"It is not truisms which science unveils. Rather it is part of the greatness and beauty of science that we can learn through our own critical investigations that the world is utterly different from what we ever imagined - until our imagination was fired by the refutation of our earlier theories."

"The wrong view of science betrays itself in the craving to be right."

"...only through criticism can knowledge advance."

"the growth of our knowledge proceeds from problems (scientific inconsistencies with establishd "truth") and our attempts to solve them."

Karl Popper, The Logic of Scientific Discovery.

"The erroneous belief that science eventually leads to the certainty of a definitive explanation carries with it the implication that it is a grave scientific misdemeanor to have published some hypothesis that eventually is falsified. As a consequence scientists have often been loath to admit the falsification of such an hypothesis and their lives may be wasted in defending the no longer defensible. Whereas according to Popper, falsification in whole or in part is the anticipated fate of all hypotheses, and we should even rejoice in the falsification of an hypothesis that we have cherished as our brain child. One is thereby relieved from fears and remorse and science becomes an exhilirating adventure where imagination and vision lead to conceptual developments transcending in generality and range the experimental evidence. The precise formation of these imaginative insights into hypotheses opens the way to the most rigorous testing by experiment, it being always anticipated that the hypothesis may be falsified and that it will be replaced in whole or in part by another hypothesis of greater explanatory power."

J. C. Eccles, Facing Reality.

# HYDROTHERMAL PHENOMENA IN THE WESTERN LOBE OF THE ST. AUSTELL GRANITE, CORNWALL

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## ABSTRACT

This thesis is a study of the granite of the western lobe of the St. Austell granite cupola and the fluids which interacted with it and their effects upon it.

The western lobe is composed of a phenocryst rich, coarse grained, biotite bearing peraluminous alkali feldspar granite. It is chemically and mineralogically similar to other SW England and Sn-W bearing granites.

Extensive late magmatic crystallisation resulted from high volatile contents which depressed the solidus. Pegmatitic zones, miarolitic cavities, tourmaline banding and autometasomatic alteration resulted from the periodic separation and localised concentration of immiscible aqueous phases from the residual interstitial melt.

Greisenisation, tourmalinisation and kaolinisation are the main types of alteration caused by the passage of successive generations of fluids through the granite. The mineralogical and chemical changes accompanying these alteration processes have been studied using petrological and statistical techniques. Tourmalinisation is the principle alteration type accompanying tin mineralisation. There is a correlation between cassiterite and tourmaline of schorlitic composition.

Hydraulic fracturing in the granite was the result of the interaction between cooling stresses, the regional stress field and fluid overpressures generated by the separation of aqueous phases from the differentiating melt at depth. A breccia body formed as a result of fracturing down an extreme pressure gradient.

The possible origin and mineralisation potential of the successive generations of hydrothermal fluid have been determined from their thermal and compositional characteristics and in the light of contemporary models for magmatic differentiation processes and the initiation of hydrothermal convective systems caused by the intrusion of igneous bodies. The available stable isotope data has been reappraised. Deuteric fluids are largely responsible for greisenisation, tourmalinisation and tin mineralisation. Meteoric hydrothermal waters caused kaolinisation and possible uranium mineralisation. These represent the early and late stages of a single hydrothermal convective system of extended duration which persisted due to the high radiogenic heat content of the granite.

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# PREFACE

This research project developed in a similar fashion to the majority of such studies, that is, the objectives were constantly changing with time as work progressed. Initial interest for this project was stimulated by a spectacular tourmaline breccia pipe exposed during routine development work in Wheal Remfry, a china clay pit in the western lobe of the St. Austell granite. This was of particular interest since similar tourmaline breccias associated with porphyry copper and porphyry tin mineralisation have been well described from the Andean metal provinces, Sillitoe & Sawkins (1971), Sillitoe et al (1975), Grant et al (1980). A reconnaissance investigation of the breccia was subsequently undertaken by Halls et al (1977). Following this a CASE studentship was set up between the NERC and English Clays Lovering Pochin Co. Ltd. (ECLP) to study this and related phenomena in the pit.

It became immediately apparent that the breccia pipe could not be studied in isolation since it formed an integral part of the structural fabric of the area and its origin was related to the igneous and hydrothermal evolution of the granite. The scope of the research was therefore broadened to include the structures and their associated hydrothermal alteration.

The large volume of wall rock alteration present in the western lobe of the St. Austell granite raised questions on the nature of the fluids responsible, the quantity of fluid necessary to effect it and the way in which such volumes could be passed through the rock. Taylor (1977) published evidence to indicate that large amounts of water circulated through high level granite intrusives through the mechanism of large scale hydrothermal convective cells. Considerable theoretical work was being undertaken at the same time by Norton and his co-workers, (Norton & Knapp 1977, Norton and Knight 1977, Villas and Norton 1977) on the

subject of the hydrothermal convective cells generated by the intrusion of igneous bodies into the upper crust. Their concepts on the origin of the hydrothermal fluids were applied to SW England.

Having begun as an investigation of a tourmaline breccia pipe the research evolved into a study of the evolution of the granite and the fluids which passed through and interacted with it.

In summary it was hoped that the following objectives could be achieved:

1. To explain the origin and mechanism of formation of the structures
2. To define the morphology, controlling factors, mineralisation potential and genesis of the tourmaline breccia pipe.
3. To identify the different alteration facies and their sequence of formation.
4. To describe the mineralogical and chemical changes accompanying alteration.
5. To characterise the fluids responsible for alteration and their evolution with time.
6. To establish a reasonable model for the origin of the hydrothermal fluids consistent with the observed data and the theoretical models.

This study has benefitted from a great deal of advice, discussion and argument from and with a large number of people, in particular however: Dr Andrew Rankin, Dr Chris Halls, Colin Bristow, Dr Clive Gronow, Dr Jan Hawkes, John Dangerfield, Dr David Alderton, John Moore and Dr Neville Price.

I am indebted to the IGS for the use of their rock crushing

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Without the consent of ECLP Co. Ltd. this project could not have been undertaken and I should like to express my gratitude to all of the geological, mining, surveying and laboratory staff for their help and co-operation.

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# CHAPTER 1

## SOUTH-WEST ENGLAND

## 1.1 ECONOMIC INTRODUCTION

SW England has been an area of considerable economic importance for a long time, possibly since the bronze age (circa 1800 BC). It is also said that both the Phoenicians and the Romans obtained tin from here, probably from placer deposits. Mining activity only reached its peak however towards the end of the 19th century under the stimulus of The Industrial Revolution. The main ore minerals were those of tin and copper but significant quantities of argentiferous lead, zinc, arsenic, iron and barite were also extracted. Small amounts of fluorite, uranium and antimony have been mined on a local scale. Gold, bismuth, nickel, cobalt and molybdenum benefitiate some deposits and have been recovered occasionally as by-products. The total value of metals extracted at current market prices is estimated to be of the order of $\$28 \times 10^{9}$ based upon information from Jackson (1979). Increasing costs of production, low capitalisation and poor technology forced most of the mines to close.

After nearly a century of relative inactivity, interest has been revitalised by a combination of factors, incentives for exploration from the EEC, the present buoyant metal market, improved technology and better geological knowledge. Tin and tungsten are the current target ore minerals. There are currently four active mines working such deposits, Geevor, South Crofty, Pendarves and Wheal Jane- Mount Wellington. The Hemerdon tungsten prospect looks promising and several other prospects are being re-examined.

Despite the focus of geological attention on metalliferous mineralisation the most important mineral resource in SW England is kaolinite (china clay). The deposits, scattered throughout the granites but particularly concentrated in the St Austell granite mass are the

single largest in the world and makes Britain the second largest producer after the USA. Current annual production is 3,800,000 tonnes (1978).

## 1.2 PALAEOGEOGRAPHIC RECONSTRUCTION

By the end of the Caledonian orogeny, roughly 370 my ago Northern Europe formed part of the stable Laurasian Craton. The developing Hercynian belt lay to the south. Much of the northern foreland was elevated to form the Old Red Sandstone continent which supplied detritus to the developing Hercynian geosyncline. A fluctuating shoreline ran roughly east-west from Poland into southern Britain and on into Ireland.

The main events of the Hercynian orogenic cycle affecting SW England can be summarised as follows:

I. A transgression (in the Devonian) began the geosynclinal phase. In the northern part adjacent to the ORS continent alternating shallow marine and continental phases contained a few volcanic rocks. Further south the assemblage was entirely marine, pelitic and calcareous rocks predominating with abundant basic volcanic material.

Regression occurred during the end of the period accompanied by some tectonic disturbances of the "Bretonic Phase". It is possible that the Lizard complex (possible Precambrian basement) was emplaced at this time along the Lizard - Dodman - Start thrust fault. Although hypothetical, the presence of this structure fits the geophysical evidence (Bott and Scott 1964).

II. At the beginning of the Carboniferous period a transgressive sea advanced over and more or less completely submerged the ORS continent. In the geosyncline a great thickness of black shales, cherts, black limestones and sandstones, dominantly "flysch" type sediments with pillow lavas and tuffs were deposited to form the Culm facies.

Near the end of the Dinantian the powerful "Sudetic" tectonic phase occurred (circa 325 my). Its focus was further south in central Europe resulting in virtually all of the land to the south of Cornubia emerging as a new land mass.

III. The effects of the Sudetic orogen are barely seen in SW England as deposition of marine shales with their turbidite sandstones continued more or less without break up into the Westphalian. By contrast Asturic disturbances (c.290 my) which marked the end of this period is most important since it was then that the strata was thrown into overturned folds or displaced northwards on low angle thrusts. The intrusion of the granitic pluton and consequent metamorphism of the country rocks occurred during the closing stages of these movements.

At the end of the Hercynian orogenic cycle, SW England was part of an extensive land mass situated near the equator. The hot arid climate lead to severe denudation and widespread deposition of piedmont, desert and sabkha facies. The lowest formations are Hercynian molasse of breccia, conglomerates and coarse sandstones containing fragments of predominantly local origin forming the basal Permian. The sporadic occurrance of tourmaline rich pebbles and kaolinite in these deposits indicate that some high level expression of the granite was unroofed by Permian times (Dangerfield & Hawkes 1969). Studies of heavy minerals occurring in Jurassic and Cretaceous marine sediments however indicate that the main body of the granite was not exposed until Wealden times (Groves 1931). Marls and sandstones were laid down in fresh water in broader basin areas. Late orogenic volcanics including andesites and tuffs are associated with the molasse type clastic formations - the Exeter volcanic series. They are the remnants of formerly extensive lava

flows extruded at or soon after the beginning of the Permian. Non-marine breccias, pebble beds, sandstones and marls of Triassic age were laid down during continuing arid conditions.

It is not known whether SW England remained as a substantial land mass from the Jurassic onwards because any sediments which may have been deposited have subsequently been eroded.

The effects of the Alpine orogeny which reached its peak during the Miocene are limited to the development of a number of dextral wrench faults, Dearman (1964).

## 1.3 THE CORNUBIAN BATHOLITH

### 1 MORPHOLOGY OF THE BATHOLITH

Gravity studies have shown that a granitic batholith forms the backbone of the Cornubian peninsula (Bott et al 1958, Bott & Scott 1964). It stretches about 200 km from Dartmoor to the Scilly Isles in a NW-SE orientation. Granite samples have been dredged from the sea floor 150 km west of Land's End at Haig Fras (Edmonds et al 1975) but if this represents an extension of the batholith, there must be a substantial offset of 60 km due to transcurrent faulting. Similar wrench faulting of Tertiary age has affected the exposed granite causing disturbances in the gravity anomalies by displacing the granite outcrops with respect to each other (Dearman 1964).

The batholith is exposed as six major units, Figure 1: Dartmoor, Bodmin Moor, St Austell, Carnmenellis, Land's End and the Scilly Isles (not shown) and several minor ones including Tregonning - Godolphin and St Agnes - Cligga Head. Subordinate outcrops are associated with the major cupolas e.g. Castle-an-Dinas and Belowda Beacon on the north flank of the St Austell granite.

The depth of cover between each exposure is estimated to be as little as 2 or 3 km along the axis of the batholith. The present level of erosion has therefore only skimmed the roof of the batholith. The sub-surface shape of the granite was believed to be laccolithic (Bott et al 1958). Subsequently the geophysical data has been more satisfactorily interpreted as being due to an increase in density of the granite northwards (Bott & Scott 1964). The granite extends to a depth of approximately 12 km.

## 2 THE GRANITE

The majority of those working on the Cornubian batholith believe it to be a single intrusive mass showing minor variations in texture and composition. The most obvious difference is the contrast between the porphyritic and non-porphyritic varieties. The former has been interpreted by Booth (1968) as being the peripheral development of a fundamentally homogenous body. Exley & Stone (1964) also believed it to be a peripheral phenomenon but due to the outward migration of potassium rich fluids. Although this view is widely accepted, it is not substantiated by an analysis of potash contents in the Dartmoor granite varieties by Tammemagi and Smith (1975). They demonstrated a progressive decrease in potash content with increasing phenocryst abundance.

The granite masses have been recently reclassified and remapped by the IGS. A number of different granite types have been identified, Hawkes & Dangerfield (1978), Figure 2. The differences have been attributed to the effects of assimilation, contaminination and autometasomatism. The lithium mica granite is an exception and is considered to be the residual product of differentiation of the ordinary granite which has been intruded into its host and parent.

## 3 OTHER INTRUSIVE ROCKS

Fine grained aplite dykes occur in SW England. They are spatially closely related to the granite masses and their sharp contacts and parallelism suggest that they have been forcefully injected into the host rock.

"Pegmatites are remarkably scarce in view of the high proportion of volatiles in the granites", Exley & Stone (1964). Although manifestly true of pegmatitic dykes (although some have been commercially exploited), pegmatitic zones are quite common in the granite and aplites (Bray 1980).

Elvans are fine grained, often porphyritic, quartzitic rocks occurring as dykes cutting both granite and killas (country rock). Chemically they are siliceous, hyperpotassic and hyposodic. They are generally considered to be late granitic differentiates but the difference in $K_2O/Na_2O$ ratios between them (11.3) and the granite (2.7) would seem to exclude any direct genetic relationship (Hall 1970). Goode (1973), Henley (1972), Stone (1968), Hawkes et al (1975), Hawkes (pers. comm.) have suggested that they represent fluidised systems; an intimate mixture of late differentiated fluid expelled under pressure from the granite containing partially or completely digested granitic material.

## 4 ORIGIN OF THE GRANITE

Most authors investigating compositionally restricted granites associated with tin-tungsten mineralisation are of the belief that they are of lower crustal origin, Table 1. Chappell and White (1974) differentiated between granites of primary, juvenile, mantle origin (I type) from those of lower crustal, anatectic origin (S type). Table 2 lists the criteria upon which this discrimination is based and the features of the Cornubian batholith are included for comparison. This shows the Cornubian batholith to have 'S' type granite characteristics with the exception of the $Sr^{87}/Sr^{86}$ ratios and the presence of magnetite as the ubiquitous iron oxide. These two discrepancies are insufficient to prove a mantle contribution (Simpson et al 1979), particularly in view of the large variation in initial ratios obtained for the elvans: 0.7130, 0.7080, 0.7064 (Hawkes et al 1975). However, the assimilation of sufficient quantities of crustal material and fractionation will give a magma of mantle origin, crustal characteristics, (Burnham 1979).

The conditions under which anatexis took place are delimited by a number of bracketing parameters, Charoy (1979). The first of these is the $H_2O$ content of the magma. In order to attain high levels in the crust the anatectic melt must be undersaturated in $H_2O$ at its origin and must therefore also be the product of relatively anhydrous parental material. The amount of $H_2O$ dissolved has been estimated to be about 3 wt%. The subsequent parameters relate to the mineralogy of the granite, the presence of garnet and cordierite which have been presumed to have crystallised from the magma and the assumed metasomatic origin for the protolithionite. The pressure and temperature conditions of anatexis thus lie: to the left of the liquidus for granite containing 3 wt% $H_2O$, slightly above the phase line separating the stability fields of

cordierite from cordierite and garnet and to the right of the incongruent melting curve for protolithionite, Figure 3. This corresponds to the following conditions: 860-60 $^{+}_{o}$C, 5.2-0.4 kb, 3 to 5 wt% $H_2O^{+}$.

## 5 MECHANISM OF MAGMA FORMATION

The volume of the granitic batholith implies that a considerable quantity of crustal material must have undergone anatexis. This requires either a substantial and persistant supply of heat or water in order to produce the requisite quantity of magma. There are four ways in which this may be achieved.

1. Subduction. The subduction of crustal material generates magma of basaltic or andesitic composition which may generate granite magmas indirectly by impinging upon and partially melting the lower crust (Presnall & Bateman 1973) or directly by assimilation of crustal material on ascension (Burnham 1979). The Andean mountain chain is a classic example of this orogenic process. Numerous contradictory models for subduction during the Hercynian orogeny have been proposed, Floyd (1972), Bromley (1976), Badham and Halls (1975). Moreover, granites generated in such environments are characterised by being "I type", Atherton et al (1979), Thorpe & Francis (1979), Pitcher (1979).

2. Crustal thickening. Mitchell (1974) proposed a continent to continent or Himalayan type collision for the Hercynian. In this kind of orogeny crustal shortening results in thickening sufficient to partially melt the lower crust and give rise to "S type" granites, Pitcher (1979). This is in contrast to the European Hercynian which is characterised by a distinct lack of nappe structures, large scale thrust faulting, areas of strong post collision uplift or (in south-west England) any regional

negative gravity anomalies other than those due to the granite (Simpson et al 1979).

3. Mantle hot spots. Hot spots are imperfectly understood geological phenomena but it has been suggested (Hawkes, pers. comm.) that such a feature associated with the onset of crustal splitting in northern Europe may account for the Hercynian magmatism.

4. Transcurrent faulting. Heat generated by transcurrent faulting may be sufficient to induce partial melting of the lower crust (Halls 1981). The "jostling" of the microplates (Badham & Halls 1975) may have been capable of giving rise to the conditions necessary for the generation of the Cornubian magmatism.

## 6 EMPLACEMENT OF THE GRANITE

The Cornubian batholith shows all the classic features of a high level, post orogenic granite pluton forcibly intruded into its host rocks. It has all the following properties: a well developed (0.5 to 1 km wide) metamorphic aureole; clean contacts; apophyses cross cutting the country rock; phenocryst alignment implying flow; doming of flat lying structures with the development of marginal folding and cleavage (Exley & Stone 1964), (Hawkes, pers. comm.). The lack of migmatites and the relatively low grade of metamorphism (hornblende hornfels facies) implies a relatively passive, low temperature intrusion. The presence of cataclasis and foliation caused by crushing and mylonitisation and the granulation of certain minerals shows there to have been a large component of solid flow (Exley & Stone 1964). The magma can be imagined as an aggregate of early formed minerals capable of ascending by the lubricating effect of residual intergranular aqueous fluids enriched in

volatiles (Charoy 1979, Badham et al 1976).

## 7 MINERALISATION

Mineralisation occurs predominantly as lodes orientated NE-SW containing tin and copper with arsenic, tungsten and molybdenum and as cross cutting N-S veins (cross-courses) associated with Fe, Pb, Zn, U, Co and Ni mineralisation.

There is a close spatial relationship between mineralisation and magmatism as major mineralised bodies occur along the flanks of the pluton and within or above the apices of small accessory cusps. The early mineralised fractures also cluster around the elvan dykes which strike in the same direction (Hosking 1964). The elvans are usually cut by the fractures but the inverse relationship also occurs (Badham et al 1976, Bray 1980), which indicates a close temporal as well as spatial relationship. Similar relationships are observed in the Erzgebirge - Krusny - Hory district and Stemprok & Skvor (1974) suggest a deep and common origin for both mineralisation and late magmatism.

The traces of the elvans and mineralised fractures were used by Moore (1975) to show that they both formed under the same stress conditions interpreted as the result of the interaction between the regional stress field and the fluid pressure within the crystallising granite cupola. Brittle fracture occured on the flanks of the plutons and the fractures engendered in the endozone of the granite and in the country rock were used as the conduits for the late magmatic and hydrothermal residua.

SW England has been described as a classic area showing vertical

and lateral mineral zonation. Concentric mineral zones in the sequence Sn-Cu-Zn-Pb-Fe were described by Dewey (1925), Dines (1934) reflecting the thermal gradient away from the granite (Hosking 1964). Subsequent work has shown the mineralisation to be polyascendant, that is, older "hypothermal" and younger "epithermal" assemblages share the same structure (Moore 1982). The simple model of concentric zoning was incompatible with the discontinuous pattern of mineralisation and was replaced by the concept of "emanative centres", Dines (1933) Figure 4. These were imagined to be the exit points of solutions from the granite cupolas. In cross section they consist of a central "feeder" of tin-tungsten mineralisation overlain and and flanked by successive copper and lead zones. In plan the centres are subcircular and 3 to 4 km in diameter.

Moore (1982) has pointed out that the size and shape of the emanative centres is compatible with contemporary geothermal systems such as those in New Zealand. He has reinterpreted the emanative centres in terms of individual hydrothermal convective cells each having its own independant evolutionary history, Figure 5. Under steady state conditions the mineral distribution will be in response to changing physical criteria (falling P and T) resulting in mineral zoning, but the collapse of the geothermal cell with time will give rise to apparent telescoping, Moore (1982).

The activity and life span of these hydrothermal cells will depend upon heat and water supply and the maintenance of permeability. Isotopic age dating has shown that the formation of the lower temperature minerals (particulary uranium) has continued sporadically until Tertiary times (Darnley et al 1965, Bray 1980, Jackson et al 1982) and so also, by implication, the hydrothermal cells from which they were deposited.

Hydrothermal activity may even have continued to the present as the thermal springs which issue into the mine workings. The extensive life span of these hydrothermal cells (over 200 my) is undoubtedly connected with the anomalous heat production of the Cornubian granites (Tammemagi and Wheildon 1974, 1977) caused by radiogenic decay.

## 8 GEOCHEMICAL CHARACTERISTICS

The granite contains anomalously high concentrations of: Fe, Mg, K, Ni, Cu, Cr, Sn, U, Li, Th, Pb, Rb, Be, B, F, As, Cl, Zn and Cs and low concentrations of Ba, Sr and low K/Rb ratios (Jackson 1979, Simpson et al 1979, Ahmad 1977, Hall 1973, Floyd 1972, Harding and Hawkes 1971) compared to average values for low calcium granites (Turekian & Wedepohl 1961). These are largely the same elements as those reported as being enriched and depleted in other tin bearing granites, Table 3.

This assemblage is compatible with enrichment due to magmatic differentiation. The low K/Rb ratios are additional evidence that the granite at its present level has already undergone considerable differentiation (Exley & Stone 1964). The ratios for what is considered to be the least evolved facies (biotite granite) lie between 58 and 102 and decrease in the latest differentiates (lithium mica granite) to between 20 and 30 (Tammemagi and Smith 1975). Geophysical evidence (Bott et al 1970) shows the existence of more basic rocks at depth which can be interpreted as being the more refractory fraction which crystallised from the anatectic magma.

Some of the elements (Fe,Mg,Ni,Cu,Cr,As,Pb and Zn) are more irregularly distributed and their enrichment has been explained as the assimilation of metavolcanics and pelitic country rocks (Floyd 1972,

Jackson 1979, Ahmad 1977).

The enrichment in radiogenic elements was explained by Simpson et al (1979) as scavenging of the overlying mantle wedge by the juvenile, subduction generated magma but this is incompatible with the probable anatectic origin of the granite. Lower crustal contamination is an equally possible source for the uranium (Zentilli and Dostal 1977).

## 9 RELATIVE AND ABSOLUTE AGE DATING

The age relationships from geometrical criteria are as follows: granite intrusion, aplites and pegmatites, elvans, mineralised pegmatites, normal hypothermal deposits, mesothermal deposits, barren quartz and clay filled veins. There are so many exceptions to this generalised sequence (Hosking 1964) that Charoy (1979) considers it to be useless.

Absolute ages are obtained from radiometric age dating studies (Dodson & Rex 1971, Hawkes et al 1975). Potassium/argon ages reflect the age at which the host mineral (muscovite, biotite) cools below its blocking temperature, the temperature at which the argon is effectively retained. The rubidium/strontium method is considered to give the time of magmatic crystallisation. In summary, the K/Ar dates for the granites average at $284^{+}_{-}11$ my, the Rb/Sr dates for St Austell being $301^{+}_{-}25$ my. The "true" age of the batholith is probably closer to the latter age. The elvans would appear to have been intruded rather later (K/Ar=$272^{+}_{-}6$, Rb/Sr=$278^{+}_{-}4$) at much the same time as the main greisenisation (mineralisation) event (K/Ar=$273^{+}_{-}8$, Rb/Sr=$276^{+}_{-}7$) confirming their

contemporaneity. However, all these ages are indistinguishable within experimental and statistical error.

## 10 SUMMARY

The Cornubian batholith is a high level, post orogenic granitic body with 'S' type characteristics derived by anatexis of continental crust ($T=860^{o}C$, $P=5.2$ kb). In order to be able to supply above average quantities of B,F,Rb,Sn,Cl and As to the anatectic melt the source material must have included a large pelitic component which had not previously undergone extreme metamorphism (Jackson et al 1982).

Initially strongly undersaturated with water, the magma was able to rise to within 1.5 to 4 km of the surface (Floyd 1971, Hall et al 1977) by forceful injection, block stoping and cauldron subsidence (Jackson 1979). Differentiation took place during ascension giving rise to high contents of elements such as Rb. Assimilation, contamination, and further differentiation gave rise to the different granite types.

Hydrothermal convective cells initiated on the flanks of the plutons at points where rupturing had occurred were responsible for mineralisation. The cells may have been periodically rejuvinated during later outbursts of magmatic activity whilst abnormally high heat flows due to radiogenic decay have maintained at least some of them up to the present.

## 1.4 THE ST. AUSTELL GRANITE CUPOLA

The St Austell granite is positioned more or less centrally in the south west peninsula, Figure 2. It has a subelliptical outcrop pattern stretching 20 km E-W and 12 km N-S. The dip of the contact to the south and west is steep but uneven (Gronow pers. comm.). The extensive metamorphic aureole on the northern side of the mass indicates that the body of the granite is not far below the surface. The roof zone is undulatory since outcrops of the granite occur at St Dennis, Belowda Beacon and reportedly at Roche (Ussher et al 1909), Figure 6. The morphology of the granite is such as to suggest that it is only the very highest level of the cupola which has been intersected by the present erosion surface.

### 1 THE GRANITE

The granite is grey and porphyritic in which the large potash feldspars vary between 2 and 10 cm in length. Ussher et al (1909) recognized the existence of different granite varieties, even proposing that they might represent separate intrusions but could not map their boundaries.

Richardson (1923) was the first to describe the mineralogy of the different types in detail and to delineate them spatially. He recognised three main varieties: 1- biotite muscovite granite to the east, 2- lithionite granite in the centre and extreme west and 3- gilbertite granite in the centre. Following the survey geologists, he proposed that the last two granites formed a later separate intrusion in which the

gilbertite variety represented the last volatile rich phase to crystallize.

Exley (1959) expanded and modified the earlier scheme. He too suggested that lithionite granite was intruded into the earlier biotite-muscovite granite but he remapped the contact between them. He put forward some evidence to substantiate the intrusion hypothesis whose validity has been questioned by Bray (1980). Exley's classification is summarised in Table 4. He divided the lithonite granite into two types on the basis of textural differences. The porphyritic variety he considered to have been intruded earlier than the non-porphyritic variety. Richardson's gilbertite granite was regarded as an alteration effect. Instead a discrete fluorite granite was proposed as the last differentiate, Figure 6. Plagioclase feldspar analyses (Table 4) would seem to substantiate the proposition that the lithium and fluorine bearing varieties were later differentiates of the early biotite muscovite granite.

The St Austell granite has been remapped by the IGS and their subdivision, based in part upon their experience of, and in comparison to, the other major granite exposures, differs considerably from Exley's, (Hawkes & Dangerfield 1978, Dangerfield et al 1980), Figures 2 and 7. Table 5 summarises the different subtypes proposed by the three authors. Hawkes & Dangerfield (1978) recognize only two fundamental granite types, the coarse grained megacrystic biotite granite and the non megacrystic lithium mica granite. The megacrystic lithium mica granite is considered to be the result of pervasive lithium metasomatism of the biotite granite due to the intrusion of the lithium mica differentiate. This hypothesis is largely substantiated by the distribution of lithium contents in the rocks, Figure 8. The lithium contents show a sharper fall than expected

in the western lobe which is explained by faulting along the line of the deeply incised River Fal valley. The contact between the lithionitised "biotite" granite and the lithium mica granite is no longer exposed. Exley (1959) described it as being gradational but it could be equally well interpreted as the result of partial digestion of the earlier by the later granite. A small outcrop of lithium mica granite occurs in Goonbarrow, Bray (1980), Hawkes & Dangerfield (1978). There is a most definite transgressive contact between the two granite types. A contact pegmatite developed by the growth of minerals out from the earlier biotite granite into the volatile rich later lithium rich granite. The evidence for the intrusion of the biotite granite by the lithium mica granite and its subsequent "lithionitisation" by fluids emanating from the later phase is convincing.

The third granite variety is fine grained and is considered to be incompletely granitised country rock which also explains its irregular distribution. Both Richardson's (1923) gilbertite granite and Exley's fluorite granite are considered to be alteration varieties in keeping with Ussher et al (1909) and Dewey (1948).

## 2 OTHER INTRUSIVE ROCKS

Ussher et al (1909) described a pegmatite at Trelavour Downs which at one time was worked for lithium (Edmonds et al 1975) and another near Roche worked for use in glass making. Bray (1980) describes several other occurances and suggests that they are not as uncommon as has been suggested (Badham et al 1976).

Numerous elvans were described in the 1909 memoir, the bulk of which occur outside the granite. They occur predominantly to the north and south of the granite, coincident with the areas of most important mineralisation. Elvans which do outcrop in the granite cut both the megacrystic biotite granite (Goonbarrow, Wheal Remfry, Melbur, Virginia), the lithionitised biotite megacrystic granite (Gunheath, Bluebarrow) and the lithium mica granite (Hendra, Trelavour, Goonvean & Restowrack), Bray (1980), Dines (1956) & Ussher (1909).

## 3 MINERALISATION

St Austell has been an important mining district in the past producing significant quantities of tin, copper and iron. Mineralisation occured predominantly to the south of the granite indicating that this was the flank which failed first, releasing the late stage fluids into the surrounding country rocks (Moore 1975). Mineralisation within the granite is not well developed but tin, copper and tungsten have been mined predominantly from the Hensbarrow region. The old mine workings are now intersected by the open pit workings of Goonbarrow clay pit.

## 4 ALTERATION

The most important zones of alteration are associated with joints and veins in the granite.

The three major alteration types are tourmalinisation, greisenisation and kaolinisation. Tourmalinisation is characterised by the formation of abundant tourmaline and quartz at the expense of feldspar and mica. The original fabric of the granite is frequently destroyed but sometimes the quartz phenocrysts and feldspars pseudomorphed by tourmaline can be preserved as a palimpsest texture. Although usually of limited dispersion the tourmalinised selvedges of intersecting veins can overlap and form blocks of tourmalinised ground sometimes of considerable size. Roche rock is an example. Greisenisation generally occurs outside the tourmalinised zone and is more pervasive. White mica and quartz replace feldspar whilst topaz is often present as an accessory. At St Mewan Beacon the topaz content is abundant enough for it to be termed a true topazfels. The two alteration types are not completely distinct. They are both hydrogen metasomatic processes but in one the boron content is also extremely high. Thus tourmalinised granite often contains white mica and greisenised granite is usually rich in tourmaline.

Kaolinisation, where the feldspars pass into kaolinite, white mica and quartz is the most widespread and pervasive of all the alteration types. It is currently of greater economic importance than the base metal mineralisation. The distribution of the kaolinised granite and the china clay pits can be seen in Figure 6.

## 5 SUMMARY

1. The St Austell granite is composed of a coarse megacrystic biotite granite which has been intruded and metasomatised by a more highly differentiated volatile rich, lithium mica granite. The patchy distribution of fine grained granite may partly represent the incomplete granitisation of country rock.

2. Expulsion of hydrothermal fluids through the southern flank of the pluton gave rise to the tin and copper mineralisation.

3. Tourmalisation, greisenisation and kaolinisation are the most important alteration types, arranged in order of increasing pervasiveness. Kaolinisation is the most widespread and is of great economic importance.

# CHAPTER 2

# THE IGNEOUS ROCKS AND HYDROTHERMAL PHENOMENA IN THE WESTERN LOBE

## 2.1 IGNEOUS ROCKS

### 1 GRANITE

The granite of the western lobe of the St Austell cupola has been variously described as a lithionite granite (Richardson 1923), early lithionite granite (Exley 1959) or a megacryst rich coarse biotite bearing granite with fine grained granite to the north (Dangerfield et al 1980), Figure 7. The last interpretation is supported by the levels of lithium found in these rocks, Figure 8.

In mapping the western lobe a more generalised scheme than that of Hawkes & Dangerfield (1980) was used to classify the granite. The method is summarised in Table 6. Briefly, the classification is based upon three main criteria; firstly the identity of the predominant mafic mineral, secondly the grain size of the groundmass and lastly the size and abundance of the phenocrysts. Additional information pertaining to the degree and nature of the alteration and replacement minerals may be appended in parentheses. Although developed particularly for the area under consideration, the principles may be applied to the mapping of any igneous body.

Field work in the southern part of the western lobe showed the granite to be megacrystic, coarse grained and biotite rich. Detailed mapping of the northern part shows it to be predominantly the same. Table 7 enumerates the number of different observations made for each rock type. The conclusion that the granite is predominantly phenocryst rich, coarse grained and carrying primary biotite as its mafic phase is a fair one. The lithium contents in the granite (Figure 8) provide additional supporting evidence. If the northern part did represent a different

granite type this would be clearly reflected in a diminution in the lithium contents. No such evident variation in lithium content is observed.

Table 7 and Figure 9 also express the disparate nature of the granite. The distribution of the subtypes is extremely irregular as can be seen from Figure 9. No discrete contacts can be observed between the rock types. There is also a complete gradational relationship between coarse and medium grained groundmass. Similarly, the phenocrysts are often on the verge of becoming megacrysts whilst they fluctuate in abundance. In places the granite can become extremely coarse grained. These "pegmatitic" pods are conformable with the host rock and are not intrusive. Bray (1980) has used the same term to describe similar features from elsewhere in the St Austell granite. Miarolitic cavities are related phenomena and Plate 1.1 shows an example from Wheal Remfry. The grain size of the host rock coarsens towards the cavity. The minerals infilling the cavity are potash feldspar, quartz and abundant coarsely fibrous tourmaline.

The distribution of granite types, pegmatitic pods and miarolitic cavities have a twofold significance. Firstly, and most importantly, these texturess are indicative of a locally fluctuating volatile content in the granite during an extended crystallisation history. In places the volatile content became critical leading to the development of the coarse "pegmatitic" facies (Krauskopf 1959). Secondly the occurrance of tourmaline within the cavity places the crystallisation of at least some of the tourmaline within a late magmatic context. It is obvious that in this case the formation of tourmaline straddles the magmatic/hydrothermal boundary. Previous controversies concerning the primary or secondary nature of the tourmaline are a reflection of an attempt to separate late

magmatic and hydrothermal events which are, in fact, chronologically continuous. The causes of an extended crystallisation history may be a high volatile content in the magma leading to the depression of the solidus (Manning 1981).

## 2 CONTACT BETWEEN GRANITE AND KILLAS

The contact between the granite and the country rock is exposed in a small bench face to the north east of Wheal Remfry, Figure 9. The knife edge sharpness of the contact is immediately striking. The contact dips steeply at about 80° away from the granite. In plan view it is controlled predominantly in a North-South and 290 direction. A chill margin about 2 metres wide has formed in the granite. The groundmass becomes finer grained and the phenocrysts small and sparce. The biotite flakes and phenocrysts are aligned parallel to the contact giving the rock a banded appearence. The banding is discontinuous but suggests that some degree of flow in the granite occurred against the contact.

The killas itself is noticeably undisturbed and unaltered. The effects of later alteration (kaolinisation) may have obscured the metamorphic mineral assemblage but the killas appears to have been only slightly baked and hornfelsed. This conforms to the rest of SW England where the degree of contact metamorphism never exceeds the hornblende hornfels facies. The contact relationships would seem to suggest that the magma was close to or at its solidus during intrusion.

The contact is complicated by the occurrance of an aplitic and pegmatitic phase, Figure 10. The "aplite" is a sill like body some 5m wide and 2.3m thick which penetrates the killas in a northerly direction.

It is probably an apophysis of the marginal granite facies rather than a separate aplitic phase (ss). The "pegmatite" is comprised of very large megacrysts of potash feldspar in a coarse groundmass of quartz, plagioclase, light purple mica, green mica and tourmaline. It has a more enigmatic relationship with the granite, complicated by incomplete exposure. Detailed mapping, Figure 10, suggests that the killas in part forms a westward dipping inlying wedge representing a small roof pendant. The simplest interpretation is that the fine contact facies penetrated the killas as a sill-like apophysis, the northern offshoot of which was the "aplite" sill already described. Subsequently the pegmatite "squeezed up" along the contact, largely swamping the original fine grained granite leaving relics here and there.

There are two possible modes of origin for the pegmatitic facies. A metasomatic origin is possible due to the ponding of volatiles up against a suitable structural trap. However, the weight of evidence is in favour of a partially intrusive origin. The relic portions of fine grained granite are difficult to reconcile with pervasive metasomatism and there is good field evidence to support some degree of differential movement in the pegmatite with the flow alignment of the felspars and the incorporation of killas clasts.

**Conclusions**

The lack of extreme contact metamorphism and small chill margin show that the granite magma was not sustained at high temperatures above its solidus. This was itself severely depressed by the high volatile content in the magma.

The contact relationship shows evidence of differential flow in the granite past the country rock. The intrusion mechanism (at least on a relatively small scale) is therefore one of digestion and assimilation of country rock rather than of faulting. Granite apophyses penetrated the country rock. The pegmatite is in all probability intrusive in origin but some component of metasomatism cannot be ruled out.

## 3 IGNEOUS FABRIC

The granite fabric such as schlieren and feldspar alignments provides information on early structural conditions which can be used to interprete and explain the formation of the later structures. Both feldspar alignments and schlieren are well developed in the western lobe.

**Flow alignment of phenocrysts.**

Only the traces of the feldspar phenocrysts were mapped due to the difficulty of defining the plunge of the phenocrysts.

The traces give a good indication of the direction of flow of the granite, Figure 9. The fabric is more strongly developed to the west reflecting the proximity of the granite contact in this direction. The fabric is sufficiently well developed over the whole area to distinguish an approximately circular flow pattern. This would seem to imply that the northern part of the western lobe was intruded to a slightly higher structural level. Feldspar orientations frequently intersect. This is either the result of co-crystallisation under an imposed stress field or the modification of an original flow fabric by an imposed stress field.

The orientation of the feldspars in the southern part of the western lobe is also strongly developed. The crystals are also aligned parallel to the contact indicating that flow occurred in the granite during its intrusion. A strong east-west component in the middle region of the western lobe confirms that the northern part was probably intruded to a slightly higher structural level.

**Schlieren**

Schlieren are extremely well developed in the western part of Wheal Remfry pit, Figure 9. They are composed of diffuse bands enriched in fine grained disseminated tourmaline separated by greisenised granite. Potash feldspar phenocrysts are generally fewer and smaller than in the ordinary granite but the quartz phenocrysts become extremely large, Plate 1c. The banding varies in thickness from 1 to 40 cm, the thicker bands becoming extremely tourmaline rich. There is no apparent spatial distribution of band thickness which changes gradationally and irregularly. The banding displays an overall gneissic appearance. The contact between the "tourmaline" banded and ordinary granite is indefinite and clearly gradational.

The feldspar phenocrysts are geneally orientated parallel to the banding but occasionally they lie discordantly or even cut accross it. This indicates that there has been some degree of overlap between crystal growth and the formation of the tourmaline banding. There is incontrovertible evidence that movement occurred in the granite after the formation of the tourmaline bands; the bands themselves show well developed flow folds, Plate 1d and can contain small granite xenoliths.

There are a number of possible models for the genesis of the tourmaline banding. Palingenesis of country rock is discounted because the country rock is depleted in boron with respect to the granite (Bawden 1962). The distribution of the banding and its parallelism with the feldspar orientations, Figure 9, show that it is related to flow in the granite against the contact. Straight forward differential concentration of tourmaline would not be sufficient to account for the quantities present in the banding. A model is favoured in which a late magmatic, boron rich aqueous fraction separating from the residual, interstitial silicate melt (also responsible for the formation of the quartz and tourmaline rich miarolitic cavities) was concentrated into discrete horizons by differential movement in the incompletely consolidated granite.

## 4 ELVANS

A number of elvans outcrop in the western lobe at Wheal Remfry, Burthy, Melbur and Virginia pits. They display quite a wide range in textures but have a number of features in common. They are all green in colour indicating a high muscovite (or possibly gilbertite) content. They have all been severely affected by later kaolinisation which may have obscured their original mineralogy and textures. They are all generally fine grained but can contain large twinned megacrysts of potash feldspar (Plate 1e) and bipyramids of quartz. At the contact with the granite they become glassy and fissile with good parallel cleavage, Plate 1b. The elvans post date and cross cut the quartz tourmaline alteration (Plate 1b) in line with other elvans from the St Austell granite (Bray 1980) but in contrast to the norm for the province as a whole (Dines 1956). They

are in turn cut by quartz veins. The elvans vary from a few centimeters up to 10 metres in width, strike more or less east-west and are subvertical.

There are two major hypotheses on the genesis of the elvans. Textures showing the apparent incorporation and partial digestion of granite material in the elvans lead some authors to propose a predominantly metasomatic origin (Stone 1968, Henley 1972, Goode 1973, Hawkes et al 1975). A fluidised mode of intrusion is proposed, the volatile component originating from late differentiates at depth (Hawkes per comm.). However, the chilled contacts, the fine grained nature of the elvans and the spherulitic textures caused by the devitrification of volcanic glass (Burthy pit) attest to a magmatic origin from some late residual silicate fraction.

## 5 CONCLUSION

The granite of the western lobe is phenocryst rich (often becoming megacrystic) coarse grained and has biotite as the primary mafic mineral. Sharp, clear contacts with the killas, a narrow chill margin and apophyses penetrating the country rock all indicate a passive emplacement process. Flow alignment of the feldspars imply that the northern part subsequently reached a slightly higher level in the crust.

Evidence that the granite spent a considerable period at or near its (considerably depressed) solidus is supplied by the occurrance of coarse pegmatitic pods, miarolitic cavities, tourmaline banding, the low grade contact metamorphism and the late metasomatic growth of the potash feldspars. The extremely high volatile content in the magma is considered

to be the reason for this extensive solidus history.

The elvans are relatively late phenomena, postdating tourmalinisation. Field evidence supports the emplacement of late silicate melts rather than fluidised systems as their mode of formation.

## 2.2 STRUCTURES AND HYDROTHERMAL PHENOMENA

This section describes the brittle structures which are developed in the western lobe, including a tourmaline cemented breccia pipe exposed in Wheal Remfry and the alteration associated with them.

### 1 STRUCTURES

Fractures supply information on the structural evolution of the stresses associated with the intrusion, differentiation and subsequent cooling of the granite pluton.

#### A Classification of fractures

Seven fracture types were distinguished on the basis of their fill mineralogy and associated alteration : 1 Tourmaline-quartz, 2 Quartz-fluorite, 3 Early quartz, 4 Late quartz, 5 Kaolin, 6 Umnineralised late fractures, 7 Igneous joints.

#### Tourmaline-quartz veins

There are several generations of this fracture type. The earliest are associated with a selvedge of intense tourmalinisation, Plate 1f. The fractures themselves are usually very fine being a mm or so wide. Occassionally the fractures widen to form irregular "nests" of coarsely fibrous tourmaline. The presence of small euhedral quartz crystals, often coated in iron oxide can always be accounted for by a later quartz

feeder, Plate 2a. The later tourmaline veins consist of a two to three mm wide fracture filled by compact fine grained tourmaline and generally without a well developed alteration selvedge. The colour of the tourmaline changes from dull grey to grey green to dark brown and finally yellow brown in response to its changing chemistry. Reveining and even brecciation of one generation by another is common, Plate 2b.

**Quartz-fluorite veins**

These are rather small fractures rarely exceeding one cm in width in proportion to which they show considerable persistance along strike. The vein fill comprises, milky rather massive quartz without good crystal terminations and idiomorphic purple fluorite. Pyrite is the predominant accessory sulphide but green weathering stains confirms that chalcopyrite is also present.

**Early quartz veins**

These fractures are infilled by milky quartz. There are abundant vughs containing well terminated clear crystals. These (usually rather small) crystals are commonly coated in a fine layer of iron oxide or haematite, Plate 2a. The vughs are frequently infilled by massive white kaolinite. Pyrite is a relatively common accessory. These veins are generally narrow reaching 5 or 6 cm and locally a little more in width. They show a marked persistance not only along strike but also with depth. They have a tendency to revein earlier tourmaline veins, Plate 2a, and can often become deflected along the central parting of a tourmaline vein. These veins are associated with relatively mild but appreciable silification.

