblages include: A) Quartz (qtz), pyrite (py), chalcopyrite, (ccp) and rutile (rt) intergrown with apatite in EDPPB (EB17037). B) Quartz, pyrite and chalcopyrite with less apatite in DIOP (EB18039). C) Biotite (bt), rutile and pyrite encased in irregular apatite in EDPPB (EB17037). Sericitic assemblages: D-E) Sericite (ser), pyrite and chalcopyrite in LQP2M (EB17051). F-G) Sericite and pyrite in LQP2M (EB17053). H) Sericite, pyrite and chalcopyrite in LQP2M (EB17051). I) Sericite, pyrite and chalcopyrite in LQP2M (EB17053).

apatite is less evident (about 40 % of analyses show some evidence for metasomatism compared to 50 % of magmatic apatites) and many of the textural features used to infer metasomatism are also common in ‘unaltered’ hydrothermal apatite. Because of this, and as the grains are already interpreted as hydrothermal, the alteration score of hydrothermal apatite will not typically be plotted, or used to screen apatite as was in *Chapter 6*. However, the compositional changes observed in metasomatised apatite are investigated below.

7.3 Hydrothermal apatite composition

The composition of hydrothermal apatite was determined using EPMA for major elements (such as S and halogens), followed by LA-ICP-MS for minor and trace elements. Description of the instrument set up and analytical procedures are given in *Chapter 3*, as are the detection limits and analytical precision associated with each method. Representative results, separated by apatite and alteration type, are given in tables 7.3 and 7.4. A table of results by sample are included in the *digital appendices*.

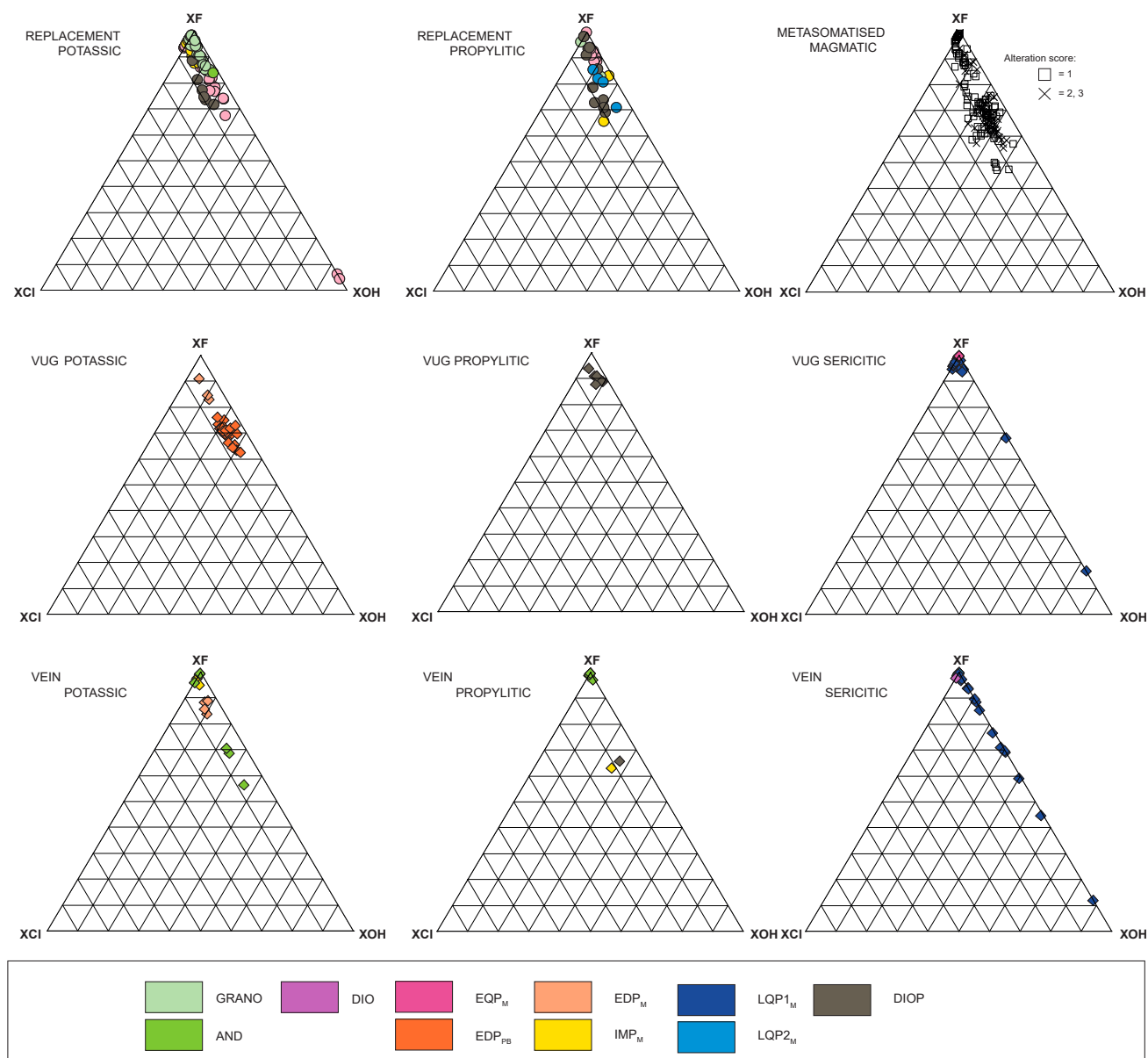


Figure 7.4 Ternary diagrams of mole fractions of halogens split by hydrothermal apatite type. Calculations are described in chapter 6.

7.3.1 Replacement apatite

The compositions of apatite from potassic and propylitic replacement assemblages are broadly very similar. All replacement apatites are fluorine-rich (Fig. 7.4) with S concentrations at or below detection limit (Fig. 7.5). Replacement apatites from potassic alteration zones have higher concentrations of Mn, Sr (Fig. 7.6A) and typically higher concentrations of U, Pb (Fig. 7.6E) than apatite in propylitic zones. The REE profiles are comparable to those of magmatic apatite REE profiles, or be it with more positive Eu anomalies (Fig. 7.8A). This includes a peak in concentrations at Pr and Nd, especially in potassic replacement apatites (Fig. 7.7). In general propylitic apatite has flatter pattern than potassic and magmatic apatite i.e. La/Sm, Gd/Yb ratios are closer to 1 (Fig. 7.8B). Overall, replacement apatites have a smaller range in composition compared to other hydrothermal apatites, and their compositions are comparable with metasomatised magmatic apatite (Figs. 7.6; 7.7). The compositions of replacement apatites are also comparable to vein and vug apatite of the same alteration.

Table 7.3 Representative compositions of hydrothermal apatite from a number of EPM analyses (n). The minimum (Min.), maximum (Max.) for each element in each apatite type and alteration domain are given as well as the calculated mean and associated standard deviation (Sd.). Values in *italics* are below the limits of detection (see Chapter 3).

	Replacement potassic (n = 107)				Replacement propylitic (n = 29)				Potassic vein (n = 15)				Propylitic vein (n = 9)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
wt. %																
Ca	36.26	39.77	38.62	0.51	37.82	39.62	39.03	0.38	37.52	39.65	38.59	0.61	38.93	39.34	39.16	0.14
P	17.31	19.23	18.87	0.31	18.00	19.52	18.72	0.38	17.55	19.22	18.54	0.48	18.37	19.31	19.00	0.27
Fe	0.01	0.80	0.22	0.20	0.02	0.76	0.20	0.19	0.05	0.69	0.21	0.19	0.13	0.53	0.28	0.12
Mg	0.01	0.67	0.04	0.08	0.01	0.28	0.03	0.06	0.00	0.29	0.06	0.08	0.00	0.11	0.02	0.03
Mn	0.00	0.70	0.32	0.14	0.03	0.34	0.17	0.07	0.02	0.47	0.18	0.14	0.08	0.33	0.14	0.08
Na	0.02	0.16	0.06	0.05	0.02	0.10	0.04	0.03	0.01	0.14	0.05	0.04	0.01	0.08	0.03	0.03
Al	0.02	1.11	0.04	0.14	0.02	0.25	0.03	0.07	0.01	0.46	0.14	0.19	0.01	0.15	0.04	0.06
S	0.01	0.48	0.04	0.05	0.01	0.20	0.05	0.05	0.01	0.17	0.05	0.04	0.01	0.12	0.04	0.04
Si	0.00	1.43	0.08	0.20	0.01	0.64	0.09	0.14	0.01	1.18	0.35	0.43	0.01	0.19	0.07	0.07
Sr	0.02	0.17	0.04	0.03	0.01	0.09	0.03	0.02	0.00	0.09	0.04	0.03	0.01	0.17	0.06	0.05
Y	0.02	0.26	0.09	0.05	0.01	0.26	0.05	0.06	0.00	0.16	0.05	0.05	0.01	0.04	0.02	0.01
F	2.46	4.45	3.52	0.46	2.47	4.63	3.32	0.50	2.13	4.42	3.49	0.67	2.48	4.45	3.85	0.57
Cl	0.06	0.80	0.29	0.12	0.00	0.79	0.28	0.21	0.04	0.52	0.26	0.15	0.02	0.52	0.10	0.16
O	38.38	40.77	40.22	0.32	39.10	41.05	40.12	0.50	39.45	41.12	40.16	0.49	39.80	40.83	40.49	0.29
Total	99.68	104.29	102.56	0.96	99.93	103.90	102.22	1.08	100.04	104.19	102.27	1.36	101.07	104.10	103.30	0.95
O=F	1.04	1.87	1.48	0.19	1.04	1.95	1.40	0.21	0.90	1.86	1.47	0.28	1.04	1.87	1.62	0.24
O=Cl	0.01	0.18	0.06	0.03	0.00	0.17	0.06	0.05	0.01	0.11	0.06	0.03	0.00	0.11	0.02	0.04
Corr. total	98.63	102.24	101.02	0.74	98.89	101.78	100.76	0.82	99.13	102.21	100.74	1.05	100.02	102.11	101.66	0.67
XF	0.65	1.18	0.93	0.12	0.66	1.23	0.88	0.13	0.57	1.17	0.93	0.18	0.66	1.18	1.02	0.15
XCl	0.01	0.12	0.04	0.02	0.00	0.12	0.04	0.03	0.01	0.08	0.04	0.02	0.00	0.08	0.01	0.02
XOH	0.30	0.34	0.33	0.86	0.34	0.35	0.34	0.84	0.25	0.43	0.30	0.80	0.34	0.34	0.34	0.82
	Sericitic vein (n = 60)				Vug potassic (n = 37)				Vug propylitic (n = 5)				Vug sericitic (n = 33)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
wt. %																
Ca	36.78	39.24	38.39	0.58	37.49	39.48	38.79	0.51	38.72	39.33	39.00	0.25	36.02	39.27	38.01	0.87
P	16.24	19.19	18.12	0.65	17.67	18.93	18.48	0.33	18.25	19.01	18.68	0.29	16.29	18.75	17.86	0.50
Fe	0.01	1.08	0.14	0.18	0.19	0.72	0.37	0.09	0.11	0.21	0.14	0.04	0.02	1.48	0.23	0.31
Mg	0.03	0.08	0.00	0.02	0.04	0.55	0.10	0.08	0.00	0.03	0.01	0.01	0.03	0.13	0.04	0.03
Mn	0.06	0.49	0.21	0.10	0.19	0.28	0.23	0.02	0.16	0.30	0.21	0.07	0.12	0.82	0.34	0.18
Na	0.01	0.65	0.22	0.19	0.03	0.18	0.07	0.03	0.01	0.07	0.03	0.03	0.00	0.19	0.06	0.05
Al	0.02	1.16	0.11	0.19	0.02	0.68	0.05	0.17	0.01	0.01	0.00	0.01	0.01	1.25	0.20	0.34
S	0.02	1.11	0.38	0.34	0.01	0.08	0.03	0.02	0.01	0.03	0.02	0.01	0.01	1.04	0.15	0.22
Si	0.01	1.10	0.15	0.26	0.00	0.80	0.10	0.21	0.00	0.02	0.01	0.01	0.00	1.35	0.26	0.41
Sr	0.01	0.10	0.04	0.03	0.02	0.09	0.05	0.01	0.00	0.03	0.02	0.01	0.01	0.15	0.08	0.04
Y	0.03	0.30	0.02	0.06	0.02	0.21	0.10	0.05	0.05	0.15	0.09	0.04	0.01	0.03	0.01	0.01
F	2.23	5.04	3.91	0.54	2.36	3.43	2.69	0.20	3.31	3.54	3.41	0.09	3.53	4.60	4.05	0.32
Cl	0.02	0.15	0.03	0.03	0.15	0.53	0.43	0.09	0.13	0.32	0.23	0.07	0.00	0.33	0.08	0.09
O	37.17	40.88	39.75	0.76	38.44	40.28	39.88	0.46	39.40	40.29	39.89	0.37	35.88	40.98	39.17	1.01
Total	95.73	103.46	101.47	1.60	97.78	102.73	101.52	1.13	101.18	102.49	101.81	0.54	92.99	103.04	100.59	2.04
O=F	0.94	2.12	1.64	0.23	0.99	1.44	1.13	0.09	1.39	1.49	1.44	0.04	1.49	1.94	1.71	0.14
O=Cl	0.00	0.03	0.01	0.01	0.03	0.12	0.09	0.02	0.03	0.07	0.05	0.02	0.00	0.07	0.02	0.02
Corr. total	94.80	101.30	99.82	1.37	96.75	101.17	100.29	1.03	99.76	100.93	100.32	0.49	91.50	101.03	98.86	1.89
XF	0.59	1.34	1.04	0.14	0.63	0.91	0.72	0.05	0.88	0.94	0.91	0.02	0.94	1.22	1.08	0.09
XCl	0.00	0.02	0.00	0.00	0.02	0.08	0.06	0.01	0.02	0.05	0.03	0.01	0.00	0.05	0.01	0.01
XOH	0.36	0.41	0.04	0.85	0.01	0.35	0.22	0.93	0.01	0.10	0.06	0.97	0.06	0.27	0.09	0.90

Table 7.4 Representative compositions of hydrothermal apatite from a number of LA-ICP-MS analyses (n). The minimum (Min.), maximum (Max.) for each element in each apatite type and alteration domain are given as well as the calculated mean and associated standard deviation (Sd.). Values in *italics* are below the limits of detection (see Chapter 3).

ppm	Replacement potassic (n = 80)				Replacement propylitic (n = 30)				Potassic vein (n = 8)				Propylitic vein (n = 3)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Na	119	4470	857	558	105	1131	401	270	320	822	514	184	210	394	306	93
Mg	111	7477	708	1162	89	9567	941	1811	174	1737	735	500	81	852	363	425
Al	0.3	8866	746	1614	14	6073	894	1257	1	910	322	351	14	569	207	314
Si	133	23782	1792	4017	302	122051	6165	22001	416	2319	1009	664	291	2698	1378	1220
Ti	0.05	7582	131	857	0.05	375	26	73	0.05	47	7	16	0.05	18	6	10
V	0.2	45	4	6	1	44	9	11	1	27	8	10	1	34	12	19
Mn	109	5963	3425	1195	305	3861	1757	724	358	4410	1973	1304	922	2682	1566	971
Fe	251	2143	746	468	261	3439	852	692	490	1727	894	432	374	2035	973	923
As	4	287	36	65	5	282	90	95	14	37	21	8	4	13	7	5
Sr	134	1289	498	195	106	694	261	138	227	497	384	102	400	1055	670	343
Y	80	1520	796	294	164	968	461	240	215	955	500	251	206	414	282	114
La	16	870	295	177	14	647	119	142	76	899	411	269	37	528	212	274
Ce	46	2231	945	517	43	1503	335	369	245	2229	1059	715	120	1239	511	631
Pr	7	313	144	76	8	216	50	51	40	332	147	109	22	159	69	78
Nd	40	1528	661	330	47	1001	250	240	213	1345	634	453	120	644	299	299
Sm	19	358	170	72	23	264	80	50	60	324	143	96	47	134	78	48
Eu	6	46	30	10	5	36	20	10	12	35	24	7	17	22	20	2
Gd	25	290	154	58	33	213	95	41	50	290	121	80	55	110	78	28
Tb	3	48	24	9	6	27	16	7	7	38	17	10	10	15	12	3
Dy	15	298	149	52	36	170	96	44	44	203	98	53	53	84	67	16
Ho	3	58	30	11	6	37	18	10	8	35	19	9	8	15	11	3
Er	8	158	89	33	15	106	48	28	22	92	52	24	20	37	27	9
Tm	1	22	13	5	2	16	7	4	3	11	7	3	2	4	3	1
Yb	5	148	88	35	10	106	41	28	23	73	45	17	14	25	18	6
Lu	1	22	13	5	1	16	6	4	3	10	6	2	2	3	2	1
Pb	0.3	29	5	4	0.4	10	2	2	1	3	2	1	1	4	2	2
Th	0.2	187	24	43	0.4	17	4	4	2	152	38	52	1	10	4	5
U	0.3	44	21	11	0.2	82	13	19	2	56	19	18	0.5	2	1	1
Ce/Ce*	0.6	1.3	0.9	0.2	0.6	1.3	1.0	0.2	0.7	1.3	0.9	0.2	0.9	1.1	1.0	0.1
Eu/Eu*	0.3	0.9	0.6	0.1	0.4	1.1	0.7	0.2	0.3	1.2	0.7	0.4	0.4	1.3	0.9	0.4
LaSm	0.6	8.3	1.7	1.0	0.5	5.5	1.3	1.1	1.0	5.9	3.1	1.6	0.7	4.0	2.0	1.7
GdYb	1.0	4.6	1.9	0.6	1.2	8.6	2.9	1.6	1.4	5.7	2.7	1.4	3.8	5.1	4.4	0.6
LaYb	1.0	44.5	3.6	4.9	0.9	63.9	5.2	12.8	1.2	17.6	9.8	5.8	2.7	21.2	9.6	10.1
SrY	0.1	2.1	0.7	0.4	0.2	3.7	0.8	0.8	0.4	2.3	1.0	0.7	1.0	5.1	2.8	2.1
ΣREE	254	5864	2804	1320	253	3676	1180	888	1052	5890	2782	1768	571	3013	1408	1391

Table 7.4 (cont.)

ppm	Sericitic vein (n = 45)				Vug potassic (n = 14)				Vug propylitic (n = 4)				Vug sericitic (n = 36)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Na	179	5034	2259	1331	491	1298	688	219	372	1083	579	337	178	5214	1239	1169
Mg	7	1925	123	302	181	3265	1272	762	263	4255	1559	1826	24	7650	1387	2178
Al	1	5057	360	1124	2	1428	133	377	123	4394	1757	1849	0	53096	3172	9437
Si	228	10582	1054	2157	134	1884	531	463	500	8362	3472	3554	174	156623	11401	31658
Ti	0.05	13	1	2	0.05	632	132	242	1	349	133	161	1	440	87	112
V	0.4	4	0	1	0.3	11	4	3	2	7	5	3	0.02	12	1	3
Mn	587	5681	2475	1290	1946	2663	2313	211	2040	2751	2371	322	795	5977	3144	1296
Fe	80	1585	231	231	349	2134	1255	373	578	2472	1325	818	92	23178	1292	3818
As	1	55	10	10	3	29	12	9	6	23	15	7	1	42	10	9
Sr	146	1226	367	250	478	794	566	94	269	361	302	42	182	1264	650	356
Y	2	1712	162	322	217	1831	884	529	683	1834	1002	556	4	2046	252	406
La	0.2	243	40	55	146	1011	309	226	144	235	170	43	2	392	73	104
Ce	0.03	869	108	186	515	2049	981	554	413	614	471	96	4	1303	199	306
Pr	0.01	157	19	33	79	375	158	99	58	87	67	13	1	220	32	50
Nd	0.3	919	109	197	320	1780	764	495	270	452	334	81	4	1139	163	261
Sm	0.1	381	46	82	64	479	210	139	91	164	117	33	1	379	55	89
Eu	0.5	224	34	48	21	40	28	6	28	46	34	8	1	284	40	72
Gd	0.4	439	52	92	46	411	191	125	118	242	161	56	1	412	59	97
Tb	0.08	61	8	13	7	63	29	18	23	48	30	12	0	62	9	13
Dy	0.4	325	38	68	43	369	174	107	148	340	202	92	1	335	47	69
Ho	0.1	57	6	11	8	73	34	21	30	74	42	21	0.1	60	9	12
Er	0.2	138	14	26	24	207	96	56	81	223	122	68	0.3	148	22	32
Tm	0.01	16	1	3	4	29	14	8	11	31	17	10	0.04	18	3	4
Yb	0.1	89	8	16	24	196	92	49	77	213	114	66	0.2	106	16	25
Lu	0.01	10	1	2	3	26	13	6	11	29	16	9	0.03	13	2	3
Pb	2	55	21	13	2	3	2	0.1	3	6	4	1	3	36	17	9
Th	0.01	26	1	4	2	270	34	69	4	30	16	13	0.02	43	3	7
U	0.1	2210	674	694	8	49	19	11	11	144	64	64	4	2249	299	575
Ce/Ce*	0.6	2.7	1.2	0.4	0.6	1.0	0.8	0.1	1.1	1.2	1.1	0.0	0.7	2.3	1.0	0.3
Eu/Eu*	0.9	19.0	3.6	3.6	0.2	1.7	0.6	0.4	0.7	0.8	0.8	0.1	0.8	18.7	2.6	3.4
LaSm	0.2	20.6	2.5	4.4	0.7	7.8	2.0	1.9	1.4	1.6	1.5	0.1	0.4	15.2	1.9	2.4
GdYb	1.6	14.6	7.4	2.9	1.3	2.7	2.0	0.4	1.1	1.8	1.5	0.3	1.1	18.1	5.7	4.3
LaYb	0.3	160.0	17.6	34.0	1.4	28.2	5.1	7.0	1.1	1.9	1.7	0.4	1.8	114.9	10.2	19.4
SrY	0.1	454.2	35.3	81.2	0.3	3.2	1.0	0.8	0.2	0.4	0.3	0.1	0.1	63.6	10.5	14.1
ΣREE	5	3684	517	826	1562	6230	3093	1659	1504	2801	1897	608	17	4758	727	1089

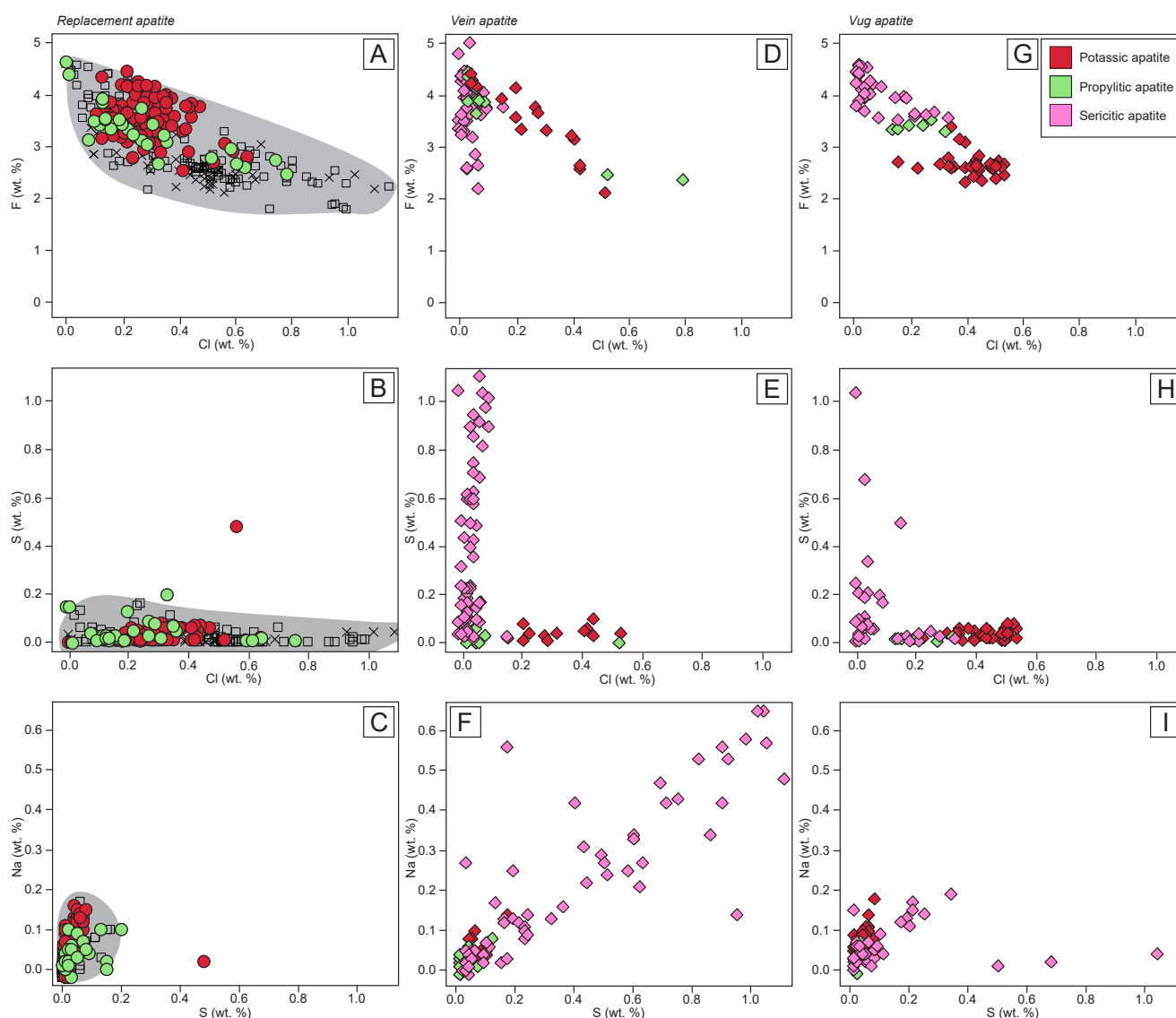


Figure 7.5 EPMA results from hydrothermal apatite as a function of apatite type and alteration assemblage. The compositions of metasomatised magmatic apatites are indicated by the grey field and black points. Empty squares - alteration score of 1, crosses - alteration score > 2. A-C). Replacement apatite associated with potassic and propylitic alteration has similar composition to magmatic apatite. Apatite in sericitic veins contains low Cl concentrations (D) and high S (E), which increases with Na (F). G-I) The composition of vug apatites is broadly similar to the composition of vein apatites from the same alteration assemblages, with the exception of some Cl-rich, S-poor sericitic vug apatites which look more like potassic-propylitic vein type. Analytical error is smaller than symbol size.

7.3.2 Vein apatite

Vein apatites have the largest variation in composition of all apatite types. All vein apatites are fluorapatite; however the majority of the sericitic vein apatites contain Cl contents near to or below the EPM detection limit (Fig. 7.5D). Apatites from propylitic and potassic alteration zones show low S concentrations. By contrast apatite in sericitic veins contains between 0 – 1.1 wt. % S, with apatites from coarse D-veins (EB17047; Qtz + Py + Ccp) contain the highest concentrations of S (Fig. 7.5E-F). The composition of low S sericitic apatite is more comparable to those of potassic and propylitic veins (Fig. 7.5). The two groups of sericitic vein apatites also have different trace element composition. The high S apatites (i.e. EB17047) have lower Y, Sr and higher U and Pb than the lower S sericitic apatite (Fig. 7.6). Again these concentrations overlap those of potassic and propylitic apatites. In general though, sericitic apatite can be distinguished from potassic and propylitic vein apatite by lower V, Fe, As and higher Na, U, Pb concentrations (Fig. 7.6). Potassic and propylitic

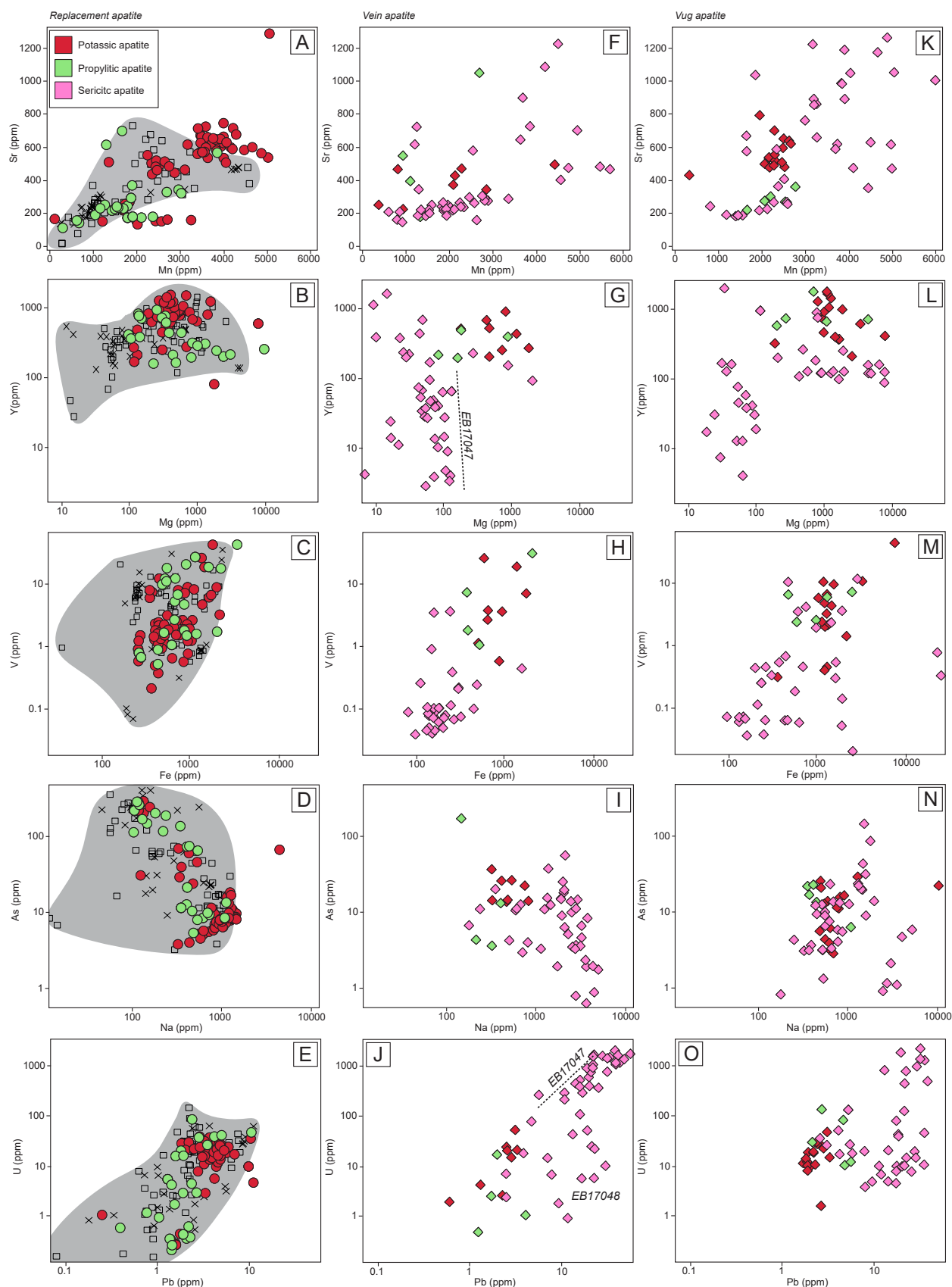


Figure 7.6 LA-ICP-MS results from hydrothermal apatite as a function of apatite type and alteration assemblage. The compositions of metasomatised apatites are indicated by the grey field and black points. Empty squares - alteration score of 1, crosses - alteration score > 2. A-E) replacement potassic and propylitic apatite are similar in composition and comparable to metasomatised magmatic apatite from the same samples. F-J) Vein apatites from potassic and propylitic assemblages tend to fall at one end of the arrays observed for the replacement apatites whereas sericitic vein apatites have a much wider range in composition that spreads beyond the range of the other two alteration types. K-O) Vug apatites show broadly similar compositions to vein apatites from the same alteration assemblages. Analytical error is smaller than symbol size.

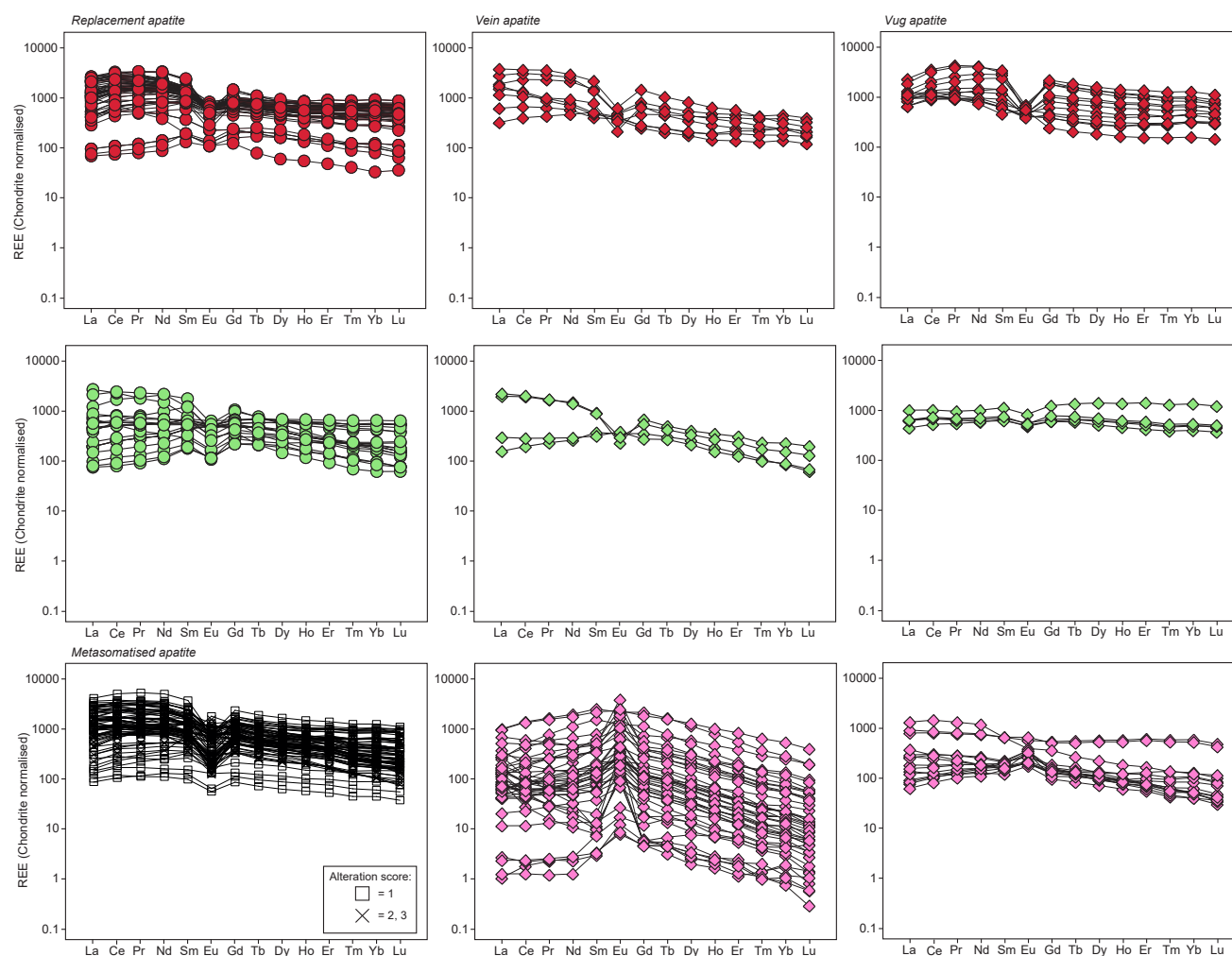


Figure 7.7 Chondrite-normalised REE patterns of hydrothermal apatite as a function of apatite type and alteration assemblage (red = potassic, green = propylitic, pink = sericitic). The compositions of metasomatised apatites are indicated by the black points. Empty squares - alteration score of 1, crosses - alteration score > 2. Normalisation parameters from Sun & McDonough (1989). Analytical error is smaller than symbol size.

have a much more restricted range in composition in both minor (Fig. 7.5) and trace element composition (Fig. 7.6). This can also be seen in the REE pattern which is comparable to replacement apatite from the same alterations (Fig. 7.7). Sericitic vein apatites have a large range in REE patterns with higher Gd/Yb, Ce/Ce* and Eu/Eu* and lower total REE than all other apatite (Fig. 7.8D-F).

7.3.3 Vug apatite

Sericitic vug apatites have the highest F concentration followed by propylitic, and then by potassic vug apatite (Fig. 7.5G). Sericitic vug apatites also show the same separation in S concentrations as vein apatite, with higher S associated with sericite (EB17047; Fig. 7.5H). The trace element compositions of vug apatite are broadly comparable to vein apatites from the same alteration association, although the range in concentrations is typically smaller (Figs. 7.5; 7.7). Similar to minor element composition, the trace element concentrations of sericitic vug apatite show the same separation between assemblages. However, the variation in REE pattern is much more limited. In addition, potassic and propylitic vug apatite have comparable REE profiles to replacement and vein apatite (Fig. 7.7), although be it some grains have flatter profiles (lower Gd/Yb; Fig. 7.8H). Potassic vug apatites have the lowest Eu/Eu* values while sericitic have the highest values (Fig. 7.8G).

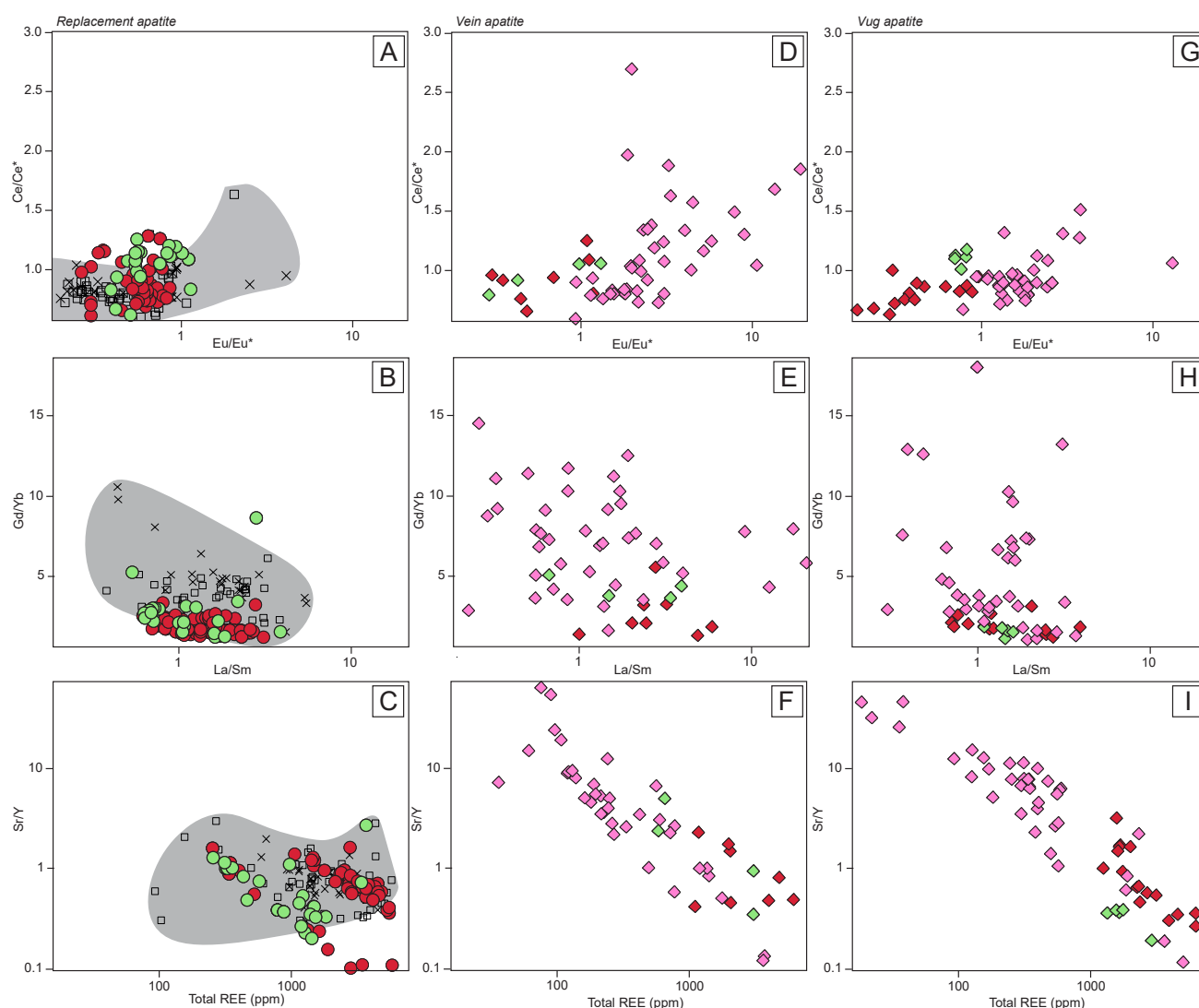


Figure 7.8 Element ratios and total REE content of hydrothermal apatites as a function of apatite type and alteration assemblage. The composition of metasomatised magmatic apatites are indicated by the grey field and black points. Empty squares - alteration score of 1, crosses - alteration score > 2. A-C) Replacement potassic and propylitic apatite are comparable in composition and are similar to metasomatised magmatic apatite. Sericitic vein apatite exhibits higher Eu/Eu^* and Ce/Ce^* (D), higher Gd/Yb ratios (E) and higher Sr/Y (F) than potassic and propylitic vein apatite which are comparable to the replacement potassic and propylitic apatites. G-I) Vug apatite shows similar compositions to vein apatites from the same alteration assemblage. Analytical error is smaller than symbol size.

7.3.4 Metasomatised apatite

As noted in *Chapter 5*, compositional changes from metasomatism are accompanied by textural alteration; most notable is the formation of pits on the surface of the grain which can be infilled by secondary, LREE-rich monazite (Harlov 2005, 2015). The presence of these alteration textures can be used to classify the degree of metasomatism (see *section 5.2.4*). Typically, metasomatised magmatic apatite has lower total REE concentrations relative to the least altered magmatic apatite, with the largest decrease observed in the LREE. In addition, lower Th concentrations in more metasomatised apatite are consistent with the formation of monazite (Miles et al. 2013; Fig. 7.9A). Mn and Sr concentrations show no consistent changes with metasomatism (Fig. 7.9B), whereas the concentration of more mobile elements like Pb and Na are similar for all metasomatised magmatic apatite (Fig. 7.9C). Across all the apatite analyses the composition of metasomatised magmatic apatite is most comparable to sericitic apatite, especially for REE, Th, Pb and Na (Fig. 7.9) and also overlaps considerably with potassic and propylitic replacement apatite composition (Figs. 7.6; 7.8).

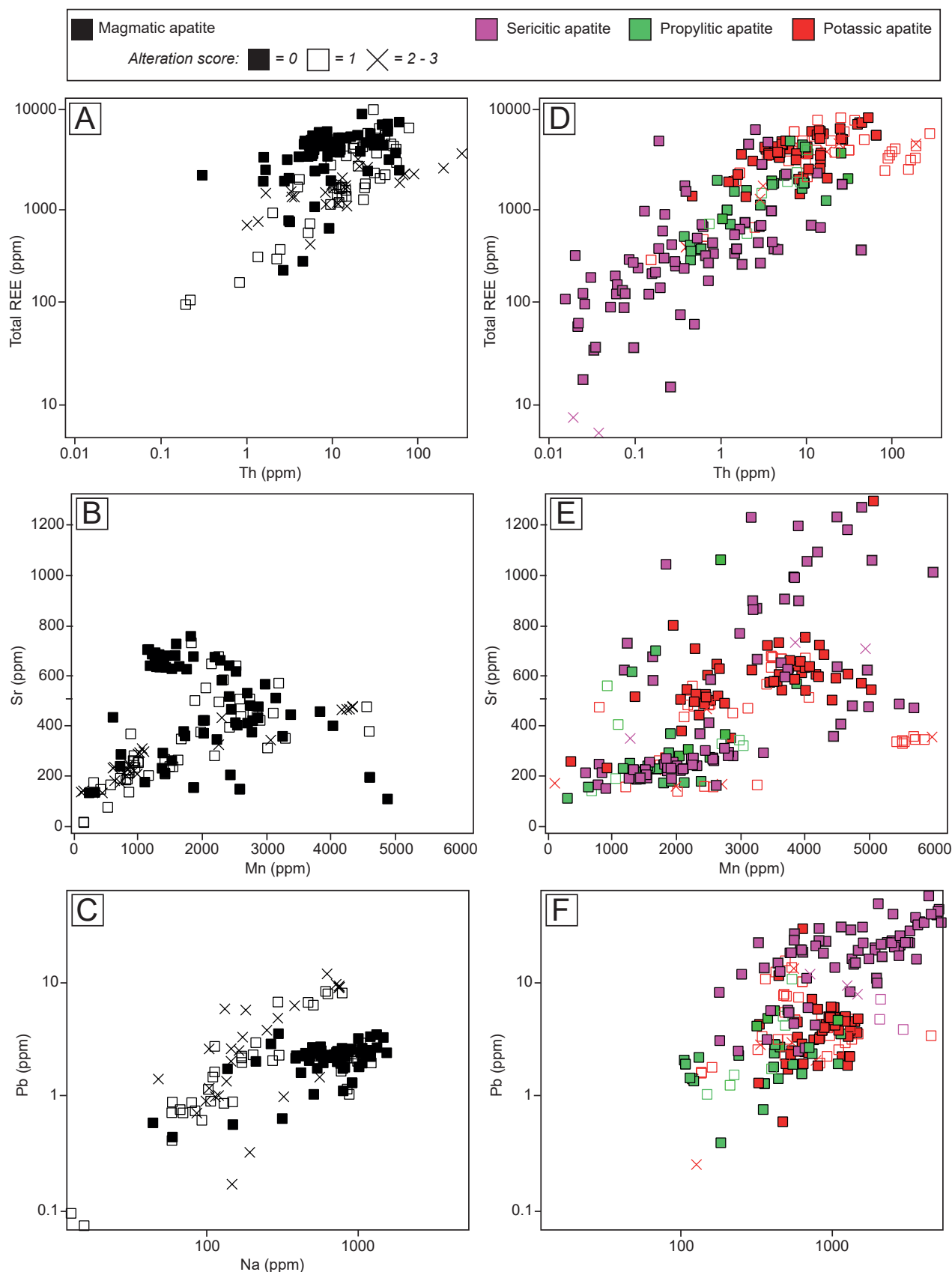


Figure 7.9 Composition of metasomatised A-C) magmatic apatite and D-F) hydrothermal apatite by with alteration score (see Chapter 5: filled squares - 0, empty squares - 1, crosses - 2). A) Metasomatised magmatic apatite has lower Th with respect to total REE, however; B) concentrations of Mn and Sr are not consistent with alteration score. C) Metasomatised magmatic apatite lies along a positive Na and Pb trend. Hydrothermal apatite is coloured by alteration association (red – potassic, green – propylitic, pink – sericitic). Changes with metasomatism are smaller than those for magmatic apatite. D) There is little systematic difference in total REE of Th E-F) or Mn-Sr as with metasomatised magmatic apatite. Metasomatised potassic apatites have lowered Sr concentrations closer to those of propylitic and sericitic apatite. Analytical error is smaller than symbol size.

7.4 Controls on hydrothermal apatite composition

The three types of hydrothermal apatite (replacement, vug and vein) are inferred to have different modes of formation that controlled the different textures and mineral assemblages observed in each type. The variations in composition of the hydrothermal apatites suggest that the hydrothermal fluid composition, precursor minerals, co-precipitating minerals and bulk chemistry of the host lithology may all have influenced apatite chemistry. In order to interpret changes in the apatite chemistry, we must first understand the relative controls.

Apatites in replacement assemblages are formed from the interaction of hydrothermal fluid with an existing mineral phase in the rock. The compositions of replacement apatites are comparable in many respects to metasomatised magmatic apatites from the same sample (Fig. 7.10). This implies that both replacement and former magmatic apatite have responded to fluid-rock interaction in a similar way. This could be an influence of the precursor minerals or that the hydrothermal fluid within that sample is controlling composition. As the compositions of replacement

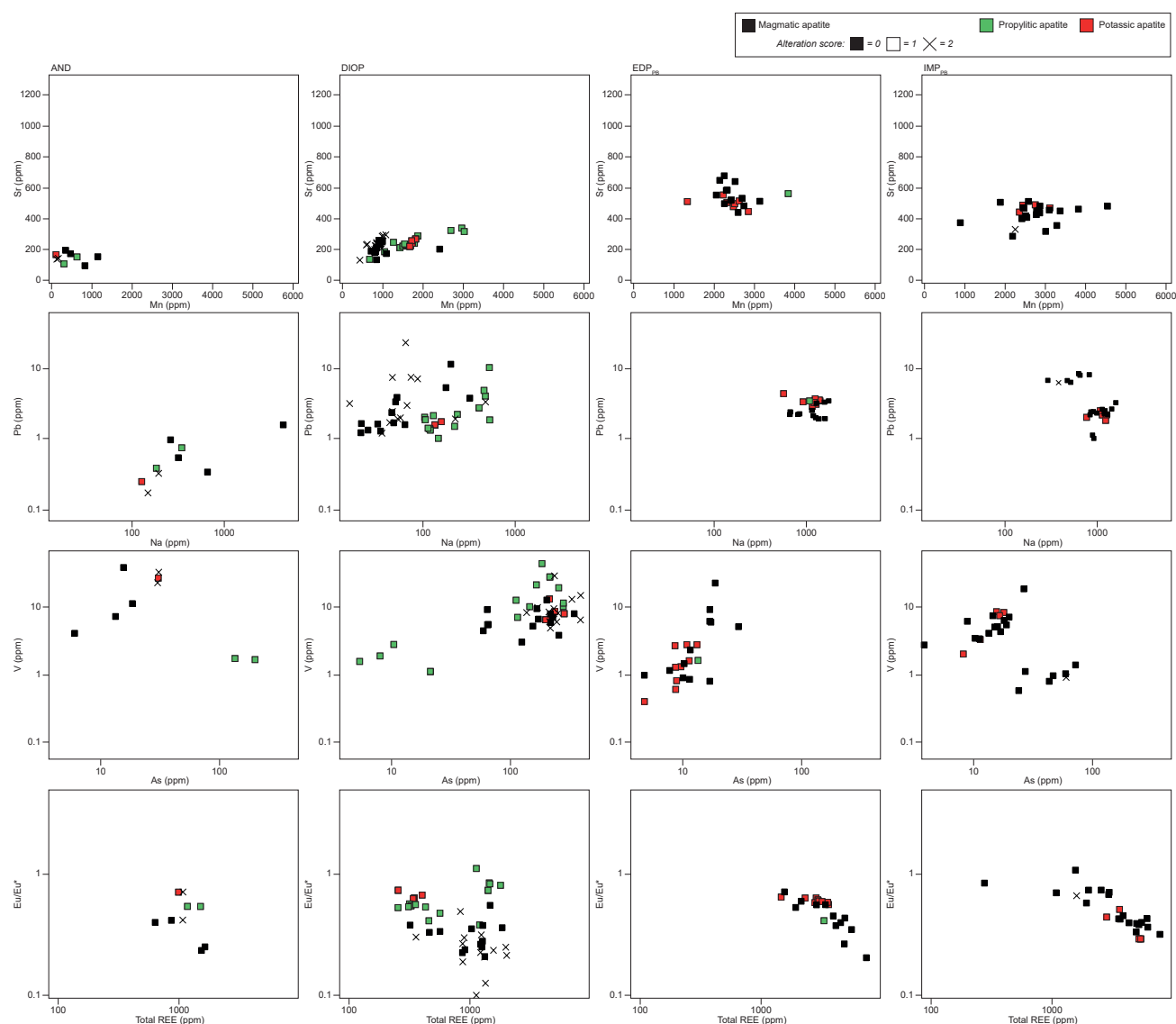


Figure 7.10 Plot of replacement apatite (red - potassic, green – propylitic) and metasomatised magmatic apatite (black) by host unit. The degree of metasomatism of the magmatic apatite is indicated by alteration score (see Chapter 5: filled squares - 0, empty squares - 1, crosses - 2). Analytical error is smaller than symbol size.

apatite show little systematic distinction between potassic and propylitic assemblages, this could be used to infer a greater control from the precursor minerals than the fluid on the apatite composition. However, the potassic and propylitic vein apatite (the composition of which is inferred to be strongly controlled by the fluid) are also comparable to magmatic apatite composition (Figs. 7.5; 7.6). Given that magmatic apatite is changing chemistry principally by interaction with a fluid phase, it follows that the nature of the precursor mineral in replacement apatite does not have an overriding influence, and that both types of apatite acquire their signature mainly from the fluid. This does not mean that local fluid-rock interaction is not affecting apatite chemistry, rather that it does so on a larger scale than just the immediate environment of a pseudomorphic replacement reaction. This can be demonstrated by the composition of hydrothermal apatite from two units of similar bulk rock composition, but different timings of emplacement and therefore fluid exposure (EDP_{PB} and IMP_{PB} ; see *Chapter 4*). Whereas least altered magmatic apatite is broadly comparable in composition, the hydrothermal apatite show more varied compositions (Fig. 7.10).

By contrast, vein apatites are inferred to have precipitated directly from a fluid within fractures in a higher fluid:rock ratio environment than for replacement apatite. As a result, vein apatites would be expected to show less host lithology or precursor mineral control, and are more likely to be influenced by the physico-chemical characteristics of the infiltrating fluid. This inference is supported by the fact that the data group more strongly by alteration style than by host lithology (Figs. 7.5; 7.6; 7.8), with similar assemblages from different samples exhibiting comparable apatite composition (Fig. 7.11). Furthermore, the widest range in compositions is observed for apatite in the thicker, sericitic veins (for example as in sample EB17047- Qtz + Py + Ccp) where the effective fluid:rock ratio is highest. As a result (of being isolated), apatite from different assemblages in veins, but the same host lithology, can have very different compositions.

Vug apatite forms within vugs or large areas of secondary porosity and is not observed to be directly replacing a mineral. Vug apatites are classified separately to vein apatite as they have not crystallised in distinct fractures, rather in small pockets of fluid that developed during fluid-rock interaction. Thus, these apatites could be anticipated to have formed under intermediate fluid:rock ratios – more rock influenced than the vein apatites but less rock influenced than the replacement apatites. For the most part, the vug apatite tends to approach the vein-type equivalent within the same alteration association (Figs. 7.6; 7.7; 7.8) so, for the subsequent plots, these have been grouped together

7.4.1 Multiple generations of hydrothermal apatite

The relative influence of precursor minerals and the hydrothermal fluid on apatite composition can be illustrated by comparing the compositions of different textural associations of apatite within a single sample (Fig. 7.12). Plots confirm that overall the fluid phase has a dominate control on the hydrothermal apatite composition. Least altered magmatic apatite reflect a magmatic end-member compositions, the opposite to vein and vug apatite which are the most fluid-dominated composition. Overprinted magmatic apatite and replacement apatite lies on approximate mixing lines between the two, with replacement and more metasomatised apatites closer to the vein apatite compositions.

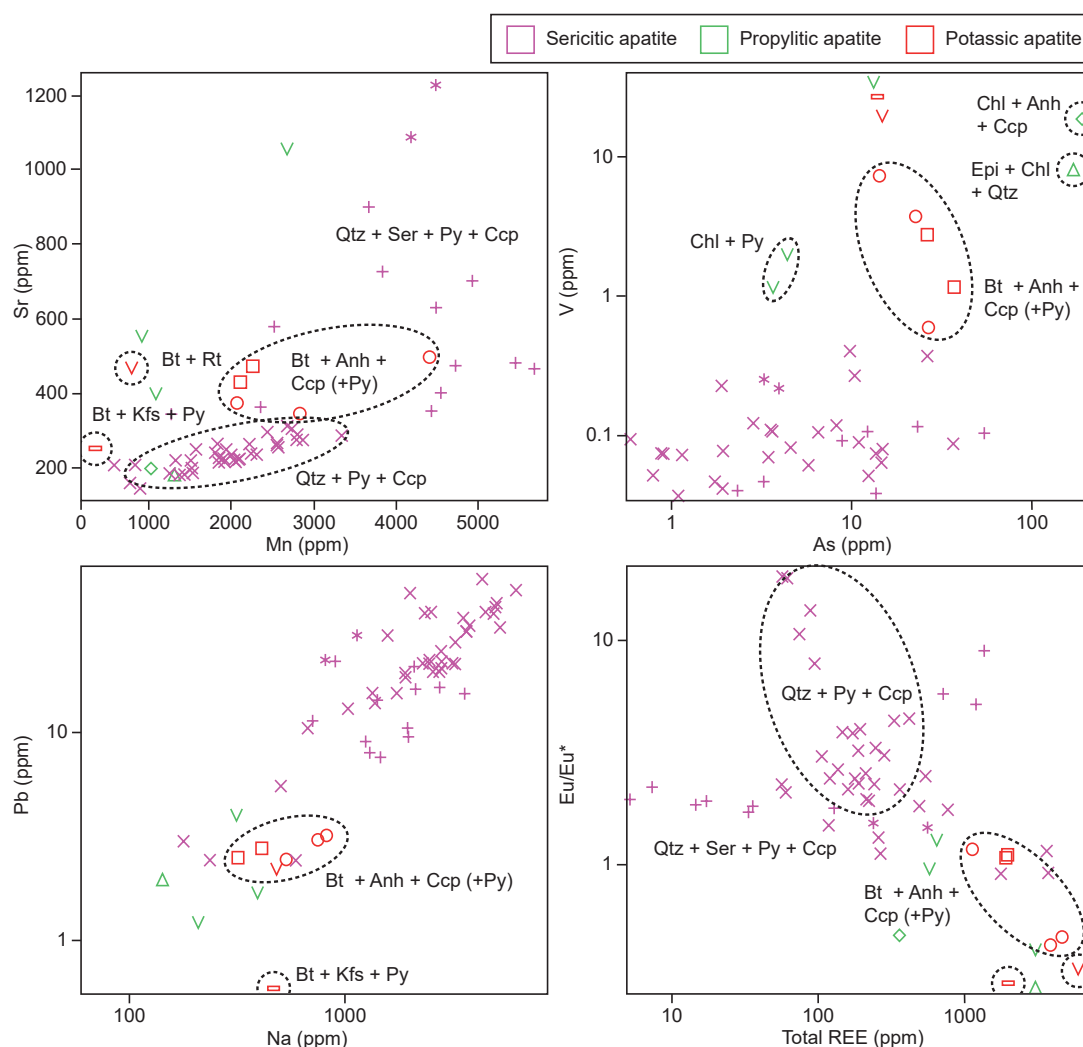


Figure 7.11 Composition of vein apatite by sample (shape) and coloured by alteration style (red – potassic, green – propylitic, pink – sericitic). Like assemblages are highlighted and show the composition of apatite from like assemblages can be comparable across different samples. In addition, multiple assemblages within a single sample have distinct compositions. Analytical error is smaller than symbol size.

The spread in the hydrothermal compositions within a sample depends on the alteration style. In proximal propylitic altered samples, propylitic-related apatite show very little compositional change and are similar to potassic and metasomatised magmatic compositions (Fig. 7.12; EB17018). However, in more distal samples, propylitic alteration may result in more significantly modified compositions (Fig. 7.12; EB17039). The overprinted magmatic apatites within samples with sericitic assemblages have a large range in compositions implying the original composition is furthest from equilibrium with the fluid (Fig. 7.12; EB17047).

As with magmatic apatite, different textural associations of hydrothermal apatite can be inferred to represent different stages of a system's hydrothermal evolution. This is made even more complex as the fluid composition changes with space and time producing the different alteration zones. In addition, as there is evidence for metasomatism of hydrothermal apatite grains, this indicates that earlier hydrothermal stages can also be overprinted, consistent with models of porphyry formation and grade development (Audétat et al. 2012; Sillitoe 2010; Seedorff et al. 2005). It has been suggested that zonation within hydrothermal apatite could record equilibration with multiple fluids (e.g. Krneta et al. 2017; Li & Zhou 2015) however for

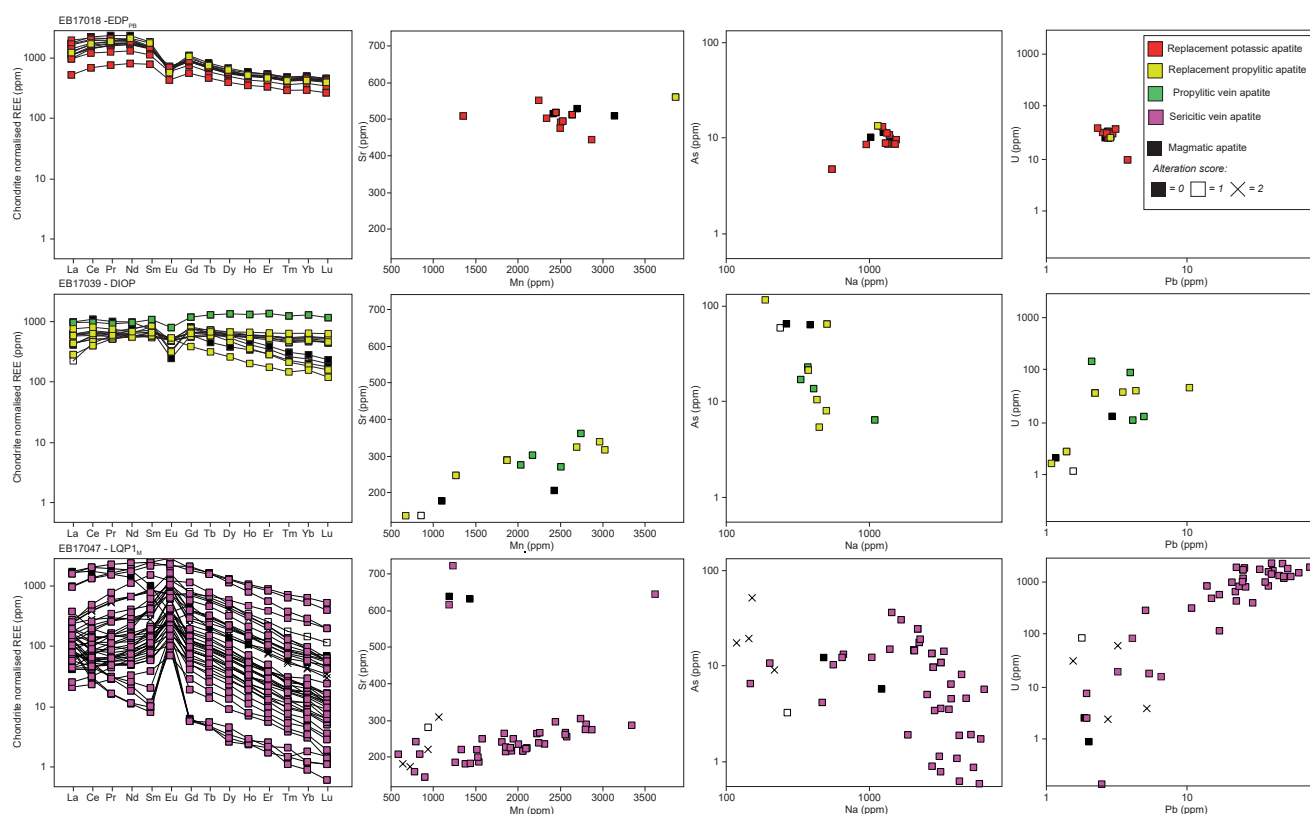


Figure 7.12 Compositional variations in hydrothermal apatite and metasomatised magmatic apatite observed within a single sample. The composition of vein apatite (green – propylitic, pink – sericitic) are more distinct from least altered magmatic apatite (black squares) with replacement (red – potassic, yellow – propylitic) and metasomatised magmatic apatite (alteration score: empty squares – 1, crosses – 2) lying on a mixing line between the two. Analytical error is smaller than symbol size.

this study, analyses were focused at the centre of the grains avoiding areas of more intense alteration, but thereby results may only capture part of the layered hydrothermal history.

7.5 Inferring hydrothermal fluid compositions from apatite

As has been demonstrated so far, the composition of replacement apatite is in part determined by the precursor mineral. By contrast, the vein apatite is thought to more directly reflect the properties of the hydrothermal fluids and so these compositions are used to speculate on the origin and controls of evolution of the fluids involved.

The variability in vein apatite composition arising from direct precipitation from fluids can be explained by temporal variations in source fluid composition and variable degrees of fluid-rock interaction prior to precipitation of a given apatite grain, along with changes in pressure, temperature, pH and $f.O_2$ that might influence fluid-mineral partitioning.

