

The ~~geochemistry of the~~ baryte deposits
of central and southern Scotland

by

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Abstract.

The various occurrences of baryte in the project area have been studied and, mainly with respect to their mineralogical assemblages, are subdivided into three 'types'. It was found that these types could be correlated in general terms with the lithologies of the surrounding country rocks. Geochemical investigation of the baryte, and associated sulphides, was carried out in order to determine whether the chemistry of these minerals reflected a similar grouping to that of the mineralogies, or indeed if any systematic variation existed between individual deposits. Neither presupposition was found to be the case.

A mechanism of emplacement for the type of veining observed is advocated, and an explanation, in terms of geological structure, for the location of the veins, postulated. The age at which the mineralisation took place is discussed, and in the light of new potassium-argon isotopic data the Permo-Trias is submitted to be an important episode, along with the Permo-Carboniferous.

A study of the fluid inclusions present in baryte is made with respect to temperature of homogenisation, salinity and alkali ratios of their fluid leachates. This is then used, along with the aforementioned mineralogical data, and the geochemical and mineralogical data from the wall rocks, to place limits on the physico-chemical

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conditions prevailing during the deposition of the veins.

An attempt is then made to reconcile all the data obtained, with a single hypothesis of origin for the deposits. The process suggested is an isothermal one, where precipitation of baryte occurred when oxidising groundwaters mixed with a fluid containing barium and sulphide ions, which had been drawn into established fault zones during seismic activity.

Finally, a mineralogical and fluid inclusion study of a calcite-baryte sample from Muirshiel, using scanning electron microscopy and an energy dispersive analysis technique, is presented.

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Chapter 1 : Introduction

Chapter 1. Introduction.

The deposits of baryte in central and southern Scotland forming the basis of this project are shown in Fig.1. In addition, other deposits lying outside the specific area were sampled for purposes of comparison, and are labelled in parentheses.

In general terms the initial aim for the project was to study this mineral province as a whole, and the veins individually, from geological and geochemical stand-points. Then an assessment could be made of any common factors or systematic differences which could provide evidence with which to qualify the generally held, broad hypothesis of low-temperature hydrothermal origin.

The veins are always intimately associated with faulting but occur in rocks of differing ages and lithologies. Hence, in order to comprehend the mechanisms of the mineralisation process, and also be able to establish when the mineralisation took place, the general geological history of the area must first be considered.

Geological evolution of the area.

The area of central and southern Scotland encompasses the Midland Valley and Southern Uplands. The Southern Upland fault forms the common boundary
....between

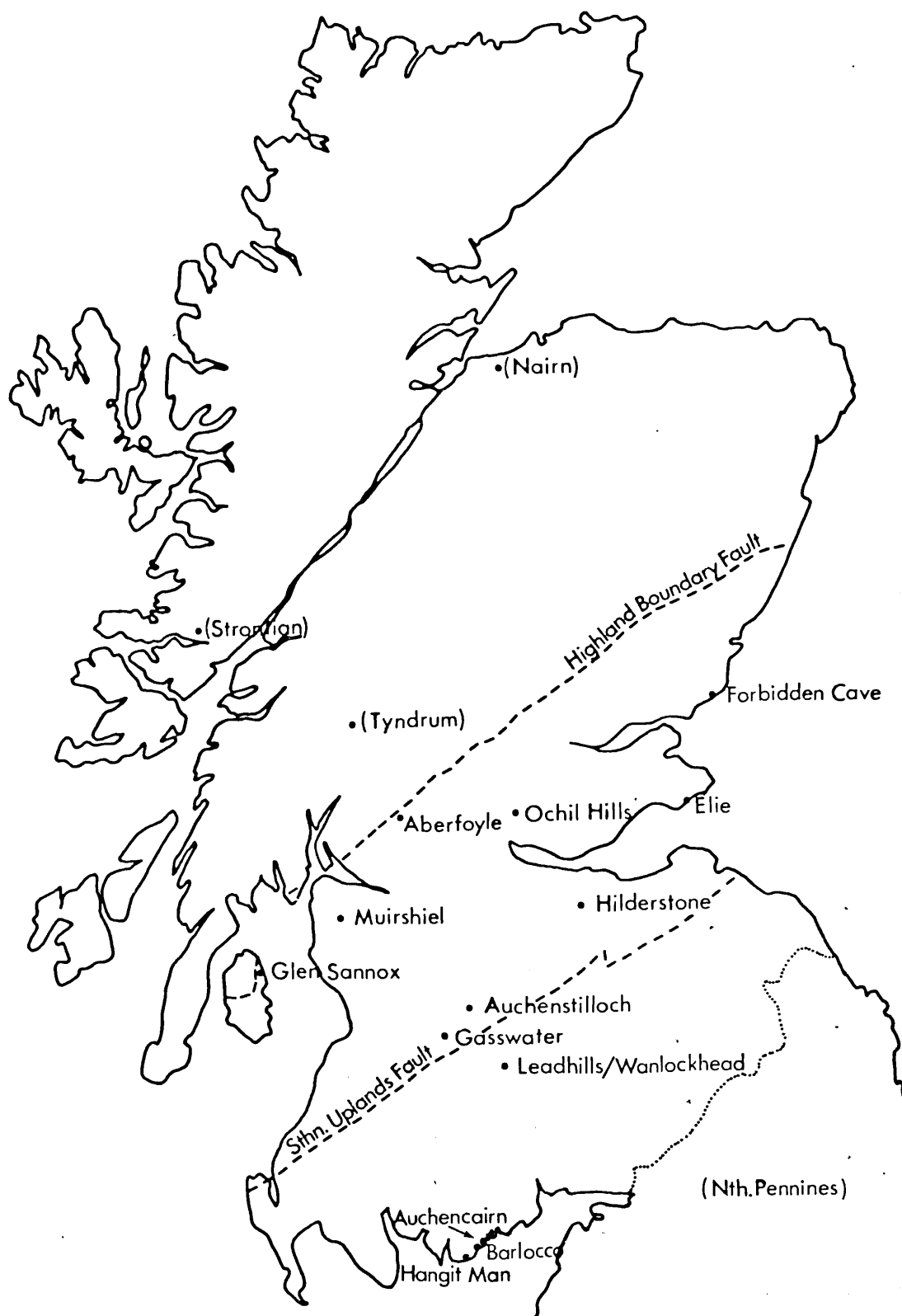


Fig.1 Locations of the baryte deposits studied; plus those others (in parentheses) which have been used for comparison.

between the two regions, and the Highland boundary fault the northern boundary for the Midland Valley. It is the movement on these two faults, throughout much of the Palaeozoic, that has had the major effect on sedimentation during that time.

The Midland Valley, although existing as a true rift valley for a significant part of the Palaeozoic, was in Cambrian times not defined by the marginal faults, and deposition of Arenig spilitic lavas, shales and cherts blanketed the whole of the area, right into the present-day Highland region. Before the rest of the Ordovician was laid down a period of folding occurred in which the Highland boundary fault was initiated, having a northerly downthrow (Fig.2). The Southern Upland area developed into a geosyncline, which existed until near the end of the Silurian. The sediments were deep-water turbidites and muds deposited on the ocean floor of a trough which was evolving in response to the deep-seated stress from which the Caledonian earth movements were soon to follow (Fig.3). The trough was elongate S.W.-N.E., between fluctuating shorelines lying in the Scottish Highlands and English Midlands (George, 1960).

