MINERALISATION, GREISENISATION AND KAOLINISATION AT GOONBARROW CHINA CLAY PIT, CORNWALL, U.K.

Colin James Bray, B.Sc.

Pembroke College

Thesis presented to the University of Oxford

for the degree of Doctor of Philosophy

Trinity 1980

Volume I : TEXT

FRONTISPIECE

Goonbarrow china clay pit looking north east. The water monitor is being operated in the Old Beam area. Imperial Goonbarrow lies off to the extreme right. The china clay suspension is pumped up from the pit bottom to the rotary classifiers in the centre of the photograph. Coarse unkaolinised granite is taken by the conveyor to the waste heap.

Nothing worth knowing can be understood by the mind.

Woody Allen, in Manhattan, 1979.

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Short Abstract

Goonbarrow, a China Clay pit situated within the St. Austell granite China Clay region, is the subject of a varied geochemical and isotopic study to determine the mode of genesis of the kaolinite and associated tin/tungsten mineralisation. Detailed geological mapping in conjunction with a geochemical study of the micas indicated that Goonbarrow is situated at the junction of the petrographically distinct phases of the St. Austell granite. An unusual assymmetric curved-feldspar-crystal pegmatite is found at the junction. Elvans at Goonbarrow and three other locations within the St. Austell granite are shown to be intruded during hydrothermal activity and in some cases after major vein formation. Three main types of vein were recognised in Goonbarrow, the major ones being spatially associated with zones of kaolinised granite. A potassium/ argon age study showed that the granites, pegmatite and greisens (and by inference tin/tungsten mineralisation) were formed at about 280 $\pm$ 10 m.y. Four elvans, including Goonbarrow, were dated at around 272 m.y. Three of these elvans crosscut major vein swarms. Age determinations on fine grained muscovite produced predominantly during kaolinisation and several kaolinised potassium feldspars also gave Hercynian ages. Scanning electron microscopy studies on daughter minerals in fluid inclusions indicated the presence of Al, As, Ca, Cl, Cu, Fe, K, Mg, Mn, Na, S, Sn and Zn although many of these elements were not present in minerals in the pit. Temperatures, pressures and salinities of vein fluids were determined by conventional fluid inclusion studies, which also indicated that the veins were boiling. Hydrogen and oxygen isotope studies on vein quartz and greisen muscovites coupled with a re-interpretation of previous work and the fluid inclusion study produced a new model for the genesis of Cornish China Clay. Kaolinite genesis from the vapour phase of hot boiling fluids intimately associated with greisen bordered quartz/tourmaline veins of Hercynian age is favoured.

Long Abstract

Goonbarrow, a China Clay pit situated within the St. Austell granite China Clay region and on the site of two nineteenth century tin mines, is the subject of a varied geochemical and isotopic study to determine the mode of genesis of the tin, tungsten and kaolinite.

Detailed geological mapping in conjunction with a geochemical study of the micas indicated that Goonbarrow is situated at the junction of two petrographically distinct phases of the St. Austell granite - a biotite-muscovite and a lithionite granite. Situated at this junction is an unusual assymmetric curved - feldspar - crystal pegmatite. The direction of growth and branching of feldspars show that it developed on a hanging wall of biotite-muscovite granite and was followed by crystallisation of lithionite granite. Elvans at Goonbarrow, Gunheath, Melbur and Dorothy China Clay pits, within the St. Austell granite, are shown from petrographic studies to be intruded during hydrothermal activity and, at the first three locations, after some major vein formation - unlike other areas of Cornwall. Three main types of vein were recognised in Goonbarrow (i) quartz/tourmaline $\pm$ cassiterite/wolframite veins with greisen borders, spatially associated with zones of intensely kaolinised granite, (ii) multimineral veins (fluorite, topaz, apatite, lollingite, arsenopyrite, wolframite), with no greisen borders and not associated with kaolinisation zones, (iii) barren quartz veins with no greisen borders.

A potassium/argon age study showed that the granites, pegmatite and greisens (and therefore the associated tin/tungsten mineralisation) were formed at about 280 $\pm$ 10 m.y. Previous U-Pb dates for Cornish mineralisation, producing ages between 50 and 290 m.y., were

re-interpretated using more modern graphical techniques to give an age of 290 m.y. The elvans at Goonbarrow, Gunheath, Melbur and Dorothy were dated at around 272 m.y. and are in excellent agreement with conventional rubidium-strontium dates on unkaolinised Cornish elvans. In this case the elvan dates place further constraints on the date of tin/tungsten mineralisation since they crosscut these veins. It is considered on mineralogical and textural grounds that the elvans were intruded during hydrothermal activity, and that the major kaolinisation event occurred between 301 m.y. (the Rb/Sr intrusion date of the St. Austell granite) and 272 m.y. Fine grained muscovite from kaolinised granite, produced predominantly during kaolinisation, and a combined sample of several kaolinised potassium feldspars (a mixture of sericite and kaolinite) also gave Hercynian ages. All these results indicate that kaolinisation at Goonbarrow is of Hercynian age.

A novel adaptation of scanning electron microscopy was utilised to determine the composition of daughter minerals in fluid inclusions from vein, greisen and granite quartz from Goonbarrow. This indicated the presence of Al, As, Ca, Cl, Cu, Fe, K, Mg, Mn, Na, S, Sn and Zn although many of these elements were not present in minerals in the pit. This suggests that the chalcophile elements were deposited in rock above the present land surface which has since been eroded away and is in agreement with classical Cornish mineralisation theories.

The fluid inclusion study can be summarised as follows:-

1. Boiling was much more intense in kaolinised granite than unkaolinised granite.

2. All veins and greisens were formed from boiling fluids.
3. Quartz/tourmaline and multimineral veins formed at between 140° and 440°C and salinities of 6-40 wt.% NaCl.
4. Cassiterite veins formed from similar fluids to the quartz/tourmaline - multimineral veins i.e. 8-42 wt.% NaCl and from temperature of 140°-480°.
5. The wolframite veins are distinct from other veins in the pit being formed within a very close temperature range 220°-300°C but still from a wide range in salinity, 12-40 wt.%.
6. Inclusions within the elvan were probably of secondary origin, chemically much simpler than the vein fluids, of about 22 wt.% NaCl, were not boiling and were trapped at between 360° and 440°C.
7. Barren quartz veins contained no fluid inclusions.

The presence of boiling inclusion assemblages enabled the calculation of pressure and therefore depth at time of intrusion. The quartz/tourmaline ± cassiterite/wolframite veins were shown to have been intruded at 450°C, 450 bars (1.7 km depth) and 10 wt.% NaCl equivalent, and by boiling and irreversible adiabatic expansion to have cooled to 200°C and increased their salinity to 40 wt.% NaCl equivalent. The elvan was formed at a minimum of 250 bars pressure. The quartz/tungsten veins were formed at about the same depth as the elvan and around 300°C, and were probably intruded after the elvan.

The hydrogen isotopic compositions of fluid inclusion waters, released by decrepitation at about 500°C, for vein quartz vary between $\delta D = -30$ and $+4‰$, although the oxygen isotopic compositions of the mineral vein quartz have a very restricted range ($\delta^{18}O = +13.2$ to $+13.9‰$). The δ L values for greisen muscovites associated with these veins range from -57 to -62‰ and are much more negative than values

obtained by other workers for Cornish alteration micas.

Re-interpretation of previous work coupled with this new data on the hydrogen/oxygen isotopic compositions of vein fluids and greisens produced a new model for kaolinite genesis which was in excellent agreement with the fluid inclusion study. This involved the intrusion of boiling hydrothermal fluids, which cooled, concentrated NaCl and produced the large hydrogen isotopic fractionation. The vapour phase of the boiling fluids was considered to have deeply penetrated the granite altering it to the large areas of kaolinised granite found today. The hydrogen isotopes indicate that the veins were produced from the liquid fraction and the greisens from an early fraction of the boiling fluid.

Previous work in favour of a hydrothermal or weathering origin for the genesis of Cornish China Clay is discussed in the light of this new data. Data previously considered in favour of a weathering origin is able to be re-interpretated in favour of the alternative view. In conclusion a hydrothermal origin is favoured for Cornish China Clay genesis which is intimately associated in this area with tin/tungsten mineralisation of Hercynian age.

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ACKNOWLEDGEMENTS

The writer wishes to offer his sincere thanks to his supervisors, Drs. B.C.M. Butler, K.G. Cox, T.J. Shepherd and E.T.C. Spooner, who provided continual encouragement and much needed advice during the writer's stay in Oxford. The writer's original supervisor, Dr. E.T.C. Spooner, is especially thanked for his insatiable enthusiasm for the project even after moving several thousand miles away, to Canada, in 1978.

The management and staff of English Clay, Lovering and Pochin Ltd., (ECLP) are gratefully acknowledged for their permission to enter several of their China Clay pits and providing base maps of Goonbarrow pit. In particular thanks are extended to Mr. C.M. Bristow, Dr. C. Gronow, Mr. A. Francis, Mr. J. Howe and Dr. I. Wilson, on the geological staff, and Mr. K. Menadue and Dr. M. Pemberton on the pit management side. Very special thanks are due to Mr. Cyril Hancock - pit captain at Goonbarrow.

Professor E.A. Vincent and the entire staff of the Department of Geology and Mineralogy at Oxford are thanked for their cooperation and assistance. In particular Colin Fagg, for help with the electron microprobe, John Arden, Mike Hepher, Clive Johnson, Pam Shreeve and Stephen Wyatt, with the geochemical study, Roy Goodwin and Dr. Paul Taylor, with the geochronological work, Richard ("no chance") McAvoy and Stephen Baker, with photography, Gillian Collins, with draughting, Dr. P.J. Hatchett, with the interpretation of the stable isotopes, and Dr. Don Fraser for help with thermodynamics, are all gratefully acknowledged.

Mr. D. Wesolowski from the Pennsylvania State University, U.S.A., is acknowledged for supplying several of the oxygen/hydrogen isotope analyses.

Dr. Norman Snelling and the staff of the isotope geology group of the Institute of Geological Sciences, London, are thanked for their cooperation and assistance in the K/Ar study. Chris Rundle deserves special mention in showing the writer the intricacies of the I.G.S. high vacuum argon extraction line. Drs. Ian Swainbank and Bob Pankhurst helped on isotope problems and Bob Beckinsale and Max Coleman in interpreting the oxygen/hydrogen work. As well as being the writer's supervisor Dr. Tom Shepherd analysed several samples for their hydrogen isotopic composition. He is also both thanked and cursed for introducing the writer to fluid inclusions in 1974!

Tony Holland helped in collecting specimens in the writers first fieldwork season.

Jerry Skarnulis and Adam Ray-Smith are gratefully acknowledged for help in using the JEOL scanning electron microscope.

The writer wishes to acknowledge the help of his fellow research students, particularly Dr. Tim Barrett, Dr. Mike Carpenter, Roger Gollop, Ian Jarvis, Dave Jones, Mike Watson and Dr. Andy Wood.

Richard Giles helped with photocopying a large proportion of the figures and tables.

Mrs. Kathleen Webb is thanked for typing this thesis with remarkable speed and accuracy.

Financial support for three years is gratefully acknowledged from the Natural Environment Research Council as well as additional funding from the Burdett-Coutts fund.

Finally I wish to thank my parents for assistance in all sorts of ways, particularly financial.

CHAPTER 1

Introduction

The South West peninsula of England, consisting of Cornwall and western Devon, has long been known for its metal mining and in more recent times china clay. These economically important materials are closely associated with the Cornubian granites which occupies the centre of the peninsula. Although Cornwall is recognised as a classic metallogenic province the area still presents many unsolved problems in ore genesis. Good quality china clay deposits of economically extractable size are relatively rare in the world. What special conditions produced such high quality china clay in such a small area? This thesis seeks to answer this question. The Cornish china clay district is in fact one of the largest in the world, the clay being in great demand due to its brightness, smoothness, gloss and opacity, important properties in the manufacture of high quality paper. About 30% of Cornish china clay is used for this purpose. Other major uses include paper filling (50%), ceramics (15%) and miscellaneous purposes (5%) (Menadue, 1979).

Over the past 150 years the origin of the Cornish kaolinite deposits has been very controversial. Two totally different hypotheses have been suggested, a low temperature, supergene, weathering origin and alternatively, production by hot ascending, magmatically derived solutions. The following list shows, chronologically, how this controversy developed until the present day.

1824 Von Buch proposed that Cornish china clay was produced by
1841 Daubree
pneumatolytic action by fluids containing fluoro-silicates or fluoro-borates acting from below.

1878 Collins recognised the association of veins with kaolinised granite and also that fluorine (and to a lesser extent boron) bearing minerals (lepidolite, fluorite, topaz, tourmaline) are present throughout the St. Austell china clay district.

1877 Collins dismissed the hypothesis that kaolinisation was produced by the action of carbonic acid (CO_2) either from the atmosphere or as a solution in water since there was no trace of this gas or of carbonates in the Cornish clay districts.

1908 Hickling was in favour of an atmospheric weathering origin and suggested that the secondary muscovite present in feldspars represented the first stage of the process. He also claimed that the kaolinised granite was shown to be in the form of an irregular surface sheet from borehole data.

1909 Collins presented evidence that kaolinised granite existed under an impermeable roof of country rock (killas) at Carpalla and interpreted this as strong evidence of a hydrothermal origin, a view supported by Butler (1908) and Coon (1913).

1911 Coon suggested that ground water infiltrated the granite via joints and while circulating in the deeper parts, took into solution the agents needed to produce kaolinisation.

1955 1959 Exley substantiated Collins association of veins with kaolinised granite. Late magmatic, initially acid solutions were considered responsible for greisening and later kaolinisation. Boron and fluorine bearing solutions were not favoured since tourmaline and fluorite were attacked by this solution. Carbon dioxide, chlorine or sulphur were also considered unlikely to be involved with kaolinisation since no minerals containing these components had been identified in the china clay pits.

1964 Exley showed that the crystallinity index of kaolinite increased towards major quartz/tourmaline veins thus suggesting that the vein fluids actually caused kaolinisation.

1968a Bristow was in agreement with the work of Exley and described the funnel-like morphology and great depth of the kaolin deposits as also being indicative of a hydrothermal origin.

1969 Konta described the mineralogical similarities between the Cornish and Czechoslovakian deposits. He was not prepared to accept, on the sole occurrence of kaolinised granite overlain by unaltered country rock at Carpalla, that the kaolinite must have been produced by ascending solutions. He also pointed out that no undecomposed granite had been found overlying kaolinised material. The similarity of the appearance of fluid inclusions in unkaolinised and kaolinised granite was also used as good evidence in favour of a non-hydrothermal origin.

1969 Walker (in the discussion of Konta (1969)) mentioned that 40ft of undecomposed granite had been found overlying 100ft of kaolinised granite at Gunheath china clay pit thus invalidating one aspect of Konta's argument.

1976 Keller showed using scanning electron microscopy that texturally Cornish kaolins are relatively open, as occurs in a weathering environment. He also suggested that hydrothermal production of kaolinite would result in a tight texture since the kaolinite would have formed beneath a thick, heavy cover of rock.

1977 Sheppard studied the oxygen and hydrogen isotope ratios of Cornish kaolinites and interpreted the data as being indicative of a low

temperature weathering environment. The possibility of re-equilibration was rejected (see Chapter 7 for full discussion).

1977 Bristow reviewed the evidence for the origin of the Cornish kaolin deposits and was in favour of a preliminary "softening up" phase followed by the main supergene kaolinising event.

This thesis is primarily concerned with contributing to a better understanding of the processes involved using modern geochemical techniques and also investigating the spatially related mineralised veins. Goonbarrow, a china clay pit within the St. Austell granite, offered excellent exposure of tin/tungsten mineralisation and intensely kaolinised granite. Although at one time economic, the tin/tungsten ore is now only produced as an occasional by-product from the high quality china clay. The pit also enabled study of some other important Cornish geological features, notably a quartz-porphyry dyke which crosscuts mineralised veins and an unusual pegmatite developed at the junction of two petrographically distinct phases of the St. Austell granite.

After an initial study of the geological framework of the area, Goonbarrow china clay pit was mapped in order to ascertain the relationships between the various geological features, particular attention being made to any temporal relationships. Three main lines of research were then followed

1. A potassium-argon geochronological study of primary and alteration micas and the Goonbarrow and some other Cornish elvans, to elucidate the date of kaolinisation, greisenisation and mineralisation in the St. Austell granite.

2. A study of the fluids involved with vein formation and granite alteration, to determine such parameters as temperature, pressure and salinity. Some data on the chemistry of the fluids has also been obtained using a novel adaptation of scanning electron microscopy.

3. A preliminary study of the hydrogen isotopic composition of vein fluids, and oxygen/hydrogen isotope study of vein quartz and greisen micas, coupled with a reinterpretation of previous data.

The data and conclusions from the above studies resulted in a new theory for the formation of Cornish china clay.

CHAPTER 2

Geological Relationships

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Geological Relationships

2.1. Geological relationships in S.W. England

The following section is a brief description of geological relationships in south west England in general and the St. Austell district in particular. Many authors have covered this subject more extensively. For a fuller description the reader is referred to Edmonds et al., 1975.

The south west peninsula of England, sometimes referred to as Cornubia, consists of intensely folded, faulted and weakly metamorphosed Devonian and Carboniferous sediments (locally termed killas) and contemporaneous volcanics, into which have been intruded five major and a number of minor adamellite granite plutons. These plutons have been shown to be joined at depth forming a batholith 250 kms in length, stretching from Dartmoor to the Isles of Scilly (Bott et al., 1958). Into these rocks were intruded quartz porphyry dykes, minettes and a complex series of veins. The Lizard, Start and Dodman peninsulas are composed of schists, basic, ultrabasic and acid igneous rocks of probably pre Cambrian age and these rocks are not intruded by the granite batholith. The veins are spatially associated with the granite bosses and intrude the granites, metasediments and metavolcanics. These veins have been the source of the important copper and tin ores, the latter having been mined since phoenician times (Dines, 1956). S.W. England is normally regarded as a tin province but it is not usually realised that Cornwall in particular was much more important for its copper, total production still exceeding that of tin although reserves have now been exhausted

(Dines, 1956, p.32). Iron, manganese, lead, zinc, arsenic and tungsten have also been mined in reasonable quantities. Small amounts of antimony, silver, uranium, bismuth, cobalt, nickel, molybdenum and gold have also been produced, usually as by-products. Generally speaking the mineral lodes have two main strike directions, East-West and North-South, although in the Lands End granite region these directions are more typically ENE-WSW and NNW-SSE. It may be noted that the Cornubian batholith strikes ENE-WSW and it is probable that the strain produced by emplacement produced this simplified pattern (Moore, 1977). It has long been suggested that the earlier E-W lodes contain mainly tin, tungsten, copper and arsenic and that the later N-S crosscourses carry lead, zinc, iron (as siderite) and rarely antimony, silver, cobalt, nickel, bismuth and uranium. Broadly speaking this hypothesis is true, however there are many exceptions. A good resume on current thoughts on this subject can be found in Hawkes (1974) and also in an excellent earlier paper by Hosking (1964). The granite adjacent to the veins is often altered to greisen, where the feldspars have been destroyed producing a predominantly quartz/muscovite assemblage. The composite nature of the Cornubian granites has been described by several workers namely Richardson (1923, St. Austell granite), Ghosh (1934, Carnmenellis granite) and Brammall and Harwood (1932, Dartmoor granite).

Elvans, the local term for quartz porphyry felsite dykes (and not to be confused with "blue elvans" - the greenstones) usually strike ENE-WSW or E-W although a few are found in a N-S or NNW-SSE direction (Hawkes et al., 1975). There is little doubt that the elvans are connected spatially and temporally with the mineral lodes. They strike in the same directions and the abundance of elvans in the Camborne-

Redruth area, by far the most mineralised area, has long been known. At one time the elvans were considered to have been derived from late stage differentiates of the Cornubian batholith. However Stone (1968) and in particular Henley (1972, 1974) proposed that they were produced by the action on solid granite of ascending silica poor, potassium and chlorine rich aqueous fluids. As the granites were eroded and the superincumbent load reduced, regional fracturing occurred resulting in explosive pressure release in areas of partial solution of solidified granite; the fluidisation of such material producing the elvan "volcanism". Many of the elvans have brecciated country rock along their margins supporting Henleys proposals (Goode, 1973). Laminated flow structures and the general fine grained nature of the elvans also support Henleys ideas of rapid fluidised flow and intrusion into cooler solid granite. This latter point is also substantiated by many elvans having finer grained textures at their margins compared with their cores.

The sequence of igneous events in Cornwall is as follows:

1. Emplacement of granite and pegmatites.
2. Development of elvans.
3. Formation of mineral veins; the E-W sets usually predating the N-S set.
4. Kaolinisation.

However Hosking (1964, p.204) found a few exceptions to this order, namely that

1. Pegmatites developed before, during and after emplacement of the granite (Hosking (1952).
2. Barren quartz veins (which were thought to post date mineralised veins) cut tin lodes (Garnett 1961).

3. Microgranite apophyses cut a wolfram lode at Castle-an-Dinas (St. Columb) (Dines, 1956).

4. Elvans at Hawkswood mine (Bodmin moor) and Great Wheal fortune (Breage) cut wolframite/arsenopyrite and cassiterite bearing veins respectively. These are the only two reported occurrences of this relationship and are of particular importance to the present studies on the St. Austell granite.

Superimposed on the granites and associated igneous features are the large areas of kaolinised granite. All the major plutons show extensive development of kaolinisation many of the minor intrusions are also kaolinised. By far the most kaolinised is the St. Austell granite which accounts for the bulk of china clay production in the south west and is one of the worlds largest non-sedimentary kaolin deposits. Kaolinite has been produced by the alteration of the primary feldspars. The genesis of these important kaolin deposits have been studied for over a hundred years. Generally they are thought to have been produced by the alteration of feldspars by ascending hydrothermal solutions. However there are other geologists who have advocated a weathering origin, or more recently a combination of these two processes. The controversy will be discussed further in chapters six and seven.

2.2. The Geology of the St. Austell granite

2.2.1. The Granites

Richardson (1923) described the mineralogical variation of the St. Austell granite and divided the pluton into three main varieties

1. Biotite-muscovite granite in the east.

2. Lithionite granite in the centre and extreme west.

3. Gilbertite granite in the western part of the centre.

He suggested that the biotite-muscovite granite was in fact a separate intrusion, being intruded by the lithionite and gilbertite phases; the latter, containing much volatile material and crystallising last. Exley (1955, 1959) agreed with Richardsons general outline but suggested four main changes.

1. Richardson's lithionite† granite was divided into two types - porphyritic (early) and non porphyritic (late) varieties.
2. The gilbertite† granite was considered to be an alteration product of earlier granite and not of primary origin.
3. The existence of a further type of granite was ascertained - a fluorite granite - in the western lobe of the pluton. Previous authors (Ussher et al., 1909, Dewey 1948, Hatch et al., 1949) had also recognised this granite but had considered it was the product of some form of alteration. Exley however asserted that this was not the case.
4. Richardson's limit for the biotite-muscovite granite was considered to be drawn too far to the east.

† Lithionite and Gilbertite are obsolete terms for types of micas. Lithionite refers to a group of lithium rich micas of which zinnwaldite is one of its members (Exley, 1955, p.25). Gilbertite refers to the green variety of mica first found at Stennagwyn, Cornwall. No complete chemical analysis exists although it is generally thought to be rich in lithium.

Exley put forward two pieces of evidence to show that the granite is a composite of two intrusions (Exley, 1959, p.198).

1. "The metamorphic aureole, as mapped by the geological survey, is shaped like the figure eight lying on its side. If the circles forming the figure are completed it is seen that the western circle intersects the eastern along a line almost coincident with the western boundary of the biotite-muscovite granite". (fig. 1).
2. "The strikes of lodes east of St. Austell change from NE-SW to NW-SE as the town is approached. The western lodes, have a strike that is discordant with the neighbouring granite margin but concordant with the perimeter of the eastern circle just described, while all dip towards its centre". (fig. 1).

Exley's second point needs more clarification since he suggests that as the biotite-muscovite granite was emplaced, joints or fractures were produced approximately concentric to the granite contact. These were later used as channels for hydrothermal fluids that formed the quartz/tourmaline $\pm$ metal veins. The only veins shown on the geological survey map used by Exley seem to be associated with the biotite-muscovite and not the later lithionite granite. However in Dines (1956) many more veins around the granite were shown and it is quite obvious that Exleys argument does not stand up well in the light of this new evidence. The veins generally strike ENE-WSW (fig. 2) and are more probably controlled by the intrusion of the batholith as a whole, since it strikes in the same direction. This does not refute Exley's suggestion of two intrusions but implies the evidence is tenuous. The contact between biotite-muscovite and lithionite granites cannot actually be seen in the field and hence the nature of the contact cannot be verified.

Table 1 shows an abbreviated description of Exley's granite types. The plagioclase in the biotite-muscovite granite is strongly zoned with cores of An_{28} and rims of An_{8}. However Exley (1959, p.201) reported that plagioclases from the boundary region between biotite-muscovite and early lithionite granites had intermediate compositions. Some had cores of An_{17} and rims of An_{13} "while in other rocks there are two generations, with compositions of An_{10} and An_{6} respectively". It is significant that the biotite-muscovite granite is very rarely sufficiently altered to produce economically extractable deposits of china clay, the only pits worked over the last twenty years being Bodelva and Carclaze Bal. By comparison the lithionite granites are extremely kaolinised producing some of the finest quality Cornish china clay.

The distribution of Exley's four granite types are shown in figure 3 along with other geological features and all working china clay pits as of July 1978. These pits offer superb geological exposure although the speed at which the material is extracted means that any one exposure is often not available for more than a short period of time.

The small amount of alteration in the biotite-muscovite granite was mentioned earlier and requires further discussion. The only mineralisation known to exist in this granite is at Lady Rashleigh consols near the eastern junction with the killas. Of the two china clay producing pits, Bodelva is close to the contact between granite and killas and Carclaze Bal is near to the junction between biotite-muscovite and early lithionite granites. In the area around Luxulyan peculiar veins of tourmalinised granite have been produced, the rock being known as luxulyanite (Ussher et al., 1909, pp.66-67). However in general the biotite-muscovite granite is virtually free of alteration, certainly when compared to the

Table 1

The four main varieties of the St. Austell granite (after Exley, 1955, 1959)

Type of Granite	Appearance	Plagioclase composition	Type of micas	Remarks
Biotite-muscovite granite	Porphyritic, coarse grained	Strongly zoned, An_{28} (but see text)	Biotite, muscovite	
Early lithionite granite	Porphyritic, coarse to medium grained	Unzoned, An_7	Lithionite	
Late lithionite granite	Non porphyritic, medium grained	Unzoned, An_4	Lithionite	Contains appreciable quantities of fluorite (1.1%) and topaz (2.1%)
Fluorite granite	Non porphyritic, medium grained	Unzoned, An_4	Muscovite	Contains fluorite (1.6%)

Note: All granites contain secondary muscovite

lithionite granite; a factor which is considered pertinent to kaolinite genesis.

2.2.2. Pegmatites

Contrary to Badham et al., (1976) pegmatites have been described within the St. Austell granite. The Trelavour Downs pegmatite was described in some length by MacAlister (in Ussher et al., 1909) and was at one time worked for lithia (Edmonds et al., 1975). This pegmatite was of the symmetrical type intruding early lithionite type granite although very near the junction with the later lithionite non porphyritic granite. MacAlister also described briefly the pegmatite at Tresayes near Roche which was worked until 1880 for its feldspar for use in glass making and indeed is known locally as the "glass pit". The author has also seen and sampled two separate pegmatites from Kernick near to the western junction between early and late lithionite granites. One of these localities is now covered by the newly constructed Kernick mica dam. Gunheath also has several pegmatite veins, some yielding the uncommon mineral columbite (Hodkinson and Clark, 1977). The author has also seen several irregular veins and pods of pegmatite containing large masses of a green "gilbertite" mica (maximum of 4 cms long). Several horizontal veins of pegmatite have also been reported from this pit (Exley, pers. comm. 1978). Bristow and Wilson (1977) in a reply to the paper by Badham et al., (1976), pointed out that pegmatites in Cornwall and in particular the St. Austell granite, are not uncommon at all and the authors work in this area has substantiated this.

2.2.3. Elvans

According to maps produced by the geological survey very few elvans occur within the St. Austell granite mass. There are quite a number

both north and south of the pluton. The area to the south is highly mineralised and was the site of such great mines as Fowey Consols, Charlestown United, Polgooth and South Terras. The elvan at Brannel has been dated by Hawkes et al., (1975) (see chapter 3). The geological survey one inch map show elvans within the early lithionite granite at Goonbarrow, Gunheath, Bluebarrow, Wheal Remfry and within the late lithionite granite at Hendra and Trelavour. MacAlister (in Ussher et al., 1909) also reports an elvan at Chytane china clay pit near Burthy Row, within the western section of the early lithionite granite. Extrapolation of this strike direction probably leads to the elvan now seen outcropping in Melbur china clay pit. An elvan is also exposed in Dorothy pit and is almost certainly an extension of the Trelavour elvan described in Ussher et al., (1909). It is also possible that the elvan at Gunheath is a further extension of the same elvan although this elvan has often been correlated with that at Goonbarrow; its strike altered by a large fault with rotational displacement. However there is no sign of faulting on the scale needed to achieve this displacement in the Gunheath area and the former statement is considered more likely. On a visit to Rostowrack pit in June 1978, large blocks of elvan were found in the pit bottom. However the source of the material could not be found and it is probable that the exposure has been covered with overburden. An elvan was shown on a map produced by Dines (Map VIIIA, 1956) which could correspond to this locality. Of the elvans mentioned the following are still exposed - Dorothy, Goonbarrow, Gunheath, Hendra, Melbur and Wheal Remfry.

2.2.4. Mineralisation

The St. Austell district has in the past been important for the production of tin, copper and iron; lying fourth in total production of these metals after the Camborne, St. Just and Callington mining districts (see Dines, 1956, p.32). The tin and copper lodes to the north of the granite and in the far eastern area strike ENE-WSW and dip to the south (Dines, 1956, Maps VIII A and B). In the area 2 kms east of St. Austell the lodes strike E-W to WNW-ESE and continue this orientation until in the Polgooth and St. Stephen districts all veins strike WNW-ESE. The iron lodes found north of the granite and also in the St. Stephens area, strike between N-S to NW-SE. Very few mineralised veins are found within the St. Austell granite, although all the china clay pits are cut by swarms of quartz/tourmaline veins often with marked greisen borders. However tin, copper and tungsten has been mined from Stennagwyn, Tin hill, Lady Rashleigh Consols and in particular the Hensbarrow region, encompassing Goonbarrow, Bunny, North Bunny, Old Beam and Rocks and Carnsmerry. In all areas the lodes strike roughly NE-SW. The elvans, both within and around the St. Austell granite, have the same approximate strike direction as the veins which may indicate why there are no crosscutting elvans. The widely held Cornish relationship between elvans and mineralisation is borne out in areas around the granite and also in the Hensbarrow region, but the elvans mentioned earlier, although developed within a multitude of quartz/tourmaline veins are not associated with tin/tungsten lodes. It is quite possible that zones in which tin and tungsten are to be found were removed when the granite was unroofed. However it is considered more significant that the most mineralised area within the granite - Hensbarrow, is found near to the contact between biotite-muscovite and early lithionite granites. Carclaze, the once famous open cast tin mine, was also located near the contact.

Table 2. Description of the unkaolinised granite specimens collected by the author from the St. Austell granite

	Exley's Classification	Porphyritic/ Non porphyritic	Matrix Grain size	Mica types	Remarks
Luxulian (Tregordan quarry)	Biotite-Muscovite	Porphyritic	large	Biotite, Muscovite	potash feldspar phenocrysts up to 5 cms in length
Carclaze Bal	Biotite-Muscovite	Porphyritic	large	Biotite, Muscovite	potash feldspar phenocrysts up to 1 cm in length
Rocks	Biotite-Muscovite	Porphyritic	large	Biotite, Muscovite	potash feldspar phenocrysts up to 1 cm in length, sample highly weathered, supplied by J. Hawkes, I.G.S.
Gunheath	Early Lithionite (porphyritic)	Non porphyritic	small	muscovite	mica light brown in colour
Littlejohns	Early Lithionite (porphyritic)	Non porphyritic	small	muscovite	
Longstone	Early Lithionite (porphyritic)	Porphyritic	medium	Biotite, Muscovite	Biotite predominates
Dorothy	Early Lithionite (porphyritic)	Non porphyritic	small	muscovite	
Rostowrack	Late Lithionite (non porphyritic)	Non porphyritic	large	muscovite	mica light brown in colour. however in china stone varieties mica loses its colour
Goonvean	Late Lithionite (non porphyritic)	Non porphyritic	large	muscovite	same remarks apply as Rostowrack
Trethosa	Late Lithionite (non porphyritic)	Non porphyritic	large	muscovite	same remarks apply as Rostowrack, except a few mica flakes have pleochroic haloes
Melbur	Early Lithionite (porphyritic)	(a) Porphyritic	large	Biotite, Muscovite	potash feldspar phenocrysts to 3 cms in length having pinkish colour
		(b) Porphyritic	medium	Biotite, Muscovite	
		(c) Non Porphyritic	small	muscovite	very similar to Littlejohns Dorothy

2.3. Comments on the composite nature of the St. Austell granite

A number of unkaolinised granite specimens were collected from various china clay pits and their appearance in hand specimen and thin section does broadly conform with Exley's model. Table 2 lists the samples and their descriptions. However there are a few discrepancies, the Gunheath and Dorothy granites being porphyritic and therefore possibly of late lithionite not early lithionite type. Melbur exhibited three types of granite two of which were the biotite-muscovite type. These samples were compared with Exley's collection at the University Museum, Oxford and it became clear that his division of the central and western areas is an oversimplification. However a further more detailed study of the St. Austell granite is outside the scope of this work although Exley's model for the composite nature of the St. Austell pluton is particularly important for the interpretation of the geology at Goonbarrow as will be shown.

2.4. Summary of the geology of the St. Austell granite

1. The St. Austell granite is a composite of four different types - biotite-muscovite (porphyritic), early lithionite (porphyritic), late lithionite (non porphyritic) and fluorite (non porphyritic).
2. The biotite-muscovite granite was probably intruded first and is relatively free of any mineralisation. Kaolinisation only occurred near the killas and lithionite granite junctions.
3. The lithionite granite types are intensely kaolinised.
4. Pegmatites and elvans are widely dispersed within the granite.
5. Mineralisation is confined to two main areas (a) the area 2 kms east of St. Austell and (b) the Hensbarrow area.

2.5. Geological relationships in Goonbarrow china clay pit

Goonbarrow china clay pit is situated about 3 kms north of St. Austell in a formerly deserted moorland area known as Hensbarrow. The present pit is an amalgam of several smaller pits which have been producing china clay since the mid nineteenth century. The position of the old pits in relation to the present Goonbarrow pit is shown in fig. 4 and their names have been retained when describing the sample locations and other exposures at Goonbarrow. The pit is also situated on the site of several old tin mines. These were Old Beam (otherwise known as Great Beam and thought to date from Henry VII's time (Collins, 1912, p.64)), and Goonbarrow and Molinnis. Even during the mid nineteenth century boom in tin mining, Old Beam was well known as a difficult mine to work since the ground in which the tin occurred was very soft and liable to "run-in" on the miners. It is a tribute to Cornish mining techniques that the mine eventually reached a depth of 92 fathoms (about 600 feet) in order to remove the rich lodes of tin and tungsten. The "soft ground" referred to is of course kaolinised granite and it is ironic that at the time this was considered worthless. Nowadays the Goonbarrow china clay, because of its high quality, is a very valuable commodity; the minor amounts of tin and tungsten being of secondary economic importance.

The most important geological features at Goonbarrow may be subdivided into five main groups.

1. The Granites
2. The Pegmatite
3. The Elvan
4. The veins
5. Kaolinised granite

2.5.1. The Granites

Goonbarrow is located within Exley's (1955) early lithionite granite, some 1-2 km from its contact with the biotite-muscovite granite as mapped by Exley. However, three types of granite have been found within the Goonbarrow pit (Plate 1), all of which are porphyritic to some extent. They are described below.

2.5.1.1. "Big feldspar" granite (BFG)

Very porphyritic dark grey rock containing large potash feldspar phenocrysts up to 10 cms in length (normal size 5-6 cms) (Plates 1 and 2). The granite looses its phenocrysts in the Imperial part of Goonbarrow pit. The groundmass is medium to coarse grained (0.1 - 0.6 mm), with the dark minerals, tourmaline and biotite, in sharp colour contrast against the white plagioclase feldspars (Plate 2). The following minerals were seen in thin section:

Quartz	Anhedral, large with many fluid inclusions, some occurring in long trains and probably of secondary origin.
Biotite	Medium to large flakes. Strongly pleochroic from light brown to a very dark red brown. Contains great numbers of pleochroic haloes (Plate 3) with occasionally small zircon crystals at their centres.
Primary muscovite	Medium to large flakes frequently intergrown with biotite.
Secondary muscovite	Very small flakes, found in both feldspars (Plates 3 and 4) and altered primary muscovite (Plate 5).

Potash feldspar	Large phenocrysts euhedral, others subhedral to anhedral. Coarse perthitic texture. Often slightly altered (Plate 4), secondary muscovite being found along cleavage.
Plagioclase	Composition An_{10}. Euhedral to subhedral. Displays predominantly albite twinning with some chessboard twinning. Often altered to secondary muscovite, the cores being particularly altered (Plates 3 and 4). The secondary muscovite flakes are often found in a criss cross pattern but not always parallel to chessboard twinning.
Tourmaline	Interstitial, of variable size, brown often containing blue pleochroic haloes. Strongly zoned.
Fluorite	Very rare, small grains seen intergrown with biotite.

2.5.1.2. "Small quartz-feldspar" granite (SFG)

Porphyritic rock containing quartz and potash feldspar phenocrysts up to 1 cm in length (normal size 0.3 - 0.5 cms). The groundmass is fine to medium grain (0.05 - 0.25 mm). In colour this rock is a slightly lighter grey than BFG (Plate 1). The following minerals were found in thin section:

Quartz	Anhedral, large with many fluid inclusions, some occurring in long trains and probably of secondary origin.
Primary muscovite	Medium to large flakes, frequently intergrown with lithionite over which it predominates.
Lithionite	Medium to large flakes, pleochroic, very light brown containing dark pleochroic haloes. Resembles biotite in relief and cleavage but not colour.

Secondary muscovite	Very small flakes, found in both feldspars (Plate 6).
Potash feldspar	Euhedral to anhedral. Coarse perthitic texture. Even freshest samples slightly altered to muscovite which is found along the cleavage (Plate 6).
Plagioclase	Composition An_8. Euhedral to subhedral. Displays predominantly albite twinning with some chessboard twinning. Often altered to secondary muscovite especially in cores (Plate 6). Secondary muscovite often found in criss-cross pattern but not always parallel to chessboard twinning.
Tourmaline	Interstitial, of variable size, brown, strongly zoned (Plate 6), contains blue pleochroic haloes. Less tourmaline present than in BFG.