7.5.1 Alteration zones at La Granja

In porphyry systems the hydrothermal fluids are exsolved from a deep, crystallising magma source and migrate towards the surface focused into conduits generated by the emplacement of porphyry stocks. At sufficient pressures, these will be supercritical and typically present as low to moderate salinity, intermediate density fluids (Sillitoe 2010; Fig. 7.13A). With decreasing depth/pressure (and temperature), the fluid will exsolve into two phases: a lower density vapour and a saline brine. The different characteristics of the phases will cause them to physically separate with the more buoyant vapour rising faster, and is responsible for the more acidic alteration facies that

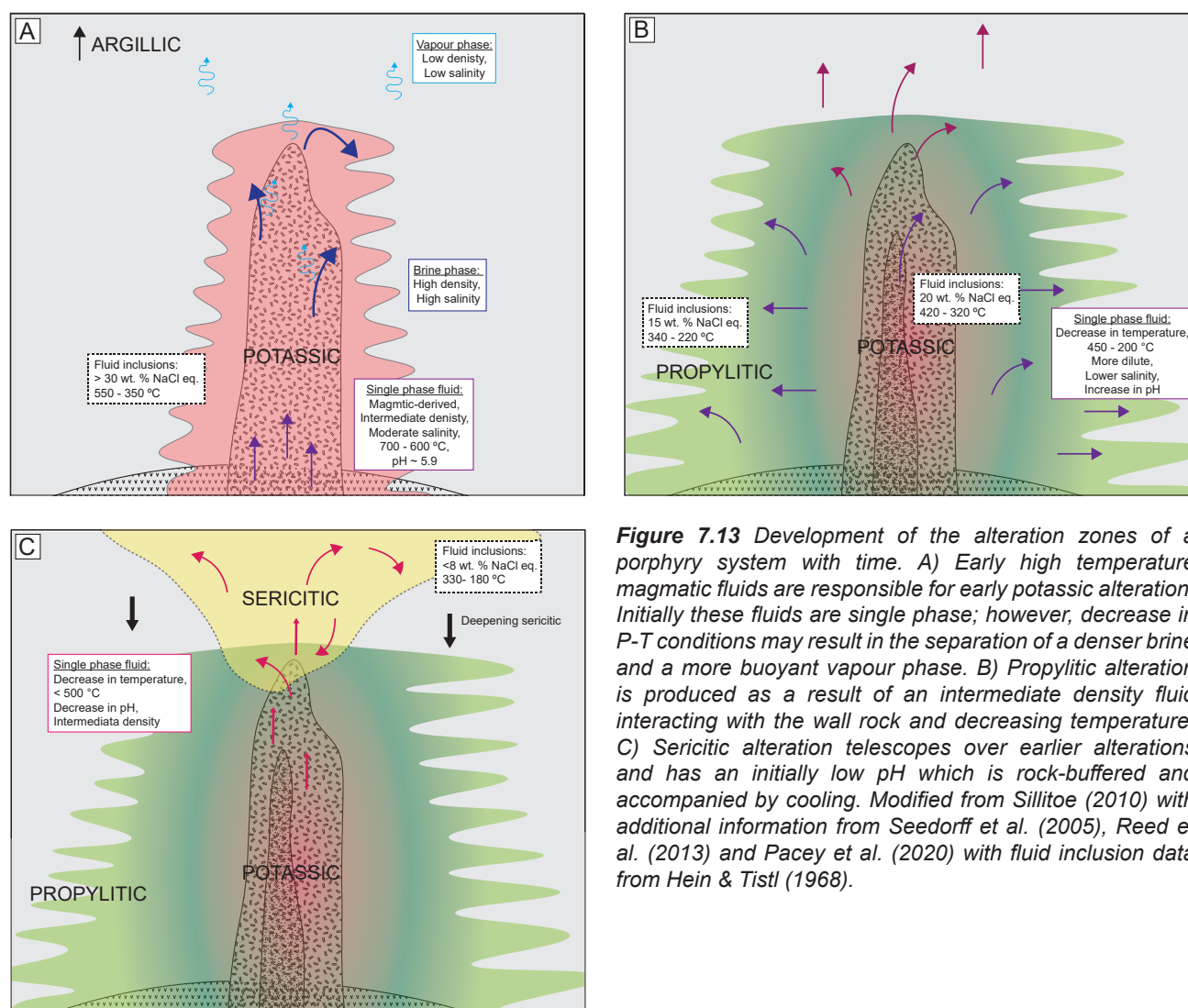


Figure 7.13 Development of the alteration zones of a porphyry system with time. A) Early high temperature magmatic fluids are responsible for early potassic alteration. Initially these fluids are single phase; however, decrease in P-T conditions may result in the separation of a denser brine and a more buoyant vapour phase. B) Propylitic alteration is produced as a result of an intermediate density fluid interacting with the wall rock and decreasing temperature. C) Sericitic alteration telescopes over earlier alterations and has an initially low pH which is rock-buffered and accompanied by cooling. Modified from Sillitoe (2010) with additional information from Seedorff et al. (2005), Reed et al. (2013) and Pacey et al. (2020) with fluid inclusion data from Hein & Tistl (1968).

generally overlie the porphyry deposit, and for the brine pooling around the base of porphyries (Fig 7.13A; Heinrich 2005). The composition of the hydrothermal fluids is largely derived from the magmatic composition and will evolve throughout interaction with the wall rock which will also affect the pH and $f.O_2$ (Seedorff et al. 2005). However, fluid phase separation can result in significant fractionation of elements between the new phases. This change in fluid conditions, coupled with a decrease in P-T conditions with time and space, is responsible for the change in alteration assemblages defining the different alteration zones (Sillitoe 2010; Seedorff et al. 2005).

Potassic alteration begins from early, high temperature (750 – 600 °C, pH around 5.9) fluids, the composition of which is principally controlled by melt-fluid partitioning. They are initially single phase, and of intermediate density and moderate salinity (Fig. 7.13A; Pacey et al. 2020; Seedorff et al. 2005; Sillitoe 2010; Reed et al. 2013). Although propylitic fluids were previously thought to be predominantly composed of meteoric fluids (Seedorff et al. 2005), the predominance of a magmatic component in these fluids is supported by recent isotopic analyses (Pacey et al. 2020). This understanding is also consistent with the model of Reed et al. (2013) who showed that propylitic, potassic (and sericitic) assemblages can all be produced from a single fluid composition undergoing cooling and wall rock reactions. Propylitic alteration occurs at temperatures between 450 – 200 °C (Pacey et al. 2020) and may be more acidic

than potassic fluids (pH of around 5.5) in proximal alterations before evolving to a slightly more alkaline composition (pH of around 6 in more distal zone ;Reed et al. 2013; Fig. 7.13B).

Despite this, it is important to note that the samples in this study are all relatively proximal to the porphyry centres. This is reflected in the mass transfer study (see *section 4.5.1*) which shows smaller changes in the propylitic samples than observed elsewhere (e.g. Pacey 2016). In addition, for the samples analysed, potassic and propylitic vein apatites are comparable in composition – compatible with their inferred contemporaneous formation (Sillitoe 2010) and therefore related fluid compositions. It is thought likely that if more distal propylitic apatites were investigated, the compositions would be more distinct.

A fluid inclusion study of the Paja Blanca porphyry by Hein & Tistl (1986) identified three types of fluid inclusions. Propylitic alteration was linked to the liquid-dominated, two phase fluid inclusions of intermediate density (~ 15 wt. % NaCl equivalent, 240–320 °C). However, more saline fluids were associated with potassic alteration: an early, saline magmatic fluid (> 30 wt. %NaCl equivalent, 550–350 °C) which cooled and was diluted (20 wt. % NaCl equivalent, 420–320 °C). Based on this, and existing understanding of the formation of porphyry alteration zones (Sillitoe 2010), potassic and propylitic vein apatite most likely precipitated from a brine or intermediate density fluid.

A review of fluid inclusion data from the literature (Landtwing et al. 2005; Rusk et al. 2004; Ulrich et al. 1999, 2001; Vry 2010) reveals broadly comparable compositions of intermediate density fluids and vapours in porphyry systems, but a distinct enrichment of elements such as Sr, Mn, Fe, Na, K and Pb in brines (Fig. 7.14). Aside from halogens, there is a limited amount of published data available for apatite-fluid partitioning of elements at upper crustal pressures. Based on apatite-fluid partitioning coefficients for Sr (at admittedly rather unrealistic conditions of 1000 °C and 1GPa) which range between 15 – 33 (Ayers & Watson 1993), the concentration of Sr in potassic vein apatite (230 – 500 ppm, Table 7.4) and in propylitic vein apatite (400 – 1060 ppm) would suggest equilibration with a low salinity, intermediate density fluid or vapour phase rather than a brine (Fig. 7.14). The apparent lack of evidence for brine-related apatite may hinder understanding of porphyry ore formation using hydrothermal apatite as studies have suggested that Cl-rich brine may be key to the generation of high-grade mineralisation (Audétat et al. 2008). However, the partition coefficient data used above may not be valid for porphyry conditions and until experimental data exist for such conditions the interpretation of the fluids responsible for apatite formation remains uncertain, and modelling their chemistry from apatite compositions will be out of reach.

Later, lower temperature liquid and/or vapour phases are more acidic and will have been much more strongly influenced by wall-rock interaction along their flow path. This includes the fluids responsible for sericitic alteration, a destructive hydrolytic alteration type in which hydrogen ions replace cations. Feldspars are altered to sericite, chlorite and clay minerals and mafic minerals are altered to chlorite, epidote and pyrite, and with strong enough alteration eventually sericite (Barton et al. 1991). This breakdown of primary minerals produces interconnected pore space that aids the mobility of cations in the fluid and also buffers the low pH of the fluid. Sericitic temperatures are typically below 500 °C and have a pH range of

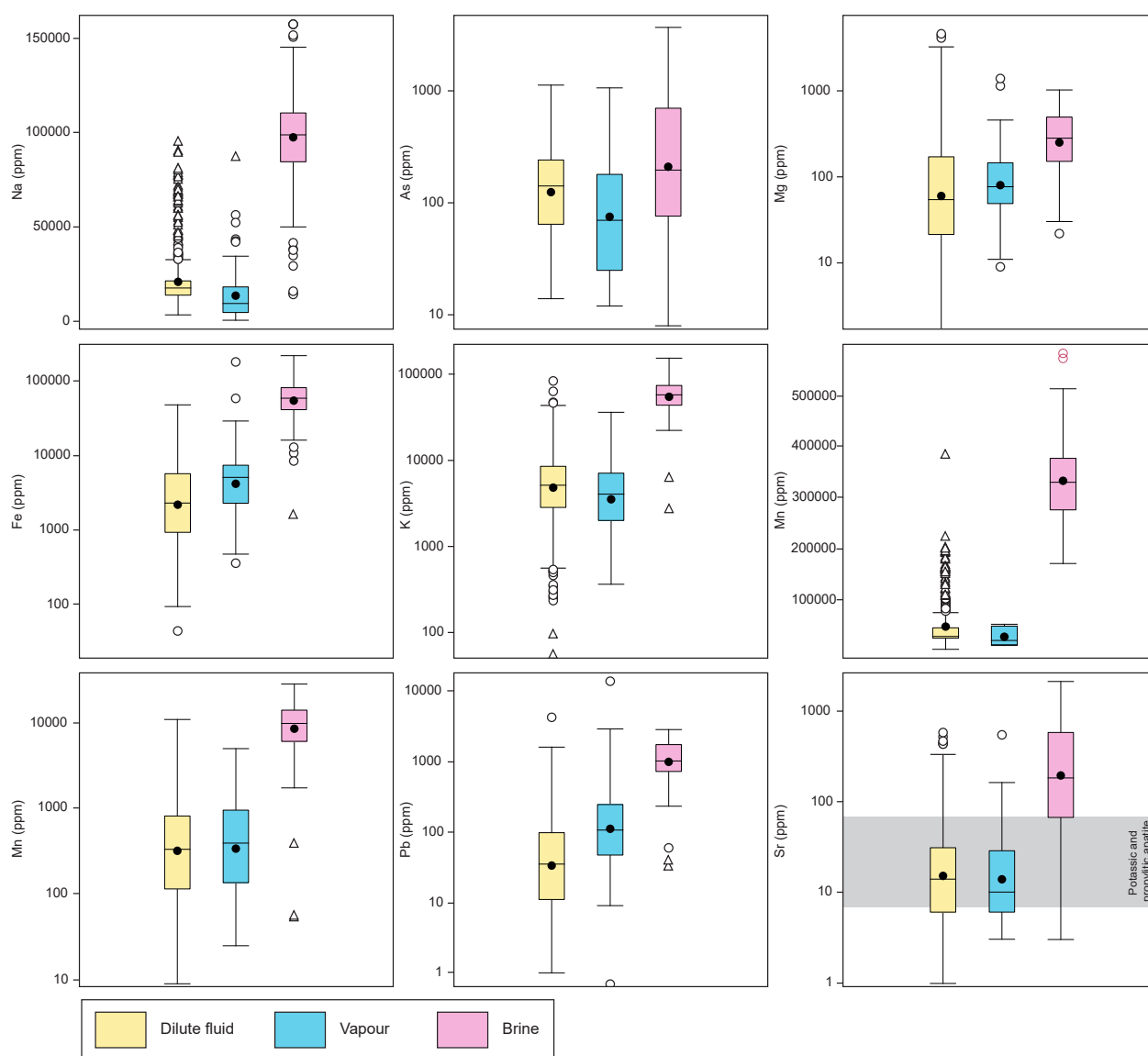


Figure 7.14 Fluid compositions of fluid inclusions from porphyry systems. (Data compiled from Klemm 2006; Landtwing et al. 2005; Rusk et al. 2004; Buckroyd 2008; Ulrich et al. 1999, 2001; Vry 2010.) The range in Sr concentrations of a fluid in equilibrium with potassic and propylitic apatite is shown in grey. Calculated using partition coefficients from Ayers & Watson (1993).

around 3 – 4.5 (Seedorff et al. 2005; Reed et al. 2013). Fluid inclusion studies at La Granja suggest sericitic alteration is linked to low salinity fluid (< 8 wt. % NaCl, 330 - 180 °C; Hein & Tistl 1986). This is also compatible with the work of Reed et al. (2013) that proposed the fluid responsible for sericitic alteration is a dilute intermediate density fluid and can be produced from a cooling of a magmatic fluid like that responsible for potassic alteration (Fig. 7.13C).

7.5.2 REE mobility and hydrothermal fractionation

Rare earth elements are transported in fluids as aqueous complexes and their mobility - which is closely tied to the availability of ligands - is a function of fluid pH, temperature, salinity, oxidation state and fluid composition (Haas et al. 1995; Bau 1991; Migdisov et al. 2014, 2016). Cl is the dominant ligand in natural aqueous fluids and is very soluble within low pH fluids; however, REE can also form complexes with OH and F ions especially in high pH and F-rich fluids (Migdisov et al. 2009, 2016). The mobility of the REE is not uniform as there is a systematic decrease in atomic radius with increasing atomic number for the 3+ cations. LREE complex more strongly

with Cl than HREE and are the most fluid mobile, evident in the greater variability of LREE concentrations (La/Sm compared to Gd/Yb; Table 7.4). In addition, mass transfer analysis (see *section 5.4.1*) reveals a net gain in LREE within propylitic and sericitic alterations relative to potassic, but comparatively little change in the HREE. Eu partitioning into apatite, as in melt, is not comparable to neighbouring REE and will be discussed separately. As a result of these different properties and controls on mobility, hydrothermal processes can result in REE fractionation.

Potassic and propylitic apatite

The REE pattern of some potassic vein apatite is very similar to magmatic apatite, indicating that REE are not significantly fractionated during initial melt-fluid partitioning, and that precipitation occurs before any further fractionation of the fluid. As further evidence, the REE patterns of potassic apatites show a peak in concentrations at Pr and Nd, like magmatic (and metasomatised magmatic) apatite (Fig. 7.7). In magmatic apatite, this feature was attributed to allanite crystallisation (see *section 6.6.2*); however, there is ostensibly no hydrothermal allanite suggesting that this signature could be inherited from the melt-fluid partitioning. Following the work of Reed et al. (2013), Pacey et al. (2020) etc., the transition from potassic to propylitic alteration can be considered as the evolution of a single, magmatic derived fluid (Fig. 7.13). Propylitic apatite, although similar to potassic apatite, does not have this 'hump' (Fig. 7.7) implying precipitation from a fluid that has undergone a greater degree of fractionation.

Lower LREE concentrations (La/Sm closer to 1) in potassic and to a greater degree in propylitic apatite (Figs. 7.8 E; 7.8F) may be explained by the increased mobility of LREE compared to total REE. Migdisov et al. (2016) modelled the effect of multiple 'waves' or fluid pulses on LREE/HREE ratios and showed how they can progressively change in the fluid and precipitated minerals. As the difference in chemical properties between the REE are so small, the initial fluid and precipitated minerals do not show much fractionation. However, with later interactions, the more mobile LREE become depleted in more proximal zones and, in stages, redistributed to further along the fluid pathway. As the propylitic samples in this study are relatively proximal to the centre of the porphyry, they are typically comparable to potassic samples. A relative enrichment in LREE relative to earlier/more proximal hydrothermal apatites would be expected with greater distance from the deposit, coinciding with peak LREE increase with mass transfer. In addition, as more distal propylitic fluids are diluted (Bowman et al. 1987) and wall rock interaction becomes less intense, continued apatite precipitation may remove REE from the fluid and therefore the total REE contents of propylitic apatite would be expected to decrease.

Notably similar apatite compositions to those reported here were identified in early hydrothermal assemblages at the Olympic Dam IOCG deposit (Krnetić et al. 2018). These apatites are present in early magnetite-bearing assemblages and are associated with fluid inclusions that suggest fluid conditions > 400 °C and 20 – 45 wt. % NaCl equivalent, comparable to early potassic fluids at La Granja (Fig. 7.13). Numerical modelling of these apatites, based on the work of Migdisov et al. (2016), suggest this REE profile of these apatites, which is produced through relatively small amounts of fractionation, could be achieved through

complexing of REE with predominately OH^- , and some Cl^- with LREE (Krnet et al. 2018).

Sericitic apatite

The REE pattern of sericitic apatite can be described as two patterns: 1) MREE-enriched concave pattern and 2) LREE-rich pattern, both of which have varying total REE (Fig. 7.7). Both of these REE patterns are present in apatite from within a single vein in sample EB17047. This is a coarse (>8 mm) sericitic vein in which the apatite is intergrown with quartz (which forms the vein selvage) and is surrounded by later sulfides (Fig. 7.15). Apatites within this vein show a large variation in Na concentrations that positively correlate with Pb and U (Fig. 7.16A-B), and negatively with total REE. In general, apatite in the vein with higher REE totals have lower Na (+ Pb, U) concentrations and are MREE enriched (Fig. 7.16C-D), while the more Na-rich apatite have lower total REE and are relatively MREE-HREE-depleted (Fig. 7.16E-F). Based on the change in composition a crystallisation sequence can be inferred from low Na, high total REE to high Na and low total REE. A decrease in REE is the result of continued crystallisation of apatite, and an increase in Na (+Pb, U) from breakdown of major minerals such as plagioclase. In addition, there is no textural evidence to support two distinct phases and so changes in relative REE enrichment are inferred to reflect continuous hydrothermal fractionation in a single evolving fluid.

Similar REE patterns are observed in apatite from a number of deposits such as Olympic Dam (Krnet et al. 2017), Wirra Well (Krnet et al. 2017) and Acropolis (Ismail et al. 2014), hydrothermal Au deposits (Chen et al. 2019) and a Fe-Cu-REE deposit in China (Li & Zhou 2015). In most cases the apatite composition is attributed to equilibration with a sericitic alteration fluid (Krnet et al. 2018; Li & Zhou 2015). These similarities in REE patterns between different deposit types and magma compositions (in addition to those of potassic apatite) imply that it is the fluid conditions rather than the co-crystallising assemblages or initial fluid composition, which determines the REE profiles of the hydrothermal apatite. This, together with petrological studies, also implies that apatite is dominant REE-phase of the hydrothermal mineral, supported by observations at La Granja.

Fractionation of the REE could be caused by the precipitation of earlier REE-rich apatite within veins acting as a closed system. This would deplete the REE concentrations in the fluid and subsequently precipitated more REE-depleted apatite as demonstrated in Brugger et al. (2000). The precipitation of other REE-rich phases, such as HREE-rich xenotime, has also been considered to be an efficient method of fractionating REE (Migdisov et al. 2016). Although such minerals were not observed within the vein samples collected, it is possible they may exist earlier along the fluid pathway. A precipitation of an initially more HREE-

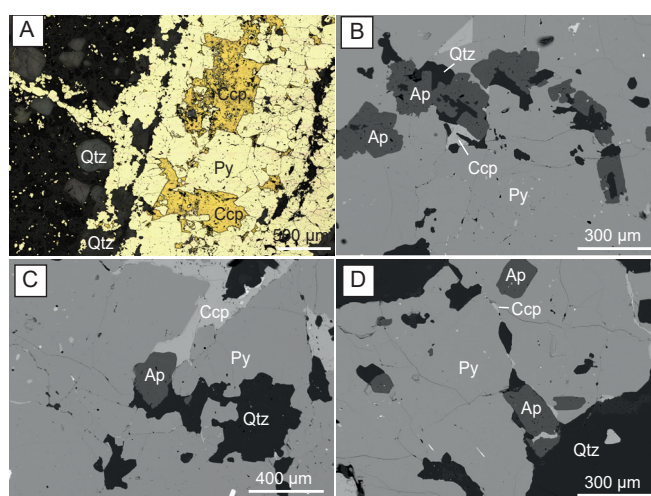


Figure 7.15 Qtz + Py + Ccp vein in EB17047. A) Reflected light image showing the sulfide zoning. B-D) BSE images of apatite within the vein.

Qtz-Py-Cpy vein - EB17047

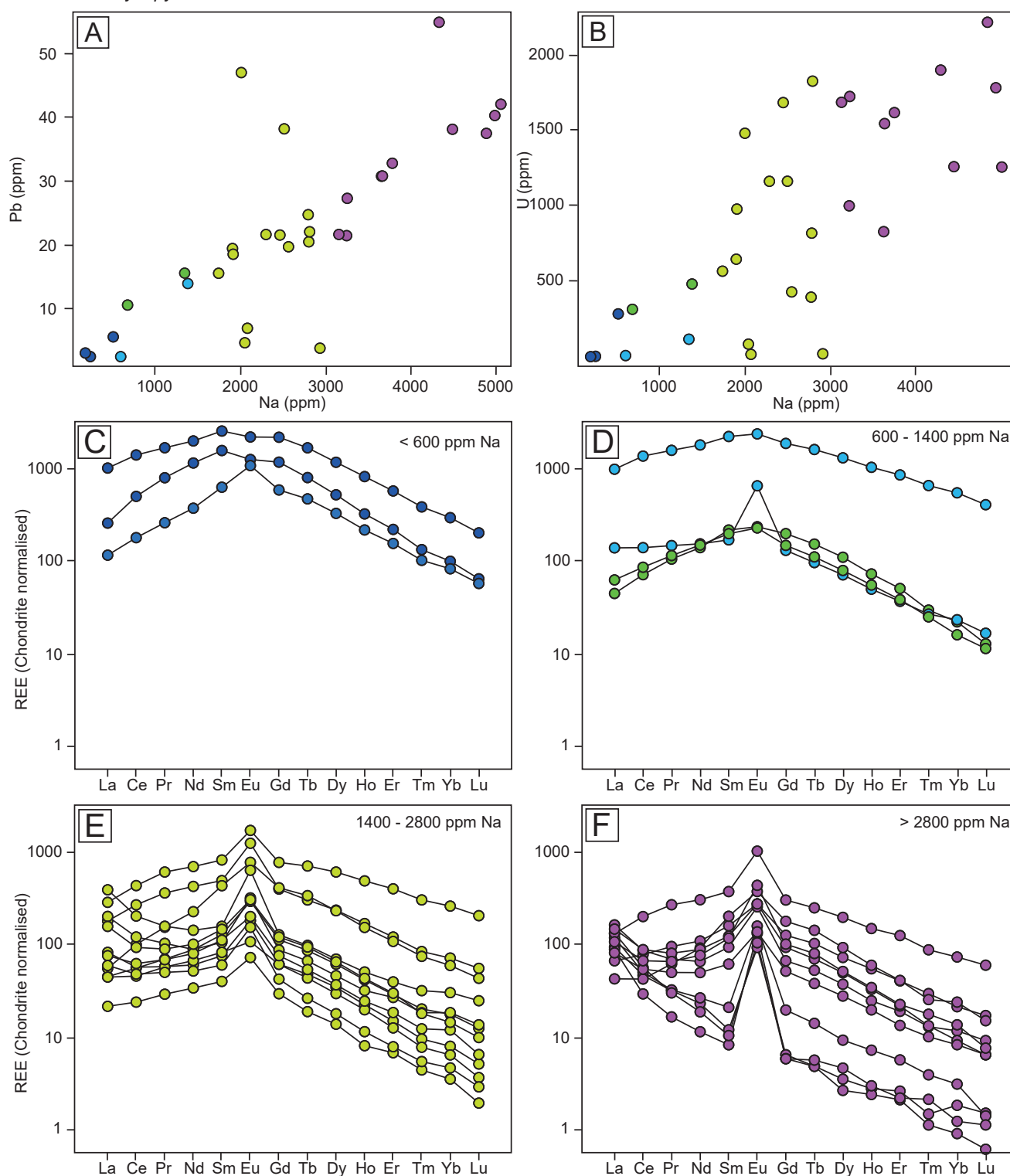


Figure 7.16 Composition of sericitic vein apatite from EB17047. A) Na concentrations increase with Pb B) and U. C-D) Low Na apatites have rounded, MREE-enriched, chondrite-normalised REE patterns. E-F) More Na-rich apatites have a more depleted HREE pattern with high Eu/Eu*. Analytical error is smaller than the symbol size.

dominated phase could produce the progressive depletion in HREE relative to LREE in apatite (Fig. 7.16D-F).

Alternatively, the fractionation of REE could be the result of contrasting mobility. Numerical modelling of REE transport suggests that selective ligand complexing can be responsible for the distinctive MREE-enriched shape by increasing LREE and HREE mobility (Krneta et al. 2018).

A decrease in apatite-fluid LREE partitioning can be produced through increased Cl^- complexing as a result of more acidic fluids. A decrease in from a potassic-like REE pattern to LREE-depleted was achieved by lowering the fluid pH to 4.4. This is comparable to independent estimations of sericitic fluids pH (Reed et al. 2013; Fig. 7.13). In addition, sufficient REE-Cl complexing was achieved with a modelled fluid of 5 wt. % NaCl equivalent (Krneta et al. 2018); this is below the NaCl equivalent fluid composition inferred for sericitic apatite at La Granja from fluid inclusions (Hein & Tistl 1986). The smaller decrease in apatite-fluid HREE partitioning can be produced from increased F^- complexes (Krneta et al. 2018). The availability of F^- in the fluid is inferred to increase due to the instability of key fluorine phases under the more acidic conditions. The shift from precipitation of LREE-depleted to LREE-enriched apatite could reflect decreased mobility of LREE. A decrease in the amount of Cl ligands could be caused by depletion in the Cl content of the fluid, or increasing fluid pH, simultaneously with increased U, Na and Pb concentrations from rock buffering (Reed et al. 2013). These suggested changes in fluid composition could occur gradually and reflect the evolution of a fluid from depth to sericitic alteration. They could also be a result of more localised variations in aqueous complexes and pH focused at the crystal edge (Sverjensky 1984; Rakavon & Reeder 1996), producing rapid changes in REE fractionation within a single fluid, resulting in the strong compositional variations observed within the apatite grains.

7.5.3 Eu anomalies in vein apatite

The partitioning of Eu into apatite does not occur in the same way as the other REE elements as it exists in two valence states, Eu^{2+} and Eu^{3+} , with only Eu^{3+} incorporated into apatite. In magmatic apatite the size of the Eu anomaly is a function of the oxidation state, which controls the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio, and competition from plagioclase which may deplete total Eu in the melt, so that Eu concentrations in apatite are typically lower than neighbouring REE concentrations (see section 6.5.1). Vein apatites consistently exhibit higher Eu/Eu^* compared to magmatic apatite. This is particularly prominent in sericitic apatite where there is a positive Eu anomaly ($\text{Eu}/\text{Eu}^* > 1$; Fig. 7.8D, G). In MREE-rich sericitic apatite, and some propylitic apatite, Eu concentrations are comparable to Sm and Gd suggesting Eu is behaving comparable to other REE (Fig. 7.16C-D). In MREE-HREE depleted sericitic apatite Eu anomalies are typically positive and Eu concentrations are independent of decreasing total REE (Fig. 7.16E-F).

Within a fluid, the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio depends on the oxidation state and also on the complexing ligands available. Eu^{2+} preferentially exists as a chloride complex, whereas Eu^{3+} favours hydroxyl complexing (Haas et al. 1995). As a result, the pH, P, T and concentration of Cl will affect $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratios (Migdisov et al. 2016). Previous work looking at $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratios in hydrothermal minerals has suggested that variations in fluid pH driven by fluid:rock interaction is the principle control. As a result, numerical models produce increasing Eu concentrations in hydrothermal apatite precipitated from higher pH, and lower salinity fluids (Migdisov et al. 2016; Brugger et al. 2008). Positive Eu anomalies are produced from higher Eu^{3+} concentrations in the fluid relative to neighbouring REE and increases with lower pH. These results are the opposite to the trends observed for sericitic apatite at La Granja, and modelled apatite compositions and conditions comparable to sericitic fluids contain $\text{Eu}/\text{Eu}^* < 1$ (Krneta et al.

2018). However, these models do consider the effect of changing Eu concentrations in the fluid.

The source of the positive Eu anomaly in sericitic, and the more positive Eu anomaly in propylitic compared to magmatic apatite is more likely a result of the lack of competition from plagioclase. Further to this, the addition of Eu to the fluid from breakdown of minerals that are otherwise REE-poor will also result in $\text{Eu}/\text{Eu}^* > 1$. In potassic alteration plagioclase is replaced by K-feldspar, and in propylitic by epidote, chlorite and calcite (Barton et al. 1991). However, the largest addition of Eu to a fluid will come from sericitic alteration of plagioclase which texturally is the most pervasive and intense. Apatite from sample EB17047 have initial Eu concentrations comparable to Sm and Gd ($\text{Eu}/\text{Eu}^* \sim 1$). The Eu/Eu^* of later apatite increases as a result of falling total REE concentrations and higher Eu concentrations following greater wall rock interaction and destruction of plagioclase (inferred from increasing concentrations of N, Pb and U), which will also act to buffer the pH of the fluid, thereby further aiding a high Eu^{3+}/Eu (Fig. 7.16).

7.5.4 XF-XCl-XOH in vein apatite

There is a non-ideal solid solution between F-, Cl-, and OH-apatite endmembers (Piccoli & Candela 2002) which means that the composition of apatite is driven by the partitioning of ions and activity of the whole system. In this section, the halogen endmember compositions are described as mole fractions XF, XCl and XOH. Ideally, OH concentrations in apatite would be measured directly. However, this is difficult so in this study XOH is calculated from stoichiometry. Due to the effect of ion migration under an electron beam (see *Chapter 5*), this means that in very F-rich apatites (in which calculated XF may be >1), XOH is underestimated.

The halogen composition of hydrothermal apatite is a function of fluid composition, temperature, pressure, pH, and fluid:rock ratio, or replenishment rate (Fig. 7.17; Kusebauch et al. 2015). F is the most compatible halogen in apatite (Zhu & Sverjensky 1991) and variations in F concentrations are found to be largely controlled by the F content of the fluid (Kusebauch et al. 2015), although thermodynamic calculations suggest that lower temperatures will also raise F content (Zhu & Sverjensky 1991). Suggested apatite-fluid partition coefficients for F are 100 times larger than those for Cl (Kusebauch et al. 2015). Thus, in contrast, the Cl content of the fluid has a much smaller effect on the Cl concentration in apatite, although experimental results and thermodynamic calculations produce different results (Kusebauch et al. 2015; Zhu & Sverjensky 1991). Cl is the least compatible of the endmembers in apatite due to its large ionic radius (Piccoli and Candela 2002), meaning that hydrothermal apatites predominantly spread along the F-OH binary as a function of fluid F content and pH (Fig. 7.17).

The activity ratios of HCl and HF in an aqueous fluid with infinite dilution allow changes in halogen content of apatite to be related to changes in the volatile phase for given P-T conditions (Zhu & Sverjensky 1991). Activity ratios cannot be directly related to fluid concentrations as Cl can exist in additional species to HCl in fluids. HF can be more loosely related to fluid as HF is the dominant form of F in an aqueous fluid. The activity ratios responsible for end-member compositions at temperatures spanning that of hydrothermal alteration at La Granja (400 and 200 °C as recorded in fluid inclusion studies; Hein & Tistl 1986) are presented in figure 7.17 (Zhu & Sverjensky 1991;

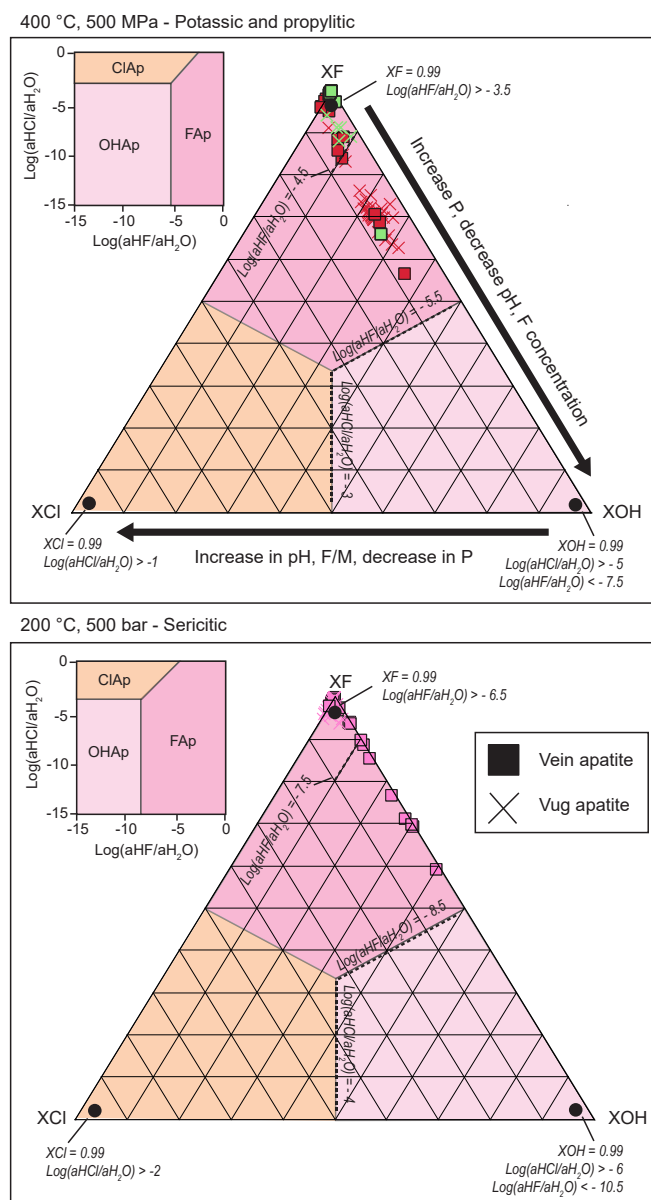


Figure 7.17 Ternary plot of the mole fraction of halogens in apatite. Activity ratios associated at temperatures of 400 and 200 °C are noted, based on data from Zhu & Sverjensky (1991); Harlov (2015), Spear & Pyle (2002). In addition, the effects of fluid conditions on the formation of endmember compositions are included (Zhu & Sverjensky 1991; Kusebauch et al. 2015; Li & Hermann 2015).

(Zhu & Sverjensky 1991; Li & Hermann 2015; Kusebauch et al. 2015). This is consistent with the known temperature, and likely pressure decrease, in the potassic to propylitic transition (Fig. 7.13). In addition, apatite XCl/XOH is also likely to be higher in lower pH fluids in which OH^- is more abundant – also consistent with the likely slightly lower pH of fluids expected in the inner propylitic halo relative to the potassic zone, especially where chlorite-sericite assemblages are developed (e.g. Cooke et al., 2014; Reed et al. 2013; Fig. 7.13).

Sericitic vein apatite

Apatite within coarse sericitic veins (EB17047, EB17048) has $\text{XCl} < 0.01$ (Cl at or near detection limits) and is predominantly rich in F with variable XF/XOH (XOH ranges from <LOD to 0.4;

Harlov 2015). The crystallisation of OH-rich apatite require low $a\text{HF}/a\text{H}_2\text{O}$ ratios and Cl-rich apatite require high $a\text{HCl}/a\text{H}_2\text{O}$. At cooler temperatures the relative activity of HF required for F-rich apatite decreases. Because halogen concentrations in apatite are readily altered through metasomatism as a result of as rapid diffusion (see Chapter 5), it is assumed here that the measured apatite compositions reflect the most recent fluid phase they equilibrated with.

Potassic and propylitic vein apatites

Potassic and propylitic vein apatites have $\text{XF}/\text{XOH} > 1$, $\text{XF}/\text{XCl} \gg 1$ and $\text{XCl}/\text{XOH} \ll 1$, reflecting the relative compatibility of the halogens in hydrothermal apatite ($D_F \sim 120$, $D_{\text{OH}} \sim 100$, $D_{\text{Cl}} \sim 2.3$; Kusebach et al. 2015; Fig. 7.18). For the potassic vein apatites, compositions spread along a line of approximately constant Cl/OH (Fig. 7.18A) consistent with a fairly uniform Cl/OH activity ratio, but variable F activity in the fluids involved. However, for the propylitic vein apatites, the XCl/XOH varies between samples (Fig. 7.18C) but is generally higher than for the potassic vein apatites. Higher XCl/XOH ratios in hydrothermal apatite may reflect lower temperatures and pressures because the stability of hydroxy-apatite decreases with decreasing temperature and pressure

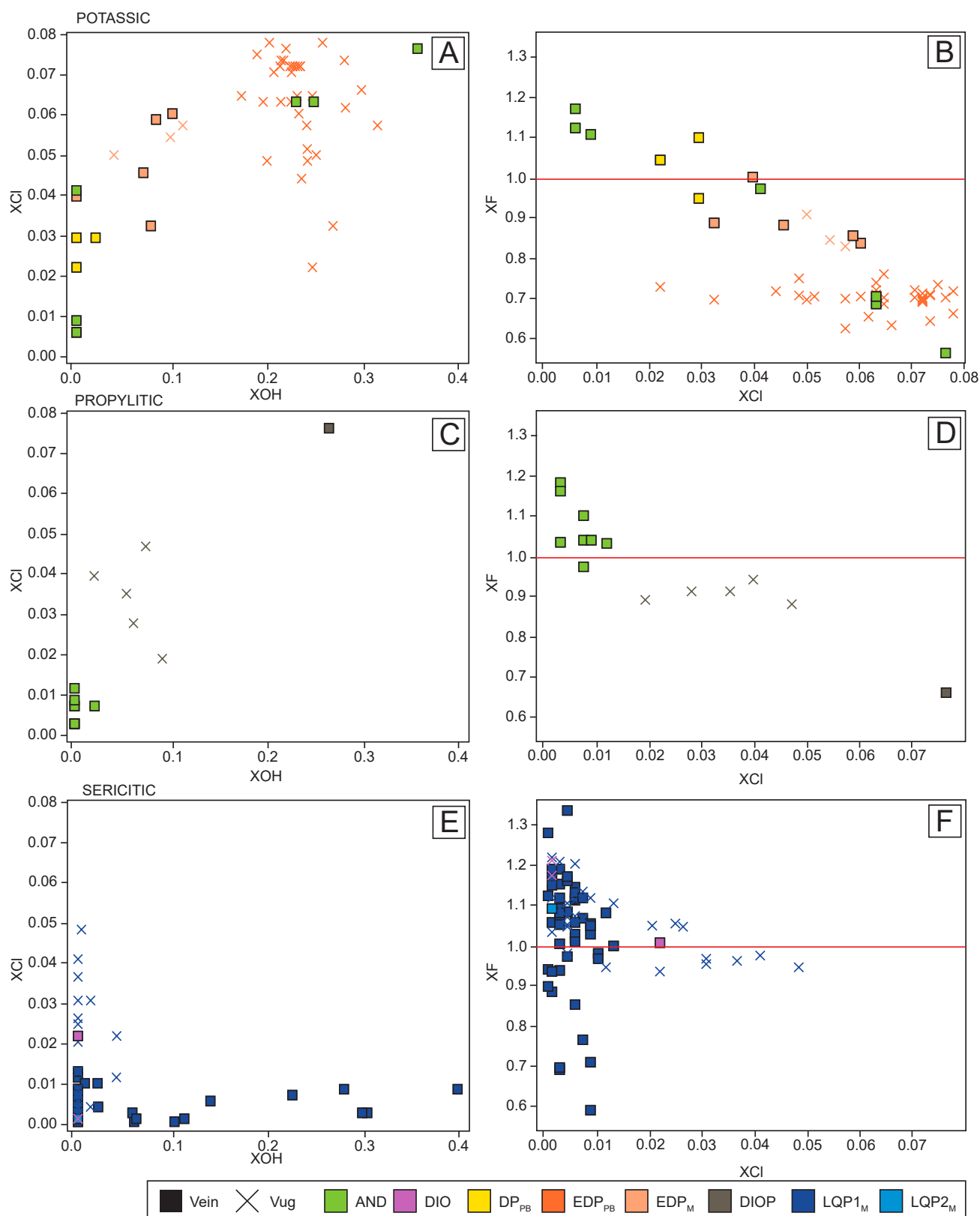


Figure 7.18 Halogen site contents of vein apatite coloured by alteration association A-B) potassic,. C-D) propylitic, E-F) sericitic. Sericitic vein apatite is characterised by very low XCl values and a range in XF but with the majority of data near the stoichiometric limit for F ($XF > 1$).

Fig. 7.18E-F). The low proportion of analyses with $XF/XOH < 1$ could reflect quantification issues with XOH; however, these analyses are associated with pyrite-dominated, lower Cu-(Fe)-sulfide assemblages and are therefore considered of interest despite this. Variation in XF/XOH could be explained by variation in F content of the fluid (Fig. 7.17). Halogens within apatite show a strong correlation with the composition of fluid trapped within cavities (Kusebauch et al. 2015). This suggests that the composition of coexisting fluid can change rapidly as a response to newly-formed apatite, which could consequently produce depleted F concentrations over time. However, within like assemblages, XF/XOH does not vary significantly and sericitic apatites are typically F-rich ($XF > 0.8$). High XF apatite may be a result of decrease in pressure or temperatures, which require a lower $a.HF/a.H_2O$ to produce F-rich apatite (Zhu & Sverjensky 1991; Fig. 7.17). This, as opposed to an increase in $a.HF/a.H_2O$, corresponds to observations of later, cooler fluids being more dilute (Rasmussen & Mortensen 2013).

Evolution of magmatic volatiles

All potassic and propylitic vein apatites fall on $XCl-XF$ and $XOH-XF$ trends that converge on $XF = 1$ (ignoring analyses with $XF > 1$ as analytical artefacts; Fig. 7.18A-D). The spread of potassic and propylitic apatite along $XF-XCl$ could reflect the evolution the fluid, such as described between potassic and propylitic apatite. Alternatively, as the composition of potassic apatite shows considerable spread along this trend, changes in $XCl-XF$ in apatite could represent changes at the fluid source.

Multiple studies using apatite and biotite as independent measures of magmatic volatiles observe a progressive decrease in the $a.HCl/a.HF$ ratio of magmatic fluids such as those exsolved from the Emerald Lake plutonic complex, Canada (Coulson et al. 2001) and mineralised pluton in the northern Canadian Cordillera (Rasmussen & Mortensen 2013). In both cases magma became enriched in more compatible HF relative to HCl with differentiation. Ap_{incl} from La Granja show similar trends of decreasing Cl contents of apatite (and Cl_{melt}) with later porphyry intrusions (see Chapter 6). In addition, Rasmussen & Mortensen (2013) identified the presence of an early Cl- and H_2O -rich fluid associated with the mineralised intrusions. At La Granja, the XCl/XF ratios are considerably higher within Ap_{incl} from the mineralised intrusions (Fig. 6.22). Therefore, the large spread in $XF-XCl$ of the potassic apatite could reflect early low $a.HF/a.H_2O$ evolving towards higher $a.HF$ and resulting in more F-rich apatites. The relative timing of the potassic veins cannot be learned from the ages of the intrusion as each unit may be subjected to multiple generations of cross-cutting veins (Fig. 7.18B). However, decreasing XCl content of potassic apatites appears to correspond to changing sulfide assemblages (Py+Bn+Ccp to Ccp+Py to Py; Tables 7.2; 7.3) consistent with the evolution of porphyry over time (Sillitoe 2010).

7.6 Apatite associated with mineralisation

Fluids are responsible for transporting and precipitating metals in porphyry systems. Mineralisation within a porphyry deposit is zoned as a response to temperature and sulfidation state of the fluid (Sillitoe 2010; Seedorff et al. 2005; Einaudi et al. 2003 Fig. 1.4). This is observed in the samples from La Granja with those closer to the centre of the system containing a higher proportion of Cu-(Fe)-

sulfides and higher bulk rock Cu grades, and more distal samples dominated by pyrite with lower bulk rock Cu (Fig. 7.19). Hydrothermal apatite is commonly present within sulfide assemblages and therefore it is inferred to have been precipitated from mineralising fluids. The objective of this analysis was to explore whether there is any relationship between Cu content of rocks on a local scale and apatite compositions, either because the apatites formed contemporaneously with sulfides and were therefore influenced by element partitioning between fluids and coeval sulfides, or because apatites present acquired distinctive compositions by being re-equilibrated with their mineralising fluids.

Composition of apatite within sulfide assemblages

The composition of vein and vug apatite directly associated with Cu-(Fe)-sulfides is, of all the apatite types, most likely to be related to the composition of fluids actively precipitating

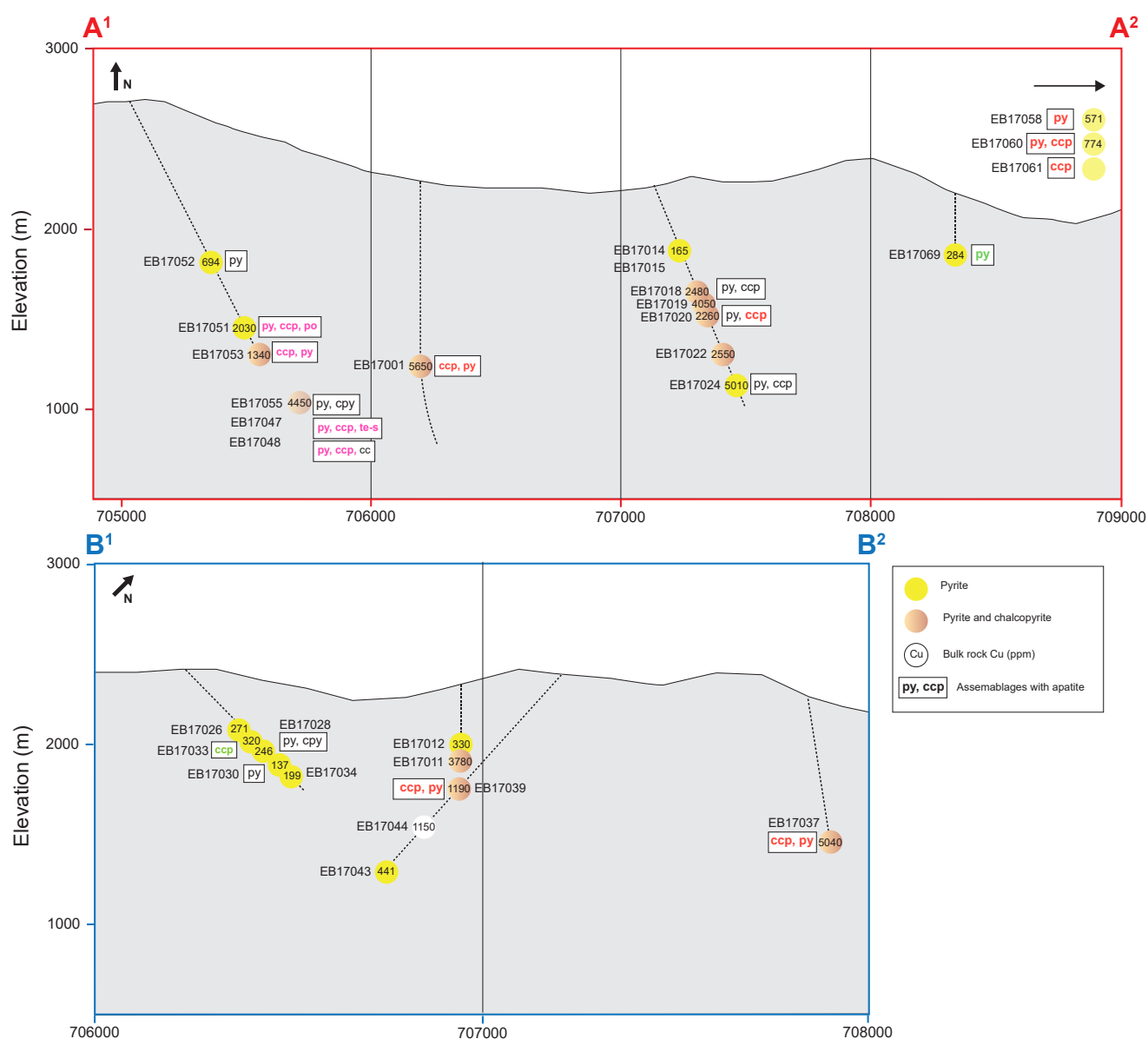


Figure 7.19 Cross sections of Paja Blanca showing positions of samples used in this chapter. For map view of cross sections see figure 4.4. A yellow circle indicates predominantly pyrite visible in bulk rock, an orange circle indicates the additional presence of chalcopyrite (see reflected light photomicrographs, appendix B). Bulk rock analyses of Cu (ppm) is indicated within the circle. Deeper, more central samples, contain higher Cu contents and chalcopyrite mineralisation. Sulfide assemblages observed with hydrothermal apatite are given within the white box (py = pyrite, ccp = chalcopyrite, bn = bornite, cc = chalcocite, po = pyrrhotite), those in bold are observed with vein or vug apatite with the colour indicating the alteration assemblage (re = potassic, green = propylitic, pink = sericitic).

mineralisation. Mineral inclusions and intergrown sulfide phases in hydrothermal apatite are key textural evidence for such a link. Sulfides range from pyrite, chalcopyrite, bornite and chalcocite, however propylitic apatite only contains inclusions of pyrite.

Potassic and propylitic apatite with close textural association to sulfides show little compositional difference to apatite with no association. However, apatite associated with Cu-(Fe)-sulfides have previously been linked to halogen variations (see section 7.5.4) and also contain higher Mn, Sr, U, Sc and Na concentrations than those with pyrite (Fig. 7.20). The majority of the sericitic apatite analysed show close association with Cu-(Fe)-sulfides. Sericitic apatite associated with more Cu-rich assemblages contain higher F concentrations than those only associated with pyrite (Fig. 7.21A). In addition, more Cu-rich assemblages contain higher Na and lower Al concentration (Fig. 7.21B).

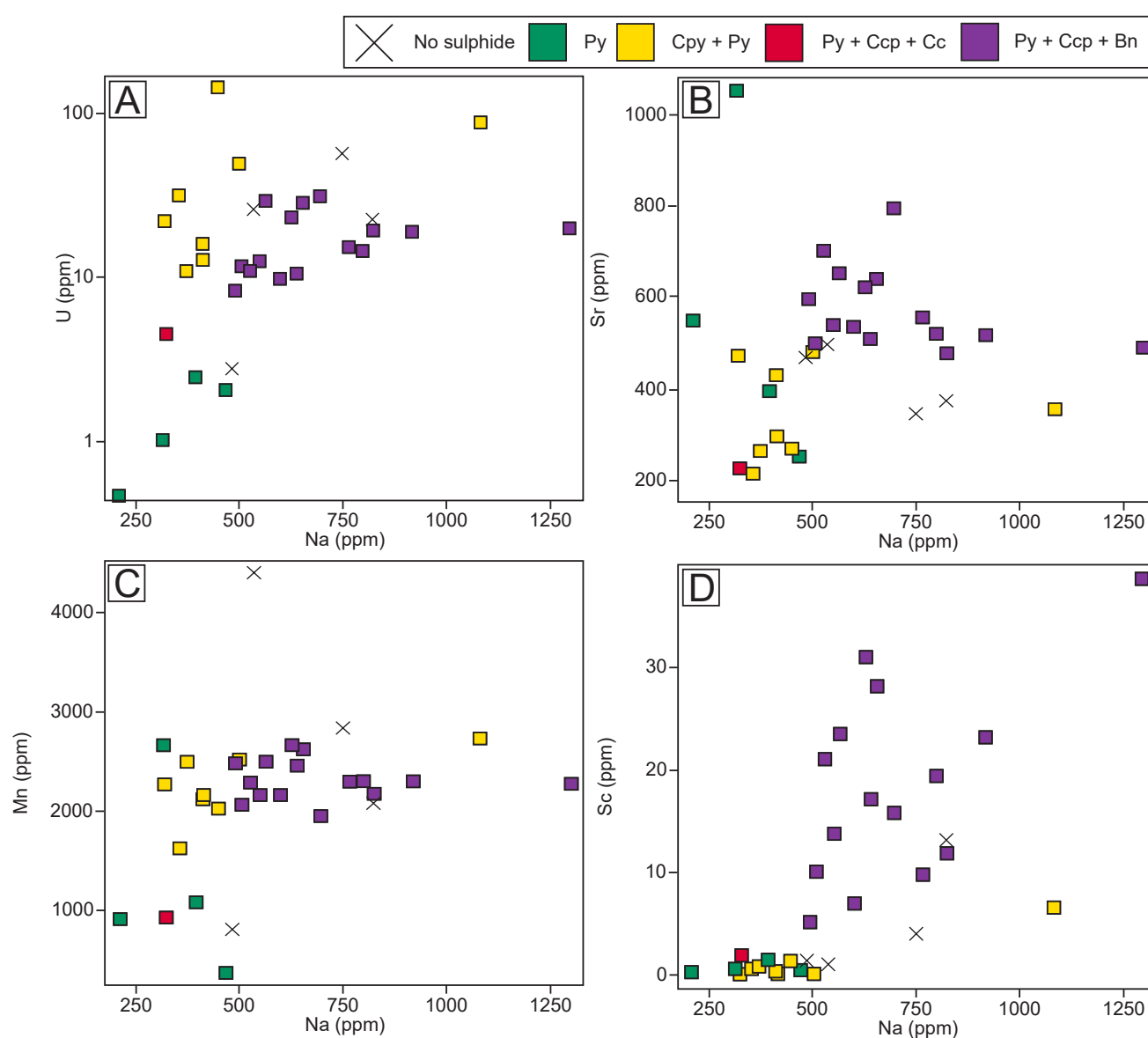


Figure 7.20 Composition of potassic and propylitic vein and vug apatite associated with different Cu-Fe-sulfides. A) Apatite with only pyrite contains lower Na, and U concentrations than those with Cu-Fe- or Cu-sulfides. B) Apatite with bornite contains higher Sr and Na than apatite without bornite. C) Apatite with only pyrite contains lower Mn concentrations than those with Cu-Fe- or Cu-sulfides. D) Apatite with bornite contains higher Sc concentrations than apatite without bornite. Analytical error is smaller than symbol size.

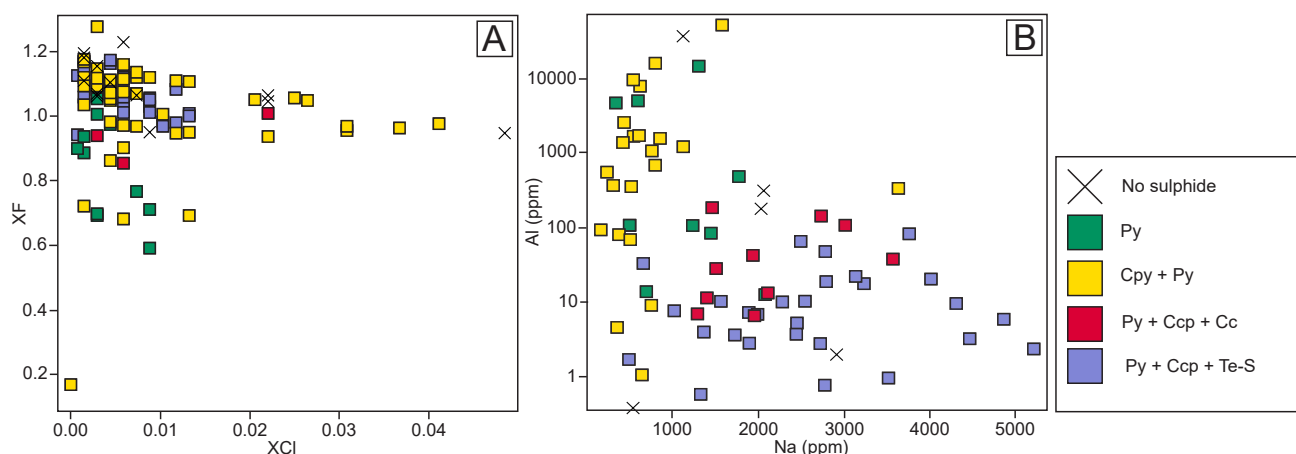


Figure 7.21 Composition of sericitic vein and vug apatite associated with different Cu-Fe-sulfides. A) Apatite with only pyrite contains lower XF B) Concentrations of Al decrease and Na increase in apatite associated with more Cu-mineralisation. Analytical error is smaller than symbol size.

Sample-scale relationships

The changes in apatite composition associated with varying degrees of Cu-mineralisation may suggest that the hydrothermal apatite also reflect some aspects of the Cu-mineralisation process. This relationship can be explored on a more practical application basis by comparing hydrothermal apatite with the degree of mineralisation, or bulk rock Cu, on a sample scale. The bulk rock samples were collected specifically for igneous petrology analysis and so that veins, or especially mineralised portions, were avoided. As a result, bulk rock Cu is mostly fairly low but ranges from < 0.01 – 0.57 wt. % Cu.

Concentrations of Na are typically higher in sericitic apatite associated with higher proportions of Cu-sulfides (Fig. 7.21B). Elevated Pb and Na concentration in sericitic apatite were previously noted within coarser veins and linked to increase rock interaction and destruction of plagioclase. Therefore, higher Na concentration may match sulfide deposition as a result of changing fluid conditions (pH, fO_2), caused in part by cooling fluids interacting with rocks (Harris et al. 2005). In addition, the interaction of fluids with calcic feldspar has been suggested as an efficient method of generating H_2S required to precipitated sulfides (Henley et al. 2015). However, on a sample-scale, the trends produced from comparison of sericitic apatites are generally weaker than those from potassic apatites. This is most likely because the mineralisation observed within the sericitic alteration is typically confined to veins. These veins often cross-cut earlier alteration and therefore did not form contemporaneously with the rest of the mineralisation within the sample. In addition, shallow sericitic alteration could be more easily effected by supergene alteration, further separating the composition of sericitic apatite from the processes within the rest of the rock.

Concentrations of Mn, Sr, Na and U in potassic (and propylitic) apatite have a strong positive correlation with bulk rock Cu. These can be ratioed against concentrations of Al which show a negative correlation (Fig. 7.22). These elements are inferred to be relatively fluid mobile and therefore are inferred to reflect fluid composition more than precursor minerals. By contrast, Al is considered relatively immobile (see section 4.5.1) with melt-fluid partition coefficients below unity (Audétat et al. 2008). It is frequently

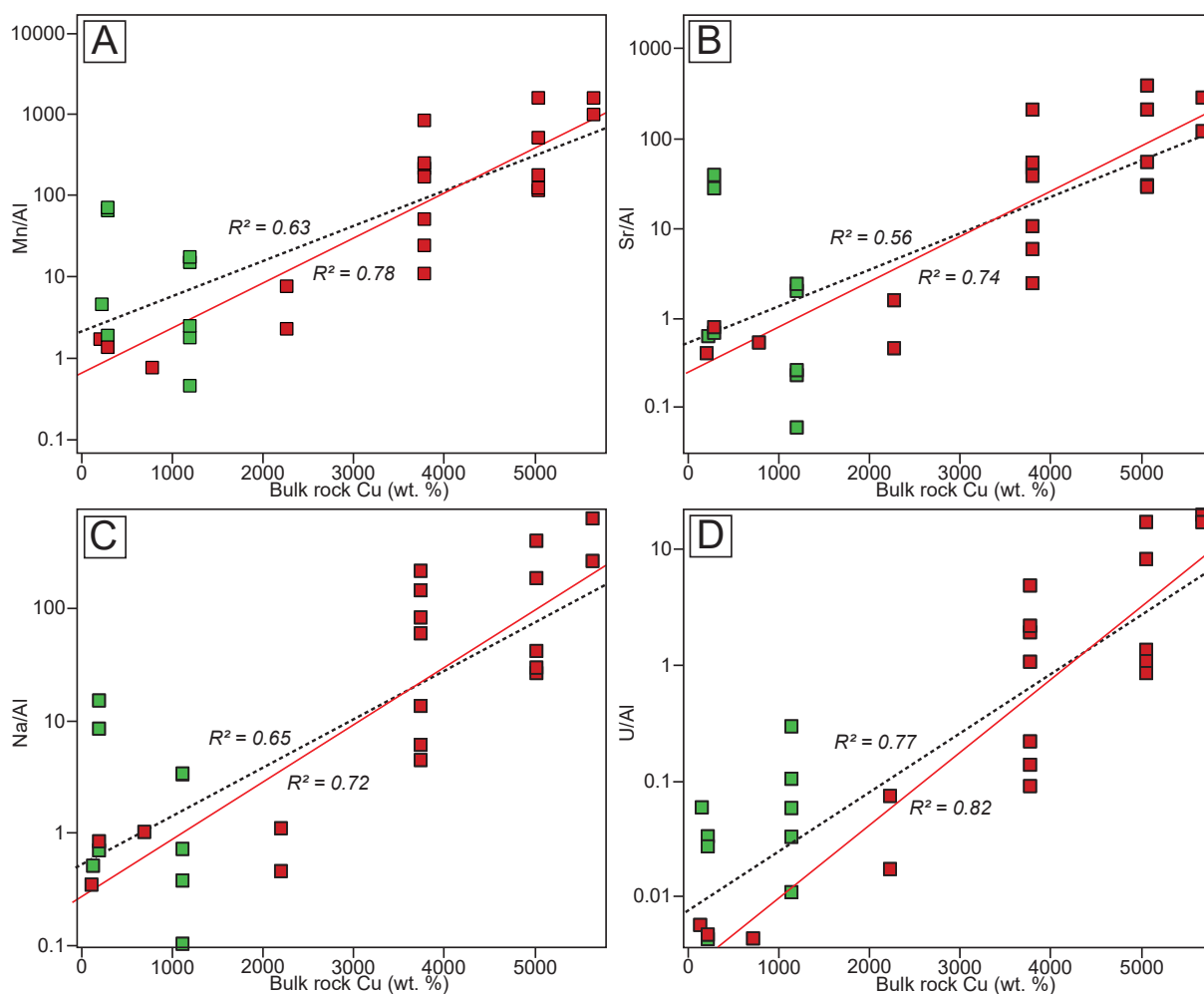


Figure 7.22 Composition of potassic (red) and propylitic (green) vein and vug apatites against bulk rock Cu. Concentrations form a positive relationship against bulk rock Cu. Least ordinary squared regression for potassic and propylitic apatite is shown by the dashed black line and the solid red line for potassic only. A) $R^2 = 0.63$, R^2 potassic only = 0.78. B) $R^2 = 0.56$, R^2 potassic only = 0.75. C) $R^2 = 0.65$, R^2 potassic only = 0.72. D) $R^2 = 0.77$, R^2 potassic only = 0.82. Analytical error is smaller than symbol size.

mobilised from one phase to the next during alteration. Thus, precipitation of a more Al-rich phase than its precursor could lead to less being available for partitioning into apatite.

Higher Cl-contents in potassic apatite has been linked to earlier fluids (see section 7.5.4) which carry the majority of the mineralisation as a result of high fluid-melt partitioning of metal (Audétat et al. 2008; Candela & Holland 1986gr). Although the Cl contents of the fluids cannot be estimated from apatite, early fluids in porphyry systems could be inferred to be Cl-rich by comparison to other studies (Heinrich 2005; Seedorff et al. 2005; Tattich & Blundy 2017). Cl-rich fluids can transport higher concentrations of Mn, Pb, Na as these cations complex with Cl (Audétat et al. 2008, Webster et al. 1989). Therefore, trends in potassic apatite composition with bulk rock Cu are possibly reflecting the presence of earlier, more saline fluids. Although high Cl contents in the fluid is no guarantee of Cu content, it may encourage a higher grade deposition. Exsolved magmatic volatile phases that pooled have been observed to be responsible for higher metal contents than fluids that migrate and precipitate mineralisation over a wider area (Davidson et al. 2005).

Higher concentrations of Mn and Pb in hydrothermal apatite composition have been observed with increase in Cu grade by Loader (2016a). However, this study needs to be

tested on a larger scale comparing between porphyry systems of different sizes in order to access how useful hydrothermal composition could be for predicting the grade of a deposit. Higher grade Cu porphyries are attributed to overprinting of multiple hypogene mineralisation events (Chiaradia 2020; Sillitoe 2010), a process that may not be recorded within a single apatite grain. In addition, depositional controls, such as redox, have been suggested to play an important control in sulfide precipitation (Harris et al. 2005; Henley et al. 2015). However, the variations observed in apatite composition do not seem to record this process.

7.7 Conclusions

- Hydrothermal apatites show greater texture variety than magmatic apatite, and their composition is a combined result of host rock composition, including any replaced minerals, fluid composition, fluid conditions and co-crystallising minerals.
- Replacement hydrothermal apatites group by host rock lithology whereas vein and vug apatite show grouping by alteration assemblage. Metasomatised magmatic apatites plot on a trend towards hydrothermal vein apatite compositions.
- Apatite is present within potassic, propylitic and sericitic assemblages reflecting a range of temperatures, salinity and pH.
- Potassic and propylitic vein apatite precipitated from early, least-fractionated magmatic fluids, consistent with an intermediate density fluid phase and therefore provide key information about the early fluid composition.
- Sericitic apatites have distinctive compositions which may easily be utilised in exploration for porphyry systems.
- Changes in halogen ratios of early fluids correspond to ratios of magmatic volatiles observed in Ap_{incl} .
- Hydrothermal apatite shows systematic changes in composition with increase in Cu-mineralisation.

Chapter 8: Discussion and comparison of Chuquicamata, Northparkes and La Granja case studies

8.1 Introduction

This study aims to describe the occurrence and understand the compositional variation of apatite in the porphyry environment in order to access the potential of apatite as a geochemical tool for porphyry exploration. *Chapters 5 to 7* consist of detailed studies of apatite in porphyry systems including descriptions of the occurrence and compositional variation of apatite assemblages, as well as suggested explanations for these observations. Here, the results from these chapters are synthesized in order to identify apatite textural types and elements that may be suitable for use in an exploration tool (reported in *Chapter 10*). Furthermore, in order for the results of this study to be of wider significance for the understanding of porphyry systems in general, the observations made at La Granja must also apply elsewhere. Likewise, if apatite is to be used in exploration for porphyry deposits, it is important to ascertain whether geochemical signatures in apatite associated with barren and mineralized porphyry intrusions are consistently present across different mineralised arcs and rock compositions. Consequently, in this chapter, results from La Granja are compared with apatite data from two other porphyry case studies – Chuquicamata in Chile and Northparkes in Australia.

8.2 Introduction to the case studies

Chuquicamata and Northparkes were selected for comparison with La Granja because they are geographically and geologically distinct systems. Chuquicamata, like La Granja, is a Cu-Mo system, formed within the major continental Eocene-Oligocene, calc-alkaline porphyry belt of northern Chile. Unlike La Granja, the host rocks at Chuquicamata are not compositionally distinct from the porphyry intrusions, which may add complexity when trying to distinguish between apatite derived from each (Zentilli et al. 2018). Samples from Chuquicamata include the host rocks and the main porphyry units that host the mineralization. Northparkes is a Cu-Au porphyry system formed in the Ordovician Macquarie Arc, New South Wales, Australia. The porphyries are alkalic and formed in an island arc environment (Pacey 2016). The samples from Northparkes exhibit extensive propylitic alteration, something that was limited in the La Granja sample set, and span the wide compositional range represented in the magmatic history of the district.