It was during the Caledonian orogeny that the Southern Upland fault was probably initiated, and the Lower Palaeozoic rocks of the Southern Uplands intensely folded. These folds are interpreted by

....Walton

Walton (1961) as complex monoclines, or strongly asymmetric anticlines which face and descend to the south-east. The broad structural pattern was due to a horizontal compression in a N.N.W-S.S.E. direction which developed folds on an E.N.E. axis, and caused strike faulting (Greig, 1971).

However, some of the Lower Palaeozoic inliers of the Midland Valley had not been folded until late in the Lower Old Red Sandstone. The Southern Upland granites were intruded in association with the orogeny, and represent the second, or non-metamorphic, of Read's Caledonian belts (1961). Dewey (1971) interpreted this area, in terms of a plate-tectonic model, to be the leading edge of a lithospheric plate under which was descending a northerly-dipping oceanic one.

In the Midland Valley at this time, in semi-arid conditions, enormous thicknesses of sediment were being deposited in the newly-formed basin situated between the new highland areas. These sediments were added to by volcanoes erupting on the flanks of the mountains.

Before deposition of the Upper Old Red strata, a third period of folding, with associated faulting, took place on the Caledonian axis (Macgregor and MacGregor, 1948): the Highlands were uplifted relative to the Midland Valley by over 3000m,

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causing the northern limb of the Strathmore syncline to be uplifted (George, 1965). This rejuvenation of the Highland boundary fault, and movement on the well-established Southern Uplands fault, caused the establishment of the true rift form of the Midland Valley (Fig.4). Then followed extensive denudation and the first Upper Old Red Sandstone sediments were probably accumulated in piedmont-like fans extending outwards into the valleys (Waterson, 1965). The detritus was derived from higher ground and the sediments overstepped the pared-down and dormant fault scarps.

In the Southern Uplands, thick lavas, sandstones and conglomerates were deposited in lakes of depressed areas on a basement of severely eroded Lower Palaeozoic. However, the Midland Valley was slowly subsiding and subject to periodic flooding and dessication under the prevailing semi-arid conditions.

The passage into the Carboniferous was generally a conformable one. Volcanic activity (commonly yielding olivine basaltic lavas) took place on the southern flank of the Southern Uplands, which was then succeeded by deposition of large thicknesses of deltaic and fluviatile sediments. Later igneous activity was alkaline and acidic in chemistry, and corresponded with the enormous outpourings

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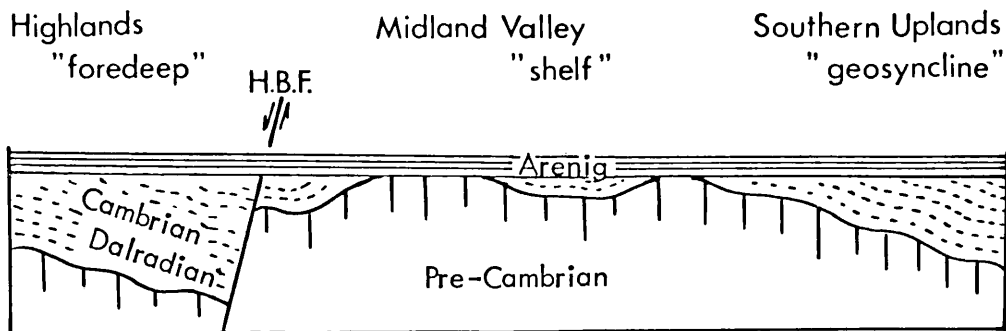


Fig. 2 Model of inferred relations of Arenig rocks to their foundation during Arenig times (after George, 1960).

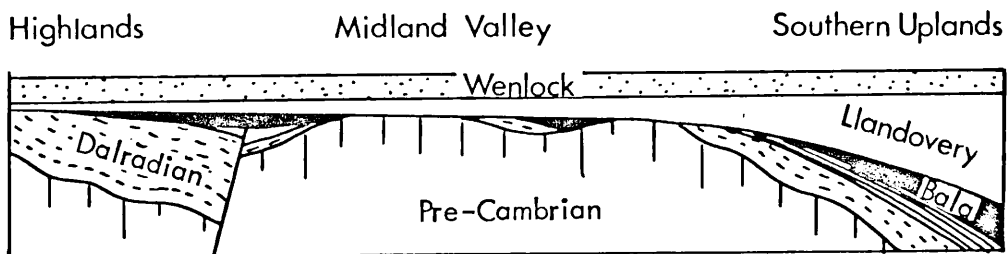


Fig. 3 Model of inferred conditions of sedimentation of the Ordovician and Silurian rocks (after George, 1960).

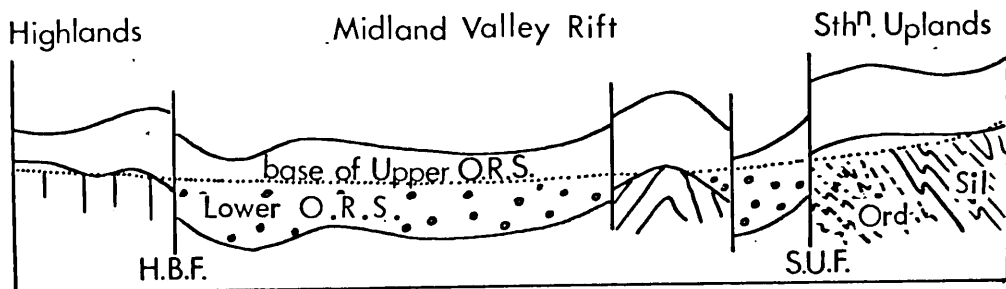


Fig. 4 Generalised model of inferred rift form in Devonian times (after George, 1960).

which had occurred in the Midland Valley in the Campsie, Renfrewshire and Garleton Hills areas (Francis, 1965). Apart from the marginal faults, it was these lavas which controlled sedimentation in the Midland Valley during the Carboniferous, effectively splitting up the area into isolated basins.

Towards the end of the Carboniferous the main phase of the Hercynian orogeny occurred, as a result of which, a period of non-deposition was experienced in the Southern Uplands. Folding and faulting took place in the Midland Valley giving rise to E.-W. and N.W.-S.E. structures (Kennedy, 1958). The folding did not always show a good correlation with the depositional troughs and highs, and according to Anderson (1951) this indicates that a compressional system prevailed, controlled by basement structures that also induced strike slip on the larger faults. Highly variable throws were the result. This would explain why the rift form was only locally re-established by the Hercynian movements.

Conditions of deposition in the New Red Sandstone were very different from those of the late Coal Measures. The sediments changed in Stephanian times from detritic to arid-continental, wind and water lain, as the sea regressed southwards.

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In the Southern Uplands differential uplift and faulting along pre-existing lines of weakness produced troughs in which breccias and sandstones were deposited. The basal breccias are of material derived from the Lower Palaeozoic, indicating that the thin layer of Carboniferous sediments in the Uplands had previously been removed.

Igneous activity at the Permo-Carboniferous boundary had resulted in the widespread extrusion of alkaline lavas and tuffs, and the intrusion of sills. Quartz-tholeiitic dykes and sills were generally restricted to the Forth area.