**Late quartz veins**

These structures are striking features due to their mineralogy, size and appearence. They are comprised of massive milky white quartz containing pyrite. Vughs are quite common into which the quartz forms large stubby terminations, Plate 2c. This generation can be overgrown in a number of ways. They can be blanketed by small spikey milky quartz crystals but more commonly they are covered in a thin (2 mm) layer of fine haematite and colloidal silica, Plate 2e, 2f. Orientated samples show well developed stoss-side deposition of this material indicating preferential precipitation from fluids passing vertically up through the fracture. This was followed by the deposition of clear amethystine quartz, Plate 2c, e,f. These last two stages can be repeated several times. Generally the last type of quartz to form is smokey rather than amethystine, Plate 2d. This sequence is generalised and in most instances one or other generation is not developed. In later veins the first material to be deposited is haematite resulting in a strong plane of failure which is significant for pit slope stabilities.

Any remaining space left in the vughs is ubiquitously infilled by very pure, massive kaolinite. This has presumably been precipitated from colloidal suspension by fluids percolating through the vughs.

The veins commonly reach a meter or so in thickness and have great persistance along strike (up to 1km) and in depth (over 150m). They tend to change in size and degree of crystal development and frequently demonstrate a flexturing and branching morphology. The late quartz veins are distributed throughout the western lobe and are an ubiquitous feature of all the clay deposits in the St Austell granite.

**Kaolin veins**

Narrow (2cm wide) fractures are infilled by compact and very pure kaolinite. It is quite competent with almost conchoidal fracture when broken. The veins are frequently branched both along strike and with depth, Plate 3a. They most commonly occur within the kaolinised granite but fractures may pass into unkaolinised granite without any apparent change in vein width or content.

It is possible that these veins formed by complete kaolinisation of some pre-existing material but the purity of the fill, lack of suitable starting material and the geometric relationships argue against this interpretation. It is considered more likely that they represent the infilling of fractures by fluids which precipitated kaolinite from suspension. The propagation of fractures through kaolinised granite could occur through a work-hardening process (E. Rutter pers. comm.). The sense of movement of the fluids is believed to be upwards on the basis of the fracture morphology. This would seem to be incidental evidence for a hydrothermal component to the kaolinising process.

**Late fractures**

The fractures are unmineralised and are associated with mild weathering and the friablisation of the granite. They can occur singly but most often form groups of fractures, Plate 3b.

**Joints**

The joint planes are well developed giving a strong blocky appearence to the granite. The planes are generally unmineralised although they may contain a little quartz and fluorite.

The subhorizontal joint planes are particularly well developed in the south of Wheal Remfry where they dip to the SSW at low angles. Movement has occurred along these planes displacing subvertical quartz-tourmaline veins and filling the fault surface with cataclastic debris. The frequency of these slip planes increases towards the surface, finally occuring at every 30 cm or so. Movement along these planes has formed tension gashes which are infilled by kaolinite. These features possibly represent off-loading structures along which slumping has occurred away from the central "high" formed by the Wheal Remfry cupola.

**B Vein paragenesis and style of fracturing**

The evolution of the structural fabric (i.e. the orientation of the stress axes) can be determined from the style of fracturing (normal, reverse, transcurrent), the orientation of the structures and their paragenetic sequence of formation.

The predominant orientations of the different types of vein were determined by taking over nine hundred strike and dip measurements. Contoured stereograms of the fracture pole densities were then plotted using a computer program written by Spiers (in prep.), Figure 11 a to g. The orientations of the major structure sets for each fracture type were determined by successively stripping out the dominant group from the data

set and replotting the residuals. These sets are summarised in Table 8 and compared for each vein type in Table 9.

From geometrical relationships the following paragenetic sequence was established: tourmaline-quartz, quartz-fluorite, early quartz, late quartz, kaolin, late fractures and joints. The relative ages of the last three structures is not completely clear due to their limited distribution. The orientation of the kaolin veins is coincident with both the joints and the late fractures and so these three structures may have formed more or less contemporaneously.

The style of fracturing shows a trend from the early to the later structures of an increasingly important strike-slip component. The early tourmaline-quartz veins show barely any movement. The later veins have a minimal strike-slip movement although some brecciation and mylonitisation of earlier vein material has been observed, Plate 2b. It is during early quartz vein formation that strike-slip movement becomes really noticable and reveining and mylonitisation textures are quite common. Strike slip reaches its apogee with the formation of the late quartz veins, some of which are associated with appreciable displacements. The later kaolin veins and late fractures have also a predominantly horizontal sense of movement attested to by small displacements on the former (a few cm) and slickensiding on the latter.

## C Discussion

The sense of movement on the fractures, their relative ages and their orientations should provide unique solutions to the orientation of the stress axes responsible for their formation. Exley (1959) contoured the poles to four hundred fractures from the whole of the St. Austell granite pluton, Figure 12. The orientation of the major fracture sets are identical to those from the western lobe, Figure 11. Any interpretation of the structures has to take their pluton-wide distribution into account.

Moore (1975) and Burnham (1979) have both emphasised the interaction between fluid pressures in a differentiating granite and the regional stress field in the formation of brittle fractures in the consolidated outer carapace of the granite and the surrounding country rock. The north-east, south-west orientation of the folds and structures in the Cornubian Peninsula (Figure 1) shows that the principal compressive stress during the Hercynian was from the south-east. Figure 14 summarises the proposed conditions for the formation of the tourmaline-quartz, early and late quartz veins in the western lobe.

The first pair of tourmaline-quartz veins to form were sets 1 and 2. The orientation of the principal stress axis is coincident with that of the Hercynian stress field. High pore pressures reduced the conjugate angle to $20^{o}$. These fractures would also be expected to be more numerous and thicker. The jacking open and infilling of these veins caused the inversion of the major and minor stress axes. Fracturing then occurred to form sets 3 and 4. Fluid pressures were lower so these fractures intersect at a higher angle. The inversion of the stress axes remained during the formation of the early quartz veins. The high conjugate angle

implies low pore pressures and these veins are usually the narrowest. The observed sense of movement on set 3 is sinistral which is opposite to that predicted. The subsequent reversion of the stress axes to their original configuration gave rise to the formation of set 2 and caused the remobilisation of set 3 resulting in the observed sense of displacement. This process was exactly reversed for the late quartz veins. Set 3 was the earliest to develope and the thickness of these veins attests to high fluid pressures. During the last phase of quartz vein formation the principal stress axis inverted once again. The moderately high conjugate angle between the resultant veins shows there to have been a drop in pore pressures. The east-west quartz veins are the last structures. They reach considerable thickness in Wheal Remfry and Melbur as a result of repeated brecciation and deposition of haematite.

The orientation of the tourmaline-quartz, early and late quartz veins can therefore be explained by the interaction between fluid overpressures (exceeding confining pressures and the tensile strength of the consolidated granite carapace and country rock) and a repeatedly inverting major and minor stress axis. It is interesting to note that the fluid pressures were high during the formation of the 320 quartz veins as the clay runs in the western lobe are coincident with this direction.

Fracture densities can be used to calculate fracture widths and rate of fluid flow. Calculated fracture widths for the tourmaline-quartz veins are in good agreement with field observations, Table 10. Since velocity of flow is roughly proportional to the square of the fracture widths these fluids passed through the rock very slowly so allowing extensive wall rock reactions to occur. The early quartz veins have much wider fractures and hence a fluid flow rate which is 400 times greater than for the tourmaline veins. This would account for the generally

insignificant alteration selvedges.

The late, unmineralised fractures were clearly formed after a considerable hiatus. Their orientation and displacement is coincident with large scale transcurrent faulting of Tertiary age (Dearman 1964). One such fault is supposed to separate the western lobe from the rest of the St Austell granite and the abrupt drop in lithium content of the granite accross this line would seem to support this, Figure 8. These late fractures are "parasitic" to the main fault plane which formed as a result of north-south compressive stresses during the Alpine orogeny.

## 2 ALTERATION

The four main alteration types are tourmalinisation, greisenisation, kaolinisation and haematisation. Tourmalinisation involves the formation of tourmaline and quartz replacing feldspar and mica. During greisenisation white mica and quartz form at the expense of feldspar and impart a greenish colour to the rock. Kaolinisation causes the alteration of feldspar to kaolinite, white mica and quartz. Haematisation is the general redening of the feldspar, sometimes to deep hues.

Kaolinisation is of economic interest and is widespread in the western lobe. Kaolinite is mined by blasting and monitoring. The veinstone refuse is termed "stent" and comprises tourmaline (30 to 40 vol%) and quartz. Approximately 1000 tons of this material is removed from Wheal Remfry pit every day which gives some indication of the extent of the boron metasomatic process which has affected the northern part of

the western lobe.

**Tourmalinisation**

Tourmalinisation is predominantly fracture controlled. Well developed alteration selvedges surround small central fractures, Plate 1f. The alteration selvedge consists of a dense quartz, tourmaline rock or "schorl". The granite fabric is usually destroyed during alteration particularly adjacent to the fracture. Further away the fabric may be preserved with the tourmaline pseudomorphing the potash feldspar phenocrysts, Plate 3c. The alteration front separating "schorl" from host granite is extremely sharp, Plate 1f. The size of the alteration selvedge varies but it is commonly about 20 cm wide. The occurance of sheeted veining, Figure 14 causes the selvedges to overlap and form large bodies of quartz-tourmaline rock such as the Carloiquitor rock in Wheal Remfry (Figure 14, 057500192500). Further away from the fracture tourmaline replaces biotite in the groundmass. When the density of tourmaline fracturing is sufficiently high these more diffused alteration zones overlap so that the granite contains tourmaline as its as its predominant mafic mineral without there otherwise being much visible alteration.

**Greisenisation**

The greisenised granite has a more pervasive distribution. The effects are generally quite mild. Plagioclase goes green giving the whole groundmass a green hue, presumably due to the introduction of white mica. The large potash feldspars become pink, altering from the outside inwards. Dark mica becomes bleached. More intense alteration causes increasing alteration of feldspars and tourmaline replaces the dark mica. The alteration is unlike that reported elsewhere from SW England in so

far as it is not clearly associated with obvious brittle fractures and there is no development of greisens (ss). This term will continue to be used to describe this alteration throughout this thesis but it is not directly comparable to the greisenisation process typically associated with vein mineralisation in other Sn-W granites.

**Kaolinisation**

During kaolinisation the granite fabric is completely preserved and the feldspars are perfectly pseudomorphed by kaolinite. Biotite is bleached to a pale purple colour, similar to the colour of protolithionite. The kaolinisation process has been divided into five stages representing different degrees of alteration, Table 11. The distribution of altered granite in Wheal Remfry is shown in Figure 14. It would appear that alteration has been pervasive but numerous blocks of relatively unaltered granite are distributed within the kaolinised body, Figure 14, Plate 3d. There is no correlation between the distribution of these blocks and the original mineralogy of the granite, Figure 9, but a strong correlation with the intensity and orientation of fractures, particularly those orientated northwest-southeast. The intensity of kaolinisation increases adjacent to these structures. It is suggested that the kaolinising fluids exploited these structures as channelways since considerable quantities of water still flow along them. The fluids then moved out into the granite along channelways of higher permeablility such as the joints, giving rise to the blocky morphology of the relatively unaltered granite relics. The overlapping of contiguous zones of alteration surrounding the channelways gives rise to the widespread distribution of this type of alteration.

An important criterion controlling the economic value of kaolinite

is its whiteness. This is dependant upon the amount of fine haematite in the clay. Kaolinite of high quality can occur directly adjacent to haematised granite. This juxtaposition is common to most clay deposits in south-west England. There is abundant evidence that the iron is removed from the granite during kaolinisation:

- partially kaolinised, haematised potash feldspar phenocrysts have a bleached rim.

- haematised granite is bleached adjacent to joint faces in response to incipient kaolinisation.

- the boundaries between altered and unaltered granite are frequently marked by an alteration front of iron oxide.

- both granite and killas are kaolinised at their contact. The granite is white due to the leaching of the iron from the feldspars but the killas remains haematised due to the more diffuse distribution of haematite through the rock.

- pink kaolinised granite occurs in the south of Wheal Remfry where the removal of the iron has been incomplete.

- there is an ubiquitous relationship between the late quartz veins carrying haematite and kaolinisation.

The iron is believed to be removed from the granite and deposited together with the silica released during alteration in the late quartz vein. An attempt was made to date the kaolinisation process by palaeomagnetic dating of the haematite veins in Wheal Remfry.

Unfortunately, the readings were below background but with the development of new, more sensitive equipment this experiment could be repeated.

**Haematisation**

Haematisation has pervasively affected the remnant granite blocks and forms a zone surrounding the kaolinite deposits. The alteration process is not associated with any particular generation of fractures. It is a blanket alteration of the iron, contained in the granite, to haematite in response to oxidising conditions. Its intensity is controlled by the amount of iron present in the granite in a readily oxidisable form. Greisenisation results in the most effective ground preparation since iron is released without being imprisoned in new resistant mineral phases such as tourmaline.

**Alteration chronology**

Greisenisation is the earliest alteration type since it is pervasive and occurred prior to the formation of brittle fracturing. It is therefore an autometasomatic process. Tourmalinisation is the alteration type associated with fracturing, the earliest phase of which was relatively muscovite rich and corresponds most closely to the vein controlled alteration elsewhere in the province. The relative ages of kaolinisation and haematisation is difficult to resolve since every texture can be interpreted as either the haematisation of iron incompletely removed during kaolinisation or as the incomplete removal of haematite during kaolinisation. The presence of haematite in the late quartz veins would suggest that haematisation preceeded kaolinisation.

## Conclusion

Greisenisation, tourmalinisation and kaolinisation are the three most significant types of hydrothermal alteration in the western lobe. Haematisation occurred in response to changes in the conditions of oxygen fugacity. Preservation of the granite fabric would imply that there has been no total volume change during alteration.

Greisenisation is the earliest, most pervasive alteration phase occuring prior to fracture development. The fluids became increasingly enriched in boron until by the onset of brittle fracturing, tourmalinisation was the predominant alteration type. Haematisation imparted a strong colour to the granite, particularly the feldspars. The kaolinising fluids were channeled by planes of permeability such as pre-existing fractures and joints. Haematite was removed during the progressive kaolinisation of the feldspars and the granite was bleached. The haematite and silica released during alteration were redeposited in the late quartz veins.

## 3 BRECCIA PIPE

The maps show the location, orientation and outline of the breccia body, Figures 9,14,15,16. The southern part of the body was surveyed using a theodelite and staff (closing error $\pm$0.5m). The northern extensions are being actively exposed by current mining and are less reliably mapped. The body is elongated N-S and is currently exposed for over 400m. It varies between 50 and 100m in width. It bifurcates at its northern end giving the whole a lobster like appearence in plan view.

It is clear from the outline of the body that its shape has been controlled by the sets of intersecting tourmaline fractures whose formation preceeded the emplacement of the breccia body itself, Figure 16.

The breccia contacts are generally sharp and subvertical as shown by the almost rectilinear form of the western contact, Plate 3e. Small breccia apophyses and veinlets branch away from this contact and run subparallel for a little way, Plate 4c. The western contact is controlled exclusively by the 350 fracture set but the eastern contact is more complex. Although maintaining an overall N-S trend the detailed geometry is controlled by the 286 and 026 fracture sets. When the contact makes an abrupt change in direction small breccia veinlets extend into the granite, Figure 16. These apophyses are of the order of 0.3 to 0.5 m wide at their point of initiation and narrow along strike until terminating after 8 or 10m in a system of anastomosing tourmaline filled fractures. This texture is akin to porphyry crackle breccias and is indicative of hydraulic rupturing of the granite by fluids under pressure. The dotted contact on the NE arm of the body, Figure 6, represents an indefinite boundary where the breccia body merges into a filigree of fine

intersecting subvertical (340 and 090) and subhorizontal tourmaline veins. Towards the outer edge of this zone negligable movement of the intervening granite has occurred. Moving inwards the fragments become progressively disrupted. The contacts thus show a variation in texture from having a transitional zone of in situ brecciation to being abrupt with complete disruption and displacement of the fragments.

The variations in composition and texture of the fragments and matrix were investigated by making observations at a series of stations located at intervals of approximately 5m along the bench levels in which the breccia was exposed, Figure 17. Measurements at each station enabled the volume ratio of fragments to matrix and the ratio of fragment types to be calculated. The results are summarised in Figures 18a,b,c. Significant variations occur between the main phase breccia and minor breccia phases in the southern part of the body.

**A Main stage breccia**

The central and northern part of the body is termed the main stage breccia, Figure 16,18c. It is the earliest and volumetrically the most important phase of breccia formation.

This phase contains predominantly granite fragments, the volume proportion lying between 40 and 70 percent, Figure 18c. The fragment populations vary with an increase in the proportion of killas (and quartz porphyry) fragments at higher levels until locally the killas fragments may comprise between 60 and 90 percent of the total. This enrichment in killas fragments suggests proximity to the granite-killas contact. Evidence from drilling and gravity surveys carried out by ECLP supports

the interpretation of the western lobe being a cupola of the main St Austell pluton. The contacts dip between 50 and 70° and by projection the roof of the intrusion should lie within 200m of the highest point now observed. The abundance of killas fragments implies that it lay even closer.

Since the elvans cut the breccia pipe, Plate 4a, these quartz porphyry fragments have either been derived from an older generation of porphyry dykes without surface expression or they have been derived from volcanoclastic extrusive material which has been brought down from higher levels. By comparison to the porphyry intrusive systems, Sillitoe (1973), these pyroclastic deposits may represent the products of sub-aerial volcanism associated with the intrusion of the granite pluton. If this is the case then these quartz porphyry fragments represent the only material of the intermediate and upper portions of the system which have been preserved from erosion. The exposed cupolas of SW England would thus seem to correspond to the bottoms of the intrusive systems in terms of Sillitoe's (1973) model. This would seem to further emphasise the parallels between the south-west England and northern Bolivian tin provinces. The occurance of these fragments would seem to suggest that the granite was intruded to very high levels in the crust, certainly within a few kilometers of the palaeosurface.

A typical exposure of the main stage breccia at an intermediate level is shown in Plate 3f. The fragment are almost exclusively of granite composition although 10 percent of killas fragments may be mixed within the breccia at this level. Fragment varieties other than ordinary phenocrystic granite and killas includes banded tourmaline granite and a few quartz porphyry fragments with an aphanitic matrix. The fragments are all tourmalinised and silicified to a greater or lesser extent.

The degree of rounding of the fragments is quite variable but the larger fragments retain an angular form. Although large fragments have been seen in parts of the breccia reaching 2m accross, the fragment population is for the most part comprised of fragments less than 0.5m in diameter.

The dark matrix is formed from finely comminuted rock and mineral particles partially or completely altered and cemented by a dense mesh of fine grained tourmaline and quartz.

**B Other breccias**

The breccia body in the centre of the rounded expansion at the southern end, Figure 16, is distinctly different from the main phase breccia. It is characterised by a fragment population of predominantly large angular killas fragments up to 2m in diameter, Figure 18a, Plate 5d, jumbled together and cemented by silica. The centres of the largest blocks have escaped the tourmalinisation and silification which affects their outer zones. The matrix is clear quartz and crystal lined vughs are common in the larger interstices between fragments. The predominance of killas fragments some 200-300m below the projected granite-killas contact together with the siliceous and vughy character of the matrix is indicative of an origin by collapse. This phase is termed the killas collapse breccia, Figure 16.

The killas collapse breccia is surrounded by a breccia type in which the matrix is dense, very fine grained, grey and siliceous. The breccia has a similar textural geometry to the main stage breccia but is

generally enriched in killas fragments, Figure 18a. However, both the fine comminuted rock fragments and the larger clasts have all suffered complete silification. Granite clasts are completely pseudomorphed by quartz and tourmaline, small terminated quartz crystals and felted patches of fine tourmaline needles infilling cavities marking the site of pre-existing feldspars.

Between the siliceous breccia and the main phase breccia is a zone in which the textures are identical to the latter but where the fragments have undergone partial silification displaying distinctive alteration haloes, Plate 5a.

The siliceous breccia evidently formed at a later stage than the main intrusive breccia and was responsible for the metasomatic silicification of the surrounding breccia types. A precise delineation of these contacts is not easy due to the masking effects of the silicification process.

Late stage, vein like breccia bodies approximately 15 x 5m cut through and therefore post date the main stage breccia, Plate 5b. They have a brownish coloured siliceous matrix. The silicified fragments of killas and granite show a wide range of textures from being numerous, small and closely packed to being large and well separated, Plate 5c. The exact relationship between these bodies and the siliceous breccia is not unequivocably resolved, Figure 16, but they are probably broadly coeval. Four other similar bodies were found elsewhere in the pit.

## C Discussion

Numerous different mechanisms have been advanced for the formation of breccia pipes (Knutson et al 1979, Grant et al 1980, Johnson and Lowell 1961, Kents 1964, Llambias and Malvicini 1969, Bryner 1961). Sillitoe and Sawkins (1971) in their account of tourmaline bearing breccia pipes in Chile decided in favour of chemical solution and in situ chemical brecciation (Sawkins 1969) followed by collapse under the influence of gravity and cementation by the residual boron rich hydrothermal solution.

At Wheal Remfry, by contrast, there is abundant evidence attesting to the dynamic process of breccia formation. The killas fragments are well mixed and widely distributed within the main phase breccia. In the lower levels this requires a vertical displacement of between 200 and 300m. They frequently occur adjacent to a contact, centimeters away from fragments which have only just spoiled away from the wall rock. Killas fragments have even been observed in the small breccialets which leave the main body of the breccia. This not only implies rigorous mixing but also that the breccia was rapidly "frozen". The fragments themselves have a highly heterogeneous size distribution showing that grading did not occur. Evidence of hydraulic fracturing and disruption can be found in the breaking away of slab-like fragments from the eastern contact, Plate 4b. All these textures point to the breccia being the result of an explosive release of fluids under high pressures causing catastrophic brittle failure.

The main stage breccia displays features which suggests that it formed as a suspension of rock particles in a turbulent fluidised medium. The "fluidisation" model was applied to geology by Reynolds (1954). In

fluidised systems solid particles are dynamically suspended by a flow of gas, vapour or fluid which may have a lower density than the suspended fragments. If this is the case then high flow rates are required to suspend the fragments within the system. This in turn requires a high volume of fluid and a suitable sink for the expended residua. In effect it necessitates that the system be grounded to "earth", i.e. open to surface. There is no conclusive evidence that this was the case. Several lines of evidence suggest the opposite. The breccia pipe contracts markedly at higher levels. The clast content becomes exclusively killas whilst the quantity of matrix becomes significantly less. This could suggest that the breccia terminates not far above the highest present level of exposure. The fluidised medium in this case is therefore believed to have been predominantly of fine comminuted rock powder fluidised by boron rich hydrothermal fluids. The rock flour is indistinguishable from the breccia matrix unless highlighted by being haematised, Plate 4f. The fluidised medium was therefore only marginally less dense than the suspended fragments. Although there was appreciable turbulence and mixing, extremely large quantities of fluid were not necessary to keep the fragments in suspension. Differential movement between fragments took place in response to the differences in hydraulic equivalence of fragments of different mass, shape and density at different levels within the system. Of the total volume of matrix, metasomatised fine rock flour made a significant contribution whilst solute dumping may not be as important as originally believed (Allman-Ward et al, 1982). Relatively large quantities of fluid are still required however to contribute the boron content for the metasomatic process. Fluidised systems are characterised by turbulent flow causing agitation and mixing of fragments causing abrasion and rounding. The fragments may not be transported far from their source and will settle without grading upon the exhaustion of the system. All these features

have been observed in the main breccia phase. The amount of rounding of the fragments, however, is appreciably less than might be expected if the mechanical attritive effects had been of long standing. There are breccia apophyses in which the population of subrounded to rounded fragments in the small size range is high, leaving no doubt that these attritive effects were important on a local scale, Plate 4c.

The impression conveyed by many of the textures of partial disaggregation is that the dynamic processes were frozen in situ by the rapid crystallisation of the matrix, Plate 4b. A possible cause would be a catastrophic fall in confining pressure. The rounded shape of certain fragments is due to concentric exfoliation, Plate 4d,e, and not attrition. The concentric spoiled layers are apparently frozen in the initial stages of disaggregation. This texture is explained by explosive rupture following just such an instantaneous drop in confining pressure. The main breccia phase was initialised as a fluidised suspension but this lasted a comparitively short time. In geological terms, it was instantaneous.

Disruptive intrusion by a turbulent fluidised system was the dominant process at the initial stages of breccia formation. This was followed by a considerably more limited phase of collapse and pervasive silicification as the fluids became less boron and more silica rich.

**D Post breccia alteration and mineralisation**

Kaolinisation post dates breccia formation. The boundary of kaolinite alteration cuts incongruently accross the northern part of the main stage breccia body, Figure 16. To the south the granite fragments have been completely kaolinised and it is clear that the breccia body was sufficiently permeable to allow the passage of the altering fluids. North of the alteration front the rock fragments show pervasive haematisation. Although the haematisaton may reflect the flushing of iron from the kaolinised parts of the system, it is more likely that the kaolinising fluids were affecting rocks which had already undergone haematisation since certain granite fragments in the silicified main stage breccia have partially resisted kaolinisation and preserve remnants of haematitic colouration.

The breccia body itself contains no cogenetic mineralisation of economic significance.

## 2.3 DISCUSSION

The hydrothermal phenomena which have been described will be synthesised to give an overall picture of the differentiation processes which took place in the granite. The hypotheses of Burnham (1979) describing the emplacement and solidification of bodies of hydrous magma are used as models. In this case they are applied to the cupola forming the western lobe of the St Austell granite.

The granite magma rose to between 3 and 8km of the surface corresponding to confining pressures of 1 to 3kb. Assuming an initial water content of 3-5 wt percent $H_2O$ (Charoy 1979) the granite crossed its saturated solidus boundary at a depth of about 3 km (Harris et al 1970). As crystallisation of the outer carapace proceeded, the interstial residual fluids became increasingly enriched in volatiles. These fluids either escaped into the surrounding country rock or remained in the granite to cause the development of miarolitic cavities, pegmatitic pods and late (autometasomatic) alteration. Slight differential movement may have caused the concentration of such fluids along the western contact to form the tourmaline banding. After complete crystallisation of the carapace the magma was effectively sealed and could not intrude further upwards.

At this stage crystallisation and differentiation began in confinement in the zone immediately adjacent to the outer carapace. The silicate melt became saturated leading to a separation of a volatile rich aqueous phase. Experimental work carried out by Pichavant (1979) shows that silica, sodium, chlorine and boron will partition into the aqueous phase. The separation of the aqueous phase causes crystallisation of the residual silicate melt which results in a volumetric increase (Burnham

1979). This cannot be accomodated by plastic deformation of the granite carapace or compression of the contiguous magma. As cooling and crystallisation proceeds internal overpressures built up sufficiently to overcome the confining pressure and tensile strength of the rocks of the envelope. Brittle failure occurs. Phillips (1973) envisaged a sequential process in which the fluid overpressure built up to its critical value causing failure and the propogation of hydraulic fractures. The escape of the hydrous fluid relieves internal overpressure. The progressive build up of fluid pressure continues as a consequence of the crystallisation of the magma. Critical conditions are achieved again and fracturing is renewed.

Early on when the granite carapace was hotter and thinner and less strong the fluid overpressures necessary for failure was relatively low. Under these sorts of conditions the fractures were small, discontinuous and without preferential orientation and fluid flow rates were very low resulting in pervasive greisenisation. As the granite carapace thickened and cooled the fluid overpressure necessary for failure increased. The onset of well developed continuous fractures is associated with boron rich hydrothermal solutions, Figure 19a. Flow rates were low and alteration well developed. The orientation of the fractures would be random in an isotropic stress field. The Hercynian regional stress field caused two fracture sets to form as the major and minor stress areas inverted in response to the wedging effects as the fractures filled under pressure.

As the outer envelope thickened and strengthened failure became increasingly episodic and violent as the fluid overpressure required for failure became concomitantly high. At some stage in the cycle of hydraulic failure and renewed pressure build up, the fluid overpressure

became sufficiently large to propogate a fracture to a low pressure regime, possibly even to the surface. Boiling would have occurred as the confining pressure fell dramatically. Wall rocks adjacent to the low pressure zone would implode in a fashion akin to rock bursting, tending to slab off along the pre-existing fracture planes. The vapour and liquid streaming down the fracture zone fluidised the fine rock powder and caused a turbulent mixing of the fragments. This dynamic state lasted for an instantaneous period in geological terms before the crystallisation of minerals from solution, the exhaustion of the fluids and the reassertion of ambient pressure froze the system. This stage is shown conceptually in Figure 19b.

The main phase of breccia formation evidently marks the climax of events in which boron rich residual fluids escaped from the apical zone of the crystallising magma. Subsequent, less well developed, spatially more restricted and chemically more siliceous breccias did form but it is evident that by this stage the residual fluids were becoming extremely depleted.

It is clear from this synthesis that the breccia body was not a feeder for surface vulcanism. Breccias in the southern Bolivian tin belt are emplaced into the roots of a volcanic system (Grant et al 1980). The abundance of quartz porphyry fragments in the upper parts of the breccia may be the only remaining evidence of just such high level volcanic activity associated with the intrusion of the Cornubian batholith. The elvan dykes cross cut the breccia body, Figure 9.14, Plate 4a and so cannot be the source for these fragments.

The fluids responsible for the formation of the quartz veins appear to have a very different chemistry and genesis. Only slight

silicification accompanies the early quartz veins due to the high flow rates of the fluids from which they formed. The late quartz veins are believed to be associated with kaolinisation as both silica and iron are mobilised during alteration (Exley 1959, Charoy 1975, 1979). Clay runs are particularly well developed in the 320 direction coincident with the thickest quartz veins formed during the period of highest fluid pressures. There is, at least, a hydrothermal contribution to the formation of the kaolinite deposits. Kaolinisation would appear to predate the Tertiary as structures of this age are unaltered.

## 2.4 CONCLUSION

The geological history of the western lobe can be summarised as follows:

1. Intrusion of phenocryst rich coarse biotite bearing granite magma by passive emplacement processes.

2. Emplacement of the northern part to a higher structural level.

3. Separation of aqueous phases from the residual interstial fluid which resulted in the formation of the miarolitic cavities, pegmatite pods and tourmaline bands and the growth of the potash feldspar megacrysts and autometasomatic alteration.

4. Solidification of the outer carapace and the differentiation of the granite magma under confining pressure.

5. Separation of the greisenising fluids and the pervasive alteration of the granite.

6. Hydraulic fracturing and tourmalinisation.

7. Hydrothermal breccia formation.

8. Elvan emplacement.

9. Quartz-fluorite veins with sulphides.

10. Formation of the early quartz veins associated with mild silicification.

11. Haematisation.

12. Late quartz vein formation associated with kaolinisation.

13. Late fractures and joint formation.

# CHAPTER 3

# PETROLOGY AND PETROCHEMISTRY AND THE EFFECTS OF HYDROTHERMAL ALTERATION

## 3.1 THE GRANITE

The western lobe is composed of a phenocryst rich coarse grained biotite granite (PRCBG). The idiomorphic phenocrysts of potash feldspar are commonly about 3cm in length. They are milky to pinky white when freshest. The groundmass is hypidiomorphic granular comprising globular quartz, greenish tablular plagioclase, black to dark bronze booklets of biotite and vitreous black rods of tourmaline.

### 1 MICROSCOPIC CHARACTERISTICS

#### Quartz

The phenocrysts are characteristically large, globular, subhedral grains up to 5mm wide. They are usually individual crystals but polycrystalline aggregates can occur. The grain edges are always ragged and irregular, blastically engulfing surrounding minerals in the matrix. The following are most commonly included : potash feldspar, plagioclase, small groundmass quartz, small biotite flakes (strongly pleochroic from colourless to dark reddish brown), muscovite flakes, zircon and small rods of a greenish birefringent mineral, Plate 7a, thought by Scrivenor (1903) to be tourmaline and Charoy (1979) to be sillimanite. The growth of the phenocrysts at the expense of the groundmass minerals must be a late magmatic or early hydrothermal feature.

The groundmass quartzes are small irregular grains sometimes forming small patches of interlocking grains.

**Potash feldspar**

The potash feldspar phenocrysts form rectangular lathes. In the groundmass the grains are anhedral and interstitial. The phenocrysts are megascopically anhedral but microscopically subhedral due to their ragged blastic edges which encroach upon the minerals in the matrix, Plate 6a. The peripheries of the lathes are strewn with small globular quartz crystals, plagioclase and less frequently biotite, tourmaline, muscovite and topaz, the last being commonly pseudomorphed by clots of white mica. The debris outlines growth zones in the phenocrysts and attests to their late development.

Carlsbad twining is ubiquitous, microcline twining was never observed. Perthitic exsolution is usually present and ranges in size from the microperthitic to a coarse exsolution of branching lamellae and irregular patches. The lamellae are of albitic composition from their extinction angles. Albite grains which have been engulfed by the growing phenocrysts can be distinguished from the exsolution blebs by the orientation of their twin planes. They persist within the phenocrysts almost unaltered despite showing a slightly strained, glassy extinction. The oligoclase grains, by contrast, are rapidly digested, commonly with the development of apatite grains or reaction rims.

Potash feldspar is in turn attacked and corroded by a number of minerals. Branching veinlets which are morphological similar to the albite exsolution lamellae penetrate from adjacent albite grains. The potash feldspar has undergone albitisation; Charoy (1979) considering that the perthitic texture itself marks the onset of the albitisation process. Muscovite sends amoeboidal fingers into the phenocrysts with the release of bleby quartz, Plate 7g. Tourmaline behaves similarly.

All the phenocrysts are slightly clouded by sericitisation, in extreme cases a small number of fluorite and apatite granules form.

**Plagioclase**

There appears to be two plagioclase phases of identical form and habit. The earlier forms tablular grains and lathes, up to 1cm in size but commonly about 5mm. The tabular grains are very occasionally zoned, emphasized by an increasing intensity of alteration towards the centre. This prevented its composition from being determined. This earlier phase is of oligoclase composition and the grains contain biotite, quartz and rare topaz inclusions sometimes in a concentric distribution.

This oligoclase phase has been overgrown, altered and pseudomorphed by both albite and potash feldspar. The albite has an identical habit but is unzoned and has less regular, more splintery twin planes.

Potash feldspar corrodes the oligoclase grains from the groundmass, engulfing and flooding cracked and brecciated grains, Plate 6b. Relic patches are left as inclusions.

The age relationships between the albitisation and potash feldspathisation of the oligoclase is uncertain. The scarcity of zoned oligoclase grains implies that the solid solution reactions between plagioclase and the interstitial residua were allowed to go to completion. The albitisation and potash feldspathisation of the oligoclase and concomitant growth of the potash feldspar phenocrysts are probably coeval, reflecting the sodic and potassic enrichment which occurs towards the end of magmatic differentiation.

The plagioclases have all been affected by sericitisation to varying degrees. They are quite strongly coloured. There is a marked increase in fluorite and apatite content accompanying alteration in the more calcic phases.

**Micas**

Although strongly coloured in hand specimen biotite is often almost colourless or only weakly pleochroic in thin section. Relic cores and unaltered flakes trapped in other minerals show it to have originally been strongly pleochoic from colourless to dark brown, Plate 7b. Zircons are scattered throughout without any particular orientation and do not have pleochroic haloes implying that their radiogenic content is low. Pleochroic haloes are quite common, Plate 7c,7d but the intensity of the radiogenic destruction makes it impossible to identify the mineral responsible. The very intensity of this destruction, however, implies a very high radiogenic element concentration. This favours uraninite as the radiogenic element bearing phase (Ball and Basham 1979). Small rods of "sillimanite" are also present together with rutile and other oxides.

Biotite is replaced preferentially along the cleavage traces. The alteration mineral has a slightly rosy-brown tinge and shows very slight pleochroism and is possibly a lithium rich muscovite. The relic grains have their cleavages outlined by iron oxides, rutile, fluorite and apatite. In the Gaverigan borehole the biotite has been replaced by chlorite (colourless to dark green pleochroism) but this is exceptional. Biotite may also be replaced by idiomorphic brown tourmaline.

The relic cores can be epitaxially overgrown by clear white

muscovite (Plate 7d) which ramifies on its outer edges into the matrix and adjacent potash feldspar grains. These epitaxial overgrowths and the occurance of bent and broken muscovite lathes shows that the growth of the muscovite was a late magmatic phenomenon. The granite could therefore possibly be classified as a two mica granite.

**Tourmaline**

The earliest tourmaline is pleochroic from light or dark brown to colourless. It is commonly rimmed by a very thin bluish variety. It is not a particularly common mineral and occurs as quite large, highly irregular anhedral grains interstial to other minerals, Plate 7e. This generation of tourmaline is clearly late magmatic.

**Accessories**

This group includes all those minerals which occur sporadically or ubiquitously but in very small quantities.

Apatite. Occassionally forms quite large discrete grains in the matrix and similar idiomorphic grains included within biotite. These are primary occurances. Most commonly it forms small granules and granular aggregates associated with the alteration of biotite and calcic plagioclase.

Fluorite. Quite common and closely associated with apatite in the alteration of biotite (where it forms bleby anhedral grains along the cleavage) and of plagioclase feldspar. It is generally colourless although purple tinges are common.

Rutile. Together with other oxides it is distributed along the cleavage in the biotite.

Sillimanite. The small greenish needles 150-300 by 10-20 microns are particularly distributed within the quartz phenocrysts and biotite

grains.

Topaz. This phase is not particularly common but this may be due to its instability and tendency to become pseudomorphed by nests of white mica. Where present it forms xenomorphic, rounded grains, cracked, corroded and rimmed by muscovite. It can be occasionally seen as quite large grains in the groundmass but it is most commonly preserved as inclusions within quartz, biotite, tourmaline and occasionally the feldspars. For this reason it would appear to be a quite an early phase.

Zircon. Almost exclusively located in the quartz phenocrysts and biotites. The lack of a pleochroic halo suggests a generally low radiogenic content. It survives the alteration of biotite.

Cordierite, andalusite and garnet have all been reported from the granite but were not observed.

## 2 CRYSTALLISATION SEQUENCE

From the inclusion and replacement relationships a tentative crystallisation sequence has been established.

Biotite was one of the first minerals to crystallise. Exley & Stone (1964) even considered it to be inherited from anatexis or incomplete palingenesis of pelitic xenoliths. The minerals included within the biotite, namely apatite, sillimanite, topaz, zircon and rutile are obviously equally early. Oligoclase or its altered plagioclase precursor was the first feldspar to form. Crystallisation rates were sufficiently low to allow complete reaction to occur between the mineral grain and magma residua. As the residua became enriched in sodium and potassium, oligoclase was destabalised and the crystallisation of albite and potash feldspar began. The calcium released by the alteration of oligoclase was fixed in fluorite and apatite. The epitaxial overgrowth of muscovite

together with the alteration of biotite and the crystallisation of tourmaline were the last truly magmatic events. The common occurance of muscovite as an inclusion in other mineral phases can be explained by the pseudomorphing of other earlier and subsequently unstable minerals such as topaz or biotite.

Although no new mineral phases appear to have crystallised, certain mineral phases continued to develop at the expense of others. Potash feldspar continued to grow before undergoing muscovitisation, silicification, tourmalinisation and albitisation. Oligoclase is also muscovitised and silicified. At this stage it becomes extremely difficult to delineate between late magmatic and early deuteric alteration, if indeed it is possible.

Quartz has an extensive crystallisation history being amongst the earliest minerals to form but it continued to grow until the final consolidation of the granite.

## 3 DISCUSSION

Exley & Stone (1964) proposed that the Cornubian granites were emplaced "dead", i.e. completely consolidated at a relatively high structural level. The different granite textures were suggested to be the result of post intrusion and crystallisation readjustments. In particular the growth of the potash feldspar megacrysts were regarded to be the result of metasomatism by potash rich fluids, emmanating from the centre of the pluton and flooding the outer parts of the granite.

The late stage growth of the potash megacrysts is well documented and supported by the petrographic observations made earlier. However,

there is no evidence that post consolidation, potash rich fluids were responsible. On the contrary, chemical evidence shows that the megacrystic granite varieties contain less potassium than non-megacrystic varieties, Tammemagi & Smith (1975). Furthermore, the rapid change in rock types in the western lobe at the same structural level presents considerable problems for such a large scale phenomenon. The critical point is believed to be the effective redistribution of potassium within the system rather than the introduction of potassium from metasomatising fluids. In megacrystic granites the potassium is predominantly located within the megacrysts themselves whereas the potassium is more evenly distributed through the non megacrystic varieties. In megacrystic varieties the diffusion of potassium in the system has been effective enough to allow the growth of a single large crystal. This did not occur in the non megacrystic granites. The diffusion of potassium between growing crystal and residual interstial fluid is therefore the critical factor. Megacrystic varieties had slow cooling histories allowing complete diffusion to occur.

Mineral phases of early magmatic origin become unstable under the ambient thermodynamic conditions and in contact with the evolving and differentiating interstitial residua. Re-equilibration reactions involved the replacement of oligoclase, the destablisation of biotite with the formation of oligoclase, muscovite and tourmaline and finally the alteration of potash feldspar.

The presence of the accessory aluminium silicate, sillimanite, has an importance in excess of its abundance. Charoy (1979) uses it as a parameter to help define the conditions of anatexis for the granite magma. This presupposes that the aluminium silicate crystallised from the magma at an early stage and was not inherited from the source material.

The presence of primary magmatic topaz supports his contention that the sillimanite was magmatic or resulted from the exsolution of excess aluminium from silicates during a slow cooling process.

## 3.2 HYDROTHERMAL ALTERATION

### 1 GREISENISATION

From the preceeding petrographic description it is clear that the "freshest" granite has already undergone a certain amount of alteration of "phyllic" character (growth of quartz phenocrysts and tourmaline, the muscovitisation of biotite and destablisation of potash feldspar). Trying to distinguish between late magmatic and deuteric alteration is almost impossible. Those changes mentioned above increase with increasing greisenisation and so would seem to belong to a truly hydrothermal alteration process.

Greisenisation is unrelated to any particular visible set of fractures. The granite acquires a generally greenish hue, white mica becomes abundant, the groundmass looses crystal definition and goes milky green and the feldspars become clouded. Alteration is pervasive due to its being preconsolidation and/or controlled by narrow (microscopic to submicroscopic), closely spaced and impersistent fractures which maximised the effects of diffusion and resulted in the overlapping of the alteration selvedges.

## A Microscopic characteristics

### Quartz

The globular quartz phenocrysts develop even more strongly blastic outlines, engulfing and including adjacent minerals, particularly potash feldspar in the groundmass, Plate 6c. Small quartz grains in the groundmass also accrete strongly at the expense of the adjacent minerals. Overgrowths are generally amoeboidal and bleby but can become graphic when replacing potash feldspar in conjunction with muscovite.

Quartz exsolved from the alteration of other minerals is distinctive from magmatic quartz in having far fewer fluid inclusions.

### Potash Feldspar

This mineral is the most susceptible to alteration, particularly the smaller groundmass grains. The phenocrysts show an increasingly coarse exsolution of albite whose twin lamellae become well defined in the coarse patches. The impression given is one of an albitisation process although the completion of such a process was never observed. Sericitisation of the phenocrysts is generally limited to a few scattered coarse needles or a coarse flake. Both muscovite and tourmaline encroach upon the phenocrysts with flame-like growths.

The smaller groundmass grains are commonly quite strongly altered, occasionally to the extent of being pseudomorphed by symplectic quartz and fine muscovite. Under these conditions a little fluorite may be present.

The phenocrysts therefore tend to become albitised whereas the groundmass is muscovitised.

**Plagioclase**

The two different varieties of plagioclase show markedly different patterns of behaviour.

Oligoclase is quite severely altered very quickly, acquiring a moderately deep colour. Muscovite forms interlocking acicular lathes which with increasing alteration recrystallise to become dots and small flakes. Quartz, fluorite and sometimes a little apatite are released during alteration. Tabular crystals showing zonation have their more calcic cores more severely altered, in one instance the core being completely pseudomorphed by idiomorphic fluorite. In the most severely altered samples the grains are covered in a golden mass of needles and patches of muscovite. Twining has been all but completely obliterated and any surviving patches, usually on the least calcic rims have a glassy aspect.

Albite by contrast remains generally clear and fresh and apparently stable. A few coarse flakes or needles of muscovite are commonly scattered widely through the grains. During intense alteration it becomes "glassy" without becoming increasingly sericitised.