2.5.1.3. "Pale mica" granite (PMG)

Slightly porphyritic. Very pale in colour and easily distinguishable in hand specimen from other granites (Plate 1). In thin section the following minerals were seen:

Quartz	Anhedral, large with many fluid inclusions, some occurring in long trains and probably of secondary origin.
Muscovite	Medium to large flakes, frequently intergrown with lithionite.
Lithionite	Medium to large flakes, much less than in SFG. Very pale in colour, very slightly pleochroic. Contains some pleochroic haloes which are fewer and much lighter than in SFG (Plate 7).

Secondary muscovite	Very small flakes, found in both feldspars (Plate 8).
Potash feldspar	Euhedral to anhedral. Coarse perthitic texture. Often altered to fine grained muscovite (Plate 8) which is found along the cleavage.
Plagioclase	Composition An_{10}. Euhedral to subhedral. Shows predominantly albite twinning with some chessboard twinning. Sometimes altered to secondary muscovite especially in cores (Plate 8). Secondary muscovite often found in criss-cross pattern but not always parallel to chessboard twinning.
Tourmaline	Few grains observed. Interstitial, brown, heavily zoned. Much less than in SFG.
Sphene	Very rare, small dark brown grains, high relief.

The big feldspar granite described above is almost certainly Exleys biotite-muscovite granite type which he described as being present at least one kilometre further east. His lithionite type corresponds most closely with the small quartz-feldspar granite, although the type material contained only a single light brown lithionite mica. The pale mica granite appears in hand specimen to resemble samples seen in the late lithionite type. Pale mica granite is found in the area around North Goonbarrow and Martins goonbarrow (fig. 4 and Map I). Small feldspar granite is found in West Goonbarrow right through to the south end of Imperial. The boundary between these two types is gradational and obscured by the intense kaolinisation in this area. Big feldspar granite is found in the Old Beam area on the northern side of the old Imperial pit. Over the last three years the contact between the big and small

feldspar granites has been superbly exposed. At every locality (for exceptions see below) the contact has been marked by a pegmatite occurring between the two granite types. This pegmatite will be described and discussed shortly. It appears that the contact between two of Exleys granite types are present within Goonbarrow.

During the summer of 1978 development work in the pit exposed kaolinised and unkaolinised granite in addition to the pegmatite. On two faces were exposed a sheet like structure of granite intruded into big feldspar granite (Plate 9). In appearance this granite sheet resembled the small quartz-feldspar granite. This was subsequently verified in thin section. On one of the faces (Plate 10) two xenoliths of big feldspar granite could be seen which had broken off and been trapped by the small quartz-feldspar granite (the photograph does not show this very well since all the rock is kaolinised to some extent). The angular nature of these xenoliths suggests that the big feldspar granite was fairly solid at the time of emplacement of the small quartz-feldspar granite.

In the Martins Goonbarrow area a xenolith of another granite was found surrounded by a pegmatitic growth of feldspar and tourmaline. It is quite probable that this xenolith consisted of big feldspar granite which fell into the small quartz-feldspar granite during intrusion but again this area of the pit is thoroughly kaolinised so the original mineralogy could not be verified (Plate 11).

2.5.2. The Pegmatite

2.5.2.1. Description of main features

The Goonbarrow pegmatite was mentioned by Badham et al., (1976) as striking at 138°, varying in thickness between two and three metres and having sharp unsheared margins. It was described as symmetrical and composite in form containing

> "an outer zone of curved fans of orthoclase that nucleate at a point, expand inward and curve upward. These fans are up to 20 cms long and 2 cms thick and are surrounded by a matrix of quartz, biotite and schorlitic tourmaline. The inner zone has a wall of orthoclase 10 cms thick and then again consists of (smaller) curved fans of orthoclase in a matrix of quartz/biotite and tourmaline. The curved crystals are confined to the vertical parts of the dyke".

They considered the pegmatite to have been a late differentiate emplaced passively into a dilatant joint. Continued observation of the pegmatite exposure over three years has shown it to be more complicated than the account given by Badham et al., (1976) whose initial interpretation was, in some cases, erroneous.

The description by Badham et al., of two distinct zones has been observed in only a few exposures and this description cannot be applied to the entire pegmatite. Generally speaking the pegmatite can be described as containing large orthoclase crystals up to 20 cms in length, often curved, surrounded by an interstitial aplitic matrix of quartz, biotite, plagioclase and tourmaline. Within this matrix are very occasionally found small amounts of torbenite and sulphides. The interstitial matrix is very variable in composition, four main types were observed:

Type 1. Fine grained matrix of quartz, plagioclase (An_8), biotite and tourmaline.

Type 2. Suitable cross sections through the pegmatite showed that the above matrix would become particularly abundant in tourmaline producing dark bands within the pegmatite that were parallel to the granite/ pegmatite contact (Plates 12 and 13). On one occasion a section was seen with long tourmaline needles formed at the contact between pegmatite and SFG (Plate 14). A further sample, from within the main core of pegmatite, supplied by Mr. C. Hancock (Pit Captain at Goonbarrow), also had good development of tourmaline needles (Plate 15).

Type 3. In some places biotite within the matrix grew to about 3 cms in length, although in very thin sheets (less than 1 mm) (Plate 16) producing similar banding to that mentioned above.

Type 4. The pegmatite exposed in the area around West Goonbarrow (fig. 4) is very kaolinised. The feldspars, which are very large in this area (up to 20 cms in length and 4 cms in width) as well as being surrounded with types 1 and 2 matrix are also enclosed by large masses of coarse grained quartz. This type of matrix occurs as lensoid pods up to about 25 cms in width and one to three metres in length (Plate 17).

Although striking in approximately the same direction throughout the pit, the dip of the pegmatite often changes suddenly producing a type of "dog leg" effect (Plates 18 to 24). The orthoclase crystals within the pegmatite are often curved (Plates 25 and 26) and display their maximum amount of curvature when the pegmatite is vertical (Plate 27).

2.5.2.2. Description and interpretation of the pegmatite-granite contacts

The pegmatite, with two exceptions, always occurs between the big feldspar and small quartz-feldspar granites. The pegmatite has been mapped for over 700 m, from the West Goonbarrow area across the pit to the extreme eastern end of Imperial (Map I). Throughout its course the

pegmatite varies in thickness from 3 to 5 m, however at the far eastern end of Imperial it pinches down to only 20 cm (Plates 28 and 29). The two granite types can be clearly seen. Badham et al., (1976) did not recognise the two granite types or their relationship with respect to the pegmatite. The BFG-pegmatite junction (Plate 30) is always fairly sharp suggesting that the BFG was essentially solid at the time of pegmatite formation. Orthoclase crystals within the pegmatite always, without exception, increase in cross-sectional area from the BFG towards SFG and also branch in this direction. At the SFG-pegmatite junction the protruding feldspars are often surrounded and overgrown by a very fine grained aplitic matrix which blends gradationally into the SFG (Plates 31 and 32). In places thin dark bands of tourmaline rich aplite have crystallised within the aplite which form around protruding feldspar crystals (Plates 31 and 32). These observations strongly suggest that the pegmatite was present before the SFG crystallised and that therefore the temporal sequence of crystallisation was BFG pegmatite SFG i.e. from hanging wall to footwall. Within 1 to 2 m of the pegmatite contact, the SFG was of a much finer grain size suggesting that the granite was quickly cooled. There is little doubt therefore that the Goonbarrow pegmatite is not of the usual intrusive type crystallising in a fracture. Its assymetric nature, direction of orthoclase growth and granite contacts rule this type of formation very unlikely. Badham et al., (1976) reported that the curved orthoclase crystals were in optical continuity suggesting that the curvature was an original feature (and not produced by later movement). This observation coupled with the "dog legging" of the pegmatite suggest that it was probably joint controlled and moving for some considerable period of time along a restricted channelway such

as a dilatant joint as originally suggested by Badham et al., (1976). However before final crystallisation of the pegmatite the granite beneath must have fallen away allowing the later SFG to crystallise on the footwall. Xenoliths of BFG in the SFG substantiate this model.

2.5.3. Elvans at Goonbarrow and other china clay pits within the St. Austell granite

The elvans (a Cornish term for a quartz porphyry dyke) are considered to have been intruded after the granites but prior to mineralisation. The only two known occurrences where elvans crosscut mineralisation were mentioned in section 2.1. Four elvans were studied, from Goonbarrow, Dorothy, Gunheath and Melbur china clay pits (fig. 3). All four elvans are light green in appearance, extremely fine grained with occasional phenocrysts of quartz and kaolinite-muscovite pseudomorphs of feldspar phenocrysts. In thin section the elvans consist of a very fine grained matrix of sericite-quartz surrounding quartz phenocrysts (Plates 33 and 34) and occasionally kaolinised feldspar, tourmaline (sometimes found as stars, Plate 34) and rarely, larger flakes of primary muscovite (Plate 33). The sericite-quartz matrix is of a recrystallised texture and is also found intergrown with kaolinite pseudomorphing feldspar (Plate 35). The Goonbarrow, Gunheath and Dorothy elvans were found to crosscut quartz/tourmaline veins. The Goonbarrow elvan was superbly exposed and must represent the finest example of such relationships found in the south west to date (Plates 24 and 36). At Goonbarrow, although no tin/tungsten mineralisation was found in the veins, their strike is very similar to veins containing such mineralisation only 200 m away in the pit. Samples of cassiterite were found within 5 m of the elvan (June 1978) but

the elvan itself was not so clearly exposed at this time. However it is considered very likely that quartz/tourmaline veins containing cassiterite (and possibly wolframite) at Goonbarrow preceded elvan intrusion. Details of the strike of the elvans are as follows:

Elvan location	Direction	Dip	Remarks
Gunheath	78°E	72°S	Crosscuts quartz/tourmaline veins, strike 42°E, dipping subvertical
Melbur	148°E	75°N	Crosscuts quartz/tourmaline veins, strike 175°W, dipping 25°E
Dorothy	98°E	80°N	-
Goonbarrow	38°E	80°S	Crosscuts quartz/tourmaline veins, strike 40°E, dipping 55° and 35°W.

At Goonbarrow a small offshoot of the elvan was discovered east of the main dyke (Map I).. This was found on both north and south faces of the old Imperial pit and ranged in width from 10 to 20 cms. The elvans often exhibit a laminated structure, as can be seen in Plate 37.

Since the elvans crosscut quartz/tourmaline veins but are themselves hydrothermally metamorphosed, this indicates that they were intruded during hydrothermal activity (see chapter 3).

2.5.4. The Veins

The veins at Goonbarrow can be divided into four groups

1. Quartz/tourmaline veins
2. Cassiterite/wolframite veins
3. Multimineral veins
4. Barren quartz veins

Cross sections of the vein systems giving strikes, dips, sample numbers and distances between veins and stereograms of the poles of the veins are shown in figs. 5 to 14.

2.5.4.1. Quartz/tourmaline veins

These strike mainly $40^{\circ} \pm 5^{\circ}$ with minor grouping at 50° and $10\text{-}30^{\circ}$; the latter being restricted to Martins Goonbarrow and the area opposite Old Beam. The veins usually have identical dip in any one area and overall range from about 30 to 80°W although the majority are about $60\text{-}70^{\circ}$W. The thickness of the veins is highly variable ranging from a few millimetres to about 15 cms. A mean value would be in the region of 1 cm. Most of the veins are bordered by symmetrical bands of altered granite referred to as greisen. These range from a few millimetres to about 10 cms in thickness (mean value about 5-6 cms). Often the veins occur in large swarms where tens of small veins may be seen over only ten metres or so. This type of veining, often referred to as a sheeted vein complex, is very characteristic of the Hensbarrow region (the old Bunny mine, about one kilometre south of Goonbarrow is another good example) and certain other parts of the Cornubian batholith (Cligga Head, St. Michaels Mount, Hemerdon Bal, Carn Brea, Hingston Down, Kit Hill and St. Agnes Beacon - Moore, 1977). Cligga Head, St. Michaels Mount and Hemerdon Bal are intimately associated with greisen haloes like Goonbarrow. The vein swarms at Goonbarrow are also intimately associated with kaolinisation. Plates 38 and 39 show a good example of unkaolinised granite grading suddenly into kaolinised granite, accompanied by an increased number of veins. In the Martins Goonbarrow area similar relationships are also displayed (Plate 40). Although kaolinised granite is sometimes found in other areas of Goonbarrow not associated with vein swarms, wherever swarms do occur the granite is always very kaolinised. Goonbarrow is cut by so many veins that the suggestion that some kaolinised granite is not associated with veining is very difficult to substantiate. Similar relationships between sheeted vein systems and kaolinised granite

are also found at Bostraze, Cligga Head and Hemerdon Bal.

The quartz/tourmaline veins at Goonbarrow consist of an intergrowth of these two minerals. In thin section the tourmaline is strongly zoned being either light brown or a pale blue colour. The tourmaline also exists in two distinct grain sizes and differs from that in the granites by being paler in colour and having a much lower content of pleochroic haloes.

The greisens associated with the quartz/tourmaline veins are of a green to grey colour in hand specimen. In thin section they consist mainly of muscovite and quartz which is anhedral and highly corroded. Tourmaline, found in the original granite, is still present. A micaceous mineral of high relief showing possible signs of pleochroic haloes is occasionaly present in greisens found within the BFG and is probably altered biotite. No feldspars are present, all have been converted to the muscovite/quartz intergrowth.

2.5.4.2. Cassiterite/wolframite veins

These veins have been found in two areas only, the Old Beam area and both north and south faces of Imperial. Both areas are on the sites of nineteenth century mines. This type of mineralisation can be further divided into two types.

(a) Cassiterite $\pm$ wolframite veins

These two minerals often occur together in veins up to 2 cms wide in the Old Beam area associated with greisens up to about 5 cms in width. They strike about $40^{\circ} \pm 5^{\circ}$ and dip around $50\text{-}60^{\circ}$W. Cassiterite is usually the dominant mineral and often grows in crystals about a centimetre in size. The Old Beam mine was very well known for the coarseness of its cassiterite and the mines output was keenly sought by tin smelters

due to its high purity. The cassiterite is highly zoned alternating between very dark brown and almost transparent varieties (Plates 41 and 42). A brief investigation of this zoning carried out on the electron microprobe indicated that the dark bands were due to a high iron content and the light zones to high titanium.

The wolframite occurs as jet black or dark red brown blades up to 2 cms in length and 3 mm wide. The jet black blades show a metallic lustre on their (010) cleavage faces unlike the dark red brown variety which may suggest that the latter variety has at some time been altered chemically. In addition to cassiterite and wolframite, blue tourmaline and quartz are also found within the veins (Plates 41 and 42). Two different forms of tourmaline were seen in thin section identical to the previously described quartz/tourmaline veins. In addition to the normal greisens, which are mineralogically similar to those found with quartz/tourmaline veins, a further type was also distinguished. This consisted of a thin band, usually between 2 and 5 mm, of fine grained topaz developed between the normal greisen and cassiterite (Plate 41). The paragenesis of the minerals is topaz border first, followed by cassiterite and tourmaline. Quartz in another part of the specimen can be seen growing from the topaz border into the central tourmaline area suggesting that it was deposited contemporaneously with cassiterite. In many cases this topaz border was found occurring instead of the normal greisen, sometimes 10 cms thick on either side of the vein (Plate 44). At the location illustrated, about 5 m further north along the vein, the topaz greisen completely disappeared being replaced by a normal greisen (Plates 43 and 45). Whenever cassiterite was found it was always associated with this topaz greisen or border and in the afore-mentioned example, when the topaz disappeared the cassiterite was

likewise absent from the vein. There is little doubt in the authors view that in the Old Beam area topaz and cassiterite deposition are intimately related. Unfortunately wolframite was not nearly as common as cassiterite and so no relationship with topaz could be found although wolframite in this area only occurred with cassiterite.

Another feature of the Old Beam area is the large number of veins which often change the strike and dip slightly forming a vein stockwork (Plate 46). This type of veining, as mentioned previously, is found in other parts of the Hensbarrow region. Samples from the now disused and overgrown Bunny mine, about a kilometre south of Goonbarrow, in the collection of the University Museum, Oxford are very similar to those found at Old Beam including the cassiterite-topaz relationship.

On the southern face of the Imperial area some large specimens of vein material have been found containing coarse cassiterite, quartz and tourmaline in combination with a normal greisen. There is no trace of topaz at all. These veins are up to 3 cms thick, were found in loose blocks and could not be found in situ. There were several areas of the face where the samples may have come from, but the unstable nature of material in this area made a thorough search very dangerous and so their exact source remains unknown. Suffice it to say that all veins in this area were striking at about 40° and dipping around $45^{\circ} \pm 10^{\circ}$W. It is very probable that the veins from which these samples were derived would be crosscut by the elvan.

(b) Wolframite veins

A very small number of veins were sampled from the north face of Imperial which contained wolframite in association with quartz and tourmaline. These veins were associated with normal greisens up to

5 cms in thickness. The wolframite was always jet black and showed the typical lustre on cleavages. Some samples from this area were found by Mr. C. Hancock which contained very large clusters of wolframite plates in a predominantly quartz matrix. The veins were sometimes 15 cms wide and have the usual greisens. A large quartz/tourmaline vein was found in this area which resembles the material in which this wolframite was found, but unfortunately no wolframite has been found to date. In veins in this area the wolframite occurred in small patches and was often difficult to find. No topaz was found in any of the greisens in this area.

Wolframite was also found in another vein and is classified under the following section.

2.5.4.3. Multimineral veins

Three examples of these types of vein were found, all in the Imperial area, their locations are shown on Map I. Sample No. Goo 76/135, strike 34°, dip 40°N. This vein contained quartz, tourmaline, purple fluorite, topaz and arsenopyrite. The three latter minerals were identified by X-ray powder photography. A normal greisen was found on only one side of the vein, about 2 cms in width. This may suggest that the vein and greisen formed in two separate episodes. Sample No. Goo 76/136, strike 50°, dip 58°N. This vein contained tourmaline, quartz, topaz and fluorite. A greisen on only one side was found like the previous sample. Sample Goo 78/329, strike 35°, dip 42°N. Vein about a centimetre wide with associated greisen which was very diffuse and up to 10 cms in width. The vein was exposed in such a way that it could not be ascertained if the vein was bordered by greisen on both sides. The vein consisted of brown and purple fluorite, tourmaline,

apatite and wolframite; the greisen of mainly topaz, apatite and purple fluorite with some associated tourmaline. In thin section the brown fluorite appeared to be the more usual honey brown variety and in the vein was intimately mixed with purple fluorite, the two blending into each other. All the above minerals were also checked by X-ray powder photography.

In addition to the above specimens a large block was found in the same general area that contained large amounts of lollingite along what appeared to be a joint face. The vein was only about a millimetre thick with a dark tourmaline greisen of similar thickness.

All these veins characteristically occurred in a buttress of hard, least altered granite. Unfortunately no crosscutting relationships were found with any other vein types so their sequence in the geological evolution of the rocks is unknown.

2.5.4.4. Barren quartz veins

In an area about midway between West Goonbarrow and Imperial, referred to as "Island facing south", a few veins of quartz were found. They were only about a centimetre wide, had no greisens and striked nearly N-S, dipping almost vertically. In thin section the veins consisted of pure quartz and contained not a single fluid inclusion. At times the quartz is amethystine and these types of vein have been seen in a number of other pits in the St. Austell granite, notably Bodelva where the quartz is often found as purple amethyst. These veins crosscut quartz/tourmaline veins and are probably the last geological event in Goonbarrow.

2.5.5. Kaolinised granite

As mentioned previously kaolinised granite is spatially associated with the greisen bordered quartz/tourmaline veins. The change from unkaolinised hard granite to kaolinised soft granite can take place over as small a distance as one metre. Kaolinisation can take place in different ways depending on the original composition of the feldspar. Exley (1959) showed that in the case of potash feldspar this altered first to secondary mica and then eventually to kaolinite. He considered that albitic plagioclase altered in two different ways, both produced intermediate products before final kaolinisation. The first process involved alteration to secondary mica similar to potash feldspar mentioned above. The second process involved altering the plagioclase to a potash enriched variety whioh altered further to a secondary mica and then to a more hydrated form. Both of these processes in their ultimate form produced an aggregate of mica and kaolinite. Exley (1976) further ascertained that albitic plagioclase altered first to muscovite and montmorillonite and then to the mica/clay aggregate. Clearly the process is quite complicated and little can be added here to Exleys work. The alteration of feldspars to secondary mica was seen in all the so called unkaolinised granites in Goonbarrow (Plates 3, 4, 8 and 47), and has also been identified in other samples within the St. Austell granite including Luxulyan, within the unaltered biotite-muscovite granite, where no clay can be found. The sudden transition between unkaolinised and kaolinised granite made studies of intermediate material difficult although the feldspars in this material could be seen to contain much more secondary mica. Intergrown kaolinite and secondary mica could be identified in thin section (Plates 48 and 49). Intergrowths of these

two minerals have been seen in single particles down to 2-4 μm size (Noble et. al., 1978). In thin section quartz appeared to be highly corroded (Plates 48 and 49) and occasionally fractured, usually breaking up into smaller pieces. Tourmaline remained unaltered and retained its zoning, biotite however was completely absent in the kaolinised BFG probably being altered to a mixture of secondary muscovite and kaolinite.

2.6. Summary and main conclusions

1. The St. Austell granite consists of four types of granite: Biotite-muscovite, early porphyritic lithionite, late non porphyritic lithionite and fluorite granites.
2. The junction between biotite-muscovite and early lithionite granites is exposed at Goonbarrow. The biotite muscovite granite (BFG) was intruded first followed by the early lithionite granite (SFG) since:

(a) An asymmetric pegmatite was found at the junction of the two granites. The direction of growth and branching of feldspars shows that it developed on a hanging wall of biotite-muscovite (BFG) granite and was followed by crystallisation of lithionite granite (SFG).

(b) A lithionite granite sheet was observed intruding the biotite-muscovite granite.

(c) A xenolith of probable biotite-muscovite granite was found in the lithionite granite.

The temporal sequence of crystallisation was: biotite-muscovite granite (BFG) → pegmatite → lithionite granite (SFG).

3. A third type of granite is exposed at Goonbarrow, characterised by pale micas. It occurred at the far western end of Goonbarrow and may be an altered version of the lithionite granite.
4. The pegmatite had variable mineralogy, was joint controlled, asymmetric and had large curved orthoclase crystals indicating that it had crystallised from a moving magma. See point 2 above.
5. Elvans in the St. Austell china clay area were intruded during hydrothermal activity and in some cases were intruded after some major vein formation.
6. Quartz/tourmaline $\pm$ cassiterite/wolframite veins with greisen borders are spatially associated with zones of intensely kaolinised granite.
7. Multimineral veins with no greisen borders do not appear to be related to kaolinisation zones.
8. Barren quartz veins with no greisen borders are probably the last geological event in Goonbarrow.

CHAPTER 3

Geochronology

CHAPTER 3

Geochronology

3.1. Introduction

South west England has been the subject of several geochronological studies and some aspects of the timing of events in the peninsula are now well established. The granites have been subjected to intense investigation mainly by potassium-argon dating of the micas and to a lesser extent by whole rock rubidium-strontium work. Other events associated with the granite intrusions have received less attention. Kaolinisation, in particular, has been considered a difficult event to date. The age of the once important tin/tungsten lodes and associated greisens are also very poorly defined.

As previously mentioned there has long been a controversy concerning Cornish kaolinite genesis and the purpose of this geochronological study was to attempt to produce new information which might enable the competing hypothesis to be distinguished or at least clarified.

3.2. Previous work

3.2.1. Rubidium-strontium whole rock and potassium-argon mineral ages

Table 3 summarises all the previous potassium-argon and rubidium-strontium ages on the granites, elvans and greisens of south west England Some of the potassium-argon ages which have been used to formulate this table are from early sources and the development of better analytical techniques place some doubt on their validity. However the greisen potassium-argon ages and rubidium-strontium data which are pertinent to this work, are more modern and consequently regarded as more reliable. All dates have been recalculated using the latest decay constants

Table 3

A. Summary of K/Ar dates on micas from S.W. England

B = Biotite, M = Muscovite, [x] = No. of dates. Recalculated from Dodson and Rex (1971) using the latest decay constant of Steiger and Jager (1977)

Dartmoor	(B)	[13]	276 ± 6
Bodmin	(B)	[2]	281 ± 6
	(M)	[1]	274 ± 9
St. Austell	(B)	[2]	283 ± 8
Carnmenellis	(B)	[2]	284 ± 6
	(M)	[1]	286 ± 9
Lands End	(B)	[5]	261 ± 10
Scillys	(B)	[1]	309 ± 9
	(M)	[2]	297 ± 15
Callington	(B)	[1]	302 ± 8
	(M)	[1]	271 ± 6
Godolphin	(M)	[2]	291 ± 9
Seven stones	(M)	[1]	287 ± 9
L'Haig Fras	(M)	[1]	283
St. Agnes Greisen	(M)	[1]	284 ± 5
Cligga "	(M)	[1]	275 ± 6
St. Michaels Mt "	(M)	[1]	267 ± 5
Bostraze "	(M)	[1]	262 ± 5

from Alex Halliday (pers. comm. 1977)

B. Summary of Rb/Sr dates from S.W. England

St. Austell granite	301 ± 25	(Harding and Hawkes, 1971)
Brannel Elvan	280 ± 5	(Hawkes, Harding and Darbyshire, 1975)
S. Crofty "	274 ± 12	
Wherry "	281 ± 12	

All recalculated using the decay constants recommended by Steiger and Jager (1977)

recommended by the subcommission on geochronology (Steiger and Jager, 1977).

With reference to Table 3 there appears to be some discrepancy between the potassium-argon and rubidium-strontium dates for the St. Austell granite. However potassium-argon dates are often slightly lower than the corresponding rubidium-strontium date due to several factors. The most important is that argon and strontium have different diffusion parameters under the same conditions (Faure, 1977, p.152) and these elements may diffuse at different rates in different minerals and rocks. When strontium diffuses out of a mineral it often enters another nearby therefore keeping the rock a closed system isotopically since it is the "whole rock" which is being dated. However should argon diffuse out of a mineral it normally leaves the system for good (York and Farquhar, 1972, p.58) and since it is the mineral, not the whole rock, that is being dated a slightly lower age is obtained.

Biotite also frequently produces a slightly lower potassium-argon age than coexisting muscovite. This may be due to some post crystallisation phenomena such as chloritisation or low temperature water/rock interaction. It may also be due to muscovite and biotite having different "blocking temperatures" - described as the temperature at which a mineral effectively retains all the argon produced by radioactive decay of potassium-40. Muscovite has a blocking temperature of 200 to 300°C compared to biotite 150-250°C (Dewey and Pankhurst, 1970, p.379) which indicates that during uninterrupted cooling of the two coexisting minerals, muscovite will produce a slightly higher potassium-argon age. However blocking temperatures are also grain size dependent (Hart, 1964, p.504) and fine grained biotite and muscovite may have blocking

temperatures as low as 100 and 150°C respectively (Dewey and Pankhurst, 1970, p.380). The rubidium-strontium whole rock isochron method is considered to give the time of initial magmatic crystallisation (Moorbath, 1967) assuming there has been no prolonged water/rock interaction which would leach out Sr^{87} producing an anomalously young age. Potassium-argon dates on micas may therefore be considered as cooling ages. In the case of the St. Austell granite even though the potassium-argon age is slightly lower than the rubidium-strontium date they are in fact the same within error.

In summary the granites can be considered to have been emplaced between 309 and 261 m.y. and the greisens, which may be associated with metallic mineralisation, at between 284 and 262 m.y. The elvans were dated at around 281 to 274 m.y., that is contemporaneous with the greisens.

3.2.2. Lead and uranium-lead ages

Tables 4 and 5 show summaries of all the previous lead and uranium-lead ages on uraninite and galena mineralisation in south west England. Darnley et. al., (1960, 1965) and Pockley (1964) concluded that there were several periods of mineralisation and/or remobilisation in south west England. The 290, 225 and 50 m.y. dates were considered to be well substantiated,with less well defined periods at 165 and 124 m.y. However more modern graphical interpretations of uranium-lead data have been used since this early work and therefore two interpretations can be made from the data (i) that there are indeed several periods of mineralisation and/or remobilisation or (ii) that the points on Darnleys graph (1965, fig.1) form a straight line intersecting concordia in the approximate region of 290 m.y. As Darnley pointed out the inaccuracy of the data and large

Table 4

Summary of Uranium-Lead ages on Cornish Uraninites

Location	Holmes-Houtermans		Model ages (m.y.)	Reference
	$^{207}/_{206}$	$^{206}/_{238}$	$^{207}/_{235}$	
Geevor	302 ± 85	290 ± 7	291 ± 15	Darnley et al.(1960)
South Terras	259 ± 100	224 ± 6	227 ± 11	Pockley (1964)
South Terras	247 ± 100	227 ± 7	229 ± 12	"
Redruth area	241 ± 160	124 ± 4	130 ± 7	"
Wheal Owles	542 ± 410	58 ± 3	71 ± 12	"
South Terras area	-ve	62 ± 3	59 ± 8	"
Geevor	257 ± 120	223 ± 5	226 ± 15	Darnley et al.(1965)
South Crofty	309 ± 370	277 ± 10	280 ± 50	"
Kingswood	268 ± 190	206 ± 5	211 ± 20	"
Wheel Bray	91 ± 140	165 ± 4	160 ± 10	"
South Terras	411 ± 400	47 ± 2	55 ± 9	"

Table 5

Summary of Lead isotope ages on Cornish galena samples (Moorbath, 1962)

Location	$^{206}/_{204}$	$^{207}/_{204}$	$^{208}/_{204}$	Model age (m.y.)
Pere Alston	18.12	15.45	37.89	270 ± 60
Wheal Rose	18.13	15.47	37.86	290 ± 70
Vottle shaft	18.20	15.49	37.88	260 ± 60
South Terras	18.24	15.52	37.96	270 ± 70
Mary Anne	18.24	15.53	38.01	280 ± 60
Lambriggan	18.25	15.52	38.13	260 ± 70
Penberthy croft	18.25	15.55	38.14	300 ± 60

errors (due to poor analytical precision) make the position of this line approximate. Clearly more analyses using modern, more accurate techniques are needed to define this line more accurately. However the extreme ease with which uranium and lead may be leached from and sometimes enriched in uraniferous minerals (Darnley, 1965) suggests that this will be difficult to achieve.

Moorbath (1962) analysed seven galenas for their lead isotopic composition and using the simple single stage model of Holmes-Houtemans showed galena mineralisation to have occurred between 300 and 260 m.y. However this data was calculated using older decay constants and the techniques used for measuring lead isotopic compositions have since been markedly improved. Some of Moorbath's samples have recently been re-analysed by Rundle and Swainbank of the Institute of Geological Sciences, London and differ considerably from the original values. Their analyses of NBS standards agree with the accepted values and so the reanalysed samples together with several other new galenas are regarded as more reliable. Their analyses plot close to the conformable lead ore growth curve of Cummings and Richards (1975) and yield model ages of between 240 and 280 m.y. with an indication of small variations of $\mu(^{238}U/^{204}Pb)$ in the source region of the lead ore bodies. The data are compatible with derivation of the lead ores from an upper mantle source region over a relatively short interval of time. It is unlikely that the lead could have been derived from crustal rocks more than a few tens of million years older than the mineralisation.

3.3. Geochronology of events in Goonbarrow and other china clay pits in the St. Austell granite

Though the St. Austell granite and Brannel elvan have been dated, no data is available for the age of greisenisation and mineralisation in the St. Austell granite. In order to resolve the detailed chronology of geological events in the Goonbarrow area, potassium-argon age determinations were carried out on fifty seven samples collected from various localities as shown in fig.15.

3.3.1. Unkaolinised granites and pegmatite

Eight samples were collected in total, two each of the three different types of granite and the pegmatite. The samples were split into pieces of about two centimetres square, jaw crushed and then sieved to recover the 40/80# size fraction which was considered to be the optimum size for mineral liberation as viewed in thin sections. The micas were then separated using several techniques (see Appendix 1). Muscovite was separated from the small feldspar (SFG) and pale mica (PMG) granites, biotite only for the pegmatite and both minerals for the big feldspar granite (BFG). These were considered to give cooling dates for the granites.

3.3.2. The greisens

Five samples in total were taken from greisens in all three granite types. These were crushed and separated as for the granite samples.

3.3.3. Kaolinised granites

Five samples were selected, four of kaolinised BFG and one only of kaolinised PMG. In chapter 2 it was shown that the feldspars produced

a fine grained muscovite on kaolinisation. This mica was of variable grain size up to about 100μm (i.e. 160#). For three of the samples four different grain size fractions were separated to elucidate if the fine grain muscovites produced a significantly lower age than the relic micas, assuming that the samples did not contain any fine grain primary mica (e.g. a Tertiary age for the kaolinisation). Due to their very altered nature the samples did not need crushing, but were disaggregated in water to remove the kaolinite which was then separated in the normal way (see Appendix 1).

3.3.4. The elvans

An unkaolinised elvan would be difficult to date by the potassium-argon method as any micas which are present are usually fine grained and would prove difficult, though not impossible to separate. They could not be reliably dated by the whole rock potassium-argon method since feldspar, a major constituent of elvans, does not retain argon to any reliable degree and would therefore give anomalously low ages. However this technique has worked well for some fine grained rocks (e.g. fine grained basalts without volcanic glass) which have not been thermally overprinted. Unkaolinised elvans have of course been successfully dated by the rubidium-strontium technique. It would have been possible to date kaolinised elvans by this technique but for intercomparison purposes with other potassium-argon dates it was considered better to use the latter method. Kaolinised elvans and especially those within the St. Austell granite, contain no potassium feldspar, large amounts of secondary mica and very little relic mica (the only other minerals present to any extent are quartz and kaolinite). Kaolinised elvans are therefore ideal for

whole rock potassium-argon dating of the secondary mica although no dates from these rocks are to be found in the literature.

In chapter 2 the Goonbarrow elvan was described as crosscutting quartz/tourmaline veins of the same strike as those containing tin/tungsten. A date on the elvan would therefore give a minimum date for the quartz/tourmaline veins and by inference an age for the tin/tungsten stockworks so typical of the Hensbarrow region. As previously mentioned in chapter 2 the elvans have been completely reconstituted to a quartz-muscovite-kaolinite-tourmaline assemblage and contain intergrown muscovite/kaolinite pseudomorphing feldspar phenocrysts. These factors suggest that the elvans were intruded during hydrothermal activity i.e. during the major kaolinising event. The elvan date may therefore represent the date of kaolinisation.

Five samples from Goonbarrow were selected together with three from the neighbouring Gunheath china clay pit and one each from Dorothy and Melbur pits in other areas of the St. Austell granite. These were then prepared as for the granite samples except that they were sieved to 60/120 # since this was the optimum mica size viewed in thin sections.

3.3.5. Miscellaneous samples including muscovites from the Goonbarrow refining process

Two further mica samples were collected for dating, both produced as waste from the kaolin refining process at Goonbarrow. Figure 16 shows their relative position in the refining process. By their nature these were mica composites, having been derived from kaolinised granite from various locations in the pit. However if it could be shown that they produced sensible ages then it may be possible to use similar samples for dating kaolinisation in other locations.

About thirty intensely kaolinised potassium feldspar phenocrysts were also collected. Thin section studies had shown these to consist of an intergrowth of kaolinite and secondary muscovite (see chapter 2). No attempt was made to remove the kaolinite since this mineral is not potassium bearing. These phenocrysts, run as one overall sample, contained no primary muscovite whatsoever but only secondary muscovite produced during the kaolinising process and a date on them should represent this event.

All the samples were analysed for their potassium content and argon isotopic composition by standard methods (see Appendix). The latest acceptable decay constants and potassium isotopic abundances were used to calculate the ages (Steiger and Jager, 1977). The final data are collated in tables 6, 7 and 8. The samples were then classified into groups according to age and a corresponding mean, standard deviation (1σ) and standard error on the mean calculated. These are listed in table 9.