Hercynian movements continued, at least locally, in the Permian as attested by the folding in the Mauchline sandstones. Rift control had by now disappeared, although in its extension in Ireland the Permian is seen thrown against Dalradian rocks, the last of its control on sedimentation. The Trias, Rhaetic and Lias are little affected by the rift in Ireland, and in the region of the Midland Valley this conformable sequence may have existed in similar thicknesses, again indicating a disregard for the rift form in Scotland (George, 1960). The Cretaceous (in Ireland) and Tertiary strata also indifferently transgress older rock structures.

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The only Tertiary rocks of the area are those of the volcanic centre of Arran and the numerous, generally north-westerly trending dykes. In mid-Tertiary times the Alpine orogeny gave rise to faulting and somewhat gentle folding on the older Hercynian lines. Following erosion, a pronounced unconformity exists below the Quaternary.

The periods of glaciation which existed in the Quaternary not only caused denudation, but on recession, with accompanying pulsatory falls in base levels, left a benched land form: a "midland valley" with flanking massifs (George, 1958).

Mineralisation.

Apart from baryte several other ores occur in important quantities in the Midland Valley and Southern Uplands (Fig. 5): lead and zinc veins have been known about in the famous Leadhills/Wanlockhead area since Roman times, but also occur at Newton Stewart (Kirkcudbrightshire), and at the Lanarkshire/Dumfriesshire border. Copper and nickel are often associated with lead and zinc, the richest deposits being found at Wanlockhead and Newton Stewart. At Leadhills, gold has been found in alluvial deposits (Duff, 1965), although only one auriferous vein (quartz) has been discovered (Temple, 1956).

....Silver

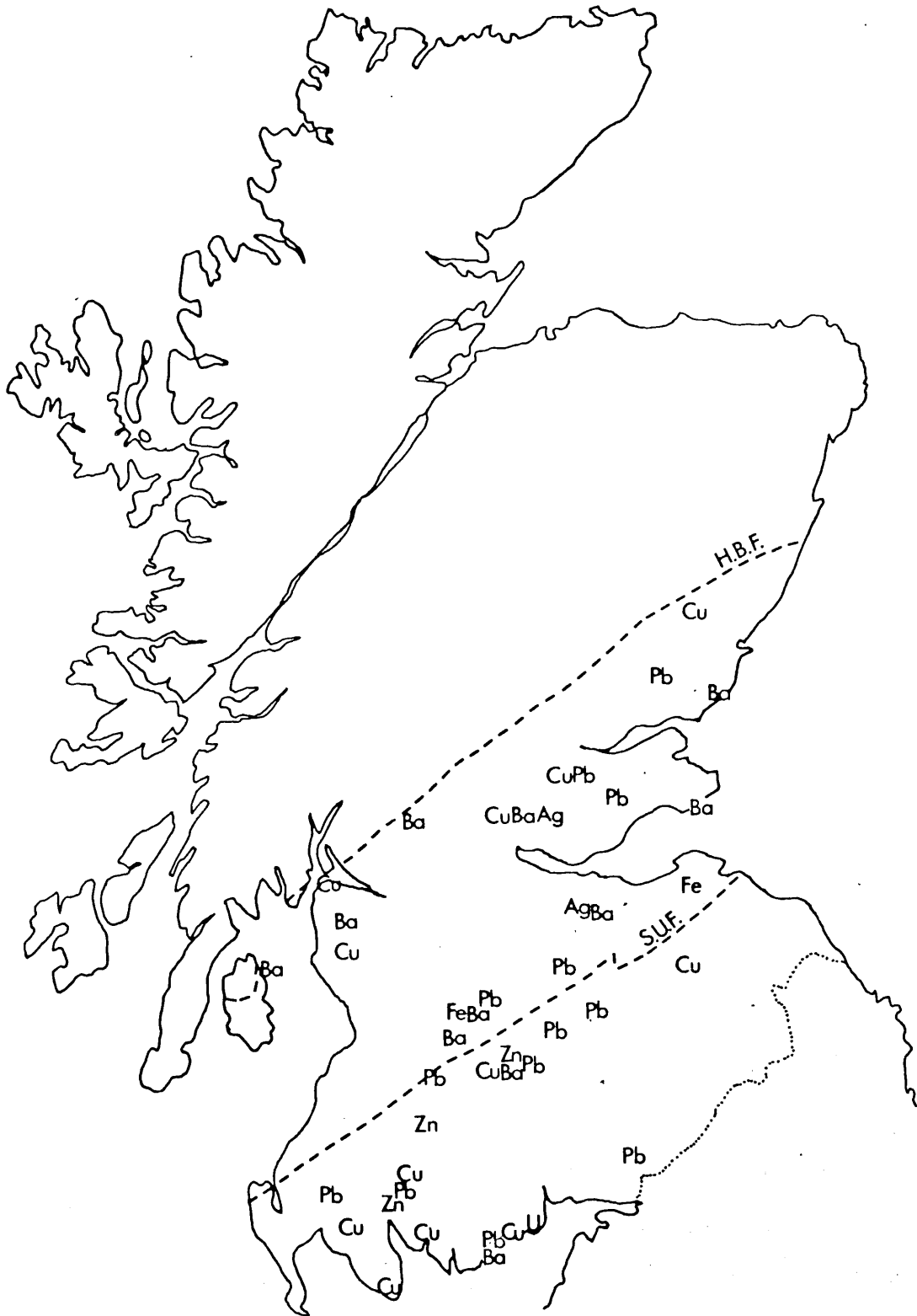


Fig.5 Mineralisation in central and southern Scotland.

Silver, as native metal, oxide ore and in-argentiferous galena occurs in Silver Glen, near Alva (Dinham ~~et al.~~^{and Haldane}, 1932), and at Hilderstone, near Bathgate (Wilson, 1921). Hematite, as vein ore is found in East Lothian (Duff, 1965) and the Muirkirk area (Scott, 1956; 1966) and Uranium-bearing veins cut the Silurian rocks to the south of the Criffel granite.

In the Cairnsmore of Fleet area, Cook (1976) believed the mineralisation to be in a zonal arrangement around the Caledonian granites, and hence inferred that there was some genetic relationship between them. This had been suggested earlier, not just in this area, but at Strontian and in the region of other plutons (George, 1961; Duff, 1965); in fact, George went so far as to suggest that it was reasonable to expect that a granitic body lay beneath the Leadhills/Wanlockhead deposits, and was similarly involved in the deposition of these veins.

Dunham (1952), in agreement with Finlayson (1910), thought that Scottish mineralisation was probably Hercynian in age. There was no conclusive evidence for this, but it was pointed out that even though there are numerous Caledonian granites, there is a general lack of associated mineralisation.

History of baryte mining.

Records of baryte mining in Scotland date back to before 1845, and it is believed that

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operations at Muirshiel mine may have started as early as 1750 (Hobson, 1959). Most of the, quite numerous, mines which were established in subsequent years proved relatively short-lived; the persistence of the ore laterally and in depth, being limited. The larger mines such as Gasswater, Muirshiel and Glen Sannox (Arran), have had lengthier, although sporadic, existences: Gasswater was worked open-cast around the turn of the century and then left for a while. The positions of the veins were re-established by trenching in 1917 and production started in 1919. It was, however, 1924 before determined efforts at large-scale production were made. Muirshiel and Glen Sannox seem to have had a sort of antipathetic relationship: in 1920 Muirshiel closed after 170 years of activity and Glen Sannox opened after 56 years of closure. Then in 1942 Glen Sannox closed and Muirshiel reopened. Being geographically quite close, the labour force merely moved from one to the other.