**Micas**

During late magmatic readjustments the biotite has already been bleached and replaced by muscovite (?protolithionite). The grains are characterised by being rather brown and murky and containing a little relic biotite. During greisenisation, muscovitisation is completed. The pale brown mica is replaced by clear muscovite. The biotite is pseudomorphed by muscovite with rutile, fluorite, apatite and oxides along the cleavage traces, Plate 7f. Zircon persists unaffected during this alteration process. Muscovite overgrowths simultaneously penetrate into the surrounding groundmass, particularly replacing potash feldspar. These patchy replacements are in optical continuity. With increasing alteration these patches coalesce to form the outlines of a larger coherent muscovite plate, Plate 6d.

**Tourmaline**

Secondary, bluey-orange tourmaline forms pointed, spikey overgrowths on the original brown magmatic grains, Plate 7h. In these murky coloured overgrowths it is sometimes possible to discern the remnants of digested feldspar. Potash feldspar is the most susceptible to alteration, the overgrowths tend to terminate against plagioclase, Plate 7h.

In cross section, tourmaline begins to show a degree of zoning from brown cores to colourless, blue and orangey rims. The order of zonation is not invariable and permutations are common.

During the tourmalinisation of other minerals quartz is released and enclosed within the growing tourmaline grains. Muscovite is never

enclosed and it would therefore appear to be unstable and readsorbed during tourmaline growth.

**Topaz**

Topaz is commonly associated with relic biotite but also occurs separately in the groundmass. Some of the grains are quite large. During greisenisation they are completely replaced by nests of very fine, completely disorientated flakes of white mica. Sometimes small rounded and corroded relics are recognizable. During more extreme alteration the flakes recrystallise to form coarser patches of small coherent muscovite plates. Their random orientation is maintained resulting in an anarchic patchwork texture.

**Conclusion**

The greisenisation process described could be split mineralogically into a number of separate processes, sericitisation, tourmalinisation, silicification and albitisation. The rates of these alteration processes do not seem to advance at a parallel rate. These processes therefore appear to be independent of each other. This is probably due to small changes in local conditions.

Muscovite-quartz rock or greisen is never developed and greisenisation is therefore an unsatisfactory collective term (Charoy 1979). Moreover it differs from the use of the term elsewhere in SW England. Nevertheless, since no better term could be substituted this one was kept for the sake of consistency.

## 2 TOURMALINISATION

Tourmalinisation includes both the tourmaline banded granite observed on the western flank of the northern part of the western lobe and the tourmaline alteration selvedges which border the tourmaline veins.

### A Tourmaline Banding

#### Microscopic characteristics

The bands are composed of an accumulation of fine tourmaline grains They are separated by "felsic" bands of fine grained, white, siliceous granite containing no dark minerals. The contacts of the tourmaline rich bands are quite sharp but not knife edge. The wider felsic bands grade into ordinary mildly greisenised granite at their centres.

In thin section the centres of the "felsic" bands show all the mineralogical characteristics of greisenised granite. The biotite has been completely pseudomorphed by muscovite. Quartz has accreted strongly. Potash feldspar phenocrysts are coarsely perthitic. The groundmass grains and all the oligoclase has been severely sericitised. Albite is generally free of alteration. Primary tourmaline is strongly overgrown by orangey-brown overgrowths. Topaz is pseudomorphed by muscovite although relic cores are preserved.

Approaching the tourmaline bands the groundmass becomes noticeably finer grained and more siliceous. The phenocrysts are predominantly of

quartz having strong blastic outlines. The quartz in the groundmass form patches with interlocking sutures. The feldspars, particularly albite, are more silicified than sericitised and are severely corroded by adjacent quartz grains. On the whole, the feldspars are smaller and less abundant, the difference being balanced by an increase in quartz content. Muscovite, pseudomorphing biotite, is itself attacked and replaced by quartz along the cleavage. Tourmaline forms very small, brown, xenomorphic grains. There is very little present and closer to the tourmaline bands the rock becomes truly felsic, containing no dark minerals.

In the tourmaline bands themselves the grains have the same small, granular, xenomorphic habit but are extremely abundant, Plate 8a. Some are light brown in colour (magmatic tourmaline) but they are predominantly orange brown with blue rims (secondary tourmaline). The fine grained character of the tourmaline is reflected in the whole rock. Quartz forms the most common phenocrysts which are fractured. Strong overgrowths develop on both the phenocrysts and the groundmass grains. The groundmass is quartz rich forming patches of interlocking grains. There is relatively little feldspar, any present being silicified and corroded by quartz. The muscovite pseudomorphs after biotite have been completely replaced by quartz and tourmaline.

**Discussion**

There is a great deal of evidence which supports a mechanical origin by differential flow for the tourmaline bands. Differential flow has undoubtably occurred since the bands are flow folded and contain xenoliths of ordinary greisenised granite. The quartz phenocrysts are shattered and the fine grained character of the bands could be explained

by cataclasis. The depletion of tourmaline in the adjacent felsic bands implies differential enrichment in the adjacent tourmaline band. However, the orange-brown variety of tourmaline is associated with greisenisation, whilst the amount of tourmaline present in the bands is too great to have been derived purely from differential enrichment.

There appears to be evidence for both a mechanical and metasomatic origin for the banding and there is no reason why both processes may not have been involved. The separation of boron and silica rich aqueous fluids from the residual interstial melt during the final stages of consolidation of the granite has already been proposed to explain the presence of the miarolitic cavities. The fluids were concentrated along zones of movement as the granite moved to slightly higher structural levels. The fluids "lubricated" the plane of movement, enhancing the effects of mineral differentiation and causing alteration of the adjacent granite.

**B Tourmaline alteration selvedges**

This phase of tourmalinisation is associated with the formation of brittle fractures. The fractures are usually unmineralised but small quartz stringers can occur, Plate 1f.

## Microscopic characteristics

### Quartz

The growth of quartz has already been observed during late magmatic alteration and greisenisation. During tourmalinisation this feature is further enhanced. The quartz phenocrysts become strongly blastic enclosing muscovite, relic feldspar and even tourmaline grains as the edges accrete. The groundmass grains grow equally strongly, corroding, silicifying and finally engulfing the adjacent feldspars. Patches of interlocking quartz grains develop in the groundmass. The original magmatic quartz retains its fluid inclusion assemblage but the newly formed quartz is much clearer with fewer inclusions and sharper exinction.

### Feldspars

The feldspars react very differently depending upon their chemical composition. Oligoclase is the most unstable, quickly degenerating into symplectic sericite and quartz. Potash feldspar is more resistant. The coarsely perthitic phenocrysts become mildly sericitised and silicified. Adjacent tourmaline grains attack it in the form of rounded or spikey apophyses. Increasingly, however, the centre of the phenocrysts become attacked and replaced by spikey patches of green tourmaline. Albite is the most resistant to change. Twining remains clear until quite late. It remains practically unsericitised but becomes increasingly glassy in appearance as it becomes increasingly corroded and swamped by quartz.

The feldspar groundmass degenerates much more quickly than the phenocrysts. Oligoclase is altered to sericite and quartz, potash

feldspar to sericite, quartz and tourmaline. The tourmaline is green and spikey and similar in size and morphology to the muscovite needles. The feldspars gradually lose their identity as twining is obliterated and they become increasingly submerged by quartz. Finally only ghost albite remains, floating, highly corroded, in a groundmass comprising quartz, muscovite and tourmaline, Plate 2b, before it too is eventually replaced. Occasionally feldspar relics may be preserved for a while where poikilitically enclosed by quartz or primary tourmaline.

**Micas**

During greisenisation biotite is completely pseudomorphed by muscovite. The opaques (rutile and minor ilmenite), fluorite and apatite released during this process are enclosed poikilitically by the muscovite along with those minerals originally enclosed within the biotite such as zircon and "sillimanite". During tourmalinisation the muscovite is replaced by quartz and tourmaline, Plate 8b,8c. Quartz initially replaces the muscovite along the cleavage but rapidly becomes bleby. Tourmaline forms small spikey green, squat, xenomorphic grains which gradually coalesce to replace the whole of the centre. The muscovite rims and overgrowths survive a little longer before being replaced as well.

The replacement of muscovite by tourmaline is ubiquitous. However in some alteration assemblages, large muscovite lathes appear to remain stable for a little longer than in others. This can result in a quartz, tourmaline and muscovite assemblage which is the closest that any rock in the western lobe comes to being a true greisen.

**Tourmaline**

During late magmatic alteration and greisenisation primary brown tourmaline is overgrown by orangey-brown to blue tourmaline. Tourmalinisation is associated predominantly with blue-green tourmaline.

Green tourmaline generally has an acicular habit. It forms overgrowths on earlier tourmaline grains, Plate 8c, penetrating and replacing surrounding minerals, particularly potash feldspar. Small radiating clusters develop around small quartz nucleii or on grain boundaries. The radiating habit is morphologically strong. Tourmaline replaces the centres of the feldspar grains (again potash feldspar is most susceptible) and finally also muscovite. Most minerals release silica during tourmalinisation and the resultant quartz grains are poikilitically enclosed within the tourmaline.

During increasing tourmalinisation, the quantity and extent of tourmaline replacement continues. The groundmass eventually comprises xenomorphic granular aggregates of tourmaline as spikey lathes or radiating groups, and quartz. The feldspar phenocrysts are distinctly pseudomorphed by symplectic quartz and short spikey tourmaline, Plate 8d, sometimes with fluorite or apatite. The muscovite grains are replaced by coarser tourmaline lathes with a parallelism mimicking the original cleavage. Quartz is enclosed poikilitically. Occassionally rutile, fluorite, apatite and zircon are preserved but they generally appear to be digested or dissolved during the tourmalinisation process.

Close to the central fracture there is some suggestion that tourmaline begins to replace and corrode even the quartz. In thin section the quartz stringer which infills the tourmaline fracture, Plate 1f, can

be seen to be a later feature as the clear quartz brecciates the wall rock, Plate 8e.

**Accessories**

There is an overall diminution in the content of the accessory minerals during tourmalinisation.

Apatite. Released during the alteration of the feldspars (particularly oligoclase) it is occasionally poikilitically enclosed in tourmaline. It very rarely occurs as large grains in the groundmass if tourmaline alteration has not been extreme.

Fluorite. Also released but more abundantly during the alteration of oligoclase. This mineral practically disappears during tourmalinisation. It is occasionally present as small poikiliths in tourmaline.

Opaques. Opaques are noticeably scarce in tourmalinised sections. They sometimes occur as small, very dark grains along grain boundaries. These are probably surviving primary grains. The opaques released during the alteration of biotite are occasionally preserved poikilitically in the tourmaline but they are more usually digested. Occassionally a large rutile lathe or lathes will be intergrown with green tourmaline. In one sample cassiterite is present in appreciable quantities as relatively coarse grains. When they are rhombohedral in outline they show a colour zonation from colourless to dark brown, Plate 8f. Stubby, lathe like grains are distributed between coarse radiating tourmaline lathes, proving their contemporaneity, Plate 8g.

Topaz. During greisenisation topaz is increasingly replaced by fine interlocking white mica lathes. This process continues during tourmalinisation. The fine muscovite needles persist into the tourmaline selvedge when all the other muscovite has been completely replaced. These

muscovite nests are finally replaced by fine radiating acicular green tourmaline. No relic topaz remains. Topaz is therefore unstable during tourmalinisation.

**Discussion**

The suddeness of the alteration front in hand specimen is reflected in thin section. The mineralogical changes are extremely abrupt. The alteration zone itself is a bimineral assemblage of tourmaline and quartz. At the edge of the alteration selvedge there is a zone of enrichment in muscovite. This zone is developed to a varying degree but never exceeds 2 or 3 cm. Further away from the fracture the alteration effects are very limited. The tourmalinising fluids would appear to have been extremely efficient over a relatively short range but did not penetrate the granite pervasively.

Unlike greisenisation, the changes accompanying tourmalinistion are consistent and predictable. Brammall and Harwood (1923) considered that the tourmaline selectively altered plagioclase. This was not confirmed since tourmaline preferentially replaced potash feldspar. Nemec (1975) suggested a reaction to account for this observation.

$$6\,K_{0.83}Na_{0.17}AlSi_3O_8 + 3B^{3+} + 3Fe^{+}_2 + 7H_2O = NaFe_3Al_6B_3Si_6O_{27}(OH)_4 + 12SiO_2 + 5K^{+} + 3H^{+}$$

orthoclase; tourmaline

The majority of the silica is believed to be deposited in situ as quartz. The other species released during alteration are presumably carried away in solution.

The tourmaline alteration zones are distinct from the tourmaline bands in a large number of ways, predominantly in their textures, mineralogy and the colour and morphology of the tourmaline (and therefore presumably also their chemistries).

## 3 KAOLINISATION

The preparation of thin sections from kaolinised material presents difficulties but they can be overcome by using impregnation techniques. It was not considered worth-while, however, since the alteration minerals are too fine grained to be identified in thin section. Use was made of the scanning electron microscope instead. Exley's (1959) mineralogical descriptions, supplimented by observations made in this study are summarised to put the SEM studies in context.

### A Microscopic Studies

#### Quartz

Recrystallisation is supposed to occur (Exley 1959) but it does not seem to be very significant. Quartz growth and silicification in the groundmass appears to accompany kaolinisation but it is impossible to determine how much of this may be due to preceeding alteration processes.

**Feldspar**

Exley proposed that potash feldspar is altered to secondary mica, finally becoming pseudomorphed by a symplectite of muscovite and quartz. This proceeds before the plagioclase (albite) is affected. With continuing alteration the albite becomes completely replaced by microcrystalline aggregates of clay and mica which pseudomorph the original grain. Present studies show that potash feldspar is on the contrary, considerably more stable than the plagioclase. The grains remain more or less fresh with only a few scattered patches of muscovitisation. Slight silicification probably helps to preserve the grains further. Oligoclase in the meantime has completely degenerated into symplectic phyllosilicates and quartz. Albite is marginally more resistant. Twining is quickly obliterated, the colour deepens and the grains become dark under crossed nicols as they become pseudomorphed by symplectic quartz and clay minerals, Plate 6e.

**Mica**

Any surviving dark mica becomes bleached, ragged and begins to alter to non-hydrous secondary mica (Exley 1959). The muscovite altering primary biotite is in turn replaced along the cleavage planes by a fine phyllosilicate mineral, Plate 6e.

**Tourmaline**

This remains stable during alteration, Exley reports that it becomes corroded but this was never observed.

**Accessories**

Apatite. Suffers from corrosion and diminishes in quantity.

Fluorite. Appears to be almost completely removed.

Topaz. Any relic cores alter strongly to the fine grained phyllosilicate flakes.

**Discussion**

Since kaolinisation is a late alteration process, it is difficult to separate the effects of this alteration from preceeding alteration processes. This is particularly so when the mineralogical phase change such as silicification accompanies all alteration processes. Nevertheless, the broad mineralogical changes involve silicification, particularly of the potash feldspar, rapid alteration of plagioclase to clay mineral aggregates and the alteration of mica by fine phyllosilicate minerals.

## B Scanning electron microscope studies

### Quartz

The phenocrysts selected for examination were derived from quite severely kaolinised material. The phenocrysts and associated parasitic grains show well developed cystal faces, Plate 9a, indicative of overgrowth. At higher magnification the surface texture has a hackled appearence with kaolinite grains within the surface pits, Plate 9b. This is believed to be the result of quartz growth accompanying kaolinisation.

### Potash feldspar

Potash feldspar appears remarkably fresh with clean surfaces and well developed cleavage. In places the crystals are "corroded" into pits which have marked striations, Plate 9c. Some pits are free of clay minerals whilst others are filled by kaolinite platelets and occasional booklets, Plate 9d. The pits are presumably areas of mechanical or chemical weakness marking the site of fractures or albite exsolution lamellae.

### Plagioclase

The sodic feldspar is much more severely decomposed. There are few fresh surfaces. The surface comprises a jumbled mass of dense kaolinite plates with the occasional rounded relic area of feldspar, Plate 9e. Microprobe analyses show these relic zones to be extremely depleted in alkalies.

## Mica

Examination of micas under high magnification clearly shows the mica plates in the process of being attacked and replaced by kaolinite, particularly at the edges of the cleavage plates, Plate 9f,g.

## Kaolinite

The degree of crystallinity of kaolinite has been used to imply a mode of genesis. Typical fields of view show that the kaolinite in Wheal Remfry is generally of the compact, platelet type, Plate 9b,e,g,h. Kaolinite "booklets" are not common.

## Discussion

SEM work has confirmed the growth of quartz during kaolinisation. The feldspars respond differently to alteration. Sodic feldspar is the most unstable, altering to kaolinite through a leached transition zone which encompases the grain. Potash feldspar is more resistant and displays textures consistent with the solution of material prior to the formation of kaolinite. In neither case has an intermediate alteration clay been observed. The micas are unstable and are being attacked along their cleavage. Kaolinite morphology is compact and dense.

## C Discussion

There are two schools of thought on the mechanism of formation of kaolinite at the expense of feldspars. The incongruent dissolution model of Hemley (1959), Hemley & Jones (1964), Hemley et al (1961) proposes that feldspar is decomposed directly to aluminosilicate minerals with the release of some components into solution. The congruent dissolution hypothesis advanced by Helgeson (1968,1969) requires the complete dissolution of the feldspar prior to the reprecipitation of clay minerals from solution.

The incongruent decomposition of feldspar is inevitably a solid state process. The nature of the intermediate alteration layer, however, is not resolved. Helgeson (1971) favours a porous blanket of newly formed minerals, Paces (1973) a "leached" layer, Wollast (1967) the direct formation of an amorphous aluminium silicate. Aluminium is considered to to be inert.

The congruent dissolution of feldspars results in the complete breakdown of the feldspar phases into their aqueous component parts. Congruent dissolution presupposes that aluminium is mobile and that the secondary minerals precipitate from solution.

The present study suggests that potash feldspar underwent congruent dissolution prior to the formation of kaolinite whilst the plagioclase was incongruently dissolved through an intermediate "leached" layer.

The degree of crystallinity of the kaolinite has been used as evidence for the genesis of kaolinite deposits. Well ordered kaolinite is associated with a hydrothermal mode of formation (Nicholas and de Rosen

1966) and badly crystallised kaolinite is found essentially in sedimentary environments (Oberlin & Tchoubar 1961). The degree of crystallinity of kaolinite increases towards quartz - tourmaline veins (Exley 1976). This would seem to imply a hydrothermal origin for the kaolinite deposits. It does not however necessarily imply a cogenetic origin as suggested by Bray (1980) since the kaolinising fluids could simply have made use of pre-existing structures as channelways.

Keller (1976) contrasted the textures developed in deposits of "indubitably" meteoric and hypogene origin. Supergene alteration is characterised by perfect automorphes developed in a loosely packed and well ordered manner (cp above). The porosity of the rock is high (up to 35%) and its density is low (<2.0) often as low as 1.39 (Baumann & Keller 1976). Small, matted, compact crystals with indefinate outlines are representative of a deep, hydrothermal origin. The porosity is low and the density is high (>2.0).

Keller (1976) showed that kaolinite from St. Austell and Brittany comprised large undeformed crystals in regular stacks having a relatively low overall density, indicative of a superficial origin. These observations are not confirmed. A range of samples of kaolinised granite from the western lobe have an overall compact texture with small, idiomorphic crystals, indicative of a "hydrothermal" origin.

## 4 SUMMARY

Greisenisation, tourmalinisation and kaolinisation are the three predominant alteration types. Haematisation did not involve any major mineralogical changes but the oxidation of the iron present in the feldspars.

Greisenisation involved six major mineralogical changes: the growth of quartz, the sericitisation of oligoclase, the albitisation of orthoclase, the muscovitisation of biotite, the growth of orangey-brown tourmaline and the alteration of topaz to fine white mica. Albite remains largely unaffected. These mineralogical changes occur independantly and are uncorrelated. A clear paragenetic sequence is therefore difficult to define.

The tourmaline banded granite is finer grained than the ordinary granite. The bands are enriched in fine, disseminated, orangey-brown tourmaline and quartz. The feldspars are silicified and less abundant. The "felsic" bands are depleted in dark minerals. The centres of the wider "felsic" bands comprise ordinary greisenised granite.

Tourmalinisation involves the extreme metasomatism of the granite to a bimineralic rock comprising quartz and tourmaline. Quartz grows, oligoclase is replaced by quartz and mica which is in turn replaced by tourmaline. Orthoclase is silicified and mildly sericitised but predominantly replaced by tourmaline. Albite is silicified without being sericitised or tourmalinised. Muscovite pseudomorphing biotite is replaced by tourmaline and quartz. Topaz is completely replaced by nests of fine white muscovite needles which are finally themselves altered to tourmaline. The tourmaline is blue-green in colour and associated with

the formation of cassiterite. The alteration front is extremely abrupt, the effects of tourmalinisation do not stretch very far beyond the visible limits of the alteration zone.

Kaolinisation involves the alteration of plagioclase rapidly to a pseudomorphous aggregate of kaolinite crystals. Orthoclase is altered more slowly and is silicified before being replaced by clay minerals. Biotite is bleached and muscovite altered to fine phyllosilicate minerals along the cleavage planes. Fluorite, apatite and topaz are destabalised and removed from the rock during alteration. There are no intermediate minerals between the destablisation of the primary minerals and the formation of kaolinite. It is difficult to distinguish the effects of preceeding alteration processes from the mineralogical phase changes brought about by kaolinisation. Considering the extensive distribution of the kaolinised granite the transition zone is sharp, generally occurring over a distance of a metre or less.

## 3.3 QUARTZ PORPHYRY DYKES

The elvans show differences in texture and appearence, often within the same body. There are two major varieties: those in which quartz and orthoclase phenocrysts are distributed through a light green matrix (Wheal Remfry, Melbur) and another in which abundant rather small phenocrysts of all types are scattered through a darker green matrix (Virginia). All the elvans have been severely kaolinised.

In thin section the quartz phenocrysts have strongly blastic, globular outlines. Accreting lobes trap groundmass between them and are finely ragged. The phenocrysts are clear and contain few inclusions, they have a sharp extinction. The feldspars are never fresh. Plagioclase forms tabular or lathe like crystals always pseudomorphed by a fine symplectite of kaolinite and quartz. Orthoclase grains are larger and slightly more resistant to alteration. Small quartzes are sprinkled through the finely kaolinised body of the grain, Carlsbad twining is preserved. More usually, bleby areas in the feldspar are replaced by quartz and muscovite and the rest by clay minerals, twining is obliterated. This texture reflects the original perthitic nature of the grain. The potash feldspars can also be tourmalinised by radiating clusters of blue to colourless tourmaline. Biotite or muscovite pseudomorphing biotite was never observed although some lathes comprising bleby quartz and radiating tufts of muscovite and coarse rutile may be the recrystallised relics. Iron oxides and apatite are also associated with these grains. An idiomorphic topaz grain was replaced by radiating tufts of muscovite, blue tourmaline, quartz and kaolinite.

The groundmass in the abundantly phenocrystic variety comprises a fine grained, homogenous mosaic of quartz and feldspar, the latter now

replaced by kaolinite. The sparcely phenocrystic variety has a groundmass with a spherulitic appearence. It is severely decomposed but originally seems to have been comprised of glassy spheruliths with a fine interstial glass probably composed origionally of feldspar and quartz.

The quartz porphyry fragments from the breccia pipe are better preserved since they have not been kaolinised. They have very similar characteristics to the elvan material, Plate 6f. The quartz phenocrysts are large and idiomorphic with blastic outlines. The potash phenocrysts have ragged, irregular, coarsely perthitic cores rimed by more homogenous material resulting in idiomorphic grains with Carlsbad twining. The plagioclase feldspars have been replaced by irregular, interlocking patches of potash feldspar, together with quartz, apatite and iron oxides, Plate 6g. The groundmass is composed of a fine interlocking quartz and feldspar mosaic.

**Discussion**

Due to the severity of the kaolinisation effects, the original textures in the elvans have been largely obscured. Nevertheless, the overall textures are compatible with a magmatic origin combined with the assimilation and partial digestion of granitic material torn from the side of the fracture.

The quartz porphyry fragments from the breccia pipe show very similar characteristics. This would seem to suggest that they were derived from an earlier generation of dykes which are no longer exposed. However the increasing frequency of their occurance at higher levels in the breccia pipe and their petrological similarity to pyroclastic material means that the question of their origin is by no means resolved.

## 3.4 KILLAS

The temperature of intrusion of the granite may be gauged by the metamorphic effects on the surrounding rocks. The country rocks in SW England are collectively termed "killas". In the western lobe they are finely banded metapelites of Lower Devonian age (Meadfoot beds) intercalated with calcareous bands. Although the diagnostic mineral phase changes for metapelites are pressure independent they are temperature sensitive. By combining the temperature of intrusion with fluid inclusion temperatures the depth of intrusion may be obtained.

The following petrographic description concerns samples taken from the Gaverigan borehole sunk close to the western lobe, within the contact metamorphic aureole. The farthest sample lies 700m away from the granite and samples were taken at regular intervals down to the contact.

There is a relatively simple petrological evolution within the metapelites towards the contact.

The country rocks have been affected by regional greenschist metamorphism of Hercynian age. The metapelites are finely banded, the phyllitic bands containing extremely fine grained minerals. The siliceous bands comprise small, granular quartz grains with raggedly recrystallised grain boundaries and coarser phyllosilicate grains; pleochroic biotite (colourless to light brown), chlorite apparently in the process of being replaced by biotite and coarse opaques, Plate 10a. The rock is cut by quartz veins which occasionally penetrate the cleavage and which also contain opaques and biotite.

With increasing grade the banding becomes less well defined and more

diffuse. The argillic bands contain biotite and chlorite with a little fine tourmaline and acicular muscovite. The micas become increasingly coarse grained but the interstial quartz remains fine grained. The siliceous bands also remain fine grained but the biotite, chlorite and opaques become increasingly coarse. Biotite replaces chlorite.

The mica content coarsens until the banding degenerates into a relative concentration of micas in relation to the fine siliceous mosaic. Small pods of coarse quartz develop containing coarse biotites, chlorites, spikey green tourmaline and opaques.

Chlorite finally disappears from the rock altogether, biotite becomes increasingly coarse and the opaques begin to concentrate into their own discrete bands. About 150m away from the contact andalusite appears as well developed poikiloblasts, Plate 10b, engulfing opaques, biotite and small tourmaline lathes. Muscovite infills the cracks in the mineral and closer towards the contact the andalusite becomes dusted with fine sericite. Biotite begins to be replaced by muscovite. This is the best developed in the hornfels "spots" where biotite is replaced by muscovite, tourmaline and opaques.

The rocks are veined and fractured to varying degrees. The mineralogy of the vein fill corresponds to the mineralogy of the immediately adjacent wall rock, Plate 10a, implying an origin through lateral secretion. Tourmaline veins, comprising a dense, xenomorphic mass of the blue-green grains are observed as far as 675m away from the contact. A microgranite vein was also seen, consisting of quartz, orthoclase (var. adularia ?), albite, abundant sphene and prochlorite in radiating "suns" and dense patches of "booklets" in the wider parts of the vein.

A calcareous band occurs 600m away from the contact. Relatively coarse quartz and chlorite bands are separated by even coarser grained tremolite. Where the rock has been sheared the tremolite becomes green and grades into actinolite, Plate 10d.

**Discussion**

Winkler (1974) has defined the stability fields for various critical minerals in the metamorphism of pelitic rocks.

- Pyrophyllite was never observed. This mineral destabilises at about 400 °C.
- Andalusite appears with the concomitant destruction of pyrophyllite between 400 & 430 °C.
- Since neither cordierite nor staurolite were observed, the pelites were not subjected to temperatures in excess of 500 to 550 °C depending upon pressure.

The presence of biotite, andalusite, chlorite, quartz, muscovite and tourmaline in the mineral assemblage defines a low to medium metamorphic grade, (Winkler 1974).

The calcareous band contains a more temperature sensitive mineral assemblage. The temperature of formation of tremolite-actinolite depends upon the partial pressure of $CO_2$ but ranges from a minimum of 490 °C to a maximum of 540 °C. This, together with the pelitic mineral assemblage directly adjacent to the granite would appear to limit the temperature of intrusion to about 500 °C, just below the medium grade metamorphic boundary (Winkler 1974).

## 3.5 BRECCIA

Several breccia phases have been identified. Volumetrically the most important is the main phase breccia, Figure 16. At the southern end of the body several other phases occur of limited distribution. The grey siliceous breccia forms a semi-circular extension to the east of the dark breccia. It is cored by the roof collapse breccia. Small "breccia dykes" cut through the main phase and grey siliceous breccias.

A thin section examination of these breccia phases should help to clarify their genetic and temporal relationships and to illuminate the mechanism of breccia formation and its mineralisation potential.

### 1 MAIN PHASE BRECCIA

In hand specimen the main phase breccia can be seen to contain an assortment of fragments, predominantly of granite but also of killas and quartz porphyry. The fragments are subrounded and cemented by a black, dull, very fine grained matrix. The fragments in the southern part of the pipe have been kaolinised whilst the remainder are quite severely haematised.

It is convenient to split the breccia into its major components for descriptive purposes.

**Fragments**

The larger granite fragments are petrographically identical to the granite of the western lobe but they have been affected by a certain amount of tourmalinisation and silicification similar to the tourmalinisation process described earlier, Plate 6h, but the tourmaline is buffer, more olive green in colour. The alteration intensifies towards the matrix. In the smaller granite fragments the alteration has frequently gone to completion due to their smaller size, becoming composed exclusively of quartz and tourmaline, Plate 11a. Alteration has not been as severe as that accompanying tourmaline fracturing because feldspar grains may survive not only in the smaller fragments but also as fragments in their own right.

The quartz porphyry fragments equally demonstrate increasing silicification towards the matrix as potash feldspar is replaced by quartz and the overgrowths on the quartz phenocrysts become even more pronounced.

The killas fragments are ubiquitously completely recrystallised to quartz and tourmaline. The banding is usually preserved, Plate 11a. The tourmaline is medium to fine grained, acicular to lathe like grains are aligned parallel to the banding. It is the same buff-green colour as the matrix tourmaline. The quartzes form a medium to fine grained mosaic and show evidence of recrystallisation. Semi-transparent opaques (rutile) are intimately associated with the tourmaline rich bands and form irregular aggregates. Veins carrying the same mineral assemblage penetrate the fragments from the matrix showing that alteration and brecciation were contemporaneous. Killas fragments containing microgranite veins were observed and fragments of microgranitic material can occur discretely in

the matrix.

The fragments have all been affected by subsequent alteration process. Any surviving feldspars have been haematised and kaolinised to varying degrees.

**Matrix**

The contact between the fragments and the matrix is sharp. The matrix comprises interlocking, radial needles and lathes of tourmaline forming matted intergrowths with interstitial quartz. The tourmaline is buff or blue to olive green in colour. The matrix is generally fine grained but can become quite coarse in patches. This coarsening is noticeably increased towards small fragments which have undergone more intense alteration. Opaques are not abundant, tending to be located within the altered killas fragments along the banding or nucleated around the edge of altered granite fragments, Plate 11a.

One of the most important features of the matrix is that at least half of it is comprised of fine rock material, predominantly quartz. The interstitial quartz cement can be distinguished from the derived material by the sparcity of fluid inclusions and the abundance of tiny tourmaline needles distributed through it.

## 2 SILICEOUS BRECCIA

The siliceous breccia samples fall into two groups. The first group comes predominantly from the eastern contact and represents a separate phase of breccia formation to the main phase breccia. The second group are main phase breccia samples which have been affected by a later phase of silicification and so they come predominantly from the western zone.

In hand specimen the two groups are very similar. Silicified and tourmalinised fragments float in a fine grained grey siliceous matrix. The size and distribution of the fragments vary. The first group contains predominantly small, well separated granitic fragments whilst the second has larger, more closely spaced fragments with numerous killas clasts. Tabular or rectangular vughs, completely or partially infilled by fine tourmaline needles and quartz crystals are common to both groups.

### Siliceous breccia

The fragments are composed entirely of quartz and tourmaline, Plate 11c. Granite fragments are pseudomorphed by interlocking quartz grains. Tourmaline grains are overgrown in optical continuity by the matrix tourmaline.

The matrix is distinctive, blue to olive green tourmaline lathes forming interlocking and interpenetrating clusters. Interstial quartz is fine grained and clear but scattered with fine tourmaline needles. Coarse patches of tourmaline and quartz either represent the infilling of voids or fragments of earlier quartz-tourmaline rock. The few opaques present are restricted to the tourmalinised and silicified killas fragments.

**Silicified main phase breccia**

The fragments have much the same characteristics except they are larger and killas clasts are more common. The smaller quartz fragments are strikingly overgrown by a ragged fringe of clear quartz, Plate 11b. The growth zones are marked by fine solid inclusions of tourmaline. Rectangular to equant vughs in the larger fragments and patches in the matrix have been replaced by a coarse mosaic of quartz and tourmaline and probably represent the site of original feldspars. The matrix is similar to that of the main phase breccia.

## 3 KILLAS COLLAPSE BRECCIA

This breccia phase is distinctive, being comprised of large, sometimes enormous, jumbled blocks of killas. The interstices between the fragments are vughy and lined or filled by quartz. The killas fragments have been silicified and tourmalinised but show concentric zoning as the intensity of alteration decreases inwards. The few granite fragments present have been completely altered to quartz and tourmaline.

In thin section the edges of the killas fragments show complete replacement by tourmaline and quartz, Plate 11e,f. The matrix comprises pale olive green to honey-yellow tourmaline needles floating in clear quartz, Plate 11e. The tourmaline replacing the fragments is of the same colour so brecciation and fragment alteration would seem to be contemporaneous. Quite large rutile grains can develop along the contact between fragments, Plate 11f.

## 4 LATE BRECCIA DYKES

Two of the small breccia dykes outcropping at the lowest level of breccia exposure were examined. The first is a grey-brown siliceous breccia from the western contact and the second is a dense brown siliceous breccialet which outcrops adjacent to the siliceous breccia.

### Grey-brown siliceous breccia

In hand specimens the fragments have all been intensely silicified and tourmalinised. A hint of kaolinisation shows that this process has not been completed. The fragment population is predominantly granitic with some killas. They float in a grey-brown siliceous matrix. Vughs are common and are partially infilled by well terminated quartz crystals.

In thin section the fragment assemblage and morphology is identical to the silicified main phase breccia, Plate 11d. Silicified granite fragments, altered killas fragments, quartz tourmaline fragments and quartz grains with overgrowths float in a matrix of interlocking buff tourmaline lathes, interstitial quartz and siliceous rock debris.

### Brown siliceous breccia

The fragment distribution is highly variable. The clasts can be few in number, large and well separated or numerous, small and closely packed. Both killas and granite fragments are present and are intensely silicified and tourmalinised. The matrix is fine grained, dense, siliceous and distinctly brown and resinous in appearence.

In thin section the fragments display the same characteristics described above, Plate 11g. The matrix however is composed of pale, honey-yellow tourmaline and is more siliceous.

## 5 CONCLUSION

On the basis of the colour of the tourmaline in the matrix and the textures of the fragments, three separate phases of brecciation have been established. These phases may not necessarily be separate events but part of a more or less continuous sequence.

The main phase breccia was the first and volumetrically most important stage of brecciation. The fragment population is comprised predominantly of granite and killas. Fragments are of variable size but generally subrounded although there is a range from angular to completely rounded forms. The presence of quartz porphyry fragments is confirmed despite the fact that the elvans postdate the breccia pipe. They may either have been derived from an earlier phase of dyke formation which is not exposed or from volcanoclastic material which was brought down from higher levels from deposits that have now been completely eroded. The juxtaposition of granite, killas and quartz porphyry fragments adjacent to each other on a microscopic scale is dramatic evidence for turbulent mixing during brecciation. The fragments have all been tourmalinised and silicified and this intensifies towards the matrix. This metasomatism is therefore contemporaneous with brecciation. The tourmaline in the matrix is buff to olive brown in colour. There is substantially less of it than expected from hand specimen. A considerable proportion of the matrix,

sometimes more than half is made up of fine grained siliceous rock debris. It would appear that the matrix or a substantial proportion of it has been derived by the metasomatism of the rock flour. Although the dumping of large quantities of tourmaline and quartz from solution (Allman-Ward et al, 1982) is now considered unnecessary and the components for tourmaline formation may easily have been cannabalised from the rock flour, largish quantities of fluid are still necessary to supply the requisite amount of boron into the system.

The second phase of breccia development concerns the formation of the siliceous grey breccia. This may largely represent the reworking of the main phase breccia by more siliceous fluids. The fragments have been completely silicified and tourmalinised with the complete replacement of the feldspars. The fragments are cemented by a siliceous matrix of bluey, olive green tourmaline. The fluids responsible for this phase of brecciation also caused the silicification and tourmalinisation of the main phase breccia and the formation of the grey-brown siliceous breccialets.

The fluids responsible for the third and final phase of brecciation were depleted in boron content and energy. The mechanism by which the space was generated for the formation of the killas collapse breccia remains unresolved. The fragments are only moderately tourmalinised and silicified as the cores of the larger blocks remain unaltered. The quantity of matrix is generally small and comprises clear quartz shot through by honey-yellow tourmaline. The brown siliceous breccialet was probably formed more or less coevally.

No phase of tourmaline breccia contains significant quantities of opaque minerals. The few opaques present are located in killas fragments.

They are formed as the result of alteration. Electron probe analyses show them to be iron and titanium oxides of a pure composition. The tin contents in particular are below detection. Although bodies of similar morphology in the Andean tin belt are associated with tin mineralisation, the Wheal Remfry breccia body would not appear to have any mineralisation potential.

## 3.6 MINERAL CHEMISTRY

Chemical analyses of mineral phases were carried out to establish the exact composition of the feldspar phases, the composition of the changing mica and tourmaline phases, to confirm the identity of the accessory mineral phases and to locate the minerals containing the radioactive elements. The analyses were carried out on a Cambridge Instruments Microscan MK5.

### Feldspars

The results of the feldspar analyses are summarised on Or-Ab-An diagrams, Figure 20a,b,c. The extreme purity of the orthoclase and albite phases is immediately striking. Even the zoned plagioclase phenocrysts with their oligoclase extinction angles are of albitic composition, Figure 20a. A poikilitically enclosed potash feldspar grain in an albite phenocryst shows partial digestion by its host mineral, Figure 20a. These relationships indicate that a period of albite growth followed the formation of the oligoclase phenocrysts and potash feldspar groundmass grains.

Albite growth was in turn followed by a period of strong potash feldspar growth. Albite lathes are engulfed and partially digested by the growing phenocrysts, Figure 20b. The potash feldspar phenocrysts are ubiquitously perthitic, the analyses confirm that the groundmass is pure orthoclase and the exsolution lamellae are pure albite, Figure 20c.

The feldspar crystallisation history is complex. Plagioclase of oligoclase composition was clearly the first to crystallise together with, or shortly followed by the potash feldspar groundmass grains. A

period of albitisation followed in which the oligoclase was completely replaced and potash feldspar grains were partially digested. Finally the potash feldspar phenocrysts began to grow, engulfing and digesting the albite grains, finally exsolving the sodic component as albite lamellae. These relationships imply that the granite underwent a very slow cooling history to allow these re-equilibration reactions to go to completion. The pure end member compositions of the feldspars in the microgranite vein, Figure 20c, show that these reactions had substantially occurred by the time the granite reached its present level of emplacement.

**Micas**

The composition of the "biotite" and "relic biotite" in the granite shows a continuous trend from biotite to muscovite, Figure 21. The composition of biotite from the killas and muscovite from the alteration of feldspars and topaz are plotted for comparison. The composition of the biotite in the killas does not coincide with the granite mica trend. The magmatic biotite would therefore not appear to have been derived by palingenesis of the country rock, Exley & Stone (1964). The wide spread in composition is a reflection of the late magmatic re-equilibrations taking place in the granite prior to final consolidation.

**Tourmaline**

In thin section the chemical composition of tourmaline clearly varied significantly to judge from the colour variations. On the basis of 135 microprobe analyses the only effective discriminator between the different colour varieties turned out to be the $\acute{F}e/Mg$ ratio , Table 12. Aluminium and titanium contents showed some small variation. Manganese contents were either very low or negligable.

The chemical changes in tourmaline composition are summarised in Figure 22. Primary magmatic tourmaline (pleochroic from light to darker yellowey brown) has an Fe/Mg ratio of 4.0 and lies towards the iron rich end of the schorl-dravite series. These tourmaline grains frequently have orangey-yellow overgrowths associated with late magmatic or early deuteric alteration (greisenisation). This generation is marginally more iron rich, having an Fe/Mg ratio of 10.1. Analyses made on the tourmalines of the banded granite and the mioralitic cavity tourmaline show that they have a similar composition with Fe/Mg ratios of 10.4 and 9.9 respectively. From their chemistries these three types of tourmaline would appear to be of the same generation. The blue-green tourmaline associated with pervasive tourmaline alteration selvedges is almost purely schorlitic, having an Fe/Mg ratio of 34.5. It is with this generation of tourmaline that the cassiterite is associated. The later tourmaline veins do not carry well developed alteration selvedges but have more massive central partings of coarse tourmaline. The colour of these later tourmaline generations passes from drab green back to pale yellow. Their chemistries also show a decreasing iron and increasing magnesium content. Mean Fe/Mg ratios are 14.2 and 1.6 respectively, although the more Mg rich varieties seem to have a wider range of values. The tourmalines show a well developed chemical trend with time. Beginning with an intermediate composition they become more schorlitic before finally reverting to a more dravitic composition towards the end of tourmaline formation.

The compostion of the tourmalines in the breccia body is highly variable. Tourmaline from the different phases show a wide range in values and a considerable degree of overlap. In general the characteristics of these tourmalines are similar to the late stage,

lightly coloured more magnesium rich vein tourmalines. Breccia formation, on the basis of the tourmaline chemistries, post dates the most intensive period of tourmaline metasomatism associated with the blue-green tourmaline variety and the crystallisation of cassiterite. This explains why the breccia body is unmineralised since the fluids responsible for its formation and from which the dravitic tourmaline was formed was already depleted in ore metals.

The tourmaline chemistries show that tourmaline banding was associated with late magmatic processes and not to the later extensive hydrothermal tourmalinisation phenomenon. This latter phase of tourmaline formation is associated with cassiterite mineralisation. Breccia formation occurred at a relatively late stage in the tourmaline paragenetic sequence, post dating stanniferous mineralisation.

**Opaques and accessories**

Rutile is the predominant opaque mineral in the granite. In 41 analyses magnetite was never recorded and ilmenite only once. This conforms with the expected opaque composition of granites derived by lower crustal anatexis.

The rutiles contain appreciable quantities of Fe, Nb, Ta and Sn, Figure 23. Mean values are 1.51, 2.58, 0.29 and 1.15 percent respectively. The distribution of compositions has a spread of values from the Fe - Nb + Ta tie line to the Sn apex. This reflects the relative charges on the different species. Nb and Ta being quinquivalent can only substitute for quadrivalent Ti if there is a concomitant substitution of trivalent Fe to maintain electrical neutrality. No such complications arise in the substitution of Ti by quadrivalent Sn. In general the early

rutiles i.e. those within the biotite cleavages, are more Nb and Ta rich whilst the later magmatic (microgranite vein) and hydrothermal rutiles are more Sn rich. The Sn contents in the rutile make it clear that this element was present in both the magmatic and hydrothermal systems.

Monazites are commonly associated with rutiles in the biotite. Analyses were carried out on thirteen for a restricted rare earth element suite. The results are plotted as chondrite normalised values against atomic number, Figure 24. The rare earth element distribution is steep and relatively straight (Eu was not analysed). There is a suggestion of light rare earth depletion. This distribution pattern suggests that the monazites crystallised very early in the magma, which in turn suggests that the host minerals, biotite and rutile, also crystallised early. The biotite is also unlikely to have been derived from parental material or incomplete palingenisis of country rock. The monazites contain radioactive elements and are frequently surrounded by pleochroic haloes. The mean thorium and uranium contents are 6.32 and 0.44 percent respectively. There is very little variation in these values. Although monazite could quite possibly represent the host mineral for thorium, it is certainly not present in sufficient quantities to account for the uranium contents in the granite.

Zircon was the remaining accessory mineral likely to contain radioactive elements. Microprobe analyses proved their radioactive elements content to be generally less than 1 percent. Uranium was slightly enriched with respect to thorium. Zircon is also unlikely , therefore, to be the host mineral for uranium. On negative evidence it would seem most probable that the uranium is located in small uraninite grains, too few in number to have been intersected in polished section.

## Conclusion

Biotite and rutile are probably magmatic in origin and not derived through anatexis or palingenesis. Monazite, biotite and rutile represent the earliest phases to crystallise from the magma. Monazites may account for the thorium levels in the granite but uraninite is thought to be the most likely source for the uranium.

The granite underwent protracted late magmatic crystallisation with slow cooling rates. This allowed the re-equilibration of the feldspars with the residual fluid, the growth of tourmaline and the muscovitisation of the biotite to occur. The tourmaline bands formed from late magmatic, deuteric fluids of similar composition to the contemporaneous or slightly later greisenising fluids. Pervasive tourmalinisation occurred later. The tourmaline was schorlitic in composition and cassiterite was deposited in association with it. The tourmaline breccia body post-dates this phase of tourmalinisation and so is unmineralised. Brecciation was coeval with the later tourmaline veins associated with tourmaline of a more dravitic composition and without pervasive alteration selvedges.