The use of textural observations coupled with compositional analyses has been crucial for identifying magmatic or hydrothermal apatite. However, analyses of apatites in-situ limits the number of analyses collected and may create a selection bias in the data. As a result, apatite mineral separates from La Granja were also analysed. These samples lack the textural information provided by thin sections but provide a significantly larger amount of data and thereby fill gaps in the dataset and potentially help to identify additional apatite populations. In this section of the study, over 800 trace element analyses from as many grains are compared, with over 600 of these linked to detailed, qualitative textural information. The results extend our understanding of the compositional variability of apatite and formation

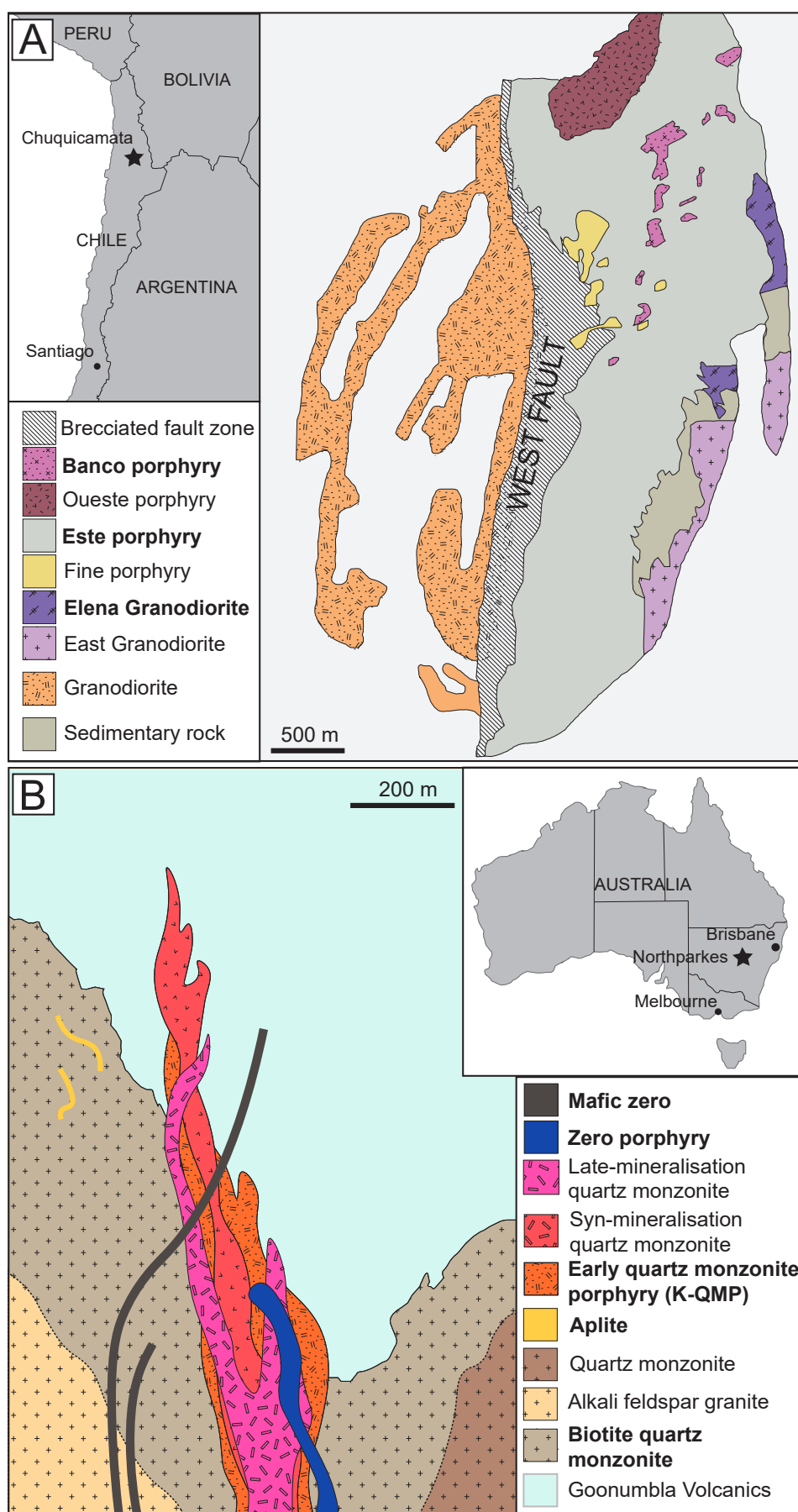


Figure 8.1 Location and geology of the Chuquicamata and Northparkes porphyry deposits. Unit names in bold within the key were sampled for this study. A) Geological map of the open pit at Chuquicamata. Mineralised porphyry units are to the east of the fault zone. B) Interpreted cross-section illustrating the relative age of units at Northparkes. Modified from Ossandón et al. (2001) and Pacey (2016).

Table 8.1 Summary of new samples analysed in this chapter. The number of trace element analyses by LA-ICP-MS for each apatite association is given, along with the type of hydrothermal apatite (if present).

Lithology	Sample number	Alteration	Magmatic apatite	Hydrothermal apatite
Chuquicamata				
Elena Granodiorite (ELENA)	P21604	Weak potassic	9	-
Este porphyry (ESTE)	P21605	Weak potassic	3	4 (Sericitic vein)
Este porphyry (ESTE)	P21606	Weak sericitic	8	7 (Vug potassic)
Banco porphyry (BANCO)	P21608	Weak potassic	10	-
Este porphyry (ESTE)	P21609	Weak potassic	28	-
Northparkes				
Biotite quartz monzonite (BQM)	P21717	Weak propylitic	8	34 (Replacement propylitic)
K-feldspar quartz monzonite porphyry (K-QMP)	P21718	Unaltered	4	-
Zero porphyry (ZERO)	P21719	Weak propylitic	13	2 (Replacement propylitic)
Biotite quartz monzonite (BQM)	P21720	Weak propylitic	1	23 (Replacement propylitic)
Biotite quartz monzonite (BQM)	P21721	Weak propylitic	-	9 (Replacement propylitic)
Aplite dyke (APL)	P21722	Unaltered	12	-
Mafic zero porphyry (MZO)	P21723	Weak propylitic	11	9 (Replacement propylitic)
La Granja				
Early dacite porphyry – Paja Blanca (EDP _{PB})	P23661	-		36
Rhyodacite dome – Mirador (RH)	P23662	-		44
Early dacite porphyry – Mirador (EDP _M)	P23663 (EB17001)	Moderate potassic/sericitic		37
Dacite porphyry – Paja Blanca (DP _{PB})	P23664 (EB17012)	Strong potassic/sericitic		15
Early dacite porphyry - Paja Blanca (EDP _{PB})	P23665 (EB17017)	Strong sericitic		25
Early dacite porphyry - Paja Blanca (EDP _{PB})	P23666 (EB17037)	Strong sericitic		14
Dacite porphyry - Mirador (DP _M)	P23668 (EB17050)	Strong potassic		22

conditions of porphyry systems, in particular with respect to the hydrothermal portions.

8.2.1 Samples

Chuquicamata Cu-Mo Porphyry System

The Chuquicamata Cu-Mo deposit lies in northern Chile about 250 km northeast of Antofagasta (Fig. 8.1A, inset). It was formed in association with intrusions of Eocene – early Oligocene age belonging to the Chuquicamata Intrusive complex, a suite of rocks that continues for over 9 km to the north of the deposit (Cuadra & Rojas 2001; Ossandón et al. 2001). The porphyries are hosted by a mixture of Paleozoic meta-sedimentary and meta-plutonic rocks, and the East and Elena Granodiorites of Mesozoic age.

The Elena Granodiorite (146 ± 15 Ma; Ambrus 1979) is exposed on the eastern side of the deposit and is mineralogically and texturally similar to the Eocene porphyry intrusions (Ossandón et al. 2001; Fig. 8.1A). Notably, it also has a distinct “fertile” signature in whole rock geochemistry (Zentilli et al. 2018). Three porphyries host the majority of the mineralisation: the Este Porphyry (34.6 ± 0.2 Ma) is granodioritic to monzogranitic in composition, the Oueste Porphyry (33.5 ± 0.2 Ma) is classified as monzogranite to granodiorite, and the Banco Porphyry (33.3 ± 0.3 Ma) is a monzodiorite (Ossandón et al. 2001; Ballard et al. 2010). The ages of the Oueste and Banco intrusions match the timing of high-temperature potassic alteration (33.4 ± 0.3 Ma; Reynolds et al. 1998). The deposit is cut by the NNE-trending, Cenozoic, West Fissure Fault, which forms part of the larger West Fault system. This has truncated the main porphyry units so that the mineralised

Chuquicamata complex is in contact with the relatively barren Fortuna Complex on the western side of the fault (Tomlinson & Blanco 1997; Ossandón et al. 2001; Ballard et al. 2010).

Samples from Chuquicamata were loaned from the Ores Collection, Natural History Museum, London. Representative samples were selected from the main intrusive units: the Este and Banco porphyries, and the Elena Granodiorite (Table 8.1), and made into 25 mm diameter polished resin blocks. The main intrusive units at Chuquicamata have been previously described in detail by Ossandón et al. (2001) and Ballard et al. (2010).

Northparkes Cu-Au Porphyry System

Northparkes is a Palaeozoic Cu-Au porphyry system located in New South Wales, Australia (Fig. 8.1B inset; Lickfold et al. 2003). It differs to La Granja and Chuquicamata as it is associated with alkalic intrusive rocks and is believed to have formed in an island arc (Glen et al. 2012). The intrusions at Northparkes span a large compositional range. The oldest and most volumetrically significant is a biotite quartz monzonite (BQM) pluton into which multiple porphyry dykes were emplaced. This unit, along with associated aplite dykes (APL), contain fine, disseminated Cu-sulfides but these intrusions are considered early or pre-mineralisation (444.2 ± 4.7 Ma; Lickfold et al. 2003; Pacey 2016). Syn-mineralisation quartz monzonite porphyries range in composition from biotite- to K-feldspar dominated (K-QMP). Post-mineralisation intrusions include monzonite porphyry dykes (436.7 ± 3.3 Ma; Lickfold et al. 2007), referred to as zero porphyries (ZERO) because they contain little or no Cu-sulfide. The trends in the bulk rock geochemistry of the intrusions suggest that the magma source region was subject to episodic injection of more mafic melt during the pre- main- and post-mineralisation stages (Pacey 2016). For example, a relatively mafic ZERO porphyry dyke (MZO) postdates the more evolved intrusions associated with mineralisation (Pacey 2016; Fig. 8.1B).

Seven samples from Northparkes were loaned from the Ores Collection, Natural History Museum, London. The sampled units span 10 Myr of mineralisation history at the deposit (Lickfold et al. 2003) and include the pre-mineral BQM pluton and associated APL, main mineralised intrusions (K-QMP) and post mineralisation ZERO and MZO porphyries (Table 8.1). All samples are only weakly altered with propylitic assemblages and hematite reddening.

La Granja concentrates

Analyses of apatite mineral concentrates from the main porphyry intrusions (EDP_{PB} , EDP_M , DP_{PB} , DP_M) were carried out, as well as from a previously unstudied sample of the rhyodacite dome (RH), which is inferred to be the final event at La Granja (Table 8.1). These samples provide additional apatite analyses where the in-situ data set (see *Chapters 6 and 7*) is sparse.

8.2.2 Methodology

For the samples from Chuquicamata and Northparkes, SEM-BSE imaging was used to locate apatite grains and to gather information of apatite textures and mineral associations. The occurrence of the different apatite types is summarised in Table 8.1. The concentrations of major components were acquired by SEM-EDS. The apatites were then analysed by LA-ICP-

MS for trace element concentrations according to the methodology described in Chapter 3.

8.2.3 Apatite textures

Chuquicamata

Magmatic apatites are euhedral to subhedral with planar mineral boundaries and few or no inclusions, suggesting a low degree of alteration (alteration score between 0 – 1, see section 5.2.1). Apatites hosted within the porphyritic groundmass (Fig. 8.2A) are common and, at an average of 100 μm in size, are easily distinguished from the finer grains of quartz and feldspar. Apatite is also present as inclusions in phenocrysts of plagioclase (Fig. 8.2B) and biotite (Fig. 8.2C). Apatite inclusions in plagioclase are common but their small size (10 – 50 μm) means that few data were collected for this type. Apatite occurring as 50-100 μm inclusions in biotite is the most abundant type. There may be multiple apatite inclusions within one biotite phenocryst; they are generally rounded and aligned parallel to the cleavage of the biotite. In the Este Porphyry and Elena Granodiorite, apatite grains > 50 μm commonly occur in zircon – titanite $\pm$ magnetite assemblages (Fig. 8.2D).

Hydrothermal apatite is considerably less common than magmatic apatite, consistent with the low degree of alteration observed in the samples. Where present, hydrothermal apatite occurs as fine grains (50-150 μm) that are irregular in shape. The grains are often intergrown with, or contain inclusions of, hydrothermal minerals from potassic (Fig. 8.2F) or sericitic assemblages (Fig. 8.2E).

Northparkes

In the samples from Northparkes, magmatic apatite is present as fine (up to 100 μm) microphenocrysts within the groundmass (Fig. 8.2H). They are generally subhedral in shape, although more irregular shapes are common. Less common are apatite inclusions in primary igneous biotite; in all examples, biotite has been at least partially altered to chlorite or epidote. Despite this, magmatic apatites from Northparkes have low alteration scores, consistent with the generally low degree of alteration observed in the samples. Apatite is also often present in propylitic replacement assemblages that include chlorite, epidote, titanite, rutile, calcite and hematite (Fig. 8.2I-L). Within these assemblages, apatite has a high abundance and a subhedral to irregular habit.

La Granja

In mineral separates from La Granja the degree of metasomatism can be classified for each grain based on intra-granular textures, but any information about mineral associations is lost (Fig. 8.3). Apatite concentrate grains from EDP_{PB} and DP_{PB} have an alteration score ranging from 0 – 2 and are euhedral to irregular in shape (Fig. 8.3A). Apatite concentrate grains from EDP_{M} are typically more altered (alteration score 1 - 2) and are generally subhedral. Apatite grains from DP_{M} have an alteration score of 0 - 3 and are subhedral to irregular in shape (Fig. 8.3B). Apatite concentrate grains from the Rhyodacite Porphyry are all relatively unaltered (alteration score 0) and predominantly subhedral in shape.

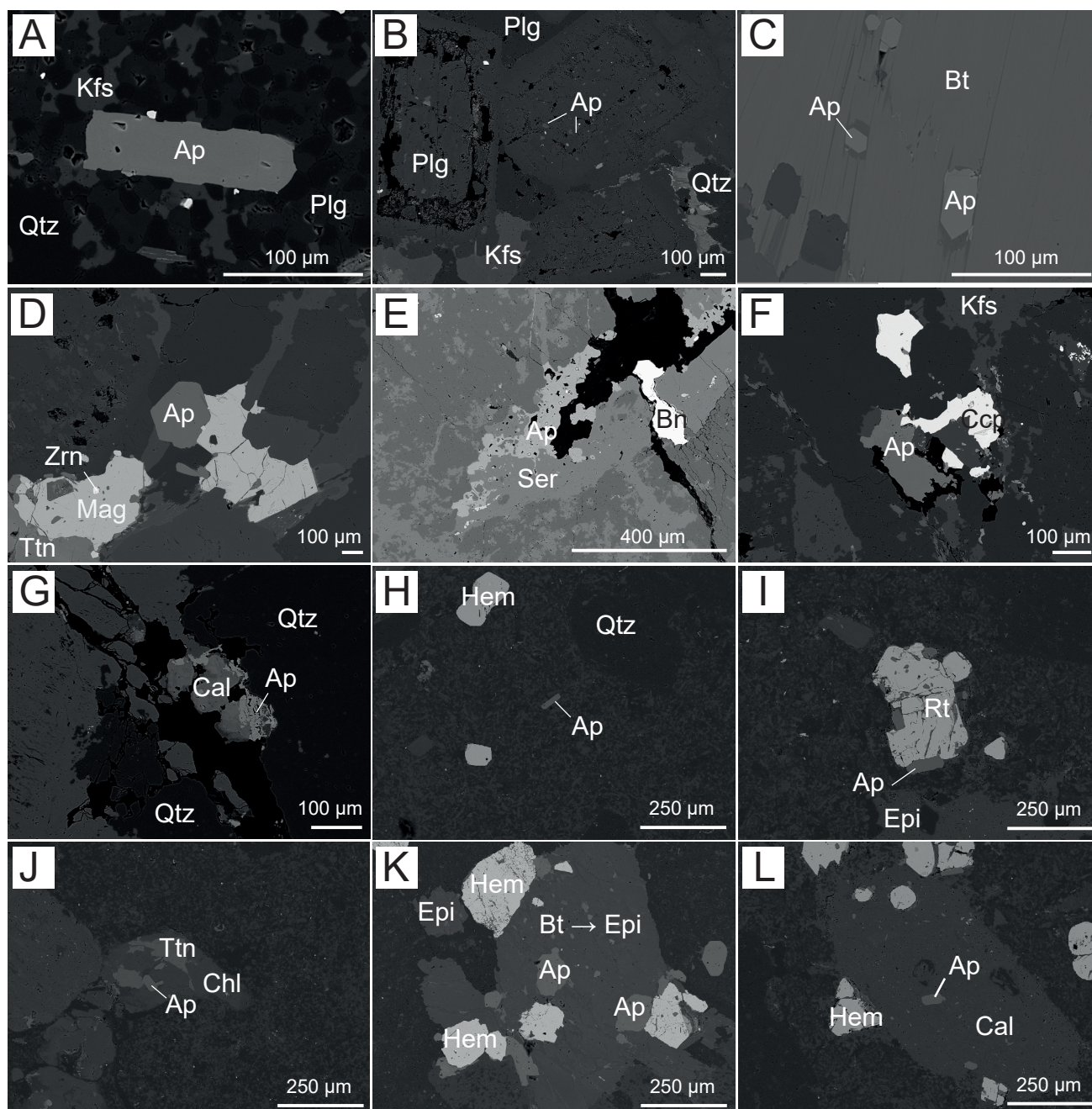


Figure 8.2 SEM back-scattered electron images of apatites from: A-G) Chuquicamata and H-L) Northparkes samples. A) Microphenocrysts of apatite in groundmass of Elena Granodiorite. B) Inclusions of apatite in plagioclase (Plg) phenocrysts. C) Inclusions of apatite in biotite (Bt) phenocrysts. D) Apatite associated with interstitial magnetite (Mag), titanite (Ttn) and zircon (Zrc) assemblages. E) Hydrothermal apatite in a vug with sericite (Ser) and bornite (Bn) in Este porphyry. F) Hydrothermal potassic apatite with disseminated chalcopyrite (Ccp) and K-feldspar (Kfs). G) Apatite and calcite (Cal) in vug. H) Microphenocrysts of apatite in ZERO porphyry. I) Apatite and rutile (Rt) replacing amphibole in ZERO porphyry. J) Replacement propylitic assemblage of apatite with titanite and chlorite (Chl). K) Hematite (Hem) and epidote (Epi) replacing biotite phenocryst. L) Calcite replacement of feldspar associated with propylitic alteration.

8.3 Textural associations of apatite

The variety of textures and mineral associations of apatites at La Granja reported in *Chapters 6 and 7* are also observed at Chuquicamata and Northparkes (Table 8.1). These include apatites that are inferred to have crystallised from the melt, such as euhedral microphenocrysts, finer apatites as part of the groundmass and inclusions within other magmatic phases (particularly biotite and plagioclase). In addition, apatite in replacement assemblages are fairly

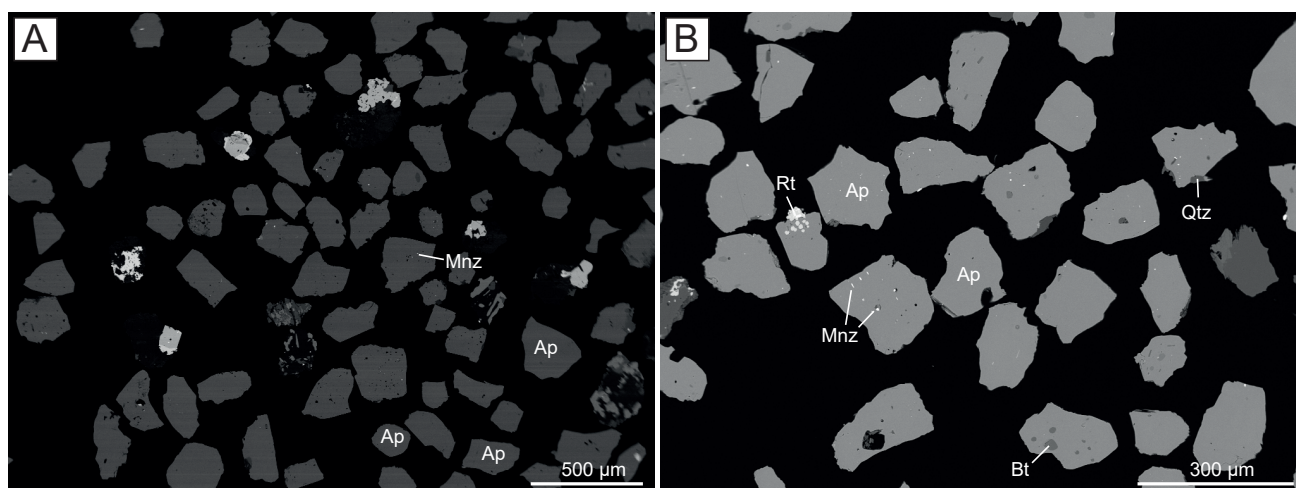


Figure 8.3 SEM back-scattered electron images of apatite concentrate blocks from La Granja. Intra-granular textural information can be established but associated minerals and textural context cannot, and therefore apatite type cannot be inferred except by the use of chemical discrimination methods. A) Apatites from sample P23666 (EDPPB) show a moderate amount of alteration in the form of fine surface pits and inclusions of monazite. B) Apatites from sample P23668 (DPM) have less pitted surfaces but contain larger inclusions of monazite, in addition to biotite and quartz. Some apatites are intergrown with rutile.

common within the porphyry intrusions at La Granja and as propylitic in Northparkes. Apatite in sericitic veins and potassic vugs are also present in samples from Chuquicamata. Grains of apatite from all assemblages may show evidence of alteration from an overprinting fluid.

The relative abundance of the different apatite types does not vary substantively between the different porphyry systems or across a range of host rock compositions (Table 8.1). However, there are spatial and temporal variations within each system that reflect the timing and intensity of hydrothermal fluid flow. For example, pre-mineralisation host rocks (if sampled sufficiently far from the porphyry centres) and late porphyry intrusions (that largely postdate mineralisation) contain greater proportions of unaltered magmatic apatite and less hydrothermal apatite. Conversely, magmatic apatites in the earliest porphyries at La Granja are generally the most affected by metasomatism. Similarly, inclusions of magmatic apatite in other minerals are less obvious in more altered porphyry intrusions because the host phases (plagioclase, biotite, pyroxene etc.) are themselves altered and may be completely pseudomorphed. In addition, magmatic apatite can be harder to locate in fine-grained intrusions. This feature tends to be more common in late porphyry intrusions, where magmatic apatite is inferred to crystallise later during melt evolution and typically occurs as part of the groundmass rather than as coarser microphenocrysts. Apatite was observed in all alteration zones sampled both within mineralised and unmineralised assemblages, apart from the argillic; however, there is evidence for overprinted apatite from such zones in the literature (Loader 2016; Krneta et al. 2017). Samples from Northparkes indicate that apatite is particularly abundant within propylitic assemblages.

8.3.1 Classification of apatite textures

Based on these observations, and comparison of apatite compositions from La Granja in *Chapters 5 to 7*, apatite can be divided into four groups: magmatic, metasomatised, replacement and hydrothermal apatite (Fig. 8.4). The classification criteria for in-situ apatite from each group are discussed in these chapters. This diversity emphasises the importance

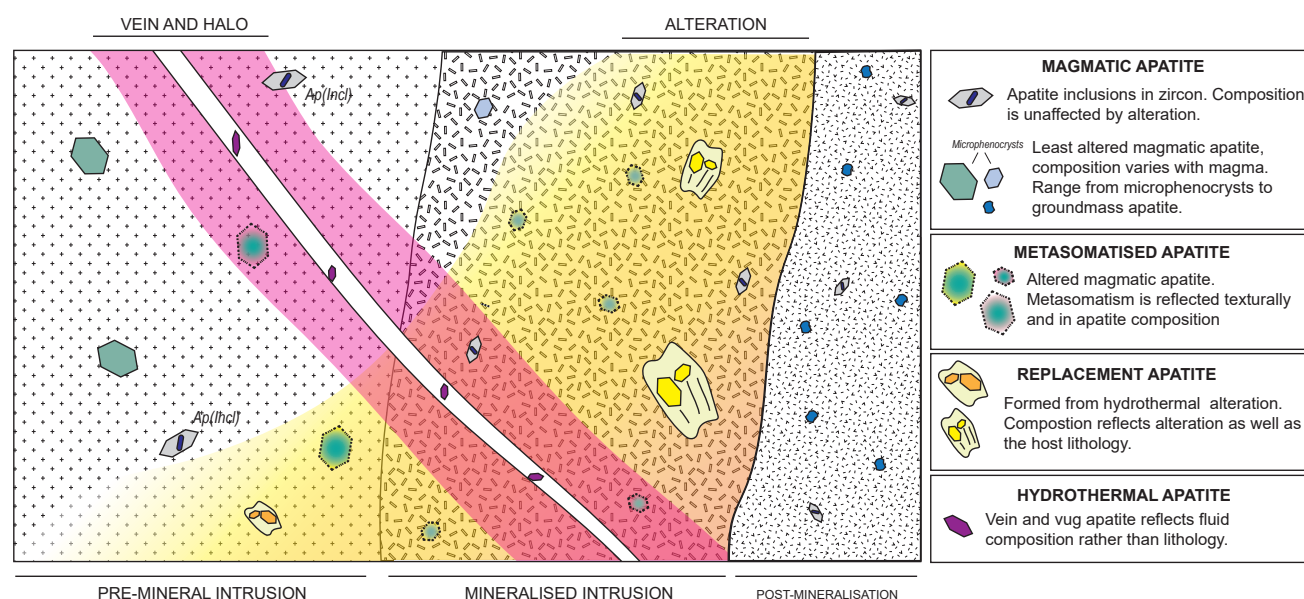


Figure 8.4 Illustration of the modes of occurrence of apatite in porphyry systems identified in this study. “Magmatic apatites” are apparently unaltered primary apatites (alteration score < 1) that have crystallised from the melt and are inferred to have experienced limited post-crystallisation modification. Magmatic apatites that have been overprinted by hydrothermal fluids are classed “Metasomatised apatites” as metasomatism has modified the primary igneous composition. “Replacement apatites” represent hydrothermal compositions as a result of replacement reactions of other mineral phases. Vein and vug apatites are classed as “Hydrothermal apatite” as they are inferred to have precipitated directly from a fluid.

of utilising mineral textures when interpreting variations in apatite compositions. In *Chapters 5 to 7* different textural associations of apatite show diverging compositions in line with their different formation histories. Understanding the controls on composition is particularly important when looking to infer melt or fluid compositions/conditions from apatite. Many previous studies (including Chu et al. 2009; Belousova et al. 2002; Mao et al. 2016; Rukhlov et al. 2016) have not comprehensively described apatite textures, aside from alteration effects, in part because of the use of mineral concentrates over in-situ grains. Some allocations can be made using composition (see *Chapter 7*) and this will be investigated further in the following chapter. In addition, grain shape and inclusion composition can be used: hydrothermal apatites are typically intergrown with other minerals of the hydrothermal assemblage (such as sulfides) and are more irregular in shape. Grain size is dependent on the grain size of the rock for magmatic apatites so cannot be used without knowledge of the host lithology.

In the porphyry environment, the effects of overprinting by hydrothermal fluids is the main issue when interpreting magmatic crystallisation compositions from magmatic apatites. In addition, hydrothermal alteration can also destroy magmatic apatite-bearing assemblages that could otherwise be used to track magmatic evolution within an intrusion (e.g. Jennings et al. 2011; Bruand et al. 2016; Stock et al. 2016). Inclusions of apatite in zircons are inferred to reflect unaltered magmatic apatite compositions (see *Chapter 5*) and can be readily found in most porphyry intrusions. However, these apatites may represent relatively late, volatile-rich crystallisation stages within a porphyry melt compared to apatite microphenocrysts or apatite inclusions within plagioclase or pyroxene. In this study, an alteration score has been applied to identify such metasomatised grains. However, it is harder to identify sericitically altered apatite using BSE-imaging alone, with a selection of grains both in this study and

Krneta et al. (2017) containing a lack of monazite inclusion within sericitic altered apatite. In this case, it has been suggested that the high activities of Na and Ca within the fluid suppress the crystallisation of monazite inclusions. However, sericitic-stage overprinting can be readily recognised by distinct CL textures, such as those described in Bouzari et al. (2016), and in distinctive changes in the relative REE concentrations (see *Chapter 7*). Therefore, it would also be of use to develop compositional-based classifications for both metasomatised apatite and hydrothermal apatite together, as they are all formed as a result of fluid interaction.

8.4 Apatite composition from case studies

8.4.1 Least-altered magmatic apatite

Least-altered magmatic apatite from La Granja is investigated in *Chapter 6* in which apatite and used to distinguish between porphyry and non-porphyry related rocks (“fertile” vs. “unfertile” igneous systems), and mineralised intrusions from unmineralised intrusions within porphyry systems. These classifications are key for exploration of porphyry systems and to aid our understanding of the fundamental controls of where and why porphyry deposits form. To explore such discrimination in magmatic apatite from the case studies, the units studied in this chapter have been classified as either porphyry-related or not porphyry-related. Those apatites not from porphyry intrusions can be further broken down: true non-porphyry-related intrusions (AND, DIO, GRANO, ELENA) which crystallised within magmatic arcs but have no temporal (over 20 Myr gap) association with mineralisation and pre-mineral plutons which have a much closer association to mineralisation (less than 10 Myr at Northparkes) but do not form part of the porphyry intrusion or stock. Apatite from porphyry intrusions can be separated into mineralised porphyries (EQP_M, EQP_{PB}, EDP_M, EDP_{PB}, K-QMP, BANCO), less mineralised porphyries (IMP_M, IMP_{PB}, DIOP, ESTE), and late- or post-mineralisation porphyries (LQP_{PB}, LQP1_M, LQP2_M, LDP_{PB}, RH, ZERO, MZO).

Because the identification of magmatic apatite grains requires textural associations, the La Granja concentrates cannot be assessed in this way and so have been kept separate. In addition, as analyses of Ap_{incl} are not available from Chuquicamata or Northparkes, magmatic apatite may have been experienced sub-solidus diffusional re-equilibration (*Chapter 5*). As a result, S and halogen concentrations will not be discussed.

Identifying porphyry-related intrusions

Most regional porphyry exploration tools based on whole rock or mineral chemistry are focused on distinguishing potentially porphyry-related from background arc rocks. This can be achieved fairly successfully using bulk rock geochemical signatures (Loucks 2014; Halley 2020). Many of these parameters within magmatic apatite, e.g. high Sr/Y, have been touched on previously (see *Chapter 6*). Eu/Eu* and HREE ratios were concluded as being the most robust melt-generated signatures in Ap_{mtx} from the effects of metasomatism and diffusion. Lower La/Yb was observed in bulk rock from ‘unfertile’ host rocks that formed in significantly different tectonic regimes to the porphyry rocks sampled, such as the Eocene units at La

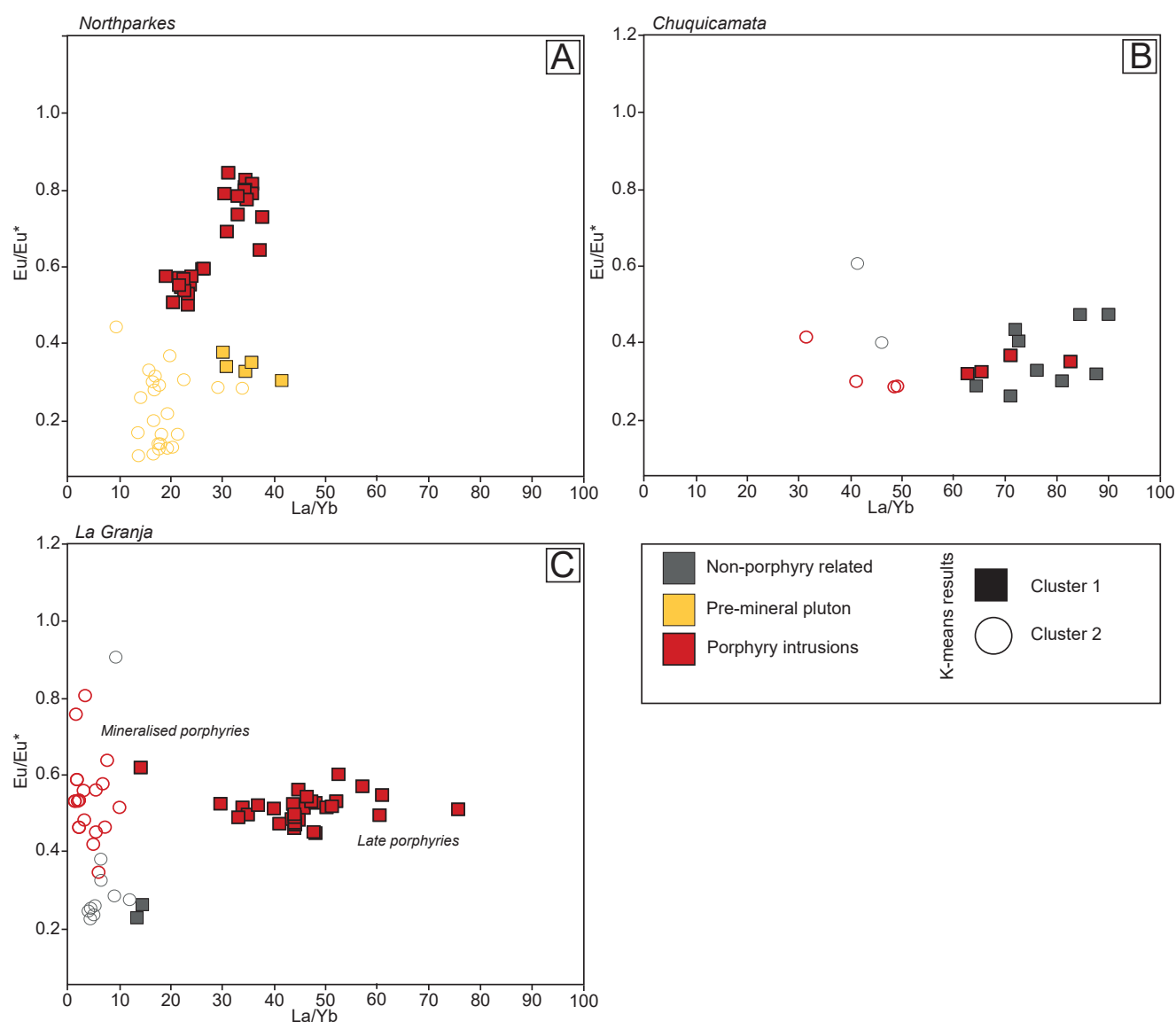


Figure 8.5 Eu/Eu^* and La/Yb in least altered magmatic apatite from porphyry and non-porphyry related intrusions (coloured). The results from K-means cluster analysis describe the distribution of the data between two centres (square and circle). A) At Northparkes Eu/Eu^* and La/Yb is lower in apatite from pre-mineral plutons and can be used to successfully classify apatite from porphyry intrusions and pre-mineral plutons. B) However, at Chuquicamata apatite from porphyry and non-porphyry related rocks have similar La/Yb and Eu/Eu^* ratios and cannot be successfully classified into two groups. C) At La Granja least-altered magmatic apatite show similar Eu/Eu^* and La/Yb concentrations, only apatite from late porphyry intrusions can be separated from non-porphyry apatites by K-means clustering. Analytical errors are smaller than the symbols.

Granja (see section 4.5.1). In addition lower Eu/Eu^* in magmatic apatite from non-porphyry intrusions is interpreted to be a result of more reduced melt conditions (see Chapter 5), supported by the low S concentrations in non-porphyry Ap_{incl} and being consistent with low and constant bulk rock V/Sc ratios (Halley 2020, see section 5.4.3). A more oxidised source melt (Mungall 2002; Sun et al. 2013) has been proposed as an important factor in the formation of porphyry-fertile magmas. In addition, low Eu/Eu^* could have been amplified by more abundant plagioclase crystallisation/fractionation in these magmas prior to apatite crystallisation, ultimately related to lower magmatic water content (see Chapter 6).

The effectiveness of apatite classification from porphyry and non-porphyry related intrusions using La/Yb and Eu/Eu^* ratios can be tested by K-means cluster analysis. K-means clustering describes the distribution of data between variables into k-clusters around the nearest mean.

Apatite analyses from Northparkes can be separated into two clusters representing apatite from porphyry intrusions and pre-mineral plutons with high success rates (100.0% and 82.1% respectively). High La/Yb signatures are inherited by apatite both within porphyry intrusions and in the precursor plutons that formed within the same geodynamic setting just prior to mineralisation. Lower Eu/Eu* in the porphyry precursor BMQ apatite from Northparkes could suggest that there was an increase in oxidation state of the system between its emplacement and the subsequent intrusion of the porphyries. However at Chuquicamata the separation is not clear and the correct classification of apatite into clusters representing apatite from porphyry intrusions and non-porphyry related intrusions is as low as 50.0% and 18.2% (Fig. 8.5B), corresponding with similarities in bulk rock compositions and petrogenetic descriptions from the literature (Ossandón et al. 2001; Zentilli et al. 2018). This is thought to reflect the intrinsic fertility of the Triassic Elena Granodiorite host rocks at Chuquicamata which may be similarly oxidised and have also undergone delayed plagioclase crystallisation in the same way as the younger porphyry units. At La Granja Eu/Eu* is higher in apatite from porphyry-related intrusions, however La/Yb ratios are comparable (Fig. 8.5C). Classification of apatite from porphyry related intrusions is low (59.6%) as only late porphyries are clustered together, classification of non-porphyry related apatite is higher (83.3%). Both REE ratios are affected by evolving melt composition. Ratios of La/Yb may increase with subsequent porphyry intrusions, as is the case at Northparkes where BQM is precursor to porphyry units and at La Granja, and within melts with respect to differentiation (see *section 6.6*). In addition Eu/Eu* could be responding to the precipitation of plagioclase alongside apatite in the shallow crust (see *section 6.5*). This means that for some deposits La/Yb and Eu/Eu* are less effective parameters for distinguishing porphyry and non-porphyry related apatite.

Intrusive phases of a porphyry system

In porphyry systems, the intrusions associated with mineralisation are typically emplaced relatively early in the magmatic centre with later intrusions hosting less mineralisation (Sillitoe 2010). In *Chapter 6*, differences in least-altered magmatic apatite compositions revealed systematic variations in relative REE concentrations between different intrusive phases at La Granja. Ap_{mtrx} from mineralised porphyries has higher HREE concentrations relative to total REE contents. The final intrusions of the porphyry systems are typically marked by a distinct change in melt composition that is reflected in the magmatic apatite as a large decrease in HREE. When modelled, these differences were inferred to reflect the crystallisation of apatite subsequent to different amounts of zircon (see *section 6.5.1*). In addition magmatic apatites from early porphyries might expect to show higher concentrations of compatible elements that then decrease in apatite from subsequent porphyry units as a result of progressive fractionation of the parental melt in an upper crustal magma reservoir (see *section 6.7*).

This decrease in compatible elements is not observed at Northparkes where magma evolution may be complicated by recurrent mafic injections between felsic porphyry emplacement events (Pacey 2016; Lickfold et al. 2007). However MREE/HREE ratios can distinguish between apatites from different intrusive phases, again K-means clustering analysis can

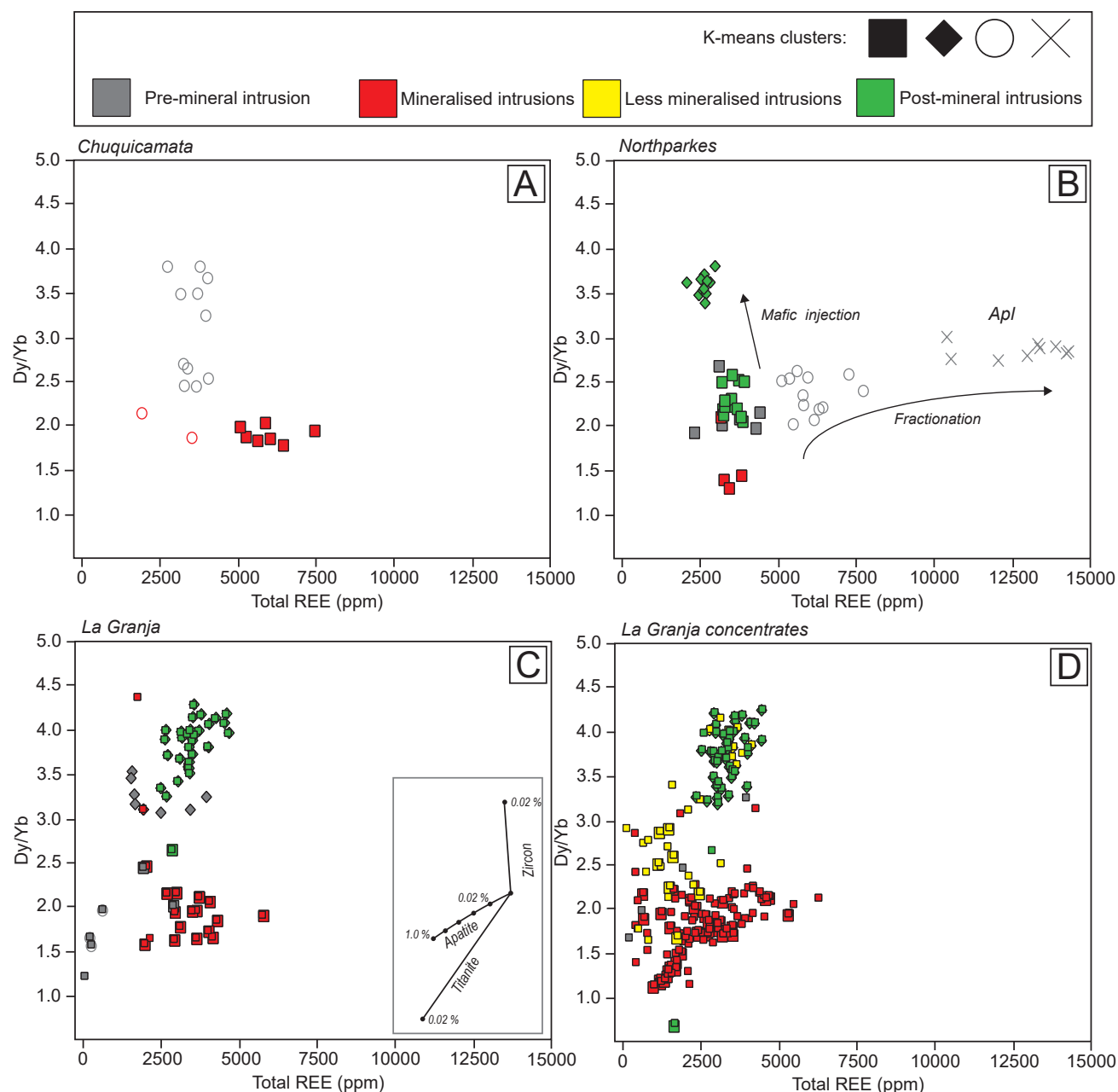


Figure 8.6 Total REE content and MREE/HREE ratios in apatite from the three case studies coloured by intrusive phase. The results from K-means cluster analyses are indicated by shape. A) Least altered magmatic apatite from Chuquicamata group into porphyry and non-porphyry related apatite (77.8 and 100% correct classification from K-means clustering respectively). B) Apatite from Northparkes show some clustering between mineralised intrusions, post-mineral intrusions and pre-mineral intrusions (66.7, 100.0 and 45.8 % respectively), however there is overlap between all three. D) Analyses from La Granja have good separation between apatite from the different porphyry intrusive phases (86.4 and 93.3 % classification of apatite from main mineralised and post-mineral intrusions) but cannot separate out those from non-porphyry related intrusions (25.0 % correct classification). Fractionation trends for apatite (up to 1 % crystallisation), and apatite co-crystallising with titanite and zircon (up to 0.02 % crystallisation) are modelled from DP_{PB} melt (see Section 6.5 for more information). D) Least-altered apatites concentrates from La Granja also show separation according to intrusive phases (main mineralised and post-mineral intrusions; 89.1 and 97.6 % respectively), however less mineralised intrusions cannot be distinguished from mineralised intrusions. Analytical errors are smaller than the symbols.

be used to identify common groups within the data distribution (Figs. 8.6A-B). Apatite from Chuquicamata can be classified into porphyry and non-porphyry intrusion. At Northparkes, apatite from the mineralised K-QMP is depleted in HREE relative to MREE (Fig. 8.5B), which could be due to the co-crystallisation of titanite. Large amounts of titanite are observed at Northparkes (Fig. 8.2J), although in the majority of grains this is inferred to be hydrothermal. In these samples magmatic apatite is observed in assemblages with zircon and titanite (Fig.

8.2D), consistent with the mineral fractionation modelling. In addition, the La Granja apatite concentrates also follow the same separation; however, they show more overlap (Fig. 8.5C), perhaps because the data have not been filtered using chemical criteria for a magmatic origin.

8.4.2 Metasomatised magmatic apatite

Hydrothermally overprinted magmatic apatite (Fig. 8.4) is the most common apatite type observed within the porphyry systems. As their compositions reflect both magmatic and hydrothermal processes, they could prove useful in exploration as recorders of the two key stages of porphyry evolution that govern metal endowment. In addition, least altered magmatic apatite is less common and would need filtering first. Elements including As, Na, Mn and Sr are relatively fluid mobile as observed within altered bulk rocks (see *section 4.5.1*) and altered apatites (see *Chapter 5*) at La Granja. Thus, these elements may not preserve primary magmatic signatures in overprinted magmatic apatite and are perhaps more likely to reflect hydrothermal signatures of mineralisation. In particular, Sr and Na in apatite have been linked to the degree of sulfide mineralisation on a hand sample scale (see *section 7.6*). Across the three porphyry systems, the concentrations of these elements in apatite show consistent differences between pre-mineralisation and porphyry-related intrusions. As concentrations are typically higher in apatite from non-porphyry-related intrusions, whereas Sr, Na and Mn ones are typically lower (Fig. 8.7). There are exceptions at Northparkes; these are the aplite-hosted metasomatised magmatic apatites, which are frequently outliers in their chemistry probably because of the highly evolved magma composition.

The incorporation of As into magmatic apatite has been linked to the oxidation state of the melt (Mao et al. 2016; Rukhlov et al. 2017) because As^{5+} can substitute easily into the PO_4 tetrahedron (Hughes & Rakovan 2002). However, there have been limited studies of As^{3+} substitution into apatite (Liu et al. 2016) so a redox control of total As in apatite is uncertain. In the three case studies, if magmatic redox were a first order control of overprinted magmatic apatite composition it would imply that the pre-mineralisation magmas were more oxidised than the porphyry-related magmas. This would contradict findings from *Chapter 6* and current understanding of porphyry formation (Richards 2005; Sun et al. 2017). Moreover, bulk rock As is higher in the porphyry intrusions (see *section 4.5*). In porphyry intrusions, a devolatilisation prior to apatite crystallisation could account for lower concentrations of As. The timing of apatite crystallisation and volatile saturation was investigated for magmatic apatite (see *section 6.7.2*) and would explain the decrease in As with subsequent porphyry intrusions (Fig. 8.7). This is supported by lower concentrations in apatite from the volcanic host rock (AND) at La Granja which may have degassed prior to apatite crystallisation. Therefore, the concentration of As in magmatic apatite from “dry” magmatic systems may reflect different controls to apatite from within porphyry systems which appear to largely reflect hydrothermal overprinting.

Alternatively the high mobility of As in fluids as evidenced by its variation in altered rock (see *section 4.5.1*), and increase with metasomatism in apatite (see *Chapter 5*), suggests a hydrothermal influence on its concentration in overprinted magmatic apatite. The distribution

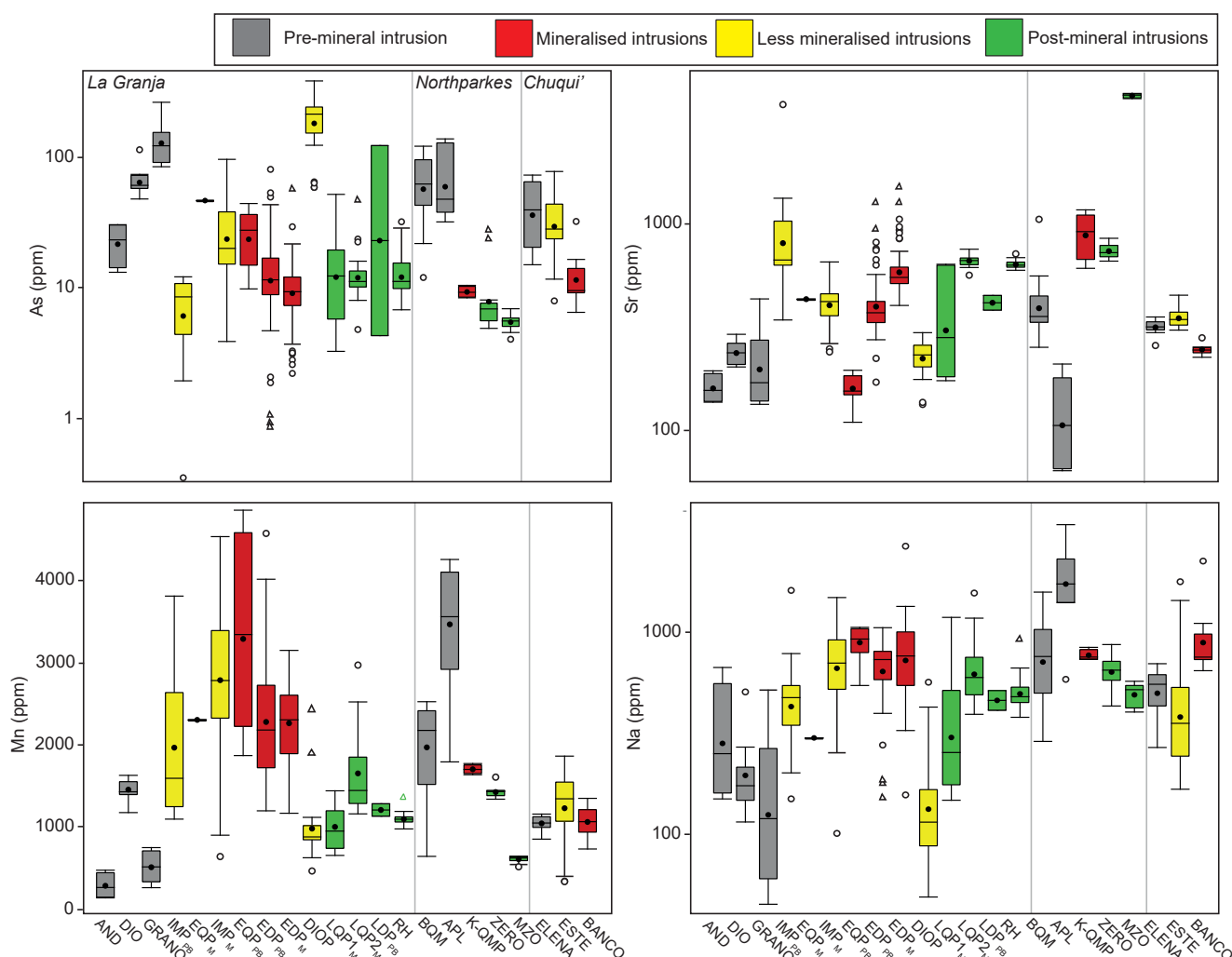


Figure 8.7 Box plots of concentrations of fluid mobile elements in metasomatised magmatic apatites, grouped by host lithology. The error on individual analyses is smaller than the range described in the box plots.

of As in porphyry deposits corresponds to the hydrothermal alteration zonation, with the majority of As-rich minerals hosted in the sericitic and argillic zones in the upper parts (Sillitoe 2010). Arsenic readily partitions into the vapour on phase separation of porphyry fluids and the low K, Na, Ca and high H^+ activities associated with acidic vapour promote the stability of arsenian sulfides, such as arsenopyrite (Kouzmanov et al. 2012; Pokrovski et al. 2013). The association of As-minerals with Au occurrence (which is also transported in the vapour phase; Zhu et al. 2011), and higher As concentrations in apatites from Au-related deposits and veins (Mao et al. 2016), is also evidence for mobilisation of As into the shallower, lower temperature regions within and above porphyry deposits, where high sulfidation epithermal gold mineralisation can form. Thus, in the porphyry systems studied here, mobilisation of As out of early magmatic apatite into later alteration fluids could couple with low As in degassed melt to produce low As concentrations in overprinted magmatic apatite.

The concentration of Sr is higher in apatites from porphyry-related intrusions than non-porphyry related, and especially mineralised intrusions (Fig. 8.7). Similar observations were reported by Loader (2016). The whole rock data from La Granja, Northparkes and Chuquibambilla all show the characteristic of increasing Sr (and Sr/Y) in more evolved magmas (Fig. 4.26). It is important to remember that in magmatic apatite, as demonstrated above and in Chapter 6,

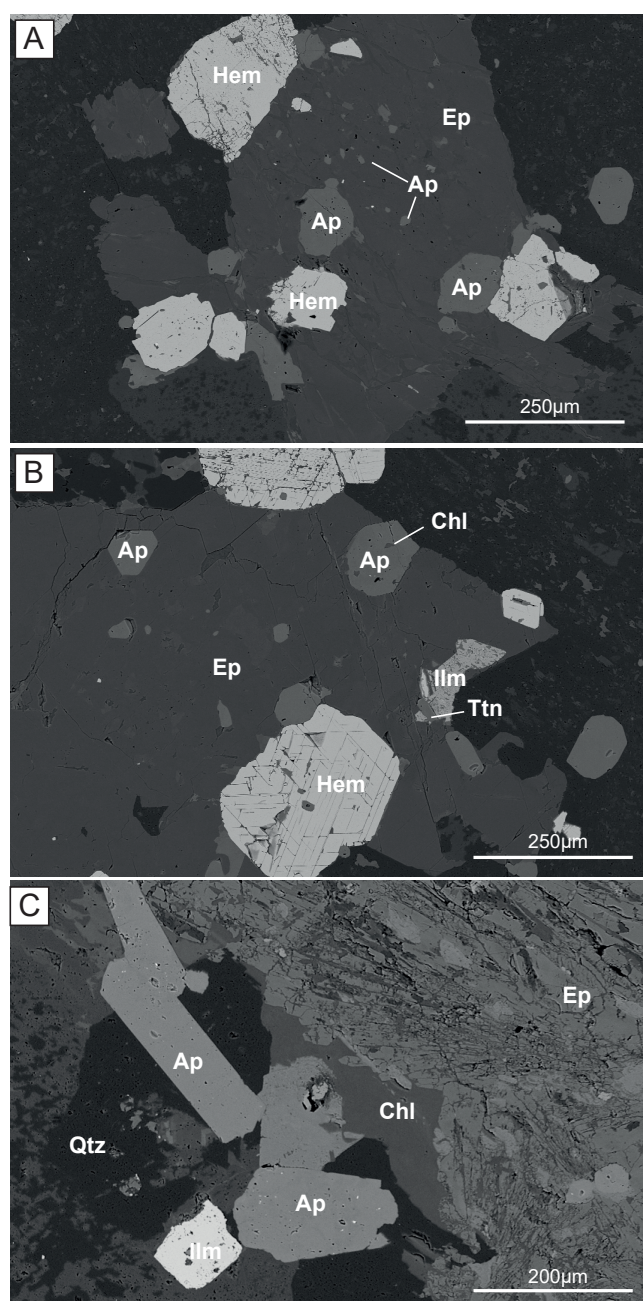


Figure 8.8 SEM backscattered electron images of apatite in typical propylitic alteration assemblages from the BQM. A) Amphibole with epidote (P21717). B) Epidote with chlorite, titanite and ilmenite (P21720). C) Chlorite with epidote and titanite (P21721).

it is the timing of crystallisation relative to plagioclase that plays an important role in controlling the Sr content, in addition to the fundamental inheritance from initial melt compositions (Nathwani et al. 2020). Irrespective of this, the fact that high Sr is observed in least-altered magmatic apatite from mineralised intrusions (see *Chapter 6*) suggests that, at least to some extent, this is a primary magmatic feature. However, it has been demonstrated that Sr is fluid mobile and can be removed from bulk rock during hydrolytic alteration (see *section 5.5.1*). Furthermore, it is also prone to mobilisation out of, or into, apatite via rapid diffusion (see *Chapter 5*). In hydrothermal apatite, Sr-rich fluids associated with the breakdown of plagioclase can show elevated Sr so that metasomatic processes could serve to enhance the high Sr signal in metasomatised magmatic apatite. Although it is difficult to deconvolve the two effects, it is clear that elevated Sr on both counts would be a useful fertile porphyry indicator and so is of potential use in any exploration tool.

Similar to Sr, Na concentrations are highest in overprinted magmatic apatites from porphyry-related, mineralised intrusions with the exception (as above) for the aplite-hosted and BQM-hosted apatite from Northparkes. The distinctly high Na in

the (relatively unaltered) aplite sample suggests that Na can be enriched in apatite by purely magmatic process, via extensive fractional crystallisation. However, as Na is mobile in bulk rock alteration (see *section 4.5.1*) and metasomatised apatite (see *Chapter 5*), it is suggested that elevated Na in overprinted magmatic apatite is largely a hydrothermal effect. A hydrothermal influence is supported by high Na concentrations in hydrothermal apatite, particularly sericitic-associated apatite, and in samples associated with mineralisation (see *Chapter 7*). Such Na-rich fluids are expected in the central 'exhaust' zone of porphyry systems generated during potassic or sericitic alteration (e.g. Sillitoe 2010). To complicate matters, Na is involved in many coupled-substitutions and so can be partly controlled by (or may itself influence) other trace elements

in apatite such as REE (see Chapter 2).

Mn concentrations are highest in overprinted magmatic apatite from porphyry-related samples at La Granja (Fig. 8.7). This was also observed by Loader (2016) at Oyu Tolgoi. Thus, high-Mn apatite seems to be a general feature of porphyry systems relative to other deposit types (Mao et al. 2016). However, the porphyry-related data from Northparkes and Chuquicamata are not especially elevated, and do not differ much from the BMQ precursor pluton at Northparkes or the Elena Grandiorite at Chuquicamata. As with some of the other trace elements, Mn is also notably enriched in the apatite from Northparkes, showing that it can be controlled by extreme magmatic differentiation. Mn is somewhat mobile during alteration of whole rocks (see section 4.5.1) and in metasomatised apatite (see Chapter 5) so that hydrothermal modification could also play a role. Hydrothermal Mn distribution is principally controlled by the brine phase in porphyry systems and so typically relates to the development of deeper alteration domains, such as the potassic core of porphyry systems (Audétat et al. 2008).

8.4.3 Replacement apatite

Apatite in replacement assemblages is common is a common component of propylitic alteration assemblages at Northparkes (Fig. 8.8). The composition of replacement apatite was identified in Chapter 7 as being largely a result of fluid composition, in addition to some control from precursor minerals. This is similar to metasomatised magmatic apatite and as a result, in proximal alteration zones, they largely share comparable compositions within like units. Despite being less abundant, replacement apatite from the case studies show the same variations in As, Sr, Mn and Na concentrations as metasomatised apatite (Fig. 8.7), supporting the conclusions that at least part of these signatures are derived from hydrothermal fluids.

At La Granja, the composition of potassic and proximal propylitic replacement apatites are comparable and have similar REE profiles to magmatic apatites, suggesting formation from early, least fractionated fluids (see Chapter 7). These similarities mean that replacement apatite from proximal alteration domains is hard to distinguish from magmatic or overprinted magmatic apatite, which is potentially advantageous when it comes to the development of discrimination tools.

More distal propylitic replacement apatite from Northparkes has a similar REE slope to

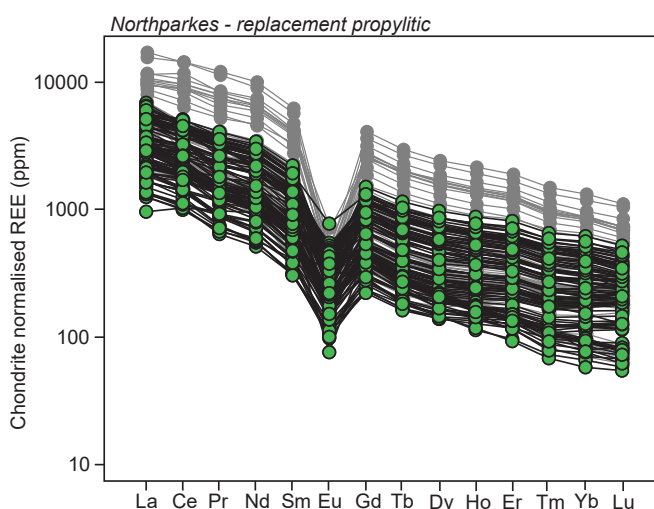


Figure 8.9 Chondrite-normalised (Sun & McDonough 1989) REE profiles of replacement apatites from Northparkes. In grey are least-altered magmatic apatite compositions from the same deposit. The analytical error is smaller than the symbol size.

Table 8.2 Distance of samples from associated mineralised centre (Pacey 2016).

Sample number	Dominant propylitic assemblage with apatite	Distance from mineralised centre (m)
P21717	Amphibole + epidote (Fig. 8.XA)	179
P21720	Epidote + titanite (Fig. 8.XB)	900
P21721	Chlorite (Fig. 8.XC)	944

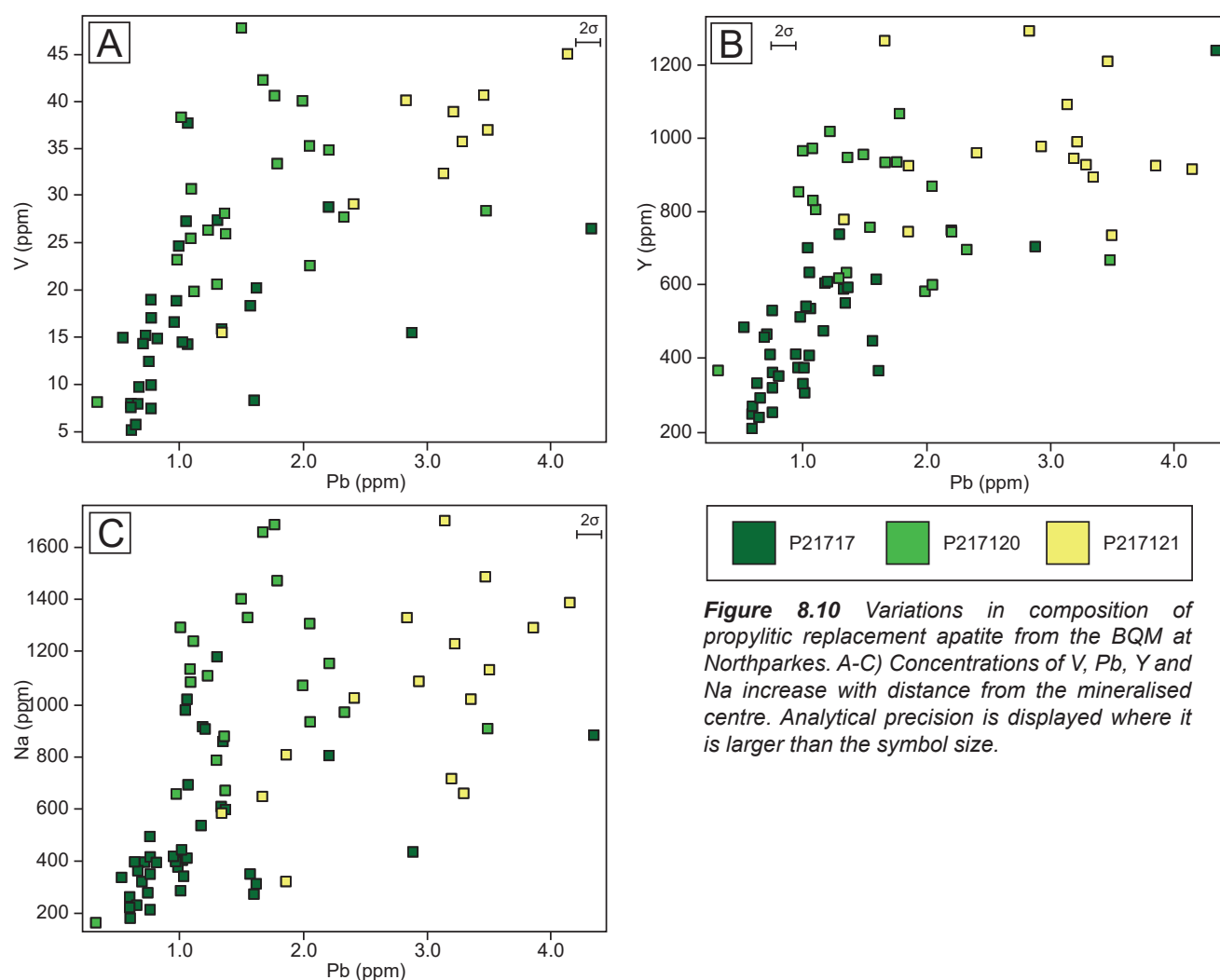


Figure 8.10 Variations in composition of propylitic replacement apatite from the BQM at Northparkes. A-C) Concentrations of V, Pb, Y and Na increase with distance from the mineralised centre. Analytical precision is displayed where it is larger than the symbol size.

magmatic apatite, but generally contains lower REE concentrations and has less negative Eu anomalies (Fig. 8.9), indicating that hydrothermal replacement apatite becomes progressively modified in composition across the potassic-propylitic transition (see *section 7.5*). Such spatial changes in chemistry have exploration applications, with a number of elements that are known to be mobile within the propylitic zone (i.e. Wilkinson et al. 2015) potentially being involved. This hypothesis was tested on samples of BQM from Northparkes that were sampled at different distances from the mineralised centre (Pacey 2016; Table 8.2). Although the distances involved do not span the full range of the propylitic zone, apatite from the more distal locations shows higher V, Pb, Y and Na concentrations, although the correlation between these elements is weak (Fig. 8.10; R^2 values of 0.38, 0.45 and 0.31 respectively). These elements have previously been identified as mobile within the propylitic environment, and have been observed to increase (to distances of ~1 to 1.5 km) and then decrease (V) or increase (Pb, Na) in concentration in other propylitic minerals with distance from the hydrothermal centre (Wilkinson et al. 2015). Thus, there appears to be potential for the use of apatite as a mineral vector for exploration, and therefore apatite can be added to the toolbox that already exists using other propylitic minerals (Neal et al. 2018; Cooke et al. 2014; Wilkinson et al. 2015). Apatite may further improve these techniques as it can host a wide range of elements and can be easier to analyse than sheet silicates, being primarily limited only by grain size.