Many baryte veins had been encountered in lead and silver mining activities long before 1750, but were treated as gangue and not exploited until well into the 19th century.

The last of the working mines in Scotland, was Muirshiel, which closed in 1969. Gasswater, the largest producer, had closed five years earlier.

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It is noteworthy that the closures were forced, not principally by lack of ore, but by economic considerations. Glen Sannox mine had reached increasingly richer veins at depth, but the ore was inherently more expensive to raise, and when much of the equipment was lost in a collapse in 1942, operations were shifted to the newly expanding Muirshiel mine. The closure of Gasswater was mainly due to the cost of the 30 miles road transport necessary to get the ore to a port (Collins, 1972). At Muirshiel, the increasing instability of the veins made the "cut and fill" method of extraction too hazardous to continue.

Demands from the North Sea oil industry, for baryte for use in drilling muds, has revived interest in British baryte over the last decade, as reflected in the increased tonnages needed to be imported. However, there are two problems which recur in the assessment of the Scottish deposits: a) the cost of necessary road transport; b) the lack of deposits which lend themselves to the techniques of open-cast mining. The second of these is of course the more basic, for whereas the near vertical veins of central and southern Scotland can yield ore of enviable purity, the stratiform deposits of Spain, Morocco and Germany may be exploited for a fraction of the cost.

Specific aims of the project.

1. To discuss the mineralogical similarities and differences between the deposits;

2. To investigate the chemistry of: a) the minerals of the deposits, and discuss the results in relation to the mineralogical comparisons; b) the immediate wall rocks, to establish to what extent the mineralisation has caused chemical change;

3. To investigate the form of the veins, and along with the evidence from the chemistry of the wall rocks, and fluid inclusion studies, to arrive at conclusions from which a probable mechanism of deposition and emplacement of the ore could be postulated.

Chapter 2 : The mineralogy of the deposits

Chapter 2. The mineralogy of the deposits.

The veins of baryte represent several generations of mineralisation, the width of the vein being governed by the number of generations. The crystal layers thus produced are generally, within one vein, of similar thickness, although the last layers to form are commonly thicker than the others and are generally coarser grained. Between veins these thicknesses vary considerably.

In the layers, the crystal growth is approximately perpendicular to the vein wall, as in normal crustiform mineralisation. If the baryte is pink, the individual generations may often be distinguished by variations in the colour. Should the colour not vary, the distinction is not as easy, as the crystal layers intermingle and changes in the crystallinity must then be relied upon.

From deposit to deposit, changes in the colour and crystal form of baryte cause its appearance to vary considerably. The differences may sometimes be quite subtle, but it has been found that, to a certain degree, it is possible to identify the deposit from which certain samples have originated on the basis of their general appearance. These characters reflect the chemistry of the mineralising solutions, the physico-chemical environment of deposition and the mechanisms of

....emplacement

emplacement, and merit definition and illustration in order that subsequent descriptions may convey a more precise idea of the mineral forms.

The colour of baryte.

In thin section baryte is colourless. In hand specimen the following factors control the colour:

i) the type of crystals and the degree to which the cleavage is expressed - samples with fibrous, well-cleaved crystals appear white, whilst coarse samples in which the cleavage has not been activated remain colourless;

ii) the population density of fluid inclusions - a high population density can cause the mineral to have a milky-white appearance;

iii) hematite inclusions - a pink colour results from dispersions of discrete, finely-divided inclusions of hematite which occur along crystal boundaries and cleavages of the baryte (Fig. 6). These inclusions, in their sparse populations, are sufficient to flood the specimen with red light. Alternatively, if they have become a little altered, as is sometimes found in the recrystallised baryte, an orangey tinge is imparted to the pink colour.

Habit.

The preferred habit of baryte is that of platy, or tabular, blade-like crystals. The general

....pattern

pattern formed by these crystals is roughly a radiating one generating a fan-like feature (Figs. 7 and 8). This occurs because, as they grow outwards, the individual blades get thicker and extra blades are incorporated. In thin sections cut perpendicular to (001) the blades appear as lath-like shapes (Fig. 9).

The variations from this general pattern are controlled by several factors: the space available for crystallisation; the rate of precipitation; the subsequent history of the vein; and occasionally the amount of hematite co-precipitating.

The term 'cockscomb' is used to describe the well-developed and generally coarse-grained crystal fans which stand proud of the rest of the mineralisation (Figs. 10 and 11). Those crystals attaining a similar form but in the body of the vein are termed (coarse-grained) tabular. However, less well-developed crystals are more common. These are generally smaller, the blades becoming very narrow, and the boundaries between adjacent crystals are indistinct (Fig. 12). In thin section, feather-like forms are observed as opposed to laths. (Figs. 13 and 14).

The terms 'compact' and 'platy' rather than tabular, are preferred for these latter specimens. Platy inferring finer blades and compact reflecting

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Fig.6 Within baryte, one of the (larger) grains of hematite to which pink baryte owes its colour.

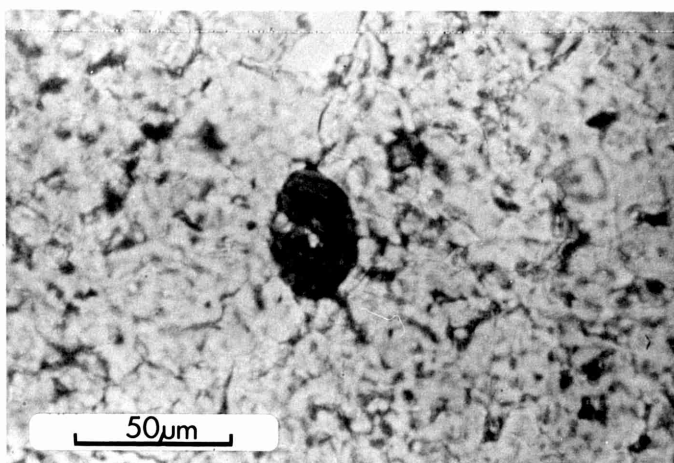


Fig.7 Medium-grained platy baryte (Ochil Hills), exhibiting a radiating, or fan-like, pattern.

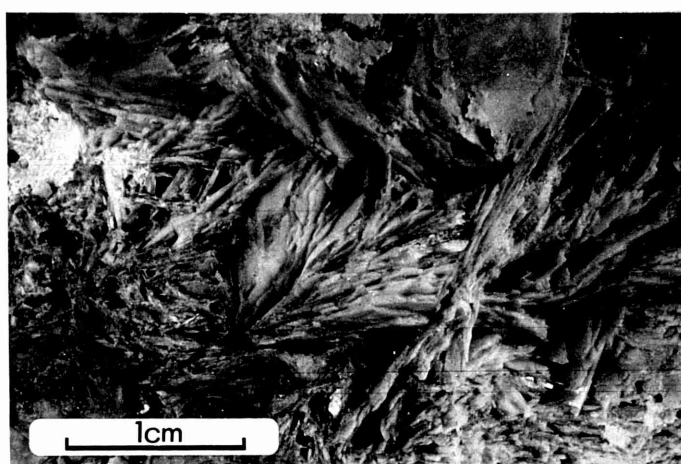


Fig.8 Course-grained tabular baryte (Nairn), exhibiting a fan-like pattern.