## 3.7 CONCLUSIONS

Charoy (1979) has determined the source region for the Cornubian granites as the lower crust. Magma was derived through anatexis. The presence of early aluminium silicate phases (sillimanite and topaz), the abundance of rutile and the scarcity of ilmenite and magnetite supports this interpretation. These minerals together with monazite and zircon and biotite, in which they are all poikilitically enclosed, were the first to crystallise from the magma. The crystallisation of precursor plagioclase and orthoclase followed. The relic zonation in the plagioclase points to a relatively rapid period of growth as the magma rose towards the surface.

The fluid content of the magma was originally 3 - 5 wt% $H_2O$, Charoy (1979). The contact metamorphic mineral assemblage shows the granite to have been intruded at about 500 $^{o}$C. The granite solidus must have been severely depressed which means that the magma was enriched in volatiles. This volatile enrichment caused an extensive late magmatic period of crystallisation. This allowed complete re-equilibration to take place between the mineral phases already present and the residual interstitial fluid. Due to changes in pressure, temperature and chemical conditions the original mineral assemblage became unstable. Oligoclase was completely pseudomorphed by albite whilst in many instances retaining the original zoning and twining textures. Fresh albite also grew. Subsequently potash feldspar grew extensively, possibly through resolution of original grains and diffusion through the interstitial fluid medium. A few large crystals consequently developed rather than numerous small ones. Depending upon local conditions this late stage growth could become extreme, resulting in the development of the coarse, almost pegmatitic facies. Other late stage re-equilibration reactions

appear to be the leaching and alteration of biotite to muscovite and the development of epitaxial overgrowths (ss). Tourmaline crystallises at this late stage and begins to grow. These features are similar to the effects of greisenisation and the granite is therefore undergoing pervasive autometasomatism.

The presence of hydrous residual phases are marked by the presence of miarolitic cavities rich in quartz and tourmaline. These boron and silica rich fluids concentrated in zones as a result of, or caused, differential flow in the granite parallel to the contact. Some mechanical enrichment in tourmaline occurred through differential concentration of primary tourmaline. The fluids caused the formation of the tourmaline bands and the alteration of the interstitial and surrounding granite. Following the formation of the tourmaline banding the granite crystallised completely.

Just after granite consolidation numerous, small, discontinuous fractures developed. The fluids passing through the fractures caused pervasive greisenisation; the sericitisation of the feldspars, the tourmalinisation of biotite and potash feldspar, the albitisation of potash feldspar and general silicification. Local variations in conditions allowed these mineralogical changes to occur inhomogeneically.

Discrete, continuous fractures were developed which guided the tourmalinising fluids and caused well developed and discrete alteration selvedges with very sharp alteration fronts. Tourmalinisation was extreme, altering the granite to a quartz and blue-green tourmaline assemblage. Cassiterite mineralisation is associated with this generation of tourmaline formation. Later tourmaline generations became more dravitic in composition and were not associated with mineralisation. The

formation of the breccia body took place during this period. Its mechanism of formation has been described. At least half of the matrix is composed of siliceous rock debris making solute dumping of large quantities of tourmaline and quartz from solution unnecessary. However considerable quantities of fluid are still required to supply the requisite amount of boron. The main phase breccia was the earliest and largest of the breccias to have formed. The grey siliceous breccia was subsequently emplaced and silicified the adjacent portions of this earlier phase. This was followed by the formation of the siliceous breccia veins, the siliceous collapse breccia and the boron rich siliceous breccia vein.

The elvans show clear cross cutting relationships with the quartz-tourmaline veins and the breccia body. The material was extremely potassic since it contains large potash feldspar phenocrysts whilst plagioclase has been completely replaced by potash feldspar. The mode of origin is likely to have been magmatic as there is evidence of relic devitrification textures. The material may have been hydrous and injected at high velocity causing blocks of granite to be torn from the wall and partially or completely digested.

Kaolinisation was the last phase of alteration and caused the preferential alteration of sodic feldspar with respect to potash feldspar, the kaolinisation of mica and the growth of quartz. Potash feldspar appears to alter by a process of congruent dissolution whilst sodic feldspar decomposes incongruently through a leached zone. No intermediate alteration mineral was observed. The kaolinite shows a dense, closely packed morphology consistent with a hydrothermal mode of formation.

# CHAPTER 4

## THE CHEMISTRY OF THE ROCK TYPES AND THE CHEMICAL CHANGES ACCOMPANYING HYDROTHERMAL ALTERATION

## 4.1 INTRODUCTION

This chapter is concerned with five major objectives.

- A comparison of the rocks from the western lobe with other SW England and Sn-W bearing granites
- An investigation of the chemistry of the alteration process, particularly their mass transfer characteristics
- An examination of the patterns of chemical behaviour of the elements during alteration
- The extraction of factors which can be used as variables to measure the degree of alteration by using statistical techniques
- Determining the distribution of ore metals within the granite in order to define mineralisation of potential economic interest

### Data

The sample preparation methods and analytical techniques are described in Appendix A and the precision and accuracy of results in Appendix B. In summary, the major and minor elements were determined by a combination of XRF and ICP techniques. Radioactive element determinations were carried out by gamma-ray spectrometry. The processing of the raw data to produce a database file containing major, minor, trace and normative data is described in Appendix A. The tabulated output is given on Microfiche 1 at the back.

The statistical techniques which are to be used in this section are parametric, which is to say that the data are assumed to be normally distributed. However, element frequency distributions are commonly skewed Figure 25, and this assumption is not therefore valid. There are a number of ways in which the data can be transformed to make this assumption hold

true. The use of a general power transformation was proposed by Box and Cox (1964). Mancey (1980) has discussed the advantages and disadvantages of using power transformations. The data from the western lobe was power transformed and the efficacy of this technique in normalising the data can be seen, Figure 26. The power transformed data are standadised (i.e. mean = 0, std. dev. = 1) and so the values represent units of standard deviation. However since some of the statistical packages which were to be used could not accept negative values, the standardised data values were shifted so as to make all values positive. This power transformed data set has been used in all the subsequent statistical analyses that have been undertaken.

## 4.2 SAMPLE GROUPING

The purpose of splitting the data into its natural groups is to enable representative subsampling to be undertaken and to allow the use of group means as the most representative measure of chemical trends during alteration.

There are several methods of grouping data. Natural cluster or groups have been defined as regions of high point density (Everitt 1974). Cluster analysis is one method by which the structure of the data can be investigated to identify the number of clusters and their membership. Non-linear mapping (NLM) is another clustering technique. N-dimensional data is mapped non-linearly onto two dimensions whilst preserving the inter-point distances as far a possible. Any intrinsic structure in the data should be present in the final plot. The method has the enormous advantage that the human eye can identify any since it is very sensitive to the presence of point groupings in such two-dimensional scatter plots. Mancey (1980) discusses the relative merits of the two techniques. Non-linear mapping is preferred for small data sets.

There are two fundamental options which affect the non-linear mapping technique, the selection of variables and the option to weight the variables equally. The variables were selected from the multi-element groups for the whole data set (see section 4.5) to reduce the redundancy in the selection of the variables. Each variable was weighted equally. The resultant maps are depicted in Figure 27 a, b, c, d, e, f.

The samples were originally classified according to their appearance in hand specimen. Group lines have been drawn around what are considered

to be the natural groupings. A certain amount of subjectivity is obviously attached to this technique at this stage.

**Greisenised granite**

The greisenised granite samples completely enclose the unaltered granite group, Figure 27a, which confirms that even the "freshest" granite has undergone some degree of alteration. The lack of spatial correlation between the greisenised samples and the elvan does not support a genetic connection.

**Tourmalinised granite**

The close spatial relationship and overlap between the greisenised and tourmaline banded granite samples (Figure 27a) contrasts with the trend of the fracture controlled tourmalinised samples (Figure 27c). This implies that greisenisation and tourmaline banding are related and distinct from the later fracture controlled tourmalinisation process. The position of the killas sample confirms the lack of any chemical relationship with the tourmaline banding. The disinct separation of moderate and intensely tourmalinised granite groups reflects the abrupt chemical changes which occur.

The breccia matrix samples, Figure 27d, overlap the intensely tourmalinised samples and are chemically indistinguishable from the metasomatic alteration selvedges around the tourmaline fractures. The matrices of the different breccia phases cannot be chemicaly distinguished.

**Kaolinised granite**

The kaolinised granite samples and kaolinite infilling vughs in late quartz veins plot well away from the other groups, Figure 27b,e. The alteration trend is dissimilar to any other. Kaolinisation is chemicaly different to the other alteration processes and therefore likely to be the product of a genetically separate process. The pegmatitic granite facies has been kaolinised and its chemistry reflects this alteration process. It is therefore impossible to determine whether it was formed by metasomatic or magmatic processes.

**Haematised granite**

The haematised granite samples, Figure 27f, do not display a coherent distribution. This confirms the hypothesis outlined in Chapter 2 that this alteration involves only a change in the oxidation state of iron . The samples have been reclassified into the groups in which they fall.

**Redefined groups**

The samples have been reclassified into six groups; unaltered granite, greisenised granite, mildly, moderately and intensely tourmalinised granite (or quartz-tourmaline rock) and kaolinised granite, Figure 27g. Any samples falling outside these redefined groups have been discarded. These reclassified samples have been non-linear mapped, Figure 28. The groups show a good separation.

## 4.3 CHEMISTRY OF THE ROCK TYPES

In this section the chemistry and normative values of the granite and its related phases are compared to other Sn-W bearing granites. The analyses for these granites have been derived from the literature and are listed on Microfiche 2 at the back. A classification of the granite was attempted using Streckeisen's (1975) criteria and normative values. The granite chemistry is discussed in the light of existing theories for the generation of the Cornubian granite magma. Hydrothermally altered granite samples have been plotted on normative diagrams to identify systematic changes during alteration. The mineralisation potential of the area is considered.

### 1 THE GRANITE AND RELATED ROCK TYPES

#### A Major and trace elements

Table 13 summarises the major element and normative data for the unaltered granite samples from the western lobe and compares them to published values for alkali granites, granites and other biotite bearing granites from SW England. A straight comparison shows the biotite granites of SW England, including the western lobe, to be chemically closer to the alkali granites than the granites (Wedepohl 1969). The calcium and normative anorthite contents are particularly critical. By contrast to the alkali granites however, the Cornubian granites are noticeably impoverished in iron and enriched in alumina and phosphorous. Despite being alkali rich these granites are still peraluminous, that is, they contain normative corundum.

The trace element data for the western lobe is compared with that from the Land's End granite and published values for low calcium granitic rocks, Table 14. The biotite granites from SW England are enriched in Rb, B, Li and Cl and depleted in V, Sr, Y, Zr and Ba. The K/Rb ratio is 83 and falls squarely within the 58 to 102 range reported for the granites or SW England by Tammemagi and Smith (1975). This range corresponds to the "pegmatitic-hydrothermal" region defined by Shaw (1968) which has been taken to indicate that the granite had already undergone considerable fractionation from its source material.

**B Radiogenic elements**

The radioactive element contents in the biotite and lithionite granite from the western St. Austell granite cupola are summarised in Table 15. The values are compared with those reported from the St. Austell granite by Tammemagi and Smith (1975), Francis (1980) and the mean value for low calcium granitic rocks quoted by Turekian and Wedepohl (1961). The St. Austell granite is enriched in potassium and uranium but depleted in thorium in line with the Cornubian batholith as a whole. The St. Austell biotite granite is marginally enriched in uranium and thorium relative to the whole batholith. The lithionite granite is depleted in all radioactive elements with respect to the St. Austell biotite granite and the batholith.

**Uranium loss lines**

In plutonic environments uranium and thorium behave similarly. Due to their close ionic size, high valencies, electronegativities and co-ordination numbers with respect to oxygen. The U/Th ratio should therefore be the same for all samples from a magma which underwent the same history of crystallisation. Under oxidising conditions uranium forms the very soluble and highly mobile uranyl complex. Thorium has no comparable chemical state and is relatively immobile. If uranium is plotted against the U/Th ratio any loss or gain in uranium can be identified. For example, a granite has an U/Th ratio of 1.0 and an initial uranium content of 10 ppm. Leaching of half the uranium leaves 5 ppm and a U/Th ratio of 0.5. Complete removal of the uranium gives a U/Th ratio of zero. All three points will fall on a straight line, called the uranium loss line. The slope of the line corresponds to the (immobile) thorium content in the rock. Similarly if uranium is added to the rock the points will be further up the loss line. The clustering of points may be used as a guide to the original uranium content in the granite. Points falling away from this group correspond to samples which have been enriched or depleted in uranium.

Uranium loss lines have been drawn using data from this work and that of Francis (1980), Figure 29. Data from two boreholes in the east of the St. Austell cupola consistently define a single loss line, data from the western lobe (including the Gaverigan borehole) define another whilst the lithionite granite shows quite considerable scatter. The wide distribution of points along the loss lines indicates that considerable leaching of uranium has occurred. The "original" uranium and thorium contents have been estimated from these loss lines, Table 16. These values confirm the enrichment in uranium and depletion in thorium in the St. Austell granite with respect to low calcium granitic rocks in

general. The western lobe is additionally enriched by comparison to the St. Austell granite pluton as a whole.

## C CIPW Norms

Normative values were calculated on the samples collected from the western lobe and are compared to norms calculated from analyses of Sn-W granites from SW England, Europe, Russia, Australia and Malaya culled from the literature. The normative values are used to classify the granites and to compare them with the haplogranite system. Their use in this context is not ideal since they do not necessarily correspond to the modal values and the granite chemistry may have been modified subsequent to intrusion by metasomatic alteration.

## Classification

The rock types have been classified according to Streckeisen's (1975) criteria. Rocks with a mafic component of less than 90% and normative quartz are classified in the QAPF diagram; the felsic constituents being recalculated to sum to 100. Q represents quartz, A the alkali feldspars including orthoclase and albite (An 00-05) and P, Plagioclase (An 05-100). The incorporation of albite within the alkali feldspar group is a convention since it is impossible to distinguish between albite which represents the end point of plagioclase solid solution and albite which has exsolved completely from potash feldspar.

According to Streckeisen's (1975) classification the granites and associated rock types in SW England, including the biotite granite of the western lobe fall into the alkali feldspar granite field, Figure 30a.

Sn-W granites and associated rock types from metallogenic provinces around the world have also been classified, Figure 31a, b and fall overwhelmingly into the same field.

Using this classification, the different rock types show remarkably little compositional variation. The incorporation of albite with the alkali feldspars also leads to a certain degree of artificiality as a rock passing from normative oligoclase (An 06) to albite (An 05) jumps accross the diagram. The presence of zoned plagioclase lead Charoy (1979) to incorporate the albite with the plagioclase, Figure 30b. According to this classification the rocks fall into the granite and monzogranite field. The compositional variation in the rock types is better displayed and shows the trend towards potash and silica enrichment in the later magmatic differentiates but the proximity of the samples to the Salave granodiorite (Harris 1979) does not truly reflect the enormous petrological difference between these rocks. The original classification criteria are therefore preferred.

**The Haplogranite system**

Tuttle and Bowen (1958) undertook an experimental investigation into the Q-Ab-Or-$H_2O$ or haplogranite system. The ternary minima were determined for the system for various saturated water vapour pressures and they were shown to migrate towards the Ab apex with increasing pressure. The line of minima coincided with the maximum concentration of granitic plutonic rocks. They concluded that the liquid phase at the ternary minimum (corresponding to the composition of most granitic melts) could be obtained by either fractional crystallisation of more basic liquids or by the remelting of sialic rocks.

The Sn-W granites and associated rock types from SW England (including the western lobe) and from around the world coincide with the granite maximum, Figure 32a,b implying that they have originated either by partial melting of the lower crust or differention from more basic magma. Granites derived by differentiation processes however are characteristically associated with a broad range of rock types such as occur in the Andean batholith. By complete contrast the Cornubian batholith and other Sn-W granites from around the world are remarkably homogenous. An origin by partial melting of the lower crust as discussed in Chapter 1 is therefore preferred. The Rb/Sr ratios of the Cornubian granites and the presence of a denser phase at depth (Bott and Scott 1964) suggests that they also underwent differentiation prior to their final emplacement. This may explain their slight displacement towards the Q-Or tie line. The position of the aplites can probably be accounted for by their greater volatile content which has been frozen in during rapid crystallisation (Pichavant, pers. comm.)

**D Sn-W granite characteristics**

The characteristics of Sn-W bearing granites reported in the literature have been summarised in Table 3. The chemical and normative mineralogical features of the Cornubian batholith, including the western lobe, are summarised in Table 7, together with what are considered to be the critical characteristics of the tin-tungsten bearing granites.

The principal criteria for tin-tungsten mineralisation would seem to be the derivation of the magma from the lower crust. This explains their universal "S" type granite characteristics. Sn-W granites occur in a wide variety of geological settings which suggests that the particular

mechanism for magma genesis is relatively unimportant, Halls (1981). The second critical criterion is the alkali rich and peraluminous nature of the granites. Both Goranson (1938) and Tuttle and Bowen (1958) both reported the immiscibility of water in such melts. Although the solubility of water is increased by high levels of volatiles such as boron (Pichavant 1979), it remains finite. During differentiation the peraluminous melt will saturate and exsolve an aqueous phase. Elements will partition into the different phases depending upon their chemical characteristics. Pichavant (1981) shows that Si, Na, Cl and B partition strongly into the aqueous phase. Patterson et al (1981) have shown that Cl plays the critical role in transporting tin and so this element (together with tungsten) will also partition into the aqueous phase. This aqueous phase represents the potential mineralising fluid which, given the requisite physical conditions, will be ejected into the crystalline carapace and country rocks. The residual silicate melt will be strongly enriched in lithium, fluorine and potassium. South-west England would appear to be a classic area in which the aqueous fluids have been expelled along fractures to cause greisenisation or tourmalinisation and the residual silicate melt has been intruded to form the elvan dykes. The close spatial and temporal relationship between mineralisation and elvan dyke intrusion (Hosking, 1964, Charoy 1979) is the result of a cogenetic origin. This relationship has also been reported from the Sn-W granite of Transbaikalia (Ontoev 1974).

## 2 HYDROTHERMALLY ALTERED GRANITE

### A Chemical and normative mineralogical changes

The analytical means of the different alteration types are given in Table 18 and the percentage changes with respect to fresh granite in Table 19. The mean normative values and their percentage changes during alteration can be found in Tables 20 and 21. Plots display the data in a more readily accessible form, Figure 33 a, b, c, d, e.

#### Greisenisation

There is a general relative decrease in most elements. Exceptions are Ca, Na and B which are relatively increased. This is reflected in the normative data where albite and orthoclase are the only minerals not to be decreased. Chemical and normative changes are generally small.

#### Mild tourmalinisation

There is an overall decrease in the trace elements with the exception of B and Zn. Amongst the majors K, Mn, P and H+ are significantly depleted. The remaining alkalis are significantly increased together with Fe and Ti. Anorthite and orthoclase are depleted whilst albite is relatively enriched. The changes accompanying mild tourmalinisation are similar to, but more extreme that those of greisenisation. The chemical effects may be interpreted as being due to the leaching of mica, the destablisation of orthoclase and the growth of tourmaline.

**Moderate tourmalinisation**

There is a general decrease in the alkalies and alkaline earths except for Li and Mg. The general increase in transition metal contents is reversed in the case of Cr, Cu, Th and Zr. All the feldspars and apatite are chemically destabilised. Elements and normative values related to the crystallisation of tourmaline increase dramaticaly (en, il and hm being the normative minerals corresponding to tourmaline).

**Intense tourmalinisation**

The changes here are similar to those above but are more extreme.

**Kaolinisation**

The aklkalis and alkaline earths with the exception of Sr and Ba are strongly depleted. The normative feldspars are concomitantly depleted, the percentage change in the plagioclase component being most marked. The strong increase in Al, H+ and normative corundum reflects their replacement by kaolinite. The increase in B and normative enstatite suggests that these samples have been slightly tourmalinised prior to kaolinisation.

**Alteration trends**

Alteration trends are most usefully summarised on Q-Ab-Or diagrams since these components comprise over 70% of the granite. Stemprok and Skvor (1974) plotted data from the Erzgebirge to show the presence of greisenisation, albitisation and potash feldspathisation trends, Figure 34. Greisenisation predominates and involves a move first towards the

Q-Or tieline and then to the Q apex. Similar greisenisation trends have been reported by Plimer (1977), Hall (1977) and Charoy (1979), Figure 35 a, b. Slightly different greisenisation trends which move first towards the Q-Ab tieline before moving on towards the Q apex also occur, Groves and Taylor (1973), Charoy (1975), Figure 35a.

The distribution of the "greisenised" granite samples from the western lobe confirms that the mineralogical changes have been slight, Figure 36a. The mineralogical equivalent of the greisenisation trends reported from these Sn-W granites is the tourmalinisation trend in the western lobe, Figure 36b. This alteration trend follows the greisenisation trends of Groves and Taylor (1973) and Charoy (1975) in moving towards the Q-Ab tie-line first. The kaolinisation alteration trend, Figure 36c, moves strongly in the opposite direction, towards the Q-Or tie-line before swinging up towards the Q apex. The difference in the trends reflects the relative destablisation of potash feldspar with respect to albite during tourmalinisation and the opposite during kaolinisation.

Modal mineral analyses were obtained using quantitative XRD for a limited number of kaolinised samples. A comparison between the alteration trends calculated from normative and modal values show a close agreement, Figure 36c and 37a. Charoy (1979) used an "exploded" Q-Musc-Kaol-Feld quaternary diagram to plot the mineralogical changes, Figure 38. Charoy (1979) concluded that kaolinisation followed two different trends, one in which the muscovite content remained constant whilst silica decreased and kaolinite increased (Dartmoor, St. Austell, Ploemeur) and a second in which both muscovite and silica decrease with increasing kaolinite content (Beauvoir, Colettes). The St. Austell granite data shows a third trend, Figure 37b in which both mica and silica decrease with increasing

alteration.

**Summary**

Greisenisation in the western lobe is not well advanced which is reflected in the relatively small changes in the bulk chemical content of the granite. This contrasts with other areas in SW England (Charoy 1979, Hall 1971), Europe (Tischendorf et al 1974) and Australia (Groves 1974, Plimer 1977). Tourmalinisation is the alteration in the western lobe which is equivalent, mineralogically and chemically to the greisenisation of other Sn-W bearing granites. It differs in being so extremely boron rich. Potash feldspar is more susceptible to alteration than albite. Kaolinisation shows a similar alteration trend to other affected granites except that both muscovite and quartz are depleted. Potash feldspar is more resistant to alteration than albite.

## B Mineralisation

### Tin

Tin mineralisation in SW England typically occurs in quartz veins associated with alteration selvedges of greisenised or tourmalinised granite. The exact temporal relationship between mineralisation and alteration is sometimes ambiguous. Mineralised quartz veins are always associated with alteration selvedges and Charoy (1979) has established that they both contain the same fluid inclusion populations. However, greisenised and tourmalinised wall rocks frequently occur without a central quartz parting containing ore minerals. This is the case in the western lobe of the St. Austell granite where unmineralised fractures are

surrounded by well developed tourmalinised granite selvedges. Quartz stringers can revein the fractures but they are unmineralised and have been formed demonstrably later. However, poor though the tin analyses were (Appendix A), they were sufficient to be able to distinguish samples of economic potential. They confirmed that a tourmaline alteration selvedge that had been observed to contain disseminated cassiterite was averaging 1.2% Sn. It has yet to be established whether this constitutes a potential ore body.

The pervasive dissemination of the tin mineralisation in the tourmaline selvedges adjacent to some of the fractures in the western lobe indicates that the physical conditions controlling the style and localisation of the mineralisation in this area differ from those pertaining during mineralisation elsewhere in SW England. High fluid pressures would have dilated the fractures and allowed the formation of a central quartz vein within which the ore minerals could have been precipitated. Instead the fluid pressures were relatively low and the fractures were under compression which caused the ore minerals to be disseminated through the alteration selvedge.

The change in physical conditions in the fluids occassioned by the extreme changes in confining pressure which took place during the formation of the breccia pipe would have been ideal for the precipitation of ore minerals had the fluids contained a significant amount of ore metals at this stage. The study of the tourmaline paragenesis (Chapter 3) shows that for some reason, by the time breccia formation took place, the boron rich fluids no longer had significant quantities of tin. Nevertheless, similar structures must represent potential targets for tin mineralisation elsewhere in SW England.

**Uranium**

The radioactive element contents for the granite samples from the western lobe are listed in Appendix A. Their uranium levels have been plotted against their U/Th ratios in Figure 39. The values plot convincingly along a uranium loss-line. This suggests that thorium is indeed immobile. The slope of the line corresponds to the thorium content of the granite which is 9.2 ppm.

The spread of values along the loss line indicates that the uranium was easily and rapidly removed during alteration. The least altered granite samples give a mean uranium vaue of 23.8 ppm. During greisenisation this has been reduced to about 5 ppm. The majority of the "fresh" biotite granite samples show similar levels. Uranium depletion is therefore an extremely sensitive indicator of alteration. This, in turn, implies that the bulk of the uranium was present in a soluble phase such as uraninite rather than diadochicaly within resistate mineral phases. This is in agreement with the conclusions of Ball and Basham (1978) rather than those of Simpson et al (1979).

Tourmalinised granite samples show an increasing depletion of uranium down to an apparent lower limit of just over 2 ppm. The clustering of points around this minimum suggests that this is the uranium level in the rock contributed by mineral phases such as zircon which are resistant to leaching or solution during the alteration processes.

The kaolinised granite samples have uranium levels of aroung 4 ppm demonstrating that uranium has also been leached from the rock during this alteration process.

Uranium has therefore been leached from the granite during every phase of hydrothermal alteration. This uranium is likely to have been redeposited in near surface, low temperature veins. Since kaolinisation is volumetrically the most important type of alteration, potential uranium mineralisation is likely to be associated with the spent fluids of this alteration phase. Uranium is enriched in the large late haemetite quartz vein in Wheal Remfry to over 50 ppm. Similar low temperature veins have been worked for uranium in the killas to the south of the St. Austell granite at South Terras mine. The bulk of the mineralised veins however would have been situated above the present level of erosion. The reworking of such deposits would make the Permian red bed sequence which surrounds the Cornubian peninsula a potential target for sedimentary type uranium mineralisation.

## 3 CONCLUSIONS

A comparison of the chemistry and normative mineralogy of the granite of the western lobe and other Sn-W bearing granites show them to have the same characteristic enrichments in $Al_2O_3$, $P_2O_5$, $K_2O$, Rb, B, Li and Cl and depletions in FeO, MgO, V, Sr, Y, Zr and Ba. They all classify as peraluminous alkali feldspar granites. Their compositions are consistent with their having been derived by anatexis of the lower crust although the Cornubian granites underwent further differentiation prior to their emplacement at their present level. Greisenisation involved little chemical or mineralogical change. The tourmalinisation alteration process in the western lobe takes a dominant role over greisenisation which is better developed in other Sn-W granites and reflects the extreme boron enrichment in the hydrothermal fluids. Tourmalinisation is associated with potentially economic disseminated tin mineralisation in some of the fracture generations. Kaolinisation processes are similar in all the Hercynian granites of north-west Europe. The granites of south west England and the western lobe of the St. Austell granite in particular are extremely enriched in uranium. The Permian red bed sequences surrounding the Cornubian peninsula are a potential location for sedimentary type uranium deposits, derived from the reworking of low temperature vein mineralisation deposited by the spent kaolinising fluids which leached the uranium from the granite.

## 4.4 MASS TRANSFER

Quantitative determinations of mass transfer during alteration is geologically and chemically desirable since real changes in composition can be established.

Gresens (1967) derived a general equation to express the relationship between the composition of altered rocks and the actual exchange of material which occurs in forming one rock from another. The equation can be expressed:

$$DXn = z\ [\ (Fv.Xn^{b}\ (p^{b}/p^{a})\ ) - Xn^{a}\ ]$$

where:

DXn = loss or gain of element n in producing rock b from rock a

Fv = Vf/Vi = ratio between final and initial volumes

$Xn^{a,b}$ = the fraction of component n in producing rocks a (parent) and b (product) respectively

$p^{a,b}$ = the specific gravities of parent and product rocks

z = initial quantity of rock. If the results are to be expressed as grams/100g rock, z=100 and Xn=weight fraction. The results may also be expressed as moles/100g or 100ml in which case z=100 and Xn=(weight fraction / formula weight) x atom proportion of element in the oxide

There are two unknowns in the equation, DXn and Fv and to achieve a unique solution one of the unknowns in the equation must be determined or assumed. The determination of volume changes based on geological criteria alone are almost impossible to achieve quantitatively. It has been common practise to assume isovolumetric alteration. It may be assumed instead that a single component has remained immobile during alteration. Fv can

then be calculated for that component since DXn=0. This volume factor can then be used to calculate DXn for the remaining components. The rare earth elements are commonly assumed to be immobile during alteration and similar assumptions have been made with regard to aluminium (Exley 1959) and oxygen (McKie 1966).

Gresens' equation is of the form $y = mx + c$ where $y$ = DXn and $x$ = Fv. A computer program was written to calculate the mass transfer values, expressed as moles/100 ml for each component for three different volume factors. The mass transfer values were calculated comparing the group means of the unaltered granite with each alteration group for each of the assumed Fv values Table 22. Component lines can be plotted using this data. The major and trace element lines for kaolinised granite have been plotted as an example, Figure 40a,b. It is likely that a certain number of components will remain immobile during any particular alteration process. If so, their component lines will cross the zero mass exchange axis (DXn=0) at approximately the same point. Clusters of crossing points on the axis are therefore indicative of a common immobility in the components concerned, Appelyard and Woolley (1979). The clustering of crossing points can be more readily discerned by plotting histograms of the log value of the crossing point (log Fv when DXn=0). This value is also calculated in the computer program and the results have been plotted in Figure 41. The mean crossing point value for the predominant cluster is taken to represent the volume factor, Gresens (1966), Appelyard and Woolley (1979). Points lying to the left of the true volume factor represent components added and those to the left, components subtracted from the rock during alteration.

**A Volume factor**

The plots of log volume factor for zero mass transfer of component elements have a similar configuration for the greisenised and mildly tourmalinised granite samples, Figure 41. In both cases a large number of elements cross the mass transfer line close to zero. The mean volume factors for greisenisation and mild tourmalinisation are 1.012 and 1.004 respectively. These alteration processes are therefore essentially isovolumetric.

During moderate and intense tourmalinisation a considerable amount of mass transfer occurs as can be seen from the large spread of component - zero mass transfer interesection points. There is no well defined conjunction of intersection values and in these two instances this method is incapable of unequivocably determining the volume factor. For the moderately tourmalinised group Si, Al and O fall near zero. These elements are often considered to be immobile and so the mean value of this group (1.010) was taken to be the volume factor. There is no hint of a cluster in the intensely tourmalinised granite components. In this case the alteration was assumed to be isovolumetric partly because the preceeding alteration stage was isovolumetric but also on the basis of field textural evidence.

A well developed clustering of components can be discerned in the kaolinised granite samples. This group is well removed from zero and has a mean value of 1.259. This implies that a 26 percent increase in volume occurred during kaolinisation. The strike-slip movement of the granite along subhorizontal planes described in Chapter 2 may be the expression of this volume increase during alteration. A 26 percent increase does, however, seem rather large given that the fabric of the granite would

appear to be perfectly preserved. The actual position of the zero mass transfer group is dependant upon the ratio of the specific gravities between the altered and unaltered granite. A reduction in the difference between the specific gravities of the kaolinised and fresh granite would also reduce the volume factor. Either the 26 percent volume increase is real or the kaolinised granite has become less dense with time. This would come about as a result of the recrystallisation of the kaolinite during the offloading of the granite. For the purpose of mass transfer calculations the volume factor of 1.259 was maintained.

Whatever the actual volume factor may be, elements such as Si, Al and O which fall outside the group of immobile elements must still have undergone mass transfer during the alteration of the granite. Thus both oxygen and aluminium have been added to the kaolinised granite in considerable quantities whilst silica has been depleted.

In conclusion the following points may be made. No single element can be assumed to be immobile. O, Si and Al are amongst those least subject to mobilisation but all are significantly affected during at least one alteration process. Oxygen contents are particularly affected during hydrolytic reactions such as kaolinisation. Alteration processes cannot be assumed to be isovolumetric. Although this is the case for the greiseniation and tourmalinisation processes it would appear that kaolinisation has been accompanied by a 26 percent volume increase. If mass transfer has been extreme and affected large numbers of elements then the volume factor cannot be defined with any certainty.

## B Mass transfer of components during alteration

Having defined the volume factor for each alteration process the component losses and gains can either be qualitatively evaluated from the component volume factor diagrams or calculated from Gresen's equation. The calculated mass transfers are listed for each type of alteration in Table 23. The final column states the threshold value below which mass losses or gains become indistinguishable from analytical error.

### Greisenisation

The chemical changes accompanying greisenisation have been quite limited. There is a definite decrease in K, H+, Rb, Cu, Li and Zr with a concomitant increase in Na, Ca and B. By comparison with mass transfers recorded fo greisenisation by other authors (Charoy 1979), these changes are very small. This confirms that greisenisation in the western lobe is not as well advanced as elsewhere. Potash feldspar is sericitised in preferance to albite, dark mica is leached and replaced by muscovite and there is new tourmaline growth.

### Tourmalinisation

During mild tourmalinisation mass transfer becomes more significant, Table 23. There are considerable gains in B and Na and losses in K, H+, Rb, Sr, Ba, Li and Zr. The alteration pattern is substantially the same as for greisenisation but more extreme.

Considerable amounts of mass transfer have accompanied the later stages of the tourmalinisation process. The patterns of the changes in composition are similar, Si, Ca, Na, K, P, Cu Rb, Zr and Ba are all lost

whilst Al, Fe, Mg H+, V, Ni, Zn, B and Li are gained.

The severe depletion of the alkali metals is a consequence of the formation of large quantities of tourmaline at the expense of both types of feldspar. Silica is the product of this alteration process (Nemec 1975). The normative data (section 4.3) suggests that the quartz content has increased, presumably through the overgrowth of quartz phenocrysts and the silicification of the groundmass. The mass transfer evidence shows that during moderate tourmalinsation some of the silica was mobilised out of altered rock. The quantity of leached silica increases with the degree of tourmalinisaion.

**Kaolinisation**

Kaolinisation is characterised by extreme changes in relatively few components, notably Si, Al, Na, Ca, K and H+ amongst the majors. The pattern for the trace elements is less readily discernable due to the effects of an earlier mild tourmalinisation. The depletion in Li and Rb and the increase in Sr and Ba however are thought to be significant, Table 23.

The enrichment of aluminium during the kaolinisation process means that it cannot be regarded as immobile even though it does not appear in the reaction equations (Charoy 1979). This confirms that some degree of congruent dissolution of the feldspars has occurred during the formation of kaolinite.

The mass transfer values for kaolinised granite given by Charoy (1979) and those recalculated from Exley (1959) using a volume factor of 1.26 are compared with these results, Table 24. There is a broad

agreement. A strong depletion in the alkalies and Rb and an increase in H+ is consistent with the kaolinisation of feldspars. The relative stability of potash feldspar with respect to plagioclase can lead to a temporary enrichment in K in completely altered granite, Table 24 (1). The decrease in lithium is believed to be a consequence of the chemical leaching of the remnant dark mica. Exley (1959) records an increase which may be due to the lithionitisation of the granite prior to kaolinisation. The behaviour of Sr and Ba is interesting and is probably caused by their absorbtion onto clay minerals (Exley 1959).

The bulk of the silica released during kaolinisation of the feldspars has been deposited in situ but all the analyses show that some has been removed from the system. This material is thought to be the source of the silica filling the late quartz veins. Similarly it has been suggested that the haematite present in these veins was derived from the alteration of the granite. The mass transfer of iron during kaolinisation of the granite in the western lobe is not significant but this is the result of the earlier tourmalinisation of the samples. If a comparison is made between the iron contents of the mildly tourmalinised and kaolinised samples then an appreciable loss is observed. A similar pattern is observed at all the other localities.

## C Conclusion

Mass transfer during greisenisation was largely insignificant, reflecting the mild but pervasive nature of this alteration process. During tourmalinisation considerable mass transfer took place. The alkalis, with the exception of Li, and alkaline earths, with the exception of Mg, were leached whilst B, Fe, Zn, Ni, V, Al, and H+ were increased. A limited number of components were intensely affected by the kaolinisation alteration process. The alkalis were depleted whilst H+ was increased. Most of the silica released during alteration was precipitated in situ. A little was carried away along with some iron to be deposited within the late quartz veins.

## 4.5 ELEMENT BEHAVIOUR DURING ALTERATION

The object of this section is to investigate the component relationships in the alteration processes. This involves the use of R-mode statistical techniques in which element associations are investigated by comparing a number of different samples. The Pearson product moment correlation coefficient is the simplest and most widely used statistic of this kind. The multivariate techniques of principal component and factor analysis will also be used.

### 1 BIVARIATE DATA ANALYSIS

#### Correlation coefficients

The simplest form of graphical bivariate analysis is the scatter plot. The correlation coefficient is a quantitative measure of the degree of covariance between the two variables. Since an extremely large number of scatter plots can be produced from relatively few variables it is usual for the correlation coefficients to be calculated first.

The Pearson product moment correlation coefficient is the most widely used. It is a parametric statistic so the data set must be approximately normally distributed. Mancey (1980) has shown that lambda transformed data generally conform to this requirement and the product moment correlation coefficient to be perfectly satisfactory when used on this type of data.

Correlation coefficients have been calculated using the lambda

transformed data shifted to make all the values positive. The reduced correlation coefficient matrices for the unaltered, greisenised, tourmalinised and kaolinised samples are depicted in Figure 42 a, b, c, d. For the unaltered samples the threshold of significance was 0.58. As the number of samples increases the critical value decreases. A minimum level of significance of 0.5 was chosen for the alteration groups to keep the number of significant correlations within reasonable limits.

**Scatter plots**

Correlation coefficients are sensitive to outlying points or fliers which may give rise to spuriously high correlations. Chapman (1976) observed that such outliers can be detected by examining the scatter plots of highly correlated variables. A correlation greater than or equal to 0.7 was chosen. The corresponding scatter plots are shown in Figure 43 a, b, c, d.

There are some good examples of spurious correlations in these plots, namely Cr-P & P-Y for unaltered granite samples and Ti-Th, Ti-Zr & Zr-Th for the kaolinised samples. When the fliers were removed and the correlations recalculated all the values fell below the level of significance. The Al-Si plot for the tourmalinised samples illustrates one of the limitations of using the Pearson (linear) correlation coefficients. In this case the relationship is clearly parabolic. Even so, the correlation coefficient is high (r=0.85). The correlation coefficients therefore seem to recognise covariance quite effectively even when the relationship is non-linear.

### Multi element groups

Reduced correlation diagrams are easier to digest than full matrices but they remain essentially two dimensional. Mutually correlated variables can be grouped together to form multi-element associations (Howarth, pers. comm., Mancey 1980). Multi element groups have been derived from the reduced correlation coefficient matrix for the different granite groups, Figure 44a, b, c, d. Elements enclosed by a loop are all positively intercorrelated. Solid lines represent other positive correlations and dashed lines negative ones. This technique is a qualitative kind of R-mode element association analysis.

## 2 MULTIVARIATE DATA ANALYSIS

Principal component and factor analysis are multivariate techniques in which the first component or factor is orientated to account for the largest possible data variance. Subsequent components are orientated so as to account for most of the residual variance. The orientation of these components are therefore determined by the variables which demonstrate the most variance. Variables which control the orientation of the component therefore correlate with it and are said to load significantly onto it. Variables that load onto the same component must therefore be correlated with eath other. The matrix of loading scores can therefore be analysed to extract mutually correlated variables.

The loading matrix can most easily be depicted as a scatter plot of one component loadng score against another. The natural clusters in the data can be identified from these plots and can be used in the geological

interpretation of the component.

In principal component analysis the successive components have to account for the maximum residual variance whilst at the same time remaining orthogonal. In data transformation this is of primary importance but in variable structure analysis it is more desirable to be able to pick out the natural clusterings of the variables. This may be done by rotating the components whilst maintaining their orthogonality. The component loading matrix for the unrotated and rotated solutions can be most satisfactorily depicted as a scatter plot of the first and second component loadings and a non-linear map of the first three component loadings. The incorporation of a larger number of components results in the obscuring of natural clusters by random variance.

In order to fulfil more realistic geological conditions in which the variables clusters may themselves be correlated, an oblique rotation of the components is necessary. This can be achieved using factor analysis. In this case however the loading matrix cannot be plotted and the variables loading significantly onto the retained factors are tabulated instead. The level of significance for the loadings was set at 0.5.

The statistical package for the social sciences (SPSS) package was used to carry out the principal component and factor analyses. Output for each alteration group is listed on Microfiche 3. Further information on Principal component and Factor analysis can be found in Kim (1975), Davis (1973), Goddard and Kirby (1976) and Mancey (1980).

**Alteration Groups**

The scatter plots and non-linear maps of the component loading matrix scores for the different alteration groups are shown in Figure 45 A, B, C. The plots which displayed the element associations most clearly were selected. The unrotated component loading matrices give the clearest element associations in the case of the greisenised and kaolinised samples. The rotated component loading matrix is more satisfactory for the tourmalinised samples. The non-linear maps are useful in identifying any spurious correlations in the scatter plots, such as the Ba-Mg association in the greisenised granites and the P-Th-Cr associations in the tourmalinised granite.

The loading matrices for the obliquely rotated factors are summarised in Table 25.

## 3 INTERPRETATION OF ELEMENT ASSOCIATIONS

The element associations derived from multi-element groups, component analysis and obliquely rotated factor analysis are in close and consistent agreement. An attempt has been made to interpret these associations in terms of the mineralogical and chemical changes which accompany the different alteration processes.

### Unaltered granite

Four element associations can be identified. The first group contains Zr, V, Ba, Ti and Al and may possibly correlate with zircon, sphene or rutile. It is difficult to imagine Ba and Al associated with zircon or rutile but all the these elements can be accommodated in sphene. However, calcium does not feature in this association of elements and the mineral sphene has not been identified in thin section. It is more likely that this group represents an association of elements contained within biotite. The second group comprising Mg, K, L.O.I., Fe and Al is typical of biotite which is the predominant ferromagnesian mineral in the granite. The third group containing Mn, Li, Cr and P is uncharacteristic but is possibly related to apatite, biotite or muscovite. If it is apatite then the lack of correlation with calcium is strange, if biotite, the negative correlation with magnesium and aluminium is difficult to explain. This leaves a lithium rich variety of muscovite as the only possible mineral host. The final group containing Na and Ca are clearly strongly interdependent due to their occurrence in plagioclase.

**Altered granite**

The element associations in the altered granite samples are summarised in Figure 46 a, b, c, together with the most likely interpretation for each association. The association of P-Mn in the greisenised granite is thought to be related to the formation of apatite. Mn has been detected in trace amounts in the probe analyses of this mineral where it is presumably substituting diadochically for Ca. However, both these elements were close to their detection limits on the ICP and their association may be spurious. The element associations during greisenisation can otherwise be related to the following mineralogical changes; the destruction of potash feldspar in preference to albite, the leaching of biotite and its replacement by muscovite and the growth of tourmaline. The element correlation groupings in the tourmalinised granite correspond to the replacement of all the rock forming minerals by tourmaline and quartz. The principal element association during kaolinisation corresponds to the destruction of feldspar and the growth of kaolinite. The second group is more difficult to interpret. The leaching and replacement of biotite is favoured since this process has been observed petrologically. The association of Ba & Sr was observed by Exley (1959) who suggested that they were both absorbed onto clay minerals. The final group is another enigmatic association which has tentatively been interpreted as reflecting the probable breakdown of apatite.

# 4 DISCUSSION

Correlation coefficients, principal component and factor analysis have been used to establish element assocciations or multi-element groups. These associations can be interpreted in terms of the probable mineralogical phase changes accompanying alteration. Of more importance is the fact that these groups can be used to select multi-element plotting variables, in order to depict alteration processes in a more scientific way. However, the presence of multi-element groups implies data redundancy. The same variance could therefore be defined using fewer variables. One variable can therefore be selected to represent each multi-element group without too much loss of variance and with a considerable saving of time and effort.

The use of component loadings displayed as scatter plots and non-linear maps has a number of advantages over the correlation coefficient method in the extraction of multi-element assocations. Once the computer programmes have been mastered it is a much faster method and it can handle very large numbers of variables that would quickly become unmanageable using the long hand technique. The plots also supply a measure of the relative degrees of correlation between the elements. The multivariate statistical methods also express the amount of data variance which has been explained by the element groups. However these advantages have to be weighed against the relative complexity of the methods, the necessity of having the necessary computer hardware and software and the inability of the scatter plots and non-linear maps to express significant negative correlations between groups. A combination of techniques is clearly most satisfactory if the necessary facilities are available.