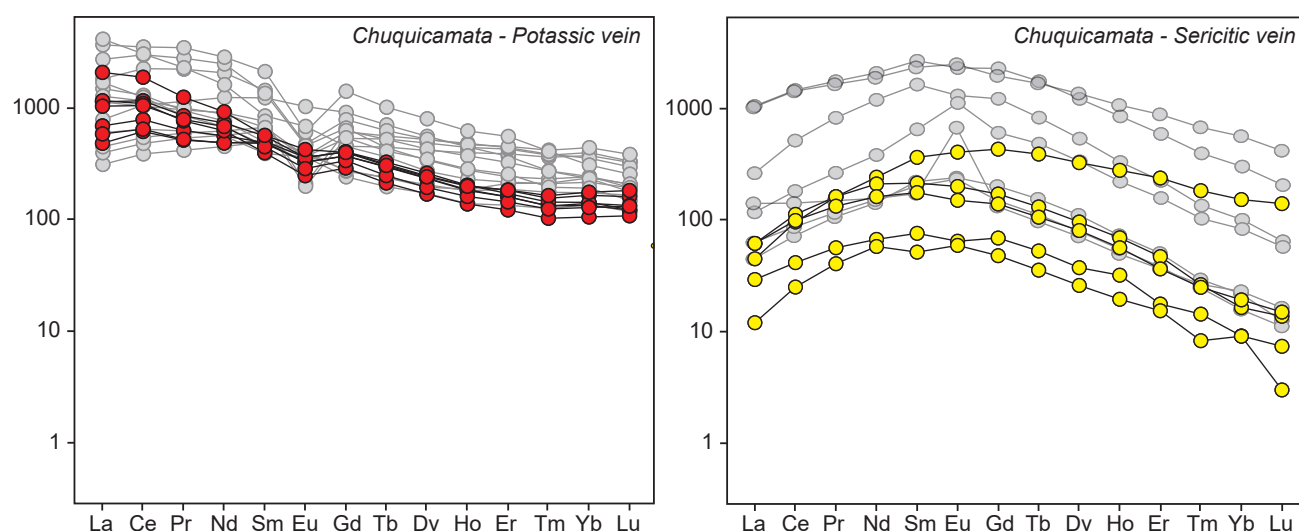


Figure 8.11 Apatite from potassic veins (red) and sericitic veins (yellow) from Chuquicamata compared to the equivalent types from La Granja (grey). The analytical error is smaller than the symbol size.

8.4.4 Hydrothermal apatite

In *Chapter 7* vein and vug apatites were concluded to be the most reflective out of the apatite types of fluid compositions. At La Granja changes in REE patterns were inferred to be controlled by fractionation resulting from hydrothermal processes, and changes in cations by fluid:rock interactions. Hydrothermal apatite is much less common in the samples from the Chuquicamata and Northparkes. Apatite is present within potassic (K-feldspar + chalcopyrite; Fig. 8.2E) and sericitic (sericite + bornite; Fig. 8.2F) veins from Chuquicamata. Potassic vein apatites from Chuquicamata are distinct to those from La Granja with lower LREE and with smaller Eu anomalies (Fig. 8.11). This difference could suggest that the apatites formed during different stages of potassic fluid evolution, or that the composition of the early fluid varies reflecting partitioning from the melt and which coincides with the different REE profiles of the magmatic apatite (Fig. 8.6). Either way it is acknowledged that the complexity of fluid compositions around a porphyry system cannot be fully captured in a study such as this one.

The apatite from sericitic veins is more similar to sericitic apatites from La Granja and also has the same distinctive MREE-enriched, LREE and HREE depleted, low Na apatites observed at La Granja (see *Chapter 7*; Fig. 8.11) and in other magmatic hydrothermal systems (Krnetić et al. 2018; Ismail et al. 2014; Chen et al. 2019; Li & Zhou 2015). These similarities of the sericitic apatite is encouraging for exploration. Signatures characteristic of specific porphyry alteration domains that are observed in most if not all porphyry systems would provide an important discriminator for porphyry-related alteration and allow the identification of specific alteration domains without textural context, such as from analyses of apatite from stream sediments.

8.5 Apatite in porphyry systems – towards a tool for exploration?

Previous work has distinguished between different mineral deposit types using the trace element chemistry of apatite (Belousova et al. 2002; Mao et al. 2016; Rukhlov et al. 2016). Bouzari et al. (2016) described changes in CL response as a result of porphyry-related hydrothermal alteration and Loader (2016) identified compositions of interest

Table 8.3 Main controls of note for apatite composition.

Element	Controls on apatite concentration	Notes	References
Sulfur	<i>Magmatic</i> : redox	Routinely below detection limit and subject to metasomatism/sub-solidus re-equilibration.	Chapter 5 Chapter 6 Chapter 7 Figs. 8.12, 8.15
Halogens	<i>Magmatic</i> : Magmatic volatile behaviour. F concentration in apatite ~ F concentration in fluids. <i>Hydrothermal</i> : Volatile behaviour in fluids. Reflects ligands associated with mineralised intrusions.	- Cl and OH often at or near detection limit and subject to metasomatism/sub-solidus re-equilibration. - Cl and F measured, OH calculated based on stoichiometry. - Beam-induced issues with F quantification.	Chapter 5 Chapter 6 Chapter 7 Figs. 8.12, 8.15
La/Yb	<i>Magmatic</i> : melt composition, strongly effected by apatite, titanite, monzanite crystallisation. <i>Hydrothermal</i> : REE fractionation with fluid evolution. Metasomatism,	- Melt composition dominated by amphibole and/or garnet at depth, variations from REE-phase crystallisation in upper crust. - Large variations in late porphyries of melts from different geotectonic settings. - Decreases as a result of metasomatism.	Chapter 5 Chapter 6 Chapter 7 Figs. 8.5, 8.9, 8.11, 8.12, 8.15
Gd/Yb	<i>Magmatic</i> : melt composition. Strongly effected by zircon crystallisation. <i>Hydrothermal</i> : REE fractionation with fluid evolution	- Increases in Gd/Yb with little change in total REE a result of zircon crystallisation. - Decrease in Gd/Yb with larger decrease in REE a result of apatite or titanite crystallisation. - Y behaves as a HREE.	Chapter 6 Chapter 7 Figs. 8.6, 8.9, 8.11, 8.15
Eu/Eu*	<i>Magmatic</i> : redox and plagioclase crystallisation. <i>Hydrothermal</i> : breakdown/co-crystallisation of plagioclase.	- Lower Eu/Eu* in more reduced melts. - Lower Eu/Eu* from increases plagioclase crystallisation prior to apatite (more mafic or high ASI, low P/Ca melt). - Positive Eu anomaly in sericitic associated apatite.	Chapter 6 Chapter 7 Figs. 8.5, 8.11, 8.12, 8.15
Total REE	<i>Magmatic</i> : melt differentiation with apatite crystallisation, metasomatism <i>Hydrothermal</i> : decrease with fluid fractionation	- Total REE decrease with apatite crystallisation. - Total REE decrease with metasomatism. - Lower total REE in sericitic apatite.	Chapter 5 Chapter 6 Chapter 7 Figs. 8.6, 8.9, 8.11, 8.15
Mn	<i>Magmatic</i> : degree of melt polymerisation. <i>Hydrothermal</i> : fluid mobile, enriched in proximal alteration zones.	- Potentially effected by sub-solidus re-equilibration and metasomatism. - Highest in mineralised porphyry units.	Chapter 5 Chapter 6 Chapter 7 Figs. 8.7, 8.12, 8.15
Na	<i>Hydrothermal</i> : Variation with hydrothermal alteration	- Effected by metasomatism - High concentrations in sericitic apatite	Chapter 5 Chapter 7 Figs. 8.7, 8.12, 8.15
Sr	<i>Magmatic</i> : Plagioclase co-crystallisation. <i>Hydrothermal</i> : Plagioclase destruction.	- High in porphyry related intrusions - Tracking timing of crystallisation relative to plagioclase	Chapter 5 Chapter 6 Chapter 7 Figs. 8.7, 8.12, 8.15
As	<i>Magmatic</i> : volatile loss. <i>Hydrothermal</i> : Alteration, competition from As-phases in hydrothermal	- As concentrations lower in hydrothermal apatite - As decrease with metasomatism.	Chapter 7 Figs. 8.7, 8.12, 8.15
Mg	<i>Magmatic</i> : melt differentiation	Can be used as a proxy for melt differentiation between apatite	Chapter 6 -
Fe	<i>Magmatic</i> : melt differentiation <i>Hydrothermal</i> : Variation with hydrothermal alteration	- Strongly correlated to Mg in magmatic apatite - Increase in proximal alteration	Chapter 6 Chapter 7 Figs. 8.10, 8.15
Pb	<i>Hydrothermal</i> : Fluid mobile. Plagioclase destruction. Variation with hydrothermal alteration	Enriched in sericitic apatite	Chapter 5 Chapter 6 Chapter 7 Figs. 8.10, 8.15

as part of a more focused assessment of apatite as a mineral indicator. These studies highlight the potential of apatite as an indicator mineral due to its highly variable major- and trace-element compositions which reflect a number of processes and conditions associated with, or required for, the formation of porphyry deposits (Table 8.3).

Textural association of apatite

The abundance of apatite in the porphyry environment renders it useful for exploration and the large range in apatite occurrence (as described in *Chapters 6 – 7* and summarised in Fig. 8.4) can aid a more complete understanding of porphyry magmatic-hydrothermal evolution. However, it is acknowledged that the recognised diversity adds complications in terms of potential exploration applications. Where the textural context of the apatite is not available, such as in samples from stream sediments, the grains should be classified as such using composition. The most effective way would be to identify hydrothermal and least altered apatite, isolating magmatic and different hydrothermal alteration signatures. Then, instead of identifying the degree of metasomatism as is done in *Chapter 6*, replacement and metasomatised magmatic apatite can be classified in terms of the hydrothermal influence on composition. In *Chapter 7* these apatite types were shown to be texturally different but compositionally similar, and should lie between magmatic and hydrothermal apatite compositions. The occurrence of Ap_{incl} are more limited and analyses are time-consuming; however, these could be incorporated as part of zircon geochronological and trace-element studies to provide additional information about the melt composition. Ap_{mtrx} provided the largest range in magmatic apatite composition and are the most useful in terms of distinguishing between intrusive phases.

The occurrence of hydrothermal apatite and textures indicating volatile-rich magmas can provide evidence of a porphyry intrusion over a plutonic intrusion. The unique composition of

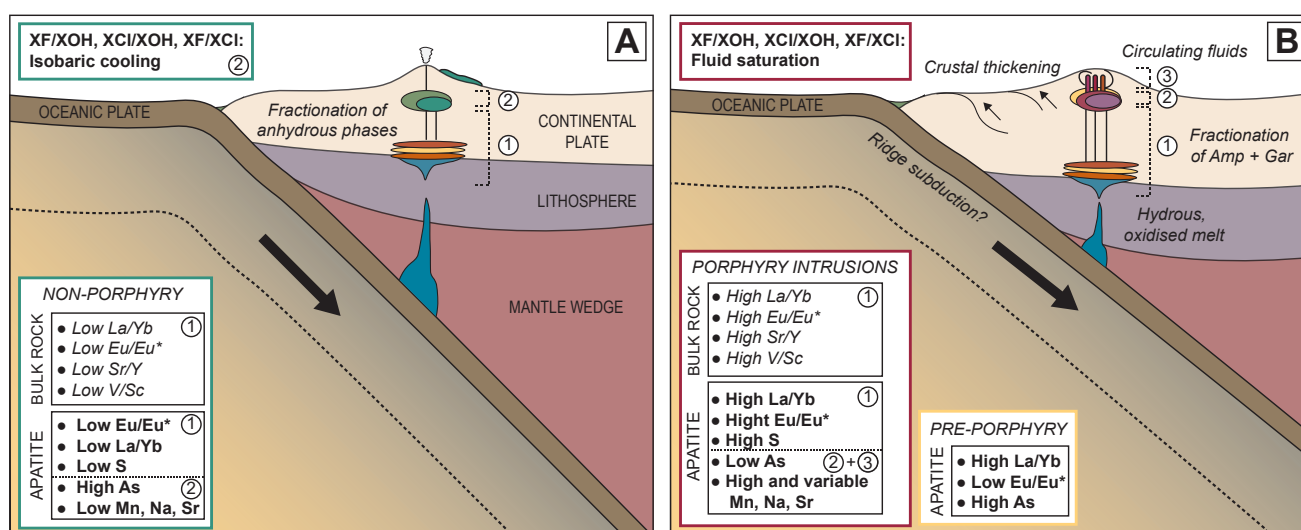


Figure 8.12 Comparison of bulk rock and Ap_{mtrx} compositions from porphyry and non-porphyry related intrusions (including pre-porphyry plutons) in this study. A) The magmas that formed the host rocks at La Granja formed in a different geodynamic setting to the younger porphyry system leading to significant differences in bulk rock geochemistry between them. Some of these differences can also be observed in the apatite within these rocks, which partly inherits the bulk rock characteristics (1). The apatites also record other differences, not observed in bulk rock data (2). B) Some host rocks, such as pre-mineralisation plutons (BQM at Northparkes), formed in more comparable settings to the porphyry systems themselves and therefore have a similar geochemical signature to them as inherited from the melt (1). Differences between pre-porphyry and porphyry apatite in this environment can occur from magmatic processes at crystallisation depth (2) or as a results of alteration (3).

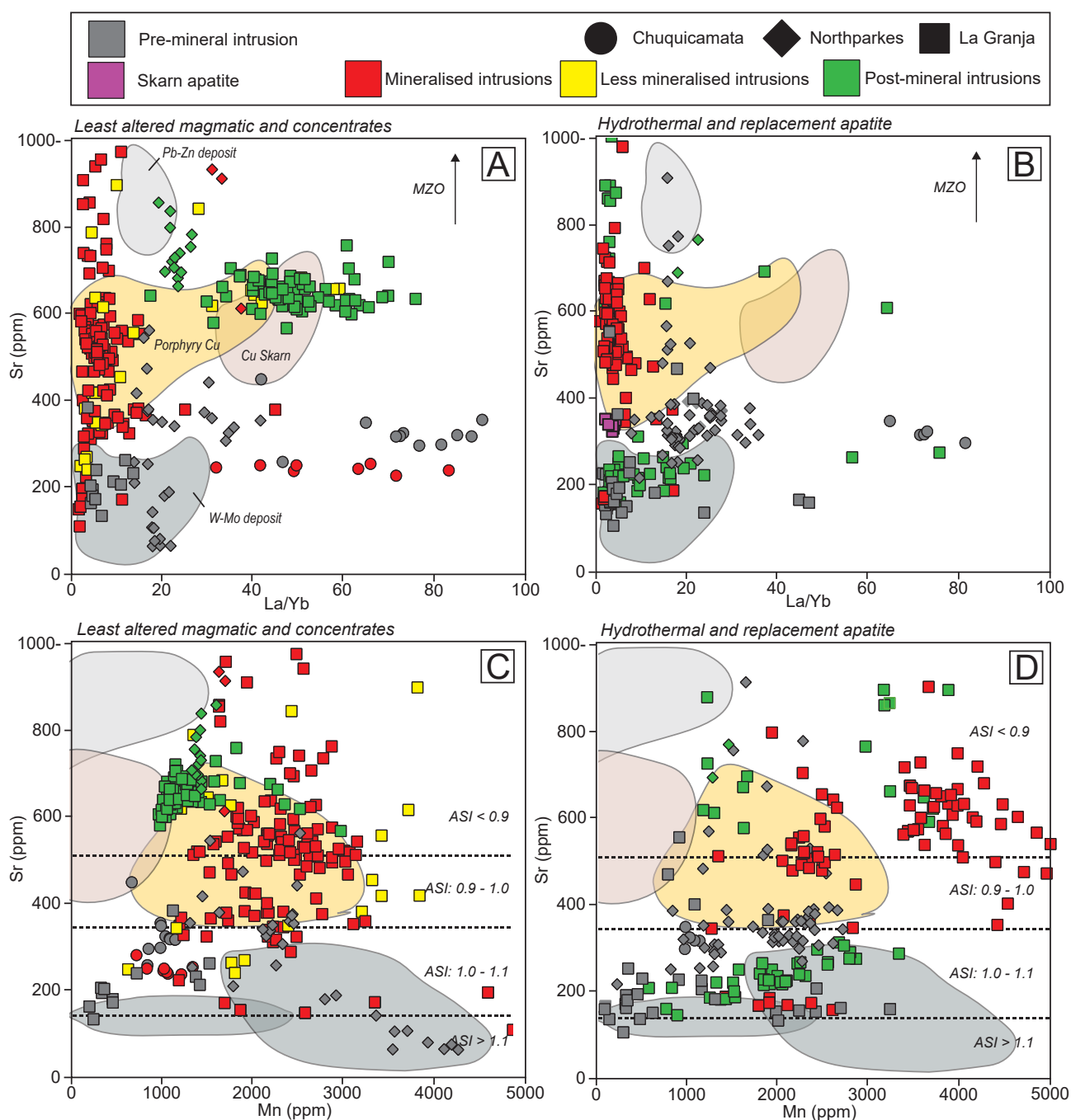


Figure 8.13 Comparison of apatite composition with literature data. Apatite from main porphyry intrusions plot within Porphyry Cu field from Cao et al. (2012) but spread over a range of ASI values (Chu et al. 2009). A) Least-altered magmatic apatite from late intrusions have higher La/Yb ratios than those in Cao et al. (2012). B) Hydrothermal fluid related apatite from main porphyry units also sits within classification scheme. C) Sr-Mn concentrations in least altered magmatic apatite also show comparable composition to those from porphyries in Cao et al. (2012). D) However, Mn concentrations in hydrothermal-related apatite show more variability. Analytical error is smaller than symbol size.

hydrothermal apatite lends itself to exploration for porphyry systems. Sericitic ($\text{Eu}/\text{Eu}^* > 1$, low ΣREE , MREE-enriched, high Na, Pb, S, see Chapter 7) and argillic overprinted apatite (depleted La/Nd, low Th and U: Loader 2016; Krneta et al. 2017) have easily identified compositions. However, the presence of such grains provides no guarantee of a mineralised porphyry system. Conversely, as shown in samples from Chuquicamata and Northparkes, hydrothermal apatite is generally less common, so could be easily overlooked from a smaller sample set.

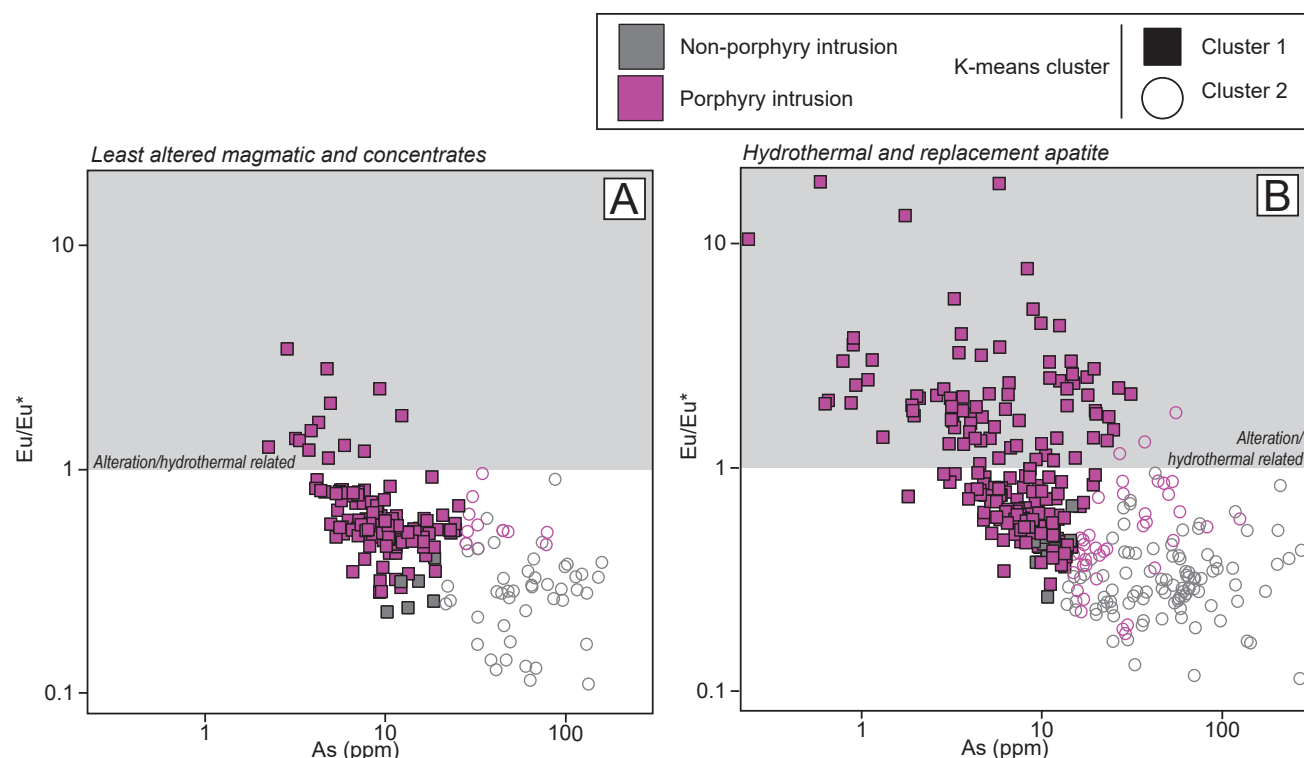


Figure 8.14 Eu/Eu^* and As concentration in apatite can be used to distinguish between those from porphyry (pink) and non-porphphy intrusions (grey). The results of K-means cluster analyses for two groups is shown as squares and circles. A) Least altered magmatic apatite and concentrates from porphyry intrusions have higher Eu/Eu^* and lower As than those from non-porphphy or pre-mineral intrusions. K-means clustering can correctly classify 92.6 and 88.2 % of the apatite into their respective groups. B) This separation also works with hydrothermal and replacement apatite with $Eu/Eu^* > 1$ produced from metasomatism or present in hydrothermal apatite (correct classification of 86.0 and 90.0 % respectively).

Fertile and non-fertile belts

There are numerous suggested controls on the formation of fertile magma, including the saturation of oxidised magma with metals and water in the lower crust, or the exsolution and concentration of metal bearing fluids in the upper crust (Wilkinson 2013). The composition of apatite could reflect some of all of these processes (Fig. 8.12). The deep crustal melt evolution that generates signals captured by whole rocks (i.e. La/Yb; Table 8.3) will be present in any rocks (and magmatic apatite) that form within the same broad magmatic cycle as the porphyries. This can be up to a few Myr before mineralisation, and potentially in the same district at the same time as mineralisation but involving non-mineralised plutons (Fig. 8.12B). As a result the bulk rock composition of the Eocene host rocks and Miocene porphyries at La Granja are distinct (Chapter 4), whereas additional comparisons of La/Yb from the case studies reveal comparable ratios. A comparison of La/Yb ratios of apatites from other arcs (Belousova et al. 2002; Chu et al. 2009; Cao et al. 2012; Mao et al. 2016) confirms that all analyses plot within the granitoid range; however, there is no discernible difference between apatite from porphyry-related and non-porphphy related intrusions (Fig. 8.13A). In addition, metasomatism of apatite will affect the results (Chapter 5), as will the type of apatite used in the classification (Fig. 8.13B).

Distinctions between apatite from porphyry deposits and unmineralised intrusions within the same magmatic district may be possible, through additional consideration of processes occurring at emplacement depth, such as fluid exsolution (Table 8.3). Magmatic water content is also considered to be a factor in the evolution of fertile porphyry systems (see section 1.2.4),

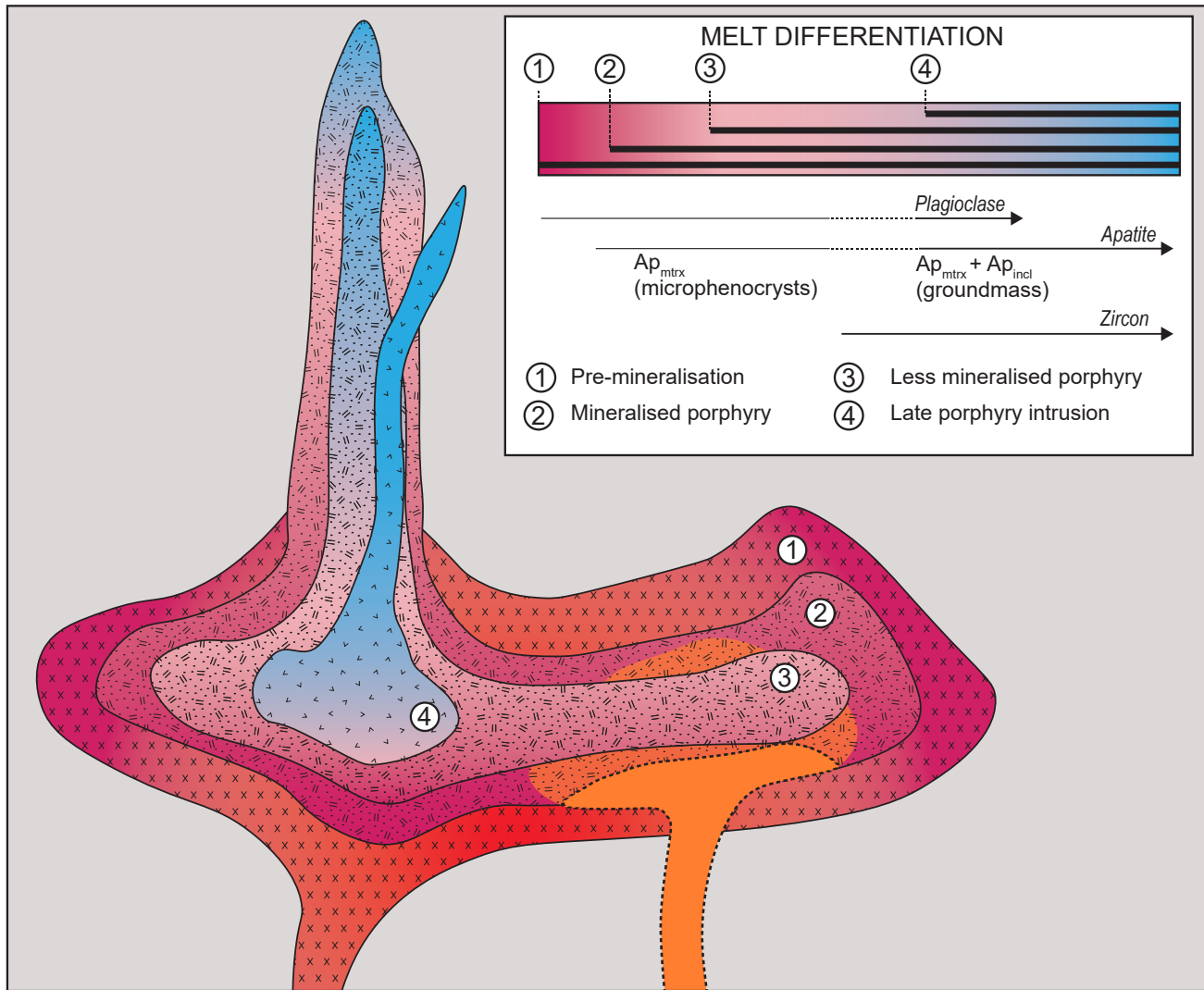


Figure 8.15 Schematic of changes in melt composition and relative timing of magmatic apatite (Ap_{mtrx} and Ap_{incl}) crystallisation between early and late porphyry intrusions (1 – 4). The bulk rock compositions of the intrusions typically follow normal melt differentiation of the shared magma source and a comparison of Ap_{mtrx} from subsequent porphyries reflect this. Ap_{incl} form at a similar time relative to melt differentiation within each intrusion so that the difference between Ap_{mtrx} and Ap_{incl} crystallisation varies between intrusions. Early, mineralised intrusions (2) have early crystallising Ap_{mtrx} relative to melt differentiation, a hiatus is then observed in apatite crystallisation before Ap_{incl} form. In late porphyries (4) the timing of Ap_{mtrx} and Ap_{incl} is more similar.

with more hydrous melts generated during the subduction of oceanic ridges (such as the Inca Plateau and the Nazca Ridge in the case of La Granja). This is thought to be the ultimate control of bulk rock Sr/Y (Loucks 2014), because of its effect on suppressing plagioclase and enhancing amphibole crystallisation, and also to be important in influencing bulk rock Th/Sm. The Eocene units at La Granja show an increase in Sm with Th, suggesting fractionation of pyroxene from relatively dry magmas, whereas porphyry units, such as the EQP_{PB} , show a decrease in Sm, consistent with the fractionation of more hydrous phases such as amphibole as also suggested by Davies (2002; see section 5.4.3). The change in mole fraction halogen ratios observed in Ap_{incl} from La Granja support these bulk rock observations, with trends in the chemistry of Ap_{incl} from the Eocene intrusions explained by isobaric cooling (see section 6.7.2). These contrast with variations in Ap_{incl} from the porphyry intrusions, which are interpreted to show increasing volatile content to the point of fluid saturation (see section 6.7.2). In addition, hydrothermally-overprinted apatite may reflect circulating hydrothermal fluids which are not

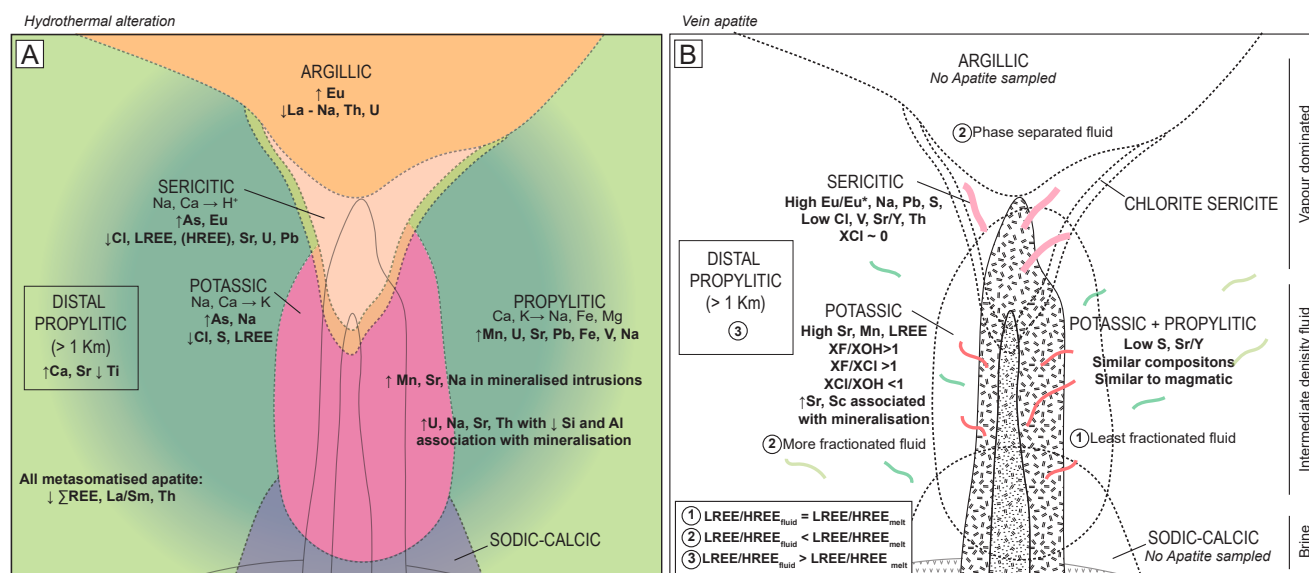


Figure 8.16 Typical composition of A) hydrothermally overprinted apatite and B) vein apatite within a porphyry system as a function of position within alteration zones and association with mineralisation. Porphyry schematic adapted from Sillitoe (2010) with additional information from Wilkinson et al. (2015), Loader (2017a), Migdisov et al. (2016) and Krneta et al. (2017).

present, or not as significant in unmineralised plutons (Fig. 8.12B). For example, in other deposits a high Cl overprint has been attributed to early fluids associated with mineralisation and can be used to distinguish mineralised and unmineralised intrusions (Rasmussen & Mortensen 2013). However, Cl concentrations in Ap_{incl} may not be routinely acquired in an exploration application. Instead, preferential, or more extensive volatile saturation in porphyry-associated magmas may be evidenced by lower As concentration observed in apatites. As a possible, simple, practical tool for identifying As-rich apatite (generally associated with less fertile rocks), CL imaging could be implemented because As is known to quench the CL response in apatite (Persial et al. 2000). Plots of Eu/Eu* against As concentration provide the best separation of apatite from porphyry intrusions as confirmed by K-means cluster analysis (Fig. 8.14), and could be inferred to reflect processes from deep to shallow crust ((Fig. 8.12), and can be applied on both magmatic and hydrothermal apatite (Fig. 8.14B).

Stages of porphyry formation

Identifying the phases of a porphyry system would enable the intrusion with highest potential for mineralisation to be identified and allow a distinction between a lower grade, main stage intrusions, which would indicate a less economic deposit, and low grade, late intrusions (Fig. 8.15). The element concentrations associated with intrusive phases can be a result of magmatic processes – usually related to melt differentiation between subsequent intrusions and timing of apatite crystallisation (*Chapter 6*) - or a result of changing composition of overprinting hydrothermal fluids associated with each intrusive phase (Table. 8.3).

Rare earth element ratios in Ap_{mtrx} show systematic difference between porphyry phases (Fig. 8.6). This is inferred to be a magmatic signature, controlled by the relative timing of apatite crystallisation (see *section 6.6*). Figure 8.15 illustrates the relative timing of Ap_{mtrx} and Ap_{incl} crystallisation within different porphyry intrusions. In late porphyries crystallisation of Ap_{mtrx} is delayed relative to earlier intrusions, and is compositionally similar to Ap_{incl} . The

stage of melt differentiation recorded by Ap_{incl} is fixed by the timing of zircon crystallisation, whereas the onset of apatite saturation is closely linked to plagioclase crystallisation (as reflected by Eu/Eu^* in apatite), melt ASI and SiO_2 content (see section 6.4). The concentration of Sr in magmatic apatite from I- and S-type granitoids has also been related to melt ASI in earlier studies (Chu et al. 2009) with Sr concentrations decreasing with increasing ASI (Fig. 8.13C-D). This is consistent with observations made in Chapter 6. Although the concentration of Sr works well for separating mineralised and less mineralised intrusions within a system (Fig. 8.7), the baseline Sr used for classification differs from one site to another. By contrast, the distinctions for REE ratios, although of a fairly broad nature, appear to be consistent across rock compositions and deposit types (Cu-Mo vs. Cu-Au) which opens up the possibility of 'global' applicability. Furthermore, discrimination using HREE concentrations which are less affected by metasomatism (see Chapter 6) means that such a discrimination approach may also be effective for overprinted magmatic apatites (Fig. 8.5D).

An additional approach to identifying porphyry phases could be to focus on elements known to be mobile within a porphyry hydrothermal environment (see section 4.5.1). Element concentrations in apatite associated with hydrothermal processes are shown in Table. 8.3. The REE pattern in hydrothermal and replacement apatite is result of fractionation processes. Early, proximal apatite towards the centre of a system has REE patterns comparable to that of the magmatic apatite (see section 7.5.2; Figs. 8.9 and 8.11). By contrast the other cation concentration in apatite is a dependant on the co-precipitating minerals and changing fluid compositions (Chapter 7). Variations observed in apatite between alteration zones, combined with interpretations from the literature (Wilkinson et al. 2015; Loader 2016; Migdisov et al. 2016; Krneta et al. 2017) are described in Fig. 8.16. The concentrations of elements in metasomatised and replacement (Fig. 8.16A) and hydrothermal apatite (Fig. 8.16B) differ, emphasizing the need to identify the textural association of the apatite.

Hydrothermally-modified apatite could be used to vector towards the centre of a system. This could utilise the changes in composition observed or hypothesised for propylitic replacement apatite (Fig. 8.16B). However, this would require further study as other propylitic minerals within the assemblage, such as chlorite or epidote, may compete for the mobile elements such as Zn, Fe and V (Cooke et al. 2014; Wilkinson et al. 2015). The varying mobility of REE within a fluid could also be exploited to vector towards a fluid source. The more distal hydrothermal apatite could exhibit higher LREE/HREE ratios than the more proximal apatites precipitated from the least fractionated fluid, and a significantly higher LREE/HREE than intermediate apatite. However, although this has been demonstrated experimentally (Migdisov et al. 2016), it has yet to be observed on a large-scale in natural systems.

In addition, concentrations of Mn, Sr and Na have all been shown to peak in metasomatised and replacement apatite from mineralised intrusions across the three deposits (Fig. 8.7). This could be utilised for deposit-scale exploration. The elevated concentrations of these elements within the early intrusions may be a result of: 1) higher Mn, Sr, and Na concentrations within early magmatic derived fluids (or higher fluid-apatite partition

coefficients for these elements at this stage); 2) liberation of Mn Sr and Na from the altered rocks contributing to fluid composition; or 3) a combination of the two, combined with more intensive alteration of the earlier, central porphyries which experience the greatest fluid flux. The concentration of Mn in hydrothermal-related apatite from the main porphyry units is significantly higher than least altered magmatic apatite from the same units (Fig. 8.13C-D).

In summary, it is evident that apatite can be used, with care, as a powerful discrimination tool in porphyry systems. However, there is potential for much more robust and distinct classifications of apatite using multivariate approaches that combine the discrimination power of some of the various parameters identified in this chapter. In the next chapter, this will be explored with the aid of machine learning algorithms.

Chapter 9: Application of apatite geochemistry to predictive tools for exploration

9.1 Introduction

Over the course of *Chapters 5 – 8* the trace element chemistry of apatite has been shown to be sensitive to environmental conditions and fluid compositions. This includes magmatic and hydrothermal processes that are believed to be important in the development of porphyry deposits and which ultimately culminate in the mineralisation of a system (*Chapter 7*). These compositional features in apatite are present in porphyry deposits from different magmatic arcs (*Chapter 8*) opening up the potential for the use of apatite as an indicator mineral for exploration purposes. However, the diversity of apatite occurrence and composition is wide, so discriminations based on a low numbers of variables – such as simple bivariate plots – are ineffective. To combat this, machine learning algorithms can be used to develop multivariate tools that can effectively classify apatite based on composition. The findings from *Chapter 8* are used here to inform choices such as variable selection and the type of predictive classifications required in the development of a series of such multivariate discrimination tools.

Predictive learning algorithms have been successfully applied to mineral geochemistry with a focus on ore deposit exploration (Gregory et al. 2019; Zuo & Xiong 2018) and, specifically, the use of apatite to distinguish between deposit types (Mao et al. 2016; Rukhlov et al. 2017). Here, trace element data presented in the previous chapters is combined with an additional 780 apatite concentrate analyses and used to build two predictive models that can be used to discriminate apatites formed in magmatic arc rocks. **Model 1** will classify the petrological occurrence of apatite where textural evidence is not available (such as in stream sediments). It will also enable the identification of different alteration associations of hydrothermal apatite. **Model 2** will aim to distinguish between porphyry and non-porphyry intrusions, and main-stage and late-stage porphyry intrusions. This would be of use for early stage exploration during the delineation of fertile intrusive complexes and later when exploring within such fertile complexes.

9.1.1 Predictive models

In this study, supervised learning has been used to build the predictive models. With supervised learning, the input variables of the data have a direct influence on the output. This differs to unsupervised techniques which describe the underlying distribution or organisation of the data (Hastie et al. 2008). Applying a supervised technique enables control over the nature of the classification model built, allowing for observations and differentiations made earlier in this study to be incorporated. The output of any models needs to be discrete, qualitative responses rather than contentious variables, so classification models, rather than regression models, are required (Hastie et al. 2008). Consequently, logistic regression and random forest were identified as suitable approaches.

Logistic regression

Logistic regression is a statistical model that uses a logistic function to model qualitative classification. It is typically used for binary outcomes with predicted outcomes given as probabilities between 0 and 1, with 1 being positive or true (Hosmer & Lemeshow 2000). However, logistic regression can also be applied to models with multiple outputs (Hastie et al. 2008).

The relationship between the independent (input) variables and output is described by a linear regression which is acted upon by a logistic function. The relationship between two variables in a linear model can be described as:

$$E(Y|x) = \beta_0 + \beta_1 x \quad \text{Eq. 9.1}$$

This can be read as the expected value of Y given x , or the probability (E) of output Y given value x . β_0 is the bias or intercept and β_1 is the coefficient of the trend. The logistic function of this relationship can be written as:

$$\pi(x) = \frac{e^{\beta_0 + \beta_1 x}}{1 + e^{\beta_0 + \beta_1 x}} \quad \text{Eq. 9.2}$$

here $\pi(x)$ is used as notation for condition mean of $E(Y|x)$ when the logistic distribution is used. Values of $\pi(x)$ will plot in as logistic function which is also known as a sigmoidal function (Fig. 9.1A). The change in $\pi(x)$ gets smaller the closer the output (Y) is to 0 or to 1 (Hosmer & Lemeshow 2000). In a dichotomous classification as shown in figure 9.1A, a classification threshold (e.g. at $Y = 0.5$) is used to assign the outcome to a qualitative output. In the case of multinomial logistic regression a classification is not applied and the results are left as probabilities.

Logistic functions are preferred over linear functions as most geochemical data sets show trends in log-space (for examples see *Chapters 6 - 7*). However, this model assumes that the input variables are normally distributed, which geochemical data are not, so pre-processing (log-transforming) the variables is required before the logarithmic function is applied. In addition, the outcome is strongly affected by multicollinearity between predictive variables (Hosmer & Lemeshow 2000; Kubat 2017).

Random forest

Random forest is a completely different type of learning algorithm. It is based on decision trees which are hierarchically organised structures that split data by class at nodes (Hastie et al. 2008). In random forest, the trees are used ensemble or as a 'forest' to produce multiple uncorrelated outcomes with a low bias (Breiman 2001). The majority vote from the collection of trees is then used in the final classification model (Fig. 9.1B).

The value in this learning technique is in the number of iterations. Individual trees will have a low variance but a high bias. A forest of uncorrelated trees will have a higher variance but a low bias, and when combined together will outperform an individual model (Breiman 2001). So long as each tree is unique, the final model will be protected from the error produced in the individual trees (Hastie et al. 2008). Low correlation between each tree can be achieved through bootstrap aggregation, or bagging, which is a method of random sampling. As the outcome of a decision tree is very sensitive to the data it is trained on it is important to use random sub-sets of data for each tree. In addition, limiting the features that can be used at each node, or feature randomness, also helps promote

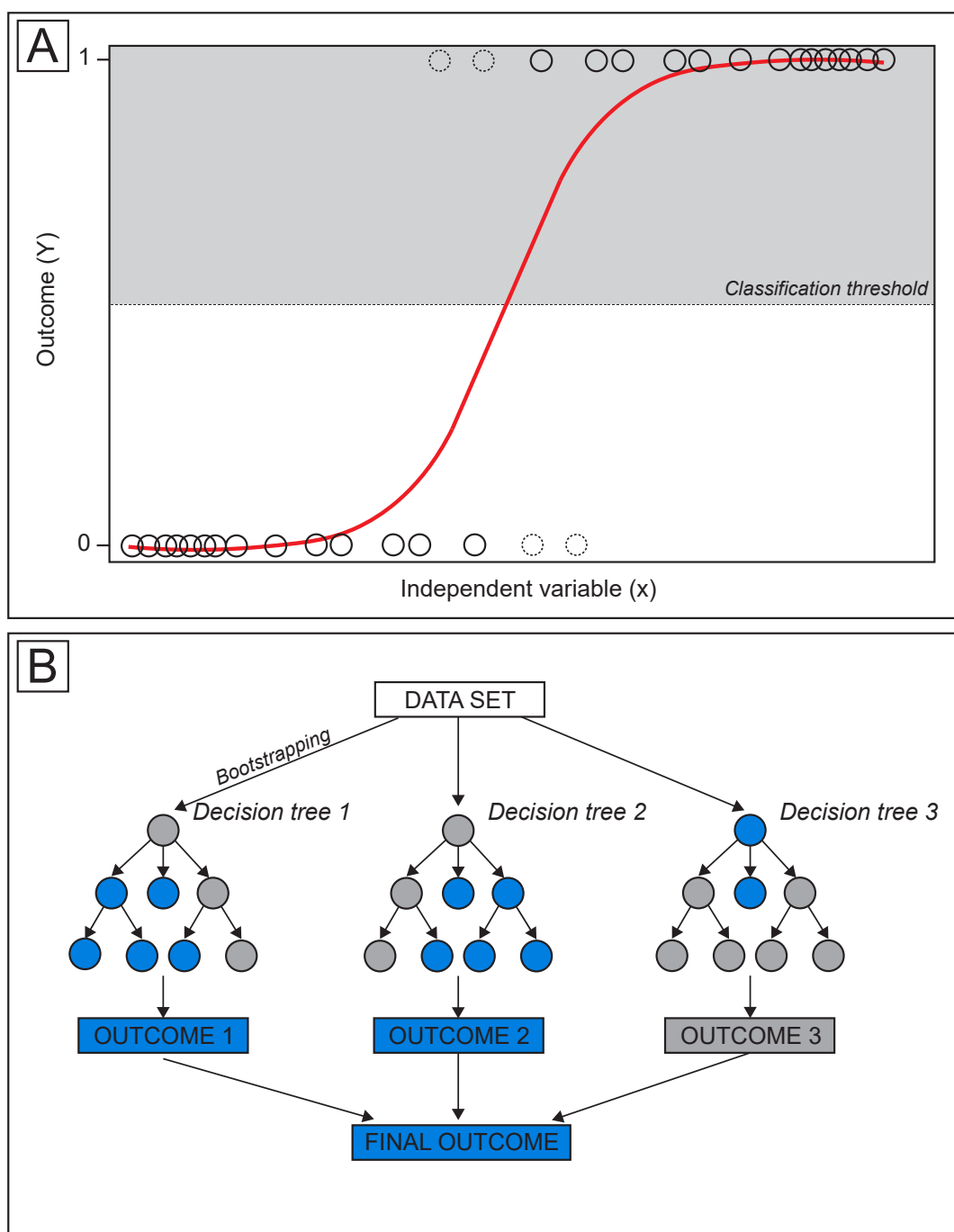


Figure 9.1 Explanation of supervised learning models used in this study. A) Classification of binary outputs by logistic regression plots a sigmoidal curve between independent variable (x) and outcome (Y). The position of the classification threshold along this regression determines the classification of the outcome. B) Random forest uses an ensemble of decision trees to classify sub-sets of the data. The final result is determined from an average of these outcomes.

diversity between trees helping to further randomise the forest (Breiman 2001; Hastie et al. 2008).

Random forest is a comparatively simple method of machine learning. In addition, it does not require extensive preparation of geochemical data and is robust about multicollinearity. However, as mentioned, the models are very dependent on the input data. This may be an issue for smaller or class-biased data sets which can produce over-fitted (high variance) models.

9.2 Methodology

A summary of the methodical process used in this chapter is described in figure 9.2. This can be

broken down into three stages: preparing the data set, fitting and evaluation of the model, and testing of the final model.

9.2.1 Preparing the dataset

The dataset is composed of 850 trace-element analyses of apatite from the three case-studies of La Granja, Chuquicamata and Northparkes (*Chapter 9*), and an additional 780 analyses from 32 blocks of apatite concentrates provided by Rio Tinto (Table 9.1). Qualitative data was also collected describing grain textures, and in the case of in-situ apatites, mineral assemblages.

Quality assurance, quality control routine

For consistency, the trace element analyses were collected using the same methodology as described in *Chapter 3*. Analyses of Durango apatite were collected with every run and a comparison of these results is given in *Appendix A*. The same quality assurance and quality control (QAQC) routine was applied to all results. This includes the analysis of elements that are typically low in apatite but high in included phases such as Si, Zr, Al which can be used to identify contaminated analyses.

Pre-processing

Geochemical data are expressed as a relative weight of a set of parts in total where all components sum to a constant (i.e. wt. %, ppm). Therefore, each component only carries relative information and cannot be considered independent from each other. This is also known as closed data and can produce ‘false’ correlations between components (Aitchison 1986). This is especially problematic for logistic regression models which are affected by multicollinearity. Also, logistic regression models require normally distributed data, which is not the case for the apatite data under consideration. Finally, the value of a component does not

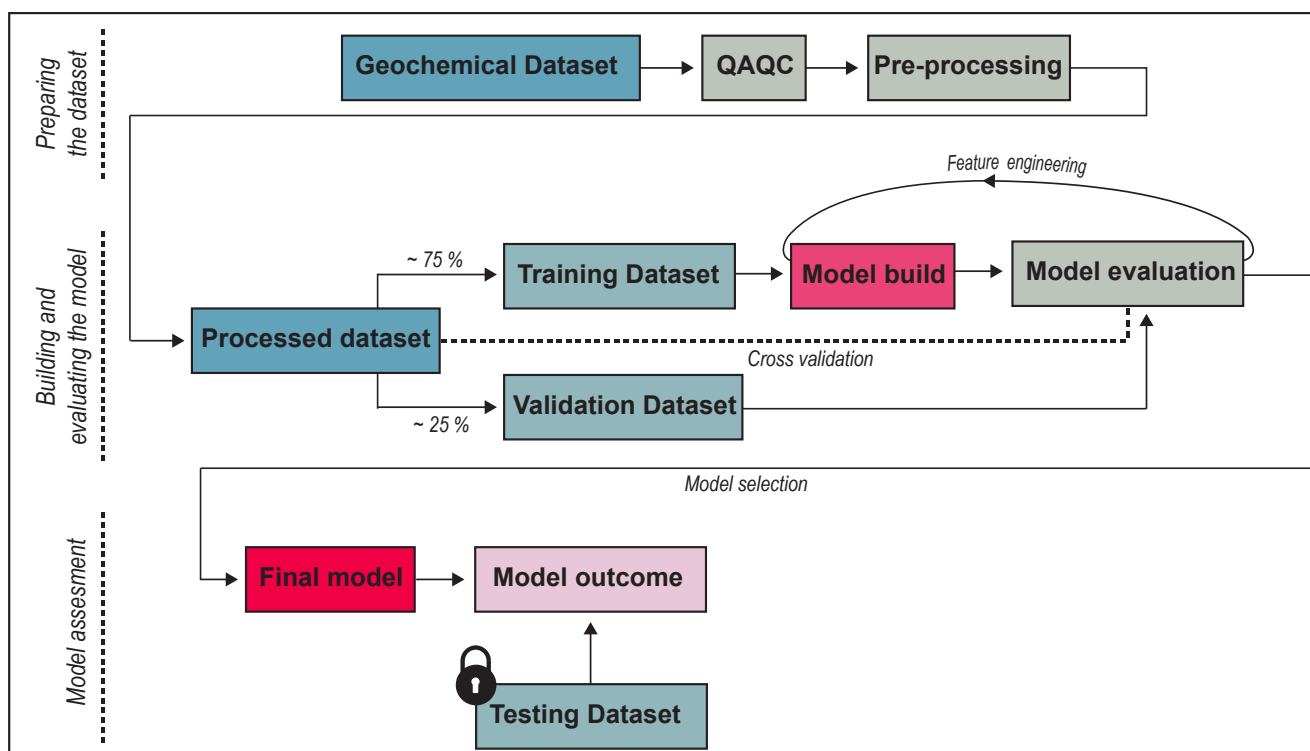


Figure 9.2 Summary of typical methodology used during development and testing of the classification models.

Table 9.1 List of analyses used in model 2. System Cu grade assigned using data from *mrdatausgs.com*¹, *miningdataonline.com*², *Hart-Madigan (2019)*³, and *Rio Tinto annual report (2019)*⁴.

	Prospect	Country	Lithology	System type	Intrusive phase	System Cu grade	Number of analyses
Model 2 validation dataset	Arroyo de las Minas	Argentina	Granodiorite porphyry	Porphyry Cu-Au	Main porphyry	N/A	19
	Bingham ^{1,2}	USA	Monzonite	Porphyry Cu-Mo	Non-porphyry	> 0.5 – 1.0 % Cu	22
			(Quartz) latite porphyry		Late porphyry		55
			(Quartz) monzonite		Main porphyry		147
	El Abra ²	Chile	Monzonite	Porphyry Cu	Main porphyry	> 0.5 – 1.0 % Cu	23
'Gravestones' Quarried rock samples	Australia	Granite	Background	Non-porphyry	Barren, < 0.1 % Cu	9	
		Quartz monzonite		Non-porphyry		6	
Model 2 training dataset	Heruga ^{3, 4}	Mongolia	Quartz monzonite	Porphyry Cu-Au	Main porphyry	> 0.1 – 0.5 % Cu	61
	Hugo ^{3, 4}	Mongolia	Biotite granodiorite	Porphyry Cu-Au	Late porphyry	> 1.0 % Cu	30
			Dacite tuff		Non-porphyry		19
	Little Cottonwood Stock	USA	Porphyritic granite	Background	Non-porphyry	Barren, < 0.1 % Cu	51
	Lomas Bayas ²	Chile	Dacite porphyry	Porphyry Cu-Mo	Late porphyry	> 0.1 – 0.5 % Cu	29
			Granodiorite		Main porphyry		28
	Resolution ¹	USA	Granite	Porphyry Cu-Mo	Non-porphyry	> 1.0 % Cu	8
			Granitic porphyry		Main porphyry		2
	SW Oyu ³	Mongolia	Quartz monzonite	Porphyry Cu-Au	Main porphyry	> 0.1 – 0.5 % Cu	52
	Valeo Stock	USA	Granodiorite	Porphyry Cu	Non-porphyry	Barren, < 0.1 % Cu	57
	White Pine	USA	Quartz monzonite porphyry	Porphyry Cu	Non-porphyry	Barren, < 0.1 % Cu	111
	Zaldivar ²	Chile	Feldspar biotite porphyry	Porphyry Cu-Mo	Late porphyry	> 0.1 – 0.5 % Cu	50
	Chuquicamata ²	Chile	Elena granodiorite	Porphyry Cu-Mo	Non-porphyry	> 0.5 – 1.0 % Cu	As in Chapter 9
			Elena porphyry	Porphyry Cu-Mo	Main porphyry		
			Banco porphyry	Porphyry Cu-Mo	Main porphyry		
	La Granja ⁴ (Mirador and Paja Blanca)	Peru	AND	Background	Non-porphyry	> 0.5 – 1.0 % Cu	
			DIO	Background	Non-porphyry		
			GRANO	Background	Non-porphyry		
DIOP			Porphyry Cu-Mo	Non-porphyry			
EDP			Porphyry Cu-Mo	Main porphyry			
EQP			Porphyry Cu-Mo	Main porphyry			
IMP			Porphyry Cu-Mo	Main porphyry			
LQP			Porphyry Cu-Mo	Late porphyry			
LDP			Porphyry Cu-Mo	Late porphyry			
RH			Porphyry Cu-Mo	Late porphyry			
Northparkes ²	Australia	BQM	Porphyry Cu-Au	Non-porphyry	> 0.5 – 1.0 % Cu		
		APL	Porphyry Cu-Au	Non-porphyry			
		KQMP	Porphyry Cu-Au	Main porphyry			
		ZERO	Porphyry Cu-Au	Late porphyry			
		MZO	Porphyry Cu-Au	Late porphyry			

reflect the importance of that variable. This means that some changes in concentration may be overlooked by the algorithm as they are orders of magnitude smaller than other variables.

Log transformations are recommended for closed geochemical data in order to unconstrain the components (Egozcue et al. 2003; Grunsky & Caritat 2019; Filzmoser et al. 2009; Muriith 2015). Consequently, the input variables were transformed using a centred log transformation (clr) as described in the equation (Aitchinson 1986):

$$clr(x) = (\log(x/(x_1 \cdot x_2 \dots \cdot x_n)^{-n})). \quad \text{Eq. 9.3}$$

here the transformed variable (x) within a sample with *n* features is the log of the ratio to the geometric mean of the sample. Scaling the results can remove bias from the relative concentration of the element, giving a more equal weighting to different variables. Therefore the variables were also scaled using:

$$y = \frac{x - \text{mean}(X)}{sd(X)}. \quad \text{Eq. 9.4}$$

here *y* is the scaled value of variable (*x*) in a sample (*X*). This results in normalised data where the components are independent and have a mean with 1 standard deviation.

Centred log ratio transformation was chosen because it is isometric, meaning that the distances in the transformed values are equivalent to the distances in the original composition (Aitchinson 1986). In addition, as most geochemical data show trends on a log-scale without logging the variable the linear algorithms may miss these features.

9.2.2 Building and evaluating the model

The models were built and evaluated using Orange, a machine-learning and data mining software.

Selection of variables

Only trace element concentrations in apatite were used as independent variables in the models. A different set of variables was used for each model and were selected based on the conclusions of the previous chapters. Elements with large uncertainties, low signal-to-noise, or analyses with a large proportion of missing data (such as values below detection limit) were immediately discounted. In addition, strongly correlated elements, such as the REE were avoided within the same model. Instead, REE ratios were used to describe the REE profile. By using variables that are affected by both magmatic and hydrothermal processes, the effects of collinearity were reduced. Overall, the number of independent variables was restricted for each model as, although adding variables may improve variance, it commonly results in over-fitting of the data (Hastie et al. 2008).

Validation dataset

The aim of evaluating a model is to estimate the prediction error and then make any adjustments accordingly to improve the prediction capability (feature engineer). After a series of iterations, the final model can be selected (Fig. 9.1). Where there is large volume of training data (as was the case for model 2; Table 9.1), the model can be evaluated using a sub-sample of the training data, or the validation data set (Fig. 9.1). However, where the training data is more limited, cross validation was used instead. Cross validation estimates the predictive error of a model by randomly dividing the training data into a specified number of groups or *folds*. All but one of the groups is used to train the model which is then tested on the remaining data. This is repeated over all the folds and the results summarised. Using cross validation may lead to inflated evaluation results and overfitting of the model (Hastie et al. 2008; Kubat 2017). This is caused by the use of similar data to both train and test the model, and is especially true for the data set used in this study where there are multiple analyses from the same sample. To combat this, the folds used were pre-defined to make sure that related analyses were contained within the same fold.

Evaluating models

The ability of a model to distinguish between classes can be assessed by describing the outcomes of the model. Outcomes can produce a true positive (TP), false positive (FP), true negative (TN) and false negative (FN). True positive and true negative results are correct predictions, whereas false positive and false negative results are incorrectly classified outcomes (Kubat 2017).

The accuracy of the predictions is the number of correct predictions as a percentage of the total number of predictions. This is only a useful description if all the output classes are the same size. Therefore, it is more appropriate to consider the ratios of all classifications.

The precision of a model is the percentage of true positives in the total number of positives:

$$Pr = \frac{N_{TP}}{N_{TP} + N_{FP}} \quad \text{Eq. 9.5}$$

The recall, also known as the sensitivity or the true positive rate (TPR), is the ratio of true positives to all observations in the class (Kubat 2017):

$$Re \text{ or } TPR = \frac{N_{TP}}{N_{TP} + N_{FN}} \quad \text{Eq. 9.6}$$

Precision and recall can be summarised by the F-score (F1) which is a weighted average of the two. This is the most useful description of fit in a data set with asymmetrical classes.

$$F1 = 2 \cdot \frac{(Re \cdot Pr)}{(Re + Pr)} \quad \text{Eq. 9.7}$$

A receiver operating characteristic (ROC) curve is a way of visualising the rate of true positives to false positives (Fig. 9.3). The false positive rate (FPR) is described as:

$$FPR = \frac{N_{FP}}{N_{FP} + N_{TN}} \quad \text{Eq. 9.8}$$

The ROC curve is calculated over different classification thresholds. The classification threshold is the defined boundary between a positive and negative output, with a lower threshold resulting in more positive classifications. The shape of the ROC curve can be measured by the area under the curve (AUC), where 1 is a perfect classification, and 0.5 means there is no class separation. The classification threshold (e.g. Fig. 9.1A) is often set at 0.5; however, results may be improved, especially for multinomial classifications, by adjusting this threshold. For each model, the effect of changing the classification threshold was considered.

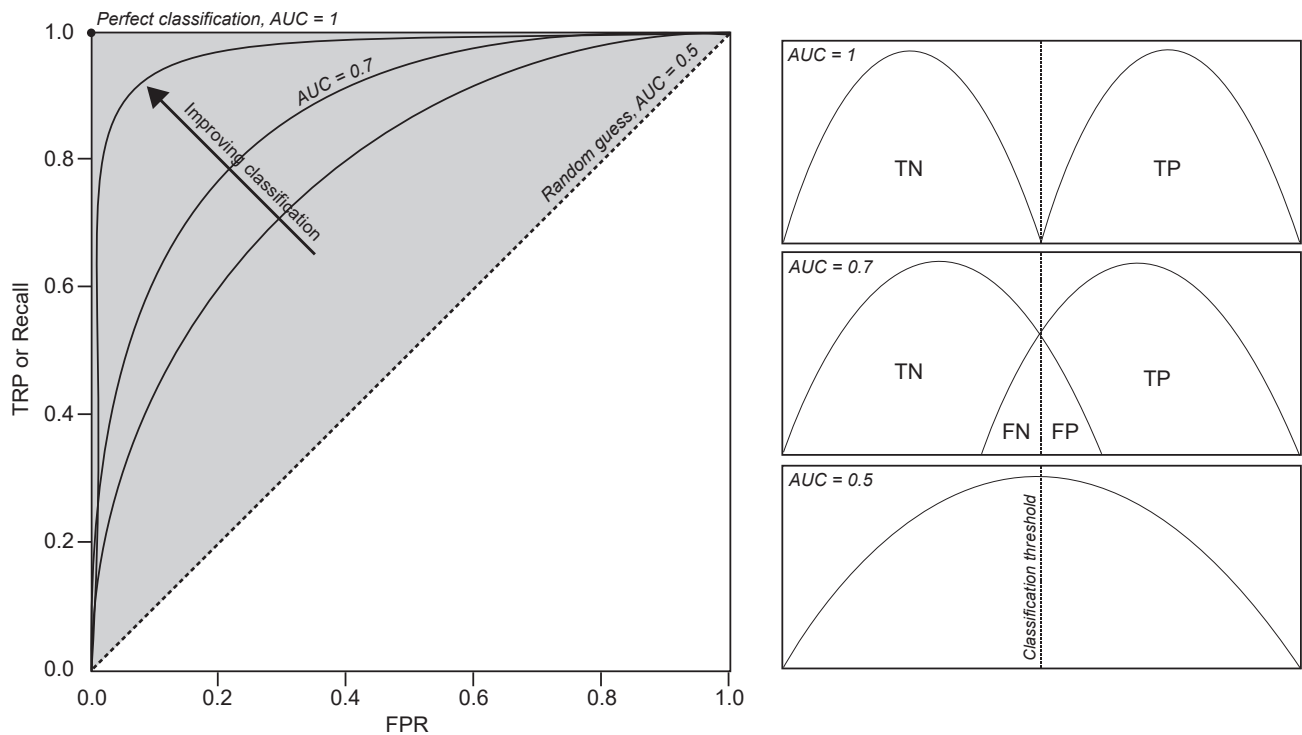


Figure 9.3 A receivers operating characteristic (ROC) curve described the ratios of outcomes from a model (TRP = true positive rate, FPR = false positive rate). The shape of the curve can be described by calculating the area under the curve (AUC). Perfect classification will only produce true positives (TP) and true negatives (TN), or TPR value of 1 and FPR value of 0 for a given classification threshold, producing an AUC value of 1. If no classifications can be distinguished then the AUC has a value of 0.5. False classifications are produced when $0.5 < AUC < 1$. The FPR and TPR will vary with the classification threshold.

9.2.3 Model assessment

Testing data set

A final assessment estimates the predictive error of the chosen model using a unique and independent dataset (Fig. 9.2). This is referred to as a blind data set as it has not been used in the building or previous assessment of the model (Hastie et al. 2008). For model 2, the final assessment was carried out using a separate data set of over 950 apatite analyses provided by Rio Tinto, collected at their lab in Melbourne, Australia. A comparison between the two labs used in this study was carried out to ensure that the data are comparable (see *Appendix H*).

9.3 Model evaluation

9.3.1 Model 1: Classification of magmatic and hydrothermal apatite

In *Chapter 8*, the need for a composition-based classification method was highlighted, particularly for identifying least-altered magmatic and hydrothermal apatite compositions. Apatite compositions were shown to spread between least-altered magmatic, potassic (and proximal propylitic) and sericitic-associated apatite compositions. It was also suggested that the degree of metasomatism (or alteration score) could also be classified at the same time, as it is also the result of the influence of hydrothermal fluids on mineral composition.

Building a supervised classification algorithm requires existing knowledge of the apatite textural associations and, as a result, only analyses of in-situ apatite from the three case study sites could be used. Analyses from La Granja and Northparkes were used to train the model and those from Chuquicamata were held separately and used as the blind dataset for model assessment. Model evaluation was conducted using cross validation with pre-defined folds of the same apatite host rock units selected at random. This reduces overfitting and prevents further reduction of the data caused by having a separate validation dataset. The classification targets were defined as least-altered magmatic (*Chapter 6*), sericitic-associated apatite, proximal hydrothermal apatite (includes potassic and propylitic vein and replacement types; *Chapter 7*) and metasomatised magmatic apatite (*Chapter 5*). More distal propylitic alteration from Northparkes was not included as it is significantly under-represented in the samples and is potentially problematic given the known compositional variation possible as a function of spatial position in propylitic alteration halos (e.g. Wilkinson et al. 2015).

Investigations found that due to the very distinctive composition of sericitic-associated apatite, better separation was achieved between by classifying in two steps. First, sericitic-associated apatite was classified (model 1A), followed by classification of magmatic, metasomatised magmatic and proximal alteration assemblages (model 1B) in the residual data. Model 1A uses elements and ratios identified as enriched in sericitic apatite in *Chapter 7* (Eu/Eu*, Pb, V and U). Full model details are provided in *Appendix G*. Results from cross validation show that both random forest and logistic

Table 9.2 Results of cross validation analysis for random forest and logistic regression classifiers for model 1A. Area under the curve (AUC), F-score (F1) precision and recall are all higher for the random forest model than the logistic regression model.

Model 1A	AUC	F1	Precision	Recall
Random Forest	0.96	0.97	0.97	0.97
Logistic regression	0.98	0.97	0.97	0.97

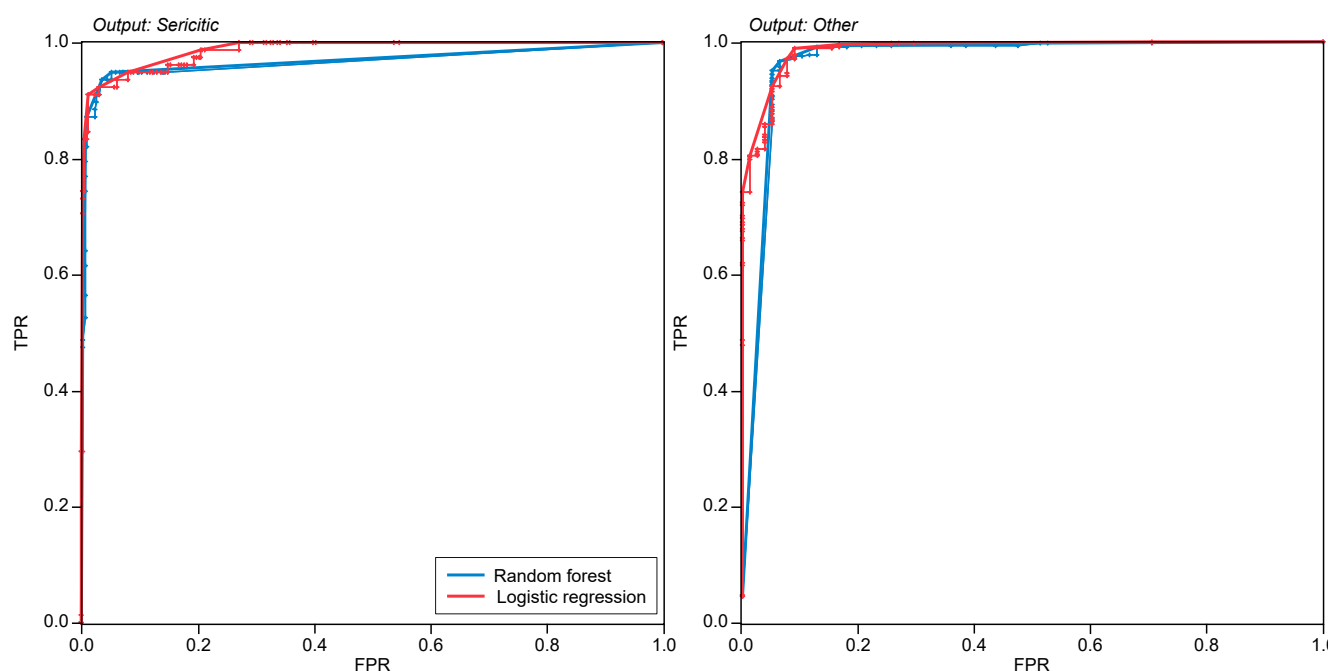


Figure 9.4 Receiver operating characteristic (ROC) curves of random forest and logistic regression classifiers for model 1A.

regression classification models work equally well (Table 9.2); however, the random forest based algorithm was selected as it provides the best classification results for given classification thresholds (Fig. 9.4) and more accurate classification of sericitic apatite (Table 9.3).