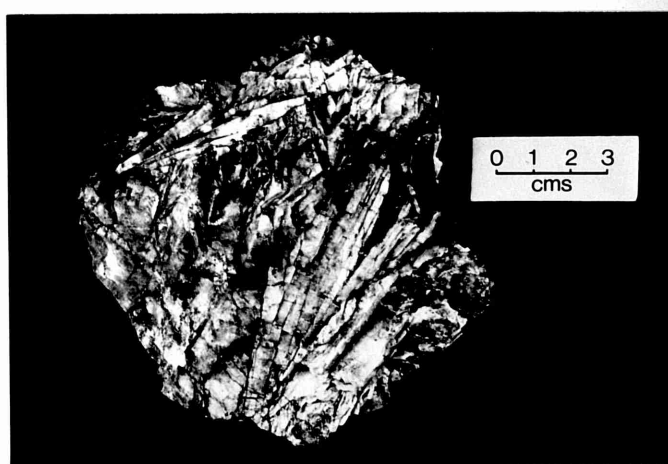


Fig. 9 Lath-shaped crystals of tabular baryte (crossed polarised light).

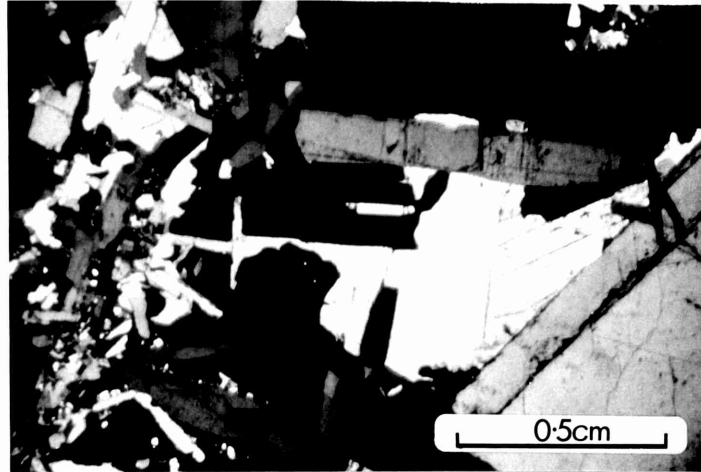


Fig. 10 'Cockscomb' baryte (Ochil Hills).

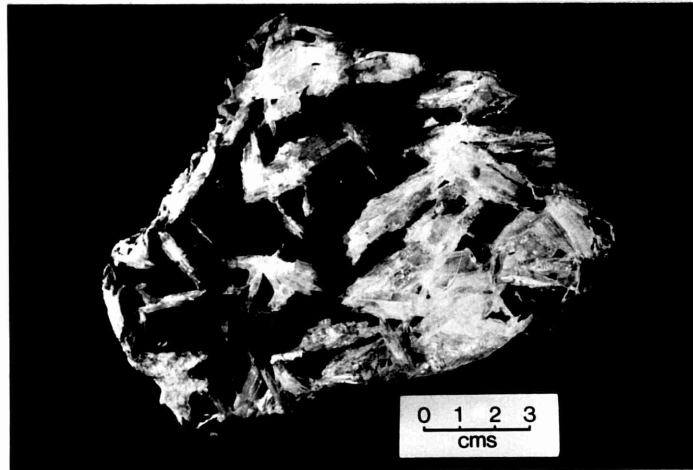


Fig. 11 Stained 'cockscomb' baryte (Wanlockhead).

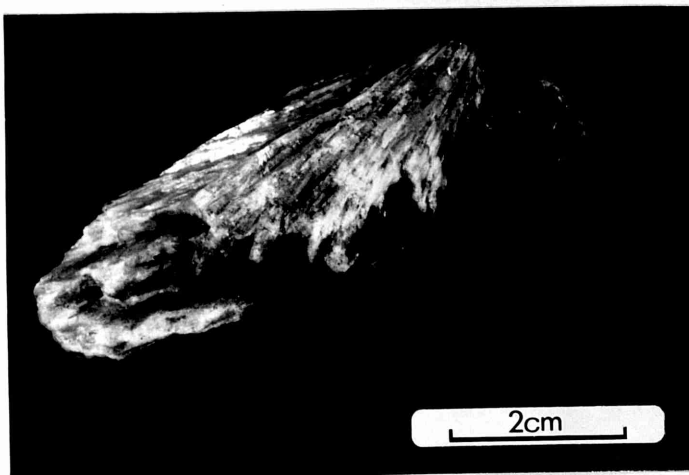


Fig.12 Pink, fine-grained
compact-platy baryte
(Muirshiel).

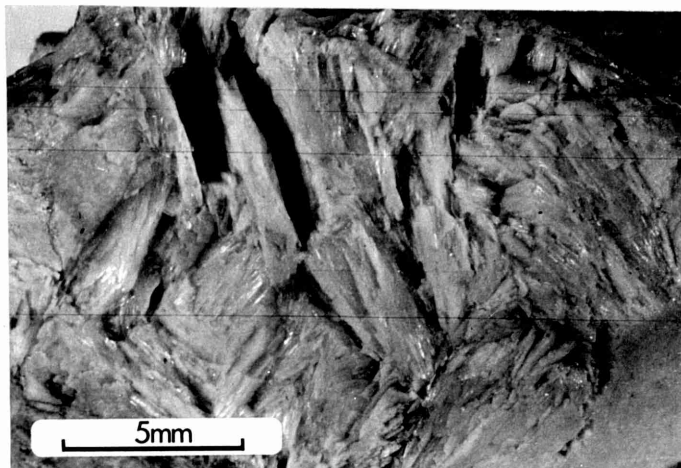


Fig.13 Thin section of
fig.12 , showing the
'feathery' effect (crossed
polarised light).

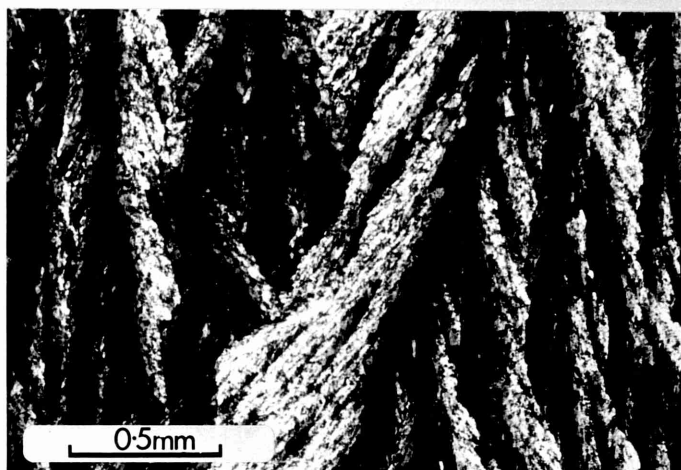


Fig.14 A feather-like
form in pink baryte from
Auchenstilloch (crossed
polarised light).



the space-competitive appearance imparted.

In references to the size of crystals those attaining around 2 cm or more (crystals of up to 20 cm have been observed) are referred to as coarse-grained, those of around 0.5 to 1.5 cm as medium-grained, and those of less than 0.5 cm as fine-grained.

Some of the fine-grained baryte is rather soft and powdery, possibly due to stress having been imposed at some time, and is termed 'earthy'. It resembles the cauk (cauk) type of baryte common in Derbyshire. The crystals are seen in thin section to be small and platy.