3.4. The statistical treatment and meaning of ages

The potassium-argon age determinations were carried out at the Institute of Geological Sciences, London and following the practice of that laboratory the errors for the potassium-argon ages were calculated by the method adopted by Rundle (1979, p.31). The errors are a combination of the standard errors for the argon isotopic composition, spike volume and potassium determination and are quoted at the 95% (2σ) confidence level. They represent estimates of the analytical precision only and do not incorporate errors in the decay constants. The mean

TABLE 6. Results of Potassium - Argon ages on Goonbarrow samples

Sample No.	Description	Mineral or rock	Mesh size	% K	Vol. Rg Ar^{40} (nl/g at NTP)	% Atm Ar^{40}	Age (m.y.)
GRANITES AND PEGMATITE							
167	BIG FELDSPAR GRANITE	Muscovite	40-80 #	5.200	55.94	13.47	257.4
187	"	Muscovite	40-80 #	5.200	57.74	17.69	265.1
262	"	Muscovite	40-80 #	4.927	59.18	16.09	285.2
262	"	Biotite	40-80 #	6.908	77.083	2.10	266.3
187	"	Biotite	40-80 #	7.265	84.63	8.05	277.1
187	"	Biotite	40-80 #	7.265	85.20	3.90	278.9
188	SMALL FELDSPAR GRANITE	Muscovite	40-80 #	5.688	62.34	7.67	261.9
188	"	Muscovite	40-80 #	5.688	65.28	36.70	273.4
247	"	Muscovite	40-80 #	7.932	93.40	10.28	280.0
247	"	Muscovite	40-80 #	7.932	94.02	8.15	278.5
248	PALE MICA GRANITE	Muscovite	40-80 #	7.909	93.04	3.93	279.7
248	"	Muscovite	40-80 #	7.909	95.00	4.51	285.2
249	"	Muscovite	40-80 #	7.473	87.59	7.08	278.8
186	PEGMATITE	Biotite	40-80 #	7.604	88.34	6.20	276.5
186	"	Biotite	40-80 #	7.604	88.64	7.31	277.3
MISCELLANEOUS							
	GOONBARROW NO. 2 UNDERFLOW	WR	-	2.896	30.40	15.91	251.6
	"	WR	-	2.896	33.00	18.78	271.5
	GOONBARROW HYDROCLONE RESIDUE	Muscovite	40-80 #	7.310	83.15	9.01	271.1

TABLE 7. Results of Potassium - Argon ages on Goonbarrow, Gunheath, Dorothy and Melbur samples

Sample No.	Description	Mineral or Rock	Mesh size	% K	Vol. Rg Ar^{40} (nl/g at NTP)	% Atm Ar^{40}	Age (m.y.)
ELVANS							
206	GOONBARROW	WR	60-120 #	3.468	39.98	10.31	274.5
213	GOONBARROW	WR	60-120 #	1.906	21.27	13.86	266.3
214	GOONBARROW	WR	60-120 #	1.762	20.10	14.04	271.8
218	GOONBARROW	WR	60-120 #	3.618	40.55	15.78	267.4
221	GOONBARROW	WR	60-120 #	3.260	37.84	4.16	174.7
223	GUNHEATH	WR	60-120 #	3.204	36.77	6.40	273.4
230	GUNHEATH	WR	60-120 #	2.735	31.48	22.41	274.1
237	GUNHEATH	WR	60-120 #	4.770	54.53	10.70	272.4
254	DOROTHY	WR	60-120 #	2.463	28.79	14.04	278.1
258	MELBUR	WR	60-120 #	4.491	49.72	2.43	264.4
GREISENS							
140	OLD BEAM	Muscovite	40-80 #	7.205	82.78	6.50	273.7
141	OLD BEAM	Muscovite	40-80 #	5.799	78.95	5.14	320.1
141	OLD BEAM	Muscovite	40-80 #	5.799	73.83	2.70	300.9
141	OLD BEAM	Muscovite	40-80 #	5.799	77.74	9.87	315.6
196	IMPERIAL	Muscovite	40-80 #	4.505	48.89	12.19	259.6
196	"	Muscovite	40-80 #	4.505	50.32	7.49	266.6
197	ISLAND OPPOSITE OLB BEAM (S.FACE)	Muscovite	40-80 #	4.818	56.42	5.81	278.6
197	"	Muscovite	40-80 #	4.818	58.34	10.05	287.3
198	NEAR MARTINS GOONBARROW	Muscovite	40-80 #	3.520	39.22	14.29	265.9

TABLE 8. Results of Potassium - Argon ages on Goonbarrow Samples

Sample No.	Description	Mineral	Mesh size	% K	Vol. Rg Ar^{40} (nl/g at NTP)	% Atm Ar^{40}	Age (m.y.)
KAOLINISED GRANITE							
265	KAOLINISED BFG-CLASSIFIERS AREA	Muscovite	40-80 #	7.623	85.73	5.41	268.3
265	"	Muscovite	40-80 #	7.623	79.45	1.15	249.9
265	"	Muscovite	80-120 #	7.173	79.89	6.42	265.9
265	"	Muscovite	120-160 #	7.275	79.75	4.98	262.0
265	"	Muscovite	160-240 #	6.438	71.83	11.69	266.3
265	"	Muscovite	160-240 #	6.438	72.56	2.40	268.8
265	"	Muscovite	160-140 #	6.438	72.57	4.92	268.9
264	KAOLINISED FMG-NR.MARTINS GOONBARROW	Muscovite	40-80 #	6.620	79.62	4.15	285.5
264	"	Muscovite	40-80 #	6.620	79.49	10.39	285.1
264	"	Muscovite	80-120 #	4.672	55.91	9.64	284.2
264	"	Muscovite	120-160 #	7.074	81.25	3.51	273.6
264	"	Muscovite	160-140 #	4.101	46.66	13.44	271.3
264	"	Muscovite	160-240 #	4.101	45.93	7.83	267.3
263	KAOLINISED BFG-OLD BEAM	Muscovite	40-80 #	7.010	80.20	8.69	272.6
263	"	Muscovite	160-240 #	5.286	58.15	5.07	262.8
	"	Muscovite	40-80 #	7.028	83.24	8.60	281.4
	"	Muscovite	40-80 #	7.028	82.12	7.93	277.9
	KAOLINISED BFG-IMPERIAL	Muscovite	40-80 #	5.235	62.26	7.85	282.5
	"	Muscovite	40-80 #	5.235	64.43	8.66	291.7
	KAOLINISED K-FELDSPAR-CLASSIFIERS AREA	Sericite Kaolinite	WR	0.539	6.19	28.5	273.9

Table 9. Grouped ages and means of results from the Potassium-argon age study

Mean ages are followed by the standard error on the mean (sem) and standard deviation in brackets (1σ)

1. Unkaolinised granites and pegmatites

BFG	Muscovite	257.4 ± 8.5		
		265.1 ± 89	269.2 ± 8.3 (14.4)	
		285.2 ± 9.1		All muscovites 274.5 ± 2.7 (9.8)
	Biotite	266.3 ± 8.5		
		277.1 ± 8.5	274.1 ± 3.9 (6.8)	All biotites 275.2 ± 2.1 (5.1)
		278.9 ± 8.6		
SFG	Muscovite	261.9 ± 8.3		
		273.4 ± 8.9		
		280.0 ± 8.9	273.5 ± 4.1 (8.2)	
		278.5 ± 8.8		
PMG	Muscovite	279.7 ± 8.9		
		285.2 ± 9.1	281.2 ± 2.0 (3.5)	
		278.8 ± 8.9		
Peg	Biotite	276.5 ± 8.6	276.9 ± 2.0 (3.5)	
		277.3 ± 8.5		

2. Kaolinised granites

BFG	40/80 #	249.9 ± 8.0 (1)		
		266.3 ± 8.5		
		272.6 ± 8.9		Overall 274.2 ± 1.4 (8.9)
		281.4 ± 8.6	279.1 ± 3.3 (8.2)	
		277.9 ± 8.6		All 40/80 280.6 ± 2.4 (7.5)
		282.5 ± 9.1		
		291.7 ± 9.3		All 80/120 275.1 ± 9.1 (12.9)
	80/120 #	265.9 ± 8.5		
	120/160 #	262.0 ± 8.3		All 120/160 267.8 ± 5.8 (8.2)
	160/240 #	266.3 ± 8.5		
		268.8 ± 8.5		All 160/240 267.7 ± 1.0 (2.9)
		268.9 ± 8.5	266.7 ± 1.4 (2.9)	
		262.8 ± 8.4		
PMG	40/80 #	285.5 ± 9.0		
		285.1 ± 9.0	285.3 ± 0.2 (0.3)	
	80/120 #	284.2 ± 9.0		
	120/160 #	273.6 ± 8.7		
	160/240 #	271.3 ± 8.7		
		267.3 ± 8.5	269.3 ± 2.0 (2.8)	

(1) Not used since almost 4σ from the mean (279.1) i.e. there is a 0.1% chance that it is a member of this population

3. Elvans

Goonbarrow	274.5 ± 8.5		
	266.3 ± 8.6		
	271.8 ± 8.5	270.9 ± 1.8 (3.9)	
	267.4 ± 8.6		
	274.7 ± 8.7		271.7 ± 1.1 (4.3) (2)
Gunheath	273.4 ± 8.5		
	274.1 ± 9.1	273.3 ± 0.5 (0.9)	
	272.4 ± 8.7		
Dorothy	278.1 ± 8.8		
Melbur	264.4 ± 8.4		

(2) sem calculated on Goonbarrow and Gunheath samples only since there is no standard deviation available for the Dorothy and Melbur samples.

4. Greisens

In BFG	273.7 ± 8.8		
	320.1 ± 9.6 (3)		
	300.9 ± 9.2 (3)		
	315.6 ± 9.6 (3)	266.6 ± 4.1 (7.1)	
	259.6 ± 8.3		
	266.6 ± 8.7		272.0 ± 2.6 (10.0)
In PMG	278.6 ± 8.8		
	287.3 ± 8.9	283.0 ± 4.3 (6.2)	
In SFG	265.9 ± 8.7		

(3) Not considered (see text)

ages and errors quoted in table 9 were calculated using standard statistical formulae (see Appendix). Comparison of groups of two or more ages to elucidate if they are significantly different was carried out using the "Students t" test. (Speigel, 1961) (see Appendix 3).

3.5. Discussion

In tables 6, 7 and 8 the potassium values are listed for the analysed micas. In some cases the potassium values for the muscovites are lower than would be expected (Deer, Howie and Zussman, 1962). Microscopic examination utilising refractive index oils revealed that some samples were contaminated with approximately 1 - 10% quartz. It was found impossible with the methods available to purify the samples further, however since quartz is a non potassium bearing mineral its presence was not considered to affect the potassium-argon age determinations. Those samples suffering from the greatest quartz contamination were 187, 188, 196, 197, 198, 262 and the fine grained fractions of 263 and 264. Some of these muscovites were also analysed using an electron microprobe and found to contain more normal potassium values although not all the low values could be attributed to quartz contamination. They are reported in chapter 4.

3.5.1. Unkaolinised granites

The muscovite and biotite ages for all the granites and pegmatite are virtually the same within error and give a mean age of around 275 m.y. As expected this value is considerably lower than the rubidium-strontium age obtained by Harding & Hawkes (1971) although still

the same within error. The 275 m.y. value is slightly lower than, although again the same within error as, the 283 m.y. dates quoted in table 3. These values, measured by Miller and Mohr (1964) and Dodson and Rex (1971), were obtained from biotite from Tregorden quarry near Luxullyan. This locality is well within Exleys biotite-muscovite granite. As described in chapter 2 the SFG and PMG at Goonbarrow correspond to Exleys early lithionite type (see also chapter 4) and were intruded after the biotite-muscovite granite. The ages of the three granite types are statistically indistinguishable, however this does not necessarily indicate that they were intruded within a short time of each other since potassium-argon dates only represent cooling ages. These dates only indicate that they cooled through the blocking temperature of the appropriate mineral or were subsequently thermally reset at about the same time.

The pegmatite date is not in disagreement with the sequence of events as concluded in chapter 2.

3.5.2. Greisens

Of the five greisen samples analysed, one (141) consistently produced an abnormally high age, much higher than any unkaolinised granite date. This consistency indicates that the argon isotopic ratio measurements are reliable. Anomalously high ages may be due to several factors (Dalrymple and Lanphere, 1969, p.200). (1) potassium loss (2) excess ^{40}Ar (3) inherited ^{40}Ar (4) poor potassium determination - in this case a low value. (1) Potassium loss could result from some form of alteration of the mineral. However argon loss would also be experienced which may counter-balance this phenomena. A laboratory study has shown that up to 80% loss of potassium in a biotite causes no affect on the potassium-argon

age (Kulp and Engel, 1963). The muscovites in question would have to lose most of their potassium to produce a higher age. The potassium content of sample 141 is 5.8% which in comparison with other values of muscovite from Goonbarrow, even taking into account the contamination problem, is very typical. It is therefore thought unlikely that this process is responsible for the anomalously high ages. (2) Excess ^{40}Ar is radiogenic ^{40}Ar incorporated into the mineral lattice during formation of the mineral. Several minerals are susceptible to trapping excess ^{40}Ar, for example beryl and tourmaline, however this phenomena is extremely rare for micas and has never been reported to explain anomalous ages in muscovites. (3) Inherited ^{40}Ar is caused by incomplete resetting of the potassium-argon clock. It is impossible for a muscovite in Goonbarrow to inherit an argon isotopic composition indicating an age older than about 280 m.y., the approximate cooling age of the granite. (4) A poor potassium determination is the most likely method for producing the high age in this case. This could be due to contamination of the sample with a mineral of much lower potassium content. The most likely candidate is tourmaline which for some samples was difficult to separate from the muscovite. Unfortunately due to the difficulty in separating the muscovite from the bulk of the rock all of this sample had to be used for potassium and argon determinations, so a repeat potassium analysis or improved separation could not be attempted. The presence of any tourmaline could add further to an anomalously high age since this mineral is well known in containing excess ^{40}Ar.

Omission of sample 141 produces a mean age for the remaining four greisens of 272 m.y. which is indistinguishable from the unkaolinised granites. The greisens are certainly associated with mineralised veins and spatially associated with zones of kaolinised granite. The age of mineralisation in Goonbarrow may therefore be inferred. These dates

also agree with the four dates obtained for greisens in the Land's End granite (see table 3) indicating a similarity in the time of stockwork mineralisation for these two areas.

3.5.3. The elvans

All four elvans are identical in age within error. The mean value of 272 m.y. is also statistically indistinguishable from the unkaolinised granites, kaolinised granites and greisens. This value also agrees extremely well with other elvan ages (Hawkes et. al., 1975) obtained by the rubidium-strontium method. The rubidium-strontium date represents the elvan intrusion age and the potassium-argon age the hydrothermal alteration date since it is the secondary muscovite which has been dated. Destruction of the original mineral assemblage to produce the new re-crystallised texture must have reset the potassium-argon clock. The fact that the two dates are so close indicates that the St. Austell granite altered elvans were hydrothermally altered immediately after intrusion. This is consistent with the fact that the elvans crosscut some veins but are themselves altered, thus indicating that they were intruded during hydrothermal activity. Their dates therefore correspond to the time at which the secondary elvan muscovite cooled through 250°C - 300°C (the approximate blocking temperature) which was after hydrothermal activity (fig. 17). Since muscovite/kaolinite intergrowths pseudomorph feldspar phenocrysts, this suggests that the major kaolinising event occurred between 271.7 $\pm$ 4.3 m.y. (the potassium-argon elvan date) and 301 $\pm$ 25 m.y. (the St. Austell granite rubidium-strontium date).

3.5.4. Kaolinised material

The problems involved with the hydrothermal vs. weathering kaolinite

genesis controversy have been discussed elsewhere. In chapter 2 thin section studies showed that kaolinite was intergrown with fine grained muscovite, produced during the kaolinite process. Therefore if this fine grained muscovite could be dated this would represent the time of kaolinisation.

The two types of granite investigated appear to produce slightly lower ages with decreasing grain size of the muscovite. For the PMG a "students t" test showed the 40/80 # and 160/240 # fractions to be statistically different at the 0.01 level of significance, although the corresponding grain sizes for BFG were not statistically different. The 80/120 # and 120/160 # fractions are not statistically different from each other or the other two fractions. They are all single age determinations which consequently prevent the errors from being reduced to similar levels as the other fractions. In the case of the BFG 40/80 # fraction, one of the seven measured ages is anomalously low (249.9) and since it is almost four standard deviations (4σ) from the mean of the rest of the group (this means there is only a 0.1% chance that it is a member of that population) it was discarded.

The low age for the 160/240 # fractions may be a very real effect suggesting that kaolinisation occurred 7 - 13 m.y. after emplacement of the granites. However, as previously mentioned, low potassium-argon ages are often produced as the grain size of a mineral is reduced (Dewey and Pankhurst, 1970). It is also possible that some of the larger relic mica flakes broke down contaminating the finer 160/240 # "kaolinised muscovite" although the very nature of the separation process minimises this possibility.

This data suggests that kaolinisation occurred during the Hercynian and is not of Tertiary origin as suggested by Bristow and Wilson (1977) and other workers.

3.5.5. Miscellaneous samples

The date on the kaolinised potassium feldspar (i.e. sericite/kaolinite mixture) of 273.9 ± 9.5 m.y. is statistically indistinguishable from the unkaolinised granite, kaolinised granite and greisen samples. This further supports an Hercynian age for kaolinisation since the secondary muscovite intergrown with kaolinite was produced during the kaolinising process.

The Goonbarrow No. 2 underflow sample produced two ages of widely differing values. The 272 m.y. date seems more sensible in comparison with the date of 252 m.y. It appears that this type of sample may not produce reliable results. The single age determination on Goonbarrow hydrocyclone residue muscovite produced a result of 271 m.y. which is very close to kaolinised and unkaolinised granite dates. The muscovites from a hydrocyclone residue are produced almost exclusively from the soft kaolinised granite and so this date may represent the age of kaolinisation assuming it has not been contaminated with relic muscovite. However due to the mechanical way in which this residue is produced contamination is quite possible in this case and so their reliability is also questioned.

3.6. Summary and conclusions

The overall sequence of geological events at Goonbarrow is summarised in fig. 17.

1. The biotite-muscovite and early lithionite granites exposed at Goonbarrow gave (cooling) ages statistically indistinguishable from one another at a mean of 275 m.y. This value was within error of (a) previous potassium-argon dates obtained for the biotite-muscovite granite only (b) a rubidium-strontium isochron date for the biotite-muscovite granite.
2. The Goonbarrow pegmatite gave a date statistically indistinguishable from the granites. Since these dates represent cooling ages they do not conflict with the temporal sequence of events suggested in chapter 2.
3. The greisens, which are associated with mineralised veins and spatially associated with zones of kaolinised granite, are of the same age as the granites and pegmatite and also with similar greisens dated in the Lands End granite.
4. Four elvans from different locations within the St. Austell granite gave the same age within error and agree extremely well with other elvan ages obtained by the rubidium-strontium technique. Since three of the analysed elvans crosscut veins and taking into account the greisen ages, this indicates that mineralisation within the St. Austell granite is of Hercynian age. This is also in good agreement with Moorbaths (1962) galena study and with the reinterpretation of previous uranium-lead work.
5. It is considered that the elvan was intruded during hydrothermal activity on mineralogical and textural grounds, and that the major kaolinising event occurred between 301 and 272 m.y.

6. Fine grained muscovite from the kaolinised PMG, produced predominantly during kaolinisation, gave a slightly lower age than the corresponding unkaolinised granite. This variation was also identified for the grouped kaolinised granite data. However this was not the case for the corresponding size fractions for the BFG. This may indicate that kaolinisation occurred just after the granite micas cooled through their blocking temperature or may be due to grain size effects lowering the mica blocking temperatures.
7. The date on the kaolinised potassium feldspar (a sericite/kaolinite mixture) was also the same as unkaolinised granite within error.
8. All the results indicate that kaolinisation at Goonbarrow, and probably elsewhere in the St. Austell granite, was of Hercynian age and intimately associated with greisen bordered veins.

CHAPTER 4

Geochemistry

CHAPTER 4

Geochemistry

4.1. Introduction

The main criteria for distinguishing the granite types in the St. Austell mass are the different varieties of mica. In chapter 2 it was shown that the big feldspar granite at Goonbarrow corresponded to Exleys (1955, 1959, 1976) biotite-muscovite granite and the small quartz-feldspar granite to his porphyritic lithionite variety. However, in the latter case two micas were recognised, identified as muscovite and probably lithionite, compared to the single lithionite mica in Exleys description. In view of the importance of the micas in classifying the granites and their use in the potassium-argon dating program, a short chemical analysis program was initiated.

Another important criterion for distinguishing biotite-muscovite and lithionite granites according to Exley, was the composition of the plagioclase feldspars. Consequently the plagioclase feldspars within the Goonbarrow granites were also analysed.

4.2. Analytical procedures

The mica separates used for potassium-argon dating plus six other samples were dissolved as described in the appendix and analysed for K_2O by flame photometry (as described in appendix 2). Li_2O and Al_2O_3 were analysed by atomic absorption under standard conditions using a Perkin-Elmer 306 atomic absorption spectrophotometer and lanthanum chloride as an ionisation buffer.

Seven samples of granite and two of greisen were analysed for Al, Ca, Fe, K, Mg, Na, Rb and Si using a Cambridge Instruments microscan 9

electron microprobe. Each mineral grain was usually analysed in three different places using a 3μm raster.

The analyses are shown in tables 10 to 19.

4.3. Discussion

4.3.1. The micas

In chapter 3 the problem of the purity of the mica separates was discussed. It can be seen from the data in table 10 that many of the Al_2O_3 values are surprisingly low for muscovite which is normally 34-39% (Deer, Howie and Zussman, 1962). Consequently the Li_2O values may also be correspondingly low although they are still of great assistance for identification of the micas.

The micas from the unkaolinised and kaolinised BFG have Li_2O values of 0.10 - 0.29 and 0.22 - 0.45% respectively which is typical for muscovite (Deer, Howie and Zussman, 1962). However it appears that unkaolinised and kaolinised SFG and PMG have very high Li_2O values. It must be remembered that all the unkaolinised SFG and PMG mica separates are a composite of muscovite and what has been tentatively described as lithionite. Only one mica was recognised in the kaolinised samples. For sample 188 it was possible to separate these two micas and it can be clearly seen from the data that sample no. 188L (light mica) has a Li_2O value typical of a muscovite (and in very good agreement with the value obtained for muscovite in the big feldspar granite) and sample no. 188D (dark mica) a much higher value. This value is typical of Lepidotite, Zinnwaldite and the Lithionite series.

Greisens, defined by Johannsen (1938) as rocks consisting essentially of quartz and mica, are formed by alteration of the granite adjacent to

TABLE 10 Atomic absorption and flame photometric results on Goonbarrow samples

Micas from Unkaolinised granites/pegmatite

Granite type	Sample No.	No. of analyses	Li_2O%	K_2O%	Al_2O_3%
Big feldspar	187M	1	0.14	6.49	15.37*
"	187Bi	2	1.07	8.76	21.90
"	262M	2	0.29	5.94	17.95
"	262Bi	2	1.16	8.33	21.99
"	403	2	0.15	5.72	-
"	407	2	0.10	5.70	-
Small quartz-feldspar	188L	2	0.28	4.60	9.69*
"	188D	2	3.03	10.76	24.01
"	247	2	3.58	9.56	21.38
Pale mica	248	2	2.20	9.53	24.47
"	249	2	1.72	9.01	23.13
Pegmatite	186Bi	1	1.14	7.60	19.98

Micas from Unkaolinised granite

Granite type	Sample No.	No. of analyses	Li_2O%	K_2O%	Al_2O_3%
Big feldspar	263 160/240 #	2	0.22	6.37	28.72
"	263 40/80 #	2	0.32	8.45	28.23
"	265 160/240 #	2	0.25	7.76	29.98
"	265 40/80 #	2	0.35	9.19	30.58
"	408	2	0.29	9.53	-
"	409M	2	0.28	6.26	-
"	409Bi	2	0.45	8.71	-
Pale mica	264 160/240 #	2	1.17	4.94	24.06
"	264 120/160 #	2	2.18	8.53	22.14
"	264 80/120 #	2	1.38	5.63	20.71
"	264 40/80 #	2	2.36	7.98	20.24
"	405	2	2.60	8.43	-

Micas from Greisens

Granite type formed in	Sample No.	No. of analyses	Li_2O%	K_2O%	Al_2O_3%
Big feldspar	140	2	0.41	8.68	23.50
"	141	2	0.41	6.99	23.09
"	196	2	0.08	5.43	19.92
Small quartz/feldspar	198	1	3.92	4.24	20.03
Pale mica	197	1	1.29	5.81	14.98*

Notes

M = muscovite, Bi = biotite, L = Light mica, D = dark mica.

Samples marked * are particularly impure.

TABLE 11 Electron Microprobe Analyses

Sample No. 187 Big feldspar granite

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe as FeO	Rb_2O	Total	Remarks
FELDSPARS											
RN	plagioclase	10.14	-	21.28	69.06	0.28	1.71	-	0	102.47	An 16.8
SN	"	10.99	-	20.44	67.94	0.20	1.12	-	0.01	100.70	An 10.9
Z	"	10.46	-	20.69	67.77	0.47	1.49	-	0.03	100.91	An 14.5
PRIMARY MICAS											
A	muscovite	0.66	-	31.19	45.57	10.29	0	-	0.29	88.00	
B	"	0.60	-	30.87	45.63	10.09	0.01	-	0.38	87.58	
C	"	0.60	-	31.17	45.48	9.94	0.01	-	0.32	87.52	
R	"	0.44	-	29.28	45.13	10.32	0.01	-	0.27	85.45	
S	"	0.52	-	28.69	46.19	8.71	0.26	-	0.27	84.64	
T	"	0.65	-	30.48	45.93	10.05	0.01	-	0.31	87.43	
TN	"	0.25	-	27.38	46.87	10.01	0.19	-	0.35	85.05	
YN	"	0.26	-	26.00	43.71	10.37	0.12	-	0.42	80.88	
SECONDARY MICAS											
F	muscovite	0.92	-	35.68	47.09	9.30	0.37	-	0.05	93.41	
L	"	0.30	-	36.87	46.77	10.07	0.47	-	0.17	94.65	
N	"	0.25	-	33.58	47.42	10.23	0.24	-	0.26	91.98	
P	"	0.52	-	30.59	49.48	10.23	0.30	-	0.30	91.42	
U	"	0.27	-	36.05	46.31	9.88	0.87	-	0.14	93.52	
W	"	0.42	-	37.45	46.36	10.07	0.28	-	0.07	94.65	

TABLE 12. Electron Microp̃e Analysis

Sample No. 200 Big feldspar granite

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe as FeO	Rb_2O	Total	Remarks
FELDSPARS											
M	plagioclase	11.48	0.02	19.51	71.29	0.11	0.26	0.01	0.02	102.70	An 2.6
N	"	11.22	0.02	20.29	70.83	0.28	0.51	0.01	0	103.16	An 5.1
T	"	11.42	0.02	19.81	71.08	0.27	0.12	0.01	0	102.73	An 1.2
U	"	10.30	0.02	21.77	69.31	0.53	1.53	0.01	0	103.47	An 15.1
AF	"	10.73	0.02	19.97	69.57	0.15	0.87	0.01	0.09	101.41	An 8.8
AG	"	10.73	0.02	19.88	69.62	0.11	0.63	0.01	0.03	101.03	An 6.6
PRIMARY MICAS											
A	biotite	0.13	3.21	21.57	36.27	9.04	0.20	21.09	0.57	92.08	
B	"	0.15	3.32	21.14	37.04	9.01	0.13	20.18	0.64	91.08	
C	"	0.08	3.38	21.61	31.44	5.42	0.07	27.66	0.40	90.06	
K	"	0.14	3.47	21.24	37.05	9.42	0.01	20.04	0.64	92.01	
L	"	0.16	3.46	21.32	37.42	9.22	0.10	19.66	0.65	91.99	
D	muscovite	0.44	1.19	33.49	47.32	10.24	0.01	2.78	0.28	95.75	
E	"	0.56	1.29	33.11	46.79	10.10	0.01	2.79	0.28	95.03	
F	"	0.66	1.19	34.03	47.17	10.31	0.01	2.59	0.28	96.24	
G	"	0.56	1.28	33.39	47.52	10.29	0.07	2.75	0.23	96.09	
H	"	0.61	1.37	32.57	46.98	10.46	0	3.22	0.40	95.61	
Z	"	0.55	1.40	31.47	47.67	10.32	0	2.83	0.31	94.55	
AA	"	0.64	1.36	32.81	47.65	9.99	0.09	2.66	0.33	95.33	
AC	"	0.68	1.40	33.00	47.31	10.16	0.01	2.65	0.33	95.54	
AD	"	0.71	1.31	33.11	46.84	10.23	0	2.70	0.36	95.26	
AE	"	0.68	1.29	33.16	46.91	10.22	0	2.69	0.36	95.31	
SECONDARY MICAS											
P	muscovite	0.45	0.09	36.61	47.34	10.22	0.12	0.81	0.14	95.78	
S	"	0.19	0.15	35.73	47.89	9.92	0.89	0.98	0.26	96.01	
V	"	0.31	0.57	35.42	46.92	9.39	0.75	1.50	0.26	95.12	
X	"	0.51	0.31	35.83	47.11	9.33	0.53	1.38	0.24	96.24	
AH	"	0.21	0.20	34.36	48.23	10.26	0.13	2.17	0.29	95.85	
AJ	"	0.26	0.07	34.41	47.87	10.66	0.01	1.94	0.38	95.60	

TABLE 13. Electron Microp Analyses

Sample No. Old Beam Kaolinised big feldspar granite

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe as FeO	Rb_2O	Total	Remarks
CLAY MINERALS											
AX	kaolinite	0.01	0.13	35.54	44.26	0.02	0.04	0.48	0.01	80.49	
AY	"	0.01	0.04	35.45	42.33	0.01	0.42	0.42	0	78.30	
AZ	"	0.07	0.17	34.19	41.70	0.01	0.91	0.42	0	77.47	
PRIMARY MICAS											
A	muscovite	0.18	1.03	31.49	46.90	10.08	0.01	2.62	0.38	92.69	
B	"	0.13	2.02	30.97	47.19	7.50	0.01	2.62	0.50	90.94	
C	"	0.21	0.90	31.17	46.16	9.96	0.04	2.56	0.24	91.24	
D	"	0.41	0.48	35.85	47.98	10.14	0.06	1.34	0.12	96.38	
E	"	0.28	1.69	28.31	42.19	10.14	0.12	4.12	0.31	87.16	
F	"	0.75	.49	32.92	47.56	10.28	0	2.46	0.21	95.67	
G	"	0.55	0.72	35.00	46.97	10.34	0	1.57	0.29	95.44	
H	"	0.63	1.76	30.37	44.96	9.80	0.01	3.16	0.30	90.99	
I	"	0.23	0.94	30.72	46.77	9.92	0.01	2.98	0.33	91.90	
J	"	0.36	0.92	31.78	46.30	9.09	0.03	2.17	0.25	90.90	
K	"	0.67	1.39	31.96	46.74	10.12	0.03	2.03	0.34	93.93	
AK	"	0.10	0.29	35.81	45.81	5.16	0.12	1.23	0.07	89.52	
AM	"	0.25	0.04	36.43	47.14	10.17	0.03	0.29	0.12	93.14	
AN	"	0.57	0.54	34.50	42.88	9.84	0.04	2.02	0.24	94.89	
AO	"	0.46	1.41	29.82	42.7	8.98	0.01	2.91	0.32	86.79	
AP	"	0.52	1.54	29.20	42.76	9.46	0	2.92	0.25	86.65	
AQ	"	0.32	1.40	30.01	43.45	7.80	0	2.66	0.18	85.82	
SECONDARY MICAS											
L	muscovite	0.16	0.13	36.81	47.68	4.82	0.06	0.69	0.13	90.48	
P	"	0.15	0.24	33.66	43.93	6.93	0.09	1.01	0.27	86.28	
Q	"	0.14	0.07	36.77	47.57	4.97	0.12	0.56	0.18	91.38	
R	"	0.12	0.28	33.33	44.54	8.30	0.07	0.18	0.39	88.21	
V	"	0.09	0.15	36.58	46.38	3.86	0.26	0.51	0.16	87.99	
W	"	0.74	0.15	36.05	45.52	7.52	0.03	1.10	0.05	91.16	
Y	"	0.59	0.17	32.72	44.56	8.78	0.12	1.50	0.16	88.60	
AA	"	0.09	0.13	34.13	44.93	3.48	0.04	0.78	0.16	83.74	
AE	"	0.06	0.28	33.30	43.57	4.57	0.03	1.43	0.21	83.45	

TABLE 14. Electron Micrope Analyses

Sample No. 138 Small quartz-feldspar granite

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe as FeO	Rb_2O	Total	Remarks
FELDSPARS											
BT	plagioclase	11.44	0.02	19.15	69.65	0.16	0.01	0	0.09	100.52	An 0.1
BZ	"	10.95	0.02	19.59	69.08	0.16	0.23	0.01	0.03	100.07	An 2.4
CB	"	11.27	0.02	19.10	68.51	0.15	0.01	0.01	0.01	99.08	An 0.1
CH	"	10.87	0.02	19.27	67.06	0.15	0.07	0.03	0.04	97.51	An 0.8
CI	"	11.00	0.02	18.89	68.33	0.13	0.04	0.03	0.02	98.46	An 0.4
CO	"	10.95	0	19.34	67.40	0.15	0.06	0.01	0.02	97.93	An 0.7
CP	"	11.14	0.02	19.15	68.98	0.18	0.07	0	0.05	99.59	An 0.7
PRIMARY MICAS											
AT	zinnwaldite	0.48	0.41	28.10	43.86	8.86	0.10	7.76	0.85	90.42	
AU	"	0.26	0.56	22.55	45.11	8.78	0.19	9.55	1.58	88.58	
AV	"	0.33	0.68	22.04	45.27	8.81	0.22	9.58	1.47	88.40	
AW	"	0.21	0.47	27.58	43.15	9.77	0	8.43	0.84	90.45	
AX	"	0.20	0.64	21.18	45.61	9.62	0	9.95	1.14	88.34	
AY	"	0.29	0.47	26.47	45.00	9.65	0.01	7.35	0.99	90.23	
AZ	"	0.18	0.53	25.84	45.25	9.74	0	7.69	1.21	90.44	
BB	"	0.17	0.60	22.31	44.62	9.50	0.03	10.07	1.60	88.90	
BC	"	0.18	0.58	24.21	45.03	9.56	0	8.30	0.85	88.71	
BG	"	0.16	0.50	25.68	43.99	9.61	0	9.16	1.13	90.23	
BH	"	0.19	0.47	29.15	44.34	9.99	0	6.90	0.75	91.79	
BI	"	0.13	0.62	20.91	46.84	9.14	0	9.42	0.23	88.29	
BJ	"	0.30	0.49	25.56	41.23	9.63	0	11.52	0.94	89.67	
BK	"	0.27	0.52	29.63	44.48	9.92	0	6.15	0.52	91.49	
BL	"	0.27	0.47	27.89	43.55	9.65	0	8.24	0.82	90.89	
BM	"	0.24	0.45	28.37	44.87	9.11	0.01	6.56	0.69	90.30	
BN	"	0.24	0.51	26.23	45.34	9.38	0.15	7.07	0.71	89.63	
BO	"	0.27	0.45	28.50	44.75	9.00	0.00	7.04	0.69	90.70	
BP	"	0.22	0.71	21.62	44.12	9.31	0.09	11.52	0.96	88.55	
BQ	"	0.18	0.63	21.90	45.35	9.38	0.04	10.49	0.75	88.72	
BR	"	0.19	0.67	24.70	45.05	8.88	0.25	7.57	0.66	87.97	
SECONDARY MICAS											
BU	muscovite	0.62	0	36.64	46.05	10.00	0	0.72	0.51	94.54	
BW	"	0.56	0.04	36.93	45.47	9.31	0.24	0.71	0.37	93.63	
BX	"	0.50	0.02	35.93	45.32	9.64	0.22	1.02	0.36	93.01	
BY	"	0.36	0.24	33.39	44.05	9.16	0.72	2.10	0.31	90.33	
CD	"	0.24	0.30	31.23	45.16	10.00	0.01	4.59	0.62	92.15	
CF	"	0.29	0.27	29.83	45.64	9.69	0.13	4.91	0.62	91.38	
CL	"	0.62	0	36.59	45.04	10.37	0	0.63	0.29	93.54	
CQ	"	0.31	0.22	34.20	44.81	8.44	1.13	1.07	0.34	90.52	
CS	"	0.47	0.13	34.69	45.17	8.85	0.63	1.12	0.30	91.36	

TABLE 15. Electron Microp Analyses

Sample No. 189 Small quartz-feldspar granite

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe as FeO	Rb_2O	Total	Remarks
FELDSPARS											
AX	orthoclase	0.39	0	18.58	66.68	16.44	0	0	0.34	102.43	
AY	"	0.51	0	18.65	64.85	16.22	0	0	0.29	100.52	
BD	plagioclase	11.38	0	19.67	70.00	0.15	0.29	0.01	0.04	102.44	An 3.0
BS	"	11.02	0.02	19.86	70.04	0.31	0.13	0.01	0.07	101.46	An 1.4
BU	"	11.32	0.02	19.46	71.34	0.14	0.19	0.03	0.03	102.53	An 2.0
PRIMARY MICAS											
BE	zinnwaldite	0.52	0.47	28.82	45.60	9.85	0.12	7.32	0.64	93.34	
BF	"	0.67	0.68	29.87	44.93	9.89	0.09	6.77	0.66	93.56	
BG	"	0.36	0.57	24.46	44.41	9.71	0.15	11.13	1.17	91.96	
BH	"	0.36	0.54	23.55	46.44	9.73	0.15	9.04	1.55	91.36	
BI	"	0.23	0.70	23.89	44.79	9.98	0.10	10.16	1.23	91.08	
BJ	"	0.23	0.49	25.66	45.99	10.32	0.07	8.89	1.36	93.01	
BK	"	0.21	0.66	23.93	43.68	9.85	0.20	10.10	1.34	89.97	
BL	"	0.21	0.74	24.45	42.93	9.41	0.32	10.17	1.33	89.56	
BM	"	0.40	0.76	25.08	42.16	9.17	0.39	10.16	1.33	89.45	
BQ	"	0.15	0.78	22.04	45.60	9.87	0.15	9.97	1.46	90.02	
BR	"	0.11	0.63	27.89	43.95	10.42	0.07	8.54	0.85	92.46	
BZ	"	0.54	0.59	29.35	44.37	9.68	0.22	7.29	0.78	92.82	
DA	"	0.28	0.46	21.70	46.49	10.09	0.07	10.23	1.53	90.85	
DB	"	0.15	0.30	22.01	48.77	8.76	0.10	11.16	1.42	92.67	
BN	muscovite	0.32	0.11	32.79	46.71	10.56	0.07	3.94	0.49	94.99	
BO	"	0.46	0	32.18	46.28	10.58	0.03	1.08	0.48	96.09	
BW	"	0.29	0.02	31.80	46.86	10.69	0	5.03	0.56	95.25	
BX	"	0.31	0.02	30.53	47.62	10.73	0	6.00	0.52	95.73	
BY	"	0.24	0.02	26.63	45.87	10.47	0.03	9.22	0.89	93.37	
SECONDARY MICAS											
Au	muscovite	0.30	0.02	31.81	47.53	10.81	0	4.88	0.52	95.87	
AW	"	0.27	0.04	29.52	46.34	10.76	0	6.95	0.78	94.66	
BC	"	0.20	0.06	31.27	47.34	10.82	0.03	4.86	0.57	95.15	
BT	"	0.31	0.11	32.39	48.98	10.21	0.07	3.65	0.55	96.27	
BV	"	0.73	0.02	28.90	48.57	10.24	0.01	6.15	0.64	95.26	