## 4.6 MULTIVARIATE DATA REDUCTION

With the significant increase in the number of elements analysed routinely there has grown the problem of depicting the data in such a way as to make it informative yet readily understood. Scatter plots are the simplest method of plotting the data but they are extremely wasteful of analytical information. Multi-dimensional scatter plots are limited by the human imagination and the dimensional constraints of the printed page. These problems can be overcome by combining elements together to form a multi-element variable. Frequently the rationale behind the choice of such variables has been obscure and the resulting plots consequently difficult to understand.

The reduction of dimensionality in data is one of the uses of principal component and factor analysis. These techniques effectively extract the elements which are significantly involved in an alteration process and weight them onto a new, dimensionless variable. Such a variable or component or factor can therefore be imagined as a chemical fingerprint for that particular alteration process. Multivariate data is thus reduced to a single variable. This variable will explain the greatest amount of data variance due to alteration. The variable can then be used as a plotting parameter to depict degree of alteration, alteration trends and the variation in mineralogical and chemical composition taking place during alteration.

## 1 EXTRACTION OF FACTORS

### A Principal component analysis (PCA)

PCA on selected groups of data is the simplest way of extracting factors corresponding to each alteration process. PCA on a selected group will extract the principal component accounting for the greatest data variance. This should be diagnostic of the alteration process. The proper selection of data in this method is critical. The samples selected must be representative of the alteration process. Objective grouping of the samples according to their chemistries is important. Three alteration processes and six data groups were identified using non-linear mapping and are summarised in Table 26.

PCA was carried out using the SPSS package available at ULCC. Full output is listed on Microfiche 4 at the back.

### Retained components

There are two methods of determining the number of significant components to be retained. In Cattell's scree test, Figure 47, the percentage variance is plotted against the corresponding component number. The sudden change in slope is diagnostic of the change from significant to insignificant (i.e. random) variance, Mancey (1980). On the basis of this scree test 7,6 and 7 components should be retained for the greisenisation, tourmalinisation and kaolinisation alteration groups respectively. The program used an eigenvalue greater than 1.0 as its test of significance which results in 8, 6 and 8 components being retained.

**Component loadings**

The component loading matrix was used in the previous section to establish element associations. In this section the loading matrix is used to try and interpret the principal component. The principal component loadings for each alteration type are compared to their mass transfers and multi-element groups, Table 27. The signs on the component loadings represent correlations and not the sense of mass transfer of the elements during alteration.

**Principal component interpretation**

The multi-element groups have already been interpreted. All these groups load onto the principal components. The components therefore correlate with the chemical and hence mineralogical changes accompanying alteration. These changes can be summarised as follows:
Greisenisation. The destruction of potash feldspar, the leaching of biotite and the growth of tourmaline.
Tourmalinisation. The replacement of all rock forming minerals but particularly the feldspars by tourmaline and quartz.
Kaolinisation. The destruction of the feldspars and the growth of kaolinite.

**Principal components and data variance**

The percentage of total variance explained by the principal component for each alteration type is not paticularly high, 22, 38 and 30 percent for the greisenisation, tourmalinisation and kaolinisation processes respectively. The reason for this is the presence of spurious variance or "noise". Elements which do no take part in, or are unaffected

by, an alteration process increase the total data variance. This decreases the percentage variance explained by the principal component. Such elements may be legitimately discarded from the data set.

Elements not significantly involved in a particular alteration process can be identified in a number of ways. The most obvious is to look at the multi-element groupings and discard any element not significantly correlated to at least one other. Elements may also be identified directly from the component loading matrix. Elements behaving independently either load individually with a high value onto a low order component or load insignificantly onto a large number of components. Its variance explained by the retained components (communality) will be low. If these noisy elements are removed from the data then the percentage variance explained by the principal components is bound to increase significantly.

Comparison of the principal component loadings with the mass transfer and multi-element groups, Table 27, shows that the principal components have extracted most, if not all, the elements actively taking part in the alteration process. A re-evaluation of the scree test diagrams would allow the cut-offs to be repositioned after the first principal component.

In conclusion, the total amount of variance explained by the first principal component for each alteration process is relatively small but this is the result of background variance. The first component adequately explains the variance due to alteration in each case. The principal component loadings show close agreement with the mass transfer values and multi-element groupings and can be interpreted mineralogically. They are therefore considered to be real chemical analogues of the alteration

processes.

**Principal Component Scores**

Every sample is "projected" upon each of the three principal components. The values obtained on the respective components are termed the principal component scores. The calculations can be summarised as follows:

$$p_x = \sum_{i=1}^{n} F(x,i).z(x,i)$$

where:

p = principal component score

x = sample number

n = number of variables

F = factor score coefficient

z = standardised variable value

The component scores were calculated for each sample for the principal components corresponding to greisenisation, tourmalinisation and kaolinisation, using the factor score coefficients output from the PCA program, Microfiche 4, Table 28. The sense of the component score depends upon that of the factor score coefficient and has no directly interpretable meaning. The degree of greisenisation and kaolinisation increases with decreasing scores whilst increasing tourmalinisation is reflected by increasing values.

The principal component scores for each sample correspond to the degree of alteration undergone by the sample for each alteration type. Plots of the principal component scores will help to determine whether the principal components do satisfactorily explain the alteration variance. Should the components prove to be satisfacory analogues of the

alteration processes then they can be used as variables to express the degree of alteration.

The plots are discussed in the following part of this section. In summary the plots show that the principal components do satisfactorily explain the data variance caused by alteration. The residual variance left unexplained by the principal components must then be caused by random variance. The derived principal components have proven themselves to be real chemical analogues of the alteration processes.

**Discussion**

In the principal component analysis of the alteration, data groups were selected from which the principal component was extracted. There is therefore an element of circularity in the logic of comparing these results to the original groupings in order to validate them. However, the groups were selected objectively from their chemistries using non-linear mapping and the results have also been substantiated on the basis of geological reasoning. Nevertheless, in order to check on the validity of this technique, factor analysis was undertaken on all the samples simultaneously.

**B Factor analysis**

There are a number of factoring programs available in the SPSS package which differ in the way the communalities are calculated. Rao factor analysis was chosen as it estimates the communalities from the amount of variance in an element which can be accounted for by all the other elements (its total variance). All the remaining variance is considered to be random error.

An oblique solution for the analysis was selected because it was considered probable that the factors corresponding to the alteration processes would be correlated. Unfortunately the program does not allow for a free rotation to give a best fit solution. A parameter (delta) has to be specified which sets the maximum amount of correlation allowed. There is no "correct" solution and the program is rerun with different delta values until the "best" solution is obtained. The optimum solution is operator determined which highlights the subjectivity of this technique. The "best" solution in this instance was considered to be the one in which the factor loadings corresponded most closely to the alteration group means, the multi-element groupings and the principal component loadings for each alteration group.

Initial solutions were extremely difficult to interpret or rather the factors corresponding to the different alteration processes could not be readily identified. This was the result of "noise" contributed by elements playing no significant part in the alteration process but whose variance had to be accounted for by the factor solution. These elements were identified on the basis of their low communalities and discarded.

Factor analysis was carried out itteratively, discarding elements

and varying the values of delta until a satisfactory solution was reached. The output is listed on Microfiche 5. The optimum solution was achieved with a value of delta of 0.05 (a value of 0.0 allows for "a fairly oblique solution" Kim (1975)) and with Mn, P, Cr, Cu, Th, Sr, Y and Nb discarded.

**Retained factors**

The scree test indicates that five factors should be retained but the eigen values fell below 1.0 after the fourth factor and so this was the number retained. Only three alteration types have been identified and the retention of four factors is one greater than expected. The fourth factor may represent a hitherto unrecognised alteration process.

**Factor identification**

The factors were identified by comparing the elements which loaded most strongly onto them with the mass transfer values, multi-element groups and principal component loadings for the three types of alteration, Table 29. This comparison shows the first and fourth factors relate to tourmalinisation whilst the second and third factors relate to kaolinisation and greisenisation respectively.

**Factor correlations**

The factor correlation matrix, Microfiche 5, shows the tourmalinisation factors to be closely correlated with each other but uncorrelated to either the greisenisation or kaolinisation factors. There is likewise no significant correlation between greisenisation and kaolinisation factors. This implies that all three alteration processes

are chemically distinct.

### Factor scores

The factor scores were output directly from the factor analysis program and are listed on Microfiche 5. These scores were plotted in the same way as the principal component scores and gave substantially the same results.

## C Discussion

Principal component and factor analyses have been used to reduce the dimensionality of the data set to three factors corresponding specifically to the greisenisation, tourmalinisation and kaolinisation alteration processes. The principal components were extracted from selected alteration groups. The reconstitution of these groups from the component scores was used as a test for the validity of the method. There is an element of circularity in this but the method is justified on the grounds that factor analysis on all the alteration groups simultaneously gave substantially the same results.

Factor analysis thus confirmed the validity of this principal component technique. It was not so successful in accounting for the total data variance due to the operating limitations of the program and higher background levels of "noise". This noise can only be reduced by dicarding the elements which do not take part in any of the alteration processes. Elements which may be involved in only one alteration process will nevertheless load onto the other alteration factors causing random variance. This increased noise is intrinsic to the factor analysis

method. There is additionally a problem in plotting the results. The factor scores should be plotted on axes which intersect at angles corresponding to their degree of correlation. Plotting the scores on orthogonal axes results in distortion. It would be possible to map the factor scores onto orthogonal axes using principal component analysis but to do so would be to move too far away from the original data and so make the results difficult to conceptualise and therefore interpret. For these reasons the factor analysis results were less satisfactory than the principal component results. The principal component scores were therefore used as the plotting variables.

The close agreement between the results from both methods and their amenability to geological interpretation suggests that the factors extracted by both techniques are realistic chemical analogues of the alteration processes. The difficulties associated with the factor analysis technique means that it is simpler and less expensive to derive factors from principal component analyses of selected alteration groups. Group selection is therefore critical and must be carried out as objectively as possible using clustering or non-linear mapping techniques.

## 2 ALTERATION FACTORS AS PLOTTING VARIABLES

The purpose of extracting factors from alteration geochemistry is to reduce the multi-dimensional element data to a single variable. This factor may be imagined as a multivariate variable involving only those elements taking a significant part in the alteration process. The factor scores are calculated from the values of the original element contents weighted in direct proportion to the importance of the involvement of these elements in the alteration process. The factor scores for each alteration process can therefore be used as a measure of degree of alteration.

The use of factor scores overcomes the problems inherent in trying to display multivariate data. The scores can be plotted against each other to specify alteration trends or against element or mineral contents or mass transfer values to gain an idea of the behaviour of these variables during increasing alteration.

### A Scatter plots

#### Greisenisation vs Tourmalinisation

The unaltered, greisenised and mildly tourmalinised granite samples all plot parallel to the greisenisation axis with little vertical variation, Figure 48a. The moderately and intensely tourmalinised granite samples have a wide distribution parallel to the greisenisation axis but are considerably displaced away from it.

The mildly tourmalinised granite group is composed predominantly of

tourmaline banded granite samples. Its position at the end of the greisenisation trend provides chemical confirmation of the conclusions drawn from field and petrological information that the tourmaline banding was formed by fluids, the same as or similar to, those responsible for greisenisation.

The trend line corresponds to a traverse from greisenised to moderately tourmalinised granite. The traverse did not extend into unaltered rock so the first part of the trend line drawn through these samples is conjectural. The sharp change in direction of the trend line emphasises the sudden chemical change that occurs during tourmalinisation which is shown by its sharp alteration front.

The well developed scatter of tourmalinised samples parallel to the greisenisation axis implies that samples underwent varying degrees of greisenisation prior to tourmalinisation. This is good chemical evidence that fracture controlled tourmalinisation was superimposed upon the granite which was at varying stages of greisenisation.

The position of the kaolinised samples implies that they were nearly all slightly tourmalinised prior to kaolinisation. This is consistent with the mass transfer data.

**Greisenisation and Tourmalinisation vs Kaolinisation**

These plots show that the unaltered, greisenised and mildly tourmalinised samples are largely unkaolinised or only incipiently altered, Figures 48 b, c. The spread of points parallel to the greisenisation and tourmalinisation axes confirms that kaolinisation was the last alteration event to affect the rocks.

The position of the kaolinised samples shows that they underwent little greisenisation but marked tourmalinisation prior to kaolinisation. The position of the moderately and intensely tourmalinised granite samples, Figure 48c, could be real as these samples have undergone substantial kaolinisation but their position may be an artefact produced by a certain similarity in the chemistries of the two processes.

**Non-linear map**

In order to express the data for the three alteration processes simultaneously the factor scores were non-linear mapped, Figure 49.

The groups show an exceptionally good separation. The tourmaline banded granite samples in the mildly tourmalinised granite group are clustered closely with the greisenised granite samples, once again emphasising their chemical similarity. This non-linear map should be compared to that of the lambda transformed data, Figure 28. No resolution has been lost in the separation of the different groups. This confirms that the residual variance left unexplained by the principal components was lagely random. The principal components of the alteration groups therefore satisfactorily explain the significant data variance. It also shows how effectively the non-linear mapping technique was in discriminating between the different alteration groups in the original data set.

## Conclusion

1. The unaltered granite samples have suffered incipient greisenisation but are largely untourmalinised or kaolinised.
2. The mildy tourmalinised banded granite samples are the product of the same or similar fluids that give rise to greisenisation.
3. The greisenisation and tourmalinisation processes are chemically and probably temporally distinct. Samples have undergone greisenisation to differing degrees before being subject to tourmalinisation.
4. Kaolinisation is a distinct, separate and later alteration process than either of the others.

## B Ternary plots

In the ternary plot, Figure 50, the greisenisation and kaolinisation factor scores increase away from their apices whilst the tourmalinisation scores increase towards its apex. This turns out to be the best combination by trial and error as the groups are most clearly depicted. Other combinations tend to squash the points into one or other corner.

The alteration groups are well separated. The unaltered samples plot close to the greisenisation-kaolinisation tie line and equidistant between the apices. The greisenised samples plot in a zone distributed about a line from the greisenisation apex. The banded tourmaline granite samples plot adjacent to the greisenised group. The moderate and intensely tourmalinised samples affected by later fracture controlled fluids plot towards the tourmaline pole in well separated groups. The kaolinised samples fall into a discrete group away from the others.

These groups have much the same distribution as in the non-linear map, Figure 49 and can be interpreted in exactly the same way.

**C Factor scores vs CIPW norms**

Plotting alteration factor scores against mineral modal analyses should help to identify the mineral changes which accompany alteration processes. Brimhall (1979) has proposed a method by which alteration processes may be split into their reaction domains on the basis of changes in mineral content with increasing alteration. This work could be paralleled by using the factor scores as a measure of degree of alteration. Unfortunately there was insufficient time to obtain statistically reasonable numbers of modal analyses so the CIPW norms were used instead. Since both the factor scores and the norms are calculated from the chemical data there is an element of artificiality in this procedure. The principal of the method however should become apparent even if the interpretation of the plots is limited.

Only quartz, corundum, potash feldspar, plagioclase, hypersthene, ilmenite and rutile were used as they were the only norms to show significant variation. Corundum, hypersthene and possibly ilmenite and rutile do not correspond to the real mineral assemblage but reflect the saturation of Al, Mg, Fe and Ti respectively. These elements are likely to be controlled by the contents of biotite, muscovite, kaolinite and tourmaline in the fresh and altered granite.

The greisenisation, tourmalinisation and kaolinisation factor scores are plotted against the normative data in Figures 52 a, b and c. Domains

are defined by a change in the rate of change of mineral abundances with increasing alteration. The domains, mineral changes and the minerological interpretation are summarised in Table 30. During greisenisation the increase in plagioclase (albite) may be real or relative. In general, greisenisation is accompanied by relatively little mineralogical change. The changes during tourmalinisation are extreme. The leaching of quartz and the relative increase in plagioclase may be due to these extremely altered samples, adjacent to the fracture, containing some tourmaline infilling the fracture. The calculated normative mineralogical phase changes accompanying a progressively kaolinised sequence of granite samples confirms that orthoclase feldspar remains stable after plagioclase has suffered complete alteration and replacement by kaolinite. The mafic minerals are not involved in this alteration process.

Accepting the limitations imposed upon the interpretations by the use of the CIPW norms rather than modal data, these plots illustrate how useful and geologically realistic the factor scores are as measures of degree of alteration. The plots of mineral stability fields can be used to determine alteration domains in the same way that Brimhall (1979) used modal mineralogies to define alteration domains.

## D Kaolinisation factor scores vs XRD mineral norms

The mineral contents of six samples collected in a traverse from unkaolinised to completely kaolinised granite were analysed quantitavely by XRD, Appendix A. These values are plotted against the kaolinisation factor scores in Figure 52.

The plot shows the very high degree of correlation between the kaolinisation factor scores and the analysed content of kaolinite in the samples. The factor scores are clearly an excellent measure of the degree of kaolinisation. Quartz increases concomitantly with kaolinite reflecting the in situ precipitation of the silica released during this alteration process. The relative susceptibility of albite to alteration with respect to orthoclase is again clearly shown. Mica is also strongly altered as suggested from petrological and SEM observations. Tourmaline remains inert.

## E Alteration factor scores against mass transfer values

Alteration factor scores have been plotted against mass transfer values for greisenised, tourmalinised and kaolinised granite major and trace element contents, Figure 53 a, b, c, d, e & f. The alteration fields have been divided into domains on the basis of the changes in the rate with which components are added to, or removed from, the system. The interpretation of the domains is summarised in Table 31. There is a close agreement with the reaction domains determined from the CIPW norms but the mass transfer values split the fields more sensitively.

## F Conclusion

The use of alteration factor scores as plotting variables is instructive in depicting alteration trends and the changing chemistry and mineralogy of the rocks during alteration.

Greisenisation, tourmalinisation and kaolinisation are three separate stages of alteration which occurred one after the other. The mildly tourmalinised, banded granite samples are the product of the same or similar alteration fluids responsible for greisenisation.

During greisenisation Si, Na, Ca and B were added to the rock whilst K, H+, Al, Rb, Sr, Ba, Th, Cu, V and Li were leached. This was accompanied by an increase in quartz, albite and tourmaline and the leaching and muscovitisation of biotite. Alteration was generally slight.

Extreme metasomatism occurred during tourmalinisation. H+, Al, Fe, Mg, Li, Ni, V, Zr and B were all added to the rock whilst Si, K, Na, Ca, Zr, Rb, Ba, Cu, Th and Nb were removed. This corresponds to an increase in tourmaline at the expense of all the other rock forming minerals.

Mass transfer values during kaolinisation show that Si, Fe, K, Na, Ca, Rb, Cu and Li have all been leached with a concomitant increase in H+, Al, Zr and Nb. The increases in Mg and V probably reflect the effects of a prior, mild tourmalinisation. Plagioclase feldspar was attacked and almost completely altered by kaolinite before the potash feldspar began to decompose. The increase in quartz which accompanies kaolinisation shows that the majority of the silica released during alteration was precipitated in situ. Some was leached and together with the iron was precipitated in fractures to form the late quartz veins.

The mass transfer and mineralogical trends gives strong support to the conclusion that the early alteration fluids were sodium rich whilst the later kaolinising fluids were relatively highly depleted in this element. This indirectly suggests a completely different origin for the two generations of fluid.

The alteration factors have been shown to be extremely effective plotting variables. Consistent and geologically realistic results show that these factors are reasonable analogues describing the alteration processes.

## 3 DISCUSSION

This section has demonstrated the effectiveness of principal component and factor analysis in reducing the dimensionality of multi-variate data. The resultant factor contains the elements weighted in direct proportion to the importance of their involvement in the alteration process. The factor scores for each sample (the projections of the old multivariate data onto the new factor) can be used as a one dimensional measure of the degree of alteration. This is a practical advantage in the presentation of geochemical data relating to hydrothermal alteration.

Alteration factor scores can be used to illustrate how certain elements or minerals change with increasing alteration which allows the alteration process to be split into a number of chemical or mineralogical domains. Alternatively, alteration trends may be distinguished by

plotting one alteration factor against another. This latter application may lead in the future to the use of alteration factors in the classification of alteration processes.

## 4.7 CONCLUSION

The unaltered granite composing the western lobe of the St. Austell cupola is chemically homogenous and is similar to other SW England granites. The Cornubian batholith has an alkaline chemistry having high $Na_2O$ and $K_2O$ and low low CaO contents. However, it is enriched in $Al_2O_3$ and $P_2O_5$ and depleted in $Fe_2O_3$, MgO and CaO with respect to alkali granites, Wedepohl (1969). Of the trace elements, Rb, B, Li, Cl and U are enriched whilst V, Sr, Y, Zr and Ba are depleted by comparison to average low Ca granites, Turekian and Wedepohl (1961).

Using calculated CIPW norms the western lobe of the St. Austell granite and the other SW England granites plot in the alkali granite field on Streckeisen's (1975) Q-A-P ternary diagram. Despite being alkali rich they are still peraluminous since they contain normative corundum.

The western lobe of the St. Austell granite and the Hercynian granites of SW England as a whole have a chemistry and normative mineralogy very similar to other Sn-W granites from around the world. Like them, the Cornubian batholith has "S" type granite characteristics implying a lower crystal origin for the magma. Support for this hypothesis is provided by the fact that the bulk of the Cornubian granites plot close to Tuttle and Bowen's (1958) ternary minimum. The low K/Rb ratios however indicate that the granites have been differentiated from their original magmatic material. Geophysical evidence suggests the presence of a denser material at depth, presumably representing the more refractory residuum.

Having reached their current level of emplacement in the crust the granites crystallised. As the peraluminous magma differentiated the

solubility of the volatiles in the silicate melt was exceeded and an immiscible aqueous phase formed. Partitioning of the elements between the phases resulted in a silica, sodium, chlorine, tin rich fluid and a potassic and siliceous melt. The former was expelled as hydrothermal fluid and the latter was emplaced as the elvan dykes.

The passage of the fluids through the granite caused alteration of the wall rock. Uranium loss lines prove to be very sensitive indicators of alteration. Four separate kinds of alteration were identified in the field; greisenisation, tourmalinisation, kaolinisation and haematisation. The last of these however, haematisation, does not involve a gross chemical change in element content but rather represents a change in the oxidation state of iron.

Greisenisation is the most pervasive alteration type. The following elements were involved in the alteration process: Si, Ti, Na, K, H+, V, Cu, Th, Rb, Sr, Zr, B and Li. They reflect the preferential sericitisation of potash feldspar, the growth of quartz, alkali feldspar and tourmaline and the replacement of biotite. These phase changes are independent and uncorrelated. Mass transfer calculations show significant depletions in Cu, Rb and Li and the enhancement of B during this isovolumetric alteration. Greisenisation is the nearest of these alteration processes to being isochemical.

The tourmaline banded granite was formed by the same or similar fluids which were responsible for greisenisation and it is concluded that the banding is therefore largely metasomatic in origin and is not the result of the partial digestion of xenoliths of country rock.

Tourmalinisation involves a simple mineralogical phase change but

extreme metasomatism. Tourmaline replaces all the rock forming minerals (potash in preference to sodic feldspar). The silica released during alteration is predominantly deposited in situ. All the analysed elements were involved in this alteration process with the exception of Ti, Cr and Zr. Numerous elements were added to the rock in considerable quantities, Al, Fe, Mg, H+, V, Ni, Zn, B and Li whilst the following were subtracted: Ca, Na, K, P, Cu, Rb, Y, Ba and even Si when the alteration becomes extreme. It is an isovolumetric alteration process. There is an abrupt chemical change between samples which have undergone tourmalinisation to varying extents reflected macroscopically by the sharp alteration front. The breccia body matrix is chemically indistinguishable from the intensely tourmalinised granite samples adjacent to the fractures. It is concluded that metasomatism was the process which produced the tourmalinised granite and it reasonable to infer that metasomatism played a predominant role in the formation of the breccia matrix.

Kaolinisation involved two major phase changes, the kaolinisation of feldspar (sodic in preferance to potash) and the destruction of mica. These two phase changes are independent. Kaolinisation is either accompanied by a 26 per cent increase in volume or the density of the kaolinised granite has decreased subsequent to its formation. A large number of elements are involved in the alteration process. Appreciable mass transfer however has only affected a few of these. The alkalies Ca, Na, K, Rb and Li with P are depleted whilst H+, Y and Ba are enriched. Most of the silica released during alteration was precipitated in situ. A significant proportion is remobilised together with the soluble iron to be precipitated in the late quartz veins. The chemistry of the kaolinisation process is incompatible with an origin by weathering.

The three alteration types have separate alteration trends and are

chemically and temporally distinct. Tourmalinisation was preceeded by greisenisation and followed by kaolinisation. The fluids responsible for greisenisation and tourmalinisation were sodium rich. During kaolinisation the fluids were depleted in sodium but were relatively potassium rich. This confirms that greisenisation and tourmalinisation were separated from kaolinisation by a considerable chemical hiatus and suggests that the fluids were derived from different sources.

Tin mineralisation occurs in association with the tourmalinisation of the granite. Since fractures in the western lobe were under compression, no central quartz stringer developed and the ore minerals were disseminated through the tourmalinised granite of the vein selvedge. In places the tenor of tin reaches one percent Sn and thus these rocks could potentially be an economic source for the metal.

The granite contains anomolously high contents of uranium in the form of highly soluble uraninite. Uranium was leached by the hydrothermal fluids and probably redeposited at higher levels as low temperature vein mineralisation. The reworking of such deposits makes the Permian red bed sequences surrounding the granites an exploration target for sedimentary type mineralisation.

# CHAPTER 5

# THE PHYSICAL AND CHEMICAL PROPERTIES OF THE HYDROTHERMAL FLUIDS

## 5.1 INTRODUCTION

The aim of this study was to characterise the physical (temperature, salinity) and chemical properties of the hydrothermal fluids which have interacted with the granite and to determine how they evolved.

The term hydrothermal in this context is defined merely as hot water (ie. above ambient temperature), probably involved in some sort of convective system. Hydrothermal fluids can be derived from numerous sources. Magmatic, juvenile or deuteric fluids synonymously describe an aqueous phase either separating immiscibly from a differentiating melt or as the end product of such a differentation process. Groundwater is fluid present in the country rocks which is in the process of chemical and isotopic equilibration with the containing rocks. Meteoric hydrothermal fluid represents relatively freshly precipitated water which has not undergone extensive re-equilibration with the rocks with which it is in contact.

These hydrothermal fluids have been trapped in mineral phases to form fluid inclusions. The fundamental assumption in studying these inclusions is that the fluids they contain are representative of the fluid from which the host mineral was crystallising. Roedder (1967) has discussed and justified this assumption.

## 5.2 INCLUSION PETROLOGY

Petrological studies of the fluid inclusions will help to define the fluid paragenesis. Roedder (1967) has described the parameters which distinguish primary, pseudosecondary and secondary inclusions. Within a section it is possible to gain an impression of the relative ages of different fluid generations as long as they are physically distinguishable. Inclusion parageneses are complicated by the relative ages of the host mineral. For example primary inclusions in one sample may form secondaries in another, slightly older sample. In order to disentangle the fluid inclusion generations it is therefore desirable to work back from the youngest to the oldest generation of host minerals.

The different generations of quartz have been described in Chapter 2. In summary, from oldest to youngest, they are magmatic phenocrysts, miarolitic cavity quartz, quartz tourmaline vein and breccia body quartz, early vein and late vein quartz.

The quartz phenocrysts have been collected predominantly from kaolinised granite due to the ease of sampling and generally display an idiomorphic bipyramidal morphology. The miarolitic cavity quartzes are coarse and well developed and penetrate towards the centre of the cavities which is otherwise filled by massive aggregates of intersecting tourmaline needles, Plate 1a. The quartz phenocrysts which have been caught up in the breccia pipe have been overgrown by a later generation of quartz associated with the formation of the breccia matrix. They show moderately good crystal morphologies. The early quartz veins are generally quite thin and comprise milky, translucent, massive quartz, Plate 2b.

Vughs contain clear well terminated quartz crystals frequently coated in iron oxides, Plate 2a. The late quartz veins are the thickest containing massive milky white quartz which can form large stubby crystal terminations in vughs, Plate 2c. This generation is generally overgrown by cylical deposits of haematitic cryptocrystalline quartz and amethystine or smokey quartz, Plate 2d, e, f.

These quartz generations are discussed in the following order; late vein quartz, early vein quartz, phenocryst quartz, miarolitic quartz and breccia body quartz. The last two are described out of sequence in order to minimise repetition as they share a number of similar characteristics with the quartz phenocrysts.

All the samples examined were of quartz. Microscopic studies were carried out either on polished thick sections or on fragments under oil immersion (using tritolyl phosphate and silicone oil). The latter technique greatly reduced sample preparation time. A scanning electron microscope (SEM) with a multi- channel energy dispersive analyser was used for high magnification and phase identification studies.

**Late quartz veins**

These quartz crystals from the late quartz veins are strongly zoned with massive milky white quartz cores and amethystine quartz overgrowths, Plate 2f, Plate 12a.

Microscopically the reason for the milky white colour of the earlier quartz generation is the abundance of small elongate fluid inclusions (generally <20 microns). The inclusions concentrate in thin zones to outline growth surfaces but also form trails of inclusions running at

right angles to and between successive growth surfaces, Plate 12b, c. The density of these growth stringers is episodic. They may be very strongly developed between two growth zones causing a marked turbidity and more or less completely absent between the succeeding growth zones so that the quartz is optically clear. This episodicity is presumably related to rates of crystal growth.

The inclusion population of the growth zones and stringers are comprised of biphase inclusions (V+L) with small vapour bubbles, Plate 12c, clear liquid monophase inclusions which are generally small and sometimes show negative crystal shapes, Plate 12c,f and large opaque or semi-opaque inclusions, Plate 12b, c, d, 13a. At high magnifications this opacity can be seen to be the result of some fine grained transparent material coating the inner surfaces, Plate 13b. SEM work has subsequently confirmed that these inclusions are coated by a thick layer of fine loosely packed kaolinite often showing classic "booklet" textures, Plate 13a,d. Due to their opacity it is impossible to tell whether these inclusions are biphase or monophase but small vapour bubbles have been observed in some semi-opaque inclusions, Plate 12d. The coexistence of biphase and monophase inclusions within the same string suggests that they are coeval. The monophase inclusions are therefore metastable which is confirmed by the nucleation of a gas phase during freezing runs. The presence of kaolinite within these inclusions shows that kaolinisation of the granite had begun through the agency of hydrothermal fluids at temperatures above 70 $^{o}$C, Roedder (1967).

The milky white basal zone contains abundant solid inclusion other than clay minerals. Pyrite cubes occur occasionally at the base of the crystal. In reflected light they can be seen to be in the process of being altered to haematite. Balls of radiating birefringent accicular

needles are distributed throughout this zone and can locally show marked abundance, Plate 12e. An attempt was made to identify this mineral. A ball was extracted and its optical properties established. The radiating fibres are colourless, they have first order birefringence, parallel extinction and are length fast. They have a moderate to high relief and by using immersion oils a refractive index of 1.602 was determined. A qualitiative microprobe analysis showed it to be composed predominantly of aluminium and silicon with appreciable quantities of Na, P, K, Ca and possibly S. This combination of elements suggests that more than one phase is present which may explain why the X-ray diffraction photographs could not be correlated to any particular mineral. The growth zones can be marked by the accumulation of abundant grains of a transparent colourless mineral, having a similar relief to the host mineral. These grains are believed to be small parasitic quartz crystals which grew as a result of changes in the crystallisation conditions, probably due to temporary interruptions in the supply of silica.

The basal zone terminates against a layer of fine grained haematite and quartz. It is opaque in thin section but towards the edges its orangey colour may be seen. Coarse orange coloured "grains" are present and are probably monophase inclusions with a coating of fine haematite. This zone clearly reflects a period of haematite enrichment in the fluids.

The haematite layer can be overgrown by numerous small parasitic quartz crystals which are subsequently swamped by the next, usually amethystine, generation of quartz. There are fewer inclusions in this zone and those present are concentrated in the growth zones so the quartz is generally clear. Monophase inclusions predominate and may be either clear or opaque or red due to the fine coatings of haematite. It is the

latter which gives this generation of quartz its amethystine colour. The rare two phase inclusions which occur have very small vapour bubbles, Plate 13f. The presence of these biphase inclusions shows that temperatures were still above 70 °C.

The amethystine quartz zone can be terminated by a strong growth zone of orange haematitic monophase inclusions, black spheruliths of haematite and quartz crystals. The quartz of the outer zone is clear in cross section due to the paucity of inclusions. There are a few monophase inclusions, some with haematite coatings concentrated on the growth zones. These zones are also remarkable for the stiking development of haematite "mushrooms" which have a peculiar and distinctive morphology, Plate 13e. In reflected light they can be seen to be comprised of bladed lathes of haematite. These can become quite dense and are responsible for the apparent smokey colour of this generation of quartz when viewed from above.

**Early quartz veins**

The early quartz veins frequently contain vughs having well terminated clear quartz crystals.

The basal zones of these crystals have been most heavily fractured and contain the greatest number of inclusions. The primary inclusions are predominantly biphase (with a degree of filling generally just below 0.9) and occasionally show good negative crystal shapes, Plate 14a. Radiating accicular "balls" of a birefringent mineral probably the same as those described earlier are quite common, Plate 14b. It varies considerably in abundance from a few strands, Plate 14c, to straggly nest-like aggregates, Plate 14d, which may even fill the whole inclusion. Very

rarely an inclusion may contain a small clear phase with a somewhat elongate trapezoidal habit, Plate 14e, f. This phase is birefringent and is possibly either $FeCl_2$ or (less likely) halite formed as a result of necking or some unidentified solid phase trapped in the fluid inclusion. Secondary strings of two phase, Plate 14g, and clear liquid monophase inclusions cut through this basal zone. Away from this zone the inclusions are scarcer and exclusively biphase. The acicular mineral phase occurs increasingly frequently. Very occasionally, small rounded phases having very low relief may be present, Plate 14h. This phase remains unidentified. Growth zones are not well developed but are occasionally highlighted by a concentration of quartz grains or tiny parasitic crystals.

This generation of quartz can occasionally be coated by a thin covering of quartz containing a late quartz vein assemblage of inclusions and/or haematite. Crystals exhibiting this characteristic would appear to span the transition between early and late quartz generations which would seem to form part of a continuum.

**Quartz phenocrysts**

The quartz phenocrysts contain an abundance of inclusions which makes them appear translucent. The inclusions are predominantly very small (<20 microns) which compounds the difficulties in studying them.

The fluid inclusions are predominantly high salinity, that is, they contain at least one daughter phase of halite, Plate 16f. These inclusions are particularly common around the edge of the phenocrysts. The number of daughter phases and possibly also captured phases increase in number towards the centre of the phenocrysts, Plate 16 a, b, e, Plate

17 a, b, c, d. These have been identified by SEM as sylvite, mixed halides of Na and K, iron chloride, silicates such as muscovite and sillimanite and oxides such as haematite and rutile, Plate 15 e, f. Very rarely, melt inclusions can be found containing no liquid but packed with solid phases and containing a gas bubble.

Most of the inclusion types are associated with boiling assemblage inclusions in pseudosecondary fractures. Boiling assemblages are taken to be an association of inclusions having highly variable degrees of filling down to zero (monophase gas inclusions). Intermittant boiling was therefore occurring during the crystallisation of the quartz phenocrysts.

The phenocrysts are cut by secondary biphase and monophase inclusions. The quartz overgrowths on the phenocrysts derived from kaolinised granite are not easily observed due to their tendency to grow in optical continuity. Their apparently limited development is probably the result of the orientation in which the sections were cut. Nevertheless, where present they contain a late quartz vein inclusion assemblage.

**Miarolitic cavity quartz**

These quartz samples are well developed crystals which penetrated a miarolitic cavity infilled by felted black tourmaline needles, Plate 1a. The distribution of the inclusions within the crystals was complicated by the multiple episodes of fracturing which had occurred and the lack of well defined growth zones.

The bases of each of the crystals contain an assemblage of high salinity inclusions (inclusions containing at least one daughter phase).

They are cut by annealed fractures containing pseudosecondary inclusions with single large halite daughter phases. Boiling assemblage inclusions are common, sometimes containing a daughter phase as well as a low degree of filling, Plate 17c. Boiling assemblage inclusions are also coeval with secondary strings of two phase inclusions which commonly contain a small greenish birefringent mineral with parallel extinction and high relief.

Large, strongly pleochioic tourmaline crystals are trapped around the edge of the quartz crystal, Plate 17f. Opaques, presumably rutile, are quite common.

Further away from the basal zone, three phase inclusions with a single halite daughter phase and biphase inclusions become increasingly important. Boiling assemblage inclusions are still common. The tourmaline needles overgrow original, trapped phases, Plate 17f,g, and penetrate the quartz more deeply until the crystal is intersected by them.

**Breccia body quartz**

The clear overgrowth on a quartz phenocryst from the siliceous breccia contains a sparce assemblage of two-phase inclusions but is shot through with tourmaline needls, Plate 17 h. The contact between phenocryst and overgrowth is irregular with small brecciated quartz and tourmaline fragments, Plate 17h.

Small quartz crystals from a vugh in a silicified killas fragment have a more interesting inclusion population. The basal zone is intersected by abundant tourmaline needles. The coexisting primary fluid phase is moderately saline as the inclusions contain a single small halite cube. Secondary two phase inclusions occur in association with

boiling assemblage inclusions. Biphase inclusions predominate towards the top of the crystals whilst monophase inclusions appear during the last phase of quartz growth.

**Conclusion**

The quartz phenocrysts have a fluid inclusion distribution which suggests a gradual decrease in fluid salinity as quartz growth proceeded. Boiling occurred intermittently particularly towards the later stages.

Boiling continued and was common during the formation of the mioralitic cavities. The fluids at this stage were also passing from being saturated (containing daughter phases) to being undersaturated (two phase inclusions).

By the time of breccia body formation the fluids were moderately saline and boiled only intermittently.

**Phase ratios**

Phase ratios (degrees of filling) can be used to calculate the homogenisation temperature and salinity of fluid inclusions. The way in which phase ratios are calculated is summarised in Appendix C.

The histograms of the calculated degrees of filling and salinities for the saturated inclusions (inclusions containing at least one daughter phase) are plotted in Figures 54 & 55. Graphical population splitting techniques resolve this multimodal distribution into three populations, Table 32. The scatter plot of calculated salinity against degree of filling, Figure 56, shows that the degree of filling remained more or

less constant at 0.88 whilst the salinities decreased from 44 to 35 to 28 wt. percent. Using the data of Lemmlein and Klevtsov (1961), the homogenisation temperatures for these three groups were found to be about 500°C (extrapolating the data), 380°C and 270°C. The highest temperature corresponds to the intrusion temperature determined from contact metamorphic mineralogy. As these dense magmatic fluids cooled, they became less saline.

Homogenisation temperatures cannot be defined from the degree of filling of two phase inclusions using Lemmlein and Klevtsov's (1961) data as the salinities remain unknown. The multimodal distribution of degrees of filling calculated for two phase inclusions, Figure 57, contains four or possibly five populations. Low salinity fluid activity would seem to have been similarly episodic. Estimates of the homogenisation temperature can be obtained for these inclusion populations by selecting a range of likely salinities, Table 33. The estimates are not too disparate for the degrees of filling observed. They can be summarised as follows: a high temperature group (>300°C), a moderate temperature group ( 260°C) and two low temperature groups at 200 and 130°C. From the number of observations the cooler populations would appear to have been most active and lasted longest. In general, the lower temperature, two phase inclusions predominate in the later quartz veins.

## 5.3 TEMPERATURE AND SALINITY OF THE HYDROTHERMAL FLUIDS

The P-V-T-X properties of fluids in the system $H_2O$-NaCl are becoming increasingly better established and consequently the behaviour of the fluids before and after trapping are better understood. Weisbrod et al (1976) give an excellent summary of the post-entrapment characteristics of fluids of variable composition and density, summarised in Figure 58.

A fluid is trapped to form an inclusion at Tt. As the inclusion cools it moves along an isochore (a line of equal density). When it intersects the vapour saturation curve at Th the fluid separates into two phases. Separation of the phases continues down to room temperature along the vapour saturation curve. If the process is reversed by heating the inclusion, the phases will rehomogenise at Th, paths 1 and 2. Th is always less than Tt unless trapping occurred on the vapour saturation (boiling) curve.

For high salinity inclusions the process is complicated by the presence of the halite phase. Such an inclusion, on heating, will progress up the halite-liquid-vapour curve. If the halite dissolves first, the inclusion will then follow the vapour saturation curve and homogenise in the normal way, path 4. If the fluid homogenises first, the inclusion will leave the halite liquid vapour curve and intersect the halite saturation curve at which point (Ts) the halite phase will dissolve, path 3. In the case of high salinity inclusions, Th gives a closer estimate of Tt if the halite phase dissolved first. Ts gives a closer estimate if homogenisation occurs first.

There are a number of conditions which have to be satisfied for the trapped fluids to behave in the fashion described. The fluid has to be

homogenous at the time of trapping, there must have been no change in the volume of the cavity or post-entrapment modification of the inclusion. Roedder and Bodnar (1980) have discussed these assumptions in more detail. In general, any inclusion can be used that shows no sign of necking or evidence of boiling.

In high salinity inclusions the salinity of the fluid can always be directly obtained from the solution temperatures of the halite phase using Keevil's (1942) data. For low salinity inclusions the salinities can be determined from the depression of the freezing point of water caused by the addition of salts. Since NaCl is usually the predominant salt, its depression curve is used. Other salts are likely to be present which will affect the freezing point (Tf) and so salinities are always expressed as equivalent weight percent NaCl.

The heating and freezing work was carried out on a Linkam TH600 instrument whose calibration is described in Appendix D. Runs were carried out on polished plates and on quartz fragments using the immersion oils tritolyl phosphate for freezing runs and silicone oil for heating runs.

Roedder (1967) and other workers after him have emphasised the necessity of discriminating between primary, pseudosecondary and secondary inclusions in geothermometric studies. This is practically impossible on the size of samples used for these runs. In any case the status of a fluid phase in a sample relates to the paragenesis of the samples rather than of the fluids. A more statistical approach is preferred. Each fluid generation can be distinguished on the basis of its temperature and salinity. If sufficiently large numbers of observations are accumulated then the homogenisation temperature and salinity

distributions can be split into their component populations. These populations should then represent the difference inclusion generations. The graphical probability plot population splitting technique of Sinclair (1974) was used.

**A Homogenisation temperatures**

Homogenisation runs were carried out on inclusions from quartz phenocrysts, quartz overgrowths on phenocrysts in the breccia pipe, quartz crystals from vughs in tourmaline veins, early clear sparry quartz and late quartz associated with amethystine overgrowths and haematite.

Since boiling assemblage inclusions was formed from inhomogeneous fluids at the time of their entrapment they were not used. All the inclusions studied homogenised to the liquid phase with the disappearance of the vapour bubble. The homogenisation temperature results, Figure 59, include the halite dissolution temperatures (Ts) if they were higher than the homogenisation temperatures (Th). The distribution has been split into four populations summarised in Table 34. The results compare closely to the temperatures estimated from the phase ratio calculations for the two phase inclusions. This also helps to confirm the validity of this technique.

Each sample type shows an extremely wide range of populations, Figure 60. The populations are unevenly distributed within each sample. The phenocrysts contain predominantly the highest temperature populations ($>300^{o}C$). The inclusions from quartz in the tourmaline veins, breccia matrix and the early quartz, all have similar, predominantly intermediate

(240-290 °C) homogenisation temperatures with a wide range in values. The late quartz inclusion population is largely low temperature (130-240 °C).

**B Salinities**

Salinities were determined on the same samples. The high salinity inclusions were found directly from the solution temperature of the halite phase using the saturated solution curve of Keevil (1942). The solution temperature of sylvite, if present, was not recorded precisely but it was generally between 50 and 150 °C and always less than the solution temperature of halite. Assuming an average sylvite solution temperature of 100 °C and halite solution temperature of 300 °C an average composition for the fluid can be calculated from the $H_2O$-NaCl-KCl diagram, Roedder (1971). The overall composition is 50% total salts composed of 20% KCl and 30% NaCl respectively (K/Na ratio = 0.33). This is in general agreement with the observations of Charoy (1979) and the analysed fluid compositions.

Values for the low salinity inclusions were determined by cryometry. Generally, first melting occurred below the NaCl-$H_2O$ eutectic, occassionally as low as about -30 °C but generally around -25 °C, indicating the presence of a small amount of other salts. This was particularly the case with the earlier, higher salinity inclusions. No hydrate melting above zero was observed implying a low $CO_2$ content in the inclusions. This was subsequently confirmed by crushing tests in anhydrous glycerine.

The salinity distribution shown in Figure 61 has been split into its component populations, Table 34. The high salinity populations compare

favourably with those derived from the phase ratio calculations of salinities, Figure 55, Table 32. The high salinity data from these two sources have therefore been combined, Figure 62 to define the final high salinity populations.