'Recrystallised' is a term used here to describe the hard cryptocrystalline baryte which has resulted from subsequent mineralising episodes causing healing of boundaries and cleavages, obliterating the original crystal forms (Fig. 15). In thin section 'feathery' shapes may be seen, but generally growing haphazardly. Palimpsest structures may also be observed (Fig. 16).

Quite separate from the above varieties are the rare, solitary well-formed orthorhombic crystals which are usually the last to have formed, having been unconfined in their growth. These are termed tabular prismatic.

....Baryte

Fig.15 Recrystallised pink baryte with some white areas (Gasswater).

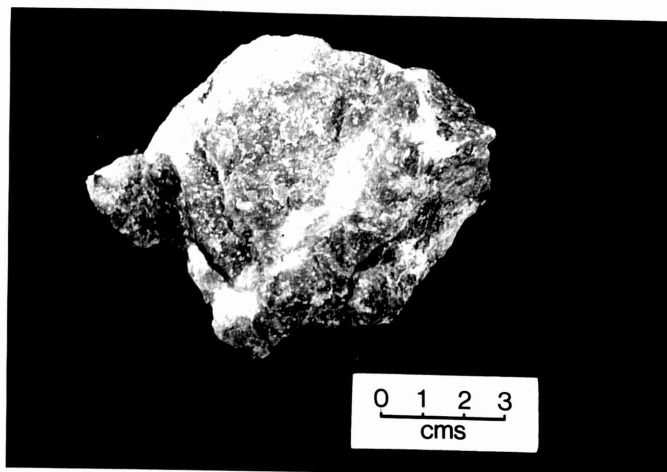
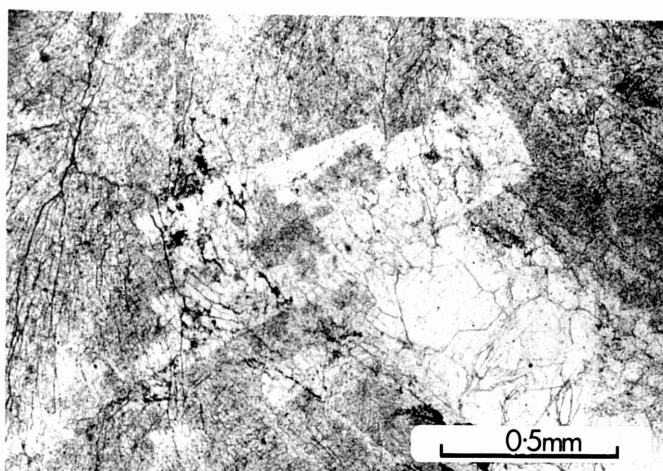


Fig.16 Palimpsest lath in fine-grained compact-platy baryte (plane polarised light, Auchenstilloch).



Baryte also occurs having replaced wall rock which has been brecciated and enclosed in the veins. It invariably presents tabular, or lath-shaped crystals in these cases (Figs. 17, 18 and 19).

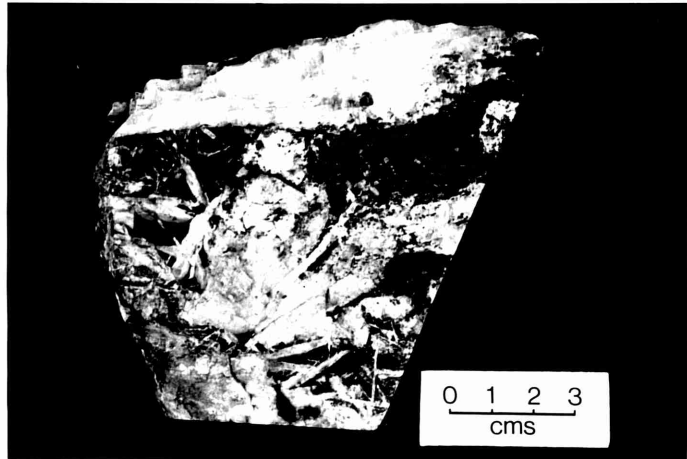
Fluorescence.

Barytes have been recorded as having white, yellow or orange fluorescence, and occasionally as being phosphorescent (Deer et al, 1962). Of the samples studied here many showed a weak creamy-coloured fluorescence in ultra-violet light, but none had any visible phosphorescence. When very pink baryte was studied the cream fluorescence was not observed, but a weak reddish one could be discerned, presumably imparted by the hematite present.

Quartz.

Quartz occurs in various modes in the veins, often forming minor veinlets, or occurring as pods of crystals within the baryte. In these cases it may contain inclusions of micaceous minerals (Figs. 20 and 23.vi.) or acicular hematite crystals. Commonly a very fine-grained mass of quartz has grown interstitially to the preceding minerals (Fig. 23.i.), or individual grains have grown at crystal boundaries and in cleavages. In these latter instances the quartz has often been able to

....attain



Figs.17 and 18
White baryte veining and replacing an altered greywacke (Barlocco).

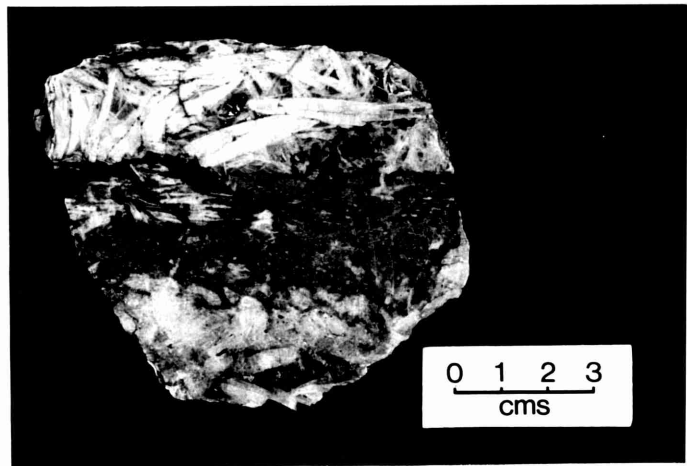
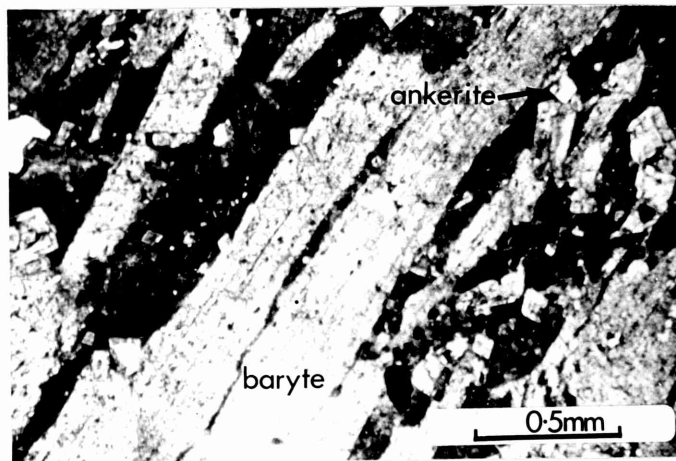


Fig.19 Baryte and ankerite replacing an iron-rich greywacke.



attain a euhedral hexagonal shape in spite of the enclosing baryte (Fig. 21). It is clearly later than the baryte as remnants of the latter are seen enclosed within the quartz (Figs. 22, 23.iii and 23.v.).

Descriptions of the mineralisation of individual deposits.

Aberfoyle (grid. ref. NN501987).