Table 9.3 Proportion of predicated outcomes compared to actual classification by random forest classifiers for model 1A.

		Predicted	
		Sericitic (73)	Other (430)
Actual	Model 1A Sericitic (78)	87.2 %	12.8 %
	Other (425)	1.2 %	98.8 %

Model 1B uses a wider range of variables including a mixture of ‘magmatic’ ratios (Gd/Yb, Eu/Eu*) and more fluid mobile (As, Pb, Mn) elements. Full model details are provided in *Appendix G*. In this classification, logistic regression models were most accurate, especially at classifying magmatic and hydrothermal apatite (Fig. 9.5). However, unlike model 1A, better classification can be achieved by adjusting the classification thresholds. Due to the nature of metasomatism, magmatic and metasomatised magmatic apatite spreads over the whole probability range. However, the best classification for least-altered magmatic apatite can be achieved with a threshold around 0.5 (Fig. 9.6). This results in high precision (Pr, Eq. 9.5) and low false positive (FPR, Eq. 9.8) responses, but low recall (Eq. 9.6), because classification of some least-altered apatites produces false negatives,

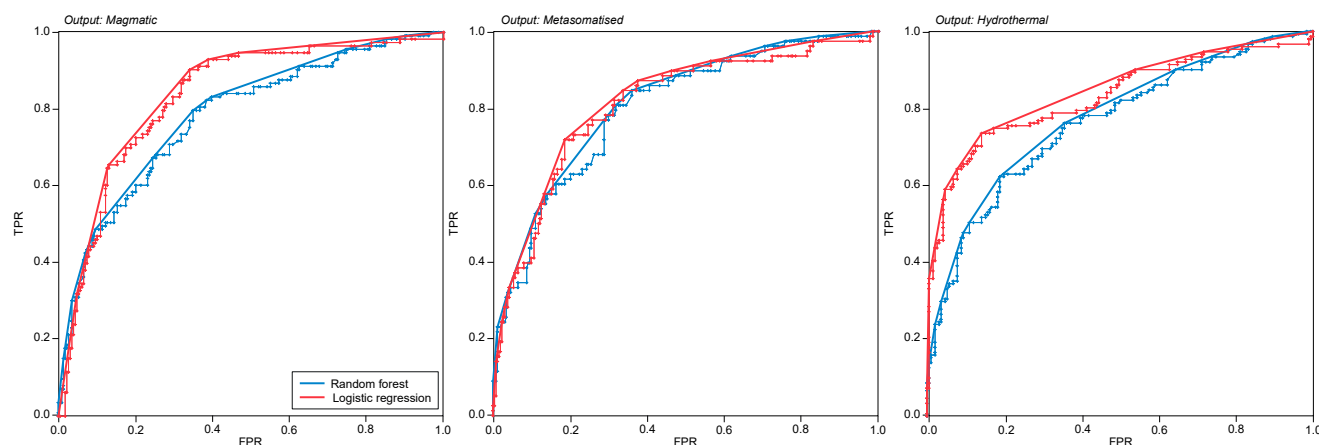


Figure 9.5 Receiver operating characteristic (ROC) curves of random forest and logistic regression classifiers for model 1B.

Table 9.4 Results of cross validation analysis for logistic regression classifier for model 1B at a classification threshold of 0.5 for least altered magmatic and 0.65 for proximal hydrothermal.

Model 1B	F1	Precision	Recall	FPR
Magmatic (least altered)	0.68	0.72	0.65	0.13
Proximal hydrothermal	0.72	0.86	0.62	0.08

mainly in the metasomatised magmatic apatite domain (Fig. 9.6; Table 9.4). Many of the false positives in this classification are also metasomatised magmatic apatite which suggests that there could be issues with the initial textural classification and emphasises the fact that magmatic and metasomatised magmatic apatite lie on a sliding compositional scale. A higher true positive rate for proximal hydrothermal apatite can be achieved with a threshold of around 0.65 (Fig. 9.6). Again, this produces lower recall but high precision and low false positive rates, illustrating how the threshold can be adjusted to suit the specific application (low false positive rate is a key requirement for a valid exploration tool).

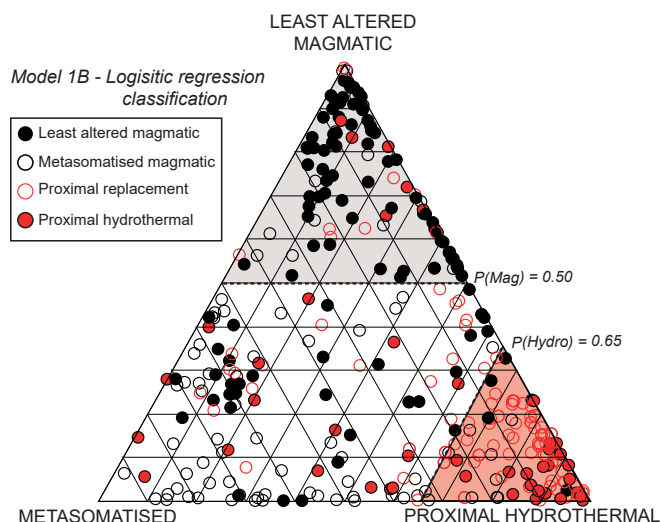


Figure 9.6 Predictions from logistic regression classifications of model 1B from cross-fold validation. A classification threshold of 0.5 is best for isolating least altered magmatic apatite, and 0.65 for hydrothermal apatite. Points are coloured according to their actual classification.

9.3.2 Model 2: Classification of intrusive phases

Model 2 is built from the outcomes of *Chapters 6 and 8*, where compositions of magmatic and hydrothermal apatite were used to distinguish between intrusive phases. It was concluded in *Chapter 8* that it is difficult to distinguish between apatite from pre-porphyry fertile arc rocks, and porphyry intrusions. As a result, for this model apatite from unmineralised arc rocks, pre-porphyry fertile arc rocks are grouped together as non-porphyry rocks and were classified against apatite from the main and late porphyry intrusions (Table 9.1). As the training dataset is of a sufficient size, a validation dataset was used to evaluate the model (which includes data from Arroyo, Bingham, El Abra, Gravestones – selected randomly by alphabetical order). Full model details are provided in *Appendix G*. If output classification is assigned based on the highest scoring probability, the logistic regression model works better than random forest (Table 9.5). However the ROC plots show the averages for the results are brought down by classification of apatite from the main porphyry intrusions (Fig. 9.7). A correlation matrix of the predicted outcomes of the validation dataset shows that over half of the apatite from the main mineralised porphyries is being classified into the other target outcomes (Table 9.6). As this is a multinomial classification, probabilities as low as 0.34 could result in a positive

Table 9.5 Results of validation test classification for random forest and logistic regression classifiers for model 2 where output classification is determined by the highest scoring probability. Area under the curve (AUC), F-score (F1) precision and recall are all higher for the logistic regression model than the random forest model.

Model 2	AUC	F1	Precision	Recall
Random Forest	0.65	0.49	0.54	0.49
Logistic regression	0.82	0.63	0.65	0.64

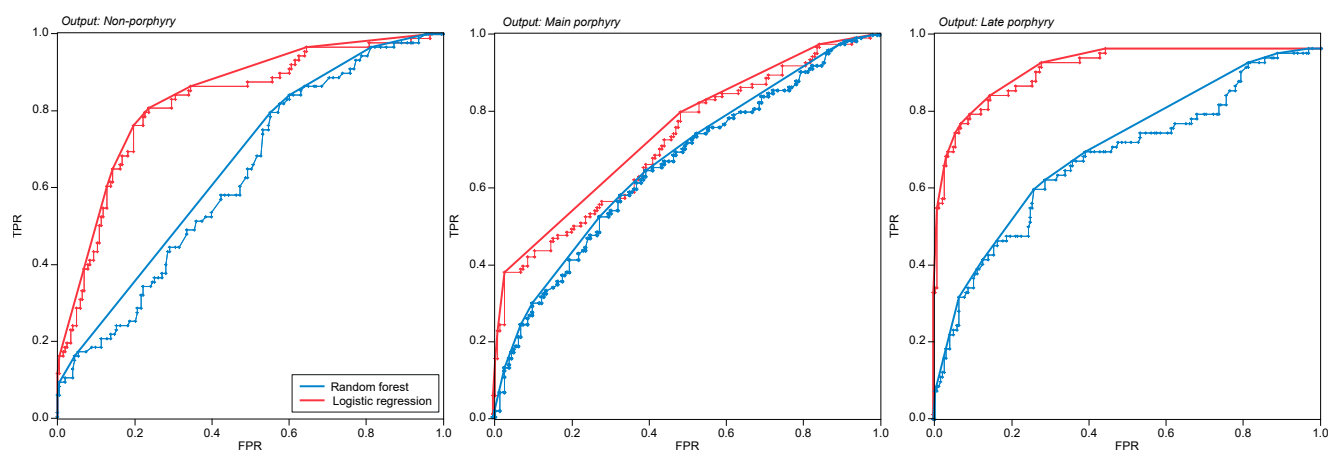


Figure 9.7 Receiver operating characteristic (ROC) curves of random forest and logistic regression classifiers for model 2. Output classification is determined by the highest scoring probability.

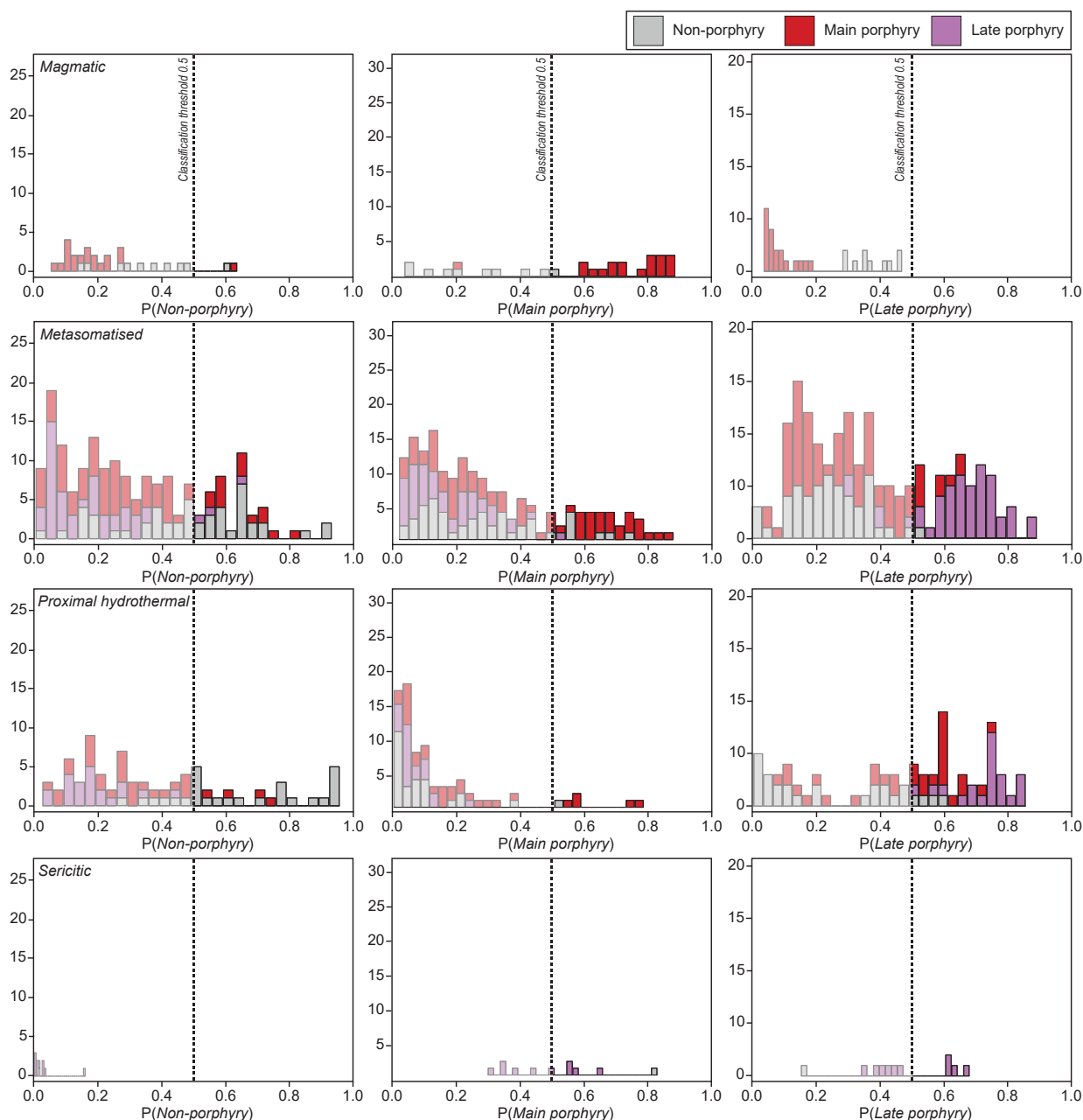


Figure 9.8 Normal distribution plots of prediction probabilities from logistic regression classification of model 2 calculated for the validation data set. The plots are split by outcomes from models 1A and 1B (least altered magmatic, metasomatised, proximal hydrothermal and sericitic associated). Classification thresholds of 0.5 produce good results for each outcome. Results are coloured according to their actual classification.

Table 9.6 Correlation matrix of predicated outcomes compared to actual classification by logistic regression for model 2 where output classification is determined by the highest scoring probability.

	Model 2	Predicted		
		Non-porphyry (97)	Main porphyry (79)	Late porphyry (116)
Actual	Non-porphyry (88)	69.3 %	18.2 %	12.5 %
	Main porphyry (79)	26.4 %	44.8 %	28.8 %
	Late porphyry (125)	3.8 %	8.9	87.3 %

classification, which is the case for many of the apatites from mineralised porphyries. A minimum classification threshold of around 0.5 would minimise this for the three outcomes (Fig. 9.8) with an additional ‘inconclusive’ classification added to capture outcomes with low probability for all three outcomes. The results from model 2 can be combined with the classification outputs from model 1 (Fig. 9.8). There are a number of important learnings from this analysis. First sericitic classified apatites are almost non-existent in the non-porphyry and main porphyry dataset. Although the data are limited, sericitic-classified apatite from late porphyries has a relatively high proportion of false negatives. Secondly, a low proportion of apatites from late-stage intrusions are classified as magmatic. The more unique composition of apatites from these intrusions (*Chapter 6*) may result in the misclassification of magmatic apatites as metasomatised. Metasomatised apatites are common in all classifications; however in non-porphyry apatites these largely belong the pre-porphyry pluton at Bingham (Table 9.1). Metasomatised apatite has a high success rate in identifying intrusive phases.

9.4 Model assessment

9.4.1 Model 1

Model 1 was assessed through testing of the blind dataset from Chuquicamata. The classification of sericitic-associated and least altered magmatic apatite is show in figure 9.9. Sericitic classification has a precision, recall and F-score equal to 1, and least altered magmatic also has classification scores close to 1 (precision = 0.98, recall = 0.94 and F-score = 0.96). There are few metasomatised apatites within the sample set and these classify close to, or within, the least altered magmatic threshold (Fig. 9.9). However, the main misclassification with this model for this dataset is for potassic-associated hydrothermal apatites that classify as metasomatised apatite rather than hydrothermal.

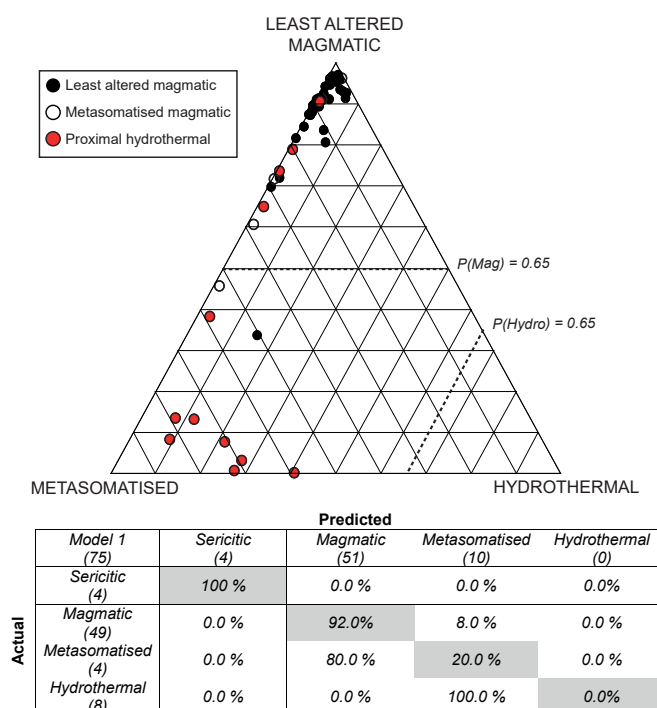


Figure 9.9 Classification results from the testing dataset (Chuquicamata) using model 1. Points are coloured according to their actual classification.

Table 9.7 Summary of Rio Tinto data set used as testing data in model2, and for additional comparison to system grade (in italics). Data from Miningdataonline.com¹, Garrido et al. (2008)², Singer et al. (2008)³, Gilmour & Carpenter (2017)⁴, Hart-Madigan (2019)⁵, Rio Tinto annual report (2019)⁶.

	System name	Country	Intrusive phase	System grade (% Cu)
Model 2 testing dataset	Alcaparrosa ² (183)	Argentina	Main porphyry	> 0.1 – 0.5
	Amarillo (4)	Argentina	Late porphyry	-
	El Teniente ¹ (29)	Chile	Main porphyry	> 0.5 – 0.1
	Escondida ¹ (42)	Chile	Main porphyry	> 0.1 – 0.5
	Galloway Plains Batholith (7)	Australia	Non-porphyry	<i>Barren, < 0.1</i>
	Grasberg ¹ (29)	Indonesia	Main porphyry	> 1.0
	Huachi ⁴ (68)	Argentina	Main porphyry	> 0.1 – 0.5
	La Voluntad ² (49)	Argentina	Main porphyry	> 0.1 – 0.5
	Pancho Arias ³ (91)	Argentina	Main porphyry	<i>Barren, < 0.1</i>
	Placetas (8)	Argentina	Main porphyry	<i>Barren, < 0.1</i>
	Radomiro Tomic ¹ (25)	Chile	Main porphyry	> 0.1 – 0.5
	Taca Taca Bajo ³ (16)	Argentina	Late porphyry	> 0.1 – 0.5
	Ujina ³ (2)	Chile	Main porphyry	> 0.5 – 1.0
Additional analyses used in Fig. 9.12	'Unknown' background (408)	Australia	Non-porphyry	<i>Barren, < 0.1</i>
	Bingham ¹ (2111)	USA	Main porphyry + Late porphyry	0.5 – 1.0
	El Abra ¹ (148)	Chile	Main porphyry	0.5 – 1.0
	Heruga ^{5,6} (598)	Mongolia	Main porphyry + Late porphyry	> 0.1 – 0.5
	Hugo ^{5,6} (274)	Mongolia	Main porphyry + Late porphyry	> 1.0
	Lomas Bayas (225)	Chile	Main porphyry + Late porphyry	> 0.1 – 0.5
	Resolution ⁵ (424)	USA	Main porphyry	> 1.0
	SW Oyu ⁵ (160)	Mongolia	Main porphyry	> 0.1 – 0.5
	Zalvidar ¹ (62)	Chile	Main porphyry + Late porphyry	0.1 – 0.5

9.4.2 Model 2

Model 2 was tested using a separate dataset provided by Rio Tinto (Table 9.7). This means that not only is this a truly blind dataset, as little was known about these samples in advance of this study, but it is also a test of the model on samples collected and analysed by industry (Fig. 9.10). There are comparatively few analyses of late porphyry apatites to compare and those that are present are mostly misclassified as main porphyry intrusions producing a lower F-score (Table 9.8).

The system type classification outcomes can be combined with the previous classification made in model 1 (Fig. 9.11). As with the validation dataset, apatite analyses classified as magmatic and metasomatised can discriminate background, main and late porphyry units with more success than hydrothermal apatite, however these can discriminate porphyry units from non-porphyry (Table 9.8). The classification of apatite from late porphyry units is significantly improved by using only magmatic (and metasomatised) apatites.

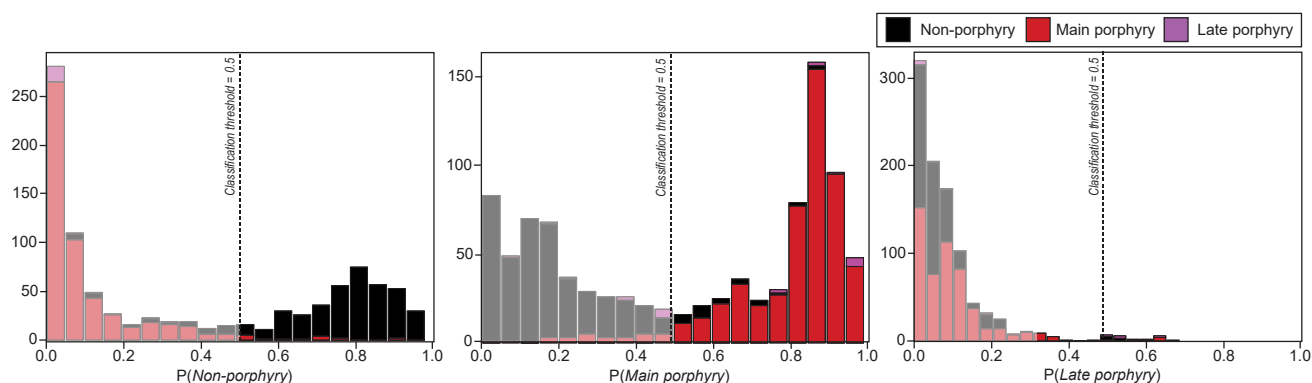


Figure 9.10 Classification probabilities for test dataset (Rio Tinto database) from model 2. Results are coloured according to their actual classification.

Table 9.8 Results for classification of test dataset (Rio Tinto database) from model 2. The classification threshold was set at 0.5 with analyses with no classification in any category assigned to inconclusive. Both results from all analyses and least altered and metasomatised apatite (as classified by model 1) are shown.

Using all apatite classifications				
Model 1A	F1	Precision	Recall	FPR
Non-porphyry	0.93	0.97	0.93	0.03
Main porphyry	0.94	0.94	0.94	0.08
Late porphyry	0.40	0.33	0.40	0.02
Inconclusive (25)				
Least altered magmatic and metasomatised (Model 1A + 1B)				
Model 1A	F1	Precision	Recall	FPR
Non-porphyry	0.92	0.94	0.86	0.03
Main porphyry	0.94	0.95	0.96	0.08
Late porphyry	0.74	0.67	0.80	0.01
Inconclusive (14)				
Least altered magmatic (Model 1A + 1B)				
Model 1A	F1	Precision	Recall	FPR
Non-porphyry	0.86	0.87	0.92	0.03
Main porphyry	0.96	0.97	0.94	0.11
Late porphyry	0.89	0.75	0.74	0.01
Inconclusive (10)				

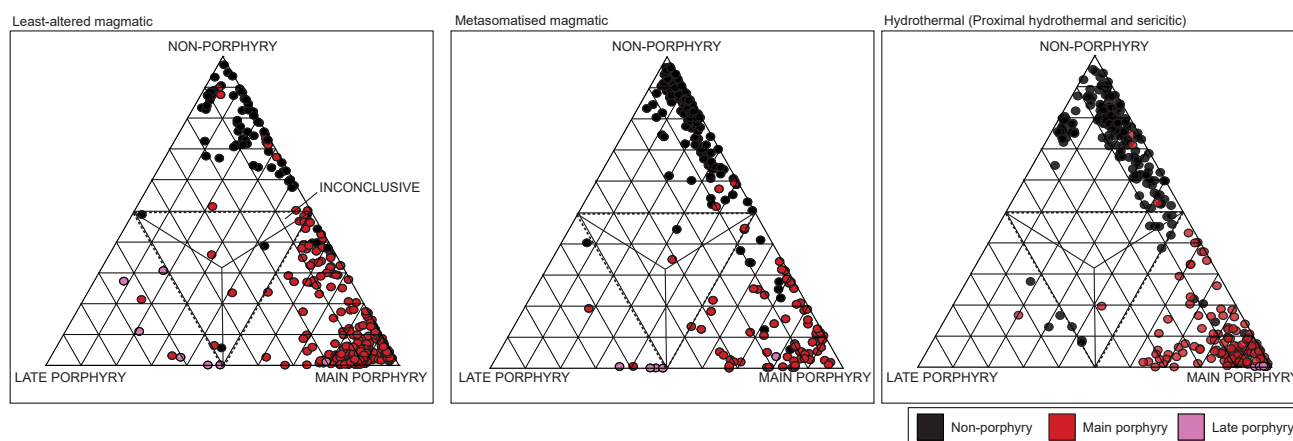


Figure 9.11 Ternary plots of results from classification of test dataset (Rio Tinto database) from model 2, split by results from model 1. Points are coloured according to their actual classification.

9.5 Discussion

9.5.1 Model evaluations

These models serve as a proof of concept that careful use of the trace-element chemistry of apatite, when combined with knowledge of apatite occurrence in porphyry systems, can be used to build powerful predictive models. Although further development of these models is suggested, the results show that meaningful outputs are possible from apatite concentrates analysed as part of large data collection drives and with limited information about the samples or geological context.

Model 1

In Chapter 8 it was stated the full complexity of the compositions of *proximal hydrothermal apatite* is not captured within the case study analyses and that only the composition of sericitic apatite appeared to be relatively consistent between deposits. This is supported by results from this chapter, which show that potassic apatite from Chuquicamata is not classified as such based on the training dataset from La Granja and Northparkes. Texturally, the potassic apatite at Chuquicamata is different to these other two systems, occurring in sulfide-filled vugs

(Fig. 8.2F), as opposed to within thin, earlier, and less mineralised veins as were sampled at La Granja (*Chapter 7*). By contrast, the composition of sericitic apatite from the case studies is comparable to that found in other systems (Li & Zhou 2015; Krneta et al. 2017; Chen et al. 2019).

Needless to say, model 1 is built on a comparatively small dataset by machine learning standards. The classification of magmatic apatite by model 1 works well, helped by the fact that there is a high proportion of magmatic apatite analyses used to train the model and which cover a wide range of host rock compositions. By contrast, the number of hydrothermal, and especially potassic, apatite compositions used to build the model is very low. In addition, the composition of apatite associated with more distal alteration is not included in the model which may be impacting results. Given the known spatial variation of mineral chemistry of the propylitic zone (Wilkinson et al. 2015; Pacey 2016; Neal et al. 2018), a regression-based model may need to be used in order to capture the full range of compositions whilst also providing an indication of distance from the fluid source.

The metasomatised magmatic apatites from Chuquicamata plot close to or above the classification threshold for magmatic apatite. This could be a result of the relatively weak alteration observed in these samples and the small amount of textural evidence for metasomatism observed on the apatite grains (Figs. 8.2A-D). Thus, the classification may actually be reasonably robust (i.e. effectively 'weakly metasomatised magmatic'). The classification of metasomatism along a continuous probability works well, as it mirrors the gradual changes inherent in metasomatic processes. Here, only geochemical data has been used to build the models, however additional observations such as presence of inclusions could be used as additional variables. These could be collected and quantified by automated image processing software in the interest of speed, data volume and to avoid human bias. In addition, such observations should make the classifications more robust as these criteria would be an independent feature.

As the model currently stands, it provides accurate and repeatable classification of least altered magmatic and sericitic apatite. These are key apatite occurrences for both the exploration of systems (i.e. indicating the presence of specific hydrothermal conditions or as a filter for additional classification models), and also for use in further study of apatite in porphyry systems (least altered magmatic being the best record of magmatic conditions). Classification of analyses by model 1 prior to their use with any further classification models is advised as it allows for a deeper interrogation of the outcomes. In order to develop the model, additional analyses of hydrothermal apatite are required to improve the training process. The ability to classify apatite in terms of alteration association ultimately could provide information from stream sediments about the erosion depth of potential porphyry systems within a basin catchment area.

Model 2

Model 2 is able to correctly predict the classifications (non-porphyry, main stage and late porphyry) for the majority of apatites from 16 different systems. The classification of non-porphyry covers a wide range of intrusion types that, importantly, include pre-porphyry plutons and unmineralised arc rocks. The most effective subsets of the data for identifying the main mineralised porphyries are magmatic/metasomatised classifying grains, suggesting that the classification relies on both

fundamental magmatic features of fertile and mineralised intrusions, combined with the overprinting effects of mineralising hydrothermal solutions (see *section 8.5*). Other classification tools using whole rock or mineral chemistry exist for distinguishing magmatic rocks from porphyry-fertile belts (i.e. Loucks 2014; Halley 2020). At present, due to the small size of the dataset all non-porphyry apatites are grouped together to avoid small class sizes and potentially producing an over fitted model. This model has not been tested on non-igneous apatites from outside the magmatic arc environment as it is beyond the scope of this study, and not especially relevant from a porphyry exploration context. However, there are numerous existing classifications and studies of apatite from a wider range of settings (Piccoli & Candel 2002; Belousova et al. 2001; Mao et al. 2016; O'Sullivan et al. 2020) that could be utilised in such an endeavour. With apatite analyses from additional sources it may also be possible to separate the non-porphyry classification used in this study further into more specific sub-types (e.g. I-type, S-type, island arc, continental arc, etc.).

The highest proportion of misclassification, from both the validation and testing datasets, is of apatite from the late porphyries which is commonly classified as main porphyry associated (Fig. 9.11). As with the classification of magmatic and metasomatised magmatic apatites from model 1, this overlap could reflect an evolving composition of the magmatic system across this period, from early to late stage porphyries (see *Chapter 6*). However, because filtering out hydrothermal apatite improves the classification (Table 9.8), this problem may have more to do with more distinct compositions of late-stage hydrothermal fluids (*Chapter 7*) that are not accounted for in the model. For example, evidence from El Teniente (Spencer et al. 2015) shows that the late stage fluids associated with the final porphyry pulses are highly evolved and relatively enriched in Mo, As, Rb and Cs and depleted in Cu.

Understanding which analyses are hydrothermal is important as they may contrast strongly with magmatic apatites from the same units. This discrepancy between the composition of hydrothermal apatites and host rock assignment may also contribute to why predictions from least altered magmatic and metasomatised magmatic apatites work best (Table. 9.8). The high positive prediction rates from metasomatised apatite suggests that collecting analyses from the centre of grains (*Chapter 5*) is sufficient to avoid alteration of the grain negatively affecting the classification results. Combining the outcomes of models 1 and 2 confirms that understanding apatite association still has relevance for exploration. In future, models could be trained using pre-filtered data (i.e. all magmatic or all hydrothermal) to improve the classification results.

Continued development of predictive models using apatite composition will ultimately aim to identify high and low grade systems. In figure 9.12, the predictions of 4950 analyses from models 1 and 2 are compared to the system grade. The analyses include those from the testing dataset for model 2, plus new analyses from deposits used to train the dataset and that were subsequently excluded from the testing set (Table 9.7). Magmatic apatite occurs in deposits of all grades but with a concentration of higher grade system data towards the main porphyry-late porphyry axis (i.e. with low 'non-porphyry' scores). It is notable that most of the low grade and unmineralised system data from magmatic apatites plot along the porphyry-non-porphyry axis. A similar pattern, though slightly less clear is observed for the metasomatised apatites. Apatite classified as proximal

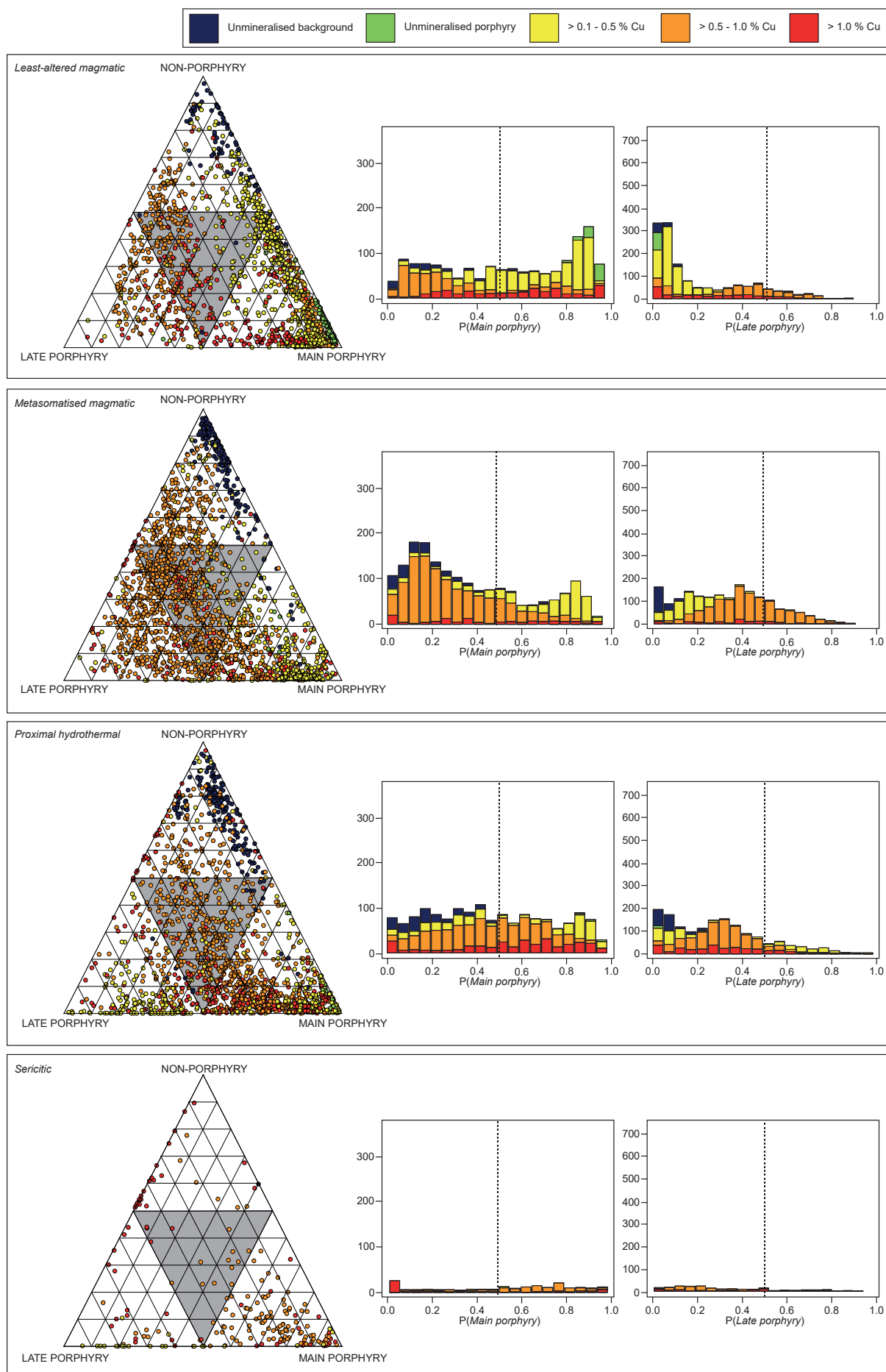


Figure 9.12 Predictions of model 2 testing dataset split by classifications from model 1. Points are coloured by system grade as reported in table 9.7.

hydrothermal appears to have a larger proportion of analyses from higher grade systems plotting within the main porphyry classification, but with less clear distinction of higher and lower grade data points (Fig. 9.12). This, combined with results from *Chapter 7*, suggests that there could be potential in developing both magmatic and hydrothermal apatite copper grade indicators. This fits in with existing understanding that the early, least fractionated magmas and associated fluids are often associated with a high proportion of the mineralisation (Halter et al. 2005; Ulrich et al. 1999). From the samples tested, few magmatic or metasomatised apatites from low grade porphyry systems plot within the late porphyry classification and therefore model 2 could help distinguish low grade porphyry systems from late, low grade intrusions that may be part of a larger, higher grade system.

9.5.2 Additional considerations

In addition to the size of the dataset, class bias and input classifications of the training data are the main areas for further improvement with the current models. There are a disproportionate number of analyses from the case studies, and in particular late porphyry apatites from La Granja, and a lower proportion of hydrothermal and non-porphyry analyses (Table 9.1). This may affect output predictions because algorithms tend to produce a bias towards the majority class (Kubat 2017). This could be acceptable where the class imbalance is representative of a true dataset, such as in number of magmatic versus hydrothermal analyses (so long as all compositions are captured). Alternatively, this could be detrimental to the model, such as in the case of the number of non-porphyry analyses, and could be accounted for by up-scaling or down-scaling of each class.

In supervised techniques, the output depends on the input variable and this is why, for models 1 and 2, a smaller, better constrained dataset was used to train the models over the data available within the larger testing dataset. Ideally, and particularly for random forest algorithms, the model should be trained over random sub-sets of the data to see how reliant predictions are on the training set and therefore assess how fitted the model is. With the datasets used for these models, one of the main issues will be the input classification. Differences arising from different geologists' interpretations or understanding of a deposit will affect the input classifications used to train the model. This is an argument for the use of unsupervised models as they will show how the data is organised without being affected by any *a priori* classification. Typically, unsupervised methods require much more computing power but could enable a larger, less constrained dataset to be used to train the model.

Future application of these models will be subject to issues with comparable detection limits and missing variables. Ideally, any future data collection would be designed around the analytical set up as described in *Chapter 3*. In the case of missing variables, substitution of values should be avoided; instead imputation should be used in which new values are calculated based on a fit of a model (Engle & Brunner 2019). For example, in the case of missing REE values, these can be interpolated quite easily from neighbouring REE concentrations.

Overall the results these early models are promising and justify the continued development of machine learning techniques for porphyry deposit exploitation. Initial testing suggests that understanding the associations of the apatite used in the models is important for both

interpreting the outputs of the models and for future development. Classification of this through predictive models needs further development, incorporating the full range of hydrothermal apatite compositions. Classification of the intrusive phases works well and could prove a useful addition to current geochemical exploration techniques. The fact that a clear separation can be made between porphyry and non-porphyry apatite suggests that the final steps that result in the formation of porphyry systems occur in the shallow crust. This follows on from the deep 'fertile' differentiation path that is developed in magmas from mineralised arcs. Within apatites classified as main- and late-stage porphyries there is a clear separation of data from higher and lower grade systems which could be developed further into an indicator of system grade.

Chapter 10: Conclusions and suggestions for further work

10.1 Introduction

This thesis focuses on understanding the occurrence and compositional range of magmatic and hydrothermal apatite in porphyry systems. In particular how changes in apatite composition relate to the development of a porphyry deposits. Key conclusions from case studies have then been used as a framework for predictive classification models which can aid exploration for deposits.

10.2 Textural occurrence of apatite in porphyry systems

Magmatic and hydrothermal apatites are common accessory minerals in the igneous rocks associated with porphyry systems and are observed in almost all the rock types and alteration zones investigated in this study. At La Granja, these include calc-alkaline rocks between 45 – 80 wt. % SiO_2 , and at Northparkes, alkaline rocks between 49 – 70 wt. % SiO_2 . Apatite is retained in hydrothermally altered rocks even when strongly altered (up to argillic alteration intensity) and is also precipitated from fluids associated with potassic, propylitic and sericitic alteration. Through petrographic study, apatite can be classified into distinct types based on its textural associations and mineral assemblages, which vary with the host lithology and alteration zone.

Magmatic apatite is most commonly observed as microphenocrysts or finer grains within the groundmass (Ap_{mtrx}). Magmatic apatite is also found as inclusions in primary igneous phases such as plagioclase and biotite, which are often significantly altered, and accessory phases such as zircon. These textures relate to differences in the inferred relative timing of crystallisation and are reflected in the apatite trace element composition. The relative timing of crystallisation of Ap_{mtrx} varies between successive porphyry intrusions at La Granja: Ap_{mtrx} from the early porphyry intrusions appears to crystallise earlier compared to Ap_{mtrx} from the late porphyry intrusions and that from non-porphyry related intrusions. Apatite inclusions in zircon (Ap_{incl}) are inferred to crystallise late relative to melt differentiation in all units.

Mineral assemblages involving hydrothermal apatite are more varied than magmatic apatite and can be split texturally into vein and vug apatite, which are inferred to have precipitated directly from a fluid into open space, and replacement apatite, which formed through interaction of a fluid with a pre-existing mineral. The abundance of each apatite type varies between porphyry-related and non-porphyry related rocks and can be used to infer the presence of a hydrothermal system. The composition of hydrothermal apatite varies between the different textural associations, reflecting the influence of melt-fluid partitioning, fluid composition and host rock chemistry. Despite their compositional diversity, hydrothermal apatites can be distinguished from magmatic apatite using multivariate techniques. In particular, sericitic-associated apatite from different deposits can be classified with excellent results. The classification of apatite associated with more proximal hydrothermal alteration types works less well, although it is recognised that a more suitable model could be developed by expanding the training data set with additional deposits.

The diversity in apatite occurrence recorded in this study and in previous work means that apatite composition can be used to help understand a wide spectrum of magmatic-hydrothermal processes in porphyry systems, from early magmatic, through the magmatic-hydrothermal transition, to final, overprinting fluid stages.

10.3 Apatite metasomatism in the porphyry environment

Apatite is physically robust which is an important property for a useful indicator mineral. However, it is less robust compositionally than other indicator minerals such as zircon and is commonly subjected to metasomatism within the porphyry environment. This process can produce changes in both texture and composition with a higher degree of alteration producing a larger response in both. These observations concur with previous research on the alteration of apatite and have been used to develop an alteration classification to 'score' the observed alteration of the apatite grains.

Concentrations of Cl, Na, Pb, As and REE show the largest changes during metasomatism, and are typically depleted with alteration, apart from As. The LREE are more mobile than HREE in apatite and so depletion in LREE is typically responsible for the lower total REE content of metasomatised apatite. Variations in other cations, such as Mn, Sr and Fe, are less consistent and depend on the overprinting fluid composition, with metasomatised magmatic apatite generally lying on a trend between least altered magmatic apatite and vein apatite compositions. Consequently, metasomatised apatite can be distinguished compositionally from least altered magmatic and hydrothermal apatite using the same predictive algorithms used for classifying magmatic and hydrothermal apatite: metasomatised apatite falls between upper and lower classification thresholds for magmatic and hydrothermal apatite. Due to the nature of metasomatised apatite, these grains show the largest spread in the predicted classification and there is some overlap with the other apatite types. Metasomatised apatite is comparable in composition to replacement apatite within the same sample; however, multivariate techniques are able to distinguish the two. As metasomatised magmatic apatites are abundant in the porphyry systems studied, it is assumed that they would also form a large component of the apatite fraction in stream sediments derived from an eroding porphyry system. Metasomatised apatite works well in the classification tools developed to distinguish variably mineralised intrusive phases so, in an exploration context, it may not always be necessary to explicitly identify them. This may be due in part to the fact that the more extreme effects of metasomatism (altered domains and overgrowths) can be avoided by analysing the centre of grains.

Apatites from the matrix of the porphyry intrusions may also be compositionally modified during post-crystallisation diffusional re-equilibration with high temperature fluids. This process does not necessarily leave a distinct textural record in apatite morphology or SEM backscattered electron response. Therefore concentrations of Cl, F and S in Ap_{mtx} should not be assumed to reflect crystallisation compositions even in apparently unaltered grains. Concentrations of Sr and Mn may also be prone to lesser amounts of diffusion and should also be used with caution when inferring magmatic compositions in least altered Ap_{mtx} . The degree of post-crystallisation diffusion depends on the relative timing and location of the host intrusion; apatites from earlier, more central porphyries are more affected. Apatite inclusions in zircon likely preserve primary records of magmatic evolution in

porphyry systems as they are shielded after crystallisation. Analysing the trace element composition of Ap_{incl} using modified analytical techniques provide a way of accurately studying the halogen and S content of porphyry melts. The compositions of Ap_{incl} are inferred to reflect melt equilibrium at the time of zircon crystallisation, which is relatively late within the history of melt differentiation, and so these inclusions therefore tend to be more consistent between porphyry intrusions than Ap_{mtx} .

10.4 Distinguishing apatite from porphyry-related intrusions

Distinguishing apatite from porphyry intrusions and unmineralised arc rocks is complicated by the fact that unmineralised rocks from within the same district and of broadly comparable age to the fertile systems may have similar bulk rock magmatic signatures (such as elevated La/Yb, Sr/Y, Eu/Eu*). In addition, the translation of such geochemical signatures into magmatic apatite may be affected by late-stage melt differentiation during emplacement of the magmas, especially from the crystallisation of plagioclase and REE-rich phases. Furthermore, apatite from porphyry intrusions or in rocks close to porphyry intrusions will also be overprinted by hydrothermal fluids, potentially obscuring these signatures.

It has been found that As concentrations and Eu/Eu* provide the best binary separation of apatite from porphyry and non-porphyry intrusions, and works best on least altered and metasomatised magmatic apatite. The variability in the concentrations of As and Eu in apatite is attributed to differences in magma redox conditions, the degree of plagioclase crystallisation - which is linked to water content - and volatile saturation, all of which are important features in the formation of porphyry systems. In this study, variations in halogen ratios in Ap_{incl} from non-porphyry intrusions are attributed to isobaric cooling. Conversely, in porphyry intrusions, such changes are attributed to an increasing volatile content leading to fluid saturation. By the same reasoning, it is also hypothesised that samples from porphyry-related intrusions will contain a higher proportion of hydrothermal apatite types (vein, replacement and metasomatised magmatic apatite).

Multivariate predictive models can produce a more accurate separation of apatite from porphyry and non-porphyry intrusions which has been tested on a range of localities. This suggests that the best differentiation can be made based on signatures that develop at the emplacement depth, such as late-stage crystallisation and overprinting hydrothermal signatures, rather than from the primary melt compositions of porphyry-related and non-porphyry intrusions from the same district which may exhibit shared characteristics. With a larger and more complete data set it may be possible to extend the tools presented here in order to effectively distinguish apatite from porphyries, porphyry-related intrusions (such as pre-porphyry plutons) and unmineralised arc magmas.

10.5 Apatite from porphyry systems

Within porphyry systems mineralisation is more commonly associated with earlier intrusive phases and tends to decrease with later intrusions. The composition of Ap_{mtx} show systematic changes between intrusions, largely following normal fractionation of the melt. Therefore apatite from earlier and likely more mineralised intrusions can be identified through comparison to the whole system. Alternatively the apatite from different intrusive phases can be identified based on

compositions resulting from differences in their relative timing of crystallisation. Ap_{mtrx} from the main porphyries crystallises early, prior to other REE phases, and therefore has high HREE content compared to total REE. Ap_{mtrx} from late intrusions (and Ap_{incl}) crystallised relatively late in relation to the melt evolution, after more significant REE fractionation especially from zircon crystallisation. Therefore these apatites have lower HREE concentrations relative to total REE. Apatite from non-porphyry related plutons can also be identified in this way as they have their own fractionation sequence. The timing of apatite crystallisation is thought to be largely a result of the SiO_2 and P/Ca content of the melt. In late, felsic, porphyries, both Ap_{mtrx} and plagioclase (the crystallisation of which increases melt P/Ca to apatite saturation) both appear to be suppressed till later in the melt evolution. Suppression of plagioclase crystallisation may lead to later apatite crystallisation. As a result the Ap_{incl} of the early porphyry units are comparable to Ap_{mtrx} of the late porphyries. The halogen contents of Ap_{incl} from early and late porphyries also slightly differ as a result of increasing fluid saturation at the magmatic-hydrothermal transition. Overall, the bulk rock, zircon and apatite composition of late porphyries indicate a fractionated, volatile-saturated melt composition that likely crystallised rapidly, supported by their finer grained texture. This evidence gives clue to the abrupt nature of the termination of porphyry systems, in line with observations made at other deposits. From an application perspective, these differences in porphyry intrusions can be used to help identify the earlier intrusions with the highest potential for mineralisation. In addition, low Cu concentrations may be explained if samples are from the late porphyries of mineralised system.

The difference between mineralised and less mineralised early intrusions in porphyry systems appears to be chiefly a result of S content. At La Granja the mineralised intrusions fall along two different bulk rock trends but the Ap_{incl} from both contain comparable Cl and S contents. By contrast, intrusions of similar compositions held varying degrees of Cu-mineralisation and S concentrations in Ap_{incl} . Ap_{incl} from pre-mineralisation intrusions contain homogeneously low S, whereas mineralised intrusions have a heterogeneous peak in S concentration. S concentrations in Ap_{incl} decreases with melt differentiation within intrusions, and also between subsequent intrusions. Due to the lack of evidence for mafic mixing, such as mingling textures or sudden changes in bulk rock or accessory mineral composition, the addition of S is suggested to be from a volatile phase rather than melt mixing. Electron probe mapping of zircons reveals occasional micron-scale band in the early porphyry units that may be formed as a result. This addition could have also provided additional Cu to the system and been responsible for triggering the emplacement of the S-enriched melt. As the peak in S concentration in Ap_{incl} occurs after initial emplacement of porphyry sequence, it suggests that this addition of S occurs relatively late and to the parental melt source. It also indicates that the S content of melt could be a key control in the mineralisation of a system, and ultimately the timing and size of injection is important.

The changes in the composition of hydrothermal apatite can be understood in the context of a single magmatic fluid evolving with interaction with the rock: cooling and changing pH. The REE and halogen content are the strongest evidence for this and reflect changes in fluid source over time and distance from the fluid source. This model explains why hydrothermal apatite associated with potassic and propylitic alteration is similar close to porphyry system. Potassic

apatite forms from early, least fractionated fluid and the REE content is similar to that of magmatic apatite, whereas the REE profile associated with sericitic apatite is more unique. By contrast the concentration of other cations in apatite is more closely related to the co-crystallising phases and the altered host phases and varies significantly depending on alteration style. The composition of hydrothermal apatite has been linked to association of Cu-(Fe)-sulfides and appears to produce the best correlation with system grade from predictive models. However more analyses from a wider range of samples are required before they can be used to train a predictive model.

10.6 Predictive classification for porphyry exploration using apatite

The viability of a porphyry deposit to be development into a mine depends on a number of factors including those which that will not have a direct influence of apatite composition. Therefore a mineral indicator aims to assess the *potential* of an apatite grain to be related to porphyry formation based off comparison to known apatite chemistry. The predictive models serve a proof of concept that trace element composition of apatite can be used to build multivariate predictive models to aid porphyry exploration. The results of the classification models confirm conclusions from the case studies, that knowledge of the apatite type or textural association is important. The compositions of sericitic apatites are easy to separate and use as evidence for presence of magmatic-hydrothermal system. In addition, when separating out intrusive phases, the analyses classified as magmatic apatite often work the best, followed by metasomatised apatite. It is suggested that proximal hydrothermal apatite has a wide range of potential compositions which may not be fully captured within the current dataset. Analyses of Ap_{mtrx} are much more practical, and the composition of Ap_{incl} were not used in the training of the model as at present there is only a limited data set. However Ap_{incl} has potential as a separate model, especially when combined with the trace element chemistry of zircon.

10.7 Suggestions for future work

A number of logical areas for follow-up research have emerged from the work done in this thesis.

For magmatic apatite:

- Collect detailed EPMA maps of apatite grains from different textural associations and with varying degrees of overprinting metasomatism. Use these to assess the extent of compositional modification versus visible alteration throughout the grain and also the effects of sub-solidus re-equilibration of halogens and sulfur. Trends in element concentrations linked by metasomatism can be evaluated using unsupervised cluster analysis approaches.
- Investigate apatite from within unidirectional solidification textures (USTs). USTs represent the magmatic-hydrothermal transition in the final stages of crystallisation of porphyry intrusions. Apatite from these textures may record the final behaviour of magmatic volatiles within an intrusion in equilibrium with the most evolved melts.
- Carry out geochronology of magmatic (and hydrothermal) apatite. Dates can be compared to zircon geochronology for magmatic crystallisation ages; variations in apatite ages may be linked to overprinting by hydrothermal fluids (U-Pb-Th mobility). Apatite has lower closure temperatures than zircon so may record the last interaction with fluids.

- Build a comprehensive library of CL images of the different textural associations with apatite from different lithologies and alteration zones. These could be compared to literature studies and potentially be utilised to aid classification of apatite grains.
- Continue investigation of S concentrations in Ap_{incl} , including analyses of samples from more porphyry units spanning the time period of mineralisation. In addition, compare these data with the S content of Ap_{incl} from a barren inclusion of a similar oxidation state and emplacement depth.

For hydrothermal apatite:

- Carry out a study of the effect of spatial position on hydrothermal apatite composition by analysing apatite from a traverse across a deposit extending to over 1 km away from the fluid source. Particularly focus on REE composition to see if there is a systematic change with distance. Changes in composition can be compared to those observed in other minerals in the literature and potentially developed into a vectoring and/or fertility assessment tool.
- Conduct a study of changes in magmatic-hydrothermal apatite with time, with particular focus on halogens reflecting magmatic volatile content. This could be achieved by analysing a greater range of hydrothermal apatite assemblages and determining a chronology for their formation.
- Compare the composition of potassic-associated apatite from successive intrusions in one porphyry system as a potential tracer of upper crustal magmatic and volatile evolution. In this research project there were too few analyses to form a robust study.
- Study additional samples of vein-hosted apatite, especially focusing on mineralised versus unmineralised assemblages.
- Carry out a fluid inclusion study of hydrothermal apatite, or quartz within apatite assemblages. This will aid interpretation of fluid chemistry from apatite composition and constrain apatite depositional conditions.

For exploration applications:

- Collect additional apatite analyses for classification models, especially analyses from a range of deposit sizes and 'background' apatite from a diversity of unmineralised settings.
- Expand the magmatic/hydrothermal classification training data set. This would require either more analyses of in-situ apatite, or the use of unsupervised machine learning techniques on concentrate samples. This could be coupled with sample descriptions (i.e. whole rock alteration) to serve as a broad classification work flow for assessment.
- Analyse the additional proximal hydrothermal apatites from systems of different grades to explore the link between the composition of early hydrothermal apatite and grade.
- Acquire more Ap_{incl} data from multiple porphyry systems and develop an exploration tool based on these to be used alongside zircon trace element classification and U-Pb dating.

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Appendix A: Comparison of laser standards over the course of this study.

Table A.1 Analyses of GSD-1G secondary standard collected by LA-ICP-MS over the course of this study (91 runs)

Date collected	Na	Mg	P	V	Mn	Fe	As	Sr	Y	La	Ca	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Pb	Th	U
19/7/18	25945	22451	959	42	206	49108	35	69	41	40	41	46	44	46	39	49	48	51	50	40	50	52	54	45	43	40
19/7/18	26723	22877	1003	43	212	49640	36	69	42	38	39	44	43	47	40	50	49	51	51	40	50	52	53	44	41	41
19/7/18	26045	22557	980	43	210	49534	36	68	41	39	40	45	45	47	39	49	48	51	51	40	50	52	53	46	41	41
19/7/18	26655	24132	1115	43	216	45682	36	70	43	41	41	46	47	49	41	51	52	53	53	43	53	53	55	47	44	41
19/7/18	26595	23846	1118	44	216	45473	36	69	42	40	41	46	47	49	41	49	49	51	53	52	43	53	54	47	42	41
19/7/18	25497	24055	1105	43	212	43911	34	69	42	39	40	45	45	48	41	50	49	51	53	52	42	52	52	45	42	41
19/7/18	26669	24083	1110	43	215	46883	36	70	43	40	41	46	46	49	41	50	51	53	52	42	53	53	55	47	43	41
19/7/18	26528	23718	1108	44	216	46943	36	69	42	40	41	46	47	49	41	49	51	53	52	43	53	54	54	47	42	41
19/7/18	25459	23276	1006	43	212	45759	34	69	42	39	40	45	45	48	41	50	49	52	52	42	52	53	52	48	41	40
19/7/18	25607	23320	1083	42	207	56596	35	68	41	38	40	45	45	48	40	48	47	50	48	40	50	52	52	48	41	40
19/7/18	26217	23748	981	42	207	57582	35	71	42	39	40	46	46	49	41	48	49	51	50	41	51	53	53	44	41	40
19/7/18	26258	23709	1003	44	215	6106	35	69	41	39	41	46	46	49	41	50	49	51	51	41	51	53	54	46	41	41
19/7/18	25459	23244	990	42	208	56060	35	68	41	38	40	45	45	48	41	49	47	50	48	40	50	52	52	48	41	40
19/7/18	26044	23673	966	42	209	58000	35	71	42	39	40	46	46	49	41	49	50	52	51	41	51	53	53	45	41	40
19/7/18	26082	23649	986	44	216	59060	36	69	41	39	41	46	46	49	42	50	49	51	51	41	52	53	54	46	42	40
19/7/18	26105	24030	842	43	215	58884	37	72	44	40	42	47	46	50	43	51	50	53	51	41	52	53	54	46	42	41
19/7/18	25670	23789	839	45	210	56062	40	77	43	40	42	47	47	50	43	52	53	52	41	52	52	54	49	44	41	41
19/7/18	26218	23877	851	44	221	6107	37	71	43	41	43	48	48	50	43	53	51	54	52	42	53	54	54	47	46	41
19/7/18	26229	24065	865	43	215	59237	37	71	43	40	42	47	46	50	43	51	50	53	51	41	52	53	54	46	42	41
19/7/18	26879	23741	874	45	210	56515	39	77	43	40	42	47	47	50	43	52	50	53	51	41	52	53	54	49	44	41
19/7/18	26272	23757	903	43	220	60486	37	72	43	41	42	48	47	51	43	53	50	54	52	42	53	54	54	47	46	41
19/7/18	25700	23174	1046	42	211	61666	36	69	42	38	41	47	43	48	40	49	47	53	51	41	50	51	50	47	42	41
24/9/18	26426	23717	1111	44	210	61939	37	72	42	40	42	47	46	49	40	49	49	52	49	40	51	54	54	48	43	42
24/9/18	25486	22876	1134	40	201	60242	36	69	42	40	40	45	44	49	40	48	48	50	49	40	51	53	54	47	40	39
24/9/18	25632	23224	1024	41	211	61515	36	69	42	38	41	47	43	48	41	49	48	53	52	41	50	51	51	47	42	41
24/9/18	26438	23843	1079	44	211	61923	37	72	42	40	42	47	46	49	40	49	49	52	50	41	51	54	54	49	43	42
24/9/18	25509	22882	1090	40	202	60153	36	70	42	39	40	44	44	48	40	48	48	50	50	40	51	53	54	47	40	39
24/9/18	24977	23178	910	43	207	60993	35	67	41	39	40	44	42	48	42	49	51	54	50	40	50	51	51	46	42	40
24/9/18	25176	23047	992	43	211	62572	35	69	43	40	40	43	42	47	40	49	49	53	52	40	49	52	53	46	42	43
24/9/18	27698	23588	963	42	215	65072	36	70	41	41	42	45	44	48	42	49	50	53	50	41	51	52	53	48	41	40
24/9/18	27698	24940	913	44	217	35906	38	74	43	41	43	47	46	50	43	51	50	53	51	41	51	52	53	50	42	41
24/9/18	26635	24379	890	43	210	34816	35	69	41	39	41	45	44	47	40	47	47	49	48	38	48	50	51	47	41	40
24/9/18	26590	24396	883	42	211	35881	38	70	41	39	42	46	45	48	41	48	48	50	48	39	49	50	52	48	40	40
4/5/19	27358	24466	1021	43	217	39788	37	70	41	39	41	46	45	48	40	49	48	51	50	40	50	53	54	49	42	42
4/5/19	27086	24094	1004	42	214	39226	36	69	41	39	41	46	45	47	40	47	47	50	49	39	48	49	52	49	42	41
20/8/19	27685	24710	1021	43	219	40081	37	70	41	39	41	46	45	48	41	49	48	51	50	40	49	52	53	50	43	42
20/8/19	27189	23997	984	42	211	39045	36	69	41	39	40	44	43	47	40	48	47	50	50	40	50	53	52	49	42	42
20/8/19	26926	23978	987	42	213	39700	36	68	40	39	41	44	44	47	40	48	48	51	50	40	50	53	53	51	42	42
20/8/19	26305	23194	981	42	214	39542	36	67	40	38	40	44	43	47	40	47	47	50	50	39	49	50	51	50	42	41
24/4/19	26309	24123	971	42	214	41284	36	68	40	38	40	45	45	47	40	50	49	53	51	40	50	51	52	51	42	41
24/4/19	26359	24443	993	43	219	41964	35	68	40	39	41	45	46	48	41	49	49	52	51	40	50	52	54	49	41	40
24/4/19	26928	24755	995	42	217	41038	35	68	40	38	40	45	44	46	40	48	48	52	50	40	50	50	53	49	40	39
24/4/19	26961	24325	883	42	216	42453	29	70	40	39	42	46	43	47	41	48	47	50	49	39	48	49	50	46	42	41
24/4/19	27023	23964	922	43	221	25690	31	70	39	38	42	46	43	47	40	46	46	49	47	37	47	49	49	50	40	42
24/4/19	26622	23826	884	43	216	24696	30	69	39	38	42	45	43	47	40	47	47	50	49	39	48	50	50	47	41	41
19/7/18	26686	23580	878	45	222	26832	37	68	39	38	42	46	45	48	41	47	47	50	48	39	48	51	50	47	40	42
19/7/18	26860	23770	883	44	218	26685	36	71	40	39	42	46	44	48	41	49	48	52	49	40	50	51	52	48	41	42
19/7/18	26684	23625	877	45	222	26811	36	69	39	38	42	46	44	48	41	48	47	50	48	39	48	51	50	47	40	42
19/7/18	26866	23836	883	44	218	26655	36	71	40	39	42	46	44	48	41	49	49	52	49	40	49	51	52	48	41	42
19/7/18	27439	24051	907	45	223	27267	37	71	41	39	42	46	43	48	41	40	48	51	49	39	49	52	51	49	42	40
19/7/18	26306	23782	780	43	213	56225	36	70	41	39	41	46	44	47	40	49	48	51	50	39	50	52	52	47	42	40
19/7/18	26440	23687	790	43	216	57694	37	69	41	39	41	45	44	47	40	48	48	51	49	39	49	52	51	47	41	40
19/7/18	27026	24234	789	44	216	57342	36	70	41	39	41	45	44	48	41	48	48	52	50	40	50	51	52	48	41	40
19/7/18	26772	24157	793	42	215	60709	37	70	41	39	41	45	45	47	41	48	48	51	50	39	49	51	52	48	42	41
19/7/18	26433	24036	799	43	215	61330	37	70	41	39	41	45	44	48	40	48	48	51	50	39	49	51	51	47	42	41