Table 16. Electron Microp Analyses

Sample No. 247 Small quartz-feldspar granite

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe as FeO	Rb_2O	Total	Remarks
FELDSPARS											
AJ	orthoclase	0.42	0	18.70	65.16	15.99	0	0.01	0.28	100.56	
AK	"	0.66	0	18.81	64.67	15.97	0	0.03	0.28	100.42	
Q	plagioclase	10.78	0.06	20.56	69.15	0.25	0.15	0.12	0.04	101.11	An 1.6
R	"	11.30	0.02	20.03	71.39	0.15	0.31	0.03	0.01	103.24	An 3.2
S	"	11.20	0.02	19.64	71.34	0.14	0.09	0.03	0.04	102.50	An 0.9
X	"	11.25	-	19.60	70.91	0.14	0.28	-	0	102.18	An 2.9
Y	"	11.37	0.02	19.44	70.72	0.11	0.06	0	0.05	101.77	An 0.6
Z	"	11.14	0.02	20.04	70.31	0.18	0.60	0.01	0.03	102.33	An 6.0
AE	"	10.99	0.02	19.87	70.52	0.11	0.03	0	0	101.54	An 0.3
AF	"	11.24	0.02	19.78	70.65	0.11	0.04	0	0.05	101.89	An 0.4
PRIMARY MICAS											
A	zinnwaldite	0.20	0.63	23.55	47.67	7.95	0	12.75	1.00	93.75	
B	"	0.32	0.77	23.25	46.45	9.59	0	12.74	0.96	94.08	
C	"	0.22	0.55	23.01	45.39	10.06	0	12.24	1.03	92.50	
D	"	0.20	0.49	21.72	45.83	10.45	0	11.62	0.66	90.97	
E	"	0.13	0.49	21.82	44.52	10.19	0	11.94	1.41	90.50	
F	"	0.15	0.54	22.89	45.37	10.28	0	10.88	1.33	91.44	
G	"	0.25	0.59	22.46	45.28	10.08	0	11.92	1.05	91.63	
H	"	0.25	0.53	22.35	45.72	10.16	0	12.52	0	92.64	
I	"	0.17	0.53	23.39	47.50	9.11	0.01	12.87	0.70	94.28	
J	"	0.24	0.57	22.21	45.61	10.64	0	12.40	0.96	91.13	
K	"	0.27	0.53	22.28	46.21	10.00	0	11.20	1.48	91.97	
L	"	0.25	0.55	22.99	45.57	10.13	0	11.49	1.44	92.22	
M	"	0.25	0.77	22.48	46.32	10.01	0	12.47	0.96	93.26	
N	"	0.15	0.27	22.53	44.80	10.22	0	12.90	0.92	91.84	
P	"	0.22	0.29	22.19	45.90	10.03	0.04	12.55	1.07	92.34	
AN	"	0.13	0.56	20.94	46.01	10.49	0.01	10.24	1.05	89.43	
AO	"	0.14	0.41	24.96	47.80	10.90	0	8.39	0.94	93.54	
AP	"	0.13	0.48	23.56	45.84	10.33	0.03	11.00	0.82	92.19	
T	muscovite	0.31	0.02	34.95	48.67	10.10	0.07	2.04	0.45	96.61	
V	"	0.32	0.28	36.08	47.85	10.45	0.04	1.66	0.41	97.07	
AA	"	0.31	0.63	31.56	46.04	5.92	0.47	1.14	0.16	86.23	
AC	"	0.28	0	36.36	46.78	10.75	0	1.22	0.47	95.86	
AD	"	0.71	0.02	35.75	47.63	8.64	0.09	1.23	0.36	94.43	
AQ	"	0.19	0.35	35.00	49.28	10.15	0.06	1.15	0.26	96.44	
AH	zinnwaldite	0.29	0.34	21.21	50.38	12.00	0.06	8.49	0.88	93.65	
AI	"	0.13	0.42	21.97	49.17	11.08	0.19	8.73	0.77	92.45	

TABLE 17. Electron Microprobe Analysis

Sample No. 248 Pale mica granite

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe as FeO	Rb_2O	Total	Remarks
FELDSPARS											
Q	plagioclase	11.28	0.02	19.39	68.35	0.17	0.03	0.01	0	99.75	An 0.3
R	"	11.33	0.02	19.26	68.53	0.12	0.25	0	0	99.51	An 2.6
X	"	11.34	0.02	19.39	70.01	0.14	0.03	0	0.05	100.98	An 0.3
AE	"	10.78	0.02	20.56	68.09	0.33	0.73	0	0	100.51	An 7.1
AF	"	10.84	0.02	19.40	68.64	0.09	0.23	0	0	99.22	An 2.5
AM	"	10.90	0.02	20.39	68.91	0.13	0.57	0.01	0.02	100.95	An 5.9
AN	"	10.43	0.02	20.66	68.27	0.26	1.08	0	0.09	100.81	An 1.5
PRIMARY MICAS											
A	zinnwaldite	0.30	2.77	24.06	45.96	9.54	0.28	5.73	1.42	90.06	
B	"	0.27	2.61	24.28	45.85	9.28	0.34	5.63	1.26	89.52	
C	"	0.19	2.57	25.17	45.42	9.70	0.34	5.64	1.29	90.32	
D	"	0.44	2.47	24.05	45.98	9.79	0.10	5.99	1.04	89.86	
E	"	0.32	2.42	22.15	46.60	9.66	0.10	6.17	1.09	88.51	
F	"	0.35	2.39	22.34	45.72	9.52	0.05	6.37	1.48	88.20	
G	muscovite	0.57	0.48	35.49	45.95	10.22	0	0.88	0.57	94.16	
H	"	0.67	0.94	33.95	46.10	9.99	0	1.63	0.57	93.85	
I	"	0.28	1.13	33.12	46.55	9.77	0.04	1.66	0.59	93.14	
J	"	0.29	0.65	33.77	47.13	10.24	0	1.38	0.42	93.88	
K	"	0.58	0.52	34.88	45.94	9.94	0	1.25	0.48	93.59	
L	"	0.64	0.31	35.77	44.99	10.12	0	0.81	0.44	93.08	
M	"	0.49	1.23	32.70	45.95	9.85	0.10	2.17	0.59	93.08	
N	"	0.47	1.10	32.44	46.54	9.37	0	2.06	0.55	92.53	
P	"	0.49	0.61	35.20	46.45	9.61	0.01	1.11	0.49	93.97	
SECONDARY MICAS											
W	muscovite	0.33	0.26	36.49	46.63	8.73	0.69	0.35	0.35	93.83	
Z	"	0.99	0.26	35.29	47.48	8.76	0.37	0.12	0.18	93.45	
AB	"	0.87	0.18	34.62	46.34	8.31	0.66	0.22	0.23	91.43	
AC	"	0.58	0.04	37.61	45.35	9.13	0.47	0.16	0.20	93.54	
AP	"	3.03	0.06	32.85	48.86	6.17	0.38	0.09	0	91.44	

TABLE 18. Electron Microprobe Analysis

Sample No. 139 Greisen in old beam area (Big feldspar granite)

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe as FeO	Total	Remarks
PRIMARY MICAS											
AP	muscovite	0.11	0.62	28.91	46.44	8.70	0.01	0.04	7.15	94.03	altered
AQ	"	0.11	0.55	25.68	41.42	8.82	0.04	0.15	5.56	82.33	"
AR	"	0.16	0.64	28.28	45.10	10.59	0.04	0.04	7.49	92.34	"
AT	"	0.14	0.68	28.45	46.11	10.40	0.03	0.15	6.35	92.31	"
AU	"	0.09	0.87	29.19	43.35	9.96	0.06	0.20	2.62	86.34	"
AV	"	0.11	0.59	25.73	41.74	9.48	0.04	0.13	5.93	83.75	"
AW	"	0.12	0.68	28.39	45.29	9.37	0.03	0.19	5.50	89.59	"
AX	"	0.12	0.89	29.38	46.55	9.81	0.07	0.17	4.01	91.50	"
AY	"	0.14	0.70	27.63	44.05	10.03	0.22	0.26	6.38	89.41	"
AZ	"	0.20	0.58	28.09	43.51	9.21	0.15	0.17	4.26	86.17	"
BB	"	0.17	0.68	29.12	44.73	10.30	0.09	0.30	5.67	91.06	"
BI	"	0.09	0.71	27.96	42.81	9.88	0.07	0.20	4.65	86.37	"
BL	"	0.06	0.76	30.35	46.16	10.21	0.06	0.13	4.71	92.44	"
BM	"	0.08	0.65	29.83	46.12	9.61	0.04	0.15	4.03	90.51	"
SECONDARY MICAS											
BC	muscovite	0.13	0.67	25.04	40.11	8.38	0.12	0.17	5.73	80.35	
BD	"	0.13	0.81	26.21	40.07	8.79	0.06	0.17	3.55	79.79	
BE	"	0.17	0.64	28.82	44.95	10.31	0.06	0.22	5.61	90.78	
BF	"	0.09	0.89	29.56	44.93	9.70	0.12	0.26	3.73	89.28	
BG	"	0.08	0.86	30.55	46.16	10.17	0.10	0.26	2.39	90.57	
BH	"	0.09	0.96	30.48	47.22	10.19	0.09	0.45	3.48	92.96	
BO	"	0.09	0.70	28.33	46.02	10.17	0.10	0.18	6.99	92.58	
BP	"	0.14	0.63	29.34	45.77	10.42	0.10	0.22	5.28	91.90	
BQ	"	0.11	0.95	29.03	46.52	10.62	0.10	0.19	4.70	92.22	
BR	"	0.16	0.66	28.32	44.98	10.56	0.12	0.22	6.39	91.41	
BS	"	0.17	0.58	28.72	45.50	10.04	0.23	0.02	6.62	91.88	
BT	"	0.10	0.69	27.50	44.95	9.82	0.20	0.04	7.73	91.03	
BU	"	0.16	0.66	28.54	46.17	10.79	0.06	0.15	6.28	92.81	
BV	"	0.19	0.41	28.00	45.02	10.22	0.07	0.09	6.25	90.25	
BW	"	0.11	0.87	26.58	41.51	9.12	0.04	0.13	4.13	82.49	
BX	"	0.15	0.69	23.50	42.67	9.39	0.12	0.15	2.07	83.74	
BY	"	0.14	0.75	28.30	45.68	10.15	0.19	0.20	5.26	90.67	
BZ	"	0.14	0.73	28.73	46.43	10.77	0.09	0.24	5.38	92.51	

TABLE 19. Electron Microbe Analysis

Sample No. 167 Greisen in Imperial area (Big feldspar granite)

Sample Point No.	Mineral	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe as FeO	Total	Remarks
PRIMARY MICAS											
A	muscovite	0.57	1.57	32.14	47.62	9.65	0.01	0.19	3.05	94.80	
B	"	0.63	1.66	31.35	46.03	10.02	0.01	0.20	3.35	93.25	
C	"	0.70	1.44	32.72	46.97	9.75	0.01	0.52	2.99	95.10	
D	"	0.69	1.54	32.20	46.63	10.07	0.01	0.09	3.05	95.08	
E	"	0.64	1.71	31.78	47.52	10.12	0	0.24	3.02	95.08	
F	"	0.70	1.48	31.75	46.76	9.96	0	0.22	2.74	93.61	
G	"	0.73	1.36	31.78	45.60	9.78	0.04	0.15	2.95	92.38	altered
H	"	0.70	1.50	32.62	47.54	9.84	0.01	0.24	2.88	95.33	"
I	"	0.15	0.44	33.38	47.55	10.26	0.04	0.07	2.46	94.32	"
L	"	0.21	0.75	30.13	42.41	8.50	0.25	0.26	1.51	84.02	"
M	"	0.62	1.84	31.44	45.22	10.26	0	0.52	4.04	93.94	"
N	"	0.65	1.01	32.77	48.09	10.32	0.03	0.34	2.51	95.72	"
P	"	0.09	1.60	32.01	45.04	10.26	0	0.67	3.35	93.02	"
Q	"	0.63	1.47	32.25	45.23	10.13	0.09	0.37	3.17	93.34	"
R	"	0.09	0.70	30.49	48.13	9.69	0.16	0.26	4.24	93.78	"
S	"	0.65	1.70	31.74	45.74	9.94	0.04	0.26	3.52	93.59	"
T	"	0.61	1.73	31.86	45.84	10.30	0.06	0.30	3.18	93.81	
U	"	0.67	1.46	33.04	46.54	9.94	0.01	0.43	2.74	94.83	
V	"	0.70	1.57	32.87	46.14	9.65	0.03	0.35	2.79	94.10	
W	"	0.69	1.76	32.75	45.53	10.31	0	0.13	3.08	94.25	
X	"	0.18	0.45	32.91	47.28	10.65	0.04	0.28	2.68	94.47	
Y	"	0.68	1.72	32.85	46.22	9.54	0.01	0.15	2.68	93.85	
SECONDARY MICAS											
Z	muscovite	0.21	0.53	31.71	46.83	10.37	0.09	0.15	3.02	92.91	
AA	"	0.17	0.49	31.89	46.47	10.82	0.01	0.15	2.94	92.94	
AB	"	0.19	0.44	34.23	42.64	10.29	0.16	0.07	1.33	94.35	
AC	"	0.16	0.41	32.45	48.54	9.96	0.16	0.04	2.89	94.61	
AD	"	0.19	0.51	31.84	41.18	8.47	0.35	0.06	0.64	83.24	
AE	"	0.18	0.52	32.36	45.94	10.03	0.13	0.11	2.12	91.39	
AG	"	0.19	0.45	32.81	45.76	9.47	0.10	0.15	1.44	90.37	
AH	"	0.15	0.56	32.41	46.61	10.70	0.09	0.17	2.10	92.79	
AJ	"	0.15	0.53	34.13	48.43	10.47	0.04	0.06	1.36	95.17	
AM	"	0.13	0.56	32.95	48.51	10.40	0.09	0.21	2.26	95.11	
AN	"	0.18	0.43	32.17	47.79	10.59	0.09	0.07	2.97	94.29	
AO	"	0.13	0.64	31.83	45.55	10.52	0.07	0.22	2.12	91.08	

veins and so it may be expected that the chemical composition of the mica may reflect the original granite composition. This appears to be the case at Goonbarrow. Sample nos. 140, 141 and 196 were formed within the BFG and have Li_2O values of 0.08 - 0.41%, higher than the unkaolinised and kaolinised BFG muscovite values, perhaps reflecting a distribution of lithium originally in both the biotite and muscovite phases. Sample no. 197 was formed in PMG and sample no. 198 in SFG, both have Li_2O values similar to the original granite mica compositions.

Examination of thin sections of PMG and SFG indicate that the PMG contains less lithionite mica and this is reflected in the Li_2O values of the composite mica separates.

Proceeding now to the results obtained using the electron microprobe, this instrument proved particularly useful since it was possible not only to analyse the primary micas but also the secondary micas found within the feldspars. The following table was assembled from data from Deer, Howie and Zussman (1962) and gives typical analyses for the micas under consideration:-

	% Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe*	Rb_2O
Biotite	0.5-0.7	10-13	13-16	35-39	7-8	1-1.6	16-21	-
Muscovite	0.5-1.5	0.1	34-39	44-46	8-10	0.1	0.1-1.5	0-1
Lepidolite	0.5-1.0	0.1	22-29	48-50	8.5-10	0.1	0.2-30	1-4
Zinnwaldite	0.5-0.8	0.3	21-23	38-46	9-10	0.1-1	11-13	0-1

Fe as FeO + Fe_2O_3

Tables 11 and 12 show analyses of the micas from the biotite-muscovite granite. Comparison with the tabulated typical analyses show Al_2O_3 and MgO values to be abnormally high and low respectively for the biotite and MgO and Fe values to be on the high side for the muscovite. The secondary micas, representing the first stages of hydrothermal alteration of the feldspars, are much more typical of muscovite having considerably lower MgO values than the corresponding primary value. Comparison of the Al_2O_3 and K_2O values with those obtained in one case from exactly the same sample (187) by analysis of the mica separate, add further weight to the impurity of the mica separates.

Table 13 lists the only analysis by electron microprobe of a kaolinised granite sample, in this case of BFG. The primary muscovites have analyses very similar to the primary muscovites of the unkaolinised samples. The secondary muscovites, were from the sericite-kaolinite intergrowth which was formed by the alteration of the feldspars. Their composition is identical to those found in the slightly altered feldspars mentioned above except for K_2O content. The fine grained muscovites from the kaolinised granite have lower K_2O values and a wider range than the secondary and primary muscovites from the unkaolinised BFG. Furthermore the relic primary muscovites retain their higher K_2O value. When utilising an electron microprobe for the analysis of minerals, on occasions composite analyses of two or more minerals are sometimes obtained. This is because the electron beam may either penetrate the mineral under analysis registering another mineral underneath or the grain size of the mineral may be below the resolution of the instrument. However in this case the analyses of the secondary fine grained muscovites from the

BFG do not appear to be composites, since if they were the presence of kaolinite (the only mineral with which the muscovite could be associated in this case) would be reflected in the Al_2O_3 value being substantially increased, which is not the case. The fall in K_2O content is probably a reflection of H_2O replacing potassium in the mineral producing a hydromuscovite. Further work is needed to substantiate this difference in K_2O content, however this suggests that the fine grained muscovite produced during kaolinisation is chemically different from that found in unkaolinised granites and that the date on this mica may reflect the true age of kaolinisation.

Analysis of the SFG and PMG (Tables 14 to 19) substantiated the presence of two primary micas. One was a muscovite of very typical composition and unlike the muscovite from the biotite-muscovite granite, in that it had more typical MgO and Fe values. The other mica had a composition very close to zinnwaldite although the corresponding mica in the pale mica granite had an anomalously high MgO value. On X-ray powder photographic evidence alone, Exley (1955) identified the so called lithionite mica in his lithionite granites as zinnwaldite. A more complete analysis, in particular a determination of the Fe^{2+}/Fe^{3+} ratio, would ensure positive identification of this mineral using the criteria of Foster (1960). The secondary micas in these granites were normal muscovite except in one case where the zinnwaldite mica was identified, probably derived from a primary mica.

The analyses of the greisen micas found within the biotite-muscovite granite indicate that both primary and secondary are normal muscovite, although the primary mica from sample no. 167 had high MgO values. They also agree with Halls (1971) analyses for muscovites from the greisens at Cligga Head.

4.3.2. The feldspars

Exley (1955, 1959) measured the composition of the plagioclase feldspars, by optical means, in his four granite types and concluded that the biotite-muscovite granite plagioclase feldspars were strongly zoned and of composition An_{28}, although in the boundary region this dropped to cores of An_{17} and margins of An_{13} and in some cases two generations were present of compositions An_{10} and An_{6} respectively. The early lithionite granite plagioclase however, were of composition An_{7}.

Analyses of plagioclase feldspars from the Goonbarrow granites are listed in tables 11 to 17 along with calculated anorthite compositions. The overall range and means are as follows:-

Granite type	Range	Mean
Big feldspar granite	An 1.2 - 16.8	An 9.1
Small quartz-feldspar granite	An 0.1 - 6.0	An 1.5
Pale mica granite	An 0.3 - 7.1	An 2.9

In the case of the big feldspar granite the majority of the compositions lie in the 8.8 to 16.8 field which is in good agreement with values obtained by Exley for biotite-muscovite granite in the boundary zone. For reasons mentioned in chapter 2 it is believed that the boundary is exposed at Goonbarrow. Anorthite values obtained for the small quartz-feldspar and pale mica granites are lower than the values obtained by Exley for his corresponding early lithionite granite. However the majority of the CaO values are under 0.1% and are unreliable since they are close to the detection limit for the instrument. It is therefore considered that the probable range is An_{2-7} which is in better agreement with Exleys values.

4.4. Summary and conclusions

1. Li_2O values for the Goonbarrow granites are consistent with the big feldspar granite corresponding to Exleys biotite-muscovite variety and the small quartz-feldspar and pale mica granites to Exleys early lithionite type.
2. The small quartz-feldspar and pale mica granites contained two micas; muscovite and a high lithia mica - probably zinnwaldite.
3. The greisen micas were identified as muscovite and were of similar composition to greisen micas analysed from another locality in Cornwall - Cligga Head.
4. Secondary micas present in slightly altered feldspars were identified as muscovite.
5. The fine grained secondary muscovite produced during intense kaolinisation of the feldspars in the big feldspar granite had a wider range and lower K_2O values than the secondary muscovites from the corresponding unkaolinised granite. This fall in K_2O content may be due to replacement of potassium by H_2O producing a hydro-muscovite.
6. Composition of the plagioclase feldspars from the Goonbarrow granites agreed reasonably with values obtained by Exley (1955, 1959).

CHAPTER 5

Fluid inclusions - Geothermometry

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5.1. Introduction

Fluid inclusions are samples of fluids that were present when the enclosing mineral grew or recrystallised. They may be considered as fossil fluids and have been used to determine the nature of solutions present during igneous and metamorphic activity and especially to ascertain the chemistry and conditions of the fluid present during ore deposition. Fluid inclusions almost always contain a bubble of water vapour, produced by the differential shrinkage of the liquid and enclosing mineral. Inclusions often contain a solid phase which has crystallised out during a decrease in temperature due to the fluid becoming saturated with respect to the particular compound. These solid phases are termed daughter crystals or minerals.

5.2. Historical Background

The first specific description of fluid inclusions was by Abu Reykhan al-Biruni a central-Asian scholar of the 11th century (Roedder, 1972). The first analysis of fluid in an inclusion was by Scipione Breislak (1811) followed by the then president of the Royal Society Sir Humphry Davy in 1822. Sir David Brewster (1826) is attributed as the first to recognise daughter minerals some of which, in view of more modern studies, appear to be halite or sylvite on account of their cubic morphology. A few other minor papers were presented on the subject before publication in 1858 of H.C. Sorby's excellent account on "the microscopical structure of crystals" which to this day is still considered as the classic treatise on the subject. Many types of inclusion were described and drawn in meticulous detail and for the first time, Sorby

attempted to use fluid inclusions to quantify certain parameters such as temperature and pressure. Much of Sorby's work was on granites and elvans of Cornwall this being the first reference to fluid inclusions in Cornish rocks. Until comparatively recently fluid inclusion studies since Sorbys paper have been of limited interest. The extensive Russian literature was reviewed by Ermakov (1950), the French by Deicha (1955) and the North American/European view by F.G. Smith (1953) who was among the first to use fluid inclusions in conjunction with the more modern theories of ore genesis. Since 1960 Roedder has been particularly active in the field and his prolific output of papers lay testimony to his important standing on the subject. Roedder's work on heating and freezing of inclusions (1962, 1963) to ascertain temperatures of trapping, pressures of formation and salinities of fluid have become the standard techniques to use. His work on describing the genesis of different types of inclusion and that fluid inclusions can, under the right circumstances, represent the original fluid from which the mineral grew (Roedder, 1968), enabled fluid inclusion studies to be viewed more favourably by the geological fraternity. From 1969 Roedder has edited a publication entitled "proceedings of the Commission on Ore Forming Fluids in Inclusions"(COFFI) which abstracts every known reference to fluid inclusions in addition to providing translations of the more important foreign papers.

5.3. Description of fluid inclusions

Most fluid inclusions are less than 10 μm in size (Roedder, 1967) and a few attain several centimetres in diameter and are usually prized museum pieces. Virtually any mineral formed from a solution will

contain fluid inclusions. Quartz and calcite sometimes contain $\sim 10^9$ inclusions per cm^3 (Roedder, 1967) which explains their milky white colour. However as the average size of the inclusions is so small the actual volume of inclusions rarely exceeds $\sim 0.1\%$. Unfortunately the inclusions in any one sample are rarely of one generation. Fluid inclusions may be classified into three types - Primary, secondary and pseudo-secondary. Primary inclusions are samples of fluid that were trapped during the growth of the enclosing mineral(s). The fluid may be trapped in several ways and the reader is referred to Roedder (1967) for further information.

Secondary inclusions are formed by any process after the cessation of mineral growth. For example by the crystal fracturing, allowing a later fluid to enter with subsequent healing of the fracture, thus trapping a later fluid of probable different chemical and physical characteristics. However should crystals fracture and heal during their growth then these inclusions are termed pseudo-secondary and do represent the initial fluid from which the crystal was growing. It is not always possible to differentiate between these types of inclusions but it is important to be able to do so. However certain characteristics may enable an observer to elucidate the origin of at least some of the inclusions. Inclusions found marking the growth zones of crystals are almost certainly primary. Long straight trails of inclusions may be either secondary or pseudo-secondary. None of the criteria for ascertaining the origin of the inclusions is absolute but their origin may often be inferred (Roedder, 1965b). Any isolated inclusions with no obvious planar arrangement are considered primary (Roedder, 1967). It is also possible for an inclusion to be altered in some way after trapping due

to physical processes such as tectonic movement or reheating. Both processes would alter the shape and physical characteristics of the inclusion and may produce "necked" inclusions (Roedder,1967). More frequently they result from the readjustment of the inclusion morphology in response to minimum surface energy requirements. If there are several phases available during growth each of the necked inclusions may contain different proportions of each phase (see fig. 18).

5.4. Quantitative data obtainable from fluid inclusions

5.4.1. Temperature

The vast majority of quantitative fluid inclusion data relates to the formation temperature. As mentioned earlier the vapour bubble results from the differential shrinkage of the fluid and enclosing mineral during decreasing temperature. If this process is reversed i.e. the mineral reheated, then the temperature at which the fluid was trapped may be inferred. This temperature will generally however be a minimum temperature since the crystal may have crystallised at a higher fluid pressure. The temperature at which the bubble homogenises into the liquid phase is termed the filling temperature (Tf) and for a simple two phase system will be identical to the homogenisation temperature. Strictly speaking this later term is the temperature at which the total inclusion including daughter phases becomes one homogenious phase.

5.4.2. Salinity

The salinity of a fluid may be ascertained in two ways. If the inclusion is subjected in some way to a very low temperature the fluid will usually freeze. It is assumed that most hydrothermal solutions

are composed mainly of sodium chloride, hence the depression of freezing point with respect to pure water is proportional to the amount of dissolved sodium chloride. The temperature at which the last ice crystal melts is termed the freezing temperature, Tm (Roedder, 1962). In the case of saturated sodium chloride solutions (i.e. those containing a halite daughter mineral at room temperature) reheating the inclusion until the halite crystal dissolves, provides an estimate of the salinity of the fluid by simple reference to the solubility vs. temperature table for sodium chloride. This temperature is abbreviated to Ts in this work.

5.4.3. Pressure

Unlike temperature, pressure may only be determined under favourable circumstances. In some inclusions CO_2 is present which if greater than 5% by weight is recognised as a thin meniscus of liquid CO_2 around the water vapour bubble (fig. 19). If these two phases were immiscible and if at the temperature of trapping it is possible for two sets of inclusions to develop; one CO_2 rich and one H_2O rich. In this case both pressure and temperature may be determined uniquely from the point of intersection of the appropriate CO_2 and H_2O isochores on a P-T plot of the systems involved (Roedder, 1967).

If a solution was boiling when the inclusions formed it is unlikely that both vapour rich and fluid rich phases will be trapped simultaneously. Boiling can often be recognised (fig. 20), the normal fluid inclusion will homogenise into the liquid phase and the vapour inclusion into the vapour phase, although the final temperature at which the latter takes place is often impossible to determine due to the vapour-liquid boundary being obscured by the internal reflections at the inclusion walls.

The presence of a boiling assemblage indicates that the aqueous fluid lies on the critical curve for that particular solution. If the salinity and temperature of the fluid is known from other inclusion evidence then the pressure may be easily obtained from the appropriate critical curve.

5.5. Composition of fluid inclusions

This section contains a summary of the methods used to ascertain the composition of fluid inclusions and is based on a more extended review by Roedder (1972). The methods range from fully quantitative to qualitative and from destructive to nondestructive techniques. Usually the techniques involve analysis of all the inclusions available in a specimen which is not very desirable should several generations of inclusions be present, this usually being the case.

5.5.1. The liquid phase

(i) Salinity measurements by freezing studies. This technique has already been outlined above and suffers from one major drawback, namely the assumption that the inclusion fluid is predominantly sodium chloride. It appears that generally this assumption holds true, however the discovery of an inclusion fluid of high K/Na ratio (see later) may indicate that the fluid is mainly potassium chloride indicating that the appropriate table of values should be used.

(ii) Chemical analysis of single fluid inclusions. When an inclusion is large enough it is possible to remove the fluid by some form of micro pipette and analyse it. This technique was first performed by Davy (1822) and subsequently by several workers. However the variety of inclusions of suitable size inhibits the use of this method.

(iii) Na/K, Na/Ca and other ratios. Crushing, subsequent leaching followed by an analysis for the appropriate elements can produce chemical ratios of elements in the fluid.

(iv) Laser-excited Roman spectroscopy. Rosasco et al., (1975) has applied this technique to the identification and partial analysis of solid, liquid and gaseous phases in fluid inclusions. It has proved particularly useful in identifying sulphur species in solution.

(v) Neutron Activation Analysis. The ability of this technique to determine minute amounts of elements has been applied to the analysis of leachants from fluid inclusions (Czamanske et al., 1963).

5.5.2. The solid phase

(i) Optical studies. The usual petrographic techniques such as birefringence and extinction angles can sometimes be used to identify daughter minerals. The nature of the host material may place severe limitations on the measurements. The morphology, colour and pleochroism of solid phases can be an extremely useful guide to identification. Opaque daughter minerals are also easily recognisable.

(ii) Removal of solid phases and subsequent analysis. If the daughter minerals are sufficiently large it is sometimes possible to extract and analyse them by several chemical techniques (Boyarskaya, 1973) or even produce X-ray powder photographs. Daughter minerals of sufficient size are however, extremely rare.

(iii) Scanning Electron Microscopy. Le Bel (1976) and Metzger et al., (1977) have successfully used this technique to identify several solid phases in opened inclusions revealed on fracture surfaces of the host mineral. This method is the most practical one yet devised to elucidate the solid phases on a routine basis and will almost certainly be used

more frequently in the future. This technique will be described fully in a later chapter.

5.5.3. The Gas phase

(i) Simple tests. Inclusions may be broken open while the sample is immersed in an immiscible liquid and the subsequent bubble of gas used to estimate pressure by simple volume comparison. This has been particularly useful when CO_2 is present in the inclusion (Roedder, 1965a). Wright (1881) managed to detect H_2S by its odour produced on crushing pegmatitic quartz.

(ii) Breaking open of inclusions and subsequent analysis. The gas/liquid phase of inclusions has been released from inclusions by either crushing (Barker, 1965, Roedder et al., 1963) or decrepitation (Wahler, 1956, Kormushin, 1962, Dolgov, 1963) under high vacuum conditions. The resultant gases and vapours have then been analysed using a gas mass spectrometer or chromatograph. In some cases the D/H, O^{18}/O^{16} ratios of the inclusion water have been measured which can provide extremely useful information for ascertaining the origin of the fluid.

5.6. Previous work on cornish material

Inclusion studies on cornish minerals have been reasonably numerous considering the previous low level of U.K. research activity in this method. Since Sorby's paper, other work has included Philips (1875), Hunt (1894, 1909), Smith, F.G. (1949) and Little (1960) who worked for the first time on inclusions in cassiterite. In the context of this thesis Sawkins (1966) work is particularly significant as he studied a limited number of quartz samples from the St. Austell china clay region.

Sawkins' data together with all subsequent fluid inclusion data is summarised in Table 20.

Davison (1926) recognised four mineral zones which were supposedly deposited concentrically around the granites. Although this hypothesis is now considered to be oversimplified his general sequence of zones is broadly correct. The vertical relationships of the ore-mineral zones in south west England are shown in fig. 21. Comparison of the temperatures of formation shown in this diagram can be compared with the observed filling temperatures in Table 20. In some cases it appears that the filling temperatures of samples from certain localities are lower than suggested by Edmonds et al., (1975). However these filling temperatures are minimum temperatures uncorrected for pressure, which may raise them by up to 50°C. From the uncorrected filling temperature data the overall range for each zone is:-

Tin/Tungsten	270 - 450°C
Copper	170 - 330°C
Lead/Zinc	115 - 170°C

Salinities of the inclusion fluids show a relatively restricted range of between 2-14 wt % NaCl although at Geevor and Levant higher values of up to 30 wt % are recorded. Penlee contains very saline inclusions ranging from about 26 to 50 wt %. Bostraze, a sheeted vein system associated with china clay similar to Goonbarrow, displays an equally large range of high salinity fluids, between 20 and 50 wt %. It is also significant that this is the only locality where definite signs of boiling have been recognised (Jackson, 1977).

Table 20. Summary of fluid inclusion data on Cornish samples

LOCALITY	AREA (DINES CLASSIFICATION)	Tf°C	SALINITY	MAIN METALS MINED	REFERENCE
GREVOR	ST. JUST : Botallack-Penceen	273-314	26	Sn	Sawkins (1966)
BOTALLACK	ST.JUST : Botallack-Pendeen	221-248	-	Sn	"
LEVANT	ST. JUST ; Botallack-Pendeen	270-370	15-30	Sn	Jackson (1977)
BOSTRAZE	ST. JUST : Morvath-Sancred	400-460	-	Sn, W	Jackson & Wilson (1977)
BOSTRAZE	ST. JUST : Morvath-Sancred	300-460	20-50	Sn, W	Jackson (1977)
BUNNIES	ST. JUST DISTRICT	275-285	8	Cu	Alderton (1977)
ST. DAY	CAMBOURNE-REDRUTH-ST.DAY : GWENNAP	176-290	-	Cu	Sawkins (1966)
GREEGBRAWSE	CAMBOURNE-REDRUTH-ST.DAY : GWENNAP	290 (max)	-	Cu, Sn	Bradshaw & Stoyel (1968)
WHEAL FRIENDSHIP	CAMBOURNE-REDRUTH-ST.DAY : GWENNAP	248-256	18-2	Cu	Sawkins (1966)
UNITED MINES	CAMBOURNE-REDRUTH-ST.DAY : GWENNAP	268-296(max)	-	Cu, Sn	Bradshaw & Stoyel (1968)
GREAT WHEEL BADDERN	CAMBOURNE-REDRUTH-ST.DAY : GWENNAP	202-231(max)	-	Pb, Sn	"
HALLENBEAGLE	CAMBOURNE-REDRUTH-ST.DAY : SCORRIER	181 (max)	-	Cu	"
PEDNANDREA	CAMBOURNE-REDRUTH-ST.DAY : SCORRIER	336 (max)	-	Sn, Cu	"
PENSTRUTHAL	CAMBOURNE-REDRUTH-ST.DAY : TROON-LANNER	270 (max)	-	Cu, Sn	"
WHEAL TRETHARRUP	CAMBOURNE-REDRUTH-ST. DAY : TROON-LANNER	226 (max)	-	Cu, Sn	"
PENLEE	PENZANCE AREA	435-440	50	Sn	Sawkins (1966)
PENLEE	PENZANCE AREA	286-309	26	Fe	"
TREWARVAS HEAD	MOUNT'S BAY : Breage	263-284	-	Cu	"
WHEAL ROSE	MOUNT'S BAY : Breage	134-138	3-4	Pb,Zn,Fe	Alderton (1977)
WHEAL FORTUNE	MOUNT'S BAY : Breage	290-320	-	Sn, W	"
ST. MICHAELS MOUNT	MOUNT'S BAY : Penzance-Ludgvan	340-400	8-14	Sn, W	Jackson & Rankin (1976)
ST. MICHAELS MOUNT	MOUNT'S BAY : Penzance-Ludgvan	280-300	8-14	Stannite	"
ST. MICHAELS MOUNT	MOUNT'S BAY : Breage	280-380	5-10	Sn, W	Moore & Moore (1979)
LAMBRIGGAN	ST. AGNES : Perranzabuloe	150-170	2-3	Zn	Sawkins (1966)
CLIGGA HEAD	ST. AGNES : Perranporth-St. Agnes	280-380	3-12	W	Jackson, Moore & Rankin (1977)
CLIGGA HEAD	ST. AGNES : Perranporth-St. Agnes	320-400	2-8	Sn	"
CLIGGA HEAD	ST. AGNES : Perranporth-St. Agnes	240-380	8-11	Cu, Fe	"
CLIGGA HEAD	ST. AGNES : Perranporth-St. Agnes	374 (max)	-	Sn, W	Bradshaw & Stoyel (1968)
CLIGGA HEAD	ST. AGNES : Perranporth-St. Agnes	290-304	0-14.5	Sn, W	Alderton (1977)
TREVAUNANCE	ST. AGNES : Perranporth-St. Agnes	394 (max)	-	Cu, Sn	Bradshaw & Stoyel (1968)
TYWARNHAYLE	ST. AGNES : Porth Towan	261 (max)	-	Cu, Pb	"
WHEAL CHARLES	ST. AGNES : Porth Towan	233 (max)	-	Cu	"
ST. AUSTELL CLAY PITS	ST. AUSTELL : St. Stephen	245-300	2.6-4.6		Sawkins (1966)
POLGOOTH	ST. AUSTELL : St. Stephen	305-312	4.2	Sn, Cu	"
WHEAL PROSPER	ST. AUSTELL : Lanivet	288-307	-	Sn	Alderton (1977)
PENDARVES	GWINEAR : Gwinear-Downs	210-370	11.5	Sn	"
MENHENIOT	LISKARD : Menheniot	115-146	-		Sawkins (1966)
BUTTERN HILL	WALKERIDGE : Bodmin Moor	243-337	-	W, Sn	Alderton (1977)
BIRCH TOR & VITIFER	DARTMOOR & TEIGN VALLEY : Central Dartmoor	216-228		Sn, Fe	"

5.7. Fluid inclusion data from Goonbarrow

Representative samples of unkaolinised and kaolinised granite, elvan and mineral veins were selected for fluid inclusion studies. Of the rock samples only those containing reasonable sized quartz grains, usually > 2 mm, were chosen. Standard petrographic thin sections were prepared first and studied for the presence of sufficient fluid inclusions of suitable size, preferably 10-40 μm. Having ascertained that the specimens were suitable, 60 μm doubly polished sections were prepared (see appendix). The fluid inclusions were then described and photographed as mentioned in 5.6.3. Finally the salinity and filling temperatures were determined on representative groups of inclusions. (See Appendix 4).

5.7.1. Types of fluid inclusions observed in minerals from Goonbarrow

In the samples studied no inclusion could be considered with any certainty, to be of undoubted primary origin. Secondary inclusions could be recognised quite easily by their occurring in long trails and planes (Plates 50 & 51). A small percentage of inclusions were of the "necked" kind and so did not represent the original fluid. Plate 52 shows a particularly good example of a necked inclusion. Plate 53 shows an inclusion which formed before the process of necking had been completed (see Section 5.3. & Roedder,1967). Had the process gone to completion it is probable that the majority of the water vapour would have been trapped in the right hand part of the inclusion and the daughter crystals on the left. Consequently subsequent heating/freezing studies would have produced very anomalous results. Inclusions not falling into any of the two above categories were considered to be primary or pseudo secondary i.e. of essentially primary origin. In a study of this kind it is inevitable that a small percentage of inclusions considered to be of

primary origin were probably secondary and this is one of the inherent problems of fluid inclusion studies. Plates 54 to 57 showed typical examples of vapour or boiling inclusions, discussed earlier in section 5.4.3. In Plate 57 two inclusions can be seen which appear to be totally vapour filled, these were particularly common in samples of quartz from kaolinised granite. Most of the other plates show inclusions containing one or more daughter crystals. Sometimes the inclusion becomes so full of solid matter that the vapour bubble has insufficient room to assume its normal spherical shape and becomes deformed (Plates 58 to 60). The most common daughter crystals are cubes (Plates 61 to 69) and anisotropic rods (Plates 70 to 72). The cubes are either halite or sylvite, probably halite, and indicate the fluids to have salinities in excess of 26 wt % NaCl. Some inclusions were observed containing a daughter crystal of hexagonal morphology which resembled a mica (Plates 73 to 75). Other daughter minerals included round sub-spherical crystals (Plates 76 to 80), a blocky birefringent crystal (Plates 81 and 82) and more rarely a fibrous mineral (Plates 83 and 84). Only on one occasion were black opaque masses observed (Plate 85). Clearly the fluids in Goonbarrow are variable and complex.