The distribution of the salinity populations in the different types of quartz sample, Figure 63, illustrate the marked contrast between the high salinity of the quartz phenocrysts with the predominantly intermediate salinities of the fluids responsible for the tourmaline veins and breccia body and the low salinities of the quartz veins. The occassional high salinity inclusion in the last category is most probably the result of necking down.

**C Homogenisation temperature - salinity data**

Scatter plots of homogenisation temperature against salinity can be most informative, Figure 64. Some data is inevitably lost as it is sometimes not possible to obtain both types of data on the same inclusion for some reason or another, consequently the number of points which have been plotted are only a fraction of the total number of the homogenisation temperature and salinity determinations made. Either liquid-vapour homogenisation temperatures or halite dissolution temperatures were plotted for the high salinity inclusions, whichever was the higher. The data has been interpreted in terms of three, separate trends, Figure 65.

### Magmatic trend

This trend line is extremely well developed and shows there to have been a continuum from high temperature, high salinity inclusions down to low temperature moderate salinity inclusions. Taking the distribution of the inclusions within the quartz phenocrysts into account, this trend line can only be interpreted as representing the progressive evolution of the deuteric fluids which were periodically separating from a differentiating melt. The deuteric fluids became progressively less saline and cooler with time. There is no evidence that the high salinity inclusions are the result of concentration due to the boiling of lower salinity fluids.

Miarolitic cavity formation, tourmaline banding and the onset of magmatic autometasomatism (greisenisation) would presmably coincide with the end of this magmatic fluid trend.

### Tourmalinisation trend

This trend lies subparallel to the first. It does not start at the same extreme high salinities but it continues further down towards the low temperature and salinity field. This trend must correspond to a second and separate pulse of fluid. Bearing in mind the brittle nature of the quartz-tourmaline fractures and the proposed mode of formation of the breccia body, this fluid phase was presumably derived by the separation of an aqueous phase from the differentiating silicate melt at depth. Cooling and dilution was possibly the result of the admixture of groundwaters beginning to encroach upon granite from the surrounding country rocks. This may also account for the greater spread of data around this trend. Since cassiterite is closely associated with

tourmalinisation, the fluids responsible for mineralisation must fall upon this trend. One may perhaps anticipate temperatures of 250-300°C and salinities of between 15 and 20 wt. percent. equiv. NaCl. These values broadly agree with those of the Sn-W mineralising fluids elsewhere in SW England (Bray 1980) although the salinities are slightly higher than those determined by Charoy (1979) for Sn-W mineralisation associated with greisenisation.

**Quartz vein trend**

This is the third and final fluid phase. Temperatures began by being high, in excess of 350°C or so but the salinities were always low, never exceeding 15 wt. percent equiv. NaCl. The trend is distinguished by having a marked thermal decay but only a slight concomitant fall in salinity. This fluid is clearly of different origin from the earlier, predominantly deuteric fluids. It is presumably composed mainly of groundwater fluids, ultimately of meteoric origin. Since the inclusions in the late quartz veins are coated in kaolinite, the kaolinisation process would appear to have been initiated towards the lower temperature end of this trend.

D Discussion

The presence of at least three separate fluid trends implies that the fluids were derived from different sources by different processes. Field evidence supports this contention.

The fluids trapped during the growth of the quartz phenocrysts and responsible for the formation of the miarolitic cavities, tourmaline banding and autometasomatic alteration (greisenisation) were of deuteric origin. They represent the periodic separation of an immiscible aqueous phase from a differentiating silicate melt. (Burnham 1979). However, Burnham (1979) goes on to demonstrate that such an aqueous phase could only contain a maximum of 5 wt. percent equiv. NaCl. The early fluid phases have salinities far in excess of this value. Boiling is the only feasible mechanism by which the salinities of the fluids could be concentrated. However, there is no evidence to suggest that the early high salinity inclusions were formed in this manner. On the contrary, the fluid trend and inclusion distribution in the quartz phenocrysts shows these fluids to have become progressively cooler and less saline with time. There are no discontinuities which would mark a period of boiling. Boiling assemblage inclusions do occur but are generally associated with the later, less saline inclusions and this reflects the intersection of the path of the evolving fluid with the vapour saturation curve in the PTX diagram of Sourirajan & Kennedy (1962).

Tourmalinisation associated with fractures, tin mineralisation and brecciation are similarly believed to have been formed from fluids of substantially deuteric origin. In this instance the fluids separated from a saturated melt beneath the consolidated outer skin and caused hydraulic fracturing, brecciation, alteration and mineralisation as they passed up

through the granite. Heat exchange between the fluid and the granite is likely to be counterbalanced by the predominantly exothermic wall rock reactions, Hemley & Jones (1964). Thermal decay and dilution of the fluids is the result of either the exhaustion of the source and/or the mixing of the fluids with progressively larger quantities of groundwaters encroaching upon the granite from the surrounding country rocks.

The final fluid trend has very different characteristics. These fluids are most likely to be groundwaters, probably without any deuteric contribution. Kaolinisation accompanied the passage of the lowest temperature fluids through the granite.

Bray (1980) has proposed an alternative model for the generation of the kaolinite deposits. He postulated that an early, high temperature (400-450 $^{o}$C), moderately saline fluid boiled to produce a low density, low salinity vapour which penetrated the granite and caused extensive kaolinisation. Although boiling assemblages are common in the St. Austell granite, there is no significant correlation, as Bray has suggested, between kaolinised granite and the abundance of vapour rich inclusions, Alderton & Rankin (in prep.).

Each new fluid pulse is considerably hotter than the last phase of the preceeding one. This is easily understood in the case of the tourmalinisation trend since these fluids were derived from a saturating magma at depth. The high temperatures of the early quartz vein fluids have to be accounted for by the deep circulation, in this case, of groundwaters combined with a significant heat input from radiogenic sources. The pre-existing fractures channelled these deeply circulated fluids back up through the top of the granite.

## E Pressure correction

All the temperatures quoted so far have been homogenisation or dissolution temperatures. No correction has been applied for the pressure at which the inclusions were trapped. The estimation of pressure corrections is subject to a large number of restrictions and limitations, Roedder and Bodnar (1980). Given the fluid inclusion assemblages present in the western lobe, the following two methods can be used.

### Geobaromety based upon the vapour pressure of the solutions

If the fluid inclusions are not part of a boiling assemblage then the confining pressure at the time of trapping exceeded the vapour pressure of the solutions at those temperatures. Such fluid inclusions do not provide any evidence concerning how much the trapping pressure may have exceeded the vapour pressure but the vapour pressure gives a minimum estimate of the pressure at trapping. The vapour pressures for each fluid phase have been calculated from the data of Haas (1971), Table 35.

It is usual when converting vapour pressures to depths to quote both hydrostatic and lithostatic depth equivalents to give a maximum and minimum estimate, Table 35. Roedder and Bodnar (1980) have pointed out that these values represent the limits of a range of possible conditions. The calculated depths for both these conditions however, are too small to be geologically reasonable.

## Geobarometry based on inclusions containing daughter phases

If the solution temperature (Ts) of the halite phase exceeds the homogenisation phase then Ts provides a minimum trapping temperature and a minimum pressure estimate from the halite-liquid-vapour curve, Figure 58, point H3.

In the overwhelming majority of high salinity inclusions, the solution temperature exceeded the vapour-liquid homogenisation temperature. The homogenisation temperatures average 260 $^{o}$C whilst the mean solution temperature is 300 $^{o}$C. This corresponds to a solution of 38 wt. percent equiv. NaCl from Keevil's (1942) solubility curve. The corresponding minimum pressure is 60 bars using the halite-liquid-vapour curve of Sourirajan & Kennedy (1962). The maximum, lithostatic depth equivalent is 230 m which is again geologically unreasonable.

Roedder and Bodnar (1980) suggest a better method of determining minimum pressure corrections. As the first step in this method, the density of the inclusion at 300 $^{o}$C, at the moment of dissolution of the halite phase, was calculated to be 1.109 g/cm$^{3}$. Extrapolation of the data of Urusova (1975) enables this isochore to be plotted which gives a maximum trapping pressure of 450 bars, Figure 66. This is equivalent to a lithostatic depth of about 1700 m. This is a geologically more realistic value and compares favourably with depth estimates made by others in SW England. Jackson and Rankin (1976) on the basis of the metamorphic mineral assemblage in the Land's End aureole reported by Floyd (1971) suggested a depth range of between 2 and 4 km. Jackson and Alderton (1974) estimated a depth of 1.5 km on the basis of the contact metamorphic garnet mineralogy in the greenstones from the same locality.

## Temperature correction

Assuming a trapping depth of two km, the temperature corrections which should be applied to the inclusion populations have been calculated, Table 36. The maximum temperature correction is 50°C which is relatively insignificant. If this correction is applied to the highest recorded solution temperature, a value of 500°C is obtained which coincides with the predicted value on the basis of the contact metamorphic mineralogy.

## 5.4 FLUID COMPOSITIONS

The principal cationic species in the fluids are likely to be Na, K and Ca. In fluids interacting with the granite, the ratios of these three elements are principally determined by equilibration with the feldspars. Studying the composition of the fluids should supply useful information on the state of equilibrium of the feldspars and how it changed with time.

Samples of magmatic phenocrysts, early quartz and late quartz were selected for analysis as they contained minimal amounts of solid impurities. Samples were prepared, crushed and leached using a modified version of Poty et al's (1974) method; details and results are provided in Appendix A. The most important difference between the methods was that the quartz samples were leached with an acidified solution and not with deionised water. The method is not absolutely quantitative as the volume of the inclusion fluid released upon crushing remains unknown. Atomic element ratios and the charge balance ratio can be calculated instead, Table 46, Appendix A. It is immediately noticeable that the change balance ratio is very erratic. This is probably due to the length of time which separated the cation analyses from those of the anions and the effects of evaporation. The difference between the anion and cation contents cannot be used to estimate acidity (H+), a dubious enough practice at the best of times, Eastoe (1978).

The principal cationic element ratios are illustrated in Figure 67. Other data derived from the literature are plotted for comparison. The plot clearly illustrates how the fluid compositions have changed markedly with time. The aqueous phases separating from the silicate melt are the earliest fluids and are sodium rich. This concurs with the theoretical

work of Pichavant (1981) on the partitioning of ionic species between an immiscible aqueous phase and coexisting silicate melt. The sodic enrichment continues in the fluids responsible for greisenisation, mineralisation and presumably tourmalinisation. This in itself suggests that these fluids were of a juvenile origin.

The compositional trend of the later fluids responsible for kaolinisation shows a sharp change towards potash and then calcic enrichment. The reason for this sudden change in fluid composition is believed to be the result of the increasing involvement of groundwaters in the hydrothermal system. The reason why groundwaters should be depleted in sodium and enriched in potassium and calcium is not clear. The extremely high calcium levels in the late stage, kaolinising fluids in the western lobe was at first believed to be the result of the acid leaching of the crushed samples. The presence of calcium sulphate was indicated in the late quartz vein samples on the SEM. However, the composition of the kaolinising fluids at Ploemeur (Charoy 1975) confirms this trend. Carbonate horizons in the country rock are a potential source for the calcium.

There is no systematic change in the anionic composition of the fluids. Chlorine is always the predominant species.

The existence of extensive wall rock alteration shows that the fluids were in profound disequilibrium with the granite through which they were passing. This is reflected predominantly in the alteration of the feldspars. Lagache and Weisbrod (1977) have shown that the K/Na ratios in a fluid are fixed for solutions that are buffered by the two alkali feldspars. The ratios are dependent solely upon temperature, the effects of pressure are minimal unless the fluid is in the vapour state.

The K/Na ratios for such buffered fluids can therefore be used as a geothermometer. The mean K/Na ratio for the magmatic fluid is 0.29 which corresponds to a temperature of 650 °C, Figure 68. The average observed solution temperature is close to 300 °C. The difference between these two temperaures implies a pressure correction of 3kb or 11.5 km lithostatic depth. As this represents half the thickness of the continental crust it is considered to be an overestimation of the depth of granite emplacement. This may be the result of a predominance of very high salinity inclusions corresponding to the earliest phase of quartz growth or contamination by solid inclusions of feldspar in the quartz or the modification of the original fluid compositions by secondary inclusions. The later fluids will, particularly, raise the K/Na ratio even though their overall salinities are very low. The mean of the three most sodic values gives a K/Na ratio of 0.18, equivalent to 470 °C corresponding to a depth of 6 km. This is more reasonable whilst the temperature of intrusion is in closer agreement with other estimates.

The use of the K/Na ratios as a geothermometer is fraught with difficulties, not the least of which is the fact that other solute species affect the slope of the equilibrium curve. Boron has been shown to be particularly important in this respect (Pichavant, pers. comm.).

If the fluids remain in equilibrium with the two feldspars during cooling then the K/Na ratios may be expected to fall with decreasing temperature. The opposite trend is observed in agreement with the results of other workers (Eastoe 1978, Charoy 1979). This reflects an increasing disequilibrium between fluid and granite. The K/Na ratios for different fluid generations are plotted against their temperatures, Figure 68. Data from similar areas in SW England and Brittany are included for comparison.

During greisenisation and Sn-W mineralisation the fluids are enriched in sodium. This would be expected if the fluids separated from a saturated silicate melt, Pichavant (1981). Potash feldspar is consequently preferentially destabilised. This corresponds to the phase of tourmalinisation and mineralisation in the western lobe. The fluids subsequently became depleted in sodium and the K/Na trend is reversed. This change is believed to be the result of the increasing involvement of groundwater in the hydrothermal system. The fluids recross the equilibrium line (field of formation of the quartz-fluorite-sulphide veins without visible alteration?) before moving into the albite destabilisation field. At high temperatures this may result in potash metasomatism but at low temperatures it results in kaolinisation. The passage of the fluids through this field is very well developed in SW England which is expressed in the intensity of the kaolinitic alteration in this region.

**Conclusion**

The granite crystallised at approximately 500 $^{o}$C at a maximum depth of about 6 km. The first fluids to evolve from the granite were enriched in sodium and caused greisenisation, tourmalinisation and mineralisation. An increasing contribution from fluids of groundwater origin changed the compositional trend of the fluids to one of increasing potassic and calcic content. The later fluids moved firmly into the field of preferential albite decomposition and remained there for the duration of the hydrothermal convective system.

## 5.5 FLUID - ROCK RATIOS

Structural and mass transfer data can be used in conjunction with the fluid inclusion results to calculate the amount of fluid which passed through the granite at different stages.

### A Structural parameters

Using the fracture widths calculated earlier, the fracture density and their vertical persistence, the volume of granite occupied by the fractures can be calculated. It is assumed that the fractures are filled by quartz. The volume of water required to flow through the fractures to precipitate the quartz can be found from the decrease in solubility of the quartz in response to a geothermal gradient. The mathematical models of Norton (1978) and the field evidence of Grindley and Browne (1976) and Steiner (1968) from the New Zealand hydrothermal systems would suggest that a geothermal gradient of 100 $^{o}$C/km is reasonable. The solubility data for quartz was derived from Holland and Malinin (1979) for hydrostatic (100 bars/km) and lithostatic (300 bars/km) regimes. Quartz solubilities are given as g/1000g solution so the densities of the phases have to be taken into account when converting to volumes. Combining the volume ratios of vein quartz to granite and vein quartz to hydrothermal fluid (water) gives the fluid-rock volume ratio.

The fluid rock volume ratios have been calculated for the tourmaline veins, the early quartz and the late quartz veins, Table 37. These values are rough approximations but the pattern emerges clearly. The volumes of water in the hydrothermal system were increasing markedly with time and not decreasing as might be expected. The highest fluid/rock ratio is

coincident with the quartz veins associated with kaolinisation.

B Mass transfer values

The mass transfer values can be used to calculate the weight of alkalies (expressed as chlorides) which have been leached from a particular alteration facies. As the salinities of the fluids responsible for alteration have been found from freezing studies, the minimum weight of water necessary to leach the alkalies can be found. Knowing the density of the fluid its volume can be derived. The fluid-rock ratio can be expressed in two ways, either as the volume ratio of fluid to total granite or as the ratio of fluid volume to altered granite volume, Table 38. The total volume of altered rock has been calculated for the tourmalinised and kaolinised granite using the following models. The tourmaline alteration selvedges are 15 cm wide and occur every 10 m, giving a volume ratio of altered to total granite of $15 \times 10^{-3}$. The kaolinised granite body is approximated by a cone of 800 m in diameter and 500 m in depth. The ratio of altered rock volume to total volume is $84 \times 10^{-3}$.

Although the results of this calculation differ by an order of magnitude from those derived using the structured parameters, the pattern and interpretation remains the same. These values should be more accurate than the earlier ones since there is better geological control and precision on the input variables. The nature of the assumption that the leached alkalies are the total contribution to the salinity of the fluid means that these values are a minimum estimate. The "true" fluid to rock ratios lie somewhere between these two values.

## C Conclusion

During tourmalinisation the fluid to rock ratio lay between .01 and 0.9. During kaolinisation the value increased dramatically to lie between 1.0 and 50. Consequently there was between 50 and 100 times more water flowing through the granite during kaolinisation than during tourmalinisation. This is believed to be compatible with the idea that a large hydrothermal convective system was in existence during kaolinisation. The source of such large quantities of water could only be the groundwaters from the surrounding country rock.

## 5.6 CONCLUSIONS

The physical and chemical characteristics of the fluids which have passed through the granite of the western lobe shows that there have been at least three separate generations of fluid affecting the rock.

The earliest phase was a magmatic fluid which separated immiscibly from the differentiating, hydrous, peraluminous magma. This phase is found in the inclusion population in the quartz phenocrysts. Both the distribution of the inclusions in the phenocrysts and the thermometric data shows that there was a progressive and steady decrease in temperature and salinity of these fluids from 450 °C, 50 wt.% (in equiv. wt.% NaCl) down to 220 °C, 30 wt.%. The average value is 300 °C, 40 wt.%. Although boiling assemblages are quite common the high salinity inclusions are unlikely to have been formed through such a mechanism since boiling would have had to be unreasonably extreme. The fluids are sodium-rich which is to be expected since sodium (and chlorine) partition strongly from a silicate melt into a coexisting immiscible aqueous phase, Pichavant (1981) and others. The later fluids underwent more frequent boiling as the path of the decreasingly saline fluids intersected the vapour saturation curve in the PTX diagram. These fluids were separating from the differentiating interstitial residual melt of the unconsolidated granite and became concentrated to form the miarolitic cavities and the tourmaline banding and to cause autometasomatic alteration ("greisenisation"). If, despite this, the fluids are assumed to have been buffered by the alkali feldspars then the fluid compositions imply an emplacement temperature of 500 °C. This value is in agreement with the highest temperatures calculated from phase ratios and the contact metamorphic mineralogy. The difference between this calculated value and the mean of the observed homogenisation values gives, as a maximum

estimate, a depth of emplacement of 6 km.

The next fluid phase was responsible for tourmalinisation and Sn mineralisation and is defined by a completely separate temperature-salinity trend. It began by having marginally higher temperatures and salinities than the last fluids of the previous magmatic trend. The fluids are predominantly undersaturated and show little evidence of boiling. They are even more sodic than the magmatic fluids, causing destabilisation and alteration of the potash feldspars. The high boron levels led to tourmalinisation rather than the ubiquitous greisenisation observed elsewhere in SW England. The sodic composition of the fluid and the low fluid/rock ratio supports the hypothesis that this fluid was predominantly of deuteric origin. It formed as an immiscible aqueous phase, which separated from the saturated melt differentiating beneath the crystalline outer carapace of the granite. Hydraulic fracturing and brecciation allowed the fluids to escape causing alteration and mineralisation. Mineralising fluids are believed to have had temperatures between 250 and 300 $^{o}$C and salinities of 15 to 20 wt %. The decreasing temperature and salinity of these evolving fluids may be due to their dilution by small quantities of groundwater or may simply reflect the exhaustion of the crystallising source region in the magma.

The final fluid phase was responsible for the formation of the quartz veins. Its composition and temperature-salinity trend shows it to be a fluid of very different character to the earlier phases. The abrupt change in composition towards potash and calcium enrichment and their predominantly low salinities are compatible with these fluids having their origin as groundwater. Their initial high temperatures (over 300 $^{o}$C) are attributed to deep circulation and a contribution of heat from radiogenic sources. The fluids cooled significantly but their salinities

decreased only slightly from 10 to 2 wt.%. The later inclusions of lowest temperature and salinity (less than 150 °C, 2wt.%) were responsible for late quartz vein formation. The abundance of inclusions with internal coatings of kaolinite in these veins indicates that these fluids were also responsible for kaolinisation. The K/Na ratios of these fluids show albite to be unstable with respect to potash feldspar, a characteristic of the kaolinisation process. The fluid to rock ratios show this alteration to be accompanied by a significant increase in the volume of fluid. The quantities required could only be derived from the country rocks. These fluids must therefore be groundwaters or meteoric hydrothermal waters.

The earliest fluid phase was hydrothermal in so far as it was hot and aqueous but it contained no element of convective flow. It is better described as a late magmatic fluid. The first hydrothermal fluids caused tourmalinisation, mineralisation and brecciation and were derived from a differentiating melt at depth. The later fluids responsible for quartz vein formation and kaolinisation had a very different origin as they were derived from the surrounding country rocks. They became involved due to the longevity of the hydrothermal convective cell assocciated with the intrusion of the granite.

# CHAPTER 6

# THE ORIGIN OF THE FLUIDS RESPONSIBLE FOR MINERALISATION AND ALTERATION

## 6.1 INTRODUCTION

Theories concerning ore genesis and the origin of the mineralising fluids are well established. The principals of lateral secretion were established in the mid 16th century by Agricola who considered vein deposits to be derived from meteoric waters seeping down into the earth from the surface. They become heated and resurgent, dissolving metals at depth and redepositing them in fissures at higher, cooler levels. In the early to mid 19th century there developed a school of thought favouring an origin through aqueous fluids associated particularly with acid magmatism. Thus the two main theories concerning the origin of the fluids responsible for vein mineralisation and alteration had already been established by the middle of the 19th century. Since then, one or other theory is temporarily in ascendence depending upon contemporary geological fashion.

The modern version of the plutonistic theory is embodied in the ideas of Burnham (1979). These ideas are strongly influenced by familiarity with the porphyry copper deposits of western North America. His model explains ore genesis through differentiation processes in acid magmas. Ore and alteration fluids are necessarily of direct magmatic origin.

Papers by Taylor (1974, 1977, 1979) have been strongly instrumental in bringing about a revival of the lateral secretion hypothesis. Stable isotope data suggests that certain high level acid plutons have acted as heat engines causing considerable quantities of meteoric water to flow through them. Norton and his co-workers (Norton & Knapp 1977, Norton &

Knight 1977, Villas & Norton 1977, Norton 1978) quantified the heat transport phenomena and created a set of computer models to describe the effect of intruding a hot granite magma into the upper crust. They concluded that the generation of hydrothermal convective systems was almost inevitable and that the majority of the fluids which passed through the pluton were not meteoric surface waters or juvenile but groundwaters derived from the country rocks. These groundwaters were then assumed to play the major role in metal transport, hydrothermal alteration and ore formation.

Both of these hypotheses are now discussed with reference to the evidence from south west England and, in particular, that from the western lobe of the St. Austell granite. A satisfactory model has to be in accord with the following features: the geological evidence provided by texture, fabric and mineralogy of the granite, the possible life span of the hydrothermal convective cell, the permeability of the rocks, the calculated fluid to rock ratios, the possible sources of the ore metals and the physical and chemical properties of the fluids.

Direct evidence regarding the origin of the fluids involved in mineralisation and alteration processes can be obtained from stable isotope compositions, Taylor (1974). The stable isotope data from SW England is re-evaluated in the light of opposing hypotheses.

Since kaolinite currently forms the most economically important mineral resource in the Cornubian region, the main lines of evidence concerning the origin of the fluids responsible for the formation of this alteration mineral are summarised and discussed.

## 6.2 EVOLUTION OF AQUEOUS PHASES FROM TIN-BEARING GRANITE MAGMAS

Tin deposits are genetically linked to granite rocks having similar chemistries and mineralogies and origins. The mechanism responsible for magma genesis can either be related to subduction processes, deep seated strike-slip faulting or mantle plumes (Halls, 1981). Whichever the mechanism, the parental magmas are all derived from the lower crust by anatexis. The resulting intrusives are compositionally restricted and are invariably granites (ss), quartz monzonites or adamellites. Biotite is the dominant mafic mineral but the rocks quite frequently contain two micas. The granites are chemically specialised and are enriched in volatiles such as Cl, F & B and a range of elements including Li, Rb, Be, U, Sn and W.

The magmas "bore" their way towards the surface under the effects of telluric pressure by a process of assimilation and crystallisation. The latent heat of crystallisation maintains the magma temperature, Burnham (1979). The marginal parts of the magma are cooled against the country rocks and some crystallisation occurs. Since the $H_2O$ content is directly proportioned to the degree of crystallinity there is a marked concentration of water around the edges and in the upper portions of the magma. The molten, comparatively dry magmatic core is encased by an $H_2O$ rich, partially crystalline rim. When the magma's progress is finally arrested the partially crystallised contact zone may show evidence of mineral abrasion and microbrecciation. As crystallisation in the outer zone continues the residual, interstitial silicate melt will become increasingly enriched in volatiles which will act by depressing the solidus, Pichavant (1981), Manning (1979), Bankwitz (1974), Charoy (1979). Magmatic crystallisation will be prolonged. The interstitial melt will no longer be in equilibrium with the previously crystallised

silicates and reactions will take place to produce a mineral assemblage stable under the new conditions.

Silicate melts of peraluminous composition show a miscibility gap with the $H_2O$ rich phase. Krauskopf (1967), Tuttle and Bowen (1958), Goranson (1938). The high volatile content has only a marginal effect upon the solubility of $H_2O$ in the melt. Pichavant (1981), Manning (1979). When the solubility of water in the interstitial melt is exceeded an immiscible aqueous phase will separate. Elements partition between the two phases depending upon their chemistries. Chalcophile incompatibles (Zn, Pb, Cu, Mo, Bi, Sn etc.) will partition towards the aqueous phase whilst the lithophile elements (Nb, Th, REE, Zr, Hf, Be etc.) remain in the silicate phase, Bowden and Jones (1974). Chlorine and boron partition strongly in favour of the fluid phase, the molality ratio between fluid and melt being 13.2 (at 750 $^{o}$C, 2kb) and 3.0 respectively (Kilinc and Burnham 1972, Pichavant 1981). Fluorine, by contrast, remains in the melt (molality ratio of 0.12 at 650 $^{o}$C, 2kb, Hards 1976). The aqueous phase is additionally enriched in alkalies with respect to aluminium and sodium with respect to potassium. The residual melt in equilibrium with the fluid phase is therefore depleted in Na, Cl, B and becomes potassic and hyperaluminous, Pichavant (1981).

Hyperaluminosity accentuates the immiscibility of $H_2O$ in the residual melt. Depending upon the original volatile content of the melt, this process of fluid saturation and separation may occur repeatedly. The exsolved fluids will react with the crystallised mineral assemblage and cause autometasomatic alteration.

The Cornubian granites display a number of the characteristics predicted from the model. They have "S" type characteristics, indicative

of a lower crustal origin, Chappell and White (1974) and in the western lobe the predominant Fe-Ti-O accessory is rutile, implying even lower oxygen fugacities and shallower derivation than the ilmenite granites, Takahashi et al (1980). The marginal microbrecciation accompanying the intrusion of the magma has been identified by Exley and Stone (1964).

The SW England granites are volatile rich and there is abundant evidence to show that magmatic crystallisation in the outer envelope was a protracted series of events. This allowed time for diffusion to occur and for exchange reactions to go to completion. This is shown by the pure end member composition of the feldspars, the growth of the potash feldspar megacrysts and the generally coarse nature of the groundmass. Late magmatic mineral readjustments largely take the form of the alteration and epitaxial overgrowth of biotite and the growth of tourmaline, Charoy (1979), Exley and Stone (1964).

The periodic separation of an immiscible aqueous phase from the residual interstitial melt is recorded by the fluid inclusion content of the quartz phenocrysts. These fluids became progressively less saline and cooler with time. They remained homogeneous as long as the pressure and temperature conditions were above the vapour saturation curve. With decreasing salinities the path of the fluids intersected this curve and boiling occurred even though there may not have been a dramatic change in ambient conditions.

Once a fluid phase has separated from the silicate melt, the character of crystallisation may change abruptly, Krauskopf (1967). The aqueous fraction allows space for coarse crystals to grow. This process may therefore explain the development of the "pegmatitic" patches. The accumulation of small pockets of fluid would have given rise to the

quartz and tourmaline-rich cavities. Slight differential movement in the partially crystallised envelope causing concentration of these fluids in narrow zones would account for the formation of the tourmaline banding.

The autometasomatic alteration caused by these sodic, siliceous, boron rich aqueous fluids would be expected to involve albitisation, silicification, tourmalinisation and muscovitisation. This is just what has been observed in the western lobe where it has been collectively termed greisenisation.

The granite fabric and observed textures either correspond very closely to the features predicted from Burnham's (1979) model or can be interpreted within its terms. This gives considerable support to his hypothesis regarding the way in which hydrous granite magmas have crystallised and suggests that the Cornubian granites followed this path of behaviour during crystallisation.

After the consolidation of the outer granite envelopes the partially crystalline, $H_2O$ saturated layer lay at deeper levels. The water-rich carapace acts as a barrier to the migration of volatiles inwards by diffusion or fluid flow, Burnham (1979). It is unlikely that water from the surrounding country rocks could mix with this primary magmatic fluid.

The separation of the aqueous phase from the saturated melt causes crystallisation. Heat is released due to the latent heats of crystallisation whilst mechanical energy is produced as a result of the accompanying increase in volume. This change in volume cannot generally be accommodated by progressive plastic deformation and expansion owing to the effects of the conflicting lithostatic pressure and the rigidity of the granite carapace and wall rocks. Consequently the internal pressure

beneath the carapace increases as cooling and crystallisation proceed. A certain finite compression of the contiguous magma system occurs but this is insufficient to absorb these internal over pressures generated through crystallisation. Internal pressures as high as 5 kb could theoretically be generated under certain conditions (Burnham 1979), but normally the rocks comprising the brittle outer shell would fail long before pressures of this magnitude were reached.

Within the apical zone of the intrusion failure would occur by fracturing when the internal overpressure (Pin) exceeded the minimal principal compressive stress (S3) and the tensile strength of the rocks (T). The density and orientation of the fractures depends upon the interplay between these three forces and the orientation of the regional stress field. The escape of the hydrous fluids into the apical zone temporarily relieves Pin but the fluid overpressures are progressively rebuilt as a consequence of the further crystallisation of the magma. Critical conditions may again be achieved and fracturing renewed. The apical portion of the intrusion may thus be subject to a series of fluid pulses.

The passage of the fluids along the fractures causes alteration. The composition of the fluids will change with time, becoming less saline, Holland (1972). At some stage conditions will be optimised for the scavenging of ore metals into the aqueous phase and mineralisation will occur.

As crystallisation proceeds the $H_2O$ saturated layer moves to greater depths. Since the amount of volatiles left in the magma decreases and the confining pressures increase with time, the conditions for critical failure are likely to occur less and less frequently with time. Failure,

if it occurs, is likely to be increasingly violent, causing brecciation.

Most of the fractures formed by hydraulic fracturing are too narrow to be intruded by highly viscous magma. Under some conditions the fractures may be widened or the magma overpressure dramatically increased by new magma arrivals and the silicate melt may be intruded into the overlying rocks.

The post crystallisation history of the western lobe of the St. Austell granite broadly fits this scheme. Hydraulic fracturing is accompanied by tourmalinisation and disseminated mineralisation. The composition of the fluids are as expected for an immiscible aqueous phase separating from a differentiating magma at depth. Several phases of fracturing and alteration are recognised, culminating in the development of a large breccia body. This would seem to terminate this phase of hydrous fluid activity but the breccia bodies are cut by quartz porphyry dykes (elvans). The chemistry of the elvan magma is compatible with an origin as the potassic, hyperaluminous, under saturated silicate residue left after repeated volatile exsolution. The close association between mineralisation and dyke formation has already been pointed out not only in SW England by Hosking (1969) but also in the Erzgebirge by Tischendorf et al (1974) and in the Transbaikalian region of the USSR by Ontoev (1974).

If alteration, mineralisation and elvan formation are all attributable to the differentiation processes of volatile rich magmas then they should all have similar ages. The ages of the granite, alteration, mineralisation and elvans have been determined isotopically using K/Ar and Rb/Sr methods. Bray (1980) concluded that all the ages were the same given the resolution of the age dating techniques.

## 6.3 GRANITE INTRUSIVES AND HYDROTHERMAL SYSTEMS

Recent work by Norton (1978) and his co-workers has succeeded in quantifying the hydrodynamic processes which accompany the thermal anomaly created by the intrusion of an igneous body into the crust. Norton et al have simulated the nature of the heat and mass transport processes by a set of partial differential equations and approximate numerical solutions of these equations.

A number of assumptions and simplifications are inherent in the derivation of these equations. The hot body is assumed to be instantaneously emplaced in the crust. The heat emitted by the body is taken to be the product of its mass, specific heat capacity and temperature. The effects of other heat generative processes such as radiogenic decay, heats of crystallisation, hydrolysis and mixing reactions are ignored. The fluids are assumed to be both composed of pure water, even though fluid inclusion evidence shows that this is not normally the case, and always above their vapour saturation curve.

The equations were used to compute models to describe the general features of heat and mass transport in the vicinity of an intrusive igneous body within the upper 10 km of the earth's crust. Heat transport phenomena around plutons depends on the heat content of the body, rock permeabilities and fluid properties. The temperature of intrusion of the body is taken to be 920 $^{o}$C. This is rather high for granitic rocks but compensates for the other heat sources which are ignored. Although some fluid circulation is an inevitable consequence of the emplacement of magmas in the crust, convection only becomes the predominant heat transport process when host rock permeabilities exceed $10^{-14}$ cm$^{2}$. The frequency of hydrothermal convection suggests that this parameter is

commonly exceeded but there is very little satisfactory data on the bulk rock permeabilities of rocks surrounding igneous intrusions. Heat transport efficiency is greatest in single phase fluids. For pure $H_2O$ it reaches a maximum between 350 and 550 $^{o}C$. In NaCl- $H_2O$ systems this temperature range is displaced towards higher temperatures and pressures.

The geometries of fluid circulation and isotherms are directly affected by variations in the distribution of permeable zones in the host rock, and the permeability, size, width and level of emplacement of the pluton. Fluid circulation cells are located in the host rocks adjacent to and above the side contacts of the pluton, the relatively low permeability pluton acting as a barrier to fluid flow. Zones of higher permeability in the host rock can take the form of more permeable stratigraphic horizons or fracture zones. In the former case, fluid circulation (represented by streamlines) is concentrated in the more permeable units whilst in the latter case, the streamlines are confined to the fracture zone. Fracturing within the pluton, modelled by sudden increases in permeability in the apical portions, allows fluid circulation to pass through the upper part of the intrusion. The vertical extent of the pluton exposed to permeable host rocks determines the lateral extent of fluid circulation. The ratio of the convective cell widths to the effective pluton heights remains approximately the same. The deeper the level of emplacement the larger the circulation cells become. Changes in the width of the pluton affect the geometry rather than the size of the circulating cells. Wide plutons have primary circulation cells located over and above the contacts as before but secondary cells also form over the middle of the pluton. With time these secondary cells predominate.

Cooling rates in average (2 km wide) intrusives average 0.4

expressed as a fraction of the initial anomaly after $2 \times 10^5$ years. Larger plutons of batholithic size cool much more slowly, to 0.8 in the same period. Increasing the permeability of the pluton through fracturing has a dramatic effect on the fluid flux and thermal decay. The increased permeability increases both horizontal and vertical fluxes which disperses the thermal energy more quickly so that temperatures in the pluton fall more rapidly. The ratio of the final to the initial thermal anomaly falls to 0.2 over the same time span.

Large quantities of fluid are redistributed through convective flow as a direct consequence of the emplacement of plutons in a permeable environment. Fluid pathlines define the distance and path along which a given fluid packet moves during the thermal event. Pathlines are dependant upon rock permeability and proximity of the path origin to the thermal anomaly. Fluids initially in the upper portions of the plutons (of juvenile origin) are transported several kilometers into the overlying host rock over a $2 \times 10^5$ year period. Fluids initially in the host rocks several kilometers away from the pluton convect towards and into the pluton. The pathlines trend parallel to the side contacts of low permeability plutons but flow into those with larger permeabilities. Pathline movement is restricted to zones of higher permeability when present.

The quantities of fluid which circulate through the pluton environment where convection is the predominant cooling process is quite high. Average fluid to rock mass ratios are 0.4. This represents the mass of rock contacted by a circulating mass of fluid and differs from the usual definition of this ratio which estimates the integrated effect of all the fluid packets circulating through an arbitrary rock mass.

The computer model which most closely parallels the geological conditions of the western lobe of the St. Austell granite is a pluton 2.7 km wide and 4.5 km deep, intruded at a temperature of 920 $^{o}$C to a depth of 5 km into stratified country rock of variable permeability. The pluton was given an initial permeability of $10^{-17}$ cm$^2$ (effectively zero). A fluid cell is initiated above and beside each contact and very little flow passes through the pluton. Fracturing was simulated in this model by arbitrarily increasing the permeability to $10^{-11}$ cm$^2$ in the upper 0.9 km of the pluton instantaneously when the temperature fell to 860 $^{o}$C (time= 1250 years). A second fracturing event was modelled to follow at time = 5000 years to further increase the permeability to $10^{-10}$ cm$^2$ in the uppermost 0.9 km and to $10^{-12}$ cm$^2$ in the lower 1.8 km. The result of the fracturing was to allow fluid to penetrate deeper into the pluton and for the fluid flux to increase markedly.

Fluid pathlines were examined for fluids originating several kilometers away, laterally and above the pluton in relatively permeable rocks; fluids adjacent to the pluton near the boundary between low and high permeability rocks and fluids near the pluton contact, deep in the system. In the first two instances the fluids move into the pluton and then out again into the overlying host rocks. The deep seated fluids moved into the pluton and remained there.

Fluid source lines are the locus of source points of all fluid packets whose pathlines intersect a fixed position of interest in the system. Source lines for fluids which flow through the top of the pluton indicate that during the initial 5 to 15,000 years the fluid sources occurred entirely within the pluton. After $10^{4}$ years the fluids were derived from surrounding host rocks. Source regions for the pluton can be defined from sets of source lines. The source area for this model pluton

extends over 50 $km^2$. After 2 x $10^5$ years of cooling only 2 percent of the fluid was derived from sources within the pluton, whilst the remainder originated from the surrounding host rock. The majority of that fluid was derived from the permeable host rock horizon.

The temperature of the pluton and the amount of fluid flowing through various points of interest in the pluton was also calculated. Temperature variation with time at the base of the pluton follows a path of simple conduction. The upper portions of the pluton affected by fracturing show very rapid cooling rates. Relatively low temperatures then persist for the remainder of the cooling period. The mass flux curves for the permeable portions of the pluton show that 60 percent of the fluid which circulates through these regions does so in approximately $10^5$ yeas elapsed time.

The following conclusions can be drawn from the work of Norton and others:

- The proportion of groundwater to magmatically derived water in the apical portions of a fractured pluton is very high
- This implies that the metals in the ore deposits within and proximal to the pluton must have been largely derived from the enclosing rocks.
- The amount of water flowing through the top of the pluton reaches its peak very early and subsequently attenuates. Mass flux ratios would be expected to decrease with time.
- The mineralogical and chemical nature of the pluton should be immaterial to the genesis of the ore deposits.
- In host rocks of varying permeability the bulk of the groundwater will be derived from the most permeable horizons.
- The temperature in the top of the fractured plutons falls rapidly but subsequently stabilises at a low temperature.

These conclusions are discussed in relation to mineralisation and wall rock alteration in SW England and specifically to the western lobe of the St. Austell granite.

**Magmatic/Groundwater ratios**

The parameters which control this ratio are the heat source, the permeabilities of the host rock and pluton and its depth of emplacement.

The greater the heat source the larger the source region and the higher the ratio becomes. The model temperature of emplacement of 920 $^{o}$C is far too high. Data from the western lobe suggests an intrusion temperature of about 500 $^{o}$C. However, this overestimation of temperature makes up for all the parameters not accounted for in the model such as the heats of crystallisation, reaction and radiogenic decay, the larger size of the St. Austell pluton and the intrustion of dykes and sills (although rather few). Whether these effects exactly balance out is impossible to determine and there remains a great deal of uncertainty in evaluating their relative influence.

Permeabilities of $10^{-14}$ $cm^{2}$ can be envisaged as a density of one fracture per meter having an aperture of about two microns. This is likely to have been exceeded in the killas and rock permeabilities would have been enhanced by the presence of calcic horizons within the predominantly semi-pelitic rocks. The pluton itself is likely to have been more permeable than this and may well have had similar permeabilities to those modelled.

The shallower the depth of emplacement the smaller the fluid cell

becomes. The depth of emplacement of the western lobe has been estimated to be between 2 and 6 kilometers which agrees well with the model.

The modelled conditions agree broadly with those observed and the predicted magmatic/groundwater ratio should therefore give a reasonable estimate of the fluids which flowed through the western lobe.

**Origin of the metals**

There has been considerable debate on the origin of the ore forming metals in SW England. The granite contains anomalously high contents of a wide range of elements and this has been variously attributed to the anatexis of a rich source rock (Hosking 1964) or the palingenesis of enriched rocks during ascent (Floyd 1972), Ahmad (1977). There is a concensus of opinion that B, Sn (& W) and Cu in the ore deposits originated from the granite. Alderton and Jackson (1974) and Bawden (1962) have shown that the country rocks have been enriched with respect to these elements emanating from the granite.

The evidence regarding the origin of the metals would seem to preclude the possibility that the ore forming fluids were of groundwater origin.

**Mass flux ratios**

The model predicts that mass fluxes should decrease with time and that hydrothermal convection should effectively cease ater $2 \times 10^5$ years. The mass flux calculations carried out on the altered granite in the western lobe show that, by contrast, mass fluxes were increasing with time from a minimum during tourmalinisation (and mineralisation) to a

maximum during kaolinisation.

It is possible to account for this difference by increasing the time during which hydrothermal convection occurred. The production of heat through radiogenic decay is a mechanism by which the life of hydrothermal convective systems can be increased. Fehn, Cathles and Holland (1978) report that the Conway granite contains 15 ppm U, 57 ppm Th, 4 percent K and has a heat flow between 1.95 and 2.21 hfu. They conclude that "within a few million years the mass of water tranported by steady state convection through such a radioactive pluton can equal the mass of water which can convect through them during initial cooling from magmatic temperatures". They incidentally go on to say that the rate of fluid convection is probably sufficient to develop a hydrothermal ore deposit containing 10,000 tons of uranium in the same period.

By comparison to the Conway granite, the western lobe of the St. Austell granite contains 23.8 ppm U, 2.3 ppm The and 4 percent K giving a heat flow of between 3.1 and 7.4 hfu. From his work on heat flow in SW England, Francis (1980) concludes that "... (there) emerges a fairly constant heat flow for the entire batholith ... the hot springs within the deep mine systems ... (and) mineralised belts, are driven by ... the high observed heat flow. Such a mechanism may well be an important factor in the mineralisation and alteration of the granites. It seems more than likely that the high heat flow is the result of the high radiogenic contribution coupled with refraction of heat flow due to the high thermal conductivity of the granite". Hydrothermal convection in the western lobe clearly persisted for far longer than $2 \times 10^5$ years and possibly for over two million years, driven by the high levels of radiogenic heat produced by the granite. The high uranium content in the granite also suggests that a high tonnage of uranium could have been deposited in veins above

the present level of erosion.

**Rock type**

Certain types of mineralisation appear to be rock type specific, White et al(1978). This correlation between mineralisation and granite types runs counter to the implications embodied in the concepts of Norton and his co-workers, McDonald (1979). In reply, Norton et al (1979) suggests that the chemistry of the plutons (particularly water content) controls their permeability through fracturing processes, Burnham (1979), which is in turn crucial to the formation of ore deposits. This argument is unsatisfactory because it still fails to explain why different types of mineralisation are associated with certain rock types such as the correlation between Sn-W deposits and peraluminous alkali granites.

**Host rocks**

The country rocks comprise a sequence of metapelites intercalated with calcareous horizons. The calcium rich compositions of the later fluids supports the hypothesis that the groundwaters would be derived predominantly from the more permeable horizons of the country rock.

**Cooling rates**

The temperature in the fractured pluton is modelled to fall rapidly and then stabilise at around 200 $^{o}$C. The pluton temperature can only be measured indirectly in terms of the temperature of the fluids passing through it and these two values are probably not the same. Nevertheless, the highest frequency of homogenisation temperatures is just over 200 $^{o}$C.

**Synthesis**

The models generated by Norton and his co-workers should not be treated too precisely. Some variables have been ignored which may have significant and unpredictable effects. These models provide a very useful picture but one which needs modification in the light of the system under investigation. It is now up to the geologists to provide more accurate values for the critical parameters so that better analogues can be generated.