19/7/18	26283	23831	24469	804	43	217	61941	37	71	42	39	41	45	44	48	41	48	49	48	48	52	50	40	50	52	52	48	42	41
19/7/18	26283	23831	24469	783	43	214	56444	36	70	41	39	41	46	45	47	40	49	48	48	48	51	50	40	50	52	52	48	42	40
19/7/18	26303	23634	791	43	216	57767	36	69	41	39	41	45	44	44	47	40	48	48	48	48	51	49	39	49	52	51	47	41	40
19/7/18	26869	24108	797	43	216	57423	36	70	41	39	41	45	44	44	48	41	48	48	48	48	51	50	39	49	51	52	48	41	40
19/7/18	26869	24079	794	42	216	60659	37	70	41	39	41	45	45	45	47	41	48	48	48	48	51	50	39	49	51	52	49	42	41
19/7/18	26419	24001	799	43	215	61317	37	70	41	39	41	45	44	44	48	40	48	48	48	48	51	50	39	49	51	51	47	42	41
19/7/18	26985	24343	802	43	217	61635	37	71	42	39	41	45	44	44	48	40	47	48	48	48	51	50	40	50	51	52	48	42	41
19/7/18	26830	24118	797	43	216	61594	37	70	41	39	41	45	45	45	47	41	48	48	48	48	51	50	39	49	51	52	48	42	41
19/7/18	26495	24012	802	43	215	61955	37	70	41	39	41	45	44	44	48	40	48	48	48	48	51	50	39	49	51	51	47	42	41
19/7/18	27104	24455	806	43	218	62392	37	71	42	39	41	45	44	44	48	41	48	48	48	48	52	50	40	50	52	52	48	42	41
19/7/18	26583	24424	794	42	213	60623	37	70	41	39	41	45	45	45	48	41	48	48	48	48	51	50	39	50	52	52	48	42	41
19/7/18	26555	24501	799	42	215	60892	37	69	41	39	40	45	44	44	48	41	49	48	48	48	51	50	40	50	52	52	49	42	40
24/9/18	26548	24478	790	42	213	61146	38	71	41	39	41	45	44	44	48	41	48	49	49	49	52	50	40	50	52	52	48	43	41
24/9/18	27003	24698	779	43	214	62698	37	70	40	39	41	45	45	45	48	40	48	48	48	48	51	50	39	50	52	52	49	42	41
24/9/18	27669	24923	800	43	216	63607	37	70	41	39	41	45	45	45	48	41	49	49	49	49	52	50	40	50	52	52	50	42	42
24/9/18	26943	24651	786	43	215	63086	36	71	41	39	41	45	45	45	48	41	49	48	48	48	51	50	40	50	52	52	48	43	41
24/9/18	27130	24585	786	43	215	62487	36	69	40	38	41	45	45	45	48	40	48	47	47	47	51	50	39	50	51	52	50	42	40
24/9/18	27091	25096	809	43	218	64018	38	71	41	39	41	46	45	45	49	41	49	49	49	49	52	50	40	50	52	52	50	43	42
24/9/18	27064	24671	787	43	216	63243	36	71	41	39	41	45	45	45	48	41	49	48	48	48	51	50	40	50	52	52	49	43	42
24/9/18	26563	24651	764	42	215	66600	35	69	41	39	40	45	43	47	40	49	47	51	49	47	51	49	39	49	51	52	48	42	41
24/9/18	26414	24520	770	43	215	66451	36	69	41	39	41	45	44	44	48	40	48	47	47	47	51	49	39	50	51	52	48	42	41
24/9/18	27099	25222	767	43	216	67295	37	70	41	39	41	45	45	45	47	40	49	49	48	48	51	49	39	49	51	52	48	42	41
24/9/18	26716	24696	769	42	215	67363	36	70	41	39	41	45	43	47	40	49	48	47	47	47	51	49	39	49	51	52	48	42	41
4/5/19	26448	24606	773	43	215	68667	36	69	41	39	40	44	44	44	48	40	48	47	47	47	51	49	39	49	51	52	48	42	41
4/5/19	26955	24959	774	43	216	67442	36	69	41	38	41	45	44	44	47	41	49	48	48	48	51	50	39	50	51	52	49	42	41
4/5/19	26958	24789	782	43	217	67173	36	69	40	39	41	46	44	44	47	41	49	48	48	48	51	49	40	49	51	51	49	42	41
4/5/19	26422	24522	779	42	212	66399	36	70	40	39	41	45	45	45	47	40	49	48	48	48	51	49	40	49	51	52	49	42	40
4/5/19	26832	24856	779	42	216	67022	36	69	40	39	41	45	44	44	47	41	49	48	48	48	51	49	39	50	51	51	49	42	40
4/5/19	26889	24709	785	43	217	66810	36	69	40	39	41	46	44	44	47	41	49	48	48	48	51	49	39	49	51	51	49	42	41
20/8/19	26355	24447	781	42	213	66196	36	70	40	39	41	45	45	45	47	40	49	48	48	48	51	49	40	49	51	52	50	42	40
20/8/19	27422	24564	1043	43	217	39959	37	70	41	39	42	46	45	47	40	48	48	48	48	48	51	50	40	50	52	54	49	42	42
20/8/19	27047	24083	1016	42	213	39284	36	69	41	39	41	46	45	47	40	47	47	47	47	47	50	49	39	48	49	52	49	42	41
20/8/19	27674	24732	1030	43	218	40054	37	70	41	39	40	45	45	45	48	40	48	47	47	47	50	49	39	49	51	53	50	43	42
20/8/19	27185	24114	994	42	211	39360	36	69	41	39	40	45	43	47	40	48	47	47	47	47	50	50	40	50	53	52	49	42	42
20/8/19	26911	24108	999	42	214	40001	36	68	40	38	40	45	43	47	40	47	47	47	47	47	50	50	39	49	51	51	50	42	42
24/4/19	26328	23280	988	42	216	39981	36	67	41	38	40	45	43	47	40	47	47	47	47	47	50	50	39	49	51	51	50	42	41
24/4/19	27400	23455	824	44	214	77784	39	69	38	37	41	44	41	46	40	44	45	45	45	47	47	37	47	47	48	51	39	40	41
24/4/19	27999	23680	846	44	217	78364	38	69	39	37	40	44	42	46	39	44	45	44	45	47	47	47	37	47	48	48	51	40	41
24/4/19	27468	23630	848	45	222	79211	38	70	40	38	41	45	43	47	40	46	47	47	47	47	49	48	38	48	50	49	50	41	41
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24/4/19	27156	23036	696	43	211	73767	36	68	39	37	40	43	42	46	39	47	46	46	46	46	49	47	38	47	50	49	48	40	41
19/7/18	27622	23682	783	42	218	75997	39	71	40	39	42	46	45	48	40	48	47	47	47	47	50	49	38	48	50	50	50	41	41
19/7/18	26243	23087	694	43	216	76731	38	71	40	39	42	45	44	47	40	50	47	47	47	47	50	48	38	48	48	49	50	40	42
19/7/18	27260	23171	673	43	213	76556	37	68	39	38	40	44	43	46	39	48	47	49	48	47	49	48	38	47	50	49	48	40	41
19/7/18	27682	23738	755	42	219	77573	39	71	40	39	42	46	46	46	49	40	48	47	47	47	50	50	39	48	50	50	51	42	41
19/7/18	27856	24463	761	43	220	75577	39	71	41	39	43	46	44	49	41	48	48	48	48	48	50	49	39	49	50	52	50	42	43
19/7/18	26788	23683	743	43	220	74229	38	70	40	39	42	46	45	48	41	49	47	47	47	47	50	49	39	49	51	50	49	41	41
19/7/18	26626	23410	732	42	214	73647	36	69	39	39	41	45	42	47	40	47	46	49	46	49	49	38	47	49	50	49	41	41	
19/7/18	27601	24340	775	43	218	74279	39	71	41	39	42	45	43	49	41	48	47	47	47	47	50	48	39	48	50	51	50	41	42
19/7/18	26731	23682	756	43	220	73530	37	69	40	39	41	45	44	48	40	48	47	50	49	49	51	50	49	39	49	51	50	49	41
19/7/18	26602	23507	745	42	213	72880	36	69	39	39	41	45	42	47	40	47	46	46	46	46	49	48	38	47	49	49	40	41	
19/7/18	28127	24396	804	45	223	38276	41	71	42	40	43	46	44	49	41	49	48	48	48	48	52	49	40	49	52	52	43	43	42
19/7/18	28542	24624	807	45	226	39515	39	68	40	40	42	46	45	49	42	49	49	49	49	49	52	50	40	49	51	52	54	42	42
19/7/18	28708	24519	799	45	224	38872	40	70	42	40	42	45	45	48	41	49	48	48	48	48	51	49							

24/9/18	27836	24670	765	44	221	60043	39	71	41	40	43	46	45	48	42	49	49	52	51	40	50	52	52	53	42	42	
24/9/18	27410	24993	778	45	224	66877	36	70	40	39	41	45	43	48	41	48	47	50	49	39	48	50	51	49	42	41	
24/9/18	27405	23611	851	42	215	62897	37	71	43	39	42	46	44	48	41	48	47	52	50	40	50	52	51	49	41	42	
4/5/19	27436	24526	890	44	225	63203	37	73	41	40	43	50	46	48	42	48	47	52	50	40	50	52	50	48	41	41	
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4/5/19	28242	24797	868	44	225	65617	38	71	41	40	42	47	46	49	42	50	49	52	52	42	51	53	53	50	43	43	
4/5/19	26379	24017	845	42	211	61326	36	69	40	39	42	45	44	48	41	47	48	51	50	40	50	51	51	49	42	41	
4/5/19	26775	23903	849	42	212	63927	36	66	39	39	43	46	43	48	42	47	47	49	48	40	49	52	53	49	41	42	
4/5/19	28141	24442	857	44	222	64712	38	71	41	40	42	47	46	49	42	51	49	52	51	41	51	53	53	50	43	43	
20/8/19	26453	24022	840	42	210	61083	36	69	40	39	42	45	44	48	41	47	48	51	50	40	50	51	51	49	42	41	
20/8/19	26700	23764	847	42	212	63854	36	66	39	38	42	46	44	48	41	47	47	49	48	40	49	52	52	49	40	42	
20/8/19	26733	24350	806	44	216	66169	37	70	40	38	41	46	44	47	39	46	47	50	49	39	49	50	50	49	41	41	
20/8/19	26516	24232	796	43	212	65487	38	68	40	38	40	45	44	47	38	45	46	49	49	39	49	50	50	49	40	42	
20/8/19	27647	25647	848	45	223	68715	40	72	42	40	42	48	46	50	42	49	49	53	52	42	51	54	55	50	42	42	
20/8/19	26719	24289	802	44	216	66103	37	70	40	38	41	46	44	47	39	46	47	50	49	39	49	50	50	49	41	41	
24/4/19	26491	24142	791	43	211	65391	37	68	40	38	40	45	44	47	38	46	46	49	49	39	49	50	49	40	41	41	
24/4/19	27609	25211	842	45	222	68582	39	72	42	40	42	48	46	50	42	50	49	53	52	42	51	54	55	50	42	42	
24/4/19	27877	25183	812	45	223	70771	37	72	41	40	42	47	46	49	42	49	49	53	50	41	50	52	53	49	41	41	
24/4/19	27165	24595	820	43	216	68594	38	70	42	39	41	45	44	47	41	45	49	52	50	39	50	51	51	50	41	41	
24/4/19	27230	24323	800	43	213	67653	37	71	42	41	42	46	46	48	41	48	48	53	51	40	51	52	52	47	41	42	
24/4/19	27794	25129	812	45	223	70306	37	72	41	39	42	47	45	48	41	48	48	52	50	40	50	52	53	48	41	41	
19/7/18	27384	24709	829	44	219	69102	39	70	42	39	41	45	44	47	41	49	49	52	50	39	50	51	51	49	41	42	
19/7/18	27236	24344	804	43	214	67338	37	71	42	40	42	46	46	48	41	48	48	52	50	40	50	51	51	47	41	42	
19/7/18	27145	24384	836	44	217	69333	38	71	41	39	42	47	46	50	42	49	48	51	50	41	50	51	53	53	42	43	
19/7/18	26163	23401	787	42	208	65787	36	67	39	38	40	45	43	47	40	47	46	49	48	39	48	50	51	46	40	40	
19/7/18	26488	24315	801	46	213	68228	37	69	39	39	41	45	45	47	40	48	45	47	47	37	48	50	50	48	40	41	
19/7/18	27169	24397	843	45	219	70280	39	72	41	39	42	47	46	50	42	49	49	51	50	41	50	52	53	53	42	43	
19/7/18	26164	23388	794	42	208	66286	36	67	39	38	40	45	43	47	40	47	46	50	48	39	48	50	51	45	40	40	
19/7/18	26628	24321	799	45	214	68877	37	69	39	39	41	45	45	47	40	48	45	47	47	37	47	50	51	47	40	41	
19/7/18	27832	25247	818	44	218	71229	36	71	42	41	42	47	48	48	42	50	50	53	51	41	51	53	54	48	42	41	
19/7/18	27574	23492	889	43	216	69276	36	69	39	38	41	45	43	45	40	46	45	48	47	37	47	49	48	48	39	40	
19/7/18	27223	23348	869	44	216	68256	36	69	39	38	41	45	45	48	40	46	45	48	47	37	47	47	48	47	39	40	
19/7/18	27120	23151	861	43	216	68258	35	69	38	38	41	45	43	45	40	46	45	49	47	37	47	49	49	48	40	41	
19/7/18	27459	23841	744	44	221	68590	37	70	39	38	42	45	45	46	40	46	46	48	47	38	47	50	49	49	41	42	
19/7/18	27241	23841	741	44	221	68770	36	69	39	38	41	45	44	46	40	46	45	49	48	38	48	48	49	49	41	41	
19/7/18	27570	24094	773	44	221	68328	36	70	39	38	41	45	44	46	40	45	46	49	48	38	48	50	49	49	41	42	
19/7/18	27532	24097	732	44	223	67744	37	70	39	38	42	45	45	46	40	46	46	48	48	38	48	50	49	49	41	42	
19/7/18	27238	23966	727	44	220	68073	36	70	39	38	41	45	44	46	40	46	46	49	48	38	48	50	50	49	41	42	
19/7/18	27536	24180	761	44	221	67702	36	70	39	38	41	45	44	46	40	45	46	49	48	38	48	50	50	49	41	42	
19/7/18	26440	23391	620	43	215	75497	35	69	39	37	40	43	42	46	39	42	45	49	47	37	46	49	49	47	40	40	
19/7/18	26674	23538	627	44	215	76487	35	69	39	38	41	44	42	47	40	46	46	48	47	37	46	49	49	47	39	40	
19/7/18	26987	23855	635	44	217	77361	34	70	39	38	41	44	44	46	41	46	46	49	47	38	47	50	49	46	40	41	
19/7/18	29873	30179	921	47	232	57484	41	70	39	38	42	46	45	48	40	46	46	48	47	38	47	50	49	52	40	44	
24/9/18	30130	29483	936	46	232	57507	42	69	38	38	43	45	44	47	40	47	45	49	47	38	47	51	50	52	40	44	
24/9/18	29470	29310	917	46	227	57209	39	68	38	38	42	46	45	47	39	45	45	49	47	38	47	50	49	51	41	44	
24/9/18	28618	29024	747	45	219	72783	38	69	38	38	41	44	42	46	39	44	45	48	47	37	47	48	47	49	39	41	
24/9/18	28363	29012	757	45	221	73876	38	68	38	37	41	44	41	46	40	46	46	46	47	37	47	48	48	49	40	42	
24/9/18	29039	29585	744	46	226	75824	40	71	39	38	42	45	44	46	40	46	46	49	47	37	47	48	49	50	40	42	
24/9/18	28594	29138	727	45	220	74960	39	69	38	38	41	44	42	46	39	44	45	48	47	37	47	46	48	48	39	41	
24/9/18	28374	29113	744	45	222	75402	38	68	38	37	41	44	41	46	39	45	45	47	46	37	47	48	47	48	39	42	
24/9/18	29035	29659	735	46	227	77022	40	71	39	38	42	45	43	46	40	46	46	49	47	37	47	48	49	50	40	42	
24/9/18	29736	29914	739	47	222	80570	36	69	38	37	42	44	43	45	40	45	45	47	47	37	47	50	48	50	40	43	
24/9/18	29076	29383	750	45	219	78710	36	69	38	37	41	43	42	44	39	43	45	47	47	37	47	46	49	48	50	39	42
24/9/18	28908	29124	754	45	221	78994	37	68	38	37	42	44	43	45	40	45	45	48	47	37	47	46	48	48	49	39	43
4/5/19	29744	29923	718	47	222	80585	35	68	37	37	42	44	42	44	40	45	47	46	47	37	47	50	48	50	40	43	
4/5/19	29192	29554	741	46	220	79064	36	69	38	37	41	43	42	44	39	44	45	47	47	37	47	45	49	47	50	38	42
4/5/19	28717	28967	745	45	220	78635	37	68	38	37	42	44	43	44	39	45	45	48	46	37	46	48	48	49	39	42	
4/5/19	28913	28633	1085	45	221	77872	37	70	38	37	41	44	43	46	39	46	46	48	47	37	46	49	48	49	39	41	
4/5/19	29480	29067	1149	47	228	81703	38	69	38	37	42	45	44	46	40	46	45	48	47	36</							

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19/7/18	27690	24671	731	44	221	71384	36	70	39	37	41	44	42	47	40	47	46	50	48	39	48	50	50	50	41	42
19/7/18	28113	24909	744	44	223	72126	37	70	40	38	42	45	44	48	41	48	47	51	49	39	49	51	51	50	41	42
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19/7/18	27681	24654	746	44	222	71733	36	69	39	37	41	44	42	46	40	47	46	49	47	39	48	50	50	50	41	42
19/7/18	28124	24877	758	44	224	72321	37	70	39	38	42	45	43	47	40	48	47	51	49	39	49	51	50	51	41	42
19/7/18	28075	24763	746	45	222	71963	36	71	40	39	42	45	44	47	41	47	47	51	48	39	48	51	50	51	42	42
19/7/18	27946	25128	717	44	219	69684	35	69	39	38	42	45	44	46	40	47	46	50	48	38	48	51	50	50	41	42
19/7/18	28247	25624	727	45	226	71376	37	70	39	38	42	45	45	46	41	46	47	50	48	38	48	50	50	52	41	42
19/7/18	28171	25334	708	44	220	70215	36	70	40	38	42	46	44	48	40	48	47	50	48	38	48	51	50	51	42	42
19/7/18	27920	25201	645	44	219	68535	35	69	39	38	42	45	45	46	40	47	46	51	48	38	48	51	50	50	41	42
19/7/18	28224	25684	670	45	226	70420	37	70	39	38	42	45	45	46	41	46	47	50	48	38	48	51	50	53	41	42
19/7/18	28154	25387	662	44	220	69426	36	70	40	38	42	46	45	48	40	48	47	50	49	38	48	51	50	51	42	42
19/7/18	27450	24734	969	44	220	74682	36	69	39	38	41	45	43	46	40	47	46	49	48	38	48	49	50	49	41	42
19/7/18	27768	24867	1005	44	219	74300	36	69	39	38	42	45	45	47	40	46	45	48	47	37	47	50	49	50	40	41
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19/7/18	27433	24706	1042	44	219	75873	36	69	39	38	41	44	43	46	40	46	46	48	47	38	47	49	49	50	41	42
19/7/18	27801	24877	1065	44	218	75474	36	69	39	38	41	44	42	45	39	45	45	47	46	37	47	49	48	49	40	41
19/7/18	28044	25168	1088	45	222	77148	38	70	40	38	41	45	44	46	40	46	46	48	48	38	47	50	50	50	41	42
19/7/18	28171	25250	1024	45	224	76890	38	70	39	39	42	47	43	48	40	47	47	50	49	39	48	50	51	51	41	42
24/9/18	28179	25081	892	43	219	74670	36	69	38	38	42	45	44	47	41	48	47	49	48	38	48	50	50	51	41	42
24/9/18	28634	25302	905	45	227	77399	39	73	40	39	43	46	43	48	41	47	47	50	49	39	49	51	51	51	42	42
24/9/18	28259	25215	1021	45	224	74949	38	70	39	39	43	47	43	48	41	48	47	50	49	39	49	51	51	52	41	43
24/9/18	28337	25125	893	43	219	72880	36	69	38	38	42	45	44	47	41	48	47	50	48	38	48	50	50	51	42	42
24/9/18	28679	25329	906	45	227	76783	39	73	40	39	43	46	44	48	41	48	47	50	49	39	49	51	51	51	42	42
24/9/18	27620	25202	688	44	222	81326	36	70	39	38	41	45	43	45	40	46	46	49	48	37	48	50	50	50	41	42
24/9/18	27447	24901	657	44	218	80291	37	70	39	38	40	44	43	45	40	46	46	50	47	37	47	49	49	49	41	41
24/9/18	27611	25369	621	44	221	82398	36	69	39	38	40	45	42	45	40	46	46	49	47	37	47	50	50	50	41	42
24/9/18	27512	25066	605	44	218	81260	37	70	39	38	40	44	43	45	40	46	46	50	47	37	47	49	49	49	40	41
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24/9/18	27570	24975	815	43	214	78652	35	69	39	38	41	44	44	47	40	46	46	48	47	37	47	50	49	50	40	41
4/5/19	27942	25109	849	43	218	78397	35	69	39	38	40	44	42	46	40	46	46	48	48	38	47	49	49	50	40	41
4/5/19	28735	25683	837	45	228	82458	36	72	41	40	42	47	46	48	41	48	47	50	49	39	49	51	51	52	43	44
4/5/19	27698	25224	649	43	220	81712	35	68	38	37	40	44	42	45	38	45	45	48	46	36	47	49	48	47	40	41
4/5/19	27590	25207	650	44	223	83117	37	71	40	40	42	46	45	49	41	48	47	50	49	38	49	51	51	50	42	42
4/5/19	27986	25299	635	45	225	83627	37	73	41	40	43	47	46	49	42	49	45	50	40	50	50	50	52	50	42	43
4/5/19	27630	25283	599	43	220	83106	34	68	38	37	40	44	42	45	38	45	45	48	46	36	47	49	48	47	40	41
208/19	27625	25339	608	44	224	84663	37	71	40	40	42	46	45	49	41	48	47	50	49	38	49	51	51	49	42	42
208/19	27956	25372	602	45	225	84875	37	73	41	40	43	47	46	49	42	49	48	51	50	39	49	50	51	49	42	43
208/19	27248	25014	649	44	222	84491	35	70	39	38	41	45	42	47	41	48	47	50	48	38	48	50	50	48	41	41
208/19	27216	3191	98	4	19	9337	3	10	3	3	3	3	4	4	3	4	3	4	4	3	4	4	4	4	3	3
208/19	27934	25225	487	44	224	75267	35	70	40	40	43	47	46	48	41	49	49	53	50	40	50	50	52	50	42	42
208/19	27278	25003	480	44	228	78568	36	70	41	39	42	46	44	47	41	47	48	50	49	39	50	51	53	50	42	42
24/4/19	27639	25394	505	44	227	76137	37	72	41	41	44	48	46	49	42	49	49	52	51	40	50	52	53	53	42	43
24/4/19	27739	25929	657	42	217	61947	36	69	39	38	41	44	43	47	39	47	46	49	48	38	48	49	50	50	41	41
24/4/19	27982	26005	691	44	226	64021	36	71	41	39	43	46	45	48	41	49	48	51	51	40	50	52	52	52	43	42
24/4/19	27469	25668	649	44	224	63518	38	72	42	40	43	47	47	49	42	51	50	53	52	40	51	53	54	52	43	43
24/4/19	27564	25330	569	44	223	66234	35	72	42	40	42	47	45	48	42	50	50	52	51	41	52	54	54	50	43	43
24/4/19	26372	24478	563	44	219	65009	36	72	41	40	42	47	45	48	41	49	48	52	50	41	51	53	53	50	42	43
19/7/18	26805	24464	556	44	221	65715	36	70	40	40	42	46	43	47	41	47	48	51	49	39	49	52	52	50	42	42
19/7/18	27438	25099	486	44	221	66277	34	72	41	40	42	46	45	48	42	49	49	52	51	41	51	54	54	50	42	43
19/7/18	26261	24277	492	43	218	64917	35	71	41	39	42	46	44	48	41	48	48	52	50	41	50	53	53	50	42	42
19/7/18	26731	24334	494	44	220	65883	36	69	39	39	42	46	42	47	41	47	47	51	49	39	49	51	51	50	42	42
19/7/18	27625	25733	917	45	225	70528	38	71	40	40	42	46	45	48	41	47	47	50	48	38	48	49	50	50	41	42
19/7/18	27227	25221	924	44	219	68503	37	71	41	40	42	46	47	49	41	49	48	51	50	40	50	50	52	49	41	42
19/7/18	26966	24988	918	44	218	68712	36	71	41	40	42	46	45	49	41	48	48	51	49	39	49	50	52	49	42	42
19/7/18	26843	23252	894	42	211</																					

197/18	27818	24491	881	44	224	45572	39	70	40	38	42	45	43	47	40	47	46	47	49	50	48	37	48	49	50	40	41		
197/18	27411	24164	869	43	216	43776	36	68	39	37	40	44	43	45	39	46	46	47	48	49	48	37	47	48	49	40	41		
197/18	27412	23888	897	43	218	45808	37	70	40	39	42	46	44	46	40	48	47	48	49	50	48	39	48	50	50	40	41		
24/9/18	27558	24088	829	43	215	48196	36	69	40	40	42	46	45	48	41	48	48	48	50	48	39	48	50	51	49	41	42		
24/9/18	26544	23044	825	43	218	48634	37	69	39	39	41	46	45	48	40	48	48	48	49	50	50	39	49	50	51	49	40	40	
24/9/18	28158	23759	826	43	213	48427	38	70	40	40	42	46	45	49	41	49	48	48	48	52	50	39	50	51	52	50	41	41	
24/9/18	27569	24064	828	43	215	47925	36	69	40	39	42	46	45	48	41	48	48	48	48	50	48	39	48	50	51	49	41	42	
24/9/18	26555	23015	825	43	219	48301	37	69	39	39	41	46	45	49	41	47	47	48	48	51	49	39	49	50	50	49	40	39	
24/9/18	28256	23687	829	43	214	48477	38	70	41	40	42	46	45	49	41	49	48	48	48	51	50	39	49	51	52	50	41	41	
24/9/18	26266	23037	819	43	215	48969	38	68	39	37	40	44	42	46	39	45	45	45	48	48	38	47	49	49	49	40	41		
24/9/18	26802	23247	815	43	219	50512	37	69	40	38	41	45	44	47	41	47	47	47	50	49	38	48	50	50	49	41	42		
24/9/18	27320	23714	818	44	216	49069	37	70	41	39	41	45	43	46	40	47	47	47	49	48	38	48	49	50	49	40	41		
24/9/18	26354	23275	837	43	215	49105	38	69	39	37	40	44	42	46	39	46	45	45	48	48	38	47	49	49	50	41	42		
24/9/18	26932	23547	835	43	219	50629	37	69	40	39	41	45	45	47	41	47	47	47	50	49	38	48	50	51	49	41	42		
4/5/19	27497	24071	843	43	216	49250	37	71	40	39	41	45	44	47	40	47	47	47	49	48	38	48	49	50	49	40	41		
4/5/19	28775	25055	947	44	222	54442	36	71	41	42	44	48	47	50	42	50	50	50	53	52	41	50	51	52	50	42	43		
4/5/19	27344	23418	886	41	207	49527	34	66	38	37	40	44	43	46	38	45	45	45	48	48	39	48	49	49	46	41	41		
4/5/19	27344	24265	927	42	212	51915	35	67	39	39	41	45	43	46	39	47	48	50	49	50	49	39	49	50	52	49	41	41	
4/5/19	27998	25335	943	44	222	54459	36	72	41	42	44	48	47	50	42	50	50	53	52	41	51	51	52	50	42	43	44		
4/5/19	26536	23309	880	42	207	49634	34	66	38	37	40	44	44	46	38	45	45	48	48	48	39	48	49	50	46	41	41		
20/8/19	27281	24133	917	42	212	52151	35	67	39	39	41	45	43	46	40	47	48	48	50	50	50	39	49	51	52	49	41	41	
20/8/19	27840	24193	882	44	220	56599	36	70	41	39	41	45	44	48	40	48	48	48	50	40	50	40	50	52	50	42	43		
20/8/19	26269	22907	862	43	217	53883	36	69	40	37	39	43	42	46	39	47	47	47	50	48	38	48	50	51	48	40	41		
20/8/19	27441	24114	892	43	216	56408	37	71	41	38	41	45	45	48	41	48	49	52	50	40	50	40	50	52	53	50	41	42	
20/8/19	26075	21954	1001	42	198	47877	33	72	38	37	39	43	41	46	39	44	44	46	45	36	45	46	47	48	47	45	38	45	
20/8/19	28258	22727	1003	41	211	50745	37	70	41	38	41	45	42	46	40	46	46	46	49	48	38	47	48	49	51	40	40	40	
24/4/19	41241	14713	560	36	150	37341	32	64	36	34	36	39	38	41	35	42	41	42	41	42	41	35	40	42	42	39	35	34	
24/4/19	42868	14456	534	37	146	35577	32	63	35	32	34	39	38	41	35	39	39	39	40	40	40	40	33	39	41	40	39	34	35
24/4/19	38051	16503	641	37	161	40700	32	65	37	35	37	41	39	42	36	43	43	43	44	44	43	36	41	44	43	41	36	35	
24/4/19	39945	16567	645	38	162	39837	32	65	36	34	36	39	37	41	35	41	42	43	43	43	35	42	44	44	43	41	36	35	
24/4/19	26508	23966	794	43	216	50895	36	69	40	39	42	45	44	47	40	49	48	51	50	40	49	50	52	48	42	41	41		
24/4/19	26300	24302	811	45	222	60608	37	72	42	41	42	46	45	48	41	49	50	53	51	50	39	50	52	53	48	42	42		
19/7/18	25938	24283	789	44	219	60797	37	71	41	40	42	46	44	47	41	49	49	49	51	50	39	50	52	52	49	42	41	41	
19/7/18	26963	23753	818	42	215	58332	35	69	40	39	42	45	44	47	40	49	48	48	51	50	40	49	50	52	52	48	42	41	
19/7/18	26916	23891	814	45	219	59678	37	71	41	41	42	46	45	48	41	49	50	53	51	50	40	50	51	52	50	48	42	41	
19/7/18	26919	23618	793	44	215	59448	37	70	41	39	41	45	44	47	41	48	48	50	49	50	49	39	50	51	52	49	41	41	
19/7/18	27457	23899	736	43	223	64814	35	70	41	39	42	45	43	48	42	48	48	48	51	50	41	50	53	52	49	41	42		
19/7/18	28020	23995	739	44	222	64975	35	71	41	40	42	45	44	49	41	49	48	48	51	50	39	49	51	52	48	41	42		
19/7/18	27750	23899	708	43	223	65064	38	72	41	39	42	45	43	47	40	48	48	48	51	49	39	49	50	52	49	41	42		
19/7/18	27184	23815	727	43	221	65168	35	69	41	39	41	45	43	48	42	48	48	48	51	50	40	49	52	51	48	41	42		
19/7/18	27886	23998	739	44	222	65600	35	71	41	40	42	45	44	48	41	49	48	48	51	50	39	49	51	52	48	41	42		
19/7/18	27629	23918	712	43	221	63833	38	72	41	39	42	45	43	47	40	48	48	51	49	39	49	50	52	49	41	42	42		
19/7/18	27436	24391	980	44	218	68809	37	71	41	40	42	46	44	47	41	48	48	48	51	50	40	50	51	53	51	42	42	41	
19/7/18	27338	24352	968	44	214	68636	36	69	41	39	42	46	44	47	41	50	49	51	51	40	50	52	53	49	43	41	41		
19/7/18	27311	24290	974	44	217	70515	37	71	42	40	42	46	45	47	42	49	49	52	50	40	51	52	53	51	42	42	41		
19/7/18	27053	23263	830	43	214	60942	38	66	38	38	41	45	45	46	40	48	47	49	49	38	48	50	48	50	47	41	41		
19/7/18	26775	23086	724	44	221	69009	38	67	40	39	42	47	45	47	41	49	47	51	49	39	48	50	50	47	42	41	41		
19/7/18	26835	23165	784	44	221	68521	38	67	40	39	42	47	45	47	41	49	47	51	49	39	48	50	50	47	42	41	41		
19/7/18	26626	23671	765	44	214	69496	36	69	40	39	41	46	44	47	40	48	47	50	49	39	49	50	52	48	43	42	41		
19/7/18	26634	23666	762	44	214	67128	36	69	40	39	41	45	44	47	40	48	47	50	49	39	49	50	52	48	43	42	41		
19/7/18	26937	24399	760	42	215	71034	36	69	40	39	40	45	44	47	40	47	47	47	51	48	38	48	50	51	47	41	40	40	
19/7/18	26954	24422	760	43	216	71006	37	69	40	39	40	45	44	47	40	47	47	47	50	48	39	48	50	51	47	41	40	40	
19/7/18	26723	23708	740	42	213	67267	37	69	40	39	42	45	43	46	39	47	47	47	50	49	39	49	51	47	42	40	40	40	
19/7/18	29144	25351	763	44	221	70851	39	71	42	39	42	46	44	47	41	48	48	48	51	50	39	49	50	51	49	43	44	44	
24/9/18	29136	25358	766	44	221	71787	39	71	42	39	42	46	44	47	41	48	48	48	51	50	39	49	50	51	49	43	44	44	
24/9/18	26854	23793	774	44	217	81648	39	70	40	39	41	45	44	48	41	49	48	48	51	49	40	50	52	52	48	41	41	41	
24/9/18	27122	23912	776	44	219	80572	39	70	40</																				

20/8/19	27634	23435	993	44	216	75398	38	69	40	38	39	45	43	45	40	47	47	50	48	39	48	50	50	47	41	41
20/8/19	27698	23877	998	44	218	83713	38	70	40	39	40	46	43	47	41	47	48	51	49	40	49	52	52	50	42	42
20/8/19	27953	24390	1053	44	221	89576	38	71	40	40	40	46	44	48	42	48	49	51	50	40	50	51	52	50	42	42
20/8/19	27790	22313	1483	44	221	50715	39	68	41	39	41	45	44	46	40	48	47	50	49	38	49	49	51	51	39	40
20/8/19	27135	22226	1461	43	217	54887	40	69	40	39	41	46	45	46	40	49	48	51	50	39	50	52	52	40	40	
20/8/19	27143	22726	1456	43	220	62137	41	71	41	39	41	46	45	48	41	49	48	51	50	39	50	51	52	40	41	
24/4/19	27183	23203	1482	43	218	67940	41	70	41	39	41	46	45	47	41	49	48	51	49	39	50	52	52	40	41	
24/4/19	26830	23036	1463	42	217	71289	39	68	40	39	40	45	43	47	40	47	48	50	48	39	49	51	52	39	41	
24/4/19	27388	23753	1486	42	218	76969	40	71	41	39	41	45	44	47	41	49	47	51	49	38	49	52	55	39	41	
24/4/19	28229	23666	1010	43	219	63978	40	71	40	38	41	44	42	46	40	48	47	50	49	39	49	50	51	42	41	
24/4/19	27967	23622	991	44	218	68940	41	70	40	38	40	44	44	46	40	47	46	49	48	38	47	49	50	51	40	40
24/4/19	27908	23269	1007	44	218	72260	39	70	40	38	41	44	42	46	40	48	46	51	48	38	48	50	50	41	41	
19/7/18	27461	23402	1021	44	218	76623	39	69	40	38	41	45	43	47	40	47	46	49	48	38	48	50	50	40	41	
19/7/18	27932	23740	1084	44	219	81687	39	70	40	39	41	45	45	45	40	47	47	50	49	39	48	51	51	50	41	
19/7/18	28929	23761	1107	44	219	85190	39	71	41	39	41	45	44	48	41	49	48	51	49	40	49	50	52	51	42	
Mean	27523	24486	841	43	217	62259	37	70	40	39	41	45	44	47	40	47	47	50	49	39	49	50	51	49	41	
Std. Dev.	1640	2175	157	2	13	14399	2	3	2	2	2	2	3	3	2	3	3	3	3	2	3	3	3	2	2	
RSD	6	9	19	6	6	23	7	5	6	6	5	6	6	6	6	6	6	6	6	6	6	6	6	6	6	

Table A.2 Analyses of Durango apatite (SDT0067) standard collected by LA-ICP-MS over the course of this study.

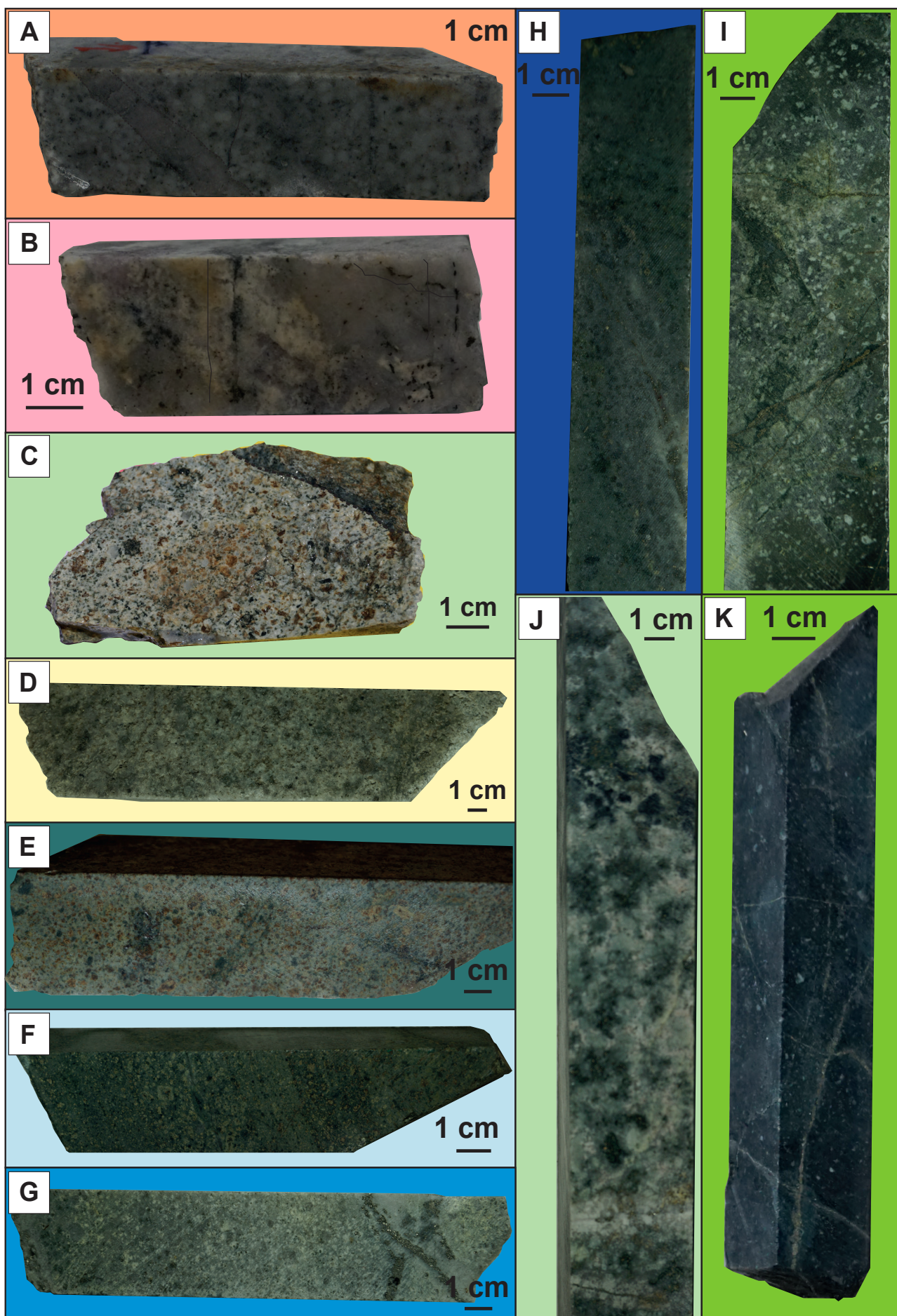
Date collected	Na (ppm)	Mg (ppm)	P (ppm)	V (ppm)	Mn (ppm)	Fe (ppm)	As (ppm)	Sr (ppm)	Y (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)	Yb (ppm)	Lu (ppm)	Pb (ppm)	Th (ppm)	U (ppm)
18/4/18	1530	119	1948 47	29.3	84.9	241	578	477	713	3393	5028	412	1282	184	16.9	161	20.4	112	22.1	60.0	7.5	42.0	4.9	0.6	215	11.8
19/4/18	1530	119	1948 47	29.3	84.9	241	578	477	713	3393	5028	412	1282	184	16.9	161	20.4	112	22.1	60.0	7.5	42.0	4.9	0.6	215	11.8
20/4/18	1517	116	2111 37	28.7	85.1	242	545	464	723	3485	5084	424	1264	177	16.5	156	19.9	113	23.1	62.1	7.6	41.9	4.8	0.6	219	12.3
21/4/18	1471	113	2128 28	29.1	85.7	246	561	470	723	3332	4840	401	1257	175	16.5	157	20.4	115	23.3	63.2	7.7	41.8	4.9	0.6	208	11.5
22/4/18	1487	115	2193 37	27.6	81.8	234	549	463	693	3327	4931	405	1223	173	16.2	150	19.4	108	21.5	58.2	7.0	39.0	4.6	0.6	211	11.7
23/4/18	1519	116	2113 35	28.7	84.6	242	544	462	720	3464	5036	423	1259	177	16.5	156	19.9	113	23.0	62.2	7.6	42.1	4.8	0.6	220	12.3
8/5/18	1520	108	2255 12	29.7	82.0	225	572	458	710	3467	4788	395	1240	178	16.0	158	20.4	115	23.2	64.3	7.8	44.8	5.0	0.7	222	12.3
9/5/18	1551	119	2565 88	28.6	87.1	207	578	502	752	3643	5133	442	1373	187	18.5	178	22.7	126	24.6	68.6	8.7	43.6	4.8	0.6	244	12.5
10/5/18	1572	118	2475 57	29.4	87.6	220	584	505	764	3742	5116	450	1389	194	18.9	182	22.9	127	25.4	69.5	8.7	44.5	4.9	0.6	240	12.6
11/5/18	1582	118	2191 71	32.0	87.2	253	578	516	814	3615	5035	450	1385	190	17.0	165	21.3	125	24.5	69.1	8.5	46.0	5.2	0.6	219	11.5
12/5/18	1526	117	1742 62	31.0	88.0	248	591	530	783	3509	5011	436	1376	190	17.4	169	21.8	121	24.8	66.7	8.5	44.4	5.2	0.6	221	11.7
13/5/18	1541	117	1931 19	30.6	87.1	252	587	521	778	3534	5018	440	1380	192	17.4	169	21.8	122	24.6	66.8	8.5	44.9	5.2	0.6	223	11.7
14/5/18	1484	113	2412 81	28.0	80.8	254	552	449	723	3512	4660	414	1256	188	16.7	158	19.6	111	22.5	61.3	7.9	43.8	5.1	0.6	218	11.5
15/5/18	1456	113	2253 58	28.0	82.0	254	549	452	721	3452	4598	403	1244	186	16.7	158	19.6	111	22.5	61.4	7.8	43.7	5.0	0.6	218	11.4
16/5/18	1489	114	2107 56	27.9	83.5	251	543	479	722	3629	4960	418	1209	173	16.1	159	20.3	113	23.6	63.5	7.7	40.5	4.7	0.6	214	11.7
8/5/18	1701	116	1985 70	29.2	90.9	277	609	521	791	3686	5328	452	1365	192	18.0	168	21.3	118	23.9	65.2	8.1	43.4	5.0	0.7	244	12.2
9/5/18	1509	109	1748 36	26.6	80.3	235	535	445	662	3478	5139	421	1257	184	16.2	144	18.5	106	22.2	61.6	7.6	41.3	4.6	0.7	223	11.7
10/5/18	1517	109	1746 67	26.7	81.1	235	539	446	663	3461	5133	421	1266	184	16.2	143	18.4	105	22.1	61.4	7.6	41.6	4.6	0.7	221	11.7
11/5/18	1817	123	1898 96	29.9	92.3	267	596	523	811	3594	5049	457	1488	210	17.8	165	21.7	120	24.4	68.2	8.3	47.3	5.3	0.8	233	12.5
12/5/18	1812	121	1877 47	29.8	91.9	266	589	520	810	3596	5034	455	1477	210	17.9	165	21.7	121	24.4	68.1	8.3	47.4	5.3	0.8	234	12.5
13/5/18	1636	108	1749 21	26.3	85.1	262	543	484	733	3567	5403	437	1262	174	15.9	158	20.7	116	22.3	60.1	7.4	40.4	4.6	0.6	241	12.6
14/5/18	1608	110	1707 80	27.4	82.0	240	554	530	746	3442	5040	420	1252	176	15.8	151	19.3	111	23.2	61.0	7.4	41.6	5.0	0.7	225	11.5
15/5/18	1641	113	1744 95	27.9	83.6	246	554	533	760	3475	5115	431	1283	178	16.2	153	19.7	113	23.5	62.3	7.6	42.4	5.1	0.6	227	11.5
19/7/18	1510	114	1761 96	28.6	86.5	243	587	479	706	3400	4776	408	1245	180	16.3	154	20.1	117	23.5	63.5	7.9	43.4	4.8	0.7	225	12.4
20/7/18	1479	108	1580 40	28.8	85.7	237	542	452	677	3376	4741	408	1270	181	16.8	160	19.5	110	21.4	56.6	7.2	40.6	4.6	0.7	226	12.0
21/7/18	1475	108	1627 90	28.8	86.2	235	544	447	672	3317	4670	403	1251	178	16.5	157	19.2	108	21.0	55.8	7.1	39.8	4.5	0.7	222	11.8
22/7/18	1467	112	1676 46	27.6	81.0	233	557	457	705	3433	4859	416	1284	179	16.6	153	19.7	112	22.2	59.8	7.2	40.2	4.6	0.7	230	12.2
23/7/18	1466	111	1641 78	27.5	81.0	235	558	459	705	3458	4881	421	1300	180	16.9	154	19.9	113	22.4	60.4	7.3	40.8	4.7	0.7	230	12.2
24/7/18	1486	110	1603 85	28.3	82.6	246	550	462	697	3525	4959	430	1353	189	17.5	165	20.7	119	23.5	61.9	7.6	43.1	4.9	0.7	234	12.3
25/7/18	1479	109	1623 24	28.2	82.7	243	550	457	694	3441	4829	419	1317	184	17.0	160	20.2	117	23.1	60.8	7.4	42.2	4.8	0.7	230	12.1
26/7/18	1428	106	1572 12	29.2	84.0	238	549	456	709	3404	4711	406	1265	178	16.6	156	20.2	116	23.3	61.6	7.3	41.4	4.8	0.7	228	11.8
27/7/18	1444	108	1630 91	29.2	84.1	240	552	461	712	3494	4830	418	1300	183	17.0	159	20.7	119	23.6	62.3	7.5	42.2	4.9	0.7	233	12.1

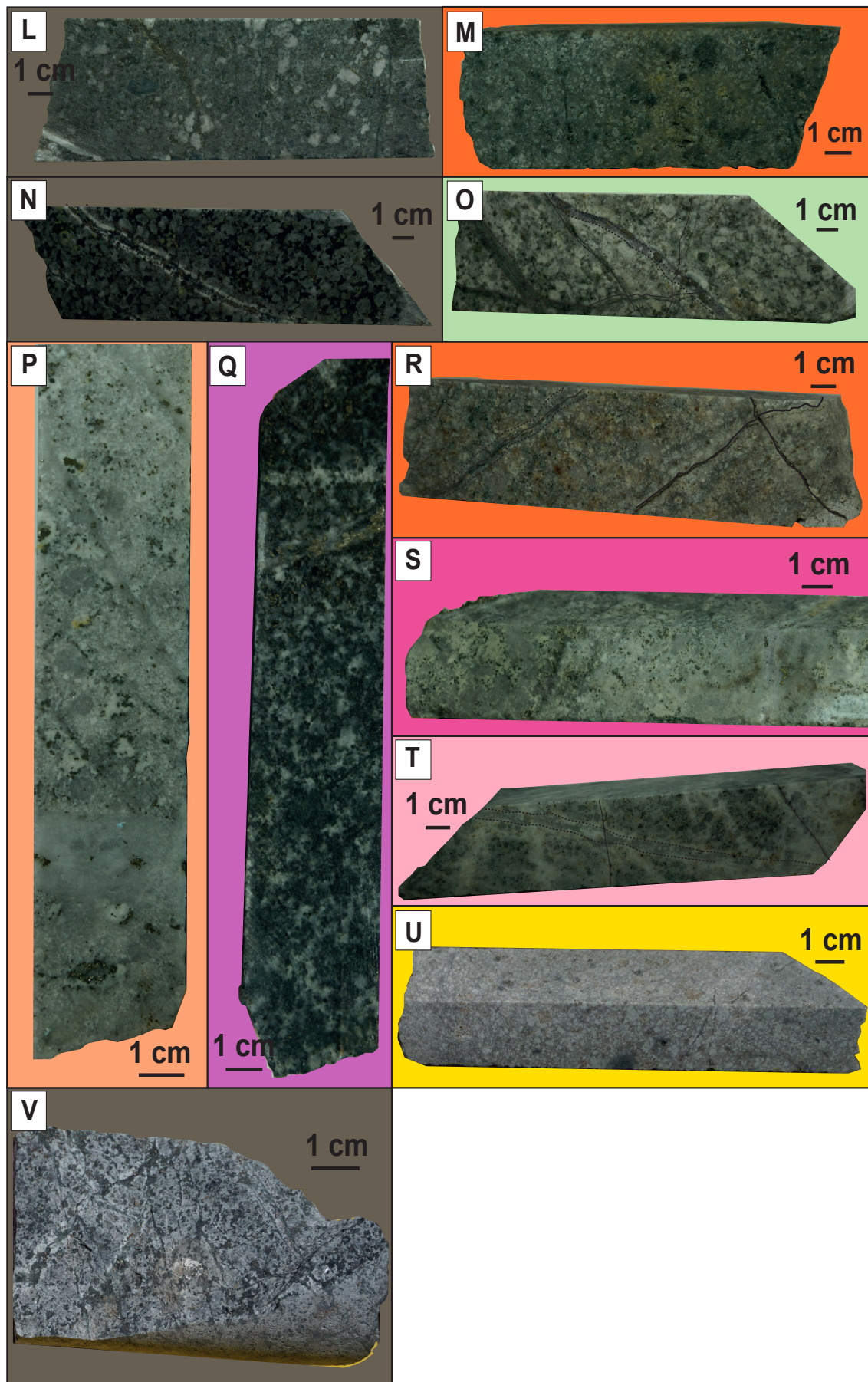
28/7/18	1546	116	179972	27.4	84.5	249	534	467	693	3478	4813	407	1249	178	16.6	155	20.1	112	22.6	61.1	7.5	41.8	4.7	0.7	242	12.8
29/7/18	1527	115	175336	27.5	84.9	250	535	466	693	3418	4716	400	1226	175	16.4	154	19.9	110	22.2	59.8	7.4	41.2	4.7	0.7	237	12.5
30/7/18	1480	110	158952	26.9	80.0	237	522	454	678	3309	4708	392	1205	175	15.6	146	19.0	111	23.0	63.0	7.9	42.8	4.9	0.7	217	11.4
3/7/18	2562	66	98455	25.3	56.4	158	500	421	625	2930	4096	342	1036	150	13.6	130	16.9	91	19.1	54.6	6.1	34.0	3.9	0.5	186	9.8
4/7/18	2180	87	136632	27.1	68.7	194	529	443	667	3171	4454	372	1132	163	14.9	142	18.6	102	21.0	58.4	6.7	38.0	4.3	0.6	202	10.7
5/7/18	1606	119	160339	30.1	86.3	256	589	488	766	3686	5052	435	1328	195	17.7	162	21.4	119	23.7	63.4	8.0	43.3	5.0	0.6	227	12.1
6/7/18	1650	123	141805	30.0	88.7	265	567	486	741	3494	4943	418	1252	186	16.9	156	19.7	113	23.5	64.3	7.7	43.3	5.0	0.6	221	12.5
7/7/18	1635	123	149146	30.0	87.7	266	563	484	738	3484	4920	418	1258	185	16.8	155	19.7	113	23.6	64.3	7.8	43.2	5.0	0.6	220	12.5
24/7/18	1993	116	159850	36.5	90.6	267	665	493	750	3763	5037	428	1367	189	16.9	168	21.8	123	24.7	66.7	8.2	45.3	5.2	0.8	237	13.9
25/7/18	1781	114	133895	36.8	90.4	283	658	478	768	3942	5327	445	1396	196	17.4	168	21.7	125	24.6	67.8	8.2	45.6	5.1	0.8	270	15.4
26/7/18	1790	115	138146	36.9	90.4	280	657	479	766	3939	5343	446	1396	196	17.4	168	21.8	125	24.7	67.9	8.3	45.6	5.1	0.8	271	15.5
27/7/18	1816	118	142384	37.2	90.4	270	646	488	763	3906	5331	450	1405	199	17.9	171	21.9	125	24.8	67.7	8.1	46.3	5.2	0.8	272	15.4
28/7/18	1816	118	142987	37.1	90.5	271	644	487	762	3905	5315	450	1406	198	17.9	171	21.9	125	24.7	67.5	8.1	46.3	5.2	0.8	271	15.3
29/7/18	1830	115	140353	36.1	91.1	283	597	473	766	3934	5294	449	1399	196	17.1	167	22.0	123	24.7	67.0	8.1	45.4	5.2	0.7	250	14.9
30/7/18	1828	115	140434	36.3	91.3	281	600	475	769	3960	5330	451	1402	197	17.1	168	22.1	124	24.8	67.6	8.2	45.5	5.2	0.7	251	15.0
31/7/18	1976	117	143178	37.2	89.2	274	617	485	750	3742	5046	429	1340	187	16.8	163	21.3	122	24.3	65.7	8.0	44.3	5.1	0.6	236	13.7
1/8/18	1878	118	148312	37.0	89.0	263	625	498	750	3770	5102	435	1354	191	16.8	166	21.3	121	24.0	65.5	8.1	44.8	5.2	0.7	240	14.2
2/8/18	1875	118	148292	37.0	88.8	269	622	497	750	3773	5105	435	1351	191	16.8	166	21.3	121	24.0	65.7	8.1	44.8	5.2	0.7	240	14.2
3/8/18	1915	119	151407	36.9	88.2	308	604	491	748	3794	5199	434	1318	191	17.1	162	21.0	117	23.9	63.9	7.9	44.2	5.1	0.7	237	13.8
4/8/18	1923	119	151491	37.0	88.3	295	601	491	750	3797	5214	435	1324	191	17.1	162	21.1	117	23.9	64.0	7.9	44.4	5.1	0.7	237	13.8
24/4/19	1541	116	193884	30.0	87.7	271	619	473	709	3360	4794	402	1291	183	17.4	156	20.7	116	23.1	62.5	7.6	42.7	4.7	0.6	217	12.2
25/4/19	1551	116	196871	29.5	86.1	273	609	468	691	3359	4836	404	1286	183	17.0	157	20.2	115	22.7	61.0	7.5	41.4	4.8	0.7	215	11.8
26/4/19	1569	118	203525	30.1	88.0	276	601	467	719	3422	4877	408	1311	183	17.3	160	20.6	116	23.4	62.4	7.7	42.9	5.0	0.7	219	12.1
27/4/19	1564	118	202972	30.0	88.4	288	596	468	714	3453	4808	409	1335	183	17.2	161	20.9	119	23.7	62.8	7.8	43.7	5.0	0.7	224	12.4
28/4/19	1563	117	213512	29.2	86.5	292	580	464	704	3430	4870	409	1323	182	17.2	162	20.7	117	23.0	62.1	7.7	42.6	5.0	0.6	221	12.4
29/4/19	1575	120	195661	29.5	88.9	267	616	481	714	3383	4900	416	1327	190	18.1	164	20.9	118	23.6	62.6	7.8	42.9	4.9	0.7	224	12.7
4/5/19	1571	111	175851	30.7	87.5	214	622	470	752	3537	4713	417	1380	199	17.6	172	21.9	124	25.1	67.9	8.4	46.4	5.3	0.7	240	12.8
4/5/19	1550	113	176418	30.5	87.9	222	610	470	744	3439	4563	405	1322	189	17.3	162	21.0	119	24.0	64.4	8.0	44.4	5.1	0.7	227	11.9
4/5/19	1624	114	180805	30.5	88.8	241	635	470	749	3471	4624	410	1332	188	17.5	167	21.4	120	24.4	67.3	8.2	44.6	5.2	0.7	229	12.5
4/5/19	1551	115	184664	30.0	88.0	254	603	467	750	3495	4614	412	1325	190	17.2	164	21.4	121	24.2	65.2	8.1	44.7	5.1	0.7	229	12.2
4/5/19	1558	117	190134	30.5	89.0	285	613	475	771	3581	4689	420	1347	192	17.5	168	21.7	123	25.0	66.8	8.2	45.5	5.2	0.7	235	12.6
4/5/19	1556	118	191310	30.1	88.9	281	609	478	771	3584	4676	423	1343	195	17.4	167	21.8	124	24.9	67.8	8.3	45.7	5.2	0.7	235	12.5
20/8/19	1679	113	219545	30.2	89.2	241	620	457	729	3460	4793	413	1336	187	17.7	168	21.2	117	23.4	64.4	7.8	43.5	4.9	0.7	227	12.4
20/8/19	1630	119	225608	30.0	89.7	243	646	467	718	3473	4877	429	1368	190	18.0	167	21.1	118	24.5	63.8	7.9	44.2	5.1	0.7	235	12.9
20/8/19	1637	114	226688	29.4	90.5	246	652	471	700	3455	4770	415	1330	187	17.2	162	20.7	115	23.6	63.3	7.7	44.8	4.9	0.7	225	12.6

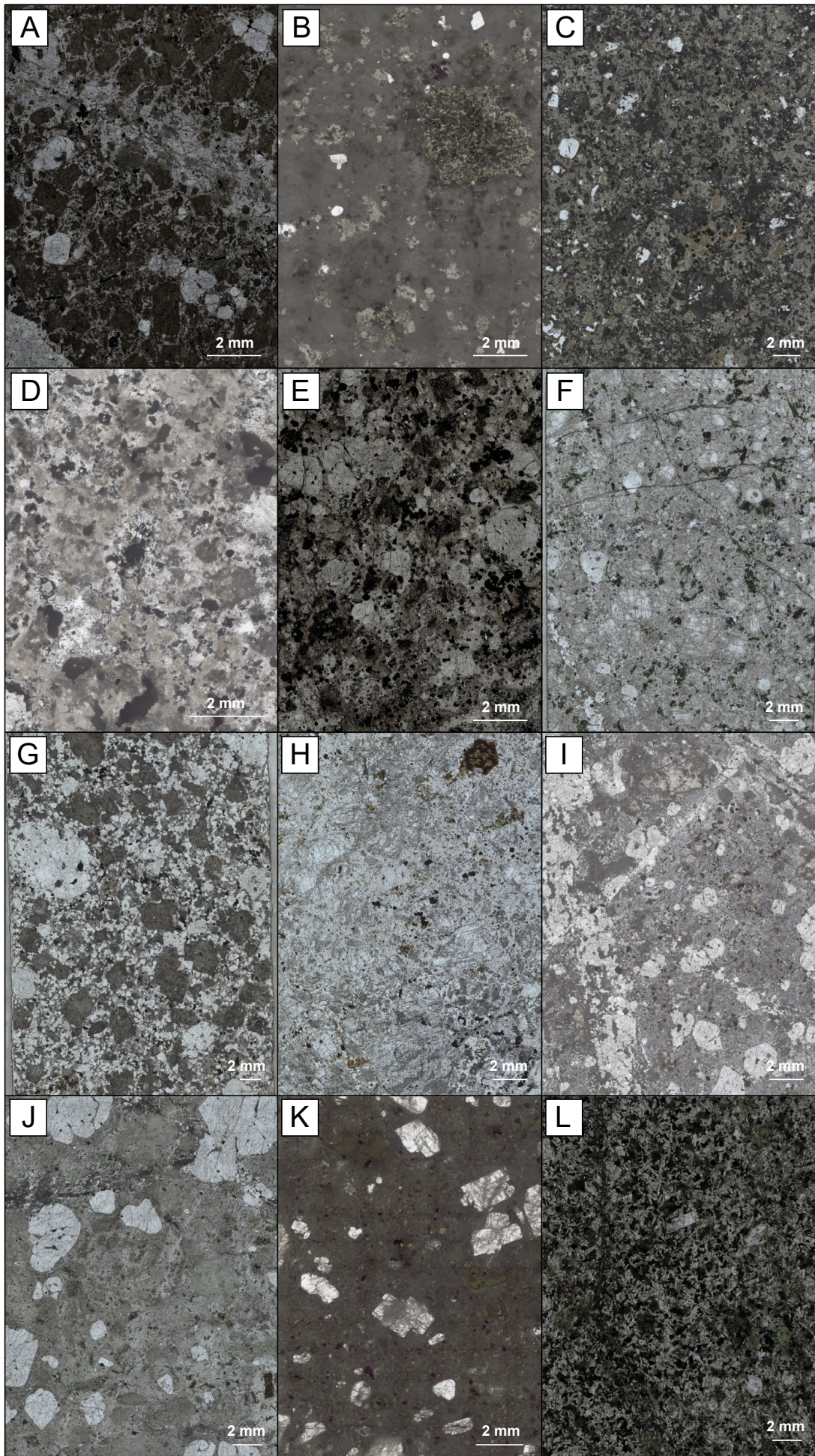
20/8/19	1681	120	231437	30.2	87.8	262	641	479	727	3539	4970	429	1333	188	17.6	162	21.5	120	23.9	65.5	8.0	44.5	5.1	0.7	228	12.9
20/8/19	1529	116	220745	28.7	87.3	266	624	462	700	3452	4739	422	1280	181	16.9	155	20.3	114	22.8	61.8	7.5	42.8	4.8	0.7	220	12.3
20/8/19	1598	123	226291	29.7	87.7	285	602	489	712	3494	4872	416	1279	184	17.2	157	20.1	113	22.6	62.3	7.6	43.5	4.8	0.7	220	12.1
MEAN	1634	114	182186	30.3	85.9	253	585	477	730	3532	4930	421	1309	186	17.0	160	20.6	116	23.4	63.5	7.8	43.2	4.9	0.7	229	12.5
Std. Dev	193	8	32203	3.2	5.2	25	38	23	37	188	240	20	72	9	0.8	8	1.1	6	1.1	3.3	0.5	2.3	0.3	0.1	15	1.1
RSD	12	7	18	10.6	6.1	10	7	5	5	5	5	5	6	5	4.7	5	5.3	5	4.9	5.2	5.8	5.2	5.1	7.5	7	8.8

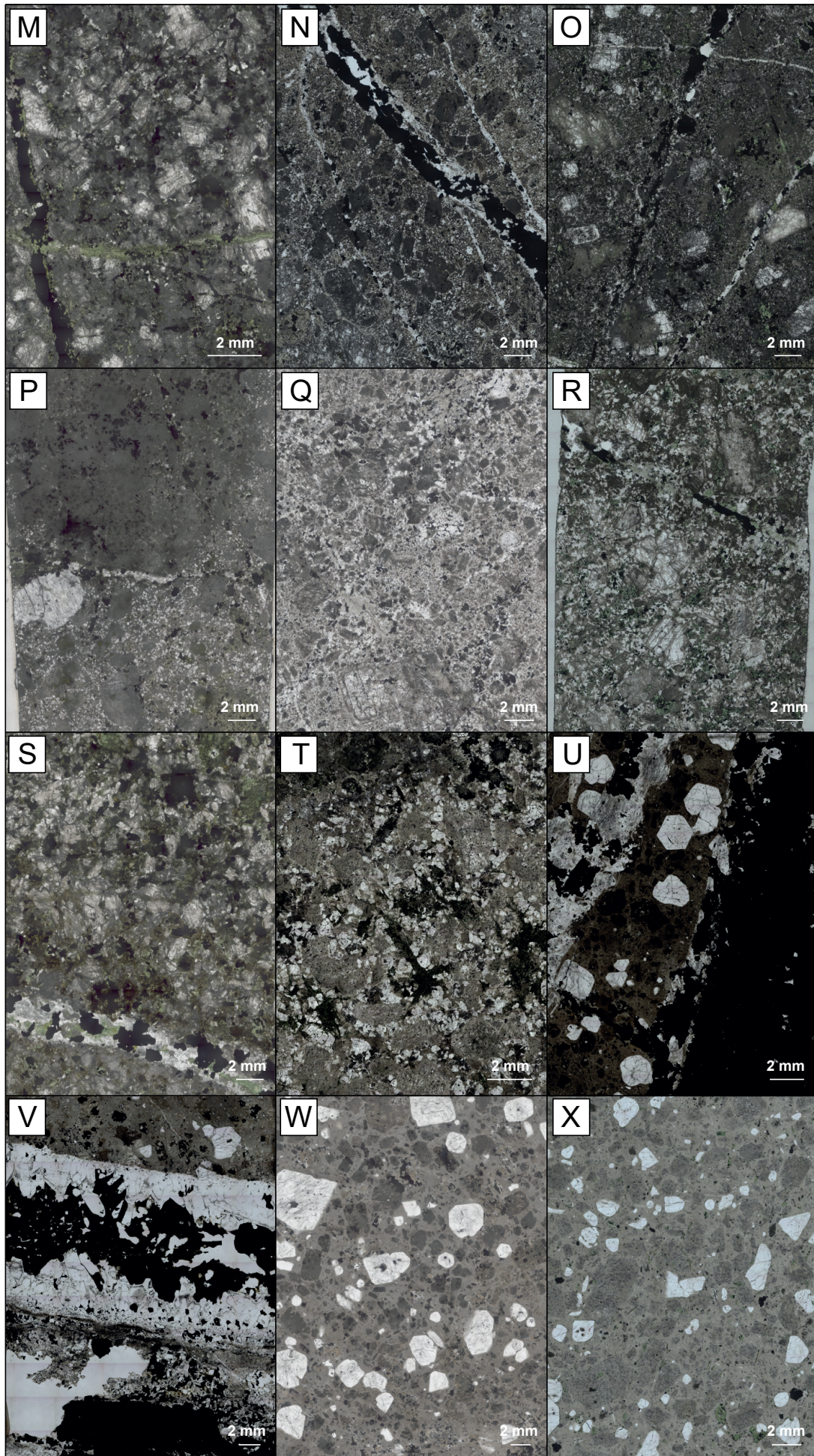
Appendix B: Hand sample photos and microphotographs of samples.

Figure B.1 Drill core sample photographs that illustrate the range of lithologies identified at La Granja. A) EDP_{PB} with thick quartz veins and early biotite veins (EB17001). B) EQP_M showing unidirectional solidification texture (EB17003). C) GRANO showing contact with diorite porphyry (DIOP). D) DP_{PB} containing little veining (EB17014). E) LQP_{PB} containing few veins (EB17005). F) LDP_{PB} with low vein abundance (EB17006). G) $LQP2_M$ with sulfide-bearing veins (EB17053). H) $LQP1_M$ (EB17052). I) Volcanic host rock with early potassic veins and sulfides (EB17059). J) GRANO containing D-veins (EB17044). K) AND (EB17060). L) DIOP (EB17033). EDP_{PB} (EB17009). N) DIOP cut by D-veins (EB17031). O) GRANO cut by A- and B-veins (EB17034). P) EDP_{PB} with quartz veins. Q) DIO (EB17043). R) EDP_{PB} (EB17016). S) EQP_M . T) EQP_{PB} (EB17022). U) DP_{PB} (EB17004). V) DIOP cut by early veins.