5.7.2. Filling temperatures and salinities of fluid inclusions within minerals from Goonbarrow

Over three hundred specimens were collected from Goonbarrow of which about two hundred were used for thin section and dating studies. Of the remaining hundred, sixteen representative samples were chosen for fluid inclusion studies. The results from the heating/freezing studies can be found in appendix 5 and are shown plotted as histograms in figures 22 and 23.

(i) Kaolinised and unkaolinised granite (specimen nos. 187 and 243).

In the unkaolinised granite sample the majority of filling temperatures occurred in the range 320-420°C with salinities ranging from 6 to 18 wt.% NaCl. Occasionally a few inclusions were observed that contained cubes but no measurements were obtained. The kaolinised granite sample ranged in temperature from 220° up to 460°C with a wider spread of salinities, 0.7 to 36 wt.% NaCl. However it must be pointed out that there were very few measurements of salinity on either specimen so these results are only an indication of some of the fluids present. A large percentage of observed inclusions did not freeze when cooled to -90°C thereby preventing salinity measurement. Boiling was recognised in the unkaolinised sample, however the kaolinised specimen was quite different in containing large numbers of vapour rich inclusions indicative of intense boiling or trapping of steam bubbles rising from below. Although no other specimens of granite were studied on the heating/freezing stage, much larger numbers of boiling inclusions were recognised in kaolinised granite samples when viewed under a normal petrographic microscope, than unkaolinised specimens.

(ii) Elvan (specimen no. 206).

Quartz within the elvan matrix contained very few inclusions. Most were in long trains and considered to be of secondary origin. Of the few isolated inclusions there were no indications of boiling or daughter crystals. The inclusion fluids also proved very difficult to freeze and consequently only a few salinity measurements were obtained, mainly from secondaries.

(iii) Quartz/tourmaline veins (specimen nos. 10, 12, 82 and 97).

Vein samples ranged mainly from 180-420°C with salinities of 8-40 wt.% NaCl. The single greisen specimen appeared to be of somewhat lower temperature, mainly 120-240°C with a similar range in salinity. Boiling was recognised in all specimens.

(iv) Veins containing cassiterite (specimen nos. 110 and 131B).

Vein and greisen specimens range in temperature from 140-480°C. Sample no. 110 (vein) contained two peaks on the salinity plot at 20 and 32 wt.% NaCl. This may be due to a statistical problem, insufficient inclusions being measured and outlines one of the difficulties in inclusion research. Often ten inclusions will be observed at any one time, some will not freeze at all even down to -100°C and for the remaining inclusions all but one or so of the final melting temperatures of ice can be observed. For this material somewhere in the region of a hundred salinity measurements should really be obtained but this was impossible due to time factors. However a random selection of inclusions was thought adequate to give some indication of the fluids present.

The greisen accompanying 110V although of similar temperature characteristics ranged from salinities as low as 2 wt.% up to 38 wt.%. Sample 131BV ranged from 8 to 42 wt.% NaCl. Boiling was recognised in all specimens.

(v) Multimineral veins (specimen nos. 26 and 133).

Temperatures ranged from 140-440°C and salinities 6-40 wt.% for 26V and mainly 18-20 wt.% for 133 although very few measurements were obtained in this case. Boiling was recognised in all specimens.

(vi) Veins containing wolframite (specimen nos. 143 andGB2).

Unlike all the vein specimens described above quartz from the two wolframite veins gave filling temperatures within a fairly narrow range 220-300°C. Specimen GB2V ranged in salinity from 30 to 48 wt.% - virtually every inclusion contained a salt cube! Specimen 143V had a much wider range of salinities 12 to 48 wt.% NaCl. The corresponding greisen specimen (GB2g) ranged in temperature from 140 to 460°C and

Table 21. Summary of fluid inclusion data for the world's major tin/tungsten mineralised districts

Location	Mine name or area	Reference	Geological features	Fluid inclusion data	Remarks
TIN DEPOSITS					
JAPAN	Ashio mine	Imai et al. (1975)	Xenothermal vein type deposits intruded into rhyolitic rocks. Associated with late cretaceous/ tertiary granites	Sn 300-350°C, Cu 230-270°C } 0-5 wt% NaCl Boiling	Reversed zoning as in Cornwall
	Akenobe mine	"	"	Sn 135-355°C (decrepitation method-unreliable)	Associated with felsite dykes in mineralised areas, intruded just before and after mineralisation
	Ikuno mine	"	"		Identical zoning of the same metals as Cornwall
	Tada mine	"	"		Associated with felsite, rhoylite and andesite dykes
AUSTRALIA	Mount Bischoff (Tasmania)	Groves & Solomon (1969)	Intruded into quartzites, shales and dolomites. Associated with adamellite intrusions.	In Qtz 200-245°C, In fluorite 195-370°C } 5-16 wt% NaCl + some 50 wt%	Associated with felsite dykes P≃ 775 bars
RUSSIA	Komsomolsk region	Sushchevskaya et al (1966)	Intruded into sandstone/shale strata	270-320°C K/Na ≃ 0.2	
FRANCE	La Villeder (S. Brittany)	Charoy & Weisbrod (1975)		150-300°C, 6-9 wt% NaCl K/Na = 0.1	P≃ 800 bars
BOLIVIA	E. Andes	Kelly & Turneaure (1976)	Intruded into folded palaeozoic formations. Associated with small granite batholiths.	In Qtz 209-530°C, 23-44 wt% NaCl; In Cassiterite 320-510°C, 19-46 wt% NaCl } Boiling	P≃750 bars
	Charloque & Llallagua (E.Andes)	Grant et al. (1977)	Subvolcanic. Associated with altered quartz porphyries	Charloque 250-300°C } 26 wt% NaCl, Llallagua 300-400°C } Boiling	P≃800 bars
TUNGSTEN DEPOSITS					
PERU	Pasto Bueno	Landis & Rye (1974)	Associated with biotite bearing porphyritic quartz monzonite	400-500°C, 5-40 wt% NaCl Boiling; 175-270°C, 2-17 wt% NaCl No Boiling	
ENGLAND	Carrock	Shepherd et al. (1976)	Intruded into gabbros, metamorphosed slates and granites with which it is associated	220-250°C, 5-10 wt% NaCl Na/K = 17 to 114	P≃ 800 bars
RUSSIA	Kholtoson (W.Transbaikal region)	Shapenko et al. (1976)	Intruded into Paleozoic diorites	150-340°C No Boiling	
EGYPT	Igla mine	El Shatoury et al. (1974)		190-390°C Boiling	

Note: All temperature and salinity determinations are on inclusions in quartz unless otherwise stated.

salinity ranging from 14 to 48 wt.%. Again boiling was recognised in all the specimens.

With the exception of the elvan, daughter crystals were common to all specimens. Nothing more will be said about them here, they were examined much more closely by other methods and the results can be found in chapter 6.

5.8. Comparison of Goonbarrow with other major tin/tungsten areas of the world

Table 21 shows a summary of all known fluid inclusion data available for tin/tungsten mineralised districts. Malaysia is noticeably absent from the tin deposit data. The temperatures found in these deposits are similar to Goonbarrow. Salinity measurements are not available for all the deposits, however several, like Goonbarrow, contain supersaline (> 25 wt.% NaCl) inclusions and were found to be boiling. The deposits at Mount Bischoff and the Japanese group contain many features found in Cornwall, notably association with felsite dykes and identical zoning sequences.

In summary Goonbarrow contains fluids very similar to some of those found in other major tin/tungsten areas in addition to many geological similarities.

5.9. Summary of Goonbarrow fluid inclusion data

1. Boiling was much more intense in kaolinised granite than unkaolinised granite.
2. All veins and greisens were formed from boiling fluids.

3. Quartz/tourmaline and multimineral veins formed at between 140° and 440°C and salinities of 6-40 wt.% NaCl.
4. Cassiterite veins formed from similar fluids to the quartz/tourmaline - multimineral veins i.e. 8-42 wt.% NaCl and from temperatures of 140°-480°C.
5. The wolframite veins are distinct from other veins in the pit being formed within a very close temperature range 220°-300°C but still from a wide range in salinity, 12-48 wt.%.
6. Inclusions within the elvan were probably of secondary origin, chemically much simpler than the vein fluids, of about 22 wt.% NaCl, were not boiling and were trapped at between 360° and 440°C.

5.10. Pressure and estimation of depth

Any suggested model for ore deposition and kaolinite formation must explain three main features:

1. The large variation in salinity.
2. The large variation in temperature.
3. The association of relatively small veins with very large masses of kaolinised granite.

Variation in salinity of inclusion fluids may be explained in two ways. Imai et al., (1971) and Kim et al., (1972) recognised that the filling temperatures of fluid inclusions decrease with decrease in NaCl equivalent concentration and explained this as being due to the dilution of ascending ore forming fluid by meteoric water. Conversely low salinity fluids can be concentrated into high salinity fluids by simply boiling, the resultant vapour phase would correspondingly be of very low salinity.

In a system which is periodically boiling and being constantly recharged, as may be the case in the formation of veins from a granite magma, a whole range of salinities could be produced. The inclusion data for Goonbarrow as shown in fig. 24, unlike the data used by Imai et al., (1971) and Kim et al., (1972) shows there is no apparent straight line relationship indicative of a simple mixing model. The higher salinity inclusions tend to be associated with lower temperatures but the low to intermediate salinity inclusions encompass the whole temperature range. For reasons mentioned earlier pervasive boiling has been recognised in all the veins in Goonbarrow. Hence the large variation in salinity is interpreted as being a result of this process.

The recognition of boiling in the veins at Goonbarrow is extremely fortunate since good estimates may now be made concerning the pressure and therefore depth of formation. Boiling of an aqueous solution will occur whenever the conditions are such that the solution lies on the boiling curve, indicating the two phase boundary between liquid and vapour. The position of these curves is dependent on the solute and its concentration.

The boiling point curves for 10 and 25 wt.% NaCl were constructed from the data of Haas (1971) and are shown in fig. 25. Unfortunately no data are available for temperatures above 330°C, therefore the curves were extrapolated to higher temperatures. For the following calculation we shall assume that the fluids in the quartz/tourmaline and cassiterite veins were originally of 10 wt.% NaCl composition (the lowest measured) and that subsequent pervasive boiling would concentrate them to 40 wt.% NaCl (the highest measured). Selection of the true vein formation temperature is more difficult but for the moment we shall assume the veins formed at around 450°C (the highest recorded filling temperature).

From fig. 25 a pressure of formation for the veins can be found - about 450 bars. Fig. 26 was also constructed from Haas' data (1971) and, if the veins at Goonbarrow were produced under hydrostatic pressure conditions, then they would have been formed at a depth of 5.5 kms. If the veins were formed under lithostatic conditions then the depth may be calculated from the simple expression

$$P = pgH \quad . \quad . \quad . \quad . \quad (1)$$

where P = Pressure in $N\ m^{-2}$

p = Density of rock in $kg\ m^{-3}$

g = acceleration due to gravity = $9.8\ m\ sec^{-2}$

H = depth in metres

For a pressure of 450 bars ($450 \times 10^5\ Nm^{-2}$) and assuming the superincumbent load is due to granite of density $2.7 \times 10^3\ Kg\ m^{-3}$ (Stacey, 1969) the calculation gives a depth of 1.7 kms. However this value may be a little on the low side since it has been assumed that the fluid consists mainly of dissolved NaCl. It is known from SEM studies (see chapter 6) that several other elements are present in abundance which may lower the vapour pressure in complex brines (Moore & Nash, 1974, p.644).

It is considered more likely that the granites were intruded into sediments that were above sea level and that therefore the veins were initially produced under lithostatic load.

5.11. Mechanisms to explain conditions of ore deposition

The aforementioned correlation between salinity and boiling has also been recognised in inclusions from a porphyry copper deposit (Chivas and Wilkins, 1977). This study along with results from another porphyry copper deposit (Moore and Nash, 1974) also revealed large

variations in filling temperatures. In both cases these filling temperature variations were interpreted as being due to reduction of pressure by altering from lithostatic to hydrostatic load conditions. It is reasonable to assume that the ore fluids were intruded at the top end of the temperature range i.e. 450°C, and that these then cooled variably in some way. Several processes may produce this cooling (Toulmin and Clark, 1967)

1. Mixing with Ground Water.
2. Heat exchange with the environment.
3. Expansion of the fluid.

1. Mixing with ground water. This process would produce a linear plot of points on a filling temperature vs. salinity graph as previously mentioned (Imai et al., 1971, Kim et al., 1972). A stable isotope study could be extremely useful in recognising this process and some preliminary work was attempted in trying to ascertain if this process took place at Goonbarrow. The Goonbarrow data plotted in fig. 24 suggests that this process contributed little, if at all, to the temperature variation.

2. Heat exchange with the environment. It is safe to assume the fluid intruded rock of lower temperature. The K-Ar data showed that the granite muscovites cooled through their blocking temperatures ($\sim$ 250-300°C) at around the same time as the greisen alteration muscovites. Therefore the ore fluid - granite temperature difference was at most around 200°C. Although this temperature difference is around the value found from fluid inclusion studies it appears that this process is usually relatively unimportant in cooling the fluid unless the duration of deposition is short (Toulmin and Clark, p.459, 1967).

3. Expansion of the fluid. As a fluid rises from depth it undergoes expansion as a result of decrease in pressure. If the fluid begins to boil it will also expand since the vapour phase has a higher molar volume (at low pressure only) than the equivalent liquid phase. These processes will also effect a drop in temperature the magnitude of which depends on the type of process taking place. The expansion of the ore fluid as it rises is an extremely complex process and certain approximations have to be made in order to calculate the temperature drop. Toulmin and Clark (1967) assumed the expansion to be an adiabatic process i.e. one which takes place without thermal contact between the fluid and its environment. They also assumed that the fluid may expand in one of two ways; "slowly as it rises along open stretches of vein and rapidly, where the vein system becomes constricted and strong pressure gradients occur". The first process is similar to reversible adiabatic expansion and the latter to an irreversible adiabatic expansion. We shall calculate the temperature drop for each of these two cases by considering firstly the reversible adiabatic expansion of an ideal gas followed by the same for real H_2O fluid, and finally consider the situation for an irreversible adiabatic expansion.

5.11.1. Reversible adiabatic expansion (boiling)

From the 1st Law of thermodynamics the sum of the heat (q) and work (w) effects on a body is equal to the change of the function of state u :-

$$U_B - U_A = q + w \qquad \text{. . . .} \qquad (2)$$

The differential form of equation (2) becomes

$$dU = dq + dw \quad . \quad . \quad . \quad . \quad (3)$$

Now $$dW = -PdV \quad . \quad . \quad . \quad . \quad (4)$$

and substituting into (2) we obtain

$$dU = dq - PdV \quad . \quad . \quad . \quad . \quad (5)$$

since $$C_v = \frac{dU}{dT} \quad . \quad . \quad . \quad . \quad (6)$$

then $$C_v dT = dq - PdV \quad . \quad . \quad . \quad . \quad (7)$$

Since we are assuming no heat is exchanged with the surroundings $dq = 0$ and therefore

$$C_v dT = PdV \quad . \quad . \quad . \quad . \quad (8)$$

For reversible isobaric boiling (i.e. at the boiling point), the expansion is simply $V_{(g)} - V_{(l)}$ and so

$$\int_{V^\circ}^{V} PdV = P\,(V_g - V_l) \quad . \quad . \quad . \quad . \quad (9)$$

and so $$\Delta T = \frac{-P(V_{(g)} - V_{(l)})}{C_v} \quad . \quad . \quad . \quad (10)$$

where
- ΔT = change in temperature
- $V_{(g)}$ = Molar volume of H_2O gas at appropriate pressure and temperature
- $V_{(l)}$ = Molar volume of water in inclusion fluid at appropriate NaCl concentration
- C_v = Heat capacity at constant volume of steam at appropriate pressure and temperature
- P = Pressure

The fluid was assumed to have the following characteristics - 10 wt.% NaCl at 450°C and 450 bars (chosen because of reasons mentioned earlier in section 5.10). For the purposes of this calculation the following values were used:-

$V_{(g)}$ = 54.11 cm^3 $mole^{-1}$ extrapolated from Burnham, Holloway and Davis (1969) see fig. 26.

$V_{(l)}$ = 40 cm^3 $mole^{-1}$ extrapolated from Urusova (1975)

C_v = 24.47 cal $mole^{-1}$ deg^{-1}. Calculated assuming $C_v = C_p - R$ where C_p = 2.653 BTU/lb (Handbook of chemistry and physics, 1975, p.E-25) 2.653 BTU/lb = 1.47 cal gm^{-1} = 26.46 cal $mole^{-1}$ deg^{-1}.

P = 450 bars

$$\Delta T = -\frac{450\ (54.11 - 40)}{24.47 \times 41.84} = -6.2^{\circ}C$$

In other words the fluid would only be cooled by about 6°C. However there would be further cooling should the gas expand to a lower pressure. For this process $f_i V = RT$ per mole, where f_i is the fugacity of the gas, and if the gas is ideal $f_i = P_i$

$$\therefore \quad \int PdU = \int \frac{RT}{V} dV = R \ln \frac{V_2}{V_1} \qquad \ldots \qquad (11)$$

since $PV=RT$, $V_1 = \frac{RT}{P_1}$ and $V_2 = \frac{RT}{P_2}$, therefore $\frac{V_2}{V_1} = \frac{RT}{P_2} \frac{P_1}{RT} = \frac{P_1}{P_2}$

$$\text{and also} \quad \int PdV = \int C_v dT \qquad \ldots \qquad (12)$$

$$\text{we obtain} \quad -C_v \Delta T = RT \ln \frac{P_1}{P_2} \qquad \ldots \qquad (13)$$

However H_2O vapour is non ideal. An extension of equation (13) can be used to calculate the temperature drop:-

$$\Delta T = -\frac{RT}{C_v} \ln \frac{f_1}{f_2} \qquad \ldots \qquad (14)$$

where f_1 and f_2 are the fugacities of H_2O vapour at the appropriate pressures. Fugacity may be related to the pressure of a non-ideal gas by the expression

$\frac{f}{p} = \Gamma$ where Γ is the fugacity coefficient which will alter over the whole pressure range (Denbigh, p.125, 1971).

Equation (14) will therefore become

$$\Delta T = -\frac{RT}{C_v} \ln \frac{P_1}{P_2} \frac{\Gamma_1}{\Gamma_2} \quad . \quad . \quad . \quad . \quad (15)$$

The temperature change due to further cooling by the vapour expanding to a lower pressure was calculated for an ideal and non-ideal gas using equations (13) and (15) respectively and the following values:-

R = The gas constant = 1.987 cal mole^{-1} deg.
T = 450°C = 723°K
C_v = 24.47 cal mole^{-1} deg^{-1}
P_1 = Initial pressure = 450 bars
P_2 = Final pressure = 150 bars
Γ_1 = fugacity coefficient for water at 450°C and 450 bars = 0.580
Γ_2 = fugacity coefficient for water at 450° and isobars = 0.856

extracted from Burnham, Holloway and Davis (1969).

The pressure drop from 450 to 150 bars was specifically chosen since if the fluid was originally intruded at 450 bars under lithostatic load and then the rock cracked in some way, allowing the fluid to replace the rock and possibly reaching surface, the final pressure would be due to hydrostatic load. Chivas and Wilkins (1977) used a similar model to interpret their data from a porphyry copper deposit. Assuming that the 1.7 kms of granite was replaced by a 10 wt.% NaCl brine this would reduce the pressure to around 150 bars (Haas, 1971). The calculations gave the following results:-

Ideal gas = -64.5°C

Non-ideal gas = -41.6°C

The variation according to fluid inclusion evidence is about 250°C. It is quite apparent therefore that the work done by the volume change during isobaric boiling is inadequate to produce the temperature drop because of the similarity in the molar volume of $H_2O(g)$ and the partial

molar volume of $H_2O(l)$ at this pressure. Expansion of the vapour, produced during boiling, to a lower pressure although more significant does not explain the large temperature drop found in practice. Toulmin and Clark (1967) point out that it is unlikely that reversible expansion ever takes place. However in vein systems expansion and boiling may well be irreversible and Toulmin and Clark (1967) considered the effects of throttling, or Joule-Thomson expansion.

5.11.2. Irreversible adiabatic expansion

In order to derive an equation to calculate the temperature change during an adiabatic irreversible expansion reference must be made to a classic experiment first carried out by Joule and Thomson in the period 1852-62. The principle involved throttling the gas flow in a tube from one side of high pressure, to another side of lower pressure, by interposing a porous plug. This situation is analogous to throttling in a vein. Since the entire system was thermally insulated, the process was an adiabatic one and $q = 0$. It can be shown (Moore, p.45, 1968) that the enthalpy on either side is identical. Whenever the gas is imperfect there will be a change in temperature. Since the process takes place at constant enthalpy, this temperature change can be described by the Joule-Thomson coefficient (μ).

$$\mu \equiv \left(\frac{dT}{dP}\right)_h \qquad \ldots \quad (16)$$

Whenever μ is positive this corresponds to cooling on expansion. Now it can also be shown that

$$\mu = -\frac{1}{C_p}\left(\frac{dH}{dP}\right)_T = -\frac{1}{C_p}\left[V(1-\alpha T)\right] \text{ (Denbigh, 1971)} \quad . \quad . \quad . \quad (17)$$

where α is the coefficient of expansivity of the gas.

Combining (15) and (17) gives

$$\frac{dT}{dP} = \frac{V}{C_p}(\alpha T-1) \quad . \quad . \quad . \quad . \quad (18)$$

$$\int dT = \int \frac{V}{C_p}(\alpha T-1)dP \quad . \quad . \quad . \quad . \quad (19)$$

and $$\Delta T = \frac{V}{C_p}(\alpha T-1)\left[P_2 - P_1\right] \quad . \quad . \quad . \quad . \quad (20)$$

where ΔT = change in temperature
C_p = Heat capacity at constant pressure of water at appropriate temperature and pressure
V = Molar volume of water at appropriate temperature and pressure
T = Temperature of the fluid
α = Coefficient of expansivity of water
P_1 = Pressure before throttling
P_2 = Pressure on other side of constriction

Unfortunately we have no idea what the pressure drop during throttling actually is so various values of P_2 were used in the calculation, so that some idea of the magnitude of T produced by this process could be ascertained. The following values were used during the calculation:-

C_p = 26.46 cal $mole^{-1}$ deg^{-1} (from Handbook of chemistry and physics, 1975)
V = 40 cm^3 $mole^{-1}$ (from Burnham, Holloway and Davis (1969) converted into cal bar^{-1} by dividing by 41.84)
T = 450°C = 723°K
α = 0.011 (extracted from Burnham, Holloway and Davis (1969) Fig. 27 shows a plot of ln specific volume vs. temperature α calculated from tangent at point 450°C, 450 bars)
P_1 = 450 bars
P_2 = variable

The calculations gave the following results for various pressure drops:-

ΔP (bars)	ΔT (^{o}C)
50	-13
100	-25
150	-38
200	-50
250	-63
300	-75
350	-88
400	-100
440	-111

It can be seen that these idealised equations show that throttling could produce temperature variations approximating to those seen in the inclusion studies from samples at Goonbarrow. If during throttling the fluid intersected the boiling curve and non isobaric boiling ensued, then it has been shown that significant further cooling could be produced. If isobaric boiling took place at lower pressures than 450 bars then the molar volume of H_2O vapour would be much higher and recalculation of the temperature drop using equation (10) would be much higher. For example at 250 bars $V_{(g)}$ = 166 instead of 54.11 at 450 bars. This would give a temperature drop of $55^{o}C$. The temperature drop in fact rises exponentially with lowering of pressure and so even lower pressures can produce temperature drops of very large proportions. Heat exchange with the environment could produce yet further cooling, although much smaller, it may add significantly to the temperature drop.

In practice if the vein were to become completely blocked and the resultant pressure become so high that it suddenly unblocked, the sudden drop in pressure could force the fluid to boil thus producing a drop in temperature.

In fact Ridge (1973) describes this very process in his paper on volcanic exhalations and ore deposition. He states

> "If the amount of open space into which these constituents were dropped was filled before boiling ceased, the vapour pressure would rise, and the remaining liquid would cease to boil until (and if) the pressure produced was sufficient to rerupture the overlying rocks or to allow connection to be made with other (and still open) fracture systems. Then boiling would recommence".

In the authors opinion this is considered a very good description of the processes which may have taken place at Goonbarrow. Explosive pressure release has been recognised in many of the cornish deposits as brecciated veins and the Wheal Remfry pipe breccia in the eastern lobe of the St. Austell granite is a particularly good example.

5.12. Suggested model and discussion

5.12.1. Fluids involved in kaolinisation and formation of quartz/tourmaline and cassiterite veins

One can consider a rising fluid of 10 wt.% NaCl composition which begins to boil possibly by repeated choking and unblocking at about 450°C. Variable incipient boiling and therefore expansion produces fluid of variable composition, up to 40 wt.% NaCl, and variable temperature, down to about 200°C. What effect would these conditions have on the formation of the ore and kaolin deposits? Toulmin and Clark (1967) have suggested that any site of throttling would be a very likely place for the formation of ore deposits since the solubility of most solid substances in supercritical fluids decreases drastically as density decreases in response to decompression (Kennedy, 1950). They also suggested that some of the peculiar details of zoning, for example apparent reverse zoning, may be explained by allowing the locus of throttling to shift through time. Throttle locus shift would explain why apparently tin/tungsten mineralisation occurs only very locally in

the veins of Goonbarrow, since the boiling and rapid cooling conditions necessary would be variably changing in time and position (Kelly and Turneaure, 1970, p.674-675). Kamilli and Ohmoto (1977) have shown that boiling was responsible for the formation of the Finlandia vein, a peculiar bonanza type gold-silver deposit. Gold/silver mineralisation is restricted to those parts of the veins where there has been boiling and have suggested that the presence of boiling may be a powerful tool in discovering other blind bonanza ore shoots.

At this stage only the normal fluid inclusions have been discussed and of course during boiling, a vapour phase is also produced. One of the main differences in physical properties between $H_2O(l)$ and $H_2O(g)$ is viscosity. $H_2O(g)$ is much less viscous and therefore on these grounds alone one would expect $H_2O(g)$ to be much more penetrative than $H_2O(l)$. One of the problems with the formation of the Cornish kaolin deposits has always been a suitable explanation for the large masses of kaolinised granite apparently associated with relatively small veins with greisen borders. However if the fluids were pervasively boiling and being constantly recharged then it would be reasonable to suppose that the vapour would travel both up the vein and out into the enclosing rock, in this case granite. Flow restrictions may encourage the vapour to predominantly penetrate the host rock. It may even be considered that the greisen borders were produced predominantly from the liquid phase and the vapour phase being much less viscous penetrated the host rock and kaolinised the granite. Microscopical examination of thin sections have shown that kaolinised granite contains many more vapour rich inclusions than unkaolinised granite. It is also very significant that boiling, variable filling temperatures and variable salinity were

also recognised in veins and kaolinised granite associated with the only other cornish china clay deposit studied to date - Bostraze (Jackson, 1976, Jackson & Wilson, 1977). The conditions of the fluid, 300-450°C, 15-50 wt.% NaCl (see table 20) are very similar to the fluids found at Goonbarrow. Their recognition of several generations of fluid of differing temperature and salinity, on the evidence from Goonbarrow, could be interpreted along very similar lines to that discussed above.

In Sorby's classical paper of 1858, he drew and described several inclusions in samples from Cornwall and other parts of the world and it is unknowingly due to him that the first recognition of boiling in the St. Austell granite was identified. The caption to fig. 111 in his paper states "A portion of the quartz of the granite of St. Austell (sic), Cornwall, X200, with many fluid cavities, and one vapour or gas cavity"!

5.12.2. Fluids in the quartz/wolframite veins

Unlike the quartz/tourmaline, cassiterite and multimineral veins which all seem to have formed under similar conditions, the quartz/wolframite vein fluids are very different. The two veins studied formed at the following conditions - both about 300°C, one of 30-48 wt.% NaCl the other 12-46 wt.% NaCl although this small difference may be due to a sampling bias. Since both veins were boiling and assuming that the vein fluids were originally of 30 and 12 wt.% NaCl composition, these conditions would correspond to the veins having formed at a pressure of about 80 bars. It can be clearly seen that these veins were formed at much lower pressures than the other veins which at the very least were subject to pressures of ultimately 150 bars. The only explanation

that can be suggested for this drop in pressure during quartz/wolframite vein formation is that these veins were of a later generation, although perhaps only a few millions of years later, and that at this time the superincumbent load has been reduced quite significantly (about 800 m) by erosion. The narrow filling temperature range may indicate that throttling in these veins was a rare occurrence. The small range in temperatures could easily be explained by simple isobaric boiling.

It is also possible that the quartz/wolframite vein fluid interacted with some of the earlier veins in the area, since there is some evidence that the filling temperatures ($260 \pm 40^{\circ}C$) are reflected in the other vein samples (see fig. 22). This effect has been recognised at the Carrock tungsten mine, Cumbria, where early ore bearing veins reflect fluids which generated the later barren quartz (pers. comm. T.J. Shepherd, 1979). The filling temperatures, for the other veins, obtained at the lower end of the temperature range may therefore be due to either the original fluid or from the later quartz/wolframite vein fluid or even a mixture of both. Whichever is correct the overall model remains unchanged although if the lower filling temperatures were due to a secondary source the data is in even better agreement with the overall boiling model.

5.12.3. The Elvan

Unfortunately the inclusions in the quartz from the elvan were secondary and it is considered that they have nothing to do with the main kaolinising event. It has been suggested elsewhere that the elvan was recrystallised by the kaolinising event in which case one might expect to find boiling inclusions in the quartz from the elvan. However if the elvan were intruded at the later stages of kaolinisation, perhaps after the boiling had subsided then one may expect the fluids to be

still hot enough to recrystallise the groundmass. These fluids may be represented by the secondary inclusions in the quartz. No indication of boiling was found whatsoever and the inclusions were formed at around $400 \pm 40^{\circ}C$ and with a very restricted salinity range 20-24 wt.% NaCl which may also be indicative of a non boiling environment. In order to prevent these fluids from boiling the pressure must have been greater than 250 bars (see fig. 25), but no better constraints can be made. It is already known that the overlying load was equivalent to 1.7 km of rock and it was suggested that this may have been replaced by hydrostatic load if the rock cracked allowing further ascent of the vein fluid. The latter conditions would give a pressure of 150 bars. However the elvan fluid inclusion data shows that the pressure cannot be any lower than 250 bars although the elvan would almost certainly be subjected to lithostatic load conditions. Calculation of the depth of elvan intrusion using equation (i), $P = \rho g H$, where

$P = 250$ bars $(250 \times 10^5 \ Nm^{-2})$
$\rho = 2.7 \times 10^3 \ Kgm^{-3}$
$g = 9.8 \ msec^{-2}$

gives a depth of 950 m. However 250 bars is the minimum pressure needed to prevent any fluid in the elvan from boiling and so 950 m is the minimum depth of intrusion.

From the fluid inclusion data the boiling quartz/wolframite vein fluids were intruded at about $300^{\circ}C$ (the upper limit of the filling temperatures) and with a salinity of about 10 wt.% NaCl (the lower limit of the salinities). Boiling lowered the temperature and raised the salinities by processes explained elsewhere in this chapter. For a 10 wt.% NaCl fluid at $300^{\circ}C$ to boil and assuming that the fluid reached surface, from fig. 26 this is equivalent to a hydrostatic depth of

about 900 m. This figure is extremely near the intrusion depth of the elvan although in all probability slightly lower due to the elvan intrusion depth of 950 m being only a minimum value. The elvan crosscuts the main generation of veins and so therefore was probably not recrystallised by the main mineralisation/kaolinisation event. The recrystallised elvan may indicate the last waning post-boiling stages of kaolinisation since boiling solutions in this area (indicating kaolinisation) would leave their mark as boiling inclusions in the elvan quartz. No crosscutting relationships were found between the quartz/wolframite veins and the elvan. On pressure constraints alone one would expect the wolframite veins to have formed slightly later than the elvan. There is some indication that some of the lower temperature inclusions in other vein quartz in the area may be due to these boiling quartz/wolframite vein fluids. It is proposed therefore that it is these fluids which were responsible for recrystallising and kaolinising the elvan.

5.13. Summary and conclusions

1. The quartz/tourmaline $\pm$ cassiterite veins were formed at about 450°C and 450 bars. This corresponds to a depth of 1.7 kms (lithostatic load). A combination of isobaric and non-isobaric boiling, heat exchange with the environment and irreversible adiabatic expansion cooled the vein fluid to around 200°C. These processes were probably initiated by sudden pressure release by replacing lithostatic load with a hydrostatic load and by throttling.

2. The elvan fluids formed at a minimum of 400 $\pm$ 40°C and at a minimum pressure of 250 bars (950 m).

3. The quartz/wolframite veins formed at 300°C and 80 bars.

The small temperature range could be explained by simple isobaric boiling and probably indicated that throttling in these veins was a rare occurrence.

On pressure constraints alone they are considered to have been formed shortly after the elvan at a depth of about 900 m and to have been responsible for kaolinising and recrystallising the elvan.

CHAPTER 6

Fluid inclusions - Scanning Electron Microscopy of Daughter Phases

CHAPTER 6

Fluid Inclusions - Scanning Electron Microscopy of Daughter Phases

6.1. Introduction

In the previous chapter a summary of the methods used to determine the composition of fluid inclusions was presented. The analysis of the solid phases in individual inclusions has prompted much research but until recently daughter crystal analysis was only possible under very favourable circumstances.

In 1976 a breakthrough was made in this field. Le Bel (1976) managed to analyse several daughter crystals in inclusions from a porphry copper deposit in south Peru. The technique had the advantage that individual phases could be qualitatively analysed as well as giving an improved study of morphology. The analyses gave data on individual inclusions and were a vast improvement on other techniques which only produced data on the fluids from a large number of inclusions in combination with several serious contamination problems.

Inclusions in samples from Goonbarrow contained many daughter crystals mostly unidentified, and their complex nature would greatly benefit from a study of this kind.

6.2. Previous work and discussion of techniques

Le Bel (1976) was the first to publish a paper on this subject. He used a JEOL - 03 SEM combined with a Nuclear Conductor diode and Tracor treatment device NS 880 PDP 8K and occasionally an ARL EMSQ Scanning electron micro quantometer. The former instrument is basically a SEM with an attached energy dispersive X-ray analyser.

The electron beam on impinging the specimen will produce X-rays characteristic of the elements within the specimen. With an instrument of this type it is impossible to analyse for elements below sodium in the periodic table. The latter is an electron microprobe and is complimentary to the previous instrument. It has a major disadvantage that its imaging capabilities are nowhere near as good as an SEM, however its analytical capabilities are much superior. Le Bel prepared his specimens by breaking them into fragments by either crushing or thermal shock on a heating stage. The submillimetric fragments were then mounted directly on a specimen holder and coated with gold by means of a cathode anodising treatment under low argon pressure. This is to prevent "charge buildup" on the specimen arising from poor electrical conduction and thereby producing a better image. From his analyses he identified the following minerals and substances: Anhydrite, ilmenite, chalcopyrite, pyrite, muscovite, franklinite, Iron-Manganese-potassium chloride and a sodium-Iron-potassium-copper-Barium sulpho-chloride complex.

Metzger et al., (1977) used an SEM (of undiclosed make) to identify daughter phases from a fluorite deposit in Colorado, gold-quartz veins from California and a carbonatite at Magnet core, Arkansas. The technique used appears to be very similar to that of Le Bel except that the specimens were coated with carbon instead of gold since this produces no interfering X-rays under electron bombardment. Daughter crystals identified in this study included: Anorthite, Arcanite, Barite, Celestite, Ferroan rhodochrosite, Glaserite, Gypsum, Halite, Phlogopite, Sylvite, Thenardite, Dawsonite and an unusual caesium-lanthanum carbonate. A more thorough investigation of the carbonatite

at Magnet cove, Arkansas (Nesbitt & Kelly, 1977) revealed twenty four daughter minerals and it was possible to say much about the chemistry of the fluids in the various phases found within the carbonatite.

The only other work of this kind was on rocks from a cornish locality - St. Michaels Mount (Moore and Moore, 1979). The inclusions in quartz intergrown with cassiterite and wolframite contained daughter minerals which on analysis with a JEOL JSM35 coupled with an ELSCINT PROXAN energy dispersive analyser identified the following elements Al, Ca, Cl, S, K and Mg. The Ca - S minerals were tentatively identified as gypsum or anhydrite and the K - Al - Si minerals as mica or clay minerals.

6.3. Experimental procedure

6.3.1. Sample preparation

Specimens were selected on the basis of observations under a high power microscope. Small chips of quartz from veins were ground on a diamond wheel to a tabular shape about 3 mm x 8 mm x 8 mm. These were then split in a small vice and the resultant chip mounted on small brass holders using RS components cement with the broken surface uppermost. These were then coated with carbon by a vacuum technique and "Aquadag" painted on at the contact between the specimen and the holder to ensure good electrical contact. The specimens were then placed in the bulk specimen holder and loaded into the scanning electron.

6.3.2. Analytical procedure

The instrument used was a JEOL 100CX coupled to a LINK SYSTEMS energy dispersive semiconductor X-ray detector. This instrument has

variable magnification from 10 x to 300,000 x, resolution 15Å and a selection of accelerating voltages 20, 40, 60, 80, 100 kv. Although the best image is obtained at 100kv it was sometimes impossible to focus on the surface of some specimens as due to their large thickness, their surface was not in the focal plane of the instrument. However the instrument had an extra facility known as the "bulk specimen mode", which only operated at voltages of 10, 20 and 40kv which effectively moved the position of the focal plane thus enabling thicker material to be studied. Fig. 28 shows the essential features of the energy dispersive analysing system. The X-rays, produced by bombardment of the electron beam, are detected by a Si(Li) detector which is a lithium drifted p-type silicon single crystal. The detector produces pulses, the amplitudes of which are proportional to the incident X-ray energies. This pulse is then amplified by the pre-amplifier using a field effect transistor cooled with liquid nitrogen. The output from the pre-amplifier is further amplified with a linear amplifier, the signals are then classified by pulse height or X-ray energy with a multichannel pulse height analyser and then displayed as an energy spectrum on the cathode ray tube (TV screen). A data processing system using a NOVA mini computer was used for storage, peak smoothing and stripping of overlapped peaks with small energy differences. There were also facilities for plotting and printing the energy spectra. The computer also enabled a user to identify the X-ray peaks immediately on the TV screen, thus saving time in referring to standard tables. The detector had to be kept topped up with liquid nitrogen to prevent diffusion and precipitation of the lithium and an increase of noise and subsequent loss of energy resolution. The detector is covered by a thin window

of beryllium to cut off the low energy continuous X-rays, however this limits the range of detectable elements to Na to U. Apparently a windowless detector is available which can detect lighter elements but extreme care must be taken not to contaminate the detector surface. The particular instrument used in this work was not fitted with such a detector.