The overall effects of the extraneous heat sources in the St. Austell granite should be to increase the size of the fluid circulation cells in relation to those predicted from the model. This may be patrtially offset by the closer proximity of the western lobe to the surface.

The origin of the elements and the composition of the fluids indicates that Sn-W mineralisation and tourmalinisation were produced by fluids of predominantly magmatic origin. This is not incompatible with Norton's (1978) model since the source of the fluids passing through the top of the pluton in the first 5-15,000 years is from within the pluton itself. If this corresponds to the period in which mineralisation effectively occurred then its age should coinside with that of the granite. This is untestable until the resolution of age dating methods improves considerably. The relatively brief life-span of these magmatic fluids could be increased by delaying the onset of fracturing in the upper portion of the pluton. The fracturing periods in the model were arbitrarily set. Fractures formed in the outer shell of a consolidating pluton through fluid overpressures (Burnham 1979) will be vertical to subvertical, at right angles to the direction of flow of the

groundwaters. This anisotropy in the permeability is not accounted for in the model. Its effect would be to delay the onset of groundwater influx making a predominantly magmatic origin for the mineralising and tourmalinising fluids more likely.

The last, spectacularly developed kaolinisation process is believed to be related to the later stages of the hydrothermal convective system. The composition of the fluids suggests that by this stage they were exclusively of a groundwater origin as Norton's (1978) model implies.

This multiphase model for the origin of the fluids responsible for tourmalinisation, mineralisation and kaolinisation is substantiated by the fluid inclusion data and the fluid compositions. The fluids, although of different origins, form the early and later part of the same hydrothermal convective system. The increase in longevity of effective hydrothermal circulation to over two million years is the result of the anomalous radioactive element content in the granite causing high radiogenic heat flow.

## 6.4 STABLE ISOTOPE EVIDENCE

The origin of fluids can be interpreted according to their stable isotope compositions since waters from different environments have characteristic isotopic signatures, Taylor (1974).

Stable isotope work has been undertaken in SW England by Sheppard (1977), Bray (1980) and Jackson et al (in press). Fresh granite, greisen selvedges, quartz veins, kaolinised granite and country rocks have been analysed using individaul minerals such as biotite, sericite, muscovite, quartz, kaolinite or whole rock samples. Present day meteoric waters have also been analysed, Sheppard (1977).

### A Magmatic fluid

The Cornubian granite field is enriched in oxygen with respect to the normal granite field, Sheppard (1977). This is an "S" type granite characteristic, Chappell & White (1974), indicating that the magma could have been derived from the anatexis of argillaceous rich metasediments. Alternatively the magma may have undergone extensive isotopic re-equilibration with, or assimilated large quantities of, the same rock type. The isotopic composition of the granites may have been additionally modified by the considerable late magmatic mineralogical re-equilibration.

The isotopic composition of the Cornubian magmatic field is taken to be the same as the isotopic composition of the rock forming minerals since "at magmatic temperatures there will be virtually no fractionation between water and the granite minerals", Bray (1980). The isotopic

fractionation curves given in Taylor (1974) show this to be true for temperatures of the order of 800 to 900 °C. There is evidence that in the western lobe of the St. Austell granite the aqueous fluids were separating from the residual magmatic differentiate at temperatures of about 500 °C. Muscovite, rather than biotite, seems to be the stable mica phase under these conditions. Using the isotopic fractionation curve in Taylor (1974), the fractionation between muscovite and an aqueous fluid at this temperature is +1 and +20 per mil for oxygen and hydrogen respectively, Figure 69.

**B Greisenising fluids**

The greisenisation field is defined by the composition of the alteration micas muscovite and sericite. The analyses of Sheppard (1977) fall into a group adjacent to the Cornubian granite field, Figure 69. They are marginally enriched in oxygen and deuterium with respect to the granite. Bray (1980) obtained much lower hydrogen isotope values but did not determine their oxygen isotopic compositions which were assumed.

The isotopic composition of hydrothermal waters in equilibrium with the alteration micas of Sheppard (1977) can be calculated using the hydrogen isotope fractionation curves of Taylor (1974) and Friedman & O'Neil (1977), Figure 69. This data was originally interpreted by Sheppard (1977) as evidence for a meteoric hydrothermal origin for the fluids responsible for greisenisation. The composition of the original meteoric waters indicates a derivation at low latitudes. This is consistent with the palaeogeographic evidence which places the Cornish peninsula within 10° of the equator during the Palaeozoic when the

granite was intruded (Jackson et al, 1982). Sheppard proposed that the meteoric fluids underwent oxygen exchange with the granites and surrounding sediments prior to being involved in greisenisation.

Bray (1980) has pointed out that since hydrothermal meteoric waters cannot have a hydrogen isotopic content greater than zero, the temperature at which greisenisation occurred must have exceeded 400 $^{o}$C. This temperature is rather too high from fluid inclusion evidence, Charoy & Weisbrod (1975), Charoy (1975), Jackson et al (1977), Jackson et al (1982).

The numerical modelling of hydrothermal systems resulting from the intrusion of igneous bodies into the upper crust (Norton (1978) and co-workers) indicates that the first fluids to enter the granite are groundwaters which will be in isotopic equilibrium with their host rocks. The country rocks in SW England are pelites which have been regionally metamorphosed to the greenschist facies. The isotopic compositional field for the country rock in Figure 69 is plotted from Sheppard's (1977) data but only contains three points and is therefore not well defined. Both the numerical models and active geothermal areas indicate that an average geothermal gradient of 100 $^{o}$C/km is reasonable. The field of "metamorphic" water (i.e. groundwater) in equilibrium with chlorite at 200 $^{o}$C (assuming a depth of intrustion of about 2 km) was calculated using the fractionation curves in Taylor (1974), Figure 69.

The isotopic composition of the greisenising fluids between 300 and 400 $^{o}$C partially coincides with the best estimate of the groundwater composition. The alteration micas with lower deuterium values plot between the groundwater and magmatic water fields. If Bray's (1980) muscovite analyses had an oxygen isotopic value of +15 per mil then they

would plot firmly within the magmatic water field. Alternatively the greisenisation fluid field is elongated towards the meteoric water line indicating that some mixing with meteoric water may have occurred.

The stable isotope data for the alteration micas can be interpreted in a number of ways. An origin from more than one source would seem likely. The earliest fluids were magmatic. Mixing with groundwaters occurred later and this fluid became predominant. Finally some dilution with meteoric or hydrothermal meteoric water may have taken place.

**C Kaolinising fluids**

The bulk of the kaolinite samples analysed by Sheppard (1977) and Bray (1980) plot close to the kaolinite weathering line but with a slight displacement, Figure 70. Sheppard (1977) regarded this as proving an origin by weathering for the kaolinisation process. This interpretation assumed that no post formational isotopic re-equilibration occurred, an assumption justified on a number of grounds. Bray (1980) has re-evaluated these justifications and taking into account the possible effects of time, acidity and salinity concluded that re-equilibration cannot be discounted. A change of 20 and 12 percent in the hydrogen and oxygen isotopic contents would be sufficient to account for the discrepancy between the composition of SPS and the Geevor kaolinite which Sheppard (1977) regarded as being of hydrothermal origin.

Using the new oxygen fractionation curve of Kulla & Anderson (1978) the equilibrium curve between water and SPS was recalculated by Bray (1980), Figure 70. The projected intersection of this curve with the meteoric water line occurs at a hydrogen isotope value of -27 per mil.

This is the composition of Cretaceous meteoric water, Jackson et al (1982). The temperature of the water at the intersection is below zero. This is incompatible with an origin for the kaolinite deposits through lateritic weathering in a hot, humid, tropical to subtropical environment, McFarlane (1976), Storr (1975). A weathering origin would therefore seem unlikely. The isotopic fractionation curve intersects the field of Cornubian magmatic fluid at temperaures between 130 and 200 $^{o}$C but it is unlikely that this fluid was responsible for kaolinisation since it is difficult to imagine a magmatic fluid following one of predominantly groundwater composition. Moreover, mass transfer calculations have shown that the quantities of fluid required are too large.

It is possible that kaolinisation could have been carried out by fluids of meteoric origin which underwent isotopic re-equilibration with the country rock. Assuming that no hydrogen isotopic exchange took place then the Geevor and SPS kaolinites formed from hydrothermal meteoric fluids of Tertiary and Quaternary ages respectively, Jackson et al (1982). Although there is evidence of periodic hydrothermal rejuvenation in SW England, Jackson et al (1982), it is difficult to imagine the re-initiation of hydrothermal convective systems necessary to bring about kaolinisation on the scale observed.

Kaolinisation may alternatively have been carried out by meteoric waters of upper Palaeozoic age which were in the process of undergoing isotopic re-equilibration with the country rocks. Upper Palaeozoic meteoric waters had compositions close to SMOW, Jackson et al (1982), Figure 70. The re-equilibration curve intersects both isotopic fractionation curves for Geevor and SPS kaolinite in the region of 100-200 $^{o}$C. This is the temperature range in which kaolinisation appears

to take place from fluid inclusion data. In this model the Geevor kaolinite formed from fluids less isotopically re-equilibrated with the country rocks than those fluids which formed the bulk of the Cornish kaolinite field. If this model is correct then it is be expected that other kaolinite compositions from SW England will fall along a trend line joining the SPS and Geevor kaolinites. Although Taylor (1979) observes that geothermal (i.e. meteoric hydrothermal) waters display an oxygen but no hydrogen isotopic shift "because the rocks contain so little initial hydrogen", the rocks referred to are "silicate and cabonate country rocks". If the rocks are composed by contrast of a thick succession of pelites and metapelites then the mica content of these rocks should enable the requisite hydrogen shift to occur.

Bray (1980) proposed a radically different model which attempted to account for the greisenisation, quartz veining and kaolinisation by a single generation of fluid. This was postulated to be of predominantly magmatic origin but mixed with a little meteoric water to give rise to a high temperature fluid (450 $^{o}$C) of moderate salinity (10 wt. percent). Throttling and adiabatic expansion caused the fluid to boil intensely. The initial liquid phase entered the wall rocks and caused greisenisation, the later fluid infilled the channelways and formed the mineralised quartz veins. The vapour component of the boiling liquid penetrated and kaolinised the granite. The vapour was cooled to 125 $^{o}$C by heat exchange with the wall rocks.

It is conceivable that the rapid cooling and condensation of this vapour could produce the dilute, low temperature brines considered here and by others Charoy (1975,1979), Alderton & Rankin (in prep.) to be responsible for kaolinisation, but this model is not favoured for the following reasons:

- Boiling partitions both hydrogen and oxygen isotopes below the critical point (Friedman & O'Neil, 1977). Since the critical temperature for a 10 wt. percent solution is 485 °C (Sourirajan & Kennedy, 1962), boiling of the liquid at 450 °C would cause a hydrogen and oxygen shift in the residual fluid. This is not observed.
- Hydrogen isotopic fractionation between the vapour and the liquid was assumed to be positive due to the absence of any data on saline systems.
- The assumed oxygen isotope compositions of the alteration micas are in disagreement with the values obtained by Sheppard (1977). Sheppard's data is incompatible with this model.
- Temperatures of 450 °C for the greisening fluids are rather high with respect to the fluid inclusion evidence for greisenisation in SW England as a whole, Jackson et al (1977), Jackson et al (1982), Charoy & Weisbrod (1975), Charoy (1979).
- Intense boiling of the fluid is necessary to maintain the isotopic composition of the vapour phase close to the original fluid composition. The residual fluids would therefore be highly saline, probably greater than 25 wt. percent. This is not in agreement with the moderate salinities observed for the fluids thought to be responsible for greisenisation and mineralisation in SW England, Charoy (1979).
- Bray has indicated a significant increase in the relative abundance of vapour rich inclusions in kaolinised granite, an observation not substantiated by Alderton & Rankin (in prep.).
- Although frequently spatially correlated, kaolinised granite is not exclusively related to sheeted greisen veins. Greisen veins can frequently be observed to run from kaolinised to unkaolinised granite. Greisenisation, mineralised quartz veins and kaolinisation would therefore not seem to be universally cogenetic.

## D Conclusion

Given the amount of data currently available and the present state of knowledge, the stable isotope data from SW England is open to numerous interpretations. The following overall model is preferred since it is compatible with the observed petrological, geochemical, fluid inclusion and field evidence, the conclusions of Charoy (1975,1979), Alderton & Rankin (in prep.) and the models of Burnham (1979) and Norton (1978) and his co-workers.

The fluids responsible for greisenisation (but in the case of the western lobe, tourmalinisation) and mineralisation show a progressive evolution. Originally magmatic, the fluids mixed increasingly with groundwaters which finally became predominant. At a later stage hydrothermal-meteoric waters may also have been involved. Kaolinisation was carried out by low temperature (100-200 $^{o}$C) hydrothermal meteoric fluids which were in the process of undergoing isotopic re-equilibration with the metapelitic country rocks.

## 6.5 SUMMARY OF EVIDENCE ON THE GENESIS OF THE KAOLINITE DEPOSITS IN THE ST. AUSTELL GRANITE

Geologists were divided at an early stage into those who advocated typical weathering and those who preferred the agency of hydrothermal processes in the generation of the china clay deposits of SW England.

The evidence of the origin of these deposits has been summarised by Bristow (1977) but some additional points can be made. The morphological difference between kaolinite deposits originating through weathering and those of SW England needs further emphasis. Weathering deposits have the following characteristics, Figure 71. They have small depth to width ratios. European weathering deposits of Tertiary age have a maximum depth of development of about 50 m , Storr (1975). Kaolinisation affects a wide variety of rock types. The alteration profile is ubiquitously zoned containing a single high grade, thin kaolinite rich zone which contains a large amount of organic matter. The substrate fabric is always partially destroyed.

These characteristics contrast strongly with those of the SW England deposits, Figure 72. The granite is the only rock type to be significantly altered and its fabric is perfectly preserved. The deposits are funnel shaped and in excess of 500m deep, are unzoned and contain no visible organic component. The deposits are comparatively low grade as they contain less than 50% kaolinite but are of very high tonnage. These deposits do not share a single common morphological characteristic with the Eastern European deposits.

Although supergene alteration of vein minerals has been reported down to depths of 300 m in SW England, Edmonds et al (1975), there is a

considerable difference between the quantities of fluid necessary to cause this and those necessary to form kaolinite deposits. Conversely, a crucial piece of evidence used in support of the hydrothermal hypothesis (the increasing crystallinity of kaolinite towards major quartz-tourmaline veins, Exley 1976) merely shows that the fluids responsible for kaolinisation moved along these fractues without giving any indication as to their sense of movement, whether up or down.

Some additional evidence is now also available since the review paper was published. Strike-slip faults orientated in the same direction as those hypothesised by Dearman (1964) to be of Tertiary age and outcroping in the western lobe are unaffected by kaolinisation. This suggests that alteration occurred before this date. Kaolinite infills upward terminating tension gashes and veinlets, having presumably been precipitated from suspension. This texture is difficult to explain by a weathering model. Clay runs were observed to be controlled by vein sets of certain orientation (320), and are particularly associated with the late quartz veins. These veins have the widest development implying a correlation between the high pore pressure fluids responsible for their formation and kaolinisation. The later sets of late quartz vein are narrower and formed from fluids having lower pore pressures. They concomitantly seem to exert far less influence on the development of kaolinised zones. The correlation between the orientations of the thick late quartz veins and the clay runs is therefore a potentially useful exploration tool. These veins are characterised by an association of milky white, amethystine and smokey quartz and frequently contains abundant haematite. Field and mass evidence shows that the silica and iron for these veins has come from the kaolinisation of the granite. The development of haematite can become quite massive and palaeomagnetic dating of this material may prove to be the only feasible way of dating

the kaolinisation process. The fluid inclusions in these veins are predominantly liquid monophase and are commonly coated with a clay mineral whose morphology and chemistry show it to be kaolinite. It was probably precipitated from suspension. There is an increasing body of evidence associating these low salinity (<5 wt. percent) low temperature ($100-200^{o}C$) fluids with the kaolinising process, Charoy (1975, 1979), Alderton & Rankin (in prep.).

There seems to be incontrovertible evidence that kaolinisation was caused by low temperature, convecting hydrothermal fluids. There remains the question of how much of the alteration is attributable to hydrothermal processes and how much to the possible imposition of weathering processes. The fluid-rock ratios were calculated independently using mass transfer data for the kaolinisation process and from the structural criteria of the late quartz veins. The results suggest that the quantity of fluid responsible for the deposition of the late quartz veins was more than adequate to account for the whole kaolinisation process. Mass transfer calculations themselves show that the volume of the granite increases with kaolinisation and that the silica released during alteration is largely precipitated in situ. Both these features suggest that a single genetic process was responsible for kaolinisation.

Two pieces of evidence appear to contradict this conclusion. These are the morphology of the alteration clay minerals (Keller 1976) and Sheppard's (1977) interpretation of the stable oxygen isotope data. A reinterpretation of the stable isotope data shows it to be not incompatible with a meteoric hydrothermal origin for the kaolinising fluids allowing for isotopic exchange with the metapelitic country rocks. The scanning electron miscroscopic studies of kaolinite textures from th St. Austell granite made by Keller (1976) purported to show that the clay

mineral was predominantly loosely packed showing classic "booklet" textures. This was interpreted as being indicative of a low pressure, near surface mode of formation and hence an origin through weathering. These observations have not been confirmed. The kaolinites from the western lobe have been found to be predominantly compact. Booklet textures are comparatively rare. The discrepancy in these observations may be due to differences in sampling depth or the result of the possible recrystallisation of the kaolinite in response to changes in temperature and pressure as a result of unroofing.

Keller (1976), Sheppard (1977) and Bristow (1977) concluded that the kaolinisation of the granite was a bimodal process. The first, hydrothermal stage "softened up" the granite to allow the extensive formation of kaolinite by the second stage weathering process. No evidence has yet been found to support this hypothesis. However, there is no doubt that the Tertiary was a period of extreme lateritic weathering responsible for the formation of kaolinite deposits all over Europe (Storr, 1975). There is no reason why SW England should have escaped these climatic conditions. The degree to which weathering may have been involved in kaolinisation probably varies from deposit to deposit. In the western lobe of the St. Austell granite its influence seems to be minimal but a significant contribution may be in evidence in the clay deposits of Bodmin Moor, Bristow (1977). A certain amount of reworking of these fundamentaly hydrothermal deposits by weathering processes may account for the generally high quality of the clay in the SW England peninsula.

## Conclusion

The kaolinite deposits of the western lobe of the St. Austell granite formed through the agency of late hydrothermal fluids of meteoric origin undergoing isotopic exchange with the killas country rocks. The meteoric waters were drawn in to replace the groundwaters in the vicinity of the granite which had already convected through it. The extensive life span (probably in excess of two million years) of the hydrothermal system was the result of radiogenic decay in the uranium enriched granite. This, together with the high permeability of the granite were the crucial elements in the formation of the hydrothermal kaolinite deposits. Lateritic weathering processes may have been involved to a limited extent but the effects are not generally evident.

# CHAPTER 7

# CONCLUSIONS

The Cornubian granite is a high level post kinematic granite with "S" type characteristics intruded into Upper Palaeozoic metasediments about 290 my ago, Jackson et al (1982). The granite contains more than the average levels of B, F, Rb, Sn, Cl, As and U. The melt was derived by anatexis of predominantly pelitic material at temperatures of about 860 $^{o}$C and pressures of 5.2 kb, Charoy (1979). The source material had not undergone extreme metamorphism prior to the anatectic event, Jackson et al (1982). The initial water content at source lay between 3 and 5 wt. percent. The granite was intruded by a process of assimilation, forceful injection, block stoping and cauldron subsidence, Jackson (1979). Differentiation occurred during ascension. Assimilation, contamination and further differentation gave rise to the different granite types, Hawkes & Dangerfield (1978).

The western lobe of the St. Austell cupola is a phenocryst-rich coarse grained biotite bearing granite. Variations in the mineralogical composition, texture and macroscopic fabric of the granite are the result of late magmatic processes. It is chemically comparable to other Cornubian granites having high $Na_2O$, $K_2O$ and low CaO levels. This is reflected in its classification as an alkali feldspar granite using CIPW norms and the classificationary scheme of Streckeisen (1975). The magma was peraluminous since normative calculations give consistent corundum values of the order of 3 percent. It is additionally enriched in $Al_2O_3$, $P_2O_5$, Rb, B and Li and depleted in $Fe_2O_3$, MgO, V, Sr, Y, Zr and Ba. The western lobe shares the same chemical and mineralogical characteristics of other Sn-W bearing granites from around the world.

The earliest minerals to crystallise from the melt were the aluminium silicates (sillimanite and topaz) together with biotite, monazite, rutile and zircon. These were followed by the feldspars,

precursor plagioclase and potash feldspar. Quartz crystallised throughout the paragenetic sequence. The presence of the early aluminium silicates and the abundance of rutile is additional evidence in favour of a derivation for the melt through lower crystal anatexis, Charoy (1979). The magma was intruded passively to a level between 2 and 4 km below the surface and at a temperature of around 500 $^{o}$C causing only moderate contact metamorphism of the country rocks.

The granite solidus was significantly depressed by the presence of volatiles in concentration. The resultant extended history of crystallisation gave rise to a thorough re-equilibration of the early formed magmatic phases and the residual interstitial melt. This led to thorough unmixing of the feldspars, complete solid solution re-equilibration in the plagioclase feldspars, the growth of coarse potash feldspar phenocrysts, the muscovitisation of biotite and the growth of tourmaline. Being peraluminous an immiscible aqueous phase periodically separated from the interstitial residual melt when the volatile component in the magma reached saturation. This gave rise to the formation of the pegmatitic patches and the quartz-tourmaline rich miarolitic cavities. Differential movement in the partially crystalline magma concentrated these aqueous fluids into narrow zones causing tourmaline banding. The disequilibrium between the aqueous and mineral phases caused some early autometasomatic changes. Mineralogically this involved the sericitisation of the feldspars, the tourmalinisation of biotite and potash feldspar, the albitisation of potash feldspar and silicification. This phase of alteration has been termed greisenisation. Local variations in conditions led to a number of different alteration parageneses. A large number of elements were involved in the alteration process but only a few were changed significantly. Copper, Rb and Li were leached whilst boron was added. The alteration is deduced to have been

isovolumetric and very nearly isochemical. With time the progressive generations of aqueous fluids became less saline and cooler. As salinity decreased, intermittant boiling of the fluids occurred.

The final stages of crystallisation of the outer granite carapace occurred at temperatures as low as 350 °C. The zone of saturated melt was by then displaced to a position directly beneath this outer zone. Some of this saturated melt was emplaced along the granite-killas contact to form the pegmatite. Saturation of the melt with volatiles and the separation of an immiscible aqueous phase continued to occur episodically. Once the outer shell had become competent the fluids separating from the melt were confined by the minimum stress and tensile strength of the overlying granite. When fluid overpressures exceeded this combined confining pressure, fracturing in the granite envelope was initiated.

The earliest fractures would have been small and anastomosing as the tensile strength of the rock was low. The fluids passing along these fractures probably continued to cause pervasive greisenisation/tourmalinisation.

Continued cooling thickened and strengthened the outer hood of the granite. Fluid overpressures necessary to initiate fracturing increased concommitantly. Subvertical fractures developed. The interaction between the fluid overpressure and the regional stress field gave rise to the formation of two pairs of fracture sets. The fluids passing up these fractures were in extreme disequilibrium with the wallrocks. Mineralogical and chemical alteration was intense. The granite adjacent to the fractures was altered isovolumetrically to a quartz-tourmaline rock. Aluminium, Fe, Mg, H+, V, Ni, Zn, B and Li were added to the rock in significant amounts whilst the following were leached: Ca, Na, K, P,

Cu, Rb, Y and B and under extreme conditions, even Si. These changes took place over very small distances as the alteration front was very sharp. Both feldspars are altered reflecting the high acidity of these solutions but their K/Na ratios of about 0.05 caused potash feldspar to be preferentially destabilised with respect to albite. Tourmalinisation in the western lobe was mineralogically and chemically predominant in the greisenisation-tourmalinisation alteration continuum. The reason for this was the extremely high boron content in the evolved hydrothermal fluids. Mineralisation is associated with tourmalinisation and in particular with tourmaline of schorlitic composition. Unlike vein mineralisation elsewhere in SW England the cassiterite is disseminated through the alteration selvedge rather than located in a central quartz stringer.

The intrusion of the granite into the upper crust initiated hydrothermal convection. The convective cells were initially restricted to the country rock. When the upper part of the pluton was fractured by the centrifugal expulsion of the magmatically derived fluids it became permeable, allowing the water in the killas to flow through the granite. The mixing of the magmatic fluids with these groundwaters caused dilution and cooling from 350 $^{o}$C, 30 wt. percent equiv. NaCl down to 200 $^{o}$C and 10 wt. percent equiv. NaCl.

With continued crystallisation the saturated residual melt migrated to greater depths. Increasing fluid overpressures were required to overcome the confining pressure. This occurred less frequently but increasingly violently. The tourmaline breccia bodies resulted from the final explosive paroxysms of the deuteric system. Hydraulic fracturing down such a pressure gradient caused rock bursting and fragmentation of the granite and killas into the low pressure zone. The pre-existing subvertical fractures controlled the morphology of the breccia bodies,

guiding the explosive release of the fluids and forming natural planes for mechanical failure. The fine grained granite powder combined with the boron and silica rich fluid to form a high density fluidised matrix in which the fragments were suspended. Vigorous circulation of the fragments occurred before the system finally "froze". The comminuted rock debris reacted rapidly with the boron rich fluid during the explosive event and created a dense crystalline matrix of tourmaline and quartz cementing the larger fragments. Breccia formation persisted on a much smaller scale during which time the fluids became increasingly siliceous as the deuteric fluids became impoverished in boron and other "exotic" volatiles and the confining pressures became limiting. The final episode was the formation of the killas rich collapse breccia.

The breccias are not mineralised because the tin producing hydrothermal event had been associated with the pre-breccia fracture generations. This does not however preclude other breccia bodies in SW England from being mineralised. Given the favourable physical conditions accompanying breccia formation for the precipitation of ore minerals these bodies must still be regarded as being of considerable economic potential.

The late stage, potassic hyperaluminous silicate residuum was injected into the consolidated granite and surrounding country rocks in the form of quartz porphyry (elvan) dykes. The dykes contain large potash feldspar and quartz phenocrysts in an aphanitic mosaic of quartz and feldspar. Devitrification textures attest to a predominantly magmatic origin. Palingenesis of wall rock granite accompanied their intrusion.

The circulation of water in the hydrothermal convective cells persisted for a period of at least two million years due to the heat

produced by the abundant radioactive elements in the granite. The fluids were initially "metamorphic" in composition, groundwaters in stable isotopic equilibrium with the country rocks. The persistence of fluid convection finally drew quantities of contemporary meteoric fluid into the hydrothermal system. As they passed through the country rock they underwent re-equilibration.

These fluids were responsible for the formation of the quartz veins and associated alteration. They had initial temperatures of over 300 $^{o}$C and salinities of about ten wt. percent equiv. NaCl. These relatively high temperatures were caused by the deep circulation of the fluid and the contribution of heat from radiogenic sources. The fluids gradually became less saline as they cooled. Eventually they contained less than 5 wt. percent equiv. NaCl at temperatures less than 100 $^{o}$C. The formation of the quartz-fluorite-sulphide veins and the haematisation possibly associated with them occurred at an early stage. The K/Na ratio of the fluid increased from early (0.4) to late (0.5) quartz formation. Albite was therefore destabilised with respect to potash feldspar. The later fluids were responsible for the kaolinisation of the granite at temperatures between 100 and 200 $^{o}$C and at salinities of less than 5 wt. percent equiv. NaCl. One hundred times more fluid was involved in kaolinisation than in the earlier tourmalinisation.

The kaolinisation of the granite is calculated to have caused a 25 percent volume increase despite the preservation of the granite fabric. This increase may have been accommodated by slippage along subhorizontal joint planes. Alternatively the kaolinised granite may have undergone a decrease in density subsequent to alteration as the kaolinite recrystallised in response to decreasing pressures as unloading occurred.

The principal mineralogical change was the alteration of the feldspars to kaolinite. Albite altered preferentially with respect to potash feldspar. The plagioclase altered incongruently through an intermediate leached zone whilst the potash feldspars altered directly to kaolinite. The other main mineralogical changes were the kaolinisation of the mica and the growth of quartz. The kaolinite has a dense, compact morphology. A large number of elements were involved in this alteration process but significant mass transfer was limited to the leaching of Ca, Na, K, Rb, Li and P and the addition of H+, Y and Ba. The silica released during the decomposition of the feldspars is largely deposited in situ.

Kaolinisation is genetically related to the fluids which also formed the veins filled by a relatively small part of the total quantity of silica and iron released from the granite during alteration. The thickest vein set orientated at 320 formed under the highest fluid pressures. This corresponds to the period of most intense alteration since the veins orientated in this direction control the development of the most persistent clay runs. The later veins exert less influence on the orientation of the clay rich zones. They are narrower, formed under lower fluid pressures and alteration was concommitantly less intense. The strong strike-slip component on the late quartz veins may have additionally enhanced fluid flow through a seismic pumping mechanism, Sibson et al (1975). Weathering processes may have enhanced or enriched some clay deposits in SW England but there is no evidence of a contribution from this source in the formation of the kaolinite deposits of the western lobe of the St. Austell granite.

The longevity of the hydrothermal convective system is a direct consequence of the particularly high levels of uranium in the granite. The uranium is predominantly located in individual grains of uraninite or

associated with compound hydrocarbon-rich inclusions, Ball & Basham (1979). It is extremely susceptible to leaching during all of the alteration processes. Since kaolinitisation is the type of alteration which has affected the largest volume of the granite there is a strong probability that these kaolinising fluids caused the solution of significant quantities of uranium and their reprecipitation in high level veins. The late quartz veins at the current level of exposure contain anomolous levels of this radioactive element. The subsequent erosion of these high level deposits probably produced secondary enrichments in the Lower Mesozoic red beds in the vicinity of SW England thus making them potential exploration targets for sedimentary style uranium mineralisation.

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# APPENDIX A

# ANALYTICAL METHODS

## A.1 SAMPLE COLLECTION

Samples were given field numbers corresponding to their location and date of collection. The initial letters correspond to the area sampled, WRP being Wheal Remfry pit, MP Melbur pit and VG Virginia clay pit. For the Wheal Remfry samples the number preceding the oblique corresponds to the field trip number and the following number is the station at which sampling occurred. All the samples from Melbur and Virginia were collected during the fourth field trip.

The optimum size sample for a coarse grained granite is about 1 kg (Wager and Brown 1960). Samples were obtained as close to this as possible but were occasionally less due to sampling difficulties.

## A.2 SAMPLE PREPARATION

Samples selected for analysis were given random analytical numbers. A subsample of between 0.5 and 0.7 kg was taken.

A tungsten carbide sample splitter was used to break the samples down to 10cm sized lumps. Further size reduction down to coarse gravel was achieved with a jaw crusher. A representative subsample was obtained for Tema-ing (60-100g) by progressive splitting. The agate Tema took six minutes to reduce each sample to -200 mesh.

One hundred and thirty-five samples were prepared in this way.

## A.3 MAJOR AND TRACE ELEMENT ANALYSES

### 1 MAJOR ELEMENTS

Thirty-five samples were analysed for major elements by XRF at the ECLP Laboratories, St. Austell. The remaining one hundred samples had their major elements determined by inductively coupled plasma (ICP) at King's College, London.

#### A XRF

These analyses were carried out under the direction of Peter Salt, to whom I am most grateful. The hardware comprises a Phillips P.W. 1410/20 X-ray fluorescence spectrometer coupled to a D.C. 852 M minicomputer. Further details may be obtained from ECLP Technical Report No. 7801/2.

Analyses for $SiO_2$, $TiO_2$, $Al_2O_3$, $Fe_2O_3$, MgO, CaO, $Na_2O$ and $K_2O$ were carried out on fused glass discs prepared using a method described by Harvey et al. (1972). Output is directly in percent.

#### B ICP

Thanks are due to Professor Howie who kindly sanctioned the use of the King's College Plasma and to Dr. Nick Walsh who instructed me in its use and with whom many useful discussions were held.

The King's College ICP is a Phillips /MBLT machine coupled to a Phillips P852 minicomputer. The performance of this machine in analysing silicate rocks and minerals has been described (Walsh and Howie 1980).

The sample preparation used and described in Watkins (1980) was slightly different to that recommended in this paper. Fusion of the rock powder was carried out in graphite crucibles in an electric muffle furnace rather than using platinum crucibles and a Meker burner. In addition to the obvious economic advantages of using graphite, the molten bead separates cleanly from the crucible and shatters when poured into the solution. The shattered bead dissolves more quickly than the fused film in the platinum crucible. This greatly speeds up an otherwise slow preparative step. The presence of graphite particles requires that the solutions be filtered but this was not found to be inconvenient in routine. There does, however, seem to be a greater tendancy for the fused sample to form insoluble polysilicic acid particles (identified using SEM). This is undesirable since the silica contents are affected. Once the solutions are prepared they appear to remain stable over considerable periods (over 2 years).

Although the preparation is tedious and relatively time consuming, each analysis takes only 1 or 2 minutes. The results are output directly as whole rock concentrations for $SiO_2$, $TiO_2$, $Al_2O_3$, $Fe_2O_3$, MnO, CaO, $Na_2O$, $K_2O$, $P_2O_5$ in percent and V, Zr, Ce, Y, Sr and Ba in ppm.

It was found that the largest source of errors lay in the fluctuations in the rate of solution uptake (Walsh and Howie 1980). This problem could be largely overcome by using an internal standard. Lanthanum was used in the form of a $La(NO_3)_3$ solution to give a concentration of 100 ppm La in the solutions to be analysed.

## 2 LOSS ON IGNITION DETERMINATIONS

The technique used is fairly standard. Between 2 and 5 g of sample powder was added to a porcelain crucible of known weight. The crucible and powder were dried for 8 hours at 110 °C and reweighed to give the value of $H_2O-$. They were subsequently ignited at 1000 °C for 30 minutes before being cooled in a dessicator. Reweighing gave the $H_2O+$ or Loss on Ignition (LOI) value.

The samples contain significant quantities of hydrated minerals so the effect of igniting them at 1200 °C was tested. The results indicated that kaolinite lost more or less all its structural water and the muscovite rich samples most of theirs at 1000 °C. The biotite and tourmaline rich samples however lost significantly more water at the higher temperature. Since the powders fuse to the porcelain crucible at 1200 °C, routine determinations were carried out at the lower temperature. Biotite and tourmaline rich samples are therefore likely to have considerably underestimated values.

## 3 TRACE ELEMENTS

The trace elements V, Cr, Ni, Cu, Zn, Th, Rb, Sr, Y, Zr, Nb and Ba were analysed using the Geology Department XRF whilst B, Li, and Sn were analysed on the King's College ICP.

### A XRF

The samples were prepared by pressing the powders into small cakes, backed by compressed boric acid powder to form briquettes (Parker 1977, 1980a).

The briquettes were analysed three at a time against a reference standard chosen to give good count rates. Output is in raw counts. A series of computer programs correct for the effects of dead time, background and spectral contamination, line overlap and matrix effects (using major element compositions), (Parker 1980b).

Calibration is accomplished by recalibrating the reference sample with respect to a number of suitable standards, analysed as unknowns. Using initial reference sample concentrations established for normal working conditions the element concentrations in the standard samples are calculated and compared to their reported values, Figure 73. The percentage by which the standard results are in error is calculated for each element and the initial reference sample concentrations are adjusted to bring the standard values as close as possible to their reported values. Standards were selected in order to give the best calibration over the range of values thought to occur in the samples. Standards with granitic characteristics were therefore preferred. Some standards were also discarded if they demonstrated gross disparity with the other

standards, e.g. G-1 for Ba, Figure 73b. The standard set selected for each element is given in Table 39. The calculated and reported values for these standards are plotted after optimisation of the reference sample concentrations (Figure 74).

**B ICP**

Boron, lithium and tin were analysed on the King's College ICP as this machine is extremely sensitive to these elements. Use was made of the boron, lithium and tin spectral lines at 2497.73, 6707.84 and 3174.05 Angstroms respectively. Channels already existed for Li and Sn whilst the roving detector was used for boron. There is a certain amount of interference of boron by iron but only at high levels.

**Fusion**

The problem of analysing for these three elements is largely related to the difficulty of getting them into solution. Tourmaline and cassiterite, the main boron and tin bearing phases, are highly resistant to the $HCl/HClO_4$ attack used for the plasma trace element analytical programme. PTFE bombs could have been used but would have been too time consuming given the number of samples involved. Fusion methods are quickest and most efficient in breaking down resistate minerals. Several fluxes are available. Lithium metaborate is clearly unsuitable. Potassium and sodium carbonate both have high melting points necessitating the use of platinum crucibles. This is prohibitively expensive when at least thirty are required to maintain a reasonably efficient routine method. Sodium hydroxide has a number of advantages as a flux. Its melting point is sufficiently low to make it possible to use nickel crucibles. A busen is more than adequate to heat the flux above its melting point which

facilitates and quickens fusion due to the lower viscosity of the melt. Iron forms an insoluble hydroxide which can be filtered out if present in sufficient quantities to cause possible spectral interference.

The procedure, Table 40 was adapted from a standard technique developed by Peter Watkins. A number of limiting parameters are imposed upon the fusion method. The quantity of samples should be maximised in order to minimise any subsampling error. The ratio of flux to sample has to be kept as small as possible to keep dilution and therefore the detection limit as low as possible. The amount of solute dilution must be kept to a minimum for the same reason. The total amount of solids in solution is limited to one percent since higher levels interfere with the plasma "flame". Modified burner heads can cope with marginally higher solid levels. These parameters require the flux levels to be minimised but fusion effectiveness necessitates a significant excess of flux.

A number of different combinations were tried:

1. 0.1g sample + 0.6g flux diluted to 100ml to give 1000 ppm solution

| | | | | |
|---|---|---|---|---|
| 2. | 0.5 | 3.0 | 500 | 1000 |
| 3. | 0.5 | 2.5 | 250 | 2000 |

The melt was rather viscous in the first method making homogenisation difficult although no significant problems were encountered. Increasing the amount of flux in method 2 gave a more satisfactory fusion due to the larger quantities of excess flux but had rather poor detection limits. The last method is preferred although it gives a solution with a 1.2 percent solid content.

The detection limits and solid content restrictions could be circumvented by using an ion exchange column to remove the excess sodium. This may be worthwhile if extremely accurate results are required at low levels but for routine work it is unnecessary.

**Standard solutions**

Standards are required in ICP analyses for calibration. The concentrations of the standards should be in the range anticipated in the samples. There are, unfortunately, no suitable international rock standards containing reasonable levels of any of these three elements. Artifical standards had to be made up in the laboratory. The first set of standards used a blank NaOH solution to which appropriate aliquots of standard element solution had to be added. This does not take into account any sort of matrix, adsorbtion or interference effects. As a closer approximation to the "real" situation, standards were made up from fused rock samples. Ideally the selected sample should be as similar to the unknown samples as possible and should not contain detectable quantities of any of the elements. NIM-G was the standard sample chosen.

Despite the use of a rock solution in the preparation of the standards, any errors associated with the fusion procedure, such as volatalisation will not be accounted for. This cannot be improved until acceptable rock standards become available.

## Calibration

Calibration plots were made of element content against intensity for both standard sets. Although the gradients of the calibration curves for both blank and NIM-G standards were similar for each element they gave different intercept values. The difference in the intercept values can be calculated to be equivilant to 45ppm B, 14.5ppm Li and 85.6ppm Sn. This compares with the published values for NIM-G of 7.4ppm B, 16.4ppm Li and 5.9ppm Sn, Steele et al (1978). The values for boron and tin are wildly overestimated. This is thought to be the result of flooding of the spectrometer by the emissions from the other elements present, i.e. a matrix effect (Walsh, pers. comm.). These values therefore represent the effective minimum limit of detection for these elements analysed by this method. There is reasonably good agreement between the calculated and published value for lithium. The detection limit in this case must be extremely low. This element does not seem to suffer from matrix effects.

The plasma output from these analyses was in raw intensities. These can be converted into ppm in solution using the following equation:

$$xs = (Is-c)$$ where xs = sample concentration

Is = sample intensity

c = calibration curve intercept

m = calibration curve gradient

Having defined the calibration curve from the standard solutions the sample concentrations can be found. Unfortunately, machine conditions do not remain absolutely constant. This has the effect of changing the calibration curve. There are two major sources of variation. Short term fluctuations such as variations in power supply will be reflected in

variations in the intercept of the calibration curve whilst variations in the rate at which the sample is introduced into the "flame" will cause the gradient of the calibration line to vary. These are usually the largest contributors to error. Sudden fluctuations may be caused by hiccups in the system such as power surges or variations in gas flow rate. These can be very large and are therefore instantly noticeable.

Since the machine operating conditions change with time it is necessary to reanalyse the standards to redefine the calibration curve. This is time consuming so there is obviously a trade-off between precision and a desirable rate of analysis. The calibration curves were redefined by reanalysing three standard solutions and calculating the line of regression through the points. The standard content is the independent variable, the intensities the dependent variable. The calibration line will be the line of regression of intensity upon calibration standard values.

Implicit in the conversion of raw intensities to concentrations is the assumption that the relationship between intensity and element content is linear, at least in its working range. This is certainly the case for these three elements and appears to be true for most elements. A programme was written to convert the raw intensities into whole rock values.

### Detection limits

The fluctuations in the intercept value (intensities) of the calibration curves with time also helps to define the detection limit. The mean variation in intercept values is equivilant to 5,2.5 and 200ppm for boron, lithium and tin respectively. The analytical fluctuations have to be added to the minimum detection limits for boron and tin caused by spectral interference effects. This gives an overall detection limit (in the whole rock) of 50,2.5 and 290ppm for B, Li and Sn respectively. This is acceptable for boron and lithium but clearly unsatisfactory for tin.

### Conclusion

The technique is satisfactory for the analysis of boron if it is present in relatively large quantities and for lithium. To improve boron analyses and make acceptable tin analyses the concentration of these elements will have to be increased.

## 4 DATA PROCESSING

The stages of major and trace element data processing is summarised in Figure 75. The data files and programme functions are described briefly in Table 41. The data was manipulated in order to make it compatible with the set of integrated programmes written by Parker (1980b) to process and evaluate XRF data. This package was basically used to process the trace element data, calculate the CIPW norms and compile a database file and tabulated output containing the major, trace and norm values. The normative and analytical data is tabulated on Microfiche 1 at

the back.

## A.4 CHLORINE DETERMINATIONS

Chlorine analyses were carried out on the NaOH fusion solutions using the wet chemical spectrophotometric method described by Watkins (1980).

## A.5 RADIOGENIC ELEMENTS

The decay of all radiogenic isotopes releases energy which is dissipated as heat. Only four isotopes are geologically important heat producers. Uranium 238 and 235 of which the latter isotope comprises only 0.7 percent of the total, thorium 232 and potassium 40. The radioactive species of potassium is relatively rare, forming only 0.0119 percent of the total element abundance.

The concentration of the radioactive isotopes in the rock samples was determined by gamma-ray spectrometry. This technique depends upon the physics of decay of the radioactive isotopes. The gamma-rays emitted on decay have precise energy values and can be detected by a scintillometer. The gamma rays interact with the detector to produce a burst of light (scintillation). These are converted into electrical pulses proportional to the energy of the incident photon. The signals are amplified by a photomultiplier and then further amplified, scaled and counted on a multi-channel analyser.

The gamma-ray spectrometry equipment is housed in the Geophysics Department. I am grateful to Jim Wheildon & Jorge Gebski for instructing

me in its use. Figure 76 is a diagramatic representation of the set up.

The samples were jaw crushed to a fine gravel and packed into perspex containers which overlap the detector to give maximum geometric advantage. The perspex adsorbs the beta particles allowing only the gamma radiation to enter the detector. The containers take between 700 and 1000g of rock. Francis (1980) has shown that the size of the crushed sample has little effect on the accuracy of the measurements.

The analytical procedure set up by Strachan (1973) was broadly followed with modifications made by Francis (1980) and Gebski (in prep.). The raw data were processed using programme Heat 1, written by Strachan (1973) but subsequently modified by both Tammemagi and Gebski. The programme calculates K, U and Th contents, heat generation and the Th/U ratio for each sample. The quoted error is calculated as a function of the count rate (Francis 1980).

The samples selected for analysis covered most of the different rock types in the western part of the St. Austell cupola. The results are listed in Table 42 and the sample descriptions and localities in Table 43. I am grateful to Dr. J. Hawkes for letting me use a number of samples collected by the IGS.

## A.6 SPECIFIC GRAVITIES

Representative samples from the fresh granite and altered granite groups had their specific gravities measured in order to derive a group average for use in mass transfer calculations.