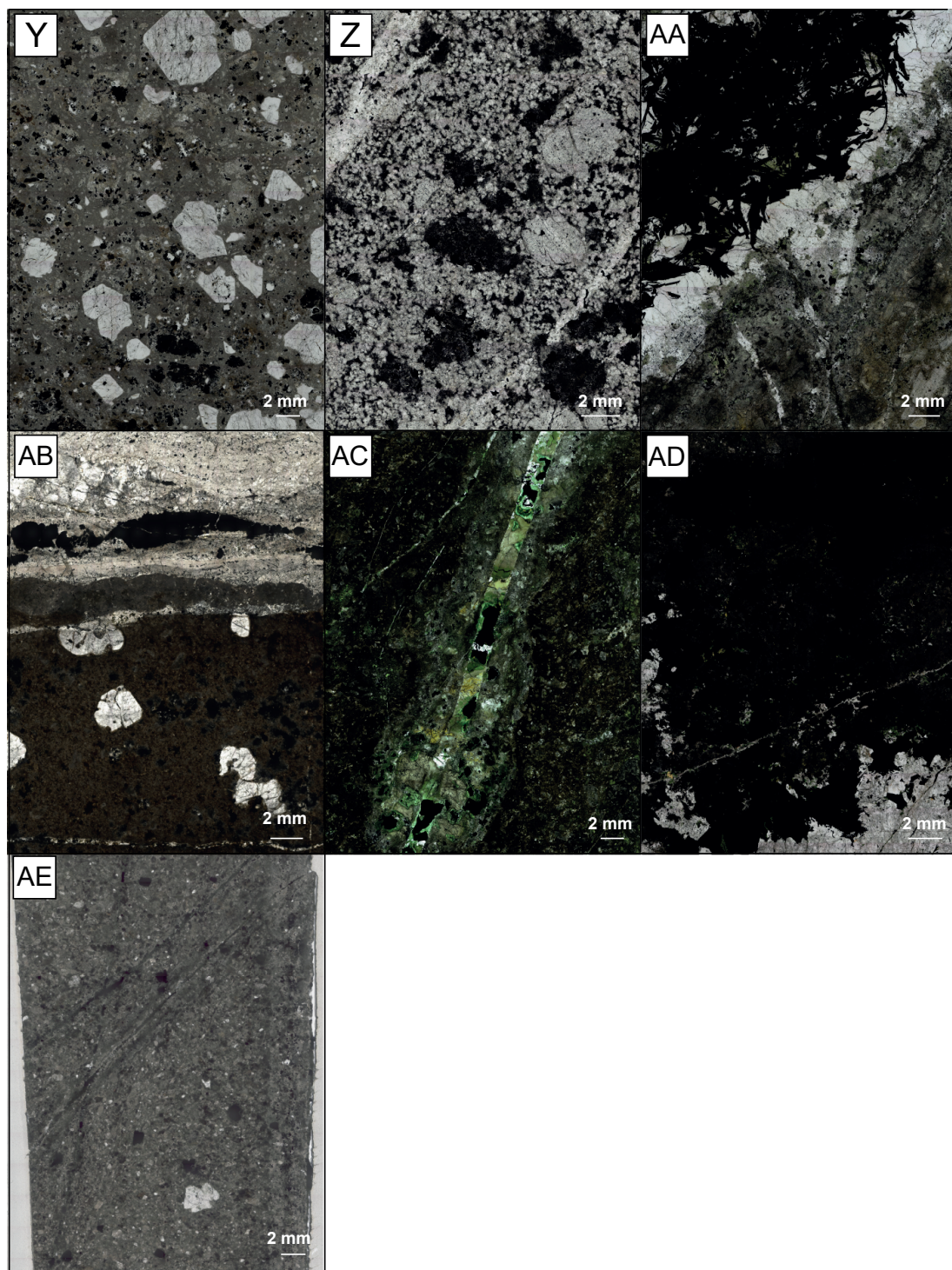
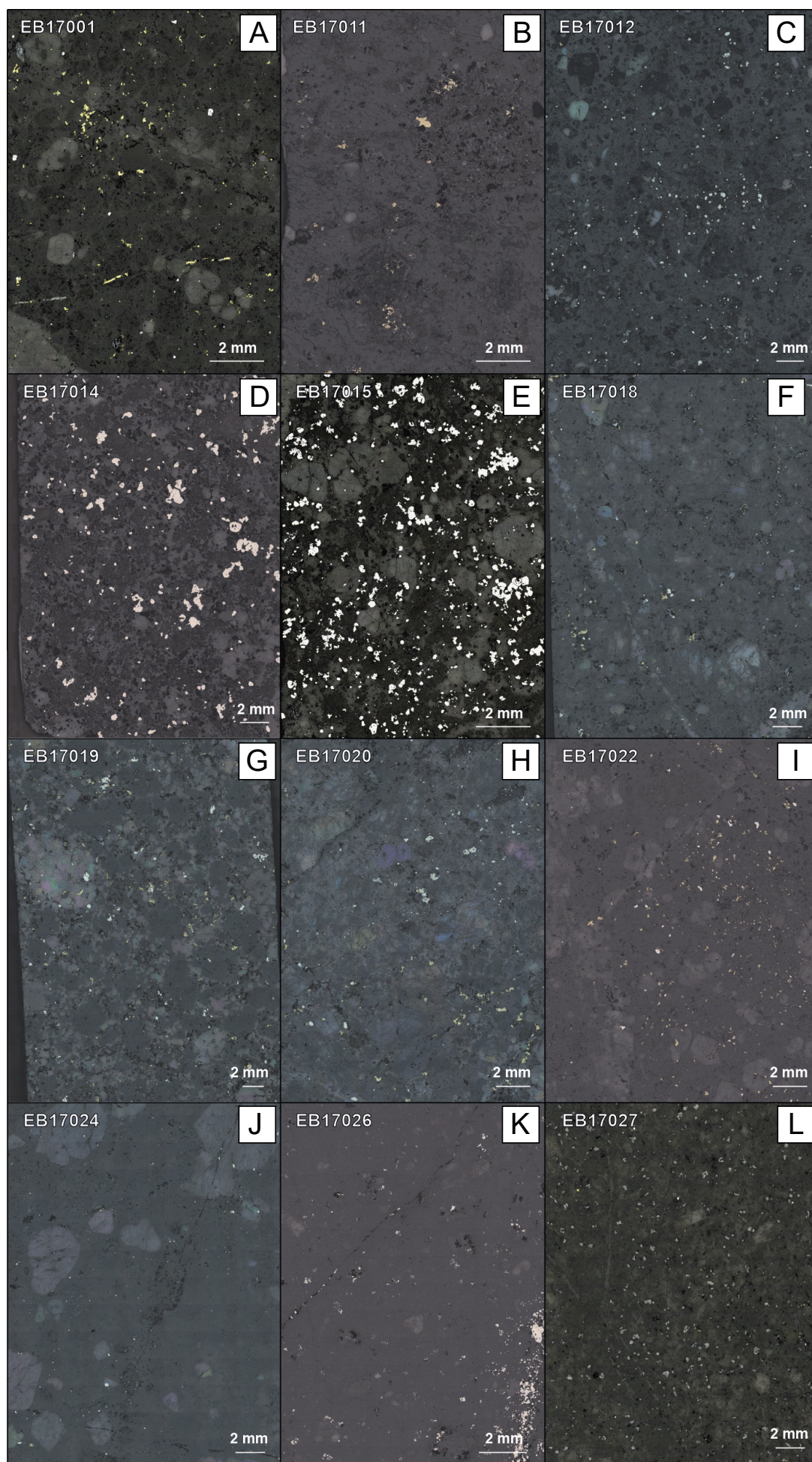
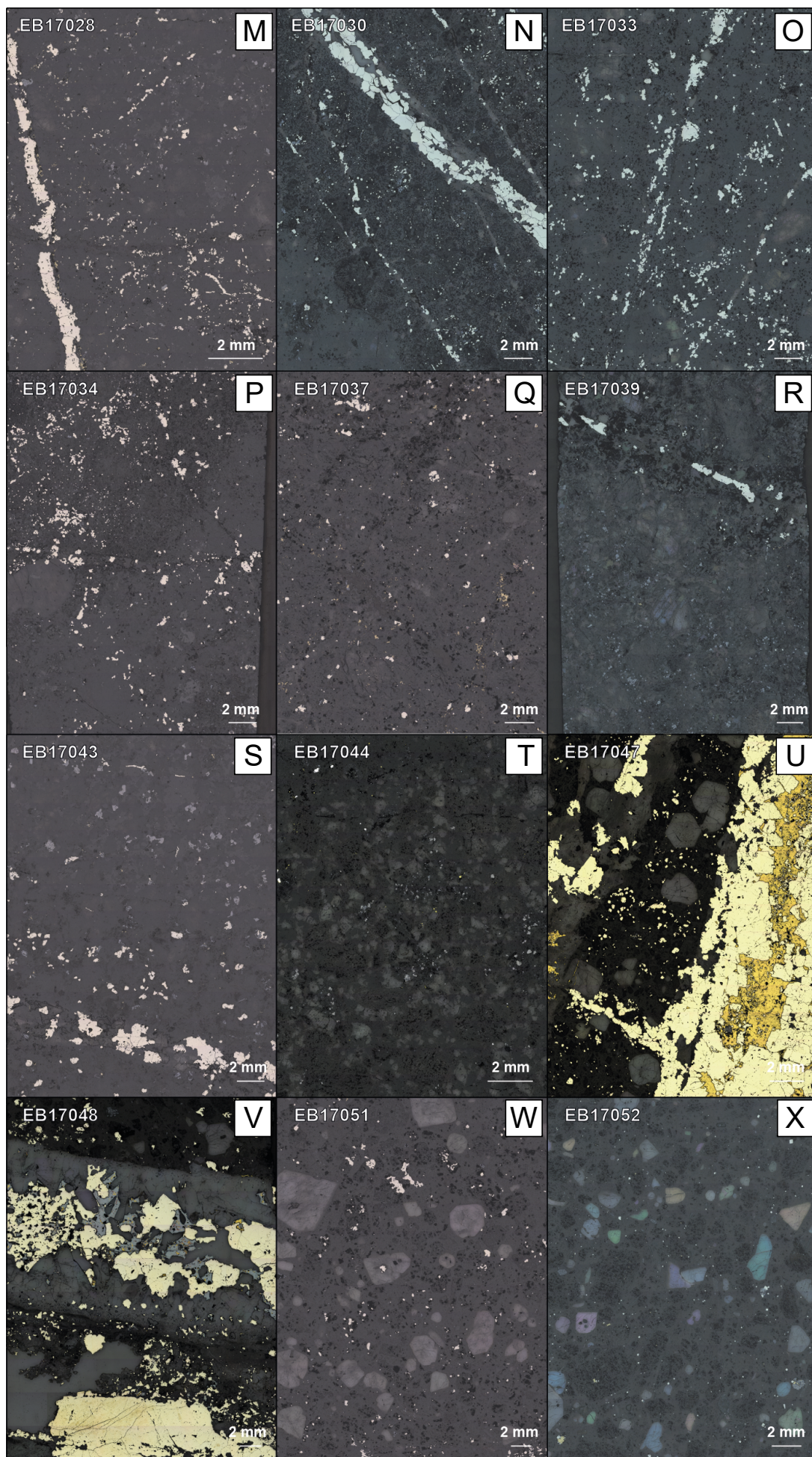


Figure B.2 Photomicrographs of thin sections viewed under plane polarized light. A) EDP_M - EB17001. B) Skarn - EB17011. C) DP_{PB} - EB17012. D) DP_{PB} - EB17014. E) DP_{PB} - EB17015. F) EDP_{PB} - EB17018. G) $EQPPB$ - EB17019. H) DP_{PB} - EB17020. I) EQP_{PB} - EB17022. J) EQP_{PB} - EB17024. K) AND - EB17026. L) DIO - EB17027. M) DIOP - EB17028. N) GRANO - EB17030. O) DIOP - EB17033. P) GRANO - EB17034. Q) EDP_{PB} - EB17037. R) DIOP - EB17039. S) DIO - EB17043. T) GRANO - EB17044. U) $LQP1_M$ - EB17047. V) $LQP1_M$ - EB17048. W) $LQP1_M$ - EB17051. X) $LQP1_M$ - EB17052. Y) $LQP1_M$ - EB17053. Z) EQP_M - EB17055. AA) DIO - EB17056. AB) AND - EB17058. AC) AND - EB17060. AD) AND - EB17061. AE) AND - EB17069.





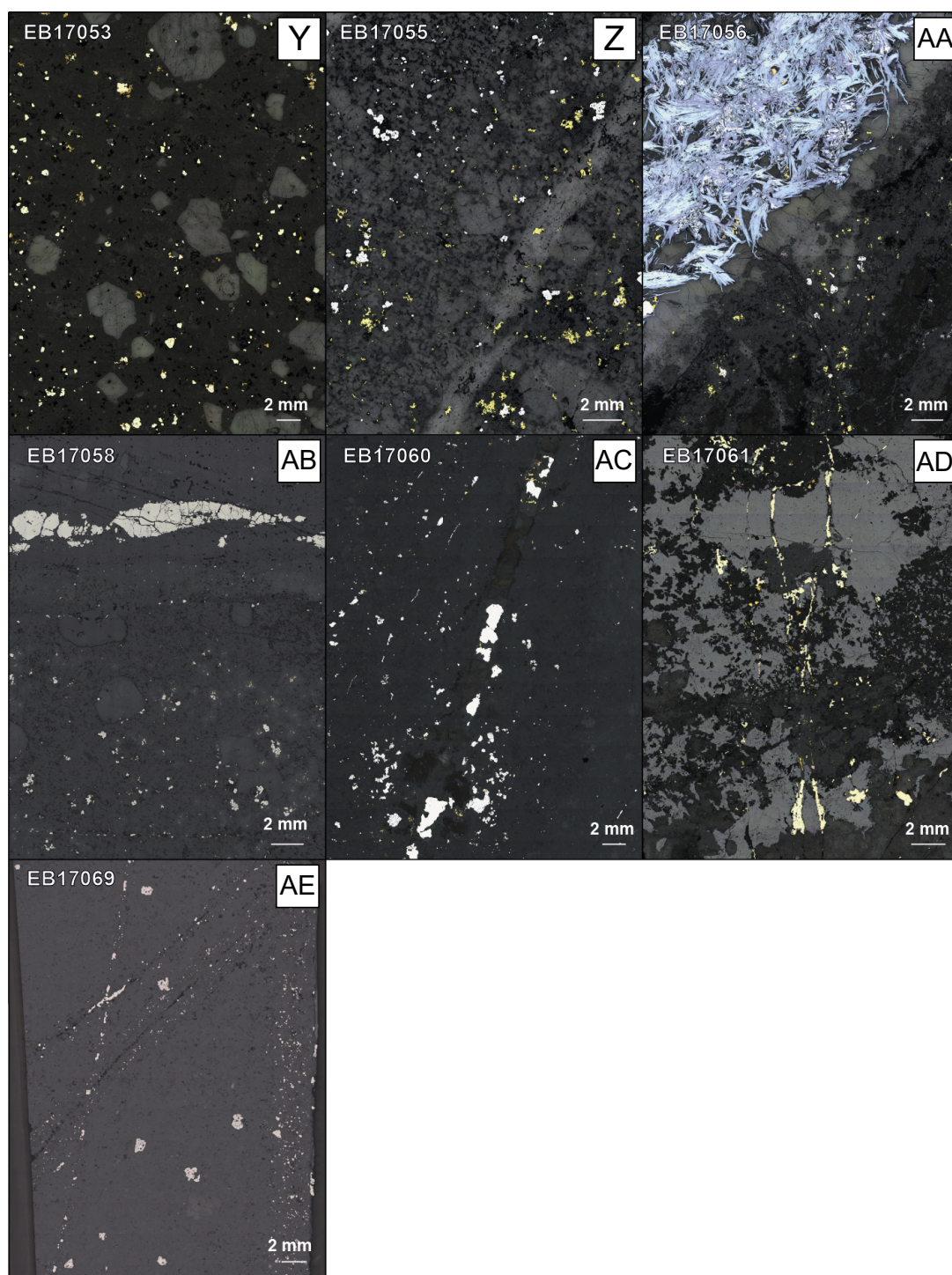


Figure B.3 Reflected light photomicrographs of thin sections. A) EDP_M - EB17001. B) Skarn - EB17011. C) DP_{PB} - EB17012. D) DP_{PB} - EB17014. E) DP_{PB} - EB17015. F) EDP_{PB} - EB17018. G) EQP_{PB} - EB17019. H) DP_{PB} - EB17020. I) EQP_{PB} - EB17022. J) EQP_{PB} - EB17024. K) AND - EB17026. L) DIO - EB17027. M) DIOP - EB17028. N) GRANO - EB17030. O) DIOP - EB17033. P) GRANO - EB17034. Q) EDP_{PB} - EB17037. R) DIOP - EB17039. S) DIO - EB17043. T) GRANO - EB17044. U) $LQP1_M$ - EB17047. V) $LQP1_M$ - EB17048. W) $LQP1_M$ - EB17051. X) $LQP1_M$ - EB17052. Y) $LQP1_M$ - EB17053. Z) EQP_M - EB17055. AA) DIO - EB17056. AB) AND - EB17058. AC) AND - EB17060. AD) AND - EB17061. AE) AND - EB17069.

Appendix C: Trace element zircon analyses se of this study.

Table C.1 Detection limit and analytical precision for zircon analyses by LA-ICP-MS. The detection limits are calculated as 3σ of the measured background. The analytical precision, given to two standard deviations, is calculated as the mean of the standard deviations that are above detection limits.

	Analytical precision $2\sigma^{\text{an}}$	Detection limit (ppm)
Zr	8553.19	0.077
Ti	0.54	0.167
V	0.05	0.058
Fe	4.62	4.189
Y	30.52	0.005
Nb	0.10	0.004
La	0.02	0.003
Ce	0.99	0.005
Pr	0.02	0.003
Nd	0.28	0.052
Sm	0.38	0.027
Eu	0.15	0.009
Gd	1.20	0.028
Tb	0.31	0.004
Dy	3.10	0.018
Ho	1.05	0.004
Er	4.99	0.018
Tm	1.03	0.004
Yb	9.83	0.028
Lu	2.03	0.005
Hf	233.97	0.021
Ta	0.04	0.004
Pb	0.15	0.030
Th	9.10	0.007
U	8.62	0.004

Table C.2 Representative compositions of zircon cores from LA-ICP-MS analyses by lithology for number of analyses (n). The minimum (Min.) and maximum (Max.) of results for each lithology is given as well as the calculated mean and associated standard deviation (Sd.).

ppm	GRANO (n = 15)				DP _M (n = 10)				EQP _{PS} (n = 3)				DP _{PS} (n = 9)				EDP _{PS} (n = 7)				DIOP (n = 10)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Zr	440000	492000	457873	13587	447000	474000	459610	9678	451000	486000	465000	18520	418500	455000	430166	11756	402400	445000	423885	18972	416000	466800	442060	18599
Ti	2.6	6.1	4.8	1.1	2.0	6.6	4.1	1.5	3.0	3.6	3.3	0.3	1.8	3.2	2.5	0.4	1.8	4.6	3.3	1.0	2.8	4.4	3.5	0.5
V	0.1	0.8	0.4	0.2	0.0	0.2	0.1	0.1	0.1	0.3	0.2	0.1	0.1	0.1	0.1	0.0	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.0
Nb	0.6	3.4	1.4	0.7	0.3	2.5	1.1	0.7	0.7	2.1	1.2	0.7	0.4	1.0	0.6	0.2	0.4	1.5	0.7	0.4	0.5	1.3	0.9	0.2
Y	698.0	2000.0	1237.7	441.9	296.0	1670.0	743.2	420.9	391.0	710.0	570.3	163.2	338.0	538.0	437.6	74.3	345.0	662.0	440.1	109.3	323.0	820.0	538.6	140.4
Ce	7.6	27.4	11.6	5.5	6.6	27.6	15.0	7.4	10.4	20.3	14.6	5.1	8.3	14.5	11.3	2.0	7.9	23.2	12.2	5.4	12.4	24.7	16.2	3.8
Pr	0.0	0.3	0.1	0.1	0.0	0.4	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.1	0.1	0.0
Nd	0.3	2.9	1.4	0.9	0.4	6.2	1.5	1.7	0.6	1.0	0.8	0.2	0.3	1.4	0.6	0.3	0.5	2.6	1.0	0.7	0.4	2.2	1.1	0.6
Sm	1.1	6.2	2.9	1.4	1.2	10.6	2.9	2.8	1.2	2.1	1.7	0.4	1.1	2.8	1.6	0.6	1.3	4.7	2.1	1.2	1.3	3.7	2.2	0.8
Eu	0.2	1.5	0.6	0.3	0.5	4.3	1.3	1.1	0.6	0.9	0.7	0.2	0.4	1.0	0.6	0.2	0.5	1.6	0.8	0.3	0.5	1.2	0.8	0.2
Gd	8.1	35.6	18.3	8.3	6.1	44.9	14.7	11.3	7.0	11.5	9.5	2.3	5.4	12.4	7.9	2.2	6.9	16.4	9.3	3.3	6.4	16.8	10.5	3.1
Tb	3.3	11.9	6.5	2.7	1.9	12.4	4.5	3.1	2.3	3.5	3.1	0.7	1.9	3.5	2.5	0.5	2.1	4.5	2.8	0.8	2.0	5.0	3.2	0.9
Dy	47.2	153.0	88.6	34.8	22.1	140.1	55.8	35.0	29.4	48.0	39.5	9.4	23.2	42.7	32.3	6.6	25.5	52.4	33.6	9.1	24.7	61.4	40.2	10.5
Ho	20.1	59.0	35.8	13.2	8.4	49.1	21.3	12.3	11.7	19.6	15.9	4.0	9.4	15.8	12.4	2.3	10.2	19.7	13.1	3.2	9.4	22.6	15.4	3.7
Er	114.5	312.0	192.8	67.6	45.5	242.0	112.1	60.4	61.9	116.0	89.6	27.1	54.1	82.2	67.4	11.6	54.6	96.9	68.5	14.2	49.6	123.5	81.9	20.4
Tm	26.6	69.0	42.9	14.0	10.2	51.3	25.6	12.7	14.7	29.1	21.3	7.3	13.1	19.5	15.8	2.4	12.7	21.6	15.9	3.0	10.9	26.5	18.7	4.3
Yb	273.3	682.0	429.4	129.3	112.0	502.0	268.2	122.7	159.0	329.0	235.0	86.4	141.0	217.0	171.0	26.7	138.9	226.6	170.2	30.4	115.5	271.0	194.9	42.7
Lu	55.2	148.3	93.0	27.5	28.7	110.8	62.6	26.4	36.8	74.0	54.6	18.7	35.0	51.4	41.0	5.6	32.4	49.6	39.8	6.0	26.8	61.4	44.8	9.5
Hf	10100.0	11360.0	10644.7	397.1	9270.0	12020.0	10927.0	741.1	11800.0	13160.0	12260.0	779.5	10580.0	11370.0	10948.9	292.3	9270.0	11120.0	10522.9	743.5	9620.0	11870.0	11041.0	703.9
Ta	0.3	1.3	0.6	0.2	0.2	0.5	0.3	0.1	0.3	1.1	0.6	0.4	0.2	0.4	0.3	0.1	0.2	0.5	0.3	0.1	0.2	0.5	0.3	0.1
Pb	3.3	16.8	6.4	3.4	0.8	2.5	1.3	0.5	1.2	3.9	2.9	1.5	1.0	1.6	1.3	0.2	0.6	2.6	1.2	0.7	0.7	1.6	1.1	0.3
Th	101.0	787.0	220.8	182.2	27.5	258.0	76.1	66.8	59.4	221.0	156.8	85.8	42.0	85.0	62.5	14.8	26.7	218.0	75.2	66.1	45.7	131.9	72.1	25.6
U	500.0	2560.0	978.6	514.3	206.0	723.0	370.0	158.9	357.0	1220.0	915.7	484.5	319.0	494.0	385.9	54.9	190.0	806.0	383.7	208.0	105.8	552.0	316.6	128.5

<i>ppm</i>	EDP_M (n = 8)				LQP_{Pg} (n = 9)				LQP_{1M} (n = 33)				LQP_{2M} (n = 23)				LDP_{Pg} (n = 7)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
<i>Zr</i>	395000.0	445200.0	429025.0	16832.4	439000.0	501000.0	461577.8	21040.5	389800.0	493000.0	423954.5	20956.2	396400.0	467000.0	424800.0	18674.4	399700.0	427800.0	412885.7	9855.5
<i>Ti</i>	2.0	4.7	2.9	1.1	2.2	5.2	3.2	0.9	2.4	7.2	4.2	1.1	1.6	5.6	3.0	1.0	2.0	5.6	3.4	1.2
<i>V</i>	0.0	0.4	0.1	0.1	0.0	0.1	0.1	0.0	0.1	0.4	0.1	0.1	0.1	0.4	0.2	0.1	0.1	0.4	0.2	0.1
<i>Nb</i>	0.4	2.8	0.8	0.8	0.4	1.5	0.7	0.3	0.3	6.2	1.2	1.1	0.5	1.8	1.1	0.4	0.3	1.7	0.9	0.5
<i>Y</i>	271.0	940.0	453.9	210.9	336.0	1050.0	539.0	224.4	215.0	3890.0	667.2	635.4	339.0	959.0	598.2	149.6	262.7	739.0	513.2	187.3
<i>Ce</i>	9.4	17.1	11.7	2.8	7.7	26.5	14.4	5.5	6.4	162.0	20.0	26.6	8.5	29.8	19.6	5.8	8.1	30.2	17.3	8.3
<i>Pr</i>	0.0	0.1	0.0	0.0	0.0	0.1	0.1	0.0	0.0	0.6	0.1	0.1	0.0	0.2	0.1	0.0	0.0	0.1	0.1	0.0
<i>Nd</i>	0.3	1.8	0.9	0.5	0.5	2.9	1.3	0.8	0.3	10.9	1.5	1.9	0.6	3.2	1.3	0.7	0.3	1.6	1.1	0.4
<i>Sm</i>	0.9	2.9	1.8	0.7	1.4	5.0	2.6	1.3	0.9	20.6	2.9	3.4	1.2	6.1	2.8	1.1	1.0	3.4	2.3	0.8
<i>Eu</i>	0.3	1.1	0.7	0.3	0.5	2.1	1.0	0.6	0.4	8.1	1.2	1.3	0.5	1.8	1.0	0.4	0.4	1.3	0.9	0.3
<i>Gd</i>	4.7	12.7	8.6	3.0	6.4	23.3	11.4	5.8	4.6	93.0	13.7	15.1	6.2	24.9	13.0	4.5	5.2	17.3	11.0	4.1
<i>Tb</i>	1.5	4.5	2.7	1.0	2.0	6.9	3.4	1.6	1.4	27.3	4.1	4.4	1.9	6.9	3.9	1.2	1.6	4.7	3.2	1.1
<i>Dy</i>	20.2	68.1	33.8	15.3	24.7	82.3	41.3	18.6	16.6	324.0	51.6	52.9	24.4	80.7	47.2	13.2	20.1	59.0	40.1	14.8
<i>Ho</i>	7.9	29.7	13.6	6.9	9.4	30.0	15.4	6.6	6.7	119.0	19.7	19.5	9.5	29.4	17.7	4.7	7.7	21.6	14.9	5.4
<i>Er</i>	43.6	181.0	75.2	44.3	51.1	154.0	79.8	32.0	35.4	570.0	103.3	93.3	52.3	144.7	91.0	22.3	41.9	110.1	78.2	27.0
<i>Tm</i>	10.5	44.8	17.7	11.2	12.2	32.1	17.7	6.3	8.0	117.0	22.7	19.1	12.5	30.7	20.1	4.5	9.1	23.8	17.1	5.9
<i>Yb</i>	111.2	496.0	189.8	126.0	131.0	316.0	184.8	60.2	89.0	1090.0	234.3	178.6	131.9	303.0	204.0	42.1	96.5	237.3	177.0	58.1
<i>Lu</i>	26.2	110.0	43.4	27.4	30.0	70.2	42.1	12.6	21.2	208.0	53.3	34.4	32.3	65.6	46.8	8.9	21.0	52.0	39.5	12.7
<i>Hf</i>	9750.0	12830.0	11336.3	919.6	10430.0	13130.0	11471.1	886.2	9730.0	13010.0	11065.8	766.4	10480.0	12840.0	11707.8	644.0	9410.0	12580.0	11285.7	1020.7
<i>Ta</i>	0.1	1.5	0.3	0.5	0.1	0.3	0.2	0.1	0.1	1.0	0.3	0.2	0.2	0.4	0.3	0.1	0.1	0.4	0.3	0.1
<i>Pb</i>	0.6	7.5	1.6	2.4	0.5	1.8	1.0	0.4	0.5	9.0	1.6	1.6	0.7	2.5	1.4	0.4	0.5	1.8	1.1	0.5
<i>Th</i>	24.4	127.0	48.7	33.8	25.9	132.0	64.4	39.4	21.6	1630.0	134.6	280.9	29.0	168.0	90.3	36.7	30.5	188.0	77.8	57.1
<i>U</i>	208.0	2230.0	504.5	688.9	193.0	624.0	346.8	128.5	53.6	1030.0	173.1	177.5	123.5	741.0	262.8	141.8	59.6	206.8	126.9	60.4

Table C.3 Representative compositions of zircon rims from LA-ICP-MS analyses by lithology for number of analyses (n). The minimum (Min.) and maximum (Max.) of results for each lithology is given as well as the calculated mean and associated standard deviation (Sd.).

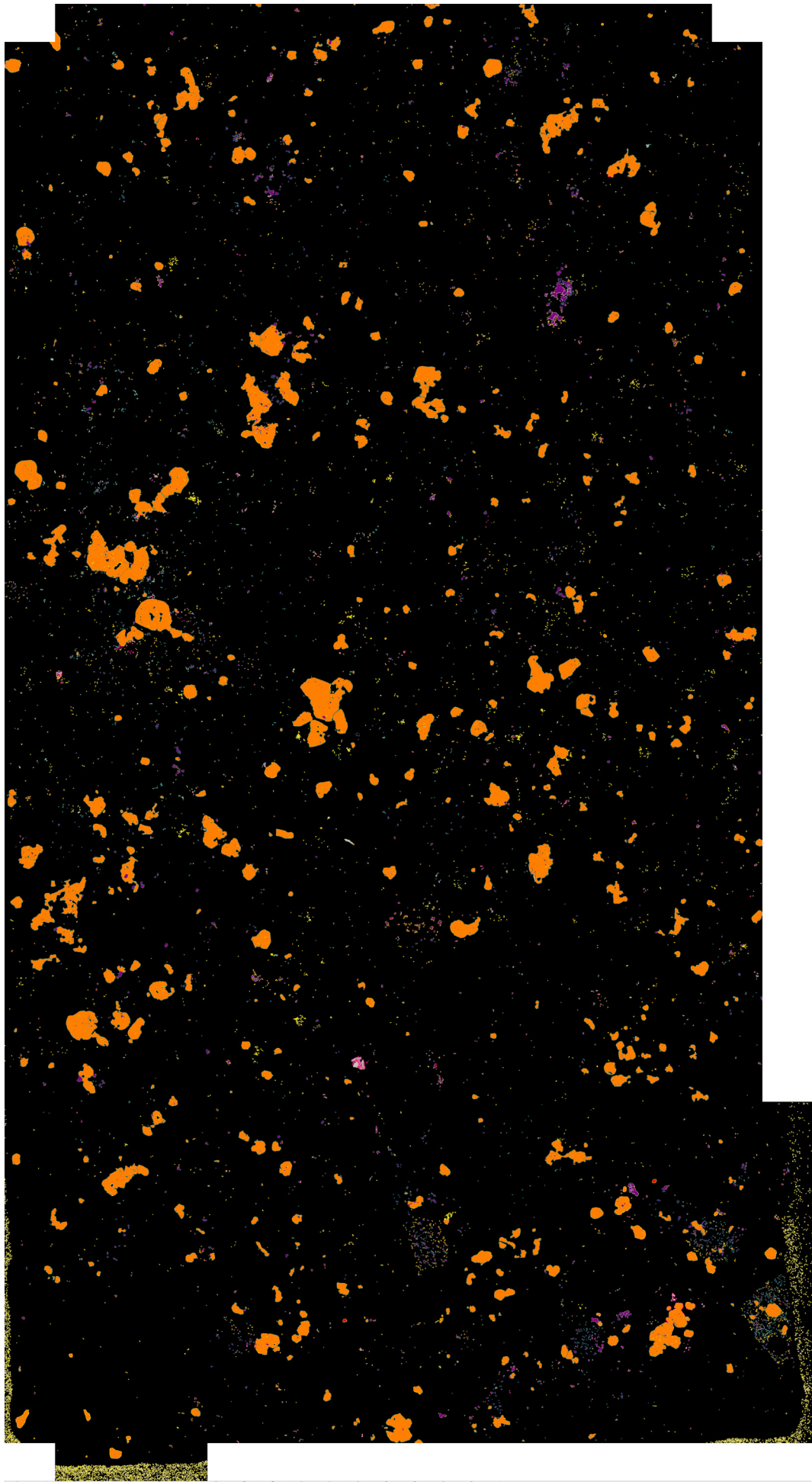
ppm	GRANO (n = 19)				DP _W (n = 35)				EQP _{FB} (n = 5)				DP _{FB} (n = 30)				EDP _W (n = 38)				DIOP (n = 10)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
Zr	437000	519000	468158	19594	426000	512000	462286	17664	460000	481000	470400	8385	426000	499000	458100	18516	436000	503000	469053	17099	415000	488000	451040	23445
Ti	2.8	9.1	5.6	1.6	2.7	7.6	4.0	0.9	1.9	8.5	3.9	2.7	1.9	4.8	3.1	0.6	2.5	6.1	4.1	0.8	2.6	5.7	3.7	1.2
V	0.0	1.0	0.3	0.2	0.1	0.2	0.1	0.0	0.1	0.2	0.1	0.1	0.0	0.2	0.1	0.0	0.1	0.3	0.1	0.0	0.1	0.2	0.1	0.0
Nb	0.7	2.6	1.2	0.4	0.3	3.8	1.4	1.1	0.9	5.3	2.7	1.9	0.4	2.4	1.1	0.4	0.3	2.6	0.8	0.4	0.7	3.6	1.3	0.9
Y	563.0	1447.0	919.8	277.2	184.7	1160.0	563.3	293.5	370.0	1826.0	1016.0	621.1	262.0	1055.0	528.4	167.9	232.6	1059.0	456.0	146.9	312.0	1265.0	542.9	281.1
Ce	6.4	18.7	9.9	3.1	4.8	37.3	14.8	9.1	11.6	46.6	22.3	14.0	8.3	33.9	16.1	6.4	6.8	35.0	13.5	5.3	11.2	54.2	20.6	12.7
Pr	0.0	0.6	0.1	0.1	0.0	0.2	0.0	0.0	0.0	0.2	0.1	0.1	0.0	0.2	0.0	0.0	0.0	0.3	0.1	0.0	0.0	0.2	0.1	0.1
Nd	0.4	3.2	1.0	0.7	0.1	3.1	0.9	0.7	0.4	3.3	1.1	1.2	0.2	4.4	0.8	0.7	0.3	1.9	0.8	0.4	0.4	3.7	1.2	0.9
Sm	0.9	4.0	2.0	1.0	0.7	5.1	2.0	1.1	1.2	8.6	3.0	3.1	0.7	6.9	1.8	1.1	0.8	3.3	1.7	0.6	1.0	7.3	2.4	1.8
Eu	0.3	0.8	0.5	0.2	0.3	1.9	0.9	0.5	0.3	4.2	1.2	1.7	0.3	2.4	0.7	0.4	0.3	1.4	0.7	0.2	0.4	2.9	0.9	0.7
Gd	6.9	24.9	13.4	5.4	3.4	21.1	10.2	5.3	7.4	47.0	18.4	16.5	4.3	27.2	9.3	4.1	4.1	18.6	8.7	2.9	5.5	35.2	11.8	8.6
Tb	2.5	8.6	4.8	1.8	1.1	6.0	3.2	1.6	2.3	13.1	5.9	4.4	1.3	7.4	2.9	1.1	1.3	6.0	2.6	0.9	1.8	10.2	3.6	2.4
Dy	39.6	117.4	68.5	23.7	13.8	82.0	41.9	21.3	28.7	152.3	77.3	51.7	17.9	84.6	38.5	13.4	16.7	75.8	34.0	10.9	23.7	113.8	43.9	26.2
Ho	17.1	44.9	27.9	8.9	5.2	32.0	15.9	8.2	10.6	53.0	29.6	18.2	7.1	29.9	14.9	4.9	6.5	29.4	13.1	4.1	9.3	40.1	16.4	9.1
Er	97.6	229.0	151.8	43.8	28.6	173.0	86.2	44.5	56.6	257.0	155.9	90.4	40.3	155.0	82.8	24.9	36.6	158.0	71.3	21.8	49.8	188.5	84.6	40.9
Tm	21.9	47.6	33.1	8.7	6.5	39.9	19.6	10.0	12.8	52.5	34.7	18.8	9.8	33.4	19.0	5.2	8.6	35.6	16.1	4.8	11.5	39.1	18.5	8.4
Yb	217.1	462.0	331.8	79.8	74.2	411.0	211.1	105.4	139.6	519.0	358.4	184.7	112.9	340.0	207.8	52.4	94.5	374.0	173.7	49.6	117.2	365.0	190.8	77.8
Lu	45.9	93.9	71.2	16.1	18.3	95.4	48.5	23.4	31.5	107.4	76.4	36.3	27.1	77.1	48.6	11.5	22.2	83.8	40.1	10.9	25.3	76.3	41.8	15.7
Hf	10110.0	12050.0	10903.7	489.0	8920.0	12710.0	11298.6	798.4	10040.0	12420.0	11398.0	884.9	10640.0	12670.0	11673.0	509.1	9830.0	12720.0	11221.8	714.5	9750.0	12370.0	11423.0	774.9
Ta	0.4	1.0	0.6	0.1	0.2	1.0	0.4	0.3	0.3	2.3	1.2	1.0	0.2	0.7	0.4	0.1	0.1	1.0	0.3	0.1	0.2	0.6	0.3	0.1
Pb	2.6	9.9	5.0	1.9	0.5	3.7	1.4	0.7	1.0	12.5	5.2	4.8	0.8	2.8	1.6	0.5	0.5	3.7	1.3	0.7	0.8	2.9	1.3	0.6
Th	66.8	562.0	157.9	110.3	23.1	326.0	87.0	60.1	50.2	375.0	205.3	127.5	32.6	247.0	84.2	46.3	19.1	327.0	84.2	68.3	41.1	311.0	102.6	86.1
U	130.6	503.0	249.5	92.3	46.1	376.0	135.7	70.6	111.7	600.0	336.6	193.7	89.3	291.0	158.8	50.7	52.3	414.0	139.9	76.8	85.2	326.0	141.6	69.8

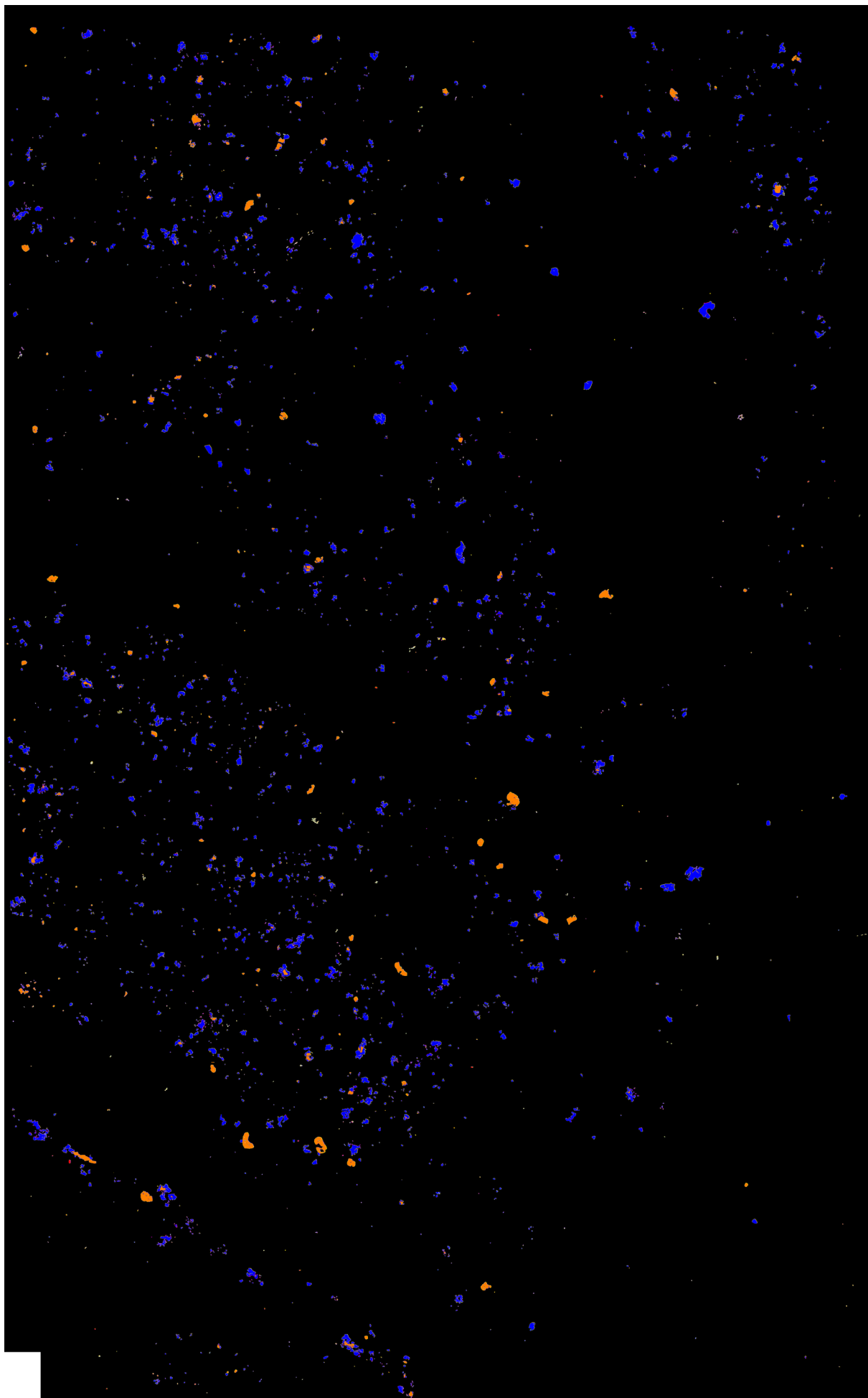
<i>ppm</i>	EDP_M (n = 40)				LQP_{PB} (n = 27)				LQP1_M (n = 39)				LQP2_M (n = 33)				LDP_{PB} (n = 8)			
	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.	Min.	Max.	Mean	Sd.
<i>Zr</i>	432000	496000	459625	16304	448000	499000	472111	13707	396300	491000	424197	17352	404300	503000	457585	29120	409100	456000	429475	15179
<i>Ti</i>	1.4	5.6	2.9	0.8	1.8	5.1	3.1	0.9	1.6	5.8	2.9	0.8	1.8	3.7	2.7	0.5	1.8	4.8	3.0	0.9
<i>V</i>	0.0	0.2	0.1	0.0	0.0	0.2	0.1	0.0	0.1	0.2	0.1	0.0	0.1	0.2	0.1	0.0	0.1	0.3	0.1	0.1
<i>Nb</i>	0.4	3.5	1.2	0.7	0.5	2.4	1.2	0.5	0.4	2.3	1.0	0.4	0.9	3.4	1.7	0.6	0.9	4.3	1.8	1.1
<i>Y</i>	132.0	1370.0	519.7	256.4	235.0	1070.0	514.7	210.2	152.7	991.0	373.2	185.1	322.1	960.0	615.8	186.2	284.7	843.0	540.0	201.5
<i>Ce</i>	8.2	52.4	21.2	9.6	11.1	44.5	20.5	8.4	8.0	36.9	17.2	6.4	13.6	45.1	27.0	8.4	14.5	73.5	30.4	19.9
<i>Pr</i>	0.0	0.2	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.1	0.0
<i>Nd</i>	0.3	4.5	0.9	0.8	0.4	4.2	1.0	0.7	0.2	2.9	0.7	0.5	0.4	2.1	1.0	0.4	0.3	2.5	1.1	0.6
<i>Sm</i>	0.5	9.6	2.2	1.6	0.7	8.3	2.1	1.4	0.4	5.5	1.5	0.9	1.0	4.6	2.4	0.9	1.1	5.2	2.6	1.2
<i>Eu</i>	0.2	3.5	0.9	0.6	0.4	2.5	0.8	0.4	0.2	2.1	0.6	0.4	0.4	1.6	0.9	0.3	0.4	1.5	0.9	0.3
<i>Gd</i>	2.4	40.7	11.2	7.5	4.1	34.1	10.8	5.8	2.7	25.3	7.7	4.5	6.1	22.0	12.8	4.5	5.4	21.3	12.2	5.0
<i>Tb</i>	0.7	10.5	3.3	2.0	1.3	8.8	3.2	1.5	0.8	7.0	2.3	1.3	2.0	6.3	3.9	1.3	1.7	5.8	3.5	1.4
<i>Dy</i>	8.9	120.0	41.0	22.8	17.6	96.0	40.2	17.5	11.0	83.0	28.9	15.2	24.9	77.8	48.7	15.5	22.0	64.9	42.7	15.8
<i>Ho</i>	3.5	40.2	15.0	7.6	7.0	32.2	15.0	6.2	4.5	29.9	11.0	5.5	9.6	28.9	18.1	5.4	8.3	24.0	15.6	5.7
<i>Er</i>	19.9	194.0	77.7	36.4	39.4	156.1	79.4	30.3	24.5	148.2	58.0	27.5	50.6	146.5	93.5	26.9	45.0	124.3	80.3	29.1
<i>Tm</i>	5.0	40.4	17.0	7.5	8.8	32.2	17.4	6.3	5.6	31.4	12.9	5.8	11.5	31.7	20.2	5.5	10.1	26.3	17.2	6.1
<i>Yb</i>	64.0	405.0	178.9	72.6	98.5	337.0	182.9	63.2	60.7	311.0	133.8	57.9	115.5	311.0	206.4	54.8	104.6	264.0	176.8	61.4
<i>Lu</i>	17.6	77.0	38.7	14.1	22.3	81.9	40.8	13.9	14.3	68.6	30.6	12.9	26.7	67.7	45.5	11.0	22.8	55.8	38.5	13.7
<i>Hf</i>	10620.0	13590.0	12335.5	694.3	11030.0	14500.0	12600.4	826.9	10960.0	13890.0	12271.3	731.5	11820.0	13970.0	12986.1	552.5	10720.0	13970.0	12730.0	999.8
<i>Ta</i>	0.1	0.6	0.3	0.1	0.2	0.5	0.3	0.1	0.2	0.6	0.3	0.1	0.2	0.9	0.4	0.1	0.3	0.7	0.4	0.1
<i>Pb</i>	0.7	4.6	1.6	0.9	0.8	6.3	1.5	1.0	0.6	3.5	1.3	0.6	0.8	4.6	1.8	0.8	1.0	5.4	2.0	1.4
<i>Th</i>	36.7	454.0	126.6	100.2	44.9	488.0	119.9	96.0	21.1	322.6	91.8	64.9	33.0	319.0	139.8	79.0	44.1	831.0	221.9	254.7
<i>U</i>	83.7	515.0	192.2	106.3	82.4	776.0	175.6	128.5	60.6	355.6	140.1	59.4	98.9	542.0	219.5	92.9	116.3	735.0	260.4	198.7

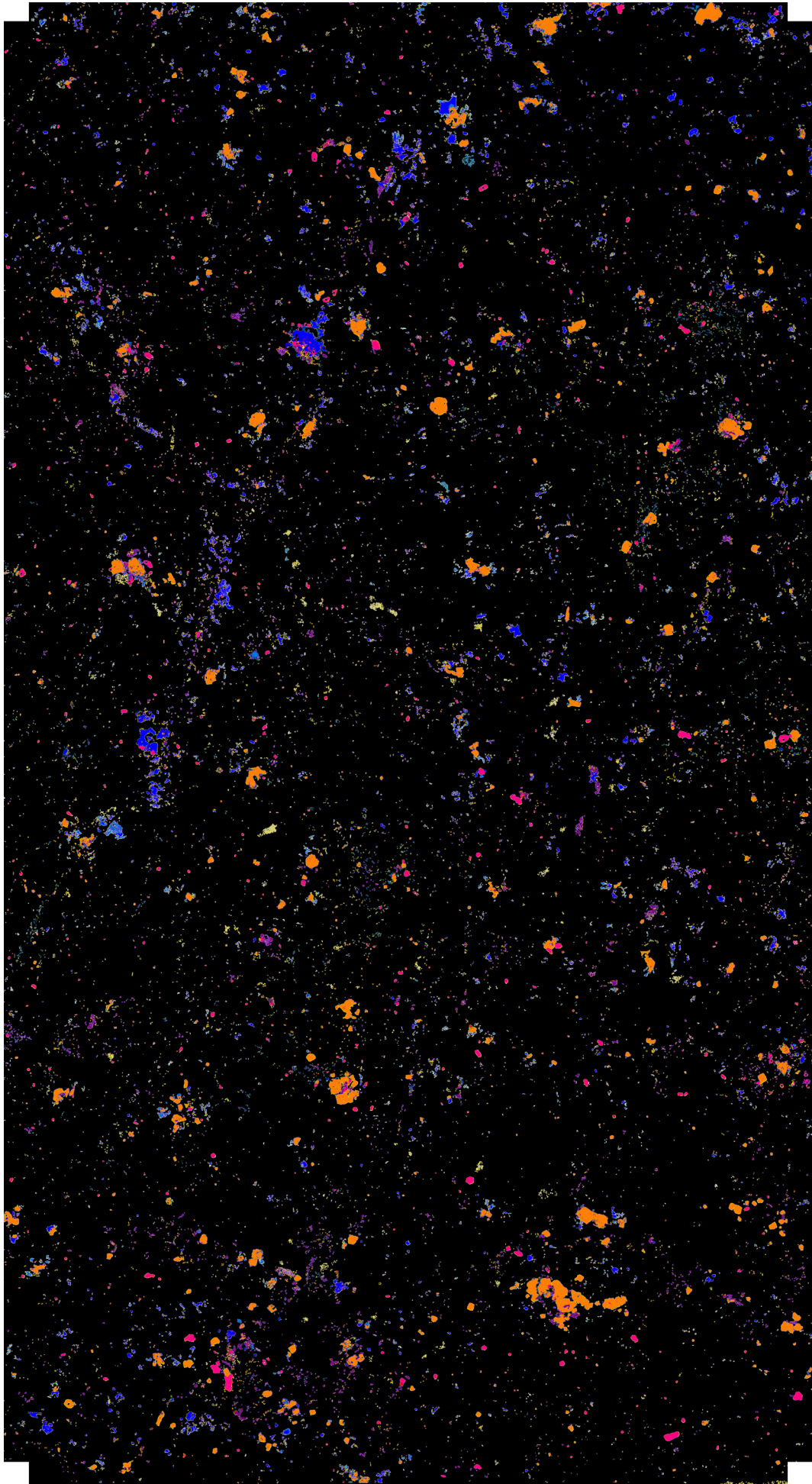
Appendix D: Automated SEM methodology

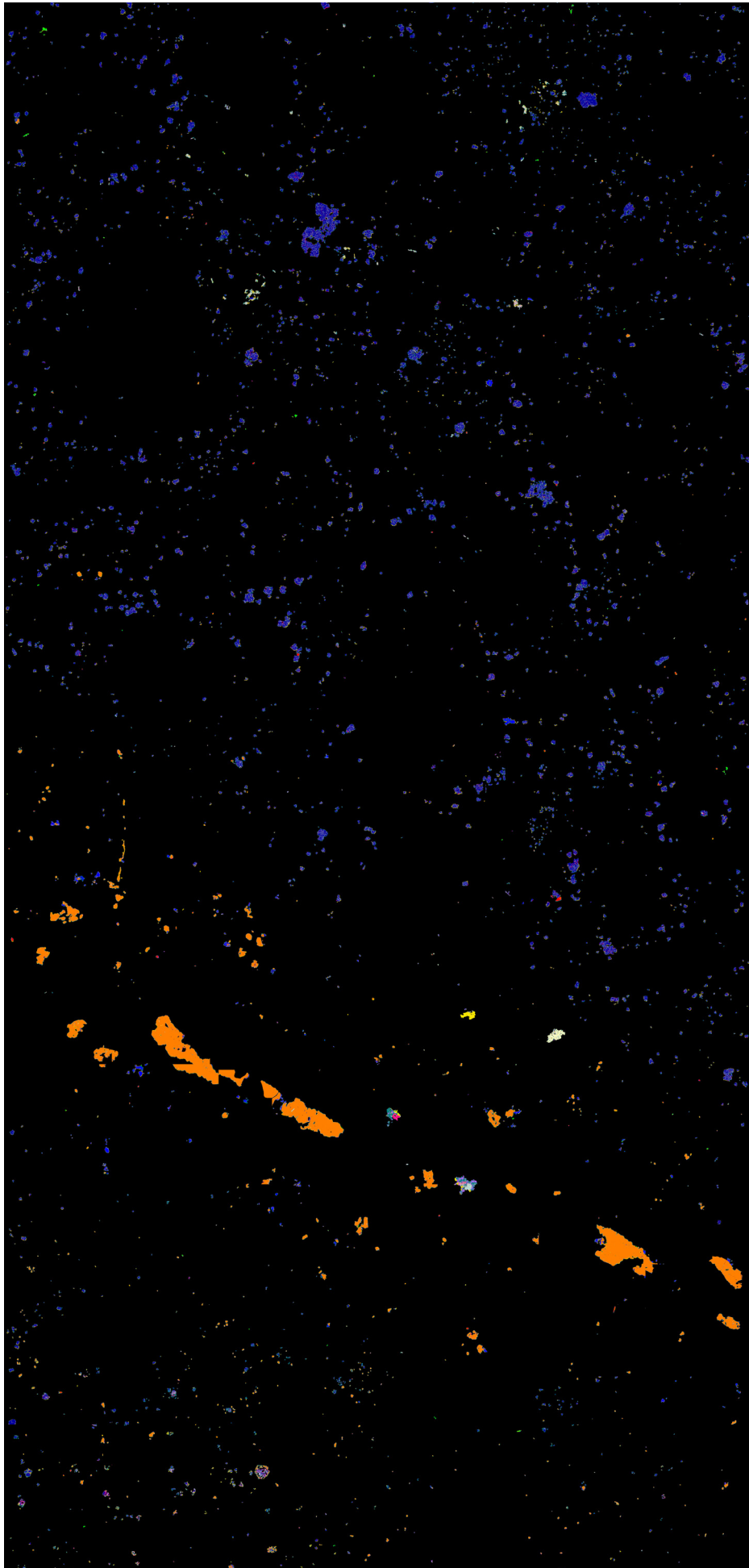
The proportion of bright phases were collected via an automated SEM scan. The thin sections were scanned using a Zeis sigma 300, at 20 kv with a 120 µm apature at Gology department at Leicester Univerisity. The relative quantities of bright phases were then normalized to the abundance of bright phases in the whole rock, calculated from stitched montages (Figure C.1). The total percentage of bright phases was determined in ImageJ by dividing the number of pixels with a value of 10 – 255 by the total number of pixels in the image. The pixel were classified as mineral compostions by comparing analyses to a pre-programmed library.

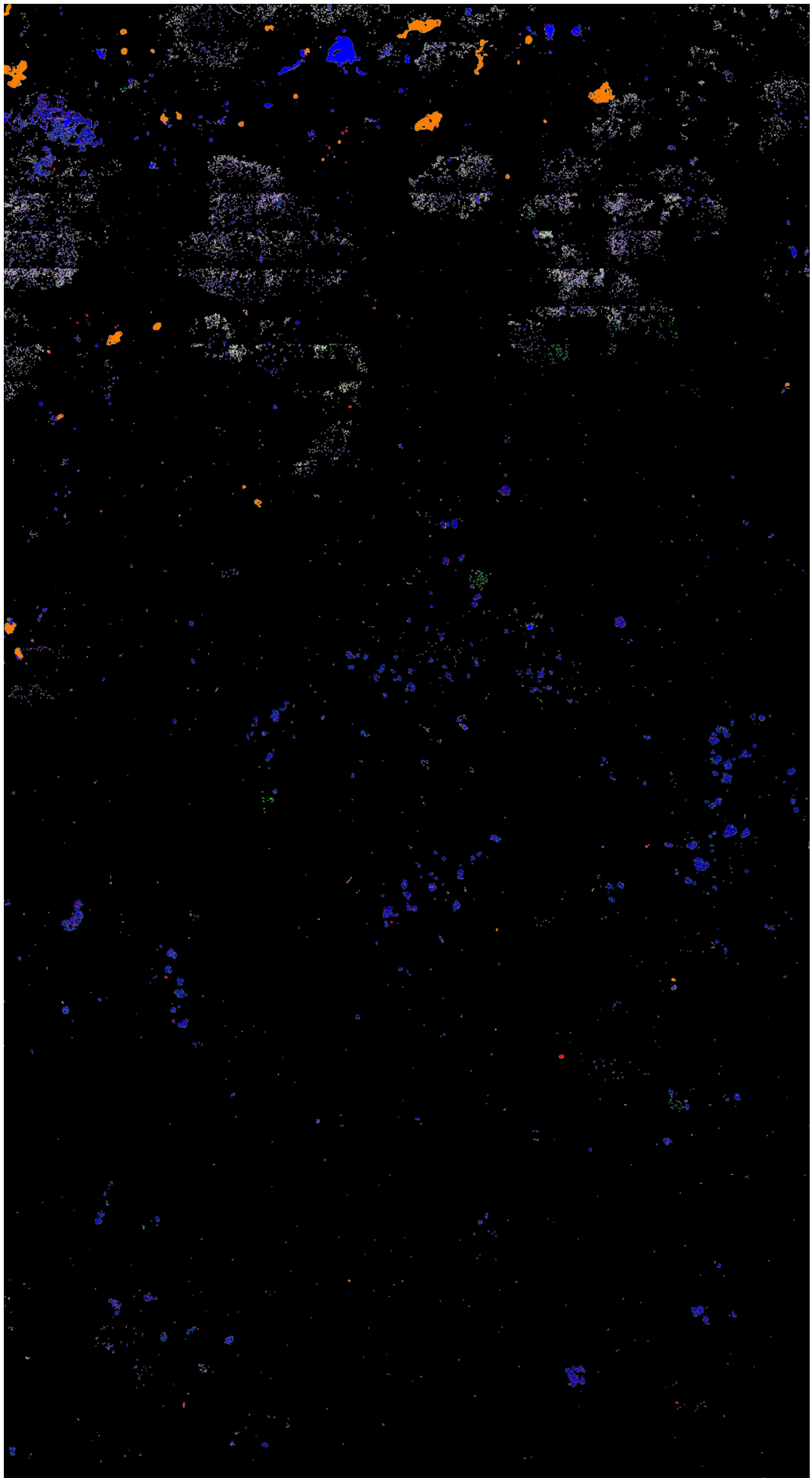
Figure D.1 Bright phase scan of samples EB17014, EB17022, EB17037, EB1703, EB170444, EB17052, EB17069

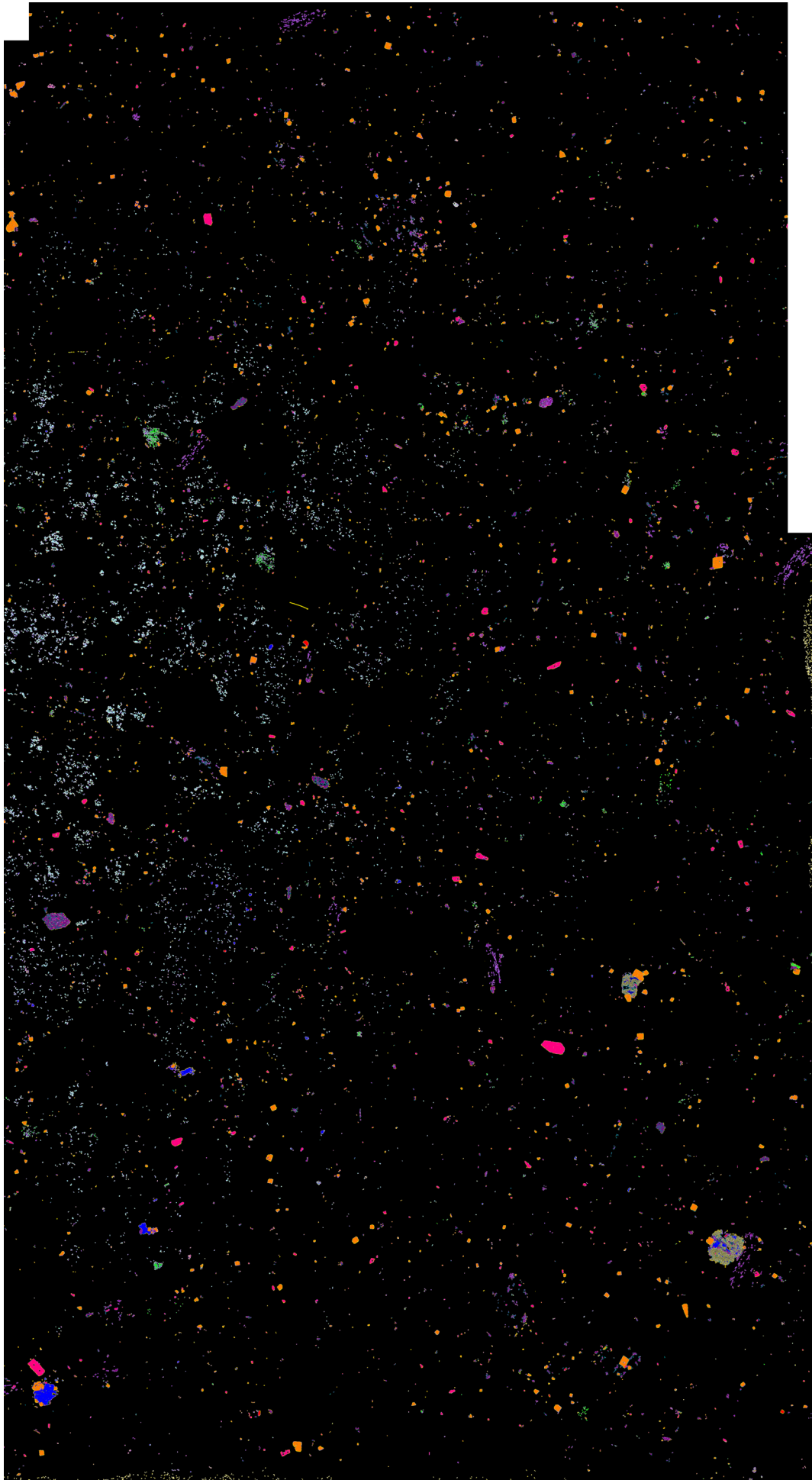


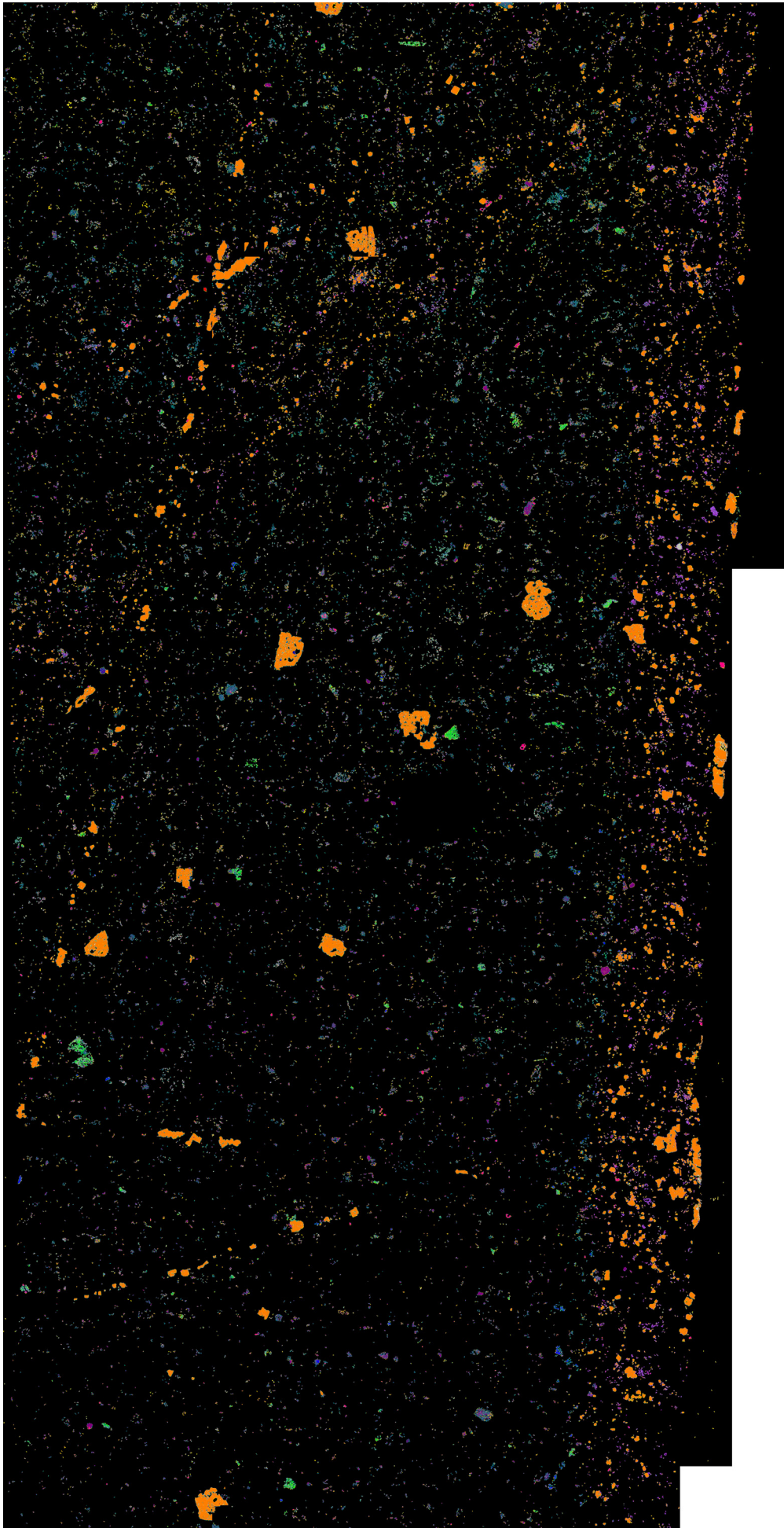












Appendix E: Bulk rock analyses

Multi-element whole rock chemistry for 61 samples from La Granja was determined by an external laboratory (ALS Perth, 31 Denninup Way, Malaga, Australia). For each sample, 1-2 kg (average 1.68 kg) of quarter core was sampled in order to minimise the effect of geochemical heterogeneities on the analyses. The method used for whole rock analysis is as follows: crush to an average grain size of 6 mm, second crush to 2 mm. From this, a smaller sample (average weight after drying, 1340 g) was taken and the grain size reduced to 75 μm . Thorough cleaning of the crusher between samples was carried out to ensure that no cross-contamination occurred between samples. Samples were then dried in an oven below 60 °C to remove excess moisture. Concentrations of the major components were determined as wt. % oxides (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , Cr_2O_3 , TiO_2 , MnO , P_2O_5 , SrO , BaO) by inductively-coupled-plasma atomic-emission spectroscopy (ICP-AES). Total C and S were measured using infra-red combustion on a LECO instrument. Trace element concentrations for most trace elements (B, Ce, Cr, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Lu, Nb, Nd, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tm, U, V, W, Y, Yb, Zr) were determined by lithium borate fusion, acid dissolution and solution ICP-MS. In this method, 200 g of sample was combined with 0.90 g of lithium metaborate flux and heated to 1000 °C in order to fuse the sample. Once cool, this was then dissolved in 100 ml of $\text{HNO}_3/2\%$ HCl_3 . ICP-MS was used to measure 44 elements. Gold, Cd, Co, Cu, Li, Mo, Ni, Pb and Sc required extra attention as they are not completely decomposed by the lithium borate fusion. Pt, Pd and Au were determined from standard lead oxide collection fire assay from 50 g of sample.

The element analyses were calibrated using 18 standards run 53 times in total. Table D.1 shows the measured values for the standards STD-OREAS-45e (laterite soil), SY-4 (diorite-glass) and SARM-48 (fluorspar granite) used in this study. The standard deviation on repeated results is less than 10 % relative to the mean values. The mean of the standard analyses show good agreement with the certified values (typically less than $\pm 5\%$ bias). In addition, 19 blank and 20 repeat analyses were collected. The analytical precision for each element is calculated as the mean of the standard deviation for each of the repeated sample where the concentration was above the limit of detection (Table. D.2). 20 samples were repeated between 4 and 6 times. The full results are presented in Table D.3.

Table E.1 A selection of the standards used for bulk rock analysis in this study. The mean and standards deviation for each is compared to the certified values for each standard.