After focussing on the surface of the specimen the holder was tilted to produce maximum count rate. Inclusions were easily identified at low power and daughter minerals at an intermediate magnification, usually about 300-500x. The daughters were studied at high power, 4000-20,000x and sometimes photographed if their morphology was particularly important. The daughters were analysed in the spot mode (spot size ~0.1μm).

6.3.3. Problems involved in the method

For reasons mentioned earlier, no elements below sodium in the periodic table can be detected which is unfortunate since ore fluids may well be composed of carbonates, nitrates, hydroxides, fluorides and borates none of which could be identified. Consequently this technique can only give limited data on the anions expected in ore fluids, although significant information concerning the transport of metals as sulphur or chloride complexes can be determined. The most awkward problem by far is the fact that the electron beam completely penetrates through the daughter crystal and into the host mineral, in this case quartz. Without exception every spectrum contained silicon. Fig. 29a shows a spectrum obtained from a cubic daughter crystal. It is quite obviously halite, however note the presence of the silicon peak. If the accelerating voltage was reduced from 40 kV to 10 kV,

resulting in less penetration (see Metzger, 1977, fig. 1), the size of the silicon peak was significantly reduced (Fig. 29b). Silicon could be tentatively identified in many daughters by its large size in comparison to other peaks. It was not usually possible to analyse the daughter at 10kV, since it was usually impossible to focus on the specimen due to the nature of the bulk analysing mode. However 40kV was always used in preference to any higher voltage wherever possible. The specimens were attached to small brass holders which at first produced large peaks for copper and zinc (Fig. 30). However this was also minimised and often removed entirely, by painting the holders with a thick covering of "Aquadag" which is essentially carbon and is undetectable to the detector. At all times it proved better to analyse daughters which extended well above the cavity thus eliminating any host mineral interferences, but of course this was not usually possible. Some other typical spectra are shown in figures 31 and 32.

6.4. Results

Table 22 lists every successful analysis of a daughter mineral in addition to some comments and their possible identification. About 1% of inclusions studied contained daughter minerals. The absence of daughters was at first thought to be surprising since the microscopical study had indicated that the presence of daughters was much more common. However many daughters were undoubtedly lost when the specimens were broken open and also during the subsequent mounting and coating process. On many occasions inclusions were found that contained daughters which would not produce any spectra including another thirty one specimens from various parts of Goonbarrow. This was considered to be due either

Table 22 Elemental compositions of daughter minerals in fluid inclusions from Goonbarrow

Elements on a single line were detected on a single daughter crystal. Lines grouped by brackets indicate that these daughter crystals were found within one inclusion.

28V, Old Beam - Cassiterite vein

Al, Fe, K	Biotite
Al, Fe, K	Biotite
Cu, Fe, Mn, Zn	
Cl, Na Ca, Mg Fe, Mn, Na, Zn	Halite
Cl, Na Al, Cl, K	Halite platey mineral
Ca	Amorphons
Fe, Mn	ferroan rhodochrosite?

53V, Old Beam - Cassiterite vein

Fe, Mn	Ferroan Rhodochrosite?
Al, Cl, K, Na	Composite, halite & muscovite
Al, K	Muscovite
Al, Cl, Fe, K	platey mineral - composite spots of evaporated NaCl present

73V, Imperial - Quartz/tourmaline vein

Al, Cl, K, Na	
Cl, K Al, Cl	Sylvite
Cl, K, Na	Sylvite/halite
Cl, Na	Halite
Al, Cl, Fe, Mn, Na, K	
Fe, K Fe, Mn	Biotite Ferroan rhodochrosite?
Cl	
Al, Fe Al, Cl, Fe Cl, Fe, K	Rod like mineral

73G, Imperial - Greisen to quartz/tourmaline vein

Al, Cl, Ka, K	

82V, Imperial - Quartz/wolframite vein

Al, K Fe, Mn	Muscovite

Table 22 cont'd

82G, Imperial - Greisen to quartz/wolframite vein

Al, K	
Fe, Mn, Zn	
Al, K	Muscovite
Al, K	
Al, Cl, Fe, Mn, K, Zn	
Fe, Mn	Ferroan Rhodochrosite?
As, Fe	Arsenopyrite?
Fe	
Fe, Mn, Zn	
Fe	
Al, K	

97V, Old Beam - Cassiterite vein

Cl, Fe, S, Zn	
Fe, S, Zn	Sphalerite/pyrite?
Cl, Fe, S, Zn	
S, Zn	Sphalerite

111, Old Beam - Cassiterite/wolframite vein

Al, K	Not platey
Fe, Mn	Ferroan Rhodochrosite?
Cl, Fe, Mn	
Mn	

124V, Old Beam - Quartz/tourmaline vein

Cl, Fe, K, Sn	
Ca, Cl, Fe, Mn	
Sn	
Cl, Fe, K, Mn	

135G, Greisen to multimineral vein

As, Cu, Fe

136, Multimineral vein

Cl, Mn	
Al, K	Muscovite
Al, K	Muscovite
Al, Fe, K	Biotite
Cl, Cu, Fe, Mn, Zn	

137V, Imperial - Cassiterite vein

Cl, Fe, Mn, Zn	
Cl, Cu, Fe, Mn	
Ca, Cl, Cu, Fe, Mn, Zn	Cubic

Table 22 cont'd

148G, Opposite Old Beam - Greisen to quartz/wolframite vein

Cl, Fe, Mn, S	
Al, Na	
Al, K	Muscovite

147V, Opposite Old Beam - Quartz/tourmaline vein

Cl, Na	Halite
Fe, Al, Ca, Cl, K, S	Amorphous Platey mineral

148A, Opposite Old Beam - Cassiterite vein

Cl, Na	
Al, K	Muscovite
Fe, Mn	Ferroan rhodochrosite?
Al, K	Muscovite
Al, Cl, Fe	
Fe, Mn Al, Fe, Mn Al, K	 Muscovite

148G, Opposite Old Beam - Greisen to Cassiterite vein

Cl, Na	Halite

152V, Imperial - Quartz/tourmaline vein

Cl, Fe, Mn Cl, Fe, Mn, K Cl, Fe, Mn Cl, Al, Fe Al, Cl, Fe	 Rod like mineral
Al, S, Zn Cl, Al, K K Fe, Mn, Zn Al, Fe, K	Sphalerite Not platey Not platey
Cu, Fe, S As, Cu, Fe, S	Chalcopyrite Arsenopyrite?
Al, K	Rod like mineral
Al, Fe, Mn, Zn	Rod like mineral
Al, K	Muscovite
Al, Cl, K, Na	Evaporated solution, complex?
Al, K Al, Cl, K	Muscovite
Al, Cl, K	rlatey mineral
Cl, Fe, K, Na	Amorphous
Cl, Na	Halite
Cl, Na Al, K Fe, Mn	Halite Muscovite Ferroan rhodochrosite?

Table 22 cont'd

152V cont'd

(Fe, Mn / Fe, K)	Ferroan rhodochrosite?
Cl	Halite
(Al, Cl / Al, Fe, K)	Biotite
(Al, K / Fe, Mn)	Muscovite
Al, K	Muscovite
(Cl, Na / Al, K)	Halite Muscovite
Al, Fe, K	Biotite

164V, Martins Goonbarrow - Quartz/tourmaline vein

Al, Fe, Mn Fe, Mn	Ferroan rhodochrosite?

165V, Martins Goonbarrow - Quartz/tourmaline vein

(Cl, K / Al, K)	Sylvite Muscovite
Al, Cl, K	Platey mineral

171V, Imperial - Quartz/tourmaline vein

Fe, Mn	Ferroan rhodochrosite?
Cl, K, Na	Halite/Sylvite
Al, Fe	Muscovite

187, Big feldspar granite

Al, K	Muscovite

262, Big feldspar granite

Al, K	Muscovite
Al, Fe, K	Not platey
Fe, Mn	Ferroan rhodochrosite?
Ca, Mn	
(Fe, Mn / Al, Cl, Fe / Sn)	Ferroan rhodochrosite?
Fe, Mn	Ferroan rhodochrosite?

Lensoid Pegmatite

Fe, Mn	Amorphous

Table 23. Summary of elemental compositions of daughter minerals in fluid inclusions from Goonbarrow

Sample No.	Description and location	No. of incs. analysed	As	S	Zn	Cu	Sn	Fe	Mn	Al	Mg	Ca	Na	K	Cl
	Geochemical associations		chalcophile elements vein mineral forming					lithophile elements water soluble							
IGNEOUS															
187	Big felispar granite	1								Al				K	
262	Big feldspar granite	6					Sn	Fe	Mn	Al		Ca		K	Cl
Peg.	Lensoid pegmatite	1						Fe	Mn						
	Total						Sn	Fe	Mn	Al		Ca		K	Cl
QUARTZ/TOURMALINE VEINS															
75V	Imperial	7						Fe	Mn	Al				K	Cl
73G	Imperial	1								Al			Na	K	Cl
124V	Old Beam	3					Sn	Fe	Mn			Ca		K	Cl
147V	Opposite Old Beam	2		S				Fe		Al		Ca	Na	K	Cl
152V	Imperial	21	As	S	Zn	Cu		Fe	Mn	Al			Na	K	Cl
164V	Martins Goonbarrow	2						Fe	Mn	Al					
165V	Martins Goonbarrow	2								Al				K	Cl
171V	Imperial	3						Fe	Mn	Al			Na	K	Cl
	Total		As	S	Zn	Cu	Sn	Fe	Mn	Al		Ca	Na	K	Cl
QUARTZ/WOLFRAMITE VEINS															
82V	Imperial	1						Fe	Mn	Al				K	
82G	Imperial	5	As		Zn			Fe	Mn	Al				K	Cl
143G	Opposite Old Beam	3		S				Fe	Mn	Al			Na	K	Cl
	Total		As	S	Zn			Fe	Mn	Al			Na	K	Cl
CASSITERITE VEINS															
25V	Old Beam	7			Zn			Fe	Mn	Al	Mg	Ca	Na	K	Cl
55V	Old Beam	5						Fe	Mn	Al			Na	K	Cl
97V	Old Beam	1		S	Zn			Fe							Cl
137V	Imperial	3			Zn	Cu		Fe	Mn			Ca			Cl
148a	Opposite Old Beam	6						Fe	Mn	Al			Na	K	Cl
148a-G	Opposite Old Beam	1											Na		Cl
	Total			S	Zn	Cu		Fe	Mn	Al		Ca	Na	K	Cl
CASSITERITE/WOLFRAMITE VEINS															
111	Old Beam	4						Fe	Mn	Al				K	Cl
MULTIMINERAL VEINS															
135G	Imperial	1	As			Cu		Fe							
136	Imperial	4			Zn	Cu		Fe	Mn	Al				K	Cl
	Total		As		Zn	Cu		Fe	Mn	Al				K	Cl

Note: All spectra include Si, part or all of which is derived from the enclosing quartz crystal.

to the daughters being too deep within the cavity, the resultant X-rays being unable to reach the detector or to the daughter consisting of elements which were undetectable i.e. lower than sodium in the periodic table.

A selection of the daughter crystals are shown in Plates 86 to 97 together with analyses and comments on their identification. Very few daughters were positively identified although halite was easily recognised and the platelike crystals are presumably micaceous minerals. Table 23 summarises all the data and gives some indication of those elements present in the ore fluids.

6.5. Theories on ore transport

Of the abundant ore minerals in the Cornubian metallogenic province the majority occur as sulphides, for example pyrite (FeS_2), chalcopyrite ($CuFeS_2$), Arsenopyrite (FeAsS), sphalerite (ZnS) and Galena (PbS). However the most economically important occur as oxides, notably wolframite ($[Fe,Mn]\ WO_4$) and cassiterite (SnO_2) although tin is occasionally found as stannite (SnS_2). It is known that these minerals are too insoluble to be transported in aqueous solution and in addition their solubilities do not follow the sequence necessary to explain the observed zoning in ore deposits (Barnes and Czamanske, 1967). The generally accepted view is that the metals were transported as complex ions, which are much more stable than the equivalent simple ions. There are two types of complexes which are considered important in the genesis of sulphide ore, these are the chloride and bisulphide-polysulphide complexes (Stanton, 1972). Although it has been shown (Barnes and Czamanske, 1967) that Cu and Zn can form sulphide complexes (e.g. of the type $Zn(HS)_3^-$ and $Cu(HS)_4^{2-}$

sufficiently stable and soluble to transport these metals, chloride complexes are considered to be more important (Helgeson, 1964, 1970) for Cu and Zn and especially Pb which forms relatively unstable sulphide complexes. In fact natural hot brines in California have been shown to carry substantial quantities of metal in the presence of sulphur (Skinner et al., 1967). The overall conditions are considered to be an abundance of chloride ion, slightly acidic pH and moderately high temperatures (Stanton, 1972).

Foster (1976) has shown that tungsten could be transported as the simple WO_4^{2-} ion in chloride rich solutions. However he does not eliminate the possibility of migration of W as the oxyfluoro complex, (WO_2F_2) suggested because of the frequent association of fluorite with greisen and pegmatitic wolframite.

The geochemical association of tin with boron and fluorine bearing minerals has long been recognised (Daubree, 1841, 1849; De Beaumont (1847)). Ferguson and Bateman (1912) concluded that boron minerals were second only to fluorine minerals in their frequency of association with cassiterite. Consequently Daubree (1849) put forward the hypothesis that tin was transported as a volatile halide and was deposited by a simple hydrolysis reaction

$$SnF_4 + 2H_2O = SnO_2 + 4HF$$

However this theory lost support when it became clear that tin was transported in a hydrothermal solution and not a vapour phase. Barsukov (1967) and Barsukov and Volosov (1968) proposed that tin was transported as an oxyfluoro complex of the type $Na_2\ Sn(OH)\ F_{6-}$ under alkaline conditions and is deposited as cassiterite when the pH is reduced to around 7.5 to 8 by interaction with wallrocks, the released fluorine forming minerals such as fluorite and topaz. Klintsova et al.,

(1975) have shown that cassiterite deposition from aqueous solutions containing Sn(IV) hydroxofluoride complexes is not governed by temperature but by reduction from a pH of 10.6 to about 8. Hesp and Rigby (1972) proposed that cassiterite was transported in Na,K and NH_4 halide solutions, presumably in a mixed liquid-vapour phase around 460° and under alkaline conditions.

Tin is also found as a sulphide mineral - stannite Cu_2FeSnS_4, especially where no fluorine or boron minerals are present. This led to F.G. Smith (1947) showing that tin could be held in aqueous solutions partly as the stannate ion and partly as the thiostannate ion, according to the following equilibrium:

$$SnS^{4-} + 4OH^- = SnO_4^{4-} + 4HS^-$$

He suggested that since the solubility of stannic sulphide was much greater than stannic oxide in aqueous alkaline solutions, that tin would precipitate late in the sequence as thiostannate minerals and as cassiterite early in the sequence. Nekrasov (1971) found that acid solutions, reducing conditions and temperatures from 200-500°C favoured the formation of tin sulphides. Stannite is rarely found in Cornwall and was certainly not seen in Goonbarrow. Generally tin sulphide minerals tend to be associated with lower temperature deposits which does not appear to be the case at Goonbarrow.

6.6. Discussion

From the SEM data the fluids which produced the veins in Goonbarrow in addition to containing Sn and W also carried Al, As, Ca, Cu, Fe, Mg, Mn, S, Zn in KCl/NaCl brines. This strongly suggests that As, Cu and Zn were transported as chloride complexes in the presence of sulphur,

probably under acid conditions, as proposed by Helgeson (1964). The Fe and Mn were presumably incorporated in wolframite and tourmaline. The transport of Sn and W under hypersaline conditions is strongly suggested although unfortunately no comment can be made on the presence or absence of the oxyfluoro (for Sn and W) or ammonium complexes (for Sn only) since nitrogen, fluorine, oxygen or hydrogen are undetectable to the instrument. In chapter 2 the ubiquitous coexistence of topaz and cassiterite in the old Beam area was mentioned which implies that fluorine and tin were coexistent. Since chlorine is in the same chemical group as fluorine an oxychloro or oxychloro/fluoro complex may also be expected to contribute to the transport of tin/tungsten although no mention of this can be found in the literature. However Barsukovs proviso of alkaline conditions is not consistent with transport of the chalcophile metals. In chapter 2 a tin vein was described from Imperial which was associated with quartz and tourmaline only, this implies that there may have been less fluorine available in this ore fluid (fluorine content of a typical tourmaline = 1% and Topaz = 17% Deer, Howie and Zussman, 1966). Of all the ore transport theories no specific tin-boron compound has been suggested in which tin can be transported although the association of boron with tin deposits has been recognised. In the cassiterite/tourmaline vein boron may be more important than the minor presence of fluorine.

In Goonbarrow wolframite was associated with two distinct type of veins, (a) with cassiterite, topaz, tourmaline and quartz in the Old Beam area and (b) alone with quartz in the Imperial area. In the first case transport of tungsten as the oxyfluoro complex, similar to tin, seems very favourable, however in the second vein type the simple

WO_4^{2-} ion may be more likely although as in the case of tin the influence of Boron on tungsten transport is unknown.

The existence of As, Cu, Fe, Mn, S and Zn and to a minor extent Ca and Mg, in the vein fluids is somewhat surprising since none of the inferred minerals (i.e. Arsenopyrite, chalcopyrite, pyrite and sphalerite) were found in the veins from Goonbarrow. Admittedly the multimineral veins do contain arsenic, in the form of Löllingite, and iron in the form of pyrite but these are very obviously of a different generation to the more important tin/tungsten lodes. It has already been suggested that the Fe and Mn could have been incorporated into wolframite and tourmaline. The absence of W in any of the daughters suggests that it had already been deposited before crystallisation of the quartz which trapped the inclusion fluid. This implies that Fe and Mn were available in a great excess to the W. Alternatively insufficient tungsten was available to form a daughter crystal when the ore fluid was trapped and subsequently cooled. Fe and Mn were invariably found together in the same daughter and although these metals were occasionally detected with Cl, in the large majority of cases the associated anion remained undetectable. From the morphology of some of the daughters they may be tentatively identified as ferroan rhodochrosite $(Fe,Mn)CO_3$ which has been reported in other inclusions elsewhere (Metzger et al., 1977). However it is clear that As, Cu, Zn and S were present in the ore fluids and that the conditions were unfavourable for deposition of sulphides. Theories of ore genesis in Cornwall have always involved fluids associated with the granites which have acted as emanative centres, producing concentric patterns of mineral zonation about them. The tin/tungsten zone is found nearest the granite (in fact usually within granite) followed outwards by copper and then finally lead/zinc. Since in the case of

Goonbarrow we are well within the tin/tungsten zone it is not surprising that copper, lead and zinc mineralisation is absent. In fact the presence of As, Cu, Zn and S in the vein fluids suggests that these elements were deposited spatially beyond the present veins, probably at a higher structural level, and have since been eroded away. It also suggests that unlike other areas in the Cornubian province the ore fluids were lead deficient. The consequences of using this method as an exploration technique are obvious. In this case the site of deposition of Cu and Zn ore is no longer present, however if a suitable generation of veins could be found on the edge of the Cornish granites which transcend the killas, these would be an obvious site for a study of this type. Unfortunately no comment can be made at present on whether the veins would be economic, only that the metals are present, which is very significant in itself.

6.7. Summary and conclusions

1. The vein fluids in Goonbarrow contained Al, As, Ca, Cu, Fe, Mg, Mn, S and Zn in KCl/NaCl brines.

2. As, Cu and Zn were transported as chloride complexes in the presence of sulphur. However conditions were unfavourable for deposition of these elements as sulphides at the present structural level exposed at Goonbarrow.

3. Fe and Mn were probably incorporated into wolframite and tourmaline.

4. Little information was found on tin/tungsten transport except that they were transported under hypersaline conditions. This was due mainly to the equipment used being unsuitable for detecting the several possible anions.

CHAPTER 7

Hydrogen and Oxygen Stable Isotope Studies

Chapter 7

Hydrogen and Oxygen Stable Isotope Studies

7.1. Introduction

One of the most useful applications of hydrogen and oxygen isotope studies has been as indicators of the origin and history of water in hydrothermal fluids (Taylor, 1974). Isotopic fractionation accompanies many of the chemical and physical processes which occur in the formation of ore deposits. However these processes can be complex or involve a variable combination of processes so that an overall model is often difficult to construct and is commonly not unique. The Cornish china clay deposits offer a problem where oxygen/hydrogen isotope studies could contribute important data on the source of the fluid that formed them. Sheppard (1977) studied the oxygen/hydrogen isotopic compositions of kaolinite and associated alteration micas from several of the Cornish china clay localities and concluded that they were produced by a supergene process during the Cretaceous-Tertiary. Initially, Sheppard's work will be described and the inherent problems discussed. His data together with data from the present study will then be used to derive an alternative model for the formation of the Cornish china clay deposits.

7.2. Previous work

Sheppard (1977) analysed the oxygen and hydrogen isotopic compositions of kaolinite, muscovite and biotite from altered and unaltered granites, sericite from greisens and sericitised granites, quartz from altered and unaltered granites and whole rock specimens from sediments and unaltered granite. This data is shown plotted in fig. 33 and was then used to construct fig. 34 (modified from Sheppard, 1977).

Before describing Sheppards interpretation the following points should be noted.

1. Of the eight points which comprise the alteration mica field only two represent true greisens associated with kaolinisation. The other six points comprise a sericitised granite, one from a sericitised sediment and four greisens from a typical tin lode. The two samples from greisens associated with kaolinisation (marked †, which can be considered very similar to the samples from Goonbarrow) plot at significantly lower $\delta^{18}O$ values than the other samples.

Sheppard constructed the hydrothermal water-sericite field from these points using the fractionation factors of Taylor (1974) (for oxygen) and Suzuoki and Epstein (1976) (for hydrogen) and assuming a temperature of between 200 and 400°C. These temperatures were obtained from fluid inclusions studies by Sawkins (1966), Charoy and Weisbrod (1975) and Jackson (unpublished work) on comparable material from Cornwall and Brittany. Since then, Friedman and O'Neil (1977) have produced an alternative plot of fractionation factor against temperature for hydrogen, based on Suzuoki and Epstein's (1976) data. The two curves differ very significantly, especially at temperatures below 400°C where the curves are extrapolated due to the unavailability of experimental data. The hydrothermal water-sericite fields are therefore plotted in fig. 34 using both curves at 200, 300 and 400°C and the uncertainty of the true position of this field must be considered in any interpretation of the data.

2. Eight samples were analysed for $\delta^{18}O$ and δD of granite micas and whole rock and seven samples of quartz for $\delta^{18}O$. This data was then used to construct the cornubian magmatic water field shown in fig. 34. At magmatic temperatures there will be virtually no fractionation between water and the granite minerals and therefore the cornubian magmatic water

field can be simply constructed from the mineral and whole rock data points. Two each of the muscovite and biotite analyses were from altered granites and may not necessarily represent primary cornubian magmatic water. The two most negative δD biotites are in fact from kaolinised granite and are significantly different from the single biotite analysis from an unkaolinised granite, although more analyses are needed to confirm this difference. However seven samples of quartz from altered (4) and unaltered (3) granites produced $\delta^{18}O$ values in the range 12.3 to 14.2 which all plot in the cornubian magmatic water field. Clearly the primary cornubian magmatic water field is poorly defined.

3. The two reference lines shown in figs. 33 and 34 are the meteoric water line (Craig, 1961) and the kaolinite line defining the isotopic variations in kaolinite from surface weathering environments (Savin and Epstein, 1970). Sheppard also analysed three samples of stream and spring water from the St. Austell and Dartmoor granites, which should represent the isotopic composition of modern day meteoric waters. These plot on the meteoric water line as shown in figures 33 and 34.

7.3. Interpretation (Sheppard, 1977)

Sheppards hydrothermal water field has D/H ratios similar to paleozoic ocean water and also meteoric waters of low to middle latitudes. On paleogeographical evidence and the unlikely event of metamorphic water being involved, Sheppard proposed that the hydrothermal fluids which produced the greisenisation were from a meteoric water source. Presumably the meteoric water must have acquired its high $\delta^{18}O$ values by isotope exchange with $\delta^{18}O$ rich country rocks such as the granite and surrounding sediments. Certainly the hydrothermal water field only slightly exceeds the highest $\delta^{18}O$ values of Cornubian magmatic water, so this theory may

be reasonable.

If Friedman and O'Neils (1977) extrapolated curve is used to define the hydrothermal water-sericite field, Sheppards interpretation is only valid for temperatures above about 400°C since meteoric waters do not exist with δD values above zero.

The kaolinite samples plotted in a very tight field close to the kaolinite (weathering) line (see fig. 33) after contamination effects by sericite were taken into account. Sample SPS, a high quality kaolinite produced from the St. Austell area by the English China Clays group, plotted centrally in the kaolinite field. The curve for water in equilibrium with this typical kaolinite sample is shown in fig. 34, plotted for the temperature range 20°C to 100°C. Sheppard argued, assuming there has been no post depositional isotope exchange, that the cornish kaolinite formed at 20°C from a water indistinguishable from modern day meteoric water and decidedly different from the water that formed the alteration micas. The association of intense kaolinisation and greisen bordered quartz veins was recognised and it was proposed that these veins "prepared the ground" for the later kaolinising event. Consequently he proposed that the Cornish china clay deposits were formed by a low temperature weathering process probably in the Cretaceous-Tertiary.

Sheppards interpretation relies on the assumption that there has been no post depositional isotopic exchange and cites four instances to illustrate his point, which are as follows.

1. Kaolinite from an argillised granite sheet in kaolinised shale adjacent to a major ore bearing vein, at a depth of 400 m, at the Geevor mine in the Lands End granite, plots between the china clay and alteration mica fields (see fig. 34). In contrast to the Geevor sample the shales

adjacent to the St. Austell china clay deposits are not kaolinised. Thus certainly not all kaolinites have undergone major re-equilibration and the field evidence suggests there may be more than one type of kaolinisation. Sheppards statement that shales adjacent to china clay deposits are not kaolinised is incorrect since a large piece of killas was found at Melbur which was intensely kaolinised (Plate 98). There is however an alternative interpretation for the Geevor data which will be presented later.

2. Kaolinite from the Czechoslavakian deposits and dickite from a Bohemian Sn-W deposit are used as an example to show that the isotopic differences of clay minerals can be preserved. In the Cornish situation this does not mean that they are preserved. The Czechoslavakian deposits arise from an environment which contains features indicative of weathering (Konta, 1969) and is unlike Cornwall.

3. Kaolinite from the Bovey formation, derived at least in part from the Dartmoor region has similar isotope characteristics to the in situ kaolinites. The fact that these kaolinites preserved their isotopic ratios in very different geological and hydrological environments is used as evidence against post depositional isotope exchange. However there is no reason why these kaolinites could not have re-equilibrated with modern day ground waters.

4. Isotopic data on kaolinites of Mesozoic and Cenozoic age from a wide variety of near surface environments indicate that they have preserved their original $^{18}O/^{16}O$ and D/H ratios. Many of these kaolinites are not out of equilibrium with modern meteoric waters. However as Sheppard states, insufficient data on Palaeozoic and older clays prevents extension of this generalisation. O'Neil and Kharaka (1976) suggested that for clays formed by surficial weathering, post-formational exchange with

ground water would not alter the original isotope ratios significantly unless the isotopic ratios of local meteoric waters changed radically and the clays were very old. They also pointed out that clay minerals formed under hydrothermal conditions may have D/H ratios significantly different from equilibrium values relative to local meteoric water and undergo subsequent exchange which alterd the original ratios.

Some experimental data is available concerning the hydrogen and oxygen isotope exchange between clay minerals, including kaolinite, and water. O'Neil and Kharaka (1976) showed that hydrogen isotopic exchange could take place at 100°C over only two years. Oxygen isotopic exchange was reported as negligible. They concluded that if isotope exchange occurred as low as 100°C in laboratory times, then in nature it must occur at this temperature and probably lower where much larger time periods are available. Their experiments were conducted at very low concentrations of NaCl (0.04 N) and in more saline waters the rates of isotopic exchange may be more rapid. Isotopic exchange was also considered to be profoundly influenced by the pH of the solution. Although much more work is needed to clarify this problem it seems likely that post depositional isotopic exchange for hydrogen and possibly oxygen, under the right conditions, may have been involved in the kaolins of the Cornish china clay region.

7.4. Hydrogen/oxygen isotope study of Goonbarrow samples

7.4.1. Introduction

On initiating this project it was hoped to obtain some $^{18}O/^{16}O$ and D/H analyses on samples of kaolinite, greisen mica, granite mica and quartz from Goonbarrow. The unavailability of equipment prevented these analyses from being obtained by the author. However Dr. T.J. Shepherd (Institute of Geological Sciences, London) kindly agreed to analyse ten

samples for the hydrogen isotopic composition of their inclusion fluid. In the latter stages of this thesis study, Mr. D. Wesolowski (Pennsylvania State University) offered to analyse the quartz samples for their oxygen isotope composition and greisen mica, kaolinised granite mica and kaolinite for both their oxygen and hydrogen isotopic composition. At the time at which this thesis was written all of these analyses were not available and so only partial interpretation of this data is possible.

Inclusion fluids have been analysed for their D/H ratio by several workers (Rye, 1966, Rye and O'Neil, 1968, Ohmoto and Rye, 1974). Measurement of the $^{18}O/^{16}O$ ratio of inclusion fluids in quartz is technically possible but not worthwhile since the vast majority of oxygen is contained in the host mineral i.e. quartz. The isotopic composition of oxygen in the inclusion fluid would alter since the water would exchange with the host mineral (quartz) during cooling. Quartz contains no hydrogen and therefore the original D/H ratio of inclusion fluids will be retained.

7.4.2. Experimental procedure

The following samples were selected for the mineral oxygen/hydrogen isotope study by Mr. D. Wesolowski:

5 of vein quartz
4 of greisen muscovite (40/80#)
2 of kaolinite
3 of muscovite associated with kaolinised granite

These were analysed by standard techniques, similar to those described by Hoefs (1973). (Precision for $\delta D \pm 1‰$ and $\delta^{18}O \pm 0.1‰$).

Nine samples of quartz from various veins and ore from the pegmatite were selected for analysis of the hydrogen isotopic composition of their inclusion fluids. After crushing the -8 to +16 mesh (approximately 1 to 2 mm) size fraction was collected and hand picked under a binocular microscope to remove any mineral impurities, including composite grains.

These were then boiled in a mixture of concentrated $HCl-HNO_3$ for one hour to remove sulphide impurities and then thoroughly washed in deionised water. Three grams of each quartz sample were taken and outgassed under vacuum for 15 mins at 120°C. The temperature was then raised to 550°C and held for 10 mins. The inclusions in the quartz were therefore decrepitated at 120°-550°C. The water released was then passed over uranium metal turnings at 750°C and the resultant hydrogen collected and analysed. The D/H ratio was corrected for H_3^+ contribution and referenced with respect to SMOW. Precision on standards was better than 1‰ (SMOW).

The results of all the analyses are shown in Table 24.

7.4.3. Discussion

The following points can be made concerning the results shown in Table 24.

1. The δD of the fluid in pegmatitic quartz is more negative than fluids in vein quartz and plots on the least negative side of Sheppards primary magmatic water fields.
2. The vein samples plot in a wide range of δD between -30 and +4‰ but have a very restricted range in $\delta^{18}O$, + 13.2 to + 13.9‰.
3. The two kaolinite samples have δD values very similar to Sheppards values.
4. The δD values for greisen muscovites plot in a tight range from -57 to -62‰. These values are much more negative than those obtained for "Cornish alteration micas" by Sheppard.
5. Fine grained muscovites associated with kaolinised granite (but possibly not contemporaneous with growth of kaolinite, see chapter 4) have about the same δD values as the greisen muscovites or possibly even a little more negative.

Table 24 Hydrogen/Oxygen isotope study of Goonbarrow samples

A. Mineral hydrogen isotope analyses

Sample No.	Location	Sample type	D^* (‰)
73	Imperial	muscovite from greisen associated with quartz/tourmaline vein	- 57
82	Imperial	muscovite from greisen associated with quartz/tourmaline vein	- 62
110	Old Beam	muscovite from greisen associated with cassiterite/wolframite vein	- 60
113	Old Beam	muscovite from greisen associated with quartz/tourmaline vein	- 61
263 160/240	Old Beam	muscovite associated with kaolinised granite (BFG)	- 55
263 240/480	Old Beam	muscovite associated with kaolinised granite (BFG)	- 66
264 240/480	Martins Goonbarrow	muscovite associated with kaolinised granite (PMG)	- 71
263	Old Beam	kaolinite	- 62
265	Old Beam	kaolinite	- 66

B. Mineral oxygen isotope analyses

Sample No.	Location	Sample type	$^{18}O^*$ (‰)
73	Imperial	Quartz from quartz/tourmaline vein	+ 13.9
82	Imperial	Quartz from quartz/tourmaline vein	+ 13.8
110	Old Beam	Quartz from cassiterite/wolframite vein	+ 13.6
113	Old Beam	Quartz from quartz/tourmaline vein	+ 13.7
165	Imperial	Quartz from quartz/tourmaline vein	+ 13.2

C. Hydrogen isotopic analyses of fluid inclusion waters in quartz

Sample No.	Location	Sample type	D^* (‰)
Lens peg	West Goonbarrow	Pegmatite quartz	- 39, - 43
82	Imperial	Quartz/tourmaline vein	- 30
110	Old Beam	Cassiterite/wolframite vein	+ 4
113	Old Beam	Quartz/tourmaline vein	- 20
120	Old Beam	Cassiterite vein	- 14
124	Old Beam	Quartz/tourmaline vein	- 22
143	opposite Old Beam	Wolframite vein	- 27, - 28
148A	opposite Old Beam	Cassiterite vein	- 18
152	Imperial	Quartz/tourmaline vein	- 19
171	Imperial	Quartz/tourmaline vein	- 14

*All relative to SMOW

Figure 35 shows most of the above data plotted on the familiar δD vs. $\delta^{18}O$ graph. $\delta^{18}O$ values for the greisen muscovites were not available at the time this thesis was written and so the $\delta^{18}O$ values were assumed to be between +9 and +11‰ for this discussion. These values were chosen on the basis of the two samples of Sheppards which most resembled Goonbarrow i.e. Cligga Head and Trethosa china clay pit. δD and $\delta^{18}O$ values for waters in equilibrium with quartz and muscovite were calculated using the fractionation factors of Friedman and O'Neil (1977) (see appendix 6). As mentioned earlier Friedman and O'Neil (1977) constructed their curve from the data of Suzuoki and Epstein (1976). Taylor (1974) had produced a different curve from Suzuoki and Epstein's preliminary data. These curves are extrapolated in different positions below 400°C due to the unavailability of experimental data. Friedman and O'Neils (1977) data is preferred simply because it is more modern and presumably they have good reason for their alternative extrapolated line.

Since Sheppards (1977) paper, new data has now become available for the fractionation of oxygen between kaolinite and water at temperatures between 172 and 319°C (Kulla and Anderson, 1978). Their data is in good agreement with the value at 300°C estimated by Taylor (in Sheppard, Nielson and Taylor, 1969); extrapolating the line to low temperatures yields data in reasonable agreement with Taylors estimated value and also with independent estimates by Savin (1967). If this new data is used in conjunction with Taylors (1974) data for kaolinite-H_2O hydrogen fractionation, then a new curve can be constructed for water in equilibrium with kaolinite-SPS (fig. 35). This differs quite markedly from the position of Sheppards line, based on estimated data, and also in being plotted to higher temperatures. The new curve intersects the meteoric

water line at about $\delta D = -27‰$ (see fig. 35) which is about 8 more positive than Sheppards values for present meteoric water. However a δD value of $-27‰$ is consistent with meteoric waters derived during the Cretaceous/Tertiary. The other eleven samples of kaolinite plot around each temperature point producing a wide band for the compositions of water in equilibrium with the overall field of analysed kaolinites (see fig. 35). The new curve also indicates that if Sheppards hypothesis is correct then the kaolins were formed at about $0^{o}C$ which is not consistent with a Cretaceous/Tertiary origin since meteoric waters would clearly be at higher temperatures due to Cornwall being at a lower latitude at this time (Smith and Briden, 1977). However this is only true if the meteoric water line has remained in the same position from the Permian to the present day, which may not be the case.

Consider now the calculated waters in equilibrium with vein quartz and greisen muscovites. There is little doubt that the veins and greisens were formed at the same time and were probably related to the kaolinising event (see chapter 2). Theoretically, since the oxygen fractionation curves are now well established for quartz-H_2O and muscovite-H_2O it should be possible to determine the temperature at which these two systems were in equilibrium with each other. This can be achieved by plotting temperature against the oxygen isotopic composition of the waters in equilibrium with these two minerals, the point at which the two lines intercept each other being the required temperature. This type of graphical approach is shown in fig. 36 for the Goonbarrow data. However the $\delta^{18}O$ value for greisen muscovite has only been assumed and therefore there is a large area of overlap making the position of the intercept difficult to determine. When the $\delta^{18}O$ values for Goonbarrow greisen muscovites are obtained this approach may prove very useful.

It appears likely however that a low temperature (200-250°C) is not favoured. As may be recalled from the fluid inclusion study temperatures of between 200 and 450°C were obtained and a model produced suggesting that the vein fluids were formed at 450°C and then cooled by various mechanisms. In conclusion therefore the oxygen isotope data is not in conflict with the veins and greisens forming initially at about 400-450°C.

With regard to the δD values of vein quartz and greisen muscovites, they appear to be radically different, the greisen muscovite δD values plotting in a very tight field in complete contrast to the vein quartz values which range from +4 to -30‰. This large range has not been reported in the literature for any other vein quartz samples. Processes which may be considered to have produced this large range may be:

1. Magmatic water mixing with meteoric water
2. Magmatic water mixing with sea water
3. Magmatic water mixing with derived sea water

A straight line mixing relationship would be obtained between the magmatic water field and the other mixing components listed above.

1. Magmatic water mixing with meteoric water. As mentioned earlier meteoric water would have δD values a little less negative than present day meteoric waters during the Cretaceous/Tertiary because of Cornwall being at lower latitudes. This would also be the case during the late Permian when these veins were formed. However this would not explain the large δD variation seen here (fig. 37a).

2. Magmatic water mixing with sea water. Mixing with sea water could produce the observed large D variations, however since the $\delta^{18}O$ composition of sea water is around zero a mixing line between sea water (δD and $\delta^{18}O = 0$) and magmatic water would be obtained (fig. 37b). This

is not the case since the vein quartz samples have a remarkably tight $\delta^{18}O$ range and do not give a mixing line.