At the Arndrum open-cast mines nearly all the mineralisation is of baryte, quartz being present in minor amounts along with traces of copper ores. (Traces of galena as reported by Wilson et al., 1922, were not found). The baryte is mainly pink, medium to fine-grained, compact-platy, with some pink, and white, medium-grained tabular baryte occurring in the later generations.

The quartz is always later than the baryte generation with which it is associated, however many generations are present and so a somewhat alternating sequence is seen (Figs. 24 and 33). Where quartz is present in higher proportions, it has caused some healing of the baryte cleavages etc. Late, vuggy quartz shows well-formed hexagonal prisms which are usually clear but occasionally contain acicular crystals of hematite.

....The

Fig.20 A mosaic of grains, commonly containing micaceous minerals, from a quartz pod within the Muirshiel vein (crossed polarised light).

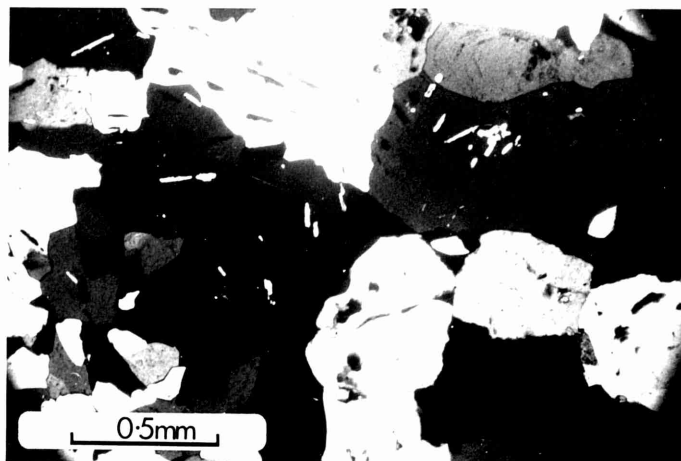


Fig.21 Scanning electron micrograph of a typical euhedral quartz grain set in baryte.

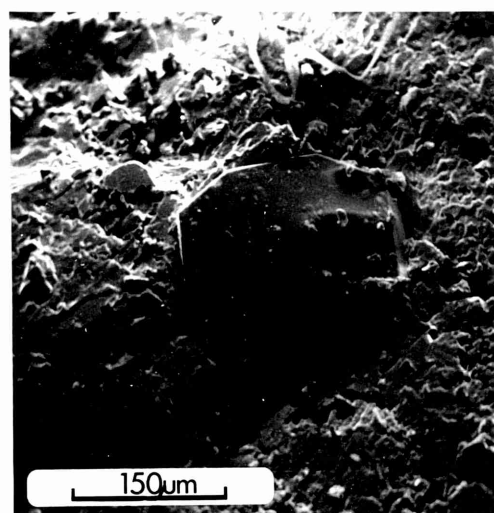


Fig.22 Euhedral quartz containing earlier baryte (plane polarised light, Auchestilloch).

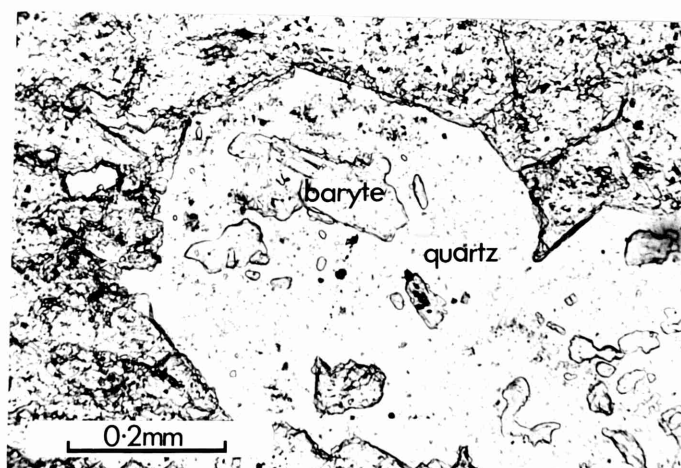
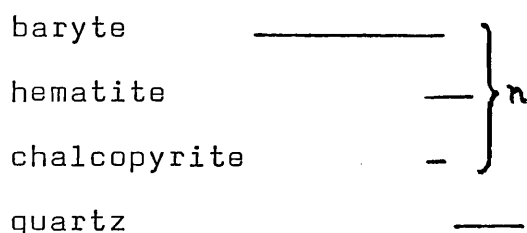




Fig.23 Micrographs of some of the various baryte occurrences.
 notation: ba - baryte; qu - quartz; ca - calcite; gal - galena;
 py - pyrite; hem - hematite; ank - ankerite; m - mica?.

The traces of green secondary copper minerals noted, were associated with the baryte rather than the quartz. In polished section rare blebs of chalcopyrite were seen, of approximately 5 μm diameter, in the body of the baryte crystals.

The schematic paragenetic sequence is:



where n = many generations, and the horizontal dimension is an approximate indication of relative time.

The wall rock of ferruginous quartz conglomerate adjacent to the mineralisation appears unchanged by the mineralisation, although some material in the body of the vein has been reduced to a quartz-clay gouge as a result of the combined effects of faulting and mineralisation.

Auchencairn (NX822485).

For most of the vein, baryte is virtually the only mineral present. It is mainly pink, coarse-grained and tabular. However, at the western extension of the vein a lot of quartz occurs with small quantities of ores of copper and iron (anhedral chalcopyrite and a little subhedral pyrite;

....altering

altering to covellite and limonite). Two yellow-stained, colourless, singly-terminating, tabular prismatic crystals of baryte, 5 mm long, were also found at this western end of the vein.

In thin section the quartz is occasionally observed to contain flakes of white mica.

Little of the vein is seen at the surface, but the wall rock of ferruginous quartz grit (Rascarrel Sandstones), close to the mineralisation, appears unaffected by the mineralisation.

The schematic paragenetic sequence is:

baryte	—————
white mica	—
quartz	— — —
pyrite	—
chalcopyrite	—

Auchenstilloch district (NS7533).

Evidence for the existence of ten main veins was seen in this area, along with a lot of minor stringers. The mineralogies fall into two groups: i) baryte and hematite, with or without chalcopyrite. ii) baryte with galena (sphalerite and pyrite have also been reported; Wilson, 1921). Quartz occurs in both groups.

Group i). The baryte is pink, generally medium to fine-grained compact-platy, and comprises virtually the total content of the veins. Brecciation and subsequent cementation of one generation

....of

of baryte, by another, is common; palimpsest structures may be seen (in thin section) although extensive recrystallisation has not occurred.

The quartz occurs as subhedral to euhedral crystals within the baryte, along cleavage planes and crystal boundaries. It is colourless but sometimes appears pink in hand specimen being flooded with red light from the enclosing pink baryte. Small amounts of chalcopyrite, altering to limonite and malachite are occasionally observed, interstitial to the baryte.

The hematite not only occurs as finely-divided crystals dispersed within the baryte but also, at two locations, as a major mineral: the first is near the head of Pockmuir burn where the latest generation of mineralising fluids were very-iron rich, causing micaceous hematite, or specularite, to crystallise. The second is a small, but hitherto unrecorded vein, having been exposed by recent track-cutting by the foresters. It is on the north side of Mannock Hill, at grid reference NS75153290, and consists of pink, fine to medium-grained compact-platy baryte with a little quartz and an encrusting layer of botryoidal hematite (Fig. 25). In polished section it is seen that the hematite initially crystallised as specularite and then graded into the botryoidal habit.