A suitable sized tablet of each rock sample was weighed and then immersed in water and reweighed. The weight difference gives the sample volume and hence the sample density can be found. This method calculates the bulk density of the rock since voids and pore spaces are taken into account.

A five figure balance was used but it was oversensitive and noticeable weight increasments occurred with increasing immersion time. This was due to water percolating into the pore spaces. Sufficient precision was obtained by taking the readings as quickly as possible.

The results are summarised in Table 44. The bulk density of kaolinised granite cannot be obtained using this method. The average bulk density of kaolinised granite from the St. Austell granite mass has been determined however by the production department of ECLP Co. Ltd using a different, bulk sampling technique. The value is about 2.0g/cm$^3$ and stays remarkably constant over the whole area (Gronow, pers. comm.).

## A.7 QUANTITATIVE MINERALOGICAL COMPOSITONS

The mineralogical compositions of ten samples were determined by quantitative X-ray diffraction techniques. Peter Salt undertook these analyses in the ECLP laboratories for which I am most thankful. He made the following comments. "The samples are assumed to be 100 percent crystalline. The kaolin and mica are estimated from the ratio of their 001 peak areas on the remainder from 100 after allowing for the other minerals which are estimated directly".

The results are summarised in Table 45. The samples comprise a sequential traverse from fresh to kaolinised granite, fresh and kaolinised pegmatite and elvan.

## A.8 DETERMINATION OF FLUID INCLUSION COMPOSITIONS

### Sample preparation

Fluid inclusion analyses were carried out on 24 quartz samples representing magmatic, early and late quartz generations. The samples had to be cleaned of physical and adsorbed adherents. Physical material can be removed by scrubbing, washing and ultrasonic cleaning. Organic material was cleaned by soaking the samples in a 2% solution of Decon 90. Cations are held on the surface of the crystals through electrostatic attraction to the lone pair electrons on the oxygen atoms in the $SiO_4$ tetrahedra. These ions can be removed through electrolysis, the use of ion exchange resins or with acids.

The electrolytic method was used by Roedder (1958) and Roedder et al (1963). The method is time consuming as the ions are pulled from the surface by the potential difference applied across a cell. The surfaces also remain highly susceptible to recontamination.

Ion exchange resins remove ions from solution. An equilibrium is then set up between the cations on the surfaces and the ions in the solution. The cations will gradually move into solution to be replaced by ions from the solution. This explains why such long periods are required (over 5 days) before effective stripping occurs, Poty et al (1974).

The use of acid has precisely the same effect except that the process is considerably more efficient. The hydronium ions in solution exchange directly with cations adsorbed on the surfaces due to its greater concentration and electronegativity. The higher the concentration the faster the exchange becomes. Too high a concentration however may

result in the ions being held in interstial sites being removed. A ten percent solution was considered to be adequate. No advantage is gained by boiling as the acid evaporates, decreasing the strength of the solution. Hot solutions however will speed up the exchange process. Nitric acid was chosen since it contains no anionic species likely to be present in the inclusion fluids. This method has the additional advantage that all the glassware and apparatus with which the samples or inclusion fluids come into contact can also be easily cleaned. This is not the case with the other two methods allowing for greater potential contamination.

**Crushing**

The inclusion fluids can be released in a number of ways. The sample can be heated and the inclusions decrepitated or crushed. Various crushing techniques have been tried. An agate pestle and mortar is extremely inefficient and susceptible to contamination. Roedder et al (1963) and Poty et al (1974) crushed their samples in a press inside copper and steel tubes respectively. The tubes were sealed by turning them over at one end and crimping them. Contamination can be kept to a minimum by thoroughly cleaning the tubes before use, discarding them afterwards and using tubing of the highest purity. Both these techniques require a lot of flushing and leaching with DDIW which results in excessive dilution of the inclusion fluids. An improvement was attempted by using crushing stamps. These were made up from a length of stainless steel tubing and two unequal lengths of stainless steel rod. The external diameter of the rods were only marginally smaller than the internal diameter of the tubing. The sample was crushed between the rods by either hammering one end of the longer rod or placing the whole stamp in an hydraulic press. After crushing, the rods can be removed and the stamps cleaned with a minimum of DDIW. This was therefore the method used to

crush the quartz samples.

In order to test the efficiency of this crushing method the crushed samples were separated into size fractions using nested sieves and a differential settling rate technique. Since the average size of fluid inclusions is about .1mm (Roedder 1979) this may be regarded as the fluid inclusion "libertion size". This corresponds to the 120 mesh which has an apperture of 0.124mm. Crushing efficiency was therefore defined as the percentage of the total crushed sample having a diameter of less than 0.124mm. Plots of the weight of the -120 mesh fraction and crushing efficiency against the total sample weight shows that although the weight of the -120 mesh fraction increases with the increasing total weight of sample, the efficiency of crushing decreases assymptotically. For most samples the crushing efficiency of this method is about 10 percent which is unsatisfactory.

The use of an agate ball mill as an alternative crushing method was investigated. This improves crushing efficiency to nearly 100 percent after only two minutes shaking. The size of the sample charge has to be less than the diameter of the crushing balls, in this case 5mm. This requires the samples to be precrushed in a jaw crusher. Although this may serve to increase sample homogeneity the largest inclusions are probably lost during this process. The rate determining step in this method is the cleaning of the agate ball mill between samples. A rinse in DDIW, followed by 10% nitric acid and six more rinses in DDIW was found to be enough to cut contamination down to less than one percent of the initial analysed value. Random high background values were caused by environmental contamination and a clean room is considered to be essential to carry out this kind of work. No significant contamination was derived from the agate itself. This method has the greatest potential

for the future.

## Leaching

Upon crushing the liberated fluids are presumably adsorbed onto the new fracture surfaces. Leaching with DDIW is the most common technique to wash the fluids from the fragments and dissolve the daughter phases. However, some daughter phases are insoluble in DDIW under ambient conditions and cations will also be left adsorbed onto the new surfaces. It would be more efficient to leach with a mildly acidified solution but this entails the possibility of contamination from solid inclusions (such as feldspar or some other rock forming mineral) released during crushing. This danger was not considered to be too great and the crushed samples were leached with an acidified solution (using nitric acid).

## Filtration

The solution and solid material can be separated by a variety of filtration techniques or by centrifuging. The filtration techniques such as Buchner funnels, millipore assemblies, Gooch crucibles or glass wool filters all suffer from the problems of being susceptible to environmental contamination and involve large scale apparatus which is difficult to clean effectively. Centrifuging was found to be the fastest, most efficient, easiest and most satisfactory method of separating the two phases. Five minutes at 2500rpm was found to be sufficient. The superlatent fluid could then be removed using a syringe and a capillary tube. Glassware was preferred since the acidified solution prevents adsorbtion. The adsorbtion characteristics of complex plastics such as PTFE are unknown but would probably affect both anions and cations.

## Analytical methods

There are considerable problems in analysing these solutions. The quantity of fluid is very small and the element concentrations are very low. Any further dilution may reduce the component levels below detection limits.

The cation content of the solutions was analysed using atomic adsorbtion spectrometry, flame photometry and the inductively coupled plasma. Using the first of these techniques Al, Fe, Mn, Mg, Ca, Na and K were analysed. Unfortunately sensitivities were not good enough, minimum detection being 0.1ppm, and a significant number of analyses fell below detection. Since the cations are predominantly alkali and alkali earth elements the flame photometer was used to analyse for Ca, Na, K and Li. This technique is extremely sensitive and good results were obtained. Both these techniques suffer from the severe disadvantage of analysing each element separately and therefore a relatively large amount of solution is consumed. ICP is an extremely sensitive multi-element technique requiring only very small volumes of solution. This will clearly be the analytical tool for the future.

The analysis of the anion composition of the fluids is still problematic since there are no multi-element techniques available. Wet chemical methods have to be used and without any micro-analytical apparatus large quantities of solution are required, necessitating dilution and a consequent decrease in sensitivity. Chlorine was analysed colourimetrically and fluorine with a specific ion electrode using procedures describe by Watkins (1980). Other anions were not analysed since suitable techniques were not developed in time.

In order to be able to quote these analyses as concentrations in ppm the quantity of inclusion fluid released must be known. This may be done using Roedder et al's (1963) method but this is complex. One technique currently under investigation involves the decrepition of the fluids directly into a mass spectrometer, (Sheppard (pers. comm.)). This has the advantage of giving stable isotopic informaion at the same time. Preliminary work was undertaken with John Lovell of the AGR group at I.C. on the use of gas chromatography and this would seem to be a promising avenue for future development work. The technique is sensitive and other gaseous species can be analysed at the same time. Failing all else, a crude estimate of concentration may be made by combining the analysed Ca, Na and K ratios with the observed last melting point temperatures to pinpoint fluids on the $CaCl_2$, NaCl, KCl, $H_2O$ quaternary diagram.

**Results**

The results of the inclusion fluid analyses are listed in Table 46. The majority of the cation analyses were carried out on the flame photometer, seven being analysed by ICP. The values are solution concentrations in ppm and do not represent absolute fluid inclusion concentrations since the quantity of fluid released was not determined. The AAS analyses are not included because the majority of the analyses fell below detection. Some significant amounts of Fe (nb there is a possibility of contamination from the steel crushing stamps) and Mg may be present. The lithium contents are generally insignificant although detectable. The anion analyses occurred after a considerable time interval and some evaporation probably occurred. The anion to cation ratios are consequently highly erratic. If the ratio is less than one, the presence of unanalysed anions is implied. If more than one then unanalysed cations are present or the solution underwent concentration

before the anions were analysed.

## Summary

The following method was used to anaylse the inclusion fluids:

- The quartz samples were cleaned ultrasonically in a detergent solution.

- The samples were subsequently cleaned in DDIW, Decon 90 (overnight), 10 percent $HNO_3$ (overnight) and finally DDIW several times.

- The samples were crushed in stainless steel stamps.

- Leaching was carried out with an acidified solution.

- Centrifuging was used to separate the solution from the solid material.

- The superlatent fluid was extracted using a syringe and capillary tube.

- The alkalies and alkali earths were analysed on a flame photometer.

- The anions were analysed wet chemically.

# APPENDIX B

## PRECISION AND ACCURACY OF THE ANALYTICAL TECHNIQUES

## B.1 MEASUREMENT OF ANALYTICAL VARIANCE

Analytical variance enables the significance of the analyses to be tested. Variability is measured by the variance statistic or its square root, standard deviation. Neither of these statistics can be immediately interpreted. The mean relative error is the standard deviation expressed as a percentage of the mean. This has the advantage of being a scale which is easily conceptualised.

Mean relative error suffers from a number of disadvantages. It is dependent upon the magnitude of the mean. Large relative errors can result from small variations if the mean value is small. The discrimination of "unacceptably" high errors is a subjective choice.

Relative error measures absolute variation in the data but this is not of critical concern. In practise it is only important to determine whether the analysed variable can be used to discriminate between different rock samples. This requires that the analytical variance should be significantly smaller than the absolute variability in the data set. The F test is the statistical method of comparing variance (Davis 1973) and in this instance is defined as the ratio of the data variance to the analytical variance. If the F statistic has a greater than critical value then the data variance is significantly greater than the analytical variance. If the F statistic falls below the critical value the variances cannot be said to be significantly different. Tables of F test critical values are widely available, Davis (1973), Shaw (1969).

The F text statistic is a better measure of error and the significance of the error since the variance generated by analytical methods and sample preparation is compared to the natural variance in the

data. In order to get a true estimate of data variance representative samples must be repeated. This requires a random selection of repeat samples.

Analytical variance can also be carried out on a single sample by re-analysing it repeatedly. This method gives a better impression of analytical variance but the F test statistic cannot be calculated unless the total variance in the data set is used.

## B.2 MAJOR ELEMENTS ANALYSED BY THE ECLP XRF

Seven out of thirty-five samples were re-analysed, a repetition of 20 percent. Repeats were taken at the sample splitting stage prior to tema-ing. The analytical variance therefore includes the variance due to sample splitting, sample preparation and analysis, Table 47.

The MRE's for the major elements (those comprising more than one percent of the total) are all less than five percent. Silica and aluminium have particularly low values. The MRE's for the minor elements are less than eight percent. All these values are considered to be acceptable. Confirmation comes from the F text statistic which is well above the critical value.

## B.3 MAJOR AND TRACE ELEMENTS ANALYSED BY KING'S COLLEGE ICP

Two methods of measuring analytical variance were used.

In the first method a single sample was selected and split ten times. One of the splits was then prepared ten times and one of these solutions was analysed ten times. A total of 28 repeat analyses were therefore derived from a single sample. The analytical repeats estimate analytical variance, the analytical and fusion repeats combined estimate the analytical and sample preparation variance. All the repeat samples together give the combined sample splitting, preparation and analytical variance, Table 48.

The mean relative errors for the major and minor elements are generally acceptable although the alkalies and alkali earths show a slightly large error. The trace elements have much higher variances. Both V and Ce have unacceptably high values, Y and Ba are borderline. Nevertheless these are not bad results for trace element analyses on a major element analytical programme. A comparison of the different variances shows that it is the analytical process itself which contributes overwhelmingly to the total analytical error.

The second method splits a single sample twice, once at the sample splitting stage and once during sample preparation. An analytical repeat gives three repeat analyses per repeated sample. Twelve repeats out of 100 samples gives a repetition rate of 12 percent.

Most of the variance is again accounted for by the analytical method, Table 49A. The total mean relative error for the different elements are again highly acceptable and show the plasma to be extremely

precise. The machine was not at its most efficient due to a deficient nebuliser and so precision should generally be better than this. The F test statistic shows all the elements to be well above the critical value with the exception of Ce, Table 49B.

The accuracy of the KC ICP analyses was checked by running standards as unknowns. Standards of granite composition were chosen, the granite NIM-G, the syenite NIM-S, the potash feldspar BCS 376 and two internal King's College standards of acidic composition, KC12 and KC13. Repeat analyses on the same solution gives the analytical variance only. Precision is quoted as mean relative error and accuracy as absolute error. This is the difference between the observed and reported value as a percentage of the reported value. The reported values for the international standards are derived from Abbey (1975), question marks signify uncertain values. Dr. N. Walsh supplied the values for the KC standards.

The results, Table 50 show that the mean relative error for most components is below five percent. The exceptions are those present in very low levels. In addition V, Ce and Sr also show unacceptably high analytical variance. Components with high absolute errors either have uncertain reported values or are present in low levels. With the exception of V, Ce and Sr the results show that the ICP analytical method is not only precise but also accurate.

## B.4 LOSS ON IGNITION DETERMINATIONS

Seventeen different sample powders were duplicated representing 13 percent of the total number of analyses.

The adsorbed water ($H_2O-$) results have a mean relative error of 21.1% and an F statistic of 11.6. Although the former seems rather high the latter value is greater than the critical value of 2.4 for 95 percent confidence limits. These analyses are therefore acceptable.

The loss of ignition analyses have a mean relative error of 2.6 percent and an F statistic of 1035. The technique clearly has good precision.

## B.5 TRACE ELEMENTS ANALYSED BY IC XRF.

Precision data for seventeen different repeat samples show that only five elements have a total (analytical + sample preparation + sample splitting) error of more than 10 percent, Table 51A. The general levels of precision for all the elements are disappointingly high. The F test statistic however shows that the natural data variance is significantly greater than the total error for all the elements. The margins for Th and Y are an order of magnitude less than for the other elements.

A comparison of total error and method error (analytical + sample preparation error) shows that zirconium and niobium both have significantly larger method errors. This is usually the result of the elements being concentrated in one, accessory, mineral, zirconium for example in zircon and niobium in rutile.

Five samples were reground to test whether the poor precision was due to the relatively coarse nature of the powder. A comparison of total error with total and regrinding error shows that some elements have increased whilst others have decreased their variance, Table 51B. There would not therefore seem to be a direct correlation between grain size and analytical precision.

Precision analyses on the repeats of a single sample, Table 51C, show that the variance for a large number of elements have been affected by sample splitting. This implies significant inhomogeneity in mineral content between the different subsamples. The sample was a fresh granite of medium grain size. The original sample was split into ten 100g subsamples. This suggests that these subsamples are insufficiently large to ensure sample homogeneity in medium grained granites.

Comparison of the precision data for the XRF and ICP trace element analyses shows that the former is more precise for every element, Table 51D. Taking into account that the trace elements were analysed on the ICP major element programme and the considerably faster rate of analysis then the results compare very favourably.

## B.6 BORON, LITHIUM AND TIN ANALYSED BY KC ICP

Errors generated at the various stages in the preparation and analysis of the samples are summarised in Table 52A. Analytical errors for boron and lithium are very low, confirming the precision of the ICP method. Both elements show a significant increase in error due to the fusion and sample splitting steps. This is due to the location of the elements in single mineral phases, tourmaline for boron and mica for lithium.

By contrast, the tin analyses are highly erratic. This is unfortunately not the result of long term drift but short term noise. The samples (with one exception, 1150) contain very low concentrations of the element. If sample 1150 is included in the precision statistics then reasonable values are obtained but since it represents a mineralised tourmaline selvedge it is unrepresentative and should be excluded. Its exclusion shows that the remainder of the data variance can be explained by analytical error so these analyses cannot be used. The analyses have however been grouped semi-quantitatively into four groups, Table 52C. From the mean of the total error (100.6ppm), a cut-off value of 300ppm has been calculated (representing the mean + two standard deviations). This compares favourably with the minimum detection limit calculated earlier. The first group representing the bulk of the samples falls below this value and therefore below detection. The remaining values are distributed in the remaining groups without any obvious pattern.

Accuracy data for B, Li and Sn is extremely hard to establish as no suitable silicate rock standards are available. NIM-G is reported to contain 16.4ppm Li (Steele et al 1978) and the observed value agrees well, Table 52B. A boro-silicate glass standard, kindly supplied by Carol

Lister from the Natural History Museum, was analysed as the boron standard. The mean value, 9.9ppm contrasts to the reported value (Carol Lister, pers. comm.) of 13.04ppm. This discrepancy may be explained by the precipitation of colloidal silica during the preparation of the standard. Boron may have been complexed and removed at the same time. The accuracy error of 24 percent is therefore considered to be an outside estimate and values are confidently thought to be better than this. No accuracy data was obtained for Sn.

## B.7 CHLORINE ANALYSED BY WET CHEMISTRY

The precision and accuracy data for the chlorine analyses show that the method has not been particularly successful, Table 53. The relative errors are all high. Although analytical error is marginally less than the data variance, the increased error associated with sample preparation and sub-sampling accounts for all the data variance and the analyses cannot be used.

## B.8 SPECIFIC GRAVITY DETERMINATIONS

Precision variance was calculated from thirteen repeats. The mean difference of 0.03 and mean value of 2.64 gives a mean relative error of 1.1%. The data variance is $1.23 \times 10^{-3}$, the analytical variance is $4.87 \times 10^{-4}$ resulting in an F value of 2.53. Both parameters indicate that the determinations have been extremely precise. No accuracy estimates were undertaken.

# APPENDIX C

## METHOD OF CALCULATING DEGREES OF FILLING

## C.1 INTRODUCTION

The underlying assumption in fluid inclusion studies is that the fluid trapped in the mineral phases are representative of the fluids from which the mineral was crystallising. The characteristics of the fluid such as its temperature and salinity may thus be derived from studying the fluid inclusions. The passage of fluids up fractures is likely to be pulsatory (Sibson et al (1975)). The evolution of the fluids with time can therefore be established by investigating the characteristics of each fluid inclusion population.

Roedder (1967) established the criteria upon which fluid inclusion generations could be resolved on the basis of their primary, pseudosecondary or secondary characteristics. In practise it is extremely difficult to classify an inclusion with any certainity into one of these three groups. This is because of the small size of the sample and its essentially two dimensional nature which does not allow for a realistic evaluation of the spatial association between fluid inclusions. This leads to considerable wastage as unclassified inclusions should not be used. Further complications arise from the relative ages of different samples. Different crystals grow at different times, secondary inclusions in one sample may be primary inclusions in a later sample.

The degree of filling of fluid inclusions provides an easier and more satisfactory method of classifying inclusion populations. The degree of filling is defined as the ratio of the liquid volume to the total volume of the inclusion expressed as a fraction or a percentage. Charoy (1975) has already distinguished between inclusion groups having high, medium or low degrees of filling. If degrees of filling could be calculated rather than subjectively quantified then large numbers of

observations could be made and the inclusions split into their component populations statistically.

Degrees of filling can be used to distinguish between different generations of fluid because it is directly related to the homogenisation temperature and salinity of the fluid inclusions. The three variables, homogenisation temperature, salinity (in equivilant wt. percent NaCl) and degree of filling are dependent, that is to say that one can be calculated from the other two. Homogenisation temperature is the easiest and most accurately measured. Salinities are the most difficult to measure and most liable to appreciable error. Salinities may be calculated instead using homogenisation temperatures and the degree of filling. Alternatively, degrees of filling can be used to estimate homogenisation temperatures if an estimate of the fluid salinities can be made.

## C.2 METHODS OF CALCULATING DEGREES OF FILLING

One of the earliest attempts to quantify degree of filling was made by Kelly and Turneaure (1970). They used a U-stage to generate clay models of the inclusions. The weight ratios of the different phases gave the degree of filling.

A number of alternative methods of obtaining degrees of filling were investigated. One possibility was the use of stereoscopic imagery adapted from a method described by Chiat (1977). Another was the use of microscopic optics to measure the various dimensions of the inclusions.

All these methods are either extremely time consuming, impractical or innaccurate. The stereological method calculates degrees of filling quickly, simply and accurately from a two dimensional image of the fluid inclusion.

## C.3 STEREOLOGICAL METHOD

Stereological techniques are widely used in ore mineralogy to determine the shape of certain mineral phases. In principal, large numbers of two dimensional observations are made to infer the three dimensional relationship between phases. Instead of looking at one object from a number of different angles, a number of different but similar objects are observed from a single angle. A picture then emerges of the "average" shape of the object. This method assumes that the objects are orientated randomly through space or that the angles of observation are random with respect to the objects. The method implicity requires a large number of observations to be made which are then processed statistically.

### 1 AREA RATIOS

Area ratios have been used directly or indirectly to calculate volume ratios, Underwood(1970), Mayhew & Cruz (1973), Mayhew & Cruz Orive (1974). Although this may be done for solid objects it will be seen that these techniques cannot be used to calculate the phase ratios of fluid inclusions.

A variety of inclusion shapes have been modelled by ellipsoids. Oblate ellipsoids have two equidimensional major axes, a smaller third axis and are discoid in shape. Prolate ellipsoids have a major axis and two equidimensional minor axes and are rugby ball shaped. The ratio of the major axis (a) to the intermediate axis (b) is here termed eccentricity and is equal to unity for oblate ellipsoids. Ellipsoidality refers to the ratio of intermediate to minor (c) axes and is unity for

prolate ellipsoids.

The relationships between degrees of filling, area ratios, inclusion shapes and orientation for oblate and prolate ellipsoids are expressed in Figure 77. When ellipsoidality is unity for oblate and eccentricity is unity for prolate ellipsoids then the inclusions are spheres. A single line defines the relationship between the true degree of filling and the area ratios. The series of lines lying above this line correspond to area ratio maximums which are observed when the intermediate and minor axes are parallel to the plane of viewing. The lines below represent area ratio minimums observed when the maximum and intermediate axes lie parallel to the plane of viewing.

These diagrams illustrate that:

- For a given degree of filling the area ratio is strongly dependent upon the ellipsoid shape. The more they diverge from sphericity the more divergent the area ratio lines become. This is summarised in Figure 77c. For an inclusion of specified shape the area ratio may lie between the maximum and minimum value depending upon its orientation with respect to the field of viewing. If the inclusion orientations are random for a fixed angle of observation then a wide range of area ratios could be observed for inclusions having a fixed degree of filling. This could lead to these orientation effects being confused with boiling assemblage inclusions.

- The area ratios cannot be used directly to obtain the true degree of filling of an inclusion unless it is spherical (unlikely) or its shape and orientation can be specified, parameters which cannot usually be measured.

## 2 CALCULATED DEGREES OF FILLING

An inclusion's degree of filling cannot be determind directly from two dimensional observation but it can be calculated if certian assumptions are made. The derivation of the equations to calcuate the phase ratios is given in Table 54. This section is concerned with justifying these assumptions and establishing the relationship between the true degree of filling and the calculated value.

The first assumption is that all inclusions are, or approximate to, ellipsoids. This cannot be proven but it is supported by circumstantial evidence. Roedder (1967) outlined the way in which fluid inclusions form and has pointed out that they undergo subsequent modification through solution and redeposition. This is in response to an energetic requirement to minimise their surface energy and hence surface area. The final shape of the inclusion will be a compromise between a sphere and a negative crystal shape. The latter is determined by the crystallographic system of the host mineral. Isomeric minerals have three equi-dimensional crystallographic axes, dimeric minerals have two equi-dimensional axes whilst trimeric minerals have three independent axes. The most common fluid inclusion host minerals are grouped in Table 55 according to their crystallography. The most important minerals for fluid inclusion studies fall within the isomeric and dimeric groups. Their entrapped inclusion are therefore likely to correspond to spheres or oblate and prolate ellipsoids.

The second assumption is that the orientation of the fluid inclusion

is such that the largest axis (a) and the intermediate axis (b) are in the plane of viewing. Lastly the inclusion is assumed to be prolate, i.e. that the third, unobservable axis is taken to be the same as the intermediate axis. The effects of making these assumptions (the difference between calculated and real degree of filling) for inclusions of different shape and orientation are illustrated in Figures 78 and 79.

**Discussion**

These figures express the relationship between the maximum, intermediate and minimum calculated degrees of filling (ADF) for inclusions of specified degree of filling but of variable shape and orientation.

The maximum apparent degrees of filling (max) occur when the calculated value of total volume is overestimated. This happens when the maximum and intermediate axes are parallel to the plane of observation. The intermediate calculated degree of filling (int) under-estimates the true degree of filling because the maximum (a) and minimum (c) axes lie parallel to the plane of viewing. The minimum calculated degree of filling (min) results from observing an inclusion with its major axis (a) at right angles to the plane of viewing. There are a series of minimum curves depending upon the degree of eccentricity (a/b ratio) of the inclusions.

The diagrams show the calculated degrees of filling for inclusions in the three most extreme possible orientations and for all reasonable inclusion shapes. They show that the maximum (ADF max) and intermediate (ADF int) calculated degrees of filling are independent of eccentricity (a/b ratio). This parameter strongly affects the minimum calculated

degree of filling (ADF min). This is because the more eccentric (elongated) the inclusion the greater the difference in observed areas when the major axis is at right angles to or parallel to the plane of viewing, e.g. Plate 14h and 14a. Thus for a true degree of filling of 0.9 and an ellipsoidality and eccentricity of 3.0, the maximum degree of filling is 0.965, the intermediate degree of filling is 0.70 and the minimum degree of filling is 0.10. Large errors can therefore arise if, in estimating the true degree of filling, the assumption that the major axis lies parallel to the plane of viewing is not fulfilled. Fortunately it is relatively easy to identify such inclusions since their perimeters do not lie within the plane of focus. If a U-stage is used to ensure that this condition is fulfilled or if the inclusion is discarded then the maximum and intermediate degrees of filling represent the limits of the apparent degree of filling for inclusions of different shape and orientation.

If the orientation of the inclusions are random then there is equal probability of making an observation anywhere between these limiting values. In the example above, the mean apparent degree of filling (ADF mean) would be 0.8325 for a population of such inclusions having different orientations. A line corresponding to the value of mean apparent degree of filling (mean) is plotted in Figure 79 for inclusions having a true degree of filling of 0.9. A series of similar lines could be constructed for different true degrees of filling.

The departure of the mean apparent degree of filling from the true degree of filling is quite considerable, particularly for extreme ellipsoidalities. However when inclusion shapes become extreme the inclusion walls begin to impinge upon the gas phase, causing it to distort. This distortion can be observed as a disc of white light in the

centre of the gas bubble, Plate 14f. Since this phase is spherical it should be completely dark due to total internal reflection. If inclusions with distorted gas phases are ignored then the ticks upon the lines in Figure 79 represent the maximum values of ellipsoidality (b/c ratio) for inclusions of different eccentricities (a/b ratio).

If there is an even spread of ellipsoidalities between minimum (1.0) and maximum value then the average apparent degree of filling will lie half way between these points. The position of these points in Figure 79 (dark circles) show that they approach acceptably close to the true degree of filling. Given that there will also be a spread in the values of eccentricity these calculated mean apparent degrees of filling will approximate even more closely to the true degree of filling. The percentage error will be negligable.

## 3 DISCUSSION

Area ratios cannot be used directly to derive degrees of filling. Degrees of filling can be calculated subject to certain assumptions and restrictions. The restrictions mean that inclusions whose major axes do not lie within the plane of viewing and those with distorted gas phases are discarded. The assumption that the inclusions are prolate is then a reasonable one. This assumption is anyway likely to be true for inclusions trapped in dimeric minerals such as quartz. A further assumption is that the inclusions will be randomly orientated with respect to the angle of viewing. This will be the case for mineral fragments observed under oil immersion or sections intersecting quartz grains at random but not for orientated sections taken from mineral

crystals.

Accepting the previous restrictions the calculated degrees of filling for a single generation of inclusions having different shapes and orientations will have a mean value close to the true degree of filling. The variance in the calculated degrees of filling will be compounded of the natural variance in the true degree of filling and the error variance due to the effect of orientation and shape. Additional error variance will be contributed by inclusions which have been included in the data set but which should have been discarded. These values will either fall outside the population distribution and can be discarded altogether or they may fall within the distribution where they will have little effect as long as they are restricted in number.

Most samples will contain several generations of inclusions which will result in a multiple distribtion of calculated degrees of filling. This compound distribtuion can be split into its component populations using conventional statistical techniques.

The calculation of the degree of filling requires that the areas of the total inclusion and the gas phase be obtained and the largest dimension of the inclusion be measured. For inclusions containing daughter phases the areas of the solid phases also have to be obtained. These areas can then also be used to calculate the salinities and densities of the inclusion fluids.

There are a number of ways in which the image of an inclusion may be recorded. The inclusions can be drawn freehand or more accurately using a microscope attachment or television camera (the inclusion image being traced directly off the screen). The images may be photographed and then

projected and traced or printed. The areas and dimension of the inclusions may be obtained using graph paper or by cutting out and weighing card or photographic paper (in which case the diameter of the gas phase has also got to be measured). The easiest and quickest method however is to use a digitiser.

A simple computer programme was written to calculate the degree of filling for inclusions whose areas had been measured directly or by weighing card. The salinities and densities of inclusions containing daughter phases can also be calculated.

The method was tested on plasticine models and on inclusions from quartz samples collected from south-west England. A number of plasticine models of fluid inclusions of different shapes and different degrees of filling were generated. Using an overhead projector the two dimensional images were traced and the areas found from which the degrees of filling were calculated, Table 56. Although the calculated degrees of filling for individual inclusions differ significantly from the true value, the mean values for each group of inclusions lies reasonably close, even though only seven inclusions were modelled.

The results of the degree of filling calculations for the inclusions have already been described and discussed in Chapter 5. In conclusion the results from the calculated degree of filling are substantially similar to the results obtained by heating and freezing studies. These two practical experiments would seem to substantiate the validity of this technique.

## C.4 CONCLUSION

The true degree of filling of an inclusion population can be derived from the mean of the calcualted degrees of filling. The salinites of saturated inclusions can also be determined.

The degrees of filling can be used to distinguish between generations of inclusions and therefore their parental fluids. They can be used in conjunction with determined homogenisaion temperatures to give the salinity of the fluid. Alternatively they can be used in conjunction with either observed or estimated salinities to give homogenisation temperatures.

The method has a number of advantages. It is extremely quick and simple and is ideally suited to handling large amounts of data. It is best used on either thin sections, grains or fragments. Useful fluid inclusion information can therefore be derived from petrological studies of rock samples. The use of mineral fragments under oil immersion obviates the need to make expensive and time consuming polished thick sections. Mineral grains from rock samples or stream sediments can be examined in the same way which has great significance with regard to the increasing use of fluid inclusions in mineral exploration.

# APPENDIX D

## STANDARDISATION OF THE LINKAM TH600 HEATING AND FREEZING STAGE

## D.1 CALIBRATION USING CHEMICAL STANDARDS

The heating and freezing stage was calibrated using standard chemicals having known melting and freezing points. Some of the melting point standards were kindly supplied by British Steel from the National Standards Laboratory, whilst the others were obtained from Reichert.

A number of problems were encountered in standardising the higher temperature range of the stage. A large number of the standards sublimed. Carbazole, Anthraquinone and Anisic Acid did so particularly badly. Recrystallisation of the sublimate occurred on the observation window, obscuring the field of view. This could be prevented for the most part by sandwiching the chemical between two microscope cover slips of thin optical glass. The flushing of inert gas through the chamber caused too great a thermal gradient across the specimen for the generation of accurate end points.

The conditions under which standardisation runs were carried out matched the likely future operating conditions. Thus although greater accuracy may have been achieved using very slow heating rates, a rate of $20\ ^{o}C/min$ was selected during the initial stages of each run. This was lowered to $2\ ^{o}C/min$ near to the melting temperature. The latent heat of sublimation for those standards which sublimed severely was sufficiently large to change the temperature of the heating block. Consequently a smooth heating rate could not be obtained.

The initial melting point of the standard was taken to be the point at which vapour, liquid and solid were in equilibrium. The 50 and 100 percent melting temperatures were also measured. Some standards, notably potassium dichromate, showed a marked disparity between these three

values, presumably due to impurities. In such instances the mean value was taken. Differences in melting points in consecutive runs on some resolidified standard samples were presumaly also the result of changing concentrations of the impurities as evaporation occurred. A fresh sample was used for each run if this occurred.

Melting points were also found to be sensitive to crystal grain size. In order to standardise the error all the samples were first ground to a very fine powder in an agate pestle and mortar. A suitable quantity which just filled the field of view was smeared thinly on a glass cover slip. This was most easily achieved by suspending the powder in some quick drying liquid which was not a solvent (usually ethanol) and then dropping it onto the cover slip. Any excess could then be scraped away. Larger quantities had to be used for chemicals which sublimed to ensure that melting occurred before the sample evaporated completely.

Few problems were encountered with the freezing standards. The liquids were trapped by meniscal forces between fragments of cover slip glass. There were occasionally problems in getting the liquids to freeze but having done so, the melting points upon reheating were sharp and easily defined.

The results of the heating and freezing standardisation runs are summarised in Table 57 and Figure 80. Very little correction was found to be necessary. The techniques evolved for standardisation runs were found to give perfectly adequate results. However, there is clearly a considerable difference between the physics of the standardisation technique and fluid inclusions. No consideration has been given to the possible effects of the mass of the standard materials in contrast to the fluid inclusion or the possible differences in thermal lag across the

glass cover slips and a polished wafer. A standardisation technique is desirable which is as analagous as possible to the nature of fluid inclusions.

## D.2 CALIBRATION USING SALT INCLUSIONS

The addition of a salt to water depresses its freezing point. The phase diagrams of salt - $H_2O$ systems show that this depression reaches a minimum at some critical salt content. This corresponds to the eutectic.

If salt crystals are grown from a saturated solution they will contain fluid inclusions. As long as the solution is pure the trapped fluid will be saturated with respect to its salt with which it is in contact. If heated, the solubility of the salt increases and the salinity of the fluid increases by dissolving more salt from the inclusion walls. Conversely, if cooled, the salt will be deposited upon the sides of the inclusion.

In the simplest system such as KCl - $H_2O$, Figure 81, precipitation of KCl around the inclusion will take place as the fluids are cooled. The inclusions will apparently shrink. At room temperature, for example, 22.7 wt. percent of KCl is dissolved in solution but by the time it has cooled to 0 $^{o}$C there is only 21.6 wt. percent KCl in solution. The difference has been deposited on the inclusion walls. If the inclusion is rapidly cooled then the KCl will not precipitate on the walls. Instead freezing will occur well below its eutectic and the salt and ice crystals will precipitate as a symplectite.

Upon reheating such an inclusion, there will be a "first melt" at the eutectic (-10.7 $^{o}$C) corresponding to the melting of the ice and the dissolution of some of the KCl crystals in the resultant liquid. The liquid will have a 12.7 wt. percent KCl content. On further heating the remaining KCl crystals will dissolve until at room temperature the inclusion fluid is back to its starting composition of 22.7 wt. percent

KCl. The eutectic of the rapidly frozen inclusion will be less definitive as crystals of KCl will remain after all the ice has melted. An inclusion which has been more slowly cooled will have the eutectic mixture concentrated in the centre and the melting point should be more easily noticed. This is rarely possible due to the metastability of the inclusions.

A number of other salts behave similarly to KCl such as KBr, KI, $NaNO_3$, CsI, RbI and $NH_4NO_3$ (explosive!). They differ only in the position of the eutectic and the exact shape of the solidus curves.

Other salts have a more complex phase relationship with water, forming hydrates. Sodium chloride is an example, Figure 82. At room temperature NaCl is stable and when cooled will precipitate on the walls of its inclusions. At $0.1^{o}C$, NaCl becomes unstable and reacts with water to form the hydrate $NaCl, 2H_2O$. Since a phase change has occurred this is termed a peritectic or reaction point. This reaction only involves the NaCl which precipitated on the inclusion walls and the solution in the inclusion. Once the hydrate has formed the system can continue to cool, precipitating more hydrate on the walls of the inclusion. When the eutectic is reached at $-21.1^{o}C$ the remaining solution crystallises as a mixture of hydrate and ice. Rapid cooling of the inclusion will cause an intimate mixture of hydrate and ice to form which will make the end point more difficult to observe precisely. Other common salts which form hydrates are NaBr, NaI, Figures 83, 84, $Na_2CO_3$, $K_2CO_3$, $KHPO_4$, $KPO_4$, $Na_2S$, $Na_2SO_4$, $NaHPO_4$, $NaP_3O_{10}$, $LiNO_3$, KOH and NaOH.

The peritectics and eutectics of a number of salt-$H_2O$ systems are accurately known and can be used as thermometers, Mellor (1963). A number of requirements have to be satisfied before this method can be used. The

laboratory standards have to be pure. Although laboratory standard reagents were used in this pilot study it would be preferable to use spec. pure chemicals. Since only very small quantities are used the cost should not be prohibitive. The salts must contain inclusions and be transparent so that they can be seen clearly. If this is not the case for the manufactured products then the salts can be recrystallised. The salts have to be examined under oil immersion. Tritolyl phosphate was found to be suitable as it remains liquid down to temperatures of $-120^{o}C$. Studies of polished quartz wafers showed that oil immersion had negligable effects upon inclusion freezing points.

Suitable salts are those which are commonly available, inexpensive, safe to use and have accurately known eutectics and peritectics which span a good range of temperatures. The following salts were selected: KCl, NaCl, KBr, NaBr, KI, NaI, $K_2CO_3$, $Na_2CO_3$ and $NaNO_3$.

**Discussion**

The results of these experiments are summarised in Table 58 and Figure 85. KBr, KCl, NaCl and $NaNO_3$ could be used directly in laboratory reagent form but the remainder had to be recrystallised. Various techniques were used. The most consistantly successful was the evaporation of a saturated solution at room temperature in a dessicator. Occasionally seed crystals were necessary to precipitate growth.

Fluid inclusions in both recrystallised and laboratory crystals were both biphase and monophase. On cooling or freezing some of the monophase inclusions nucleated a gas phase. These remained present after melting, indicating that the inclusions were metastable. Monophase inclusions which nucleate a gas phase before the last melting of the solid phases

can still be used and give accurate end points. Monophase inclusions which nucleate a gas phase with the simultaneous disappearance of the solid phases should be avoided as they give rise to spurious end points. These inclusions re-lose their gas phase upon freezing. Difficutlies were also encountered with some inclusions which would not freeze even when cooled to $-120^{o}C$. A combination of these last two difficulties together with a general scarcity of inclusions meant that $K_2CO_3$ could not be used efficiently.

Salts having a simple binary system with $H_2O$ without intermediate hydrated compounds have inclusions with simple melting histories, Plate 18. Upon freezing the inclusion contents commonly form a clear cryptocrystalline glass, Plate 18a. With increasing temperature, recrystallisation and coarsening of the ice crystals occurs, accompanied by some melting, probably caused by minor impurities. The inclusion contents take on a brown, semi-opaque aspect, Plate 18b. As the temperature continues to rise the ice crystals continue to melt. At the eutectic rapid melting of the ice crystals occurs. This end point is precise and readily observed and so makes an excellent calibration point.

Phase changes in hydrated systems are more complex, Plate 19, 20. Inclusions are generally more difficult to freeze, temperatures down to $-120^{o}C$ being commonly required. This means that the inclusions are always rapidly crystallised. It is also difficult to observe whether freezing has occurred as the solid phase is usualy a transparent glass whose presence can frequently only be detected by a slight compression or distortion of the gas phase. The glass is a cryptocrystalline symplectite of hydrate and ice crystals. As the eutectic is approached upon reheating the glass recrystallises. A discrete rim of birefringent hydrate forms around the edge of the inclusion whilst the centre comprises a coarse

mixture of hydrate and ice crystals, Plate 19b. At the eutectic all the ice crystals melt leaving the hydrate crystals. It is consequently extremely difficult to observe the precise point at which this occurs as all that can be seen is a marginal lightening at the centre, Plate 19c. The eutectics of hydrated systems are therefore unsuitable as thermometric points. As the temperature rises the hydrate rim grows and becomes better developed through diffusion, Plate 19d, 20a. At the peritectic or reaction point the hydrate begins to melt rapidly providing a precise and clearly observable end point which is thermometrically suitable. In systems containing more than one stable hydrate below room temperature e.g. NaBr and NaI, the reaction point between the two hydrates is observed. The hydrate rim and central crystals react with the fluid to form a new hydrate, Plate 19e, 20 b,c. This kind of peritectic appears to be equally clear and can also be used as a calibration point. The newly formed hydrate goes on to melt in the normal fashion, Plate 19 f, g, h, 20 d to i.

Since the peritectics in hydrated salt systems are so definite and easily observed then the observation of phase changes in fluid inclusions in salts would appear to be an excellent method of studying hydrate stability fields. Observations made in this investigation suggest the presence of three hydrates not previously described in the NaI, NaBr and $K_2CO_3 - H_2O$ systems. The peritectics in the first two systems correspond to their reported eutectics. It is probable that these reported eutectics are the peritectic temperatures and that the real eutectics have not yet been investigated. Due to the problems in determining eutectic temperatures by the inclusion method, these values can only be approximately defined at -45 and $-33\,^{o}C$ for the NaI and NaBr - $H_2O$ systems respectively. Unfortunately the actual composition of these two hydrates cannot be determined from this method. The presence of a third hydrate in

the $K_2CO_3$ - $H_2O$ system is less certain due to the limited number of observations made. A probable eutectic was observed at around $-38^{o}C$ and a further peritectic at about $-7^{o}C$. The hydrate formed at this reaction point did not melt below $100^{o}C$ and is probably $K_2CO_3$, 1.5 $H_2O$, Mellor (1963). The composition of the first hydrate remains unknown. The shape of the solidus curve would seem to support this observation, Figure 85, Mellor (1963).

Certain calibration points fall significantly away from the calibration curve generated using the fluid inclusion method, Figure 86. The most likely reason for this is either impurities or inaccurate published values. The published and observed values for these points are summarised in Table 59.

Multi-hydrate systems are useful in several ways. It is clearly convenient to obtain more than one calibration point in one run. The two points can also be used to check for drift in the temperature scale as other variables such as thermal mass or gradient are eliminated. Hydrate reactions frequently occur above $0^{o}C$ and provide useful intermediate calibration points for the lowest temperature range of the heating curve.

## D.3 CONCLUSIONS

The Linkam TH600 heating and freezing stage was calibrated using standard melting point chemicals and fluid inclusions in salt crystals. The two calibration curves are not substantially different. Problems were encountered in the first method with the sublimation of the chemicals. A satisfactory calibration curve was generated nonetheless. The fluid inclusion method offers a number of advantages. Most importantly, the calibration is carried out in conditions analogous to those of the actual fluid inclusion runs. The same variables are therefore incorporated into the calibration curve.

The fluid inclusion technique has no serious problems and it is easy and simple to perform. Some inclusions were difficult to freeze, particularly in the hydrated salts. Super-cooling was necessary to achieve freezing and consequently the frozen inclusions comprised an intimate mixture of solid hydrate and ice. This means that the eutectics in hydrated systems could not be easily seen and so could not be used. The eutectics of non-hydrated systems and the peritectics of hydrated systems however both give extremely sharp and well defined end points with good repeatability. The following salts were successfully used: KCl, NaCl, KBr, NaBr, KI, NaI, $Na_2CO_3$ and $NaNO_3$. Some salts such as NaBr and NaI contain more than one useable end point. The end points spanned a useful temperature range from -32 to +33 $^{o}C$, Figure 87. As a result of these studies, three new hydrates may have been identified in the NaI, NaBr and $K_2CO_3 - H_2O$ systems and their peritectic temperatures have been defined. Modifications to the reported KBr and $NaNO_3$ eutectic temperatures may be necessary.