3. Magmatic water mixing with derived sea water. If sea water interacted with country rock and oxygen isotopic exchange occurred, then this "derived" sea water could have the correct isotopic composition to produce the observed variations. In this case it would have to have a composition of about $\delta D=0$, $\delta^{18}O=+10$ to produce the variations seen at 450°C, the formation temperature of the veins (fig. 37c). However this would suggest that the greisen muscovites and vein quartz were not formed from the same fluid since the greisen muscovites do not show a large mixing type variation in δD. It is extremely unlikely that the veins and associated greisens could have formed from different fluids and by such different processes. In addition the fluid inclusion studies indicated that mixing between a high temperature, high salinity fluid (i.e. magmatic water) and a low temperature, low salinity fluid (ocean or meteoric water) could not have taken place (see Chapter 5).

Other processes such as boiling and irreversible adiabatic expansion, were shown to be compatible with the fluid inclusion data. Boiling was positively recognised in all the veins. Consider now the effect of boiling on the hydrogen and oxygen isotopic compositions of a fluid. The equilibrium distribution of the isotopes of oxygen and hydrogen between pure steam and water depends on the temperature and are shown in figs. 38 and 39. Thus at all temperatures below the critical point (374°C for pure water) the heavy isotope of oxygen (^{18}O) is concentrated in the liquid. At the critical point there is no fractionation but this parameter increases with decreasing temperature. At temperatures below 221°C deuterium is increasingly concentrated in water with decreasing temperature. However between 221° and 374°C (the critical point) deuterium concentrates in the

vapour phase. These fractionation patterns are for pure water only and there are no data available for hydrothermal brines. However the critical point for water increases rapidly with increasing NaCl concentration (Sourirajan and Kennedy, 1962). At 10 wt.% NaCl, the salinity of the original hydrothermal fluid obtained from fluid inclusion studies, the critical point is at 485°C. At 25 wt. % NaCl this value has risen to 685°C. No data is available for brines of around 40 wt. % NaCl, the approximate upper limit of vein fluid salinities, although it can be safely assumed that the critical point is at even higher temperatures. With such an increase in the critical point with increase of NaCl concentration it is reasonable to suggest that the magnitude and possibly sign of fractionation of hydrogen between water and steam may well be substantially different in hypersaline brines. The sign of fractionation of hydrogen between water and steam is very importance since it should be possible to determine the starting composition of the original fluid and the resultant vapour. Each case will now be considered.

A. <u>Hydrogen fractionation factor is positive at T>221°C</u>.

For the moment we shall assume that the bulk of the hydrothermal fluids were at a temperature of about 450°C (the maximum temperature from the fluid inclusion studies and for reasons mentioned earlier probably the initial temperature of the vein fluids), that deuterium was concentrated into the liquid phase (i.e. $10^3 \ln\alpha$ was positive) and that the initial hydrogen isotopic composition was $\delta D \simeq -40$ (from the measurement of the pegmatitic quartz). As the fluids boiled the residual liquid, in concentrating deuterium, would become heavier i.e. it would move to more positive δD values. Conversely the vapour or steam phase would move to correspondingly lighter (more negative) δD values. However if the fluids boiled sufficiently to produce predominantly vapour then this

vapour would alter very little from the initial δD values, although the relatively small proportion of residual liquid would shift to much more positive δD values (fig. 40a). A good example of this effect has been described by Craig (1963) for nonequilibrium evaporation of steam from some acid geothermal waters.

In the previous chapter a model was proposed which involved the veins acting as channelways for boiling fluids, the resultant vapour penetrating the granite producing kaolinisation. With regard to the oxygen/hydrogen isotopes, the veins, containing the residual liquid and some vapour, would therefore be expected to shift to more positive δD values. The results from nine samples of vein quartz show that this is in fact the case. They all have more positive δD values than the pegmatite, considered to represent Goonbarrow magmatic water. Furthermore the wide range of δD values for inclusions in vein quartz is consistent with variable boiling and throttling proposed in the previous chapter to explain several salient features of the inclusions in the veins.

B. Hydrogen fractionation factor is negative at $T>221^{\circ}C$

Alternatively we can assume that the sign for hydrogen fractionation of hypersaline solutions is negative, i.e. the same as pure water. In this case at temperatures $>221^{\circ}C$ deuterium would concentrate in the vapour phase (i.e. $10^3 \ln\alpha$ is negative). A range in δD would therefore be produced ranging from the initial composition of $\delta D \simeq -40$ down to even more negative values. This is not consistent with the measured δD values of the vein quartz (fig. 40b). However the observed δD variation could be produced as a result of competing mechanisms. If on boiling, vapour only was extracted from the boiling fluids (this would be deuterium rich say $\delta D=0$) and then this vapour condensed, the observed δD variations could be produced since the condensed vapour (i.e. liquid) would be lighter (δD

would be more negative) (fig. 40c).

At this stage either hypothesis could be used to explain the δD variation for vein quartz. As mentioned earlier the veins and associated greisens were almost certainly formed at the same time. However the greisen muscovites and the waters in equilibrium with them, have very restricted δD values. At 450°C they also plot at slightly more positive δD values in comparison to magmatic waters and in particular Goonbarrow magmatic water represented by the single analysis of pegmatite quartz. This indicates that in case A they must have been produced from the liquid at the initial stages of boiling only (fig. 40a). If they were formed throughout the main boiling event (i.e. by throttling and adiabatic expansion) then they would have a similar large range of δD values. In case B they must have been formed from the liquid still but during the last stages of condensation, since if they formed earlier they would have more positive δD values i.e. around $\delta D=0$.

At this point we must consider how the kaolins fit into these theories. In Chapter 5 it was concluded that kaolinisation was produced by vapour penetrating the granite. In case A therefore the water (or condensed vapour) from which the kaolinites formed would plot at δD values slightly less negative than the original composition of the vein fluid i.e. $\delta D = -4$ (see fig. 40a). This depletion in deuterium would only be small if predominantly vapour was produced during boiling (i.e. that boiling was very intense) which appears to be the case from the fluid inclusion study. In case B however the vapour from which the kaolinites were formed would have a composition of around $\delta D=0$ although still of restricted range due to intense boiling.

It can be clearly seen that the line for waters in equilibrium with Cornish and Goonbarrow kaolinites, transgresses the top of Sheppards

cornubian magmatic water field and is also extremely close to the single analysis of inclusion fluid from the pegmatite, considered to represent Goonbarrow magmatic water. Consequently it is considered that case A appears to be the more reasonable assuming that there has been no post depositional isotope exchange (discussed in section 7.3). The $\delta^{18}O$ composition of the vein fluids from which the kaolinite is considered to have been derived is ~10 at 450°C. This $\delta^{18}O$ composition intersects the water in equilibrium with kaolinite-SPS line (see fig. 35) at about 125°C. This suggests that the vapour cooled from 450°C to 125°C as it penetrated the cooler granite - presumably by simple exchange of heat with the environment - kaolinising the granite. It may be noticed that the vapour, derived from the initial starting composition of the fluid of $\delta D = -40$, $\delta^{18}O = +10$, is slightly less negative in δD than the H_2O-kaolinite-SPS equilibrium line. However as mentioned earlier there is a spread around this curve due to the variation in compositions of the kaolinite samples. This could in fact account for an error in the formation temperature of the kaolinite by up to $\pm$ 20°C.

The $\delta^{18}O$ composition of the vein and associated greisen fluids is at the lower end of Sheppards Cornubian magmatic water field. Although Sheppards field is badly defined and no $\delta^{18}O$ data exists for Goonbarrow magmatic water, it appears that the vein fluids may have moved to slightly lower $\delta^{18}O$ values than original Cornubian magmatic water (Messrs R.D. Beckinsale and J. Durham of the Institute of Geological Sciences, London have some preliminary data for magmatic fluids from the Cornish granites of $\delta^{18}O \simeq +12$). This suggests that the vein fluids may in fact be a mixture of magmatic and meteoric fluids. A simple calculation indicates that the vein fluids may consist of only about 10% meteoric water. However this mixing must have taken place completely and before boiling

and subsequent hydrothermal processes in order to produce the extremely tight range in $\delta^{18}O$.

Finally the fine grained muscovites associated with kaolinised granite gave δD values ranging from -55 to -71. Although only three samples have been measured they appear to give a wider range than the greisen muscovites. The waters in equilibrium with these muscovites plot in the region δD = -31 to -47 at 450°C i.e. in an area transgressing the pegmatite quartz value (Goonbarrow magmatic water). If all of these fine grained muscovites crystallised at the same time as the kaolinite, as has been suggested in Chapter 2, then they would be expected to have been derived from the vapour of the boiling fluid i.e. at δD values around and slightly more negative than the initial fluid composition (pegmatite quartz). This appears to be the case although they also plot slightly on the less negative side as well. This may be explained by them being in fact composite samples of degraded igneous muscovite and original fine grained muscovite produced during kaolinisation.

7.5. Suggested model

A graphical explanation of the model is displayed in fig. 41. For the purpose of this model we shall assume that the initial composition of the fluid is δD = -40 (from inclusions in pegmatite quartz) and $\delta^{18}O$ = + 12 (from Sheppards Cornubian magmatic water field). This magmatic fluid mixed with about 10% meteoric water and moved to a composition of about $\delta^{18}O$ = +10, δD = -40. Throttling and adiabatic expansion enabled the ascending fluid to boil and cool. The initial liquid phase altered the wallrock, forming the greisens, and ultimately infilled the channelways producing the quartz/tourmaline $\pm$ cassiterite/wolframite veins.

Deuterium was concentrated into the liquid phase which is reflected in the more positive δD values for the fluid inclusions in the veins and also for the water in equilibrium with the greisen micas. This latter point suggests that the greisens were formed at predominantly 400-450°C which is in good agreement with the fluid inclusion data. Meanwhile the other component of the boiling fluid, the vapour phase, penetrated the granite and kaolinised it. The fluid inclusion data and also examination of the fluid inclusions in petrographic thin sections, suggest that intense (i.e. more vapour than liquid) boiling was involved. In this case the fluid would be expected to produce predominantly vapour during boiling leaving behind only a relatively small proportion of residual liquid. Consequently the oxygen and hydrogen isotopic compositions of the vapour were not far removed from the initial starting composition of the fluid. The vapour probably moved to slightly more negative δD values. This water was in equilibrium with the kaolinites at about 125°C. It appears therefore that the vapour cooled from 450 to 125°C as it penetrated the cooler granite by simple exchange of heat with the environment.

The single analysis of a kaolinite sample from Geevor, quoted by Sheppard, can also be explained in a similar manner. The water in equilibrium with the kaolinite is plotted in fig. 35 This suggests that the primary magmatic water from which it was derived is probably slightly more deuterium rich than at Goonbarrow. Four analyses of greisen micas plot in a wide range at much more positive δD values than Goonbarrow greisen muscovites. Assuming the greisen and therefore the veins were formed at about 300°C (Sawkins, 1966) and that no $\delta^{18}O$ shift resulted when the fluids boiled, this would suggest that the Geevor kaolinite was formed at about 200°C indicating that the temperature

drop suggested at Goonbarrow during kaolinisation is a real effect. Sheppard interpreted the Geevor kaolinite as being of magmatic origin and the other kaolins as being formed by weathering. As can be seen there is no evidence to suggest that the two types of kaolinite were formed in a different manner.

Some of the hypotheses mentioned above may be better tested when the final batch of data is received from Mr. D. Wesolowski. However it has been shown that the data is compatible with a magmatic origin for the formation of the Cornish kaolin deposits.

CHAPTER 8

General Synthesis

CHAPTER 8

General Synthesis

8.1. Introduction

This chapter is divided into three main parts. The first discusses the observations and data of other workers in combination with some of the author's own observations and interpretation. The data presented elsewhere in this thesis will then be summarised in some detail in the second section. The information from these first two sections will then be discussed in relation to some of the geological problems apparent in Cornwall with particular reference to the hydrothermal vs. weathering controversy for the genesis of the Cornish kaolin deposits.

8.2. Discussion of previous work

The main theories for the genesis of the Cornish kaolin deposits were presented chronologically in the introduction to this thesis. The evidence used by previous workers to support each hypothesis is summarised in Table 25 and these points will now be discussed in the light of some new evidence found in the present work.

8.2.1. Evidence for a hydrothermal origin

1. The depth and shape of the deposits. Kaolinised granite is known to exceed 250 m in depth from surface and also to extend below sea level in places (Bristow, 1977). Kaolinised granite has also been found at depths ranging from 100-400 m, associated with tin/tungsten mineralisation and overlain by unkaolinised granite (Dines, 1956, Bristow, 1968a, Sheppard, 1977). The hydrothermal nature of these last examples is not disputed and reasonable inferences have been made suggesting that

Table 25

Summary of evidence presented by previous workers for the formation of Cornish china clay

Evidence for a hydrothermal origin

1. The great depth and funnel-like morphology of the deposits.
2. Unaltered killas and granite overlies intensely kaolinised granite.
3. Association of kaolinised areas with greisen bordered quartz/tourmaline veins.
4. The crystallinity index of kaolinite increases towards major quartz/tourmaline veins.

Evidence for a weathering origin

1. Oxygen/hydrogen isotope studies have been interpreted as indicating a low temperature supergene environment for the formation of kaolinite.
2. Scanning electron microscope studies show open textures for the kaolinite suggesting a low pressure environment.
3. Fluid inclusion studies of vein quartz suggest saline hydrothermal conditions. It is unlikely that kaolinite is stable under these conditions.
4. Kaolinite from a weathering source actually exists in South West England.
5. The areas of kaolinised granite are large compared to the relatively small veins.

other kaolinisation in the area is of a similar origin. The funnel shape of kaolin deposits has also been recorded (Bristow, 1968a, 1977) and is highly suggestive of ascending solutions.

2. The fact that unaltered country rock and granite overlies intensely kaolinised granite. Collins (1909) reported finding unkaolinised killas above kaolinised granite at Carpalla china clay pit. The killas at the boundary has been tourmalinised and consequently hardened. Bristow (1977) suggested that the killas was not kaolinised because it had been previously tourmalinised. However Exley (1955, p.45) pointed out that the tourmalinised killas was kaolinised to some extent near the contact but kaolinisation decreased away from the junction. There is no doubt that the killas can be kaolinised, since a large xenolith of killas that had been thoroughly kaolinised was seen in Melbur pit in 1978 (plate 98). Tourmalinised granite near the northern exposure of the elvan in Imperial Goonbarrow also contains kaolinised feldspars, so there is little doubt that tourmalinised killas and granite are permeable to kaolinising solutions. If the granite in the Carpalla pit was weathered laterally rather than directly from above, then it would be surprising that the killas was not kaolinised although granite on either side was (Collins, 1909, Exley, 1955). Walker (1969) in the discussion to Konta's paper (1969) pointed out that 40 ft of unkaolinised granite was seen overlying 100 ft of kaolinised granite at Gunheath, although it appears to have gone unnoticed that Collins (1909, p.158) had found similar relationships "in St. Stephen's and the neighbouring parishes, and it has been particularly evident at central Treviscoe". Bristow (1977, p.4) has suggested how this type of relationship can be produced by invoking an inclined trough of kaolinised granite. These observations however are highly in favour of a hydrothermal genesis.

3. Association of kaolinised areas with greisen bordered quartz/tourmaline veins. This relationship has already been discussed in Chapter 2. The author can also verify that quartz $\pm$ tourmaline veins are abundant in most of the other pits within the St. Austell granite. Admittedly tourmaline and/or greisen borders are not always associated with the veins, there is no evidence to suggest whether any single type of vein was used as channelways for the kaolinising medium. Bristow (1977, p.7) stated that the clay pits on Bodmin moor were notable for their absence of quartz/tourmaline veins. However at Stannon pit near St. Brewards, one of the largest deposits in the Bodmin granite, a large (20 cms) quartz vein runs directly down the centre of the pit. The Bodmin granite in general contains very few kaolin deposits, certainly few working pits as far as is known, and the absence of veining may well be related to this fact. This may be analogous to the eastern area of the St. Austell granite (biotite-muscovite granite) which is virtually devoid of any significant veining and kaolinised granite occurrences. Bristow (1977, p.7) also mentioned that similar kinds of veins and alteration occur in Cornish mines without significant kaolinisation. On visits to Geevor and South Crofty tin mines in 1978, a very complicated series of veins were seen which in no way resembled those seen in the kaolinised areas of the St. Austell and Bodmin granites. Formation of veins in the Cornubian batholith occurred at different times and their variable mineralogy suggests that several sources of fluid were available. The association between tin/tungsten mineralisation and kaolin deposits is also found in Spain, Portugal, France, Czechoslovakia, Malaysia and Indonesia (Bristow, in press).

4. <u>The crystallinity index of kaolinite increases towards major quartz/tourmaline veins</u>. Exley (1964) determined the crystallinity index of kaolinite for three Cornish china clay areas (St. Austell, Bodmin and Dartmoor). One suite of samples traversed a quartz/tourmaline vein into extremely altered rock and eventually into relatively fresh rock. From X-ray diffractometry the ratio of the intensities of the 3.57 and 4.46 Å peaks were recorded.

"An increase in this ratio together with an increase in the development of the reflections between 2.38 and 2.56Å indicates an increase in the order within the clay lattice". (Exley, 1964).

In each case an increase in order was obtained as the vein was approached which may be taken to indicate that the zones of kaolinisation were connected in some way with the veins.

Conversely in the Karlovy Vary area (Czechoslovakia), Konta (1979) has shown that the crystallinity index of kaolinite decreases with depth providing further evidence of a weathering origin for these deposits. No data is available on the variation of crystallinity index of kaolinite with depth for the Cornish deposits.

8.2.2. Evidence for a weathering origin

1. Oxygen/hydrogen isotope studies indicate a low temperature, weathering origin. Notwithstanding the new data presented for oxygen/hydrogen isotope studies elsewhere in this thesis, Sheppards (1977) data has been shown to be equally compatible with a hydrothermal origin (see Chapter 7) or with a weathering origin.

2. The open textures of kaolinite, from scanning electron microscopy studies, suggest a supergene origin. Kellers (1976a, 1976b, 1978) argument is based on entirely subjective data. He has compared scanning electron micrographs of Cornish kaolins with kaolins produced from certain weathering and hydrothermal environments and concludes that the "texture appears to indicate that the last significant process or stage of kaolinisation in Cornwall and Brittany was supergene weathering". However the hydrothermal kaolins he uses to compare with the Cornish samples are not produced from the same starting material (i.e. granite) - in this case a Rhyo-latitic rock. Micrographs shown in his 1978 paper of Cornish kaolins taken from drill cores in the St. Austell granite area show textures remarkably similar to that of kaolin from Sombrerate, Mexico (his fig. 28, p.11) which is certainly of hydrothermal origin. In the author's opinion the scanning electron micrographs of kaolin from Cornish china clay pits are not significantly different from those of undoubted hydrothermal origin.

Keller (1976a) also raises another interesting point, that during the first stage of hydrothermal alteration "the direction of alteration of feldspars is primarily from the interior of solid grains outward. In contrast during weathering the kaolinisation proceeds inward from the outside of mineral grains". As can be seen in Chapter 2, petrographic

studies have shown that the feldspars in the Cornish china clay area are always altered from their cores outward. This is probably due to the cores being more calcic (and therefore less stable) than the rims (Exley, 1955, 1959). A hot hydrothermal fluid would be expected to fully penetrate feldspar phenocrysts thus preferentially altering the less stable calcium-rich core. This evidence therefore favours hydrothermal alteration.

3. Fluid inclusion studies of vein quartz suggest saline fluids which are incompatible with the stability of kaolinite. As can be seen from Chapter 5, Cornish vein fluids are generally rather saline. It is generally considered that kaolinite is not stable under saline conditions. Sediments laid down in a fluvial (fresh water) environment tend to contain clay mineral assemblages dominated by kaolinite. In marine (saline) sediments (Keller, 1964, Gilkes, 1968), Bristow (1977) inferred that saline hydrothermal solutions would not lead to the formation of kaolinite but some alternative clay mineral. At first sight therefore it appears that the fluid inclusion evidence is not consistent with a hydrothermal origin for the kaolinite. Jackson (unpublished data) is reported (Bristow, 1977) to have found monophase fluid inclusions (therefore $< 70^{\circ}C$) in quartz from veins at Goonbarrow and Bostraze. Bristow (1977) interpreted this data as representing low temperature and probably low salinity fluids of late weathering origin. The author has found no appreciable numbers of monophase fluid inclusions in Goonbarrow vein quartz samples. It is considered that the thinner polished sections used in the present fluid inclusion study are superior to the normal much thicker (1 mm or more) sections used by other workers. It may be possible that the monophase gaseous inclusions present in abundance in Goonbarrow material have been inadvertently mistaken for

low temperature monophase fluid inclusions. However the author is in agreement with the hypothesis that kaolinite is probably not stable under saline conditions and the importance of the present fluid inclusion study will be discussed later.

4. Kaolinite from a weathering source actually exists in S.W. England. (Bristow 1977). Kaolinite from a weathering source is present in S.W. England. Conversely there is little doubt that the kaolinite occurrences in some of the deep mines in Cornwall are of a hydrothermal nature. As pointed out by Bristow (1977) the kaolinites produced from Woolladon (the supergene kaolinite locality described by Bristow (1968b, 1977)) are of the b-axis disordered type and therefore quite different from the well ordered kaolinites of the St. Austell granite. This may therefore suggest that the two kaolinites were formed by different processes. Lateritic weathering of rock usually produces a sequence of zones i.e. a weathering profile. In addition the morphology of this type of process will be blanket like i.e. parallel to the land surface. The Cornish kaolinite deposits are not of this shape and furthermore do not have weathering profiles, "a kaolinised granite is the same at surface as it is 200 m down" (Bristow, 1977). Coon (1911) stated that the whitest, most uniform and productive clays (in fact from the Goonbarrow pit) were from the deeper parts of the pit. The colour and properties of near surface derived clay was much less certain as well as being less productive. (Only 15% of the rock was china clay at near surface compared with 50% at a depth of 270 ft). Several workers, including pit captains, managers and geologists at ECLP have supported this observation. This is clearly not in keeping with a weathering origin. In Brittany lateritic alteration affects all types of rock (Bristow, 1977) and certainly the killas in Cornwall can be thoroughly kaolinised (see earlier). There

is absolutely no reason why the killas should not be kaolinised elsewhere in Cornwall if a purely weathering origin is envisaged. The fact that the killas is only kaolinised when in close contact with granite, as at Melbur and Carpalla, which in turn is only kaolinised in high vein density areas, is very strong evidence that the kaolinising process was in some way connected with ascending, magmatic derived, fluids.

5. Very large areas of kaolinised granite are associated with relatively small veins. It has always been considered surprising, assuming that a hydrothermal origin is accepted, that such small veins are associated with such large zones of kaolinised granite. It may be reasonable to expect the veins to be of much larger dimensions in order to transport the kaolinising fluid. This fact can however be fully explained within the model described in Chapter 5 and to be re-presented shortly.

8.3. Summary of the work presented in this study

This thesis has been primarily concerned with studying a single china clay pit within the St. Austell granite - Goonbarrow. Observations on the geological relationships in the pit are in excellent agreement with the work of Exley (1955, 1959) on the St. Austell granite. The following is a summary of the main points presented in the thesis.

1. The junction between biotite-muscovite and early lithionite granites is exposed at Goonbarrow.

2. The biotite-muscovite granite was intruded first followed by the early lithionite granite since

(a) An asymmetric pegmatite was found at the junction of the two granites. The direction of growth and branching of feldspars shows that it developed on a hanging wall of biotite-muscovite granite and was followed

by crystallisation of lithionite granite.

(b) A lithionite granite sheet intrudes the biotite-muscovite granite.

(c) A xenolith of probable biotite-muscovite granite was found in the lithionite granite.

3. The Goonbarrow pegmatite is joint controlled, asymmetric and has large curved orthoclase crystals in optical continuity indicating that it had crystallised from a moving magma.

4. Elvans in the St. Austell area have been kaolinised and recrystallised indicating that they were intruded during hydrothermal activity and three out of four elvans can be shown from field evidence to have been intruded during major vein formation.

5. Quartz/tourmaline $\pm$ cassiterite/wolframite veins with greisen borders are spatially associated with zones of intensely kaolinised granite unlike multimineral veins (containing quartz, tourmaline, fluorite, topaz, arsenopyrite, apatite, wolframite and lollingite) and barren quartz veins with no greisen borders which were probably the last geological event in Goonbarrow.

6. The biotite-muscovite and early lithionite granites exposed at Goonbarrow gave (cooling) ages statistically indistinguishable from one another at a mean of 275 m.y. The Goonbarrow pegmatite gave an age statistically indistinguishable from the granites.

7. The greisens from quartz/tourmaline $\pm$ cassiterite/wolframite veins are of the same age (260 - 287 m.y.) as the granites and pegmatite.

8. Four elvans from different locations within the St. Austell granite gave the same age within error (264 - 278 m.y.). Since these elvans crosscut major veins and are kaolinised it is considered they were intruded during hydrothermal activity and that the major kaolinising event occurred between 301 m.y. (the Rb-Sr intrusion date of the granite)

and 272 m.y. This interpretation together with the greisen mica dates indicates that mineralisation at Goonbarrow and probably elsewhere in the St. Austell granite, is of Hercynian age. This was further substantiated by reinterpreting previous uranium-lead work in the light of a more modern graphical approach.

9. Fine grained muscovite from the kaolinised PMG, produced predominantly during kaolinisation, gave a slightly lower age (by 7 - 13 m.y.) than the corresponding unkaolinised granite. This variation was also identified for the grouped kaolinised granite data although this was not the case for the corresponding size fractions for the big feldspar granite (biotite-muscovite). This may indicate that kaolinisation occurred soon after the granite micas cooled through their blocking temperatures or is related to grain size effects lowering the mica blocking temperatures. The date on the kaolinised potassium feldspar (a sericite/kaolinite mixture) was also the same as unkaolinised granite within error. These results gave no indication of kaolinisation being any other than Hercynian in age.

10. The fine grained secondary muscovite produced predominantly during intense kaolinisation of the feldspars in the big feldspar granite, had a wider range and lower K_2O values than the secondary muscovites from the corresponding unkaolinised granite. This suggests that the fine grained muscovite from the intensely kaolinised feldspars formed in a chemical environment different from the sericite from unkaolinised granite and makes the argument presented in point 8 above more valid.

11. The Li_2O values for the Goonbarrow granite micas show that they conform to Exley's classification. The high lithia mica present with muscovite in the small feldspar granite (early lithionite) was tentatively identified as zinnwaldite.

12. All veins and greisens were formed from boiling fluids. Boiling inclusions were far more numerous in kaolinised granite than unkaolinised granite.

13. The quartz/tourmaline ± cassiterite and multimineral veins were formed between 200 and 450°C with salinities from 6-42 wt.% NaCl. The wolframite veins as distinct from other veins in the pit were formed within a close temperature range 220-300°C, but still from a wide range in salinity (12-48 wt.% NaCl).

14. Inclusions within the elvan were of secondary origin. The fluids were not boiling, of about 22 wt. % NaCl salinity and were trapped between 360 and 440°C.

15. The evidence of fluid boiling for some veins enabled determination of their formation pressures. For the quartz/tourmaline ± cassiterite and multimineral veins this corresponded to about 450 bars (1.7 km), 80 bars (900 m) for the quartz/wolframite veins (assuming hydrostatic load) and a minimum of 250 bars (950 m) for the elvan.

16. From the pressure-temperature-composition data a model was produced which involved the formation of the quartz/tourmaline ± cassiterite veins at 450°C/450 bars/10 wt. % NaCl salinity (a depth of 1.7 kms assuming lithostatic load). A combination of isobaric and non-isobaric boiling, heat exchange with the environment and irreversible adiabatic expansion, cooled this vein fluid to 200°C and concentrated it up to 40 wt.% salinity. These processes were probably initiated by sudden pressure release and the change from lithostatic load to hydrostatic load (as a result of the veins reaching surface) and by throttling. Boiling and adiabatic irreversible expansion almost certainly caused deposition of cassiterite. The vapour phase produced on boiling was considered to have deeply penetrated the granite and kaolinised it. This vapour would have been

of very low salinity and is in agreement with kaolinite being only stable under non-saline conditions. It also explains the observed association of vapour inclusions with kaolinised granite.

17. The quartz/wolframite veins formed at about 300°C and 80 bars. The small temperature range can be explained by simple isobaric boiling, which would still produce a large salinity range, and probably indicates that throttling in these veins was a rare occurrence. On pressure constraints alone they are considered to have been formed shortly after the elvan at a depth of about 900 m and to have been responsible for kaolinising and recrystallising the elvan.

18. Scanning electron microscopy studies of fluid inclusion daughters indicated the presence of Al, As, Ca, Cu, Fe, Mg, Mn, S and Zn in KCl/NaCl brines. This suggests that As, Cu and Zn were transported as chloride complexes in the presence of sulphur. Conditions must have been unfavourable for deposition of these elements at the present structural level exposed at Goonbarrow. They were probably deposited at a higher structural level but have since been eroded away.

19. The hydrogen/oxygen isotope study indicated a large variation in D for the quartz fluid inclusion waters (δD = -30 to +4‰) but very little variation in $\delta^{18}O$ ($\delta^{18}O$ = +13.2 to +13.9‰). The greisen muscovites were formed from a fluid of very restricted range in δD and $\delta^{18}O$ (δD = -57 to -62‰, $\delta^{18}O$ = +9 to +11‰(assumed)). In the light of this new data coupled with a reinterpretation of previous work, a new model was produced which involved the formation of the vein quartz and greisen muscovites from the liquid phase of a boiling fluid at 450°C. The resultant vapour was considered to have kaolinised the granite and was shown to be in equilibrium with present day kaolinite at 125°C assuming that intense boiling had taken place.

8.4. Further discussion

The sequence of geological events in Cornwall has been generally accepted by previous workers as,

1. Intrusion of granites
2. Intrusion of elvans
3. Vein formation (mineralisation)
4. Kaolinisation

Although the association between veins and kaolinisation has been long recognised, the actual date of kaolinisation in Cornwall has remained unknown. Even the dating of mineralisation in Cornwall has been poorly defined. This thesis has presented data to show that in the St. Austell granite elvans postdated major vein formation and by inference the main kaolinising event. Radiometric age studies on fine grained muscovites produced predominantly during kaolinisation, and shown to have formed under a different chemical environment from the sericite present in unkaolinised granites, gave Hercynian ages. There has been no indication of a more recent age for kaolinisation. The date of mineralisation in at least three areas of the St. Austell granite has been shown to be definitely Hercynian.

The main sequence of events at Goonbarrow is shown in Table 26. It has been shown that the quartz/tourmaline $\pm$ cassiterite and quartz/wolframite veins formed at radically different pressures. It is considered that the pressure reduction was a result of erosion of the land surface. Xenoliths found in the Dartmoor granite have also been found in the Permian St. Cyres beds (Dangerfield and Hawkes, 1969) indicating that the Dartmoor granite had been unroofed by the late Permian. From the present distribution of the big-feldspar roof facies

Table 26

The main sequence of events at Goonbarrow china clay pit

age (m.y.)		
301		Intrusion of St. Austell granite (from Rb/Sr data)
280-290 (1.7 kms)		Probable date of formation of the major quartz/tourmaline ± cassiterite veins and the main kaolinising event (from Pb and U/Pb data)
275	EROSION	Cooling age (250°C) of micas in the St. Austell granite and greisens associated with the quartz/tourmaline ± cassiterite veins (from K/Ar data)
275 (950 m minimum)		Intrusion age of elvans (from Rb/Sr data)
272 (900 m)		Formation of wolframite veins and kaolinisation and recrystallisation of the elvans (from K/Ar data)

Note: Dartmoor granite unroofed by the late Permian and by inference the St. Austell granite.

of the Dartmoor granite, Dangerfield and Hawkes concluded that the granite has been eroded by no more than 50-200 m since initial crystallisation. It may be assumed that the St. Austell granite was unroofed at about the same time. The fluid inclusion evidence suggests that the level of the land surface had been eroded by about 800 m from the time of formation of the quartz/tourmaline ± cassiterite veins to formation of quartz/wolframite veins. The different temperature characteristics also support this fact. The small range in trapping temperatures but large salinity variation for the quartz/wolframite veins are indicative of simple isobaric boiling. These veins almost certainly broke to surface, probably as hot springs as envisaged by Dangerfield and Hawkes (1969), and Hawkes (1974), allowing the formation of quartz under hydrostatic pressure conditions. Irreversible adiabatic expansion, initiated by throttling, was not involved in the formation of these veins since this would produce temperature-pressure characteristics analogous to the quartz/tourmaline ± cassiterite veins - which is not the case. A minimum for intrusion of the elvan of 950 m indicates that it must have preceded the quartz/wolframite veins. The elvan has been recrystallised and kaolinised by some fluid or vapour at around 272 m.y. It is considered that this fluid or vapour was supplied from the formation of the quartz/wolframite veins. This suggests that the quartz/tourmaline veins formed at around 272 m.y. The final 900 m of overlying rock has been eroded since that time during which there was no more vein formation.

8.5. Concluding remarks

The studies presented in this thesis are all the more valuable since a wide variety of geochemical techniques have been applied to a very restricted geographical area. The fluid inclusion and oxygen/

hydrogen studies produced not only working models but were also in good agreement with each other. Kaolinite genesis from the vapour phase of hot boiling fluids intimately associated with greisen bordered quartz/tourmaline veins is favoured. Although the evidence is not unequivocal for either a hydrothermal or weathering origin for the genesis of the Cornish china clay deposits, in the author's opinion the bulk of the evidence points towards a hydrothermal, Hercynian origin. Previous work suggesting a weathering origin has been shown capable of reinterpretation to favour the alternative view.

The conditions and combination of processes needed to produce these economically important deposits have been shown to be extremely complex. Bristow's (1977) remarks could be equally well applied to this study,

"with such a formidable list of pre-requisites for the formation of the Cornwall and Devon china clay deposits it is not surprising that they are unique in the world as far as we know in terms of quantity and quality".

It is hoped also that this thesis has shown the importance of applying a variety of modern geochemical techniques to samples whose spatial relationships, relative sequence and actual age are well defined.

Appendix 1

Separation of micas

After crushing (or in the case of the kaolinised samples - disaggregation in water) the samples were thoroughly sieved to the appropriate size fraction. The kaolinised samples were usually wet sieved in order to remove every trace of kaolinite. Any biotite present in the samples was removed using a Franz isodynamic separator and separated from tourmaline using heavy liquids - Bromoform. About 25 grams of sample were then scattered over a piece of clean A4 paper and this sheet, while held in the hand at an angle of about 30°, gently shaken. Predominantly muscovite was left behind on the paper. This muscovite separate was then purified using heavy liquids - Bromoform diluted with acetone.

Appendix 2

1. Potassium determination for K/Ar age studies

Initially the potassium determinations were carried out at Oxford using atomic absorption spectrophotometry. However after the initial batch of samples which did not produce the degree of reproducibility expected, all potassium analyses were determined using a flame photometric technique at the Institute of Geological Science, Grays Inn Road, London.

(i) Potassium determination using atomic absorption spectrophotometry

About 0.1g of mica was accurately weighed out in a clean platinum dish. 15 ml of 40% HF and 4 ml of $HClO_4$ were added to the dish, using measuring cylinders, and the dishes evaporated to dryness on a sand bath. 4 ml of $HClO_4$ were then added to each dish and these evaporated to dryness again. 1 ml of conc. HCl was then added and each dish warmed gently until the residue had dissolved. The contents of each dish was then transferred to a 50 ml volumetric flask and made up to the mark with deionised water.

A stock strontium solution was then prepared by dissolving about 72g of Strontium Nitrate in 2 litres of deionised water. 1 ml of each rock solution was then taken and placed in a 50 ml volumetric flask along with 5 mls of stock strontium solution. Each flask was made up to the mark with deionised water. (The Autodiluter was used for this procedure, delivering 1.03 mls not 1 ml - calibrated by M. Hepher, Department of Geology & Mineralogy, Oxford).

The standards were prepared by adding 100, 200, 300, 400 and 500 μl of stock 1000 ppm potassium solution (from BDH) into 100 ml flasks, adding 10 mls of stock strontium solution and making up to the mark. A Blank solution was also prepared of 20 mls of stock strontium solution

made up to 200 mls in a volumetric flask.

The diluted solutions were measured on a Perkin Elmer 306 Atomic Absorption Spectrophotometer using an Air/Acetylene flame and direct readout facility in ppm. The following settings were used:-

Wavelength - 766.5 nm	Region - Visible
Operating lamp current - 12 mA	Slit width - 4
Air flow - 55 litres/min	Fuel flow - 32 litres/min
Filter - in	Burner length - 4"

The procedure used was to measure the absorbance from standard 4 (i.e. 4 ppm) and set the direct readout facility to read 4 ppm, each standard in turn was then measured and if not within 2% of what it should be (i.e. 2 ppm standard must be between 1.98 and 2.02 on direct readout - preferably within 1%) then the standard was remade. The rock solutions were measured in groups of two or three, the 4 ppm standard being used to recheck that the machine was stable after each group. After each measurement the machine was reset at zero using the blank solution.

Note:- Strontium is added to each solution, in the same concentration, to prevent ionisation of the potassium (i.e. ore requires potassium atoms to remain in the ground state in the flame), strontium is preferentially ionised.

Platinum dishes were cleaned twice with Industrial Ajax powder, then water, then 50% HCl and finally deionised water before drying in an oven.

(ii) Potassium determination using flame photometry

Crucibles were cleaned in boiling 33% HNO_3 for half an hour, washed in deionised water and then dried over a bunsen flame. About 0.1g of mica was accurately weighed out into each crucible. 6 mls of HF and 5 mls of $HClO_4$ were added using a measuring cylinder. These were then

digested on a hot plate and under IR lamps for about 3 hrs. When the samples were just dry a few mls of deionised water was added to dissolve them and then transferred to 250 ml volumetric flasks and made up to the mark with deionised water. Using an autodiluter 5 mls of sample was added to a test tube containing 5 mls of a 200 ppm Li solution. The flame photometer used this Li as a reference concentration. Meanwhile a 24 ppm K standard was prepared along with a blank solution (both solutions contained 200 ppm Li). After the electronics of the machine (an EEL Model No. 170) had warmed up the flame conditions were optimised to give the maximum output for the internal lithium standard. Potassium was determined using standard flame photometric techniques as described in the EEL instruction manual. Three sample solutions were run in between each standard measurement. Each solution was measured at least twice.

2. <u>Determination of the isotopic composition of argon for K/Ar age studies</u>

Figure A1 shows diagrammatically the high vacuum extraction line at the Institute of Geological Sciences, London. About 0.1g of three samples were weighed into molybdenum crucibles and then these loaded into the sample furnaces. The glass flasks were tightened down onto copper gaskets to prevent leaks (see Plate A1). Valves V1 and V2 were closed and then the sample furnace area pumped down using a rotary pump operating through the hoke valve. When the backing gauge indicated 0.5 torr the hoke valve was closed and V1 opened to enable the diffusion pump to operate, which reduced the pressure even further. (This pump should not be used to evacuate the vacuum system from atmospheric pressures as it would be overloaded and become contaminated).