....The

The schematic paragenetic sequence at this location is:

baryte	_____
finely-divided hematite	—
quartz	— —
specularite	_____
botryoidal hematite	_____

The general paragenetic sequence for this group is:

baryte	_____	} x n
hematite	—	
(chalcopyrite)	—	
quartz	_____	

where n = several generations.

The country rocks are of brown and red sandstones, and altered pinkish felsites. No obvious alteration has been caused by the mineralisation, save for the introduction of tiny veinlets and offshoots.

Group ii). The baryte is white generally, and fine-grained compact tabular (and platy). Galena is a common associated mineral (Fig. 23.iii). In one instance the baryte is discoloured to a creamy hue by alteration products of galena. Crystals of galena are interspersed in this earthy baryte. In thin section it was seen that very small crystals of galena altering to cerussite were ubiquitous
throughout

throughout the specimens. Quartz was also present in small amounts. The occurrence of quartz in the normal white baryte, in small amounts throughout the specimens, causes an apparent increase in hardness of the specimens.

The schematic paragenesis is:

baryte	_____
quartz	_____
galena	_____

These veins were not seen in situ, only dump material was available. However, the country rock again appeared little affected by the mineralisation, although relict crystals of a rhombohedral carbonate were seen in one thin section of a grey turbid quartz-arenite in contact with the vein baryte. There were also fine (quartz/baryte) mineralised fractures extending into the rock.

Barlocco (NX788472).

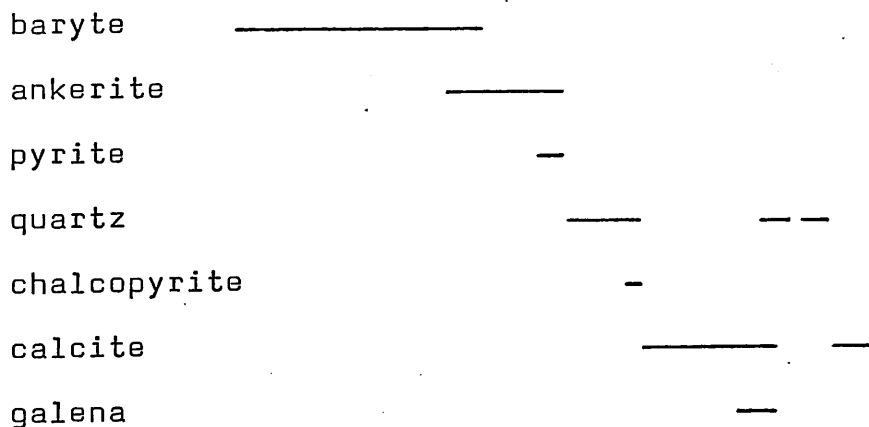
The veins are not visible at the surface, but the spoil heaps contain abundant samples of the very white, coarse-grained tabular, and sometimes beautifully cockscomb, baryte. Much calcite is also present, as coarse white rhombohedra and in the 'dog's tooth' habit, and also as clear equant rhombohedral prisms which occur as a late coating on some specimens. Quartz is also present late in the paragenetic sequence. Minor quantities of sulphide minerals occur with the calcite: galena, chalcopyrite and pyrite.

....The wall

The wall rock is a greywacke of variable lithology, ranging in colour from pale-grey to a weathered-brown. The baryte occurs as replacement crystals in the rock close to the vein and in blocks enclosed within the vein (Figs. 17, 18 and 19). In these cases a close association with ankerite[†] is seen (Fig. 23.iv). The ankerite, occurring as small rhombs, is paragenetically just later than the baryte but does not occur as a vein mineral. It may be inferred from this that the ankerite derived its chemistry from the wall rocks under the action of the baryte mineralising fluids. The pyrite probably originated in a similar manner.

Minor veining of the wall rocks has also occurred, fractures being filled with baryte, quartz or calcite.

The schematic paragenetic sequence is:



† identification was made by the staining technique of Warne (1962).

Gasswater (NS655218).

Of the two principal veins, the West Vein appears to have more of the harder recrystallised type of baryte than the Main Vein, and the Main Vein more of the coarse tabular baryte. Apart from this no other difference in mineralogy is apparent. The baryte is usually pink (or orangey-pink in the case of the recrystallised material) but all shades through to pure white are present. ("Water clear" material has previously been recorded; Hobson, 1959). Similarly all gradations from very coarse tabular baryte to fine-grained platy, and recrystallised, are present.

Scott (1956) reported large pods of calcite of various types occurring at depth in the mine, and thought they were, at least in part, paragenetically earlier than the baryte. No calcite was seen during the present study but as only the surface exposure was examined, and as the calcite was not mined, this is to be expected. Scott also reported dendritic manganese overgrowths and secondary green copper minerals associated with the baryte. The former is confirmed, but no evidence for the latter is seen in hand specimens from the surface exposures. However, in polished section small anhedral blebs of rare chalcopyrite, up to 10 μm across, were observed (identification was confirmed by electron probe analysis). They occur within baryte crystals and were not obviously related to the cleavages (Fig. 26).

Fig.24 Specimen exhibiting some of the effects of the numerous generations of baryte present in the vein (Aberfoyle, see also fig.33).

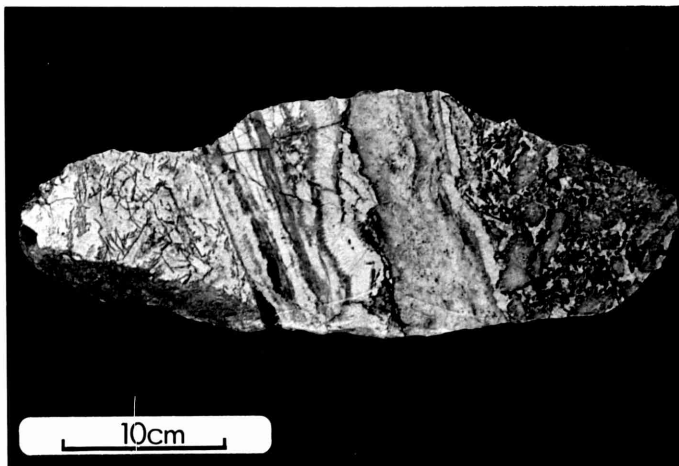


Fig.25 Pink baryte containing dispersed quartz grains (dark specs), succeeded by specular, and then botryoidal hematite, Auchenstilloch).

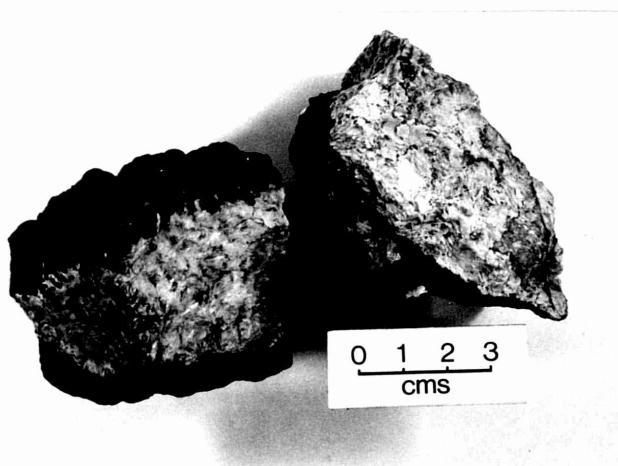