	STD-OREAS-45e			STD-SY-4			SARM-48		
	<i>This study</i>	σ	<i>Actual</i>	<i>This study</i>	σ	<i>Actual</i>	<i>This study</i>	σ	<i>Actual</i>
<i>Wt%</i>									
SiO ₂	39.72	0.48	40.13	49.94	0.63	49.90	68.23	0.68	67.11
Al ₂ O ₃	12.74	0.25	13.04	20.42	0.33	20.69	11.39	0.06	11.24
Fe ₂ O ₃	34.84	0.39	35.46	6.122	0.11	6.21	0.59	0.00	0.58
CaO	0.084	0.055	0.09	7.858	0.12	8.05	8.975	0.17	8.9
MgO	0.266	0.0089	0.27	0.512	0.01	0.54	0.08	0.00	0.18
Na ₂ O	0.076	0.015	0.08	7.066	0.11	7.10	3.33	0.07	3.22
K ₂ O	0.396	0.015	0.41	1.628	0.04	1.66	4.26	0.06	4.26
Cr ₂ O ₃	0.152	0.0045	0.15						
TiO ₂	0.978	0.0084	0.99	0.282	0.00	0.29	0.1	0.00	0.1
MnO	0.07	-	0.07	0.11	1.55	0.11	0.012	0.00	0.02
P ₂ O ₅	0.086	0.015	0.08	0.126	0.01	0.13	0.0735	0.01	0.09
<i>ppm</i>									
Ba	250.75	7.89	256	325	6.55	340.00			
Ce	24	0.72	23.50	122.67	4.36	122.00			
Cr	1105	54.47	1067	10	-	12.00			
Cs	1.2425	0.063	1.20	1.6	0.05	1.50			
Dy	2.2875	0.10	2.28	18.68	0.37	18.20			
Er	1.46	0.48	1.41	14.87	0.14	14.20			
Eu	0.535	0.034	0.55	1.99	0.03	2.00			
Ga	16.67	0.60	16.20	35.6	0.36	35.00			
Gd	2.085	0.089	2	14.72	0.20	14.00			
Hf	7.25	0.31	6.31	10.93	0.68	10.60			
Ho	0.465	0.033	0.46	4.44	0.21	4.30			
La	11.025	0.46	11.10	57.3	2.49	58.00			
Lu	0.2425	0.017	0.23	2.11	0.07	2.10			
Nb	7.425	0.17	7.40	13.53	0.25	13.00			
Nd	9.45	0.39	9.46	59.33	1.97	57.00			
Pr	2.5375	0.039	2.50	15.02	0.57	15.00			
Rb	21.25	1.16	20.80	53.6	1.95	55.00			
Sm	2.2025	0.10	2.13	12.9	0.52	12.70			
Sr	16.4	0.29	15.90	1240	10	1191.00			
Ta	0.675	0.05	0.63	0.77	0.05	0.90			
Tb	0.3725	0.013	0.36	2.72	0.11	2.60			
Th	13	0.75	13.00	1.29	0.22	1.40			
Tm	0.23	0.0082	0.22	2.33	0.04	2.30			
U	2.5875	0.11	2.54	0.88	0.05	0.80			
V	317.25	17.29	317.00	6	1.41	8.00			
W	6.75	7.32	1.06						
Y	10.85	0.31	10.60	120.33	3.75	119.00			
Yb	1.575	0.062	1.48	15.32	0.40	14.80			
Zr	268	7.62	242	566.67	33.5	517.00			
Ag	0.3	-	0.31						
Co	57.5	-	57.00						
Cu	760	-	780.00						
Li	5	-	6.58						
Mo	2.32	-	2.40						
Ni	453	-	454.00						
Pb	18.4	-	18.20						
Sc	86.6	-	93.00						
Zn	45.8	-	46.70						
Au	0.0563	0.00058	0.05						
Pt	0.1095	0.0026	0.11						
Pd	0.075	0.001	0.08						

Table E.2 List of oxides and elements measured during bulk rock geochemical analysis by ALS. The limit of detection (LOD) varies by element and method. The analytical precision is calculated as the mean of the standard deviation of repeats of unknown samples. The number of repeats is given as n. This analytical uncertainty for each element can be expressed as a percentage or relative precision by dividing by the average concentration of the each element.

	LOD	Analytical precision (σ^{AN})	Average concentration	Analytical precision (%)
<i>wt. %</i>				
SiO ₂	0.01	0.61 (n=6)	59.40	1.03
Al ₂ O ₃	0.01	0.23 (n=6)	17.00	1.35
Fe ₂ O ₃	0.01	0.09 (n=6)	6.44	1.37
CaO	0.01	0.06 (n=6)	4.77	1.23
MgO	0.01	0.04 (n=6)	3.01	1.41
Na ₂ O	0.01	0.02 (n=6)	1.68	1.40
K ₂ O	0.01	0.02 (n=6)	2.09	0.73
TiO ₂	0.01	0.01 (n=6)	0.65	0.90
MnO	0.01	0.00 (n=6)	0.10	0.00
P ₂ O ₅	0.01	0.01 (n=6)	0.14	6.83
SrO	0.01	0.002 (n=6)	0.04	5.66
BaO	0.01	0.001 (n=6)	0.04	3.06
C	0.01	0.01 (n=4)	3.58	4.67
S	0.01	0.05 (n=4)	2.36	2.17
<i>ppm</i>				
Ba	0.5	7.34 (n=5)	343.77	2.14
Ce	0.5	1.84 (n=5)	25.66	7.16
Cr	10	1.41 (n=5)	29.09	4.86
Cs	0.01	0.16 (n=5)	8.69	1.85
Dy	0.05	0.13 (n=5)	2.34	6.00
Er	0.03	0.05 (n=5)	1.43	3.38
Eu	0.03	0.03 (n=5)	0.76	4.47
Ga	0.1	0.64 (n=5)	18.27	3.48
Gd	0.05	0.09 (n=5)	2.46	3.62
Hf	0.2	0.18 (n=5)	2.92	6.30
Ho	0.01	0.01 (n=5)	0.46	2.46
La	0.5	0.89 (n=5)	12.25	7.27
Lu	0.01	0.01 (n=5)	0.22	5.74
Nb	0.2	0.07 (n=5)	4.06	1.74
Nd	0.1	0.86 (n=5)	13.00	7.01
Pr	0.03	0.22 (n=5)	3.21	7.01
Rb	0.2	1.48 (n=5)	79.90	1.86
Sm	0.03	0.20 (n=5)	2.66	7.34
Sn	1	0.14 (n=5)	2.56	5.52
Sr	0.1	5.09 (n=5)	315.19	1.62
Ta	0.1	0.00 (n=5)	0.28	0.00
Tb	0.01	0.02 (n=5)	0.38	4.82
Th	0.05	0.09 (n=5)	3.49	2.47
Tm	0.01	0.01 (n=5)	0.21	5.49
U	0.05	0.05 (n=5)	1.36	3.53
V	5	5.52 (n=5)	192.72	2.86
W	1	1.98 (n=5)	18.32	10.81
Y	0.5	0.30 (n=5)	12.96	2.29
Yb	0.03	0.05 (n=5)	1.43	3.37
Zr	2	13.72 (n=5)	108.32	12.66
As	0.1	0.62 (n=5)	25.42	2.43
Bi	0.01	0.02 (n=4)	0.77	2.08
Hg	0.005	0.001 (n=4)	0.10	0.70
In	0.005	0.005 (n=4)	0.09	5.39
Re	0.001	0.005 (n=3)	0.03	0.00
Sb	0.05	0.15 (n=4)	3.54	4.19
Se	0.2	0.23 (n=4)	2.69	8.55
Te	0.01	0.03 (n=4)	0.30	11.32
Tl	0.02	0.01 (n=4)	0.16	5.55
Ag	0.002	0.04 (n=4)	1.43	2.89
Cd	0.005	0.02 (n=4)	0.94	2.40
Co	0.005	0.20 (n=4)	15.93	1.28
Cu	0.02	22.98 (n=4)	1663.46	1.38
Li	0.2	0.69 (n=4)	7.83	8.81
Mo	0.02	1.29 (n=4)	13.70	9.40
Ni	0.08	0.17 (n=4)	9.29	1.85
Pb	0.01	0.89 (n=4)	30.90	2.88
Sc	0.01	0.37 (n=4)	13.16	2.83
Zn	0.2	0.90 (n=4)	373.32	0.24
Au	0.001	0.01 (n=4)	0.02	7.28

Table E.3 Bulk rock analyses of samples from La Granja

Sample number	Recvd Wt. (g)	Dry Wt. (g)	SiO ₂ (wt.%)	Al ₂ O ₃ (wt.%)	Fe ₂ O ₃ (wt.%)	CaO (wt.%)	MgO (wt.%)	Na ₂ O (wt.%)	K ₂ O (wt.%)	Cr ₂ O ₃ (wt.%)	TiO ₂ (wt.%)	MnO (wt.%)	P ₂ O ₅ (wt.%)	SrO (wt.%)	BaO (wt.%)	Total (wt.%)	LOI (ppm)	C (ppm)	S (ppm)	Ba (ppm)	Ce (ppm)	Cr (ppm)	Cs (ppm)	Dy (ppm)
EB17001	1.32	931	64.3	14.9	2.69	3.25	0.95	2.46	4.42	<0.01	0.35	0.07	0.15	0.04	0.06	96.47	2.83	0.3	2.17	483	31.2	<10	3.58	1.05
EB17002	1.66	1183.1	64.3	15.15	2.39	3.53	0.72	1.37	4.86	<0.01	0.37	0.09	0.15	0.04	0.05	96.53	3.51	0.19	2.75	441	23.6	10	2.29	0.84
EB17003	1.3	913.3	71.9	11.1	1.94	1.74	0.45	0.18	5.13	<0.01	0.18	0.04	0.05	0.02	0.07	95.51	2.71	0.05	1.75	655	28.4	10	1.31	1.46
EB17004	1.42	978.3	62.8	16.8	5.03	0.27	2.15	0.33	3.94	<0.01	0.61	0.14	0.19	<0.01	0.06	97.22	4.9	<0.01	3.04	505	29.9	10	3.13	1.47
EB17005	2.37	1687.5	61.3	15.2	9.44	0.45	1.3	0.83	3.83	<0.01	0.4	0.54	0.12	0.01	0.13	99.2	5.65	0.67	1.82	1135	15.1	<10	10.35	0.76
EB17006	2.15	1511.6	63.5	16.25	7.41	1.51	1.61	1.53	3.33	<0.01	0.42	0.25	0.17	0.02	0.06	99.9	3.84	0.11	1.77	535	27	<10	4.58	1.36
EB17007	2.43	1730.9	66.1	14.95	7.01	1.58	1.4	2.85	3.03	<0.01	0.41	0.23	0.16	0.03	0.06	99.95	2.14	0.08	0.46	532	18.2	<10	3.18	0.9
EB17008	2.27	1599.5	74.6	10.15	7.71	0.04	1.15	0.13	2.13	<0.01	0.26	0.07	0.05	0.01	0.04	100.02	3.68	0.01	2.89	326	17.7	10	2.6	1.02
EB17009	0.92	633.5	66	15.6	6.87	0.4	1.94	0.12	4.34	<0.01	0.4	0.11	0.17	<0.01	0.06	100.75	4.74	0.02	3.55	571	25.9	<10	6.02	0.82
EB17010	1.4	964.6	50.4	17.45	10.25	3.42	5.73	0.58	1.64	0.01	0.76	0.22	0.1	0.01	0.01	96.41	5.83	0.27	2.18	129.5	13.6	60	5.79	2.31
EB17011	0.79	537.9	67.1	16	2.96	2.59	0.75	2.22	2.72	<0.01	0.43	0.14	0.16	0.04	0.04	97.74	2.59	0.29	0.52	324	11.7	<10	7.68	0.97
EB17012	0.92	630.2	67.1	16.3	3.57	2.31	1.73	1.54	3.02	<0.01	0.43	0.12	0.18	0.02	0.04	100.13	3.77	0.43	0.91	389	17	10	8.74	1.14
EB17014	2.5	1817.2	70.3	16.45	7	0.1	0.01	0.05	0.07	<0.01	0.51	<0.01	0.13	0.05	0.01	101.15	6.47	0.01	5.54	59.4	27.6	10	0.54	0.99
EB17015	1.96	1412.7	69.9	16.1	7.33	0.1	0.02	0.06	0.08	<0.01	0.5	0.01	0.18	0.06	<0.01	101.14	6.8	0.01	5.7	39.3	27	10	0.66	0.91
EB17016	1.17	836.6	68.8	15.5	4.39	0.24	1.07	0.22	3.43	<0.01	0.51	0.01	0.19	0.02	0.04	98.83	4.41	0.01	3.07	397	24.5	10	1.21	1.1
EB17017	1.18	826.4	65.9	18.05	4.82	0.34	0.38	0.35	2.53	<0.01	0.66	0.02	0.2	0.01	0.05	99.43	6.12	0.02	2.88	472	28	10	3.41	0.95
EB17018	2.56	1866.9	64.8	16.8	4.57	4.57	1.55	3.69	1.94	<0.01	0.63	0.06	0.2	0.08	0.07	101.16	2.2	0.13	1.93	626	31.3	10	3.31	1.33
EB17019	2.72	1990.7	68.2	13.25	2.85	3.68	1.13	2.07	2.92	<0.01	0.39	0.05	0.12	0.05	0.07	98.05	3.27	0.17	3.35	581	31.7	20	2.46	1.24
EB17020	1.61	1099.5	67.8	15.35	2.14	3.98	1.06	4.09	2.2	<0.01	0.47	0.03	0.13	0.07	0.05	99.49	2.12	0.06	2.02	452	22.7	10	0.96	0.9
EB17021	0.79	549.8	62.3	15.4	4.36	4.67	1.92	4.12	1.97	<0.01	0.64	0.04	0.15	0.06	0.03	99.11	3.45	0.06	2.67	283	25.3	30	1.66	1.35
EB17022	1.63	1132	79.5	11.45	1.68	1.95	0.41	2.52	2.53	<0.01	0.14	0.04	<0.01	0.03	0.03	101.93	1.65	0.18	1.51	319	27	10	1.4	2.36
EB17023	1.4	992.4	62.1	16.6	3.05	5.89	1.97	4.31	2.02	<0.01	0.66	0.03	0.19	0.07	0.05	99.14	2.2	0.09	1.81	451	32.7	10	2.7	2.33
EB17024	1.07	747.5	74.3	10.25	3.6	2.91	1.61	2.13	1.76	<0.01	0.28	0.05	0.04	0.02	0.05	99	2	0.15	1.68	366	38.7	10	2.74	2.75
EB17025	1.76	1259.3	52.5	17.8	7.76	7.92	4.74	1.35	2.29	0.01	0.98	0.14	0.18	0.04	0.02	98.17	2.44	0.11	1.73	163	28.7	90	9.09	3.94
EB17026	2.94	2126	54.4	15.95	8.87	5.52	3.98	1.84	0.88	0.01	0.73	0.13	0.11	0.05	0.02	97.12	4.63	0.1	4.35	173.5	13	40	1.61	2.75
EB17027	2.89	2079.9	49.8	17.9	11.25	7.77	5.79	2.22	0.47	0.01	0.98	0.15	0.17	0.05	0.02	100.06	3.48	0.05	2.81	131.5	22.9	70	1.8	3.05
EB17028	2.93	2111.2	49.5	19.6	9.23	9.05	3.8	2.35	1.03	<0.01	0.86	0.13	0.21	0.07	0.02	99.42	3.57	0.04	3.47	198	18.6	30	1.33	3
EB17029	3.44	2465.5	49.1	21.2	7.84	11.05	3.83	1.73	0.61	0.01	0.59	0.09	0.1	0.05	0.01	99.44	3.23	0.05	3.31	122.5	15.3	60	0.6	2.34
EB17030	2.2	1573.4	65.9	14.85	3.84	6	1.88	3.05	1.14	<0.01	0.53	0.04	0.13	0.04	0.02	100.14	2.72	0.14	3.12	162.5	24.5	20	1.25	3.12
EB17031	2.88	2068	47.2	22.3	8.32	12.4	4.1	1.71	0.67	0.01	0.85	0.1	0.09	0.06	0.01	101.19	3.37	0.11	3.83	81.9	9.7	50	1.68	1.73
EB17032	2.95	2112.5	46.6	22	9.69	12.3	4.53	1.92	0.45	<0.01	0.9	0.14	0.08	0.06	0.01	100.8	2.12	0.03	2.18	83.4	9.8	30	0.78	2.05
EB17033	2.45	1747.7	55.7	16.35	8.16	5.7	3.65	2.37	1.08	0.01	0.73	0.09	0.12	0.05	0.02	98.34	4.31	0.19	3.86	217	26.9	50	5.6	3.1
EB17034	2.37	1667.9	62.1	14.45	6.31	6.02	2.12	2.72	1.42	0.01	0.56	0.04	0.11	0.05	0.04	99.52	3.57	0.13	4.54	333	20.5	40	1.94	2.54
EB17035	1.57	1093.2	64.9	17.05	2.5	2.55	2.3	0.69	3.27	<0.01	0.69	0.06	0.23	0.1	0.07	98.56	4.15	0.28	0.99	629	39.4	10	6.35	2.98
EB17036	1.2	830.3	68.5	8.01	3.81	9.31	3.82	0.07	0.35	0.01	0.4	0.2	0.79	0.09	0.01	99.39	4.02	0.22	1.16	46.6	47.8	50	2.21	4.08
EB17037	1.23	859.1	68.6	15.6	3	1.8	1.39	2.35	2.71	<0.01	0.5	0.07	0.18	0.04	0.07	98.84	2.53	0.18	1.34	586	29.6	10	2.2	1.11
EB17038	1.43	1019.4	65.4	16.75	3.23	3.39	1.29	3.7	1.62	<0.01	0.55	0.07	0.21	0.08	0.06	98.41	2.06	0.15	1.06	560	33.7	10	1.66	1.19
EB17039	1.93	1400	58.1	17	9.32	4.29	3.74	1.81	1.22	0.01	0.88	0.1	0.18	0.03	0.03	100.85	4.14	0.17	2.61	255	34.1	50	3.2	3.5
EB17040	1.62	1143.6	68	14.95	5.31	2.47	1.59	2.87	1.83	<0.01	0.54	0.03	0.12	0.03	0.05	100.75	2.96	0.16	2.01	431	40.9	10	5.11	3.61
EB17041	1.54	1103.1	68.6	14.4	5.02	2.92	1.19	2.73	2.63	<0.01	0.47	0.04	0.08	0.03	0.06	100.81	2.64	0.05	1.88	547	40.9	10	2.07	3.07
EB17042	1.5	1009.7	48.9	17.2	11.2	9.04	6.32	1.68	0.94	0.01	1.15	0.31	0.06	0.05	0.01	99.81	2.94	0.04	2.73	102	12.4	60	1.37	1.64
EB17043	1.45	1103.2	51.6	17.6	9.04	8.38	5.13	2.24	1.44	0.01	0.95	0.17	0.16	0.05	0.02	99.54	2.75	0.14	2.1	178.5	22.1	70	3.51	2.7
EB17044	1.69	1211.2	68.2	14.55	3.8	3.7	1.19	2.78	2.54	<0.01	0.44	0.03	0.08	0.03	0.06	99.86	2.46	0.3	1.77	498	43.8	10	7.07	3.08
EB17045	1.58	669.3	73.9	16.7	3.24	0.11	0.26	0.06	2.59	<0.01	0.81	<0.01	0.18	0.05	0.06	101.26	3.3	0.07	0.08	488	26.4	10	0.69	0.85
EB17050	1.33	942.3	69.6	16	5.72	0.24	0.5	0.13	4.86	<0.01	0.36	0.01	0.11	<0.01	0.08	101.96	4.35	0.02	3.38	701	28.1	10	2.04	1.24
EB17051	1.6	1141.3	68.9	15.65	4.26	0.23	0.84	0.08	4.92	<0.01	0.31	0.04	0.12	<0.01	0.06	99.17	3.76	0.03	2.44	521	28.2	10	4.53	0.8
EB17052	1.66	1171.9	67.1	15.6	3.99	2.81	0.87	1.85	3.26	<0.01	0.29	0.17	0.1	0.03	0.06	99.87	3.74	0.56	1.7	533	29.7	10	14.1	0.77
EB17053	1.45	1025	68.6	15.9	3.93	0.2	0.79	0.1	4.79	<0.01	0.31	0.05	0.13	<0.01	0.05	98.67	3.82	0.01	2.08	485	29.9	10	3.26	0.68
EB17054	0.88	611.8	64.3	14.2	3.96	2.87	1.31	0.33	5.47	<0.01	0.37	0.09	0.16	0.03	0.07	97.6	4.44	0.18	3.29	572	26.5	10	1.33	2.02
EB17055	0.87	595.7	74.9	10.8	4.46	1.47	0.53	0.08	3.42	<0.01	0.18	0.02	0.05	0.01	0.05	100.06	4.09	0.03	3.15	430	26.2	20	1.12	1.1
EB17057	2.8	2012.6	54.6	17.3	6.63	5.39	4.89	2.5	1.73	0.01	1.04	0.03	0.21	0.05	0.01	97.68	3.29	0.04	2.36	80.6	16.4	60	6.78	3
EB17058	2.74	1960.5	54.6	16.4	7.12	6.11	4.43	2.54	1.93	0.01	0.97	0.04												

Sample number	Er (ppm)	Eu (ppm)	Ga (ppm)	Gd (ppm)	Ge (ppm)	Hf (ppm)	Ho (ppm)	La (ppm)	Lu (ppm)	Nb (ppm)	Nd (ppm)	Pr (ppm)	Rb (ppm)	Sm (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Tb (ppm)	Th (ppm)	Tm (ppm)	U (ppm)	V (ppm)	W (ppm)	Y (ppm)
EB17001	0.56	0.61	19.8	1.72	<5	2.7	0.19	15	0.09	3.5	15.4	3.84	123.5	2.37	3	350	0.2	0.21	2.02	0.08	1.6	58	39	5.3
EB17002	0.48	0.52	18.4	1.4	<5	2.9	0.15	11.2	0.07	3.7	12.2	3.1	139.5	1.85	4	339	0.2	0.17	1.92	0.07	1.42	56	40	4.6
EB17003	1	0.44	11.6	1.54	<5	3.3	0.32	14.9	0.2	4.7	10.6	3.02	121.5	1.91	4	166.5	0.5	0.26	11.25	0.17	1.37	39	25	9.3
EB17004	0.85	0.83	21.4	2.35	<5	2.9	0.27	14	0.12	4.7	15	3.83	157	2.7	2	52.3	0.4	0.3	3.22	0.11	1.09	105	10	7.8
EB17005	0.51	0.47	21	1.07	<5	3.9	0.14	7.3	0.08	3.7	7.9	1.92	155.5	1.51	1	59.5	0.2	0.14	2.22	0.07	1.06	60	14	4.5
EB17006	0.71	0.56	24	1.77	<5	3.3	0.23	13.4	0.09	3.4	13.7	3.34	114	2.35	2	132	0.3	0.23	2.19	0.1	1.36	67	8	6.9
EB17007	0.58	0.46	20.6	1.39	<5	3.1	0.19	8.6	0.1	3.3	9.3	2.38	83.4	1.72	1	253	0.2	0.19	2.09	0.09	1.31	68	13	5.2
EB17008	0.69	0.37	16	1.12	<5	2	0.24	8.6	0.11	2.1	8.4	2.16	77.9	1.42	2	30.9	0.1	0.16	1.2	0.1	0.65	97	8	7.2
EB17009	0.51	0.48	24.9	1.1	<5	3	0.15	13	0.1	3.3	11.9	3.08	166	1.7	3	22.6	0.2	0.13	2.37	0.08	1.85	77	25	4.4
EB17010	1.64	0.81	18.3	2.44	<5	1.9	0.48	6.2	0.22	2.2	8	1.85	76.2	2.1	2	122	0.1	0.42	0.94	0.23	1.17	598	15	14.2
EB17011	0.65	0.42	17	1.04	<5	3.2	0.19	5.8	0.1	3.2	6.8	1.55	111	1.3	2	280	0.2	0.16	2.02	0.09	0.99	56	37	5.7
EB17012	0.58	0.85	21.2	2.17	<5	3	0.21	7.6	0.1	2.8	13.8	2.83	117	3.1	2	180.5	0.2	0.26	2.44	0.09	1.09	75	32	6.3
EB17014	0.52	0.63	6.8	1.54	<5	2.4	0.19	13.4	0.08	4.3	13.9	3.47	2.6	2.41	2	400	0.3	0.21	3.63	0.08	0.68	75	42	5.1
EB17015	0.61	0.64	5.6	1.58	<5	2.4	0.19	13	0.08	4.2	13.2	3.34	2.8	2.13	2	471	0.3	0.2	3.35	0.08	0.67	73	39	5.7
EB17016	0.62	0.54	16.7	1.57	<5	2.4	0.21	11.4	0.1	4.1	12.3	2.99	102	2.15	4	125	0.3	0.21	3.14	0.09	1.06	86	28	6
EB17017	0.52	0.7	23	1.85	5	3.2	0.17	12.8	0.07	5	14.9	3.65	85.5	2.75	2	104.5	0.3	0.21	3.35	0.07	1.14	104	25	4.8
EB17018	0.68	0.89	21.6	2.18	<5	2.4	0.24	14.7	0.1	4.4	17.1	4.13	57.8	2.93	1	704	0.3	0.29	2.75	0.08	0.9	93	5	6.6
EB17019	0.71	0.69	14.3	1.89	<5	4	0.24	15.5	0.11	4.3	15	4	83.9	2.61	2	390	0.3	0.25	3.83	0.11	0.93	57	11	6.9
EB17020	0.59	0.63	17.5	1.18	<5	2.9	0.19	11.4	0.1	4.7	10.2	2.83	53.5	1.91	2	597	0.3	0.16	2.54	0.08	0.78	55	13	4.9
EB17021	0.87	0.65	18.6	1.74	<5	2.8	0.27	12.4	0.14	5.7	12.1	3.15	64.9	2.29	2	533	0.4	0.27	3.23	0.13	0.9	118	6	7.9
EB17022	1.73	0.42	10.7	2.26	<5	2.8	0.5	13.7	0.27	8.1	11.6	3.11	72.1	2.5	1	222	1.1	0.4	13.85	0.25	1.54	17	4	16.1
EB17023	1.28	0.87	20.2	2.95	<5	3.1	0.4	15	0.18	5.2	17	4.34	79.7	3.21	1	628	0.3	0.42	2.7	0.18	0.97	114	7	12.2
EB17024	1.75	1.17	11.3	2.84	<5	3.7	0.57	20.6	0.32	5.8	16.4	4.25	59.7	3.07	2	164	0.5	0.45	7.9	0.29	4.1	63	40	17.7
EB17025	2.63	1.06	19.3	4.13	<5	3.1	0.84	13.5	0.36	7.4	16.9	3.77	126	3.95	4	295	0.4	0.73	3.83	0.36	1.73	236	6	23.1
EB17026	1.7	0.63	16.8	2.69	<5	2.4	0.54	7.5	0.28	3.3	7.8	1.64	30.6	2.19	3	456	0.3	0.43	3.98	0.28	1.79	192	5	16
EB17027	1.89	0.98	17.8	3.31	<5	3.1	0.66	10	0.27	4	14	3.15	15	3.41	2	363	0.2	0.55	1.36	0.29	0.57	206	11	17.2
EB17028	1.91	1.01	18.4	3.07	<5	1.8	0.59	8.5	0.26	2.3	11.2	2.48	38.8	2.59	2	590	0.2	0.51	1.84	0.27	1.05	218	6	16.8
EB17029	1.55	0.7	16.8	2.39	<5	2.3	0.49	7	0.22	2.2	9.2	2.11	24.8	2.19	1	426	0.1	0.4	1.66	0.22	0.71	165	6	13.5
EB17030	2.16	0.79	14.4	2.97	<5	4.1	0.7	10.9	0.38	4.1	12.8	3.15	43	2.96	2	347	0.4	0.52	6.45	0.32	1.49	103	6	19.8
EB17031	1.14	0.66	17.7	1.89	<5	1.4	0.38	4.3	0.17	1.7	6.4	1.35	32.7	1.55	2	563	0.1	0.31	0.79	0.16	0.64	351	8	10.4
EB17032	1.09	0.73	20.6	1.89	<5	1.4	0.38	4.5	0.17	1.3	6.1	1.34	20.8	1.61	1	486	0.1	0.34	1.05	0.16	0.46	387	6	10.6
EB17033	2.15	0.87	18.1	3.06	<5	3.3	0.66	13.6	0.32	4	13.3	3.2	45.1	2.94	2	465	0.3	0.51	5.15	0.31	1.57	188	8	18.6
EB17034	1.66	0.85	15.1	2.42	<5	3.7	0.51	8.2	0.25	4.6	11.2	2.8	64.1	2.47	2	438	0.4	0.44	7.15	0.24	1.68	112	10	15.1
EB17035	1.66	0.97	12.7	3.41	<5	3.6	0.59	19	0.26	5.9	20.4	5.02	97.6	3.91	2	938	0.4	0.52	5.57	0.23	1.6	115	17	16.8
EB17036	2.65	0.71	7.3	4.17	<5	9.5	0.92	21.1	0.47	11.6	21.9	5.68	11.5	4.45	3	764	0.9	0.68	11.75	0.41	3.56	52	10	27.2
EB17037	0.57	0.7	17.5	1.77	<5	2.9	0.21	13.9	0.09	4.2	15	3.73	76.5	2.36	2	308	0.3	0.23	2.61	0.09	0.87	72	12	6
EB17038	0.62	0.79	20.7	1.81	<5	3.3	0.21	16.2	0.1	4.3	16.5	4.24	45.1	2.53	2	745	0.3	0.22	2.65	0.09	1.24	84	11	6.2
EB17039	2.13	1.05	18.4	3.62	<5	3.6	0.69	16.1	0.34	5.3	17.7	4.25	51.1	3.65	3	250	0.4	0.56	4.82	0.29	2.11	187	19	20.3
EB17040	2.49	0.82	17.8	3.78	<5	4.9	0.76	19.7	0.4	5.9	18.3	4.83	70.2	3.88	3	241	0.5	0.58	8.17	0.38	2.9	89	40	23.2
EB17041	1.99	0.77	16.6	3.3	<5	4.3	0.66	20.9	0.34	5.6	17.5	4.6	89.5	3.4	3	245	0.5	0.49	9.67	0.31	3.03	77	35	18.7
EB17042	1.16	0.75	19.7	1.83	<5	1.3	0.37	5.5	0.16	1.9	7.4	1.7	49.7	1.8	1	435	0.1	0.29	1.24	0.15	0.79	394	24	10.1
EB17043	1.47	0.91	19.2	3.04	<5	2.4	0.53	9.9	0.25	3.7	12.8	3.02	77	2.83	1	466	0.2	0.47	1.97	0.22	0.94	231	11	15.7
EB17044	2.15	0.82	16.8	3.16	<5	4.4	0.63	22.1	0.37	5.4	18.3	4.95	93.4	3.38	2	239	0.5	0.5	9.43	0.31	2.99	71	9	19.2
EB17045	0.48	0.53	12.1	1.41	<5	3.1	0.15	13	0.1	5.7	12.9	3.26	66.3	2.04	4	458	0.3	0.17	1.85	0.07	0.77	102	24	4.7
EB17050	0.6	0.62	25.3	1.6	<5	3	0.22	12.8	0.09	4	13.3	3.57	166.5	2.28	5	35.6	0.3	0.22	2.98	0.09	1.69	57	30	6.8
EB17051	0.42	0.53	23.9	1.33	<5	3.6	0.14	13.6	0.06	3.9	13.2	3.47	182.5	2.14	4	18.6	0.3	0.15	2.56	0.05	1.92	43	39	4.1
EB17052	0.36	0.61	22.8	1.24	<5	3.1	0.15	14.6	0.07	3.6	13.5	3.66	145	2.09	2	303	0.2	0.16	2.49	0.05	1.48	41	25	4.4
EB17053	0.37	0.65	23.8	1.26	<5	3.2	0.11	14.5	0.07	3.9	13.6	3.62	171	2.02	4	36.2	0.3	0.14	2.7	0.05	2.06	43	48	3.4
EB17054	1.21	0.64	18.2	2.49	<5	3	0.39	12.5	0.18	4.1	13.8	3.49	165.5	2.82	4	241	0.3	0.36	4.58	0.16	1.92	72	73	11.2
EB17055	0.83	0.34	16	1.42	<5	3.2	0.23	13.9	0.16	4.6	9.9	2.81	98.4	1.61	4	103.5	0.6	0.2	11.6	0.13	2.05	40	40	7.4
EB17057	1.95	0.53	18.1	2.9	<5	2.7	0.63	7.8	0.3	7	8.7	2.06	84.1	2.26	9	390	0.5	0.47	4.31	0.28	1.38	219	15	18.2
EB17058	2.44	1.35	17.5	4.44	<5	2.6	0.87	18.2	0.32	6.7	21	5	92.4	4.46	15	363	0.5	0.7	4.59	0.33	1.34	216	6	22.7
EB17059	3.33	1.5	17.9	5.52	<5	4.2	1.04	22.8	0.46	8.7	24.8	5.98	67.5	5.3	10	430	0.6	0.86	5.11	0.44	1.62	130	7	29
EB17060	2.15	0.78	16.9	3.28	<5	2.4	0.63	11.8	0.33	4.6	13.6	3.24	93.7	3.29	9	367	0.3	0.55	2.81	0.3	0.95	211	2	19.1
EB17063	3.51	1.1	16.4	6.01	<5	8.1	1.28	37.8	0.56	21.6	34.4	9.1	5.6	6.79	6	142.5	1.4	0.97	15.7	0.56	3.86	60	12	34.8
EB17064	2.28	0.84	11.9	3.74	<5	8.2	0.8	23.9	0.39	10	20.4	5.6	7.9	3.89	5	35.5	0.8	0.59						

Sample number	Yb	Zr	As	Bi	Hg	In	Re	Sb	Se	Te	Tl	Ag	Cd	Co	Cu	Li	Mo	Ni	Pb	Sc	Zn	Au	Pt	Pd
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
EB17001	0.54	95	5.6	2.27	0.188	0.222	0.02	0.88	3.9	0.55	0.14	4.07	1.83	2.69	5650	6.5	25.8	2.82	16.9	3.8	700	0.012	<0.0005	0.001
EB17002	0.49	97	75.8	0.75	0.247	0.21	0.062	0.7	2.1	0.14	0.12	4.01	0.632	2.63	6890	6.5	130	2.43	67.5	3.64	252	0.004	<0.0005	0.001
EB17003	1.23	113	>250	0.5	0.823	0.16	0.204	1.97	3.7	0.18	0.06	3.77	0.634	1.26	6060	6.1	516	2.18	59.3	3.43	243	0.006	<0.0005	0.007
EB17004	0.82	99	3.2	0.86	0.22	0.222	0.011	3.77	1.5	0.23	0.13	0.514	1.525	7.71	232	10.2	4.11	5.01	7.96	7.66	522	0.005	0.001	0.002
EB17005	0.46	134	29.5	0.43	0.023	0.068	0.018	1.04	2.4	0.26	0.34	3.7	1	6.23	2910	7	7.31	2.84	37.9	4.2	587	0.061	<0.0005	<0.001
EB17006	0.65	123	5.2	1.49	0.022	0.307	0.013	0.62	2.2	0.83	0.2	3.54	1.605	7.8	2530	7.6	8.35	3.53	29.8	4.71	763	0.042	<0.0005	<0.001
EB17007	0.72	107	1.7	0.12	<0.005	0.019	0.023	0.61	2.6	0.11	0.1	4.63	0.155	6.43	4100	7.8	10.1	3.23	27.5	4.15	275	0.057	<0.0005	<0.001
EB17008	0.65	71	23.7	0.92	0.022	0.273	0.008	0.76	5.9	0.56	0.11	6.84	0.45	8.32	7580	5.8	7.05	3.4	8.08	2.85	227	0.178	0.0012	0.006
EB17009	0.59	105	35.8	2.57	0.134	0.618	0.026	0.6	1.6	1.1	0.3	5.42	7.84	7.73	3470	8	17.8	4.05	24.2	4.68	2790	0.072	<0.0005	<0.001
EB17010	1.56	74	10.6	0.92	0.011	0.075	0.036	0.24	2.5	0.37	0.15	2.66	0.425	36	2840	17.8	22.6	14.25	19.05	37.4	403	0.025	<0.0005	<0.001
EB17011	0.72	111	1.9	1.05	0.042	0.114	0.012	0.4	1.8	0.49	0.23	3.65	1.415	4.21	3780	7.7	17.05	1.71	21.8	3.75	501	0.022	<0.0005	<0.001
EB17012	0.6	102	6.8	0.56	0.025	0.039	0.166	0.53	0.6	0.22	0.19	0.531	0.045	3.27	330	7.5	67	3.87	14.55	4.9	102.5	0.006	<0.0005	<0.001
EB17014	0.6	83	16.3	0.18	0.087	0.008	0.039	1.01	5.6	0.08	0.04	0.229	0.079	22.2	165.5	18.9	17.2	7.65	28.7	3.82	35	0.009	<0.0005	<0.001
EB17015	0.53	79	13.9	0.1	0.008	<0.005	0.294	0.61	3.6	0.09	0.02	0.064	0.013	26.3	117.5	23.3	42.9	6.19	16.65	2.54	4	0.003	<0.0005	<0.001
EB17016	0.62	74	>250	0.17	0.451	0.033	0.007	25	5.1	0.12	0.13	1.635	0.225	19.15	4180	8.9	12.2	6.14	24.5	5.23	56.7	0.025	<0.0005	<0.001
EB17017	0.45	105	>250	0.16	0.294	0.027	0.052	6.07	3.8	0.12	0.23	1.315	0.081	11.5	2480	32.8	16.15	3.92	9.91	5.46	44.3	0.033	<0.0005	<0.001
EB17018	0.69	76	4.6	0.2	0.079	0.052	0.006	1.29	2.3	0.16	0.12	1.555	0.626	7.14	2480	6.1	9.41	3.35	64.6	5.5	224	0.035	<0.0005	<0.001
EB17019	0.64	216	44.8	0.18	0.119	0.064	0.009	9.38	3.8	0.08	0.08	1.695	0.37	3.94	4050	5.2	10.45	2.89	24.7	3.91	104.5	0.009	<0.0005	0.001
EB17020	0.59	96	1.4	0.14	0.012	0.03	0.021	0.33	1.9	0.1	0.06	0.954	0.084	3.39	2260	5.9	27.8	2.2	8.51	3.89	33.6	0.01	<0.0005	0.001
EB17021	0.93	105	1	0.15	<0.005	0.027	0.005	0.11	3.1	0.12	0.25	1.18	0.081	8.18	2770	8.1	5.9	5.89	6.43	10.55	47.7	0.052	<0.0005	0.001
EB17022	1.88	80	21.3	0.36	0.074	0.097	0.057	0.44	1.6	0.11	0.05	1.435	0.698	1.54	2550	3.3	36.9	1.39	100.5	3.65	190.5	0.003	<0.0005	<0.001
EB17023	1.14	97	1.5	0.06	0.017	0.033	0.013	0.43	1	0.06	0.26	0.704	0.066	7.07	2150	9.2	5.26	6.59	6.53	9.11	36.6	0.036	<0.0005	<0.001
EB17024	1.9	134	1.3	0.19	0.02	0.116	0.06	0.17	3.1	0.21	0.14	1.785	0.319	6.71	5010	9.7	82.9	9.25	7.69	5.84	93.5	0.007	<0.0005	0.003
EB17025	2.36	149	1.7	0.1	0.023	0.14	0.026	0.11	1.7	0.13	0.89	1.025	0.322	14.8	2400	11.5	9.73	24.9	5.04	26.2	150	0.044	<0.0005	<0.001
EB17026	1.86	92	6.4	1.47	0.016	0.077	<0.001	0.64	2.2	0.7	0.07	0.803	0.42	27.9	321	9.3	1.88	11.35	12.2	21.4	229	0.005	<0.0005	<0.001
EB17027	1.89	159	6.4	0.8	0.008	0.031	0.001	0.37	1.6	0.46	0.1	0.351	0.063	28.9	217	6.7	2.2	41.3	9.72	22.7	127.5	0.004	<0.0005	<0.001
EB17028	1.77	65	10.9	0.55	0.014	0.025	0.002	0.3	1	0.38	0.05	0.378	0.071	19.4	320	5.5	6.41	7.72	9.88	22	103.5	0.003	<0.0005	<0.001
EB17029	1.34	82	5.1	0.27	0.008	0.017	0.001	0.26	1.8	0.22	0.04	0.291	0.051	20.8	284	5.1	1.37	12.6	6.72	16.5	78.2	0.002	<0.0005	<0.001
EB17030	2.43	166	2.6	0.26	0.01	0.027	0.001	0.16	1.1	0.13	0.05	0.177	0.085	7.28	137.5	4.9	4.12	2.91	7.58	12.1	64.7	0.002	<0.0005	<0.001
EB17031	1.03	99	8.1	0.49	0.014	0.047	0.001	0.33	1.4	0.32	0.05	0.486	0.062	27.1	517	5	5.51	7.32	5.35	22.9	85.2	0.003	<0.0005	<0.001
EB17032	1.17	65	3.4	0.15	0.011	0.015	0.001	0.15	1.5	0.09	0.06	0.248	0.056	32.5	268	2.3	1.34	7.81	4.2	24.1	63.1	0.002	<0.0005	<0.001
EB17033	2.17	132	6.5	0.59	0.029	0.033	0.001	1.06	1.3	0.26	0.11	0.36	0.066	25.1	246	8.1	5.32	10.3	9.72	19.3	117	0.003	<0.0005	<0.001
EB17034	1.7	142	3.2	0.25	0.015	0.014	0.003	0.29	2.2	0.2	0.06	0.202	0.034	22.7	199.5	8.5	3.33	4.92	6.68	14.4	45.7	0.002	<0.0005	<0.001
EB17035	1.79	125	29.4	0.21	0.217	0.03	0.09	2.1	1.6	0.16	0.15	1.205	0.153	8.54	2350	6.3	28.3	7.14	10.95	11.25	67.7	0.008	<0.0005	<0.001
EB17036	2.85	362	37.3	0.18	0.095	0.112	0.127	3.16	3.1	0.23	0.02	1.835	0.621	7.63	3250	4.5	39.9	12.25	18.1	5.43	246	0.01	<0.0005	<0.001
EB17037	0.64	101	50.2	0.37	0.334	0.106	0.021	0.96	3.6	0.18	0.13	2.42	0.543	8.56	5040	3.6	16.6	4.48	22.4	4.9	202	0.038	<0.0005	0.001
EB17038	0.6	112	1.7	0.13	0.031	0.017	0.018	0.1	2.1	0.16	0.07	1.36	0.263	9.37	2620	5.1	4.67	4.8	18.75	5.68	123	0.023	<0.0005	<0.001
EB17039	1.99	141	3.3	0.39	0.015	0.068	0.01	0.19	1.3	0.18	0.16	0.708	0.187	20.7	1190	10.7	3.51	18.95	19.75	20.1	144	0.006	<0.0005	<0.001
EB17040	2.63	161	1.3	0.14	0.008	0.025	0.02	0.14	1.6	0.08	0.08	0.579	0.022	17.5	1110	10.3	22.3	3.87	10.8	12.1	34.5	0.007	<0.0005	<0.001
EB17041	2.18	158	5.9	0.26	0.005	0.034	0.012	0.19	1	0.1	0.11	0.688	0.019	8.01	994	7.1	11.5	2.82	11.4	9.43	57.6	0.006	<0.0005	<0.001
EB17042	1.07	48	1.9	0.15	0.01	0.023	0.003	0.09	0.9	0.14	0.24	0.777	0.095	33.7	816	4.4	4.37	33.4	3.57	37.8	130.5	0.007	<0.0005	<0.001
EB17043	1.62	90	1.8	0.35	0.005	0.03	0.001	0.16	1.3	0.19	0.63	0.33	0.127	29.6	441	4.8	5.88	31.7	13	23.6	118	0.004	<0.0005	<0.001
EB17044	2.24	169	2.6	0.19	0.016	0.029	0.021	0.09	0.8	0.08	0.1	0.774	0.037	9.27	1150	4.7	12.9	2.61	9.78	8.45	49	0.007	<0.0005	<0.001
EB17045	0.55	106	219	0.65	0.407	0.005	<0.001	24.6	9.9	0.23	0.05	1.445	0.005	0.265	151	0.7	8.62	0.47	19.8	5.71	4.6	0.029	<0.0005	<0.001
EB17050	0.61	95	53.3	1.05	0.143	0.033	<0.001	4.37	1.5	0.59	0.14	0.322	0.016	9.48	693	2.3	6.5	2.09	2.16	3.9	20.8	0.004	<0.0005	<0.001
EB17051	0.42	118	14.2	1.22	0.459	0.407	0.052	9.8	2.4	0.53	0.23	2.24	2.81	14.55	2030	2.8	36.5	2.06	72.8	2.75	1220	0.005	<0.0005	<0.001
EB17052	0.37	99	5.4	2.94	0.259	0.226	<0.001	0.36	0.5	0.96	0.27	1.35	2.03	1.79	694	3.8	0.9	1.53	22.5	2.85	813	0.004	<0.0005	<0.001
EB17053	0.35	101	22.3	0.98	0.07	0.088	0.01	2.53	1.4	0.26	0.2	2.05	1.105	5.33	1340	7.3	9.81	1.14	101.5	2.77	459	0.005	<0.0005	<0.001
EB17054	1.2	103	2.1	2.39	0.097	0.172	0.044	0.47	3.1	0.47	0.25	4.23	2.61	5.75	3880	8.3	52.1	5.25	206	6.09	974	0.006	<0.0005	0.001
EB17055	0.86	108	6.1	0.69	0.043	0.158	0.03	0.37	3.5	0.19	0.13	3.39	0.727	3.88	4450	5	34.7	3.98	43.9	3.23	243	0.01	<0.0005	<0.001
EB17057	1.98	98	1.3	0.14	0.019	0.016	0.01	0.14	1.5	0.14	0.6	0.217	0.113	23.5	246	32	8.37	31.6	6					

Appendix F: Fractionation modelling results

Table F.1 Results of Eu/Eu^* in apatite modelling as a function of variable degrees of plagioclase crystallisation (0 – 50 %) and oxidation state (FMQ+2, FMQ+1, FMQ, FMQ-1) at 900 °C.

	Plg. Crst. (%)	FMQ+2	FMQ+1	FMQ	FMQ-1		Plg. Crst. (%)	FMQ+2	FMQ+1	FMQ	FMQ-1
GRANO	0	0.97	0.83	0.67	0.50	EDP _{PB}	0	0.72	0.61	0.50	0.37
	10	0.94	0.79	0.63	0.45		10	0.58	0.58	0.47	0.34
	20	0.91	0.75	0.58	0.41		20	0.55	0.55	0.43	0.31
	30	0.87	0.70	0.54	0.37		30	0.52	0.52	0.40	0.27
	40	0.83	0.65	0.49	0.33		40	0.48	0.48	0.36	0.24
	50	0.79	0.60	0.43	0.28		50	0.45	0.45	0.32	0.21
AND	0	0.65	0.55	0.45	0.33	IMP _{PB}	0	0.79	0.67	0.54	0.40
	10	0.63	0.53	0.42	0.30		10	0.64	0.64	0.51	0.37
	20	0.61	0.50	0.39	0.28		20	0.60	0.60	0.47	0.33
	30	0.58	0.47	0.36	0.25		30	0.57	0.57	0.43	0.30
	40	0.56	0.44	0.33	0.22		40	0.53	0.53	0.39	0.26
	50	0.53	0.40	0.29	0.19		50	0.49	0.49	0.35	0.23
DIO	0	0.71	0.60	0.49	0.36	EQP _{PB}	0	0.74	0.63	0.51	0.34
	10	0.57	0.57	0.46	0.33		10	0.60	0.60	0.48	0.34
	20	0.54	0.54	0.42	0.30		20	0.56	0.56	0.44	0.31
	30	0.51	0.51	0.39	0.27		30	0.53	0.53	0.41	0.28
	40	0.47	0.47	0.35	0.24		40	0.49	0.49	0.37	0.25
	50	0.44	0.44	0.32	0.20		50	0.45	0.45	0.33	0.21
DIOP	0	0.69	0.59	0.48	0.35	LQP _{1PB}	0	0.96	0.81	0.66	0.49
	10	0.56	0.56	0.45	0.32		10	0.78	0.78	0.62	0.45
	20	0.53	0.53	0.42	0.29		20	0.74	0.74	0.58	0.41
	30	0.50	0.50	0.38	0.26		30	0.69	0.69	0.53	0.32
	40	0.46	0.46	0.35	0.23		40	0.64	0.64	0.48	0.32
	50	0.43	0.43	0.31	0.20		50	0.59	0.59	0.43	0.28

Table F.2 Results of REE modelling in apatite as a function of phase crystallisation (0.998 – 0.99 % residual melt).

EQP _{PB}	Apatite					Zircon					Titanite				
	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99
La	323.74	301.79	281.29	262.14	244.26	347.93	348.63	349.33	350.04	350.74	277.49	221.65	176.97	141.23	112.66
Ce	910.17	828.28	753.61	685.54	623.51	1001.25	1002.54	1003.83	1005.12	1006.42	641.16	410.73	262.88	168.10	107.40
Pr	125.69	110.77	97.59	85.96	75.70	142.87	143.15	143.43	143.72	144.00	67.10	31.53	14.79	6.93	3.24
Nd	599.54	514.76	441.83	379.12	325.21	699.35	700.65	701.95	703.26	704.57	194.62	54.12	15.01	4.15	1.15
Sm	200.09	166.37	138.28	114.89	95.42	240.65	240.75	240.84	240.94	241.04	37.45	5.81	0.90	0.14	0.02
Eu	37.68	33.81	30.33	27.21	24.40	41.96	41.94	41.92	41.90	41.89	11.20	2.98	0.79	0.21	0.06
Gd	241.30	187.40	145.47	112.87	87.53	241.30	187.40	145.47	112.87	87.53	56.18	10.13	1.82	0.33	0.06
Tb	47.21	38.55	31.47	25.68	20.94	55.55	53.40	51.33	49.33	47.41	9.67	1.61	0.27	0.04	0.01
Dy	318.91	274.37	235.97	202.89	174.39	318.91	274.37	235.97	202.89	174.39	57.12	8.77	1.34	0.20	0.03
Ho	67.35	59.59	52.72	46.62	41.22	64.97	55.44	47.30	40.35	34.40	16.28	3.47	0.74	0.16	0.03
Er	181.00	161.77	144.55	129.13	115.33	56.79	15.89	4.43	1.23	0.34	56.79	15.89	4.43	1.23	0.34
Tm	24.79	22.33	20.12	18.12	16.31	18.58	12.54	8.46	5.70	3.84	10.13	3.72	1.37	0.50	0.18
Yb	158.23	143.99	131.01	119.18	108.40	100.04	57.51	33.02	18.94	10.85	79.31	36.13	16.43	7.46	3.38
Lu	21.16	19.85	18.61	17.45	16.36	11.79	6.16	3.21	1.67	0.87	12.40	6.81	3.73	2.04	1.12
La/Sm	1.62	1.81	2.03	2.28	2.56	1.45	1.45	1.45	1.45	1.46	7.41	38.15	197.12	1021.82	5314.43
Dy/Yb	2.02	1.91	1.80	1.70	1.61	3.19	4.77	7.15	10.71	16.07	0.72	0.24	0.08	0.03	0.01
REE	3256.86	2863.63	2522.86	2226.80	1968.98	3341.95	3140.37	3010.51	2917.96	2848.29	1526.91	813.36	501.48	332.74	229.68
	Ap:Zrc (0.7:0.3)					Ap:Zrc:Ttn (0.6:0.35:0.05)									
	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99					
La	330.81	315.14	300.18	285.90	272.27	329.46	312.56	296.50	281.23	266.72					
Ce	936.59	877.11	821.30	768.94	719.82	924.72	855.00	790.42	730.60	675.19					
Pr	130.61	119.63	109.54	100.29	91.80	127.39	113.79	101.62	90.73	80.99					
Nd	627.88	564.64	507.66	456.33	410.11	598.13	512.34	438.72	375.56	321.39					
Sm	211.48	185.87	163.33	143.47	126.00	196.29	160.10	130.53	106.38	86.66					
Eu	38.91	36.07	33.42	30.97	28.69	36.82	32.29	28.31	24.81	21.74					
Gd	259.17	216.23	180.34	150.35	125.30	243.85	191.39	150.14	117.73	92.27					
Tb	49.57	42.51	36.44	31.23	26.76	46.17	36.87	29.43	23.48	18.72					
Dy	324.73	284.48	249.15	218.15	190.96	298.87	240.94	194.15	156.38	125.90					
Ho	66.62	58.32	51.03	44.64	39.04	61.95	50.41	41.00	33.34	27.09					
Er	172.62	147.11	125.33	106.75	90.89	161.61	128.94	102.82	81.96	65.30					
Tm	22.73	18.78	15.51	12.80	10.57	21.43	16.68	12.98	10.10	7.85					
Yb	137.90	109.34	86.65	68.64	54.34	137.90	109.34	86.65	68.64	54.34					
Lu	17.76	13.97	10.98	8.63	6.78	16.79	12.49	9.28	6.90	5.12					
La/Sm	1.56	1.70	1.84	1.99	2.16	1.68	1.95	2.27	2.64	3.08					
Dy/Yb	2.35	2.60	2.88	3.18	3.51	2.17	2.20	2.24	2.28	2.32					
REE	3327.41	2989.19	2690.87	2427.10	2193.33	3201.38	2773.14	2412.55	2107.82	1849.29					

LQP1_{PB}	Apatite					Zircon					Ap:Zrc (0.9:0.1)				
	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99
La	346.07	322.61	300.69	280.22	261.11	371.93	372.68	373.43	374.18	374.94	296.63	236.94	189.18	150.97	120.43
Ce	952.67	866.96	788.80	717.56	652.62	1048.01	1049.35	1050.71	1052.06	1053.42	671.10	429.91	275.16	175.95	112.41
Pr	122.23	107.72	94.91	83.60	73.62	138.93	139.21	139.48	139.76	140.04	65.25	30.66	14.39	6.74	3.15
Nd	540.81	464.34	398.55	341.99	293.36	630.85	632.02	633.19	634.37	635.55	175.55	48.82	13.54	3.75	1.03
Sm	122.52	101.87	84.67	70.35	58.43	147.35	147.41	147.47	147.53	147.59	22.93	3.56	0.55	0.08	0.01
Eu	11.85	10.64	9.54	8.56	7.68	13.20	13.20	13.19	13.19	13.18	3.52	0.94	0.25	0.07	0.02
Gd	121.12	94.07	73.02	56.65	43.93	121.12	94.07	73.02	56.65	43.93	28.20	5.08	0.91	0.16	0.03
Tb	19.05	15.56	12.70	10.36	8.45	22.42	21.55	20.72	19.91	19.13	3.90	0.65	0.11	0.02	0.00
Dy	127.71	109.87	94.50	81.25	69.84	127.71	109.87	94.50	81.25	69.84	22.88	3.51	0.54	0.08	0.01
Ho	27.46	24.29	21.49	19.01	16.80	26.48	22.60	19.28	16.45	14.02	6.64	1.42	0.30	0.06	0.01
Er	78.50	70.16	62.69	56.00	50.02	24.63	6.89	1.92	0.54	0.15	24.63	6.89	1.92	0.54	0.15
Tm	10.33	9.31	8.38	7.55	6.80	7.74	5.23	3.52	2.38	1.60	4.22	1.55	0.57	0.21	0.08
Yb	66.43	60.45	55.00	50.03	45.51	42.00	24.14	13.86	7.95	4.56	33.30	15.17	6.90	3.13	1.42
Lu	10.01	9.39	8.81	8.26	7.74	5.58	2.91	1.52	0.79	0.41	5.87	3.22	1.77	0.97	0.53
La/Sm	2.82	3.17	3.55	3.98	4.47	2.52	2.53	2.53	2.54	2.54	12.93	66.61	344.14	1783.93	9278.14
Dy/Yb	1.92	1.82	1.72	1.62	1.53	3.04	4.55	6.82	10.22	15.33	0.69	0.23	0.08	0.03	0.01
REE	2556.77	2267.23	2013.76	1791.39	1595.90	2727.97	2641.14	2585.82	2547.00	2518.36	1364.63	788.33	506.08	342.73	239.29
	Ap:Zrc:Ttn (0.8:0.15:0.05)					Ap:Zrc (0.95:0.05)									
	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99					
La	341.84	314.75	289.77	266.72	245.46	344.31	319.33	296.11	274.54	254.51					
Ce	916.92	803.05	703.13	615.48	538.61	925.71	818.53	723.58	639.49	565.03					
Pr	113.41	92.71	75.77	61.89	50.54	114.87	95.12	78.74	65.16	53.89					
Nd	467.50	346.88	257.23	190.63	141.19	474.75	357.74	269.42	202.78	152.54					
Sm	97.96	65.10	43.23	28.68	19.01	99.79	67.55	45.69	30.88	20.86					
Eu	10.04	7.63	5.80	4.40	3.34	10.15	7.80	5.99	4.60	3.52					
Gd	100.87	65.23	42.14	27.20	17.54	103.31	68.41	45.27	29.93	19.77					
Tb	15.39	10.15	6.69	4.40	2.89	15.64	10.48	7.02	4.70	3.14					
Dy	99.57	66.75	44.72	29.93	20.02	100.17	67.56	45.53	30.66	20.63					
Ho	22.07	15.69	11.15	7.91	5.61	21.99	15.58	11.03	7.80	5.51					
Er	64.42	47.24	34.61	25.35	18.55	62.25	44.09	31.21	22.08	15.61					
Tm	8.65	6.53	4.92	3.71	2.79	8.41	6.16	4.51	3.30	2.41					
Yb	52.82	38.20	27.61	19.95	14.40	57.89	45.90	36.38	28.82	22.81					
Lu	8.47	6.71	5.32	4.21	3.33	7.99	5.97	4.46	3.33	2.48					
La/Sm	3.49	4.83	6.70	9.30	12.91	3.45	4.73	6.48	8.89	12.20					
Dy/Yb	1.89	1.75	1.62	1.50	1.39	1.73	1.47	1.25	1.06	0.90					
REE	2319.94	1886.62	1552.06	1290.45	1083.29	2347.23	1930.23	1604.94	1348.06	1142.73					

GRANO	Apatite					Zircon					Titanite				
	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99
La	717.85	669.18	623.72	581.27	541.62	771.50	773.05	774.60	776.16	777.73	723.04	678.91	637.38	598.32	561.58
Ce	1815.48	1652.13	1503.20	1367.43	1243.69	1997.16	1999.73	2002.30	2004.88	2007.47	1832.88	1683.98	1546.92	1420.77	1304.68
Pr	236.83	208.71	183.89	161.97	142.63	269.19	269.72	270.26	270.79	271.33	239.88	214.13	191.10	170.51	152.11
Nd	970.52	833.28	715.23	613.72	526.45	1132.10	1134.20	1136.30	1138.42	1140.54	985.58	859.37	749.12	652.83	568.76
Sm	151.63	126.08	104.79	87.07	72.31	182.37	182.44	182.52	182.59	182.66	154.46	130.82	110.77	93.76	79.33
Eu	20.82	18.69	16.76	15.04	13.48	23.19	23.18	23.17	23.16	23.15	21.05	19.09	17.32	15.70	14.23
Gd	85.46	66.37	51.52	39.98	31.00	85.46	66.37	51.52	39.98	31.00	87.52	69.62	55.35	43.99	34.94
Tb	9.46	7.72	6.31	5.14	4.20	11.13	10.70	10.28	9.88	9.50	9.61	7.98	6.62	5.49	4.55
Dy	46.02	39.59	34.05	29.28	25.16	46.02	39.59	34.05	29.28	25.16	46.30	40.07	34.67	29.99	25.94
Ho	8.01	7.09	6.27	5.55	4.90	7.73	6.60	5.63	4.80	4.09	7.98	7.04	6.20	5.47	4.82
Er	18.35	16.40	14.66	13.09	11.69	5.76	1.61	0.45	0.13	0.03	18.07	15.89	13.98	12.29	10.80
Tm	2.13	1.92	1.73	1.56	1.40	1.60	1.08	0.73	0.49	0.33	2.07	1.81	1.59	1.39	1.21
Yb	11.62	10.58	9.62	8.75	7.96	7.35	4.22	2.43	1.39	0.80	11.10	9.65	8.38	7.28	6.32
Lu	1.57	1.47	1.38	1.29	1.21	0.87	0.46	0.24	0.12	0.06	1.48	1.31	1.16	1.02	0.90
La/Sm	4.73	5.31	5.95	6.68	7.49	4.23	4.24	4.24	4.25	4.26	4.68	5.19	5.75	6.38	7.08
Dy/Yb	3.96	3.74	3.54	3.34	3.16	6.26	9.37	14.04	21.05	31.58	4.17	4.15	4.14	4.12	4.10
REE	4095.76	3659.22	3273.13	2931.13	2627.72	4541.43	4512.95	4494.47	4482.07	4473.87	4141.02	3739.68	3380.56	3058.81	2770.19
	Ap:Zrc:Ttn (0.8:0.15:0.05)					Ap:Zrc (0.95:0.05)									
	0.998	0.996	0.994	0.992	0.99	0.998	0.996	0.994	0.992	0.99					
La	650.39	549.20	463.59	391.20	330.00	720.44	674.03	630.51	589.73	551.51					
Ce	1809.66	1641.55	1488.76	1349.93	1223.80	1824.16	1667.98	1524.90	1393.84	1273.82					
Pr	233.96	203.69	177.28	154.26	134.18	238.35	211.40	187.46	166.19	147.29					
Nd	938.87	779.76	647.38	537.28	445.73	978.02	846.23	731.98	632.97	547.20					
Sm	143.36	112.68	88.53	69.52	54.56	153.04	128.43	107.74	90.35	75.74					
Eu	19.92	17.09	14.66	12.58	10.78	20.94	18.89	17.04	15.36	13.85					
Gd	82.35	61.62	46.08	34.44	25.73	86.49	67.98	53.40	41.93	32.91					
Tb	8.95	6.92	5.35	4.13	3.19	9.54	7.85	6.46	5.32	4.37					
Dy	42.61	33.94	27.02	21.50	17.10	46.16	39.83	34.36	29.63	25.55					
Ho	6.45	4.60	3.27	2.33	1.65	8.00	7.06	6.24	5.51	4.86					
Er	15.18	11.22	8.29	6.12	4.51	18.21	16.15	14.31	12.68	11.24					
Tm	1.81	1.38	1.06	0.81	0.62	2.10	1.86	1.66	1.47	1.30					
Yb	11.10	9.65	8.38	7.28	6.32	11.36	10.10	8.98	7.98	7.10					
Lu	1.37	1.11	0.91	0.74	0.60	1.52	1.39	1.26	1.15	1.05					
La/Sm	4.54	4.87	5.24	5.63	6.05	4.71	5.25	5.85	6.53	7.28					
Dy/Yb	3.84	3.52	3.22	2.95	2.70	4.06	3.94	3.83	3.71	3.60					
REE	3965.97	3434.42	2980.57	2592.10	2258.78	4118.31	3699.18	3326.31	2994.13	2697.79					

Appendix G: Predictive classification models

Table G.1 Details for model 1A.

Model 1A	
Data instances	503
Input variables	Sericitic apatite, other
Features	Eu/Eu*, Pb, V, Y
Algorithm	Random Forest
Details	20 trees Unlimited tree depth Stop splitting nodes with after 5 instances

Table G.2 Details for model 1B.

Model 1B	
Data instances	343
Input variables	Least altered magmatic, metasomatised magmatic apatite, proximal hydrothermal alteration
Features	La/Sm, V, As, Pb, Na, Sr/Y, Gd/Yb, Eu/Eu*, Mn, Th
Algorithm	Logistic regression
Details	Regularisation: Lasso (L1) C = 80

Table G.3 Details for model 2.

Model 2	
Data instances	1344
Input variables	Non-porphyry, main porphyry, late porphyry
Features	Gd/Yb, V, Mn, U, Sr/Y, Eu/Eu*, Na, Pb, La/Sm, Fe
Algorithm	Logistic regression
Details	Regularisation: Lasso (L1) C = 80

Appendix H: Lab comparison

This section compares LA-ICP-MS analyses of apatite standards collected at the Core laboratories at the Natural History Museum London and Rio Tinto's laboratory in Melbourne, Australia. There are three main reasons for this study: 1) To help assess the validity of using pre-existing data collected in the Rio Tinto labs and comparing directly to new data collected at the museum. 2) To look at the reproducibility of new analyses between the museum and Rio Tinto, important for any outcomes of the projects which Rio may use

The laser set up for the NHM laser will be the same as described in section chapter 3. The laser energy was set to 5 jcm⁻² and 10 Hz, the external standard used was NIST612 and standardised to 43Ca based off of values measured by probe. At Rio Tinto a New Wave ESI 213 laser was used with a Agilent 790 quadrupole mass spectrometers, details are listed in Table H.1. The set up was ran without modifications so as to match the set up for existing data and to highlight any real changes that may need to be made. The laser sequence lasts 120 and uses no pre-ablations, 60s of washout and 40s of sample ablation. Standards are measured every 20 unknowns, with extra measured at the beginning and end of the analyses. The laser energy was set to 5.6 jcm⁻² and 5 Hz.

Here analyses of Durango apatite STD0067 are compared from each laboratory. The standard was lightly polished after laser ablation at the first lab to remove ablate build up. The location of the analyses were kept close together. A comparison of results from the two labs are given in table H.2.

Table H.1 Rio LA-ICP-MS instrument details

<i>Laser parameters</i>	
Laser type	Nd-YAG
Laser wavelength	213 nm
Analysis type	Spot
Spot diameter	35 µm
Carrier gas	Helium, (700 ml/min)
<i>Mass spectrometer parameters</i>	
Plasma gas flow	Argon, 1.10 l/min
Forward RF	1350 watts
Dwell time per isotope	10 ms
Instrument sweep time	0.579 s

Table H.2 Comparison of apatite (Durango STD0067) from both labs and average from literature solution ICP-MS (Mao et al. 2016; Chew et al. 2016)

	Literature	Natural History Museum		NHM vs Lit. (%)	Rio Tinto		Rio vs Lit. (%)	NHM vs Rio (%)
	Mean (ppm)	Mean (ppm)	RSD (%)		Mean (ppm)	RSD (%)		
Na		0.155	0.014		0.170	0.007		9.61
Fe		0.023	0.002		0.041	0.001		75.76
Mn	0.010	0.008	0.001	-13.47	0.010	0.000	1.07	16.81
Mg	0.012	0.011	0.001	-8.29	0.011	0.000	-3.14	5.61
V	0.005	0.003	0.000	-37.29	0.003	0.000	-37.51	-0.35
Sr	0.050	0.052	0.003	3.78	0.051	0.001	0.99	-2.69
Y	0.068	0.087	0.005	28.08	0.073	0.003	8.03	-15.65
La	0.388	0.397	0.027	2.22	0.346	0.009	-10.82	-12.76
Ce	0.481	0.533	0.036	10.85	0.519	0.015	7.86	-2.70
Pr	0.042	0.046	0.003	8.16	0.043	0.001	0.62	-6.97
Sm	0.018	0.019	0.001	2.89	0.019	0.001	4.00	1.08
Eu	0.002	0.002	0.000	-5.37	0.002	0.001	1.60	7.36
Gd	0.016	0.016	0.001	0.79	0.017	0.001	2.03	1.23
Dy	0.013	0.012	0.001	-9.16	0.012	0.000	-7.62	1.69
Yb	0.004	0.004	0.000	5.00	0.004	0.000	2.59	-2.29
Th	0.026	0.024	0.002	-8.02	0.022	0.001	-15.36	-7.98
U	0.001	0.001	0.000	2.13	0.001	0.001	9.79	7.50