Valve V2 was now opened. At this point the oven was lowered and the whole vacuum system baked overnight at about 180°C to remove gases clinging to the walls of the vacuum system. The next morning after the oven had been switched off and the electronics warmed up, the vacuum extraction line was checked for leaks. If there were no leaks the "getter" was switched on at 0.95A and outgassed for 10 mins. Meanwhile the spike was equilibrated into the pipette for about 10 mins. The "getter" was now turned down to its absorption temperature at 0.55A. (The getter is used to absorb certain non noble gases which can contaminate the mass spectrometer). V3 was now closed and the leak valve to the mass spectrometer opened, this part of the vacuum line was now evacuated through the ion pump. The titanium was now heated up to red heat by use of an RF coil (see Plate A1) and outgassed. After a few minutes the coil was turned off and the titanium allowed to cool for at least five minutes. The diffusion pump was now isolated by closing valve V1 and the spike allowed to equilibrate into the vacuum line for 2 minutes. The pipette valve was now closed. A sample was now fused by heating to red heat using the RF coil for about five minutes. Near the end of the fusion the cold trap was brought into use by pouring liquid N_2 into the vacuum flask. (This was used to trap easily condensable gases in the vacuum line like H_2O and CO_2). After fusing the sample the titanium furnace was heated up to red heat by the RF coil and then operated at its absorption temperature to absorb H_2. The RF coil was now switched off. When the pressure on the quadrapole gauge was below 10^{-3} torr, the leak valve was closed and valve V3 opened. The gas was allowed to equilibrate for 5 mins. The valve to the ion pump was now closed followed by valve V3 and then the leak valve opened and the gas allowed to equilibrate for at least 10 mins.

The gas was then analysed using an AEI MS10 mass spectrometer (Plate A2), for its Argon 36, 38 and 40 isotopic abundances. The mean of at least six measurements of each isotopic abundance was used to calculate the appropriate ratios needed in the age calculation.

3. Sample potassium-argon age calculation

For sample No. GOO 77/218 WR.

Measured data:	K content	=	3.618%
	sample weight	=	0.50370 grams
	measured 36/38 ratio	=	0.00158
	spike volume	=	8.3797 nl at N.T.P.

I Calculation of K^{40}

(i) Calculate grams of K

K content = 3.618%

sample weight = 0.50370 grams

Amount of K = 0.03618 x 0.50370 = 0.01822 grams

(ii) Calculate moles of K^{40}

$$K^{40} = \frac{(\text{atoms } K^{40}/\text{atoms K})(\text{grams K})}{(\text{grams K/mole K})} = \frac{(1.19 \times 10^{-4})(0.01822)}{(39.10 \text{ grams/mole})}$$

$$= 5.545 \times 10^{-8} \text{ moles}$$

II Calculation of radiogenic Ar^{40}

The contribution to the 38 peak by spike Ar^{38} is equal to:

$$\frac{\frac{36}{38} A - \frac{36}{38} M}{\frac{36}{38} A - \frac{36}{38} S}$$

where A = Atmospheric (known)

M = Mixture (measured on mass. spec.)

S = Spike (previously measured)

$\frac{36}{38} A = 5.35$, $\frac{36}{38} S = 0.000056$

This becomes $\frac{5.35 - 0.00158}{5.34994} = 0.99972$ (1)

The contribution of spike Ar^{36} to the 36 peak is given by:

$$(1) \times \frac{36}{38} S$$

$$= 0.99972 \times 0.000056 = 0.0000559 \quad (2)$$

The contribution of the atmospheric Ar^{36} to the 36 peak is therefore

$$\frac{36}{38} M - (2) = 0.0015802 - 0.0000559 = 0.0015243 \quad (3)$$

The spike component in the 40 peak is given by

$$(1) \times \frac{40}{38} S = 0.99972 \times 0.0003 = 0.0002999 \quad (4)$$

while the atmospheric component in the 40 peak is given by

$$(3) \times \frac{40}{36} A = 0.0015243 \times 296 = 0.45119 \quad (5)$$

$(\frac{40}{36} A = 296)$

The radiogenic Ar^{40} contribution to the peak is given by

$$\frac{40}{38} M - ((4) + (5))$$

$$= 2.89724 - (0.0002999 + 0.45119) = 2.44575 \quad (6)$$

The ratio Ar^{40} rad/Ar^{38} spike is 2.44575/0.99972 = 2.44644

Using the approximate formula:

$$Ar^{40}rad/Ar^{38} \text{ spike} = \frac{40}{38} M - 296(\frac{36}{38} M - \frac{36}{38} S)$$

$$= 2.89724 - 296(0.0015802 - 0.000056)$$

$$= 2.44608$$

Volume of radiogenic Ar^{40} = 2.44575 x 8.3797 nl (where 8.3797 is the spike volume)

= 20.495 nl = 20.495×10^{-9} litres

Now 1 gm mole of gas occupies 22.4 litres at N.T.P.

$$\text{Amount of } Ar^{40} \text{ rad.} = \frac{20.495 \times 10^{-9}}{22.4} = 9.15 \times 10^{-10} \text{moles}$$

III Calculation of age

Using the potassium-argon age equation (from Dalrymple and Lanphere, 1969).

$$t = \frac{1}{\lambda_\varepsilon + \lambda_\beta} \log_e \left[\frac{Ar^{40}_{rad}}{K^{40}} \left(\frac{\lambda_\varepsilon + \lambda_\beta}{\lambda_\varepsilon} \right) + 1 \right]$$

where $\lambda_\beta \left(\lambda^{40} K_{\beta^-} \right) = 4.962 \times 10^{-10}/yr$ (from Steiger and Jager, 1977)

and $\lambda_\varepsilon \left(\lambda(^{40}K_e) + \lambda'(^{40}K_e) \right) = 0.581 \times 10^{-10}/yr$

$$t = \frac{1}{(4.962 + 0.581) \times 10^{-10}} \log_e \left[\frac{(9.15 \times 10^{-10})(4.962 + 0.581}{(5.545 \times 10^{-8})(\quad 0.581} + 1 \right]$$

$$t = 1.8041 \times 10^9 \log_e (1.15743)$$

$$t = 1.8041 \times 10^9 \times 0.14620$$

$$t = 263.8 \times 10^6 \text{ years}$$

Appendix 3

Statistical formulae used in the K/Ar age study

The following formulae were used for determining the standard error on the mean (sem) and standard deviation (s.d.):

$$\text{standard error on the mean} = \sqrt{\frac{\Sigma (x - m)^2}{n(n-1)}}$$

$$\text{standard deviation} = \sqrt{\frac{\Sigma x^2 - \frac{(\Sigma x)^2}{n}}{n-1}}$$

where n = the number of dates obtained

m = the mean of the dates

x = the individual values of each date

For example for BFG muscovite three dates were obtained (see table 9):

257.4, 265.1, 285.2 ; $m = 269.2$, $n = 3$

$$\text{standard error on the mean} = \sqrt{\frac{(269.2-257.4)^2+(269.2-265.1)^2+(269.2-285.2)^2}{3(3-1)}}$$

$$= 8.3$$

$$\text{standard deviation} = \sqrt{\frac{\left[(257.4)^2+(265.1)^2+(285.2)^2\right] - \left[\frac{(257.4+265.1+285.2)^2}{3}\right]}{3-1}}$$

$$= 14.4$$

In order to determine whether groups of ages were different from one another use was made of the student "t" test. (Spiegel, 1969).

The statistic t is given by the formula

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sigma\sqrt{1/N_1 + 1/N_2}} \qquad \text{where} \quad \sigma = \sqrt{\frac{N_1 S_1^2 + N_2 S_2^2}{N_1 + N_2 - 2}}$$

where X_1, X_2 = the means from each age group being compared

N_1, N_2 = the number of ages within each age group

S_1, S_2 = the standard deviations of each age group

For example compare the overall groups of ages for the 40/80 # and 160/240 # kaolinised muscovites (see table 9):

40/80 # muscovites, $X_1 = 280.6$, $N_1 = 8$, $S_1 = 7.5$

160/240# muscovites, $X_2 = 267.6$, $N_2 = 6$, $S_2 = 2.9$

so $$\sigma = \sqrt{\frac{8(7.5)^2 + 6(2.9)^2}{8 + 6 - 2}} = 6.5$$

calculating t

$$t = \frac{280.6 - 267.6}{6.5\sqrt{\frac{1}{8} + \frac{1}{6}}} = 3.703$$

The number of degrees of freedom is given by the equation $N_1 + N_2 - 2$

In this example there are 8 + 6 - 2 = 12 degrees of freedom.

Referring now to a set of t tables, for 12 degrees of freedom at the 0.01 level of significance the critical value is 3.06. The calculated t value of 3.703 exceeds this value therefore these two populations are different at the 0.01 level of significance i.e. there is 99% confidence that the populations are different. Similarly comparing the 40/80# kaolinised muscovites a t value of 1.905 was obtained. For 8 degrees of freedom the critical value was 3.36. Therefore since t = 1.905 is less than 3.36 the two groups are not different at the 0.01 level of significance.

Appendix 4

Techniques used in fluid inclusion studies

1. Preparation of doubly polished thin sections for fluid inclusion studies

Slices amout 4 mm in thickness were cut from the specimen using an ordinary diamond cutting wheel. This usually caused some shattering, false cleavage, and similar artifacts in the crystals adjacent to the cut surfaces and it was necessary gently to grind away ½ mm or more from each surface of the slice in order to avoid this modified zone in the final polished section. This was achieved by grinding the surface to be first polished, usually for about 45 minutes, with 600 grade carborundum on a 'Logitech' LP30 lapping machine. The other surface was also briefly ground at this stage so as to make both surfaces of the slice more or less parallel.

The specimen was cleaned thoroughly with demineralized water in an ultrasonic cleaning bath and dried. It was then warmed and mounted, the thoroughly ground surface uppermost, on a glass slide using 'Lakeside 70' cement.

A batch of up to twenty-four specimens prepared in this way were then polished on 'Vibromet' polishing machines using, successively, 3 μm. 1 μm, and 0.3 μm grades of polishing alumina suspended in ethylene glycol on 'Texmet' oil- and water-resistant lap material. In these machines, the abrasive surface vibrates, with variable frequency, in a short orbital motion, producing satisfactorily relief-free polish without heating and with minimal operator supervision. Polishing times naturally vary according to the materials polished, but generally amount to 3 or 4 hours on each grade of alumina.

When the first surfaces were satisfactorily polished, the sections were again washed and dried, warmed briefly to about 80°C to soften the 'Lakeside' mounting resin, and re-mounted with the newly polished surfaces against the glass slides.

The sections were returned to the 'Logitech' lapping machine and the unpolished faces ground away to the final desired thickness (usually 60 μm).

After thorough cleaning and drying, the sections were returned to the 'Vibromet' laps and the second surface polished as before.

For the final microthermometric examination the slides were immersed in absolute alcohol for 1-3 days to dissolve the mounting resin, and the delicate doubly-polished sections cut up to provide small chips suitable for placing in the heating and freezing stage of the microscope.

Materials such as kaolinised granite and small quartz-tourmaline veins needed thorough impregnation with epoxy resin before grinding and polishing. In order to achieve adequate penetration of the resin, this was best done under vasuum using Araldite epoxy resin AY103 and hardener HY951 in the proportion 10 : 1. In the latter stages of preparing these sections an improved impregnating technique was used which involved diluting the epoxy resin with an equal quantity of isobutyl ketone prior to adding the hardener. Although the resin took longer to harden superior impregnation was obtained due to the resin being much less viscous.

2. Description of the Chaix-Meca heating/freezing stage

The design of the stage has been described by Poty et al., (1976). The stage consisted of a metal sample chamber into which had been built the condenser lenses, electrical heating coil, cooling tubes and

thermocouple (fig. A2). The sample was placed on top of the condenser lens L2 and covered during heating by a 0.2 mm thick silica disc. This enabled rapid equilibrium to be obtained within the sample chamber and enabled the lateral temperature gradient to be kept to a minimum, usually less than 1°C (Poty et al., 1976). In order to obtain freezing temperatures the stage was cooled using oxygen free nitrogen passed through a vacuum flask containing liquid nitrogen. Water vapour in the atmosphere was found to condense on both the sample and the bottom infra red filter F. A nylon collar fitting tightly over the objective lens and simply lying on top of the sample chamber was found to eliminate the first problem entirely. Removal of the silica glass disc was found to improve observation considerably during freezing determinations. The second source of condensed and frozen water vapour, on the bottom filter, which made freezing determinations impossible was eliminated by manufacturing a tube which replaced the filter F and ring holding lens L1 (see fig. A2). The latter was secured in a nylon holder by an "O" ring and the holder attached to the tube by a screw thread (see fig. A3). This addition had three main advantages in reducing condensation and subsequent freezing of atmospheric water vapour. 1. It removed the presence of the gap between the filter and condenser lens L1 where most of the condensation took place. 2. The nylon filter holder did not conduct heat as well as the metal sample chamber which enabled the filter to be at a higher temperature than the sample chamber. 3. Any frost which might build up on the bottom filter was much easier to remove by wiping with a tissue or even evaporated using a small hair dryer.

The stage is connected to a central console unit which enabled the heating rate to be varied by a variac and cooling rate by means of an adjustable valve which varied the flow of nitrogen gas. The thermocouple

embedded within the stage measured temperature and gave this as a direct reading by means of a digital readout. The equipment was also fitted with several novel design features. The first was an additional control whereby a temperature could be automatically increased to a present value, the appropriate heating or cooling rate previously having been selected. An additional feature of the apparatus was a memory control whereby a temperature could be recorded by means of a small hand control, while the operator was still observing the sample down the microscope.

The stage and associated console unit were connected to a Leitz Ortholux microscope. No condenser stage was required since the stage had this feature specially built into it. 25x eyepieces were used in conjunction with two long working length Leitz UMK series objectives - 32x and 50x. These objectives were designed for use with a universal stage but since they were used in this study without the appropriate hemispheres their effective magnification was reduced to x20 and x32 respectively (Roedder, 1972, p.84, T.J. Shepherd, 1979, Pers. Comm.).

The small doubly polished sections of rock were secured to the glass slide during polishing by "Lakeside" setting cement. In order to remove the sections from the slides for examination on the heating/freezing stage, the complete slides were immersed for one to three days in absolute alcohol in a covered petri dish. On occasions the sections needed some slight persuasion with a metal seeker to separate them from the glass slides. Small portions of these polished sections were transferred to the stage by means of vacuum tweezers.

The determination of freezing temperatures was always carried out first since some of the lower temperature inclusions in any one sample would tend to burst (decrepitate) on heating above their homogenisation

temperature. When practicable freezing and filling temperatures were determined on the same inclusion. The inclusions usually had to be cooled to -60 to -70°C in order to freeze the inclusion fluid. When measuring any phase transition temperature it is particularly important to use as low a heating rate as possible to allow the sample to thermally equilibrate. High heating rates will tend to give higher values for a phase transition temp. (see calibration procedure). The samples were allowed to warm up at about 0.5°C per minute although slightly higher heating rates were used to raise the temperature to within a few degrees of the melting temperature. On many occasions it proved difficult to observe the final melting temperature because either the inclusions were too small or the ice crystals were not visible. In these cases the inclusions were brought to as near to the final melting temperature as was possible and then they were refrozen to around -20 to -25°C. This often resulted in either the vapour bubble becoming deformed or growth of a single crystal of ice. It proved much easier to observe the final melting temperature by the bubble returning to its original shape and position or the disappearance of a single ice crystal.

Determination of filling temperatures were also measured at a heating rate of about 0.5°C/min. with similar higher heating rates being used to raise the inclusions to within five degrees or so of the filling temperature. Filling temperatures were normally fairly easy to observe since the vapour bubble would progress into more violent brownian motion as the end point was approached. Prior to freezing or heating an area of inclusions would be selected and a random number chosen for observation these being recorded as a pen sketch along with any other comments. Only these inclusions, which enabled some form of random sampling technique to be realised, were measured.

3. Calibration of stage

Since the temperature recorded on the digital voltmeter was only approximate the stage was carefully calibrated before proceeding with the temperature determinations.

(i) Choice of Standards

In the past phase transitions such as sublimation, boiling or melting of standard compounds have been used as calibration points. They include:-

Melting point of Toluene	-95° (Jehl, 1975)
-- " -- n-Hexane	-94.3° (Jehl, 1975)
-- " -- n-Heptane	-90° (Jehl, 1975)
Sublimation point of CO_2 at 1 atmosphere	-78.5° (Roedder, 1962)
Melting point of chloroform	-63.5° (Jehl, 1975)
Triple point of CO_2	-56.6° (Jehl, 1975)
Melting point of n-octone	-56.5° (Jehl, 1975)
-- " -- chlorobenzene	-45° (Jehl, 1975)
-- " -- mercury	-38.8° (Rollet, 1959)
-- " -- n-decane	-29.7° (Jehl, 1975)
-- " -- o-xylene	-25.16° (Roedder, 1962)
-- " -- carbon tetrachloride	-22.8° (Jehl. 1975)
-- " -- n-dodecane	-9.6° (Roedder, 1962)
-- " -- pure water	0.0° (Jehl, 1975)
-- " -- Benzene	5.2° (Jehl, 1975)
Boiling point of water at 1 atmosphere	100.0° (Jehl, 1975)
-- " -- Aniline -- " --	184.51° (Larson et al, 1973)
Melting point of Sodium Nitrate	306.8° (Jehl, 1975)
-- " -- Lead	327.4° (Ohmoto, 1969)

Boiling point of Mercury	356.66° (Rollet, 1959)
Melting point of Potassium dichromate	398° (Jehl, 1975)
-- " -- Iron	449.5° (Roedder, 1971)
-- " -- Barium Nitrate	592° (Rankin, 1976, pers. comm.)
-- " -- Anitomy	630.5° (Roedder, 1971)
"Signotherm" standards	40°-247° (Jehl, 1975)
"Tempil" powders	(Kelly & Turneaure, 1970)

"Signotherm" standards are marketed by Merck Co. (E. Merck - 461 - Darmstadt - W. Germany). Apparently they are mixtures of pure inorganic compounds of known composition. No further details are known on "Tempil" powders.

Of these it was decided to use similar standards to those used by Vincent Jehl since he had been responsible for calibrating a similar stage at C.R.P.G., Nancy, France. The calibration standards used were:- Toluene; Triple point of CO_2 from a series of very pure CO_2 inclusions from Calanda, Switzerland; Carbon Tetrachloride; Demineralised water; Signotherm standards SK70; SK100; SK135; SK180; SK200; SK247; Sodium nitrate and potassium dichromate. Unfortunately as yet no suitable calibration standard has yet been found for temperatures above 400°C. A. Rankin (Imperial College, personal communication) has suggested Barium Nitrate but according to V. Jehl's Ph.D. Thesis, this melts incongruently and so has not been used.

(ii) Experimental Procedure

The technique used by Roedder (1971) and most other workers to measure these phase transitions is to place a small quantity of the appropriate substance in a small capillary tube (0.5 mm O.D.), evacuate,

and then seal with an oxy-hydrogen microflame. These tubes are particularly useful as not only do they give a calibration point but also some idea of the thermal gradient vertically and horizontally across the stage due to sublimation of the compound. However Roedder (1971) found that the original crystal (on the bottom of the tube) melted at a temperature sometimes 25° above that at which the sublimed crystals on the upper wall melt (just 0.3 mm above). Consequently he quoted his results accurate to only ± 25°C.

It was therefore decided to adopt the technique used by the C.R.P.G. at Nancy, described in V. Jehl's Ph.D. Thesis. In this technique the standard substance is placed between two 0.17 mm cover slips and this then layed carefully on the stage. The powder used must be reasonably finely ground and it is important to try and use a thin layer of powder, since thicker layers tend to give higher temperatures by sometimes as much as 2°.

When measuring the phase transition temperature it is particularly important to use as low a heating rate as possible to allow the sample to thermally equilibrate. High heating rates will tend to give higher values for the phase transition temperatures and so a short series of experiments was undertaken to investigate the effect of heating rate on, in this case, the melting points of the standard substances. The results are presented in tables A1 to A8 and in figures A4 to A11. Generally speaking there tends to be a linear correlation between heating rate and melting point except for potassium dichromate. On heating potassium dichromate decomposes:-

$$2Kr_2Cr_2O_7 \rightleftharpoons 2Cr_2O_3 + 2K_2O + 3O_2$$

As the heating rate increases the melting point decreases due to contamination with Cr_2O_3 and K_2O. The evolution of some gas is also observed, presumably oxygen.

An important point must be considered here, what exactly is the melting point? It could be taken as the first point at which the compound begins to melt, although in practice this is very difficult to observe, or conversely as the point at which the last crystal melts, which is relatively easy to observe. In this calibration the mid point between the two is taken as the melting point and the accuracy quoted as the difference between this mid point and either the initial or final melting temperatures.

From the heating rate/melting point data it was decided to run all the calibration points at a heating rate of about 0.5°/min although much higher heating rates were used to raise the temperature to within 10° of the melting point. This was a compromise between very accurate results and the time factor. If fluid inclusion samples were run at a similar heating rate, then they should be consistent with the calibration curve. About five or six points were measured for each standard and both initial melting (when observed) and final melting temperatures were recorded. Crossed nicols were sometimes found to be of assistance when observing these phenomena.

A complete series of calibration points were obtained during May 1976 and five of these points were remeasured in May 1978. These results are shown in Table A9 . The temperature ranges may be attributed to several factors such as different heats of fusion, small thermal gradients within the sample, heat of crystallisation of the sample and moisture (Hollister & Burruss, 1976). On arrival all the standard compounds were stored in a vacuum desicator so this last factor was kept to a minimum. The

final calibration line is shown in fig. A12 and compares favourably with those obtained on other Chaixmeca stages (Jehl, 1975, Hollister & Burruss, 1976). Standard SK247 always produced anomalous readings and so, on comparison with other calibration curves, it was decided to ignore it during construction of the final line. The accuracy of readings up to 100°C is better than ± 1°C and for higher temperatures ± 3°C. Reproducibility for the freezing work was within 0.2°C and for the heating work between 0.1° and 0 .7°C depending on the standard.

Another interesting point is that when approaching the final melting point of the standard compound, the heating rate would decrease slightly and then rise again after this point had been attained. This is probably due to the heat of fusion of the substance, it absorbing the heat from the heating coil and using this energy to go through the process of actually melting.

TABLE A1. SIGNOTHERM SK 70

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
1.6	0.16	68.3
1.7	0.56	68.3
1.8	1.16	68.5
1.9	1.45	68.5
2.0	2.07	68.7

TABLE A2. SIGNOTHERM SK 100

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
2.15	0.06	99.0
2.2	0.58	99.4
2.25	0.99	99.5
2.25	1.03	99.7
2.3	1.00	99.7
2.4	1.70	99.5

Note: New sample used for each determination

TABLE A3. SIGNOTHERM SK 135

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
2.7	0.225	134.9
2.7	0.28	134.9
2.8	0.88	135.1
2.9	1.77	135.2
3.0	2.67	135.3

TABLE A4. SIGNOTHERM SK 180

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
3.3	0.28	179.9
3.4	0.96	180.4
3.4	1.12	180.4
3.5	1.47	180.7
3.6	2.40	180.7

TABLE A5. SIGNOTHERM SK 200

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
0.55	0.46	201.5
3.6	1.15	201.8
3.65	1.47	201.9
3.7	1.56	202.0

TABLE A6. SIGNOTHERM SK 247

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
4.1	0.40	247.5
4.1	0.50	247.2
4.15	0.89	248.4
4.2	0.93	248.4
4.3	1.70	250.0

TABLE A7. **SODIUM NITRATE**

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
4.9	0.67	308.6
5.0	1.20	308.8
5.0	1.87	309.2
5.0	1.97	309.0
5.1	2.50	309.3
5.1	2.60	308.9
5.1	2.67	309.5
5.1	2.80	309.8

TABLE A8. **POTASSIUM DICHROMATE**

Variac Setting	Heating Rate (°/min)	Final Melting Temperature (°C)
6.05	0.10	400.9
6.1	0.10	401.3
6.1	0.50	400.1
6.1	0.80	399.4
6.05	0.90	399.9
6.1	0.90	398.6
6.1	1.07	398.7

Note: Black "Specks" often observed, probably Cr_2O_3. Each sample was premelted at about 402°C and final melting point observed using crossed nicols.

TABLE A9. FINAL CALIBRATION DATA

Standard	Initial Melting Temperature (°C)	Final Melting Temperatures (°C)	Mean Initial Melting Temperature (°C)	Mean Final Melting Temperature (°C)
(i) Determinations made by May 1976				
Toluene	within 0.3° of FMT.	-94.1, -93.9, -94.2, -94.0, -94.2	-93.80	-94.08
Triple point CO	within 0.1° of FMT.	-56.3, -56.4, -56.3, 56.3, -56.3	-56.2	-56.3
Carbon Tetrachloride	within 0.2° of FMT.	-22.6, -22.6, -22.5, -22.6, -22.7	-22.4	-22.6
Water	-0.2,-0.2,-0.2,-0.3, -0.4	0.8, 0.8, 0.7, 0.8, 0.6	-0.25	0.74
SK 70	67.6, 67.6, 67.8,67.4	68.5, 68.5, 68.5, 68.5, 68.4	67.6	68.48
SK 100	95.5, 96.0, 95.5	98.0, 98.0, 98.3, 98.4	95.3	98.18
SK 135	134.4, 134.3, 134.2, 134.3, 134.3	134.9, 134.8, 134.7, 134.8, 134.6, 134.6, 134.6	134.3	134.71
SK 180	178.9, 179.0, 179.3, 179.3, 178.9, 178.8	179.8, 179.8, 179.8, 179.9, 179.9, 179.8.	179.0	179.83
SK 200	199.8, 200.6, 200.8, 200.6, 200.3	201.7, 201.7, 201.6, 201.5	200.4	201.6
SK 247	245.3, 244.6, 245.2, 244.4, 244.9	247.2, 247.2, 247.5, 247.1, 246.8, 247.1, 247.4	244.8	247.19
Sodium Nitrate	308.1, 308.7, 308.7	310.0, 309.8, 309.9, 309.8, 309.8, 309.8	308.5	309.85
Potassium Dichromate	401.0, 400.2, 399.6	404.5, 404.0, 404.7, 403.5, 404.3	400.3	404.2
(ii) Determinations made by May 1978				
Carbon Tetrachloride	within 0.2° of FMT.	-23.3, -23.4, -23.6, - 23.5	-23.3	-23.5
SK 70	69.2, 69.1, 67.6, 68.6	69.8, 69.6, 69.5, 68.9	68.6	69.5
SK 135	134.2, 132.3, 131.5	135.9, 135.8, 135.7, 135.9	132.7	135.8
SK 200	196.5, 196.9, 198.7, 196.2	203.4, 203.3, 203.3, 203.0, 203.3	197.1	203.3
Sodium Nitrate	309.2, 308.9, 309.0, 310.6, 309.3	312.7, 312.3, 312.4, 312.3, 312.2, 312.2	309.4	312.4

Appendix 5

Fluid inclusion Heating/freezing results

The following tables list the results used to construct the histograms shown in figures 22 and 23. They have all been corrected using the calibration curve shown in Appendix 4. Each line refers to data obtained on an individual inclusion. Where temperature and salinity data was available on the same inclusion this was used to construct fig. 24.

Key to tables

For explanation of the following terms see sections 5.4.1. and 5.4.2.

Tf = filling temperature

Tm = freezing temperature

Ts = halite dissolution temperature

Salinity expressed as wt.% NaCl

10 Vein Quartz/tourmaline vein

Tf	Tm	Ts	Salinity	Tf	Tm	Ts	Salinity
317				292			
332				315			
	-21		23.25	265			
	-21		23.25	274			
	-21		23.25	384			
	-18.8		21.7	352			
	-17.2		20.6	440			
	-17		20.4	351			
243				370			
264				426			
234				386			
277				234			
254				401			
234				426			
330				279			
324							

12 vein Quartz/tourmaline vein

262				333			
339				294			
379				322			
364				348			
353				352			
291				348			
364				366			
367				344			
355				338			
348				151			
365				151			
381				316			
362				234			
366				319			
361				332			
372				340			
366				331			
367				336			
398				358			
372				324			
364					-7.0		10.6
407					-7.7		11.4
400					-10		14.1
363		513	58		-5.5		8.6
352		341.5	41		-5.6		8.7

12 vein cont'd

Tf	Tm	Ts	Salinity	Tf	Tm	Ts	Salinity
	-5.6		8.7		-7.3		10.9
	-8.5		12.3		-8.7		12.6
	-6.5		9.9		-6 7		10.2
	-7.4		11.1		-6.6		10.1
	-7.1		10.7		-10.6		14.7
	-7.2		10.8		-8.0		11.8
	-7.2		10.8		-7.4		11.1
	-7.2		10.8		-8.8		12.7
12 greisen	Quartz/tourmaline vein						
	-18				-14.4		
	-19				-19.2		
	-22				-19.2		
	-22			198		290	37
	-8.8			136		310	39
	-9.0					288	37
	-9.2			161		273	36
	-8.0			197		271	36
	-12.0			229			
	-11.5			331			
	-11.0			1.57		299	37
	-11.0			1.70		377	45
	-14.0			3.51			
	-15.9			147			
	-14.5			217			
24 vein	Cassiterite vein						
	-14.6		18.45		12.8		16.8
26 vein	Multimineral vein						
	-11.5		15.6	296	-17.0		20.4
	-12.5		16.6	369	-9.3		13.3
	-13.5		17.45	355	-12.3		16.4
	-13.0		17.05		-6.3		9.6
	-12.5		16.6		-9.3		13.3
	-10.5		14.6	356	-5.0		7.9
	-8.2		12.05		14.1		18.05
	-11.7		15.8	340			
	-12.9		16.9	318			
	-12.9		16.9	323			
	-16.3		19.8	308			
	-11.0		15.1	326			
	-11.0		15.1	374			
	-14.2		18.2	245		170	31

26 vein cont'd

Tf	Tm	Ts	Salinity
248		182	32
396			
286			
242			
223		280	37
196			
180		317	39
216		224	33
		325	40
268			
299			
233		209	33
328			
328			

82 vein Quartz/tourmaline vein

313	-6.5		9.9
231	-8.2		12.05
361			
341			
341			
347	-9.1		13.05
286	-19.8		22.4
281			
371			
310	-15.1		18.9
270			
308			
130		174	31
128			
125			
208		266	268
218		261	263.4
376	-10.8		14.9
376	-10.8		14.9
375			
375			
389			
344			
305			
365			
305			
267	-16.7		20.2

Tf	Tm	Ts	Salinity
149			
237			
384			
336			
269			
388			
220			
305			
367			
385			
317			
259			
345			
434*			
267			
354	-20.2		22.7
284			
237			
360		267	36
395		286	37
273			
307	-22.5		24.3
374			
308	-13.2		17.2
202		428	4.9
294	-13.9		17.8
304			
	-23.0		24.65
	-23.0		24.65
	-23.0		24.65
210			
225			
239			
234	-6.1		9.3
313			
237			
283			
236			
343	-7.4		11.05
238	-10.6		14.7
247	-23.5		25.0

*boiling inclusion

82 vein cont'd

Tf	Tm	Ts	Salinity
310	-12.0		16.1
	-10.9		15.05
	-7.0		10.6
	-6.7		10.2

97 vein Quartz/tourmaline vein

	-11.5		15.6
408	-13.2		
385	-16.8		
260	-17.3		
180			
	-15.9		
	-10.3		
	-12.0		
211		213	33
227			
186		205	32
208			
209		219	33
219		219	33
199		315	39

110 vein Cassiterite vein

393	-15		18.8
426	-15		18.8
338	-19		21.8
405	-18		21.1
313	-18		21.1
451	-18		21.1
307	-18		21.1
372	-18		21.1
346	-18		21.1
278	-18		21.1
283			
313			
417			
396	-18		21.1
309			

Tf	Tm	Ts	Salinity
	-7.4		11.05
	-7.4		11.05
	-15.0		18.8
	-5.8		8.89
235		234	34
235		277	36
335			
336	-23.5		25.0
289	-23.5		25.0
448	-25.5		25.0
274			
268			
439			
281	-9.6		13.6
275	-11.5		15.6
278	-9.5		13.55
341	-8.4		12.3
370	-13.0		17.05
376			
154			
253		220	33
252		210	33
258		215	33
254		180	31
202			
398			
339			
422			
296			
310			
390			
324			
269			

110 greisen	Cassiterite vein						
Tf	Tm	Ts	Salinity	Tf	Tm	Ts	Salinity
402	-9.9		13.9	450			
243				390			
321	-8.2		11.95	224		297	37
141				274		200	32
141						300	37
141	-1.6		2.7	235			
170				267		260	33
131	-23.0		24.65	216			
254	-23.0		24.65	216			
463				216		292	37
463				395			
266				395			
297	-18.6		21.6	455			
248	-15.1		18.9	287			
307	-18.5		21.45	199		209	33
327	-18.9		21.8				
131B vein	Cassiterite vein						
	-12.3		16.4	239		283	36
	-11.5		15.6	240		283	36
	-9.3		13.3	223		229	34
	-7.4		11.05	255			
	-7.5		11.2	261			
	-10.0		14.05	400			
	-7.2		10.8	403			
	-8.2		12.05	285			
	-21.5		23.6	373			
	-6.1		9.3	243		201	32
	-12.8		16.8	282			
	-8.9		12.8	286			
	-12		16.1	396			
	-10.5		14.6	239			
	-17.8		20.95	425			
	-13.5		17.5	498	-15.8		19.4
	-13.9		17.9	385		351	42
	-22		23.95	425			
	-23.1		24.7	498	-17.1		20.4
	-7.0		10.6	464	-17.2		20.6
304				197		270	36
216	-11.0		15.1	136			
392	-12.5		16.6	183		288	37
402	-12.0		16.1	233		177	31
417				252			
288				276			
374				376			
360				220			
385				302			
234							

133 vein Multimineral vein

Tf	Tm	Ts	Salinity
353			
344	-18.0		21.1
294			
354			
290	-11.7		15.8
	-12.9		16.9
309			
322			
351	-11.2		15.3
268			
280			

143 vein Wolframite vein

238		209	33
		131	29
225			
273			
278			
294			
216		(i)253(KCl?) 35) both for	
		(ii)365(NaCl?)43) NaCl	
287			
244			
258			
266			
256			
254			
266			
229		268	36
281		112	27
279		377	45
239			
234			
296			

187 Unkaolinised granite

404	-6		9.2
365			
337			
406	-6		9.2
332			
278			
263			
388			
404			
321	-5.2		8.2
368			
332			
375	-12.3		16.4
259			

Tf	Tm	Ts	Salinity
341			
	-10.5		14.6
276			
383			
378			
289			
370			
352			
176		440	50
192		470	53
345			
345			
229	-15.2		18.95
381	-10.8		14.9
194	-16.5		20.05
268	-23.4		24.9
248			
248			
	-15		18.7
275	-8.3		12.1
189	-15		18.8
273	-21.9		23.9
293	-21.5		23.6
252	-24.0		25.35
253			
159		166	31
283	-21.9		23.9
235		161	30
395			
283	-21.5		23.6
375			
375			
376			
375			
375			
340	-11.1		15.2
353			
385			
361			
321			
351			
357			
354			

206 Elvan

Tf	Tm	Ts	Salinity	Tf	Tm	Ts	Salinity
375				478			
394				474			
414				424	-19		21.8
395				476			
409	-19.9		22.45	424	-19		21.8

243 Kaolinised granite

155	-1.3		2.2	436			
239	-4.5		7.2	392			
242				443			
246				375			
267				399			
265				388	-11.4		15.5
246				351			
258	-4.6		7.3	443			
336				388			
242				384			
312				305			
229	-4		6.4	384			
285		197.4	32	387			
443		239.3	34	386			
229	-0.4		0.7	372			
	-18		21.0	443			

GB2 vein Wolframite vein

224	395	747	234			
244	395	747	234		389	46
265	367	38	224		303	37
221			261			
246	372	44	277		268	36
234	337	41	265		278	36
	175	3[illegible]	237		268	36
	246	35	283			
224	284	36	272		281	36
256	351	42	268		285	36
195	219	33	328		358	42

GB2 greisen Wolframite vein

229		325	39	443			
243		313	39	320	-12.8		16.8
160				417			
145		174	31	180	-18		21.1
385						178	31
290				251			
191				279		406	47
253		151	30	246			
163		222	33	236			
178	-11.7		15.8	311	-17		20.4
422				312		204	32
410				354			

Appendix 6

Calculation of the δD and $\delta^{18}O$ values for waters in equilibrium with various minerals

1. Calculation of the $\delta^{18}O$ value for the water in equilibrium with vein quartz at 450°C

From fig. 35 $\delta^{18}O$ vein quartz = + 13.6 ‰

Using curve A of Friedman and O'Neil (1977) for the fractionation of oxygen between quartz-water at 450°C, $1000 \ln\alpha = + 3.6$

$$\ln \alpha = \frac{3.6}{1000}, \quad \alpha = 1.0036$$

From Taylor (1974, p.844)

$$\ln \alpha_{AB} = \ln \frac{1 + \frac{\delta_A}{1000}}{1 + \frac{\delta B}{1000}}$$

In this case A = Quartz, B = water

$$1.0036 = \frac{1 + \frac{13.6}{1000}}{1 + \frac{\delta H_2O}{1000}}$$

$$\delta_{H_2O} = \left(1 - 1.0036 + \frac{13.6}{1000}\right)\left(\frac{1000}{1.0036}\right) = 9.96$$

The $\delta^{18}O$ value for the water in equilibrium with vein quartz at 450°C is therefore 9.96

2. Calculation for the δD value for the water in equilibrium with greisen muscovite at 450°C.

From fig. 35 δD greisen muscovite = -59‰

Using the muscovite-water fractionation curve of Friedman and O'Neil (1977) defined by the equation $10^3 \ln \alpha = 22.1 \ (10^6 \ T^{-2}) - 19.1$ where T = temperature in °K.

At 450°C $1000 \ln\alpha = -23.1$, $\alpha = 0.9769$

from Taylor (1974, p.844)

$$\ln \alpha_{AB} = \ln \frac{1 + \frac{\delta A}{1000}}{1 + \frac{\delta B}{1000}}$$

where A = muscovite, B = water;

$$0.9769 = \frac{1 + \frac{-59}{1000}}{1 + \frac{\delta H_2O}{1000}}$$

$$\delta H_2O = \left(1 - 0.9769 - \frac{59}{1000}\right)\left(\frac{1000}{0.9769}\right) = -36.7$$

The δD value for the water in equilibrium with greisen muscovite at 450°C is therefore -36.7

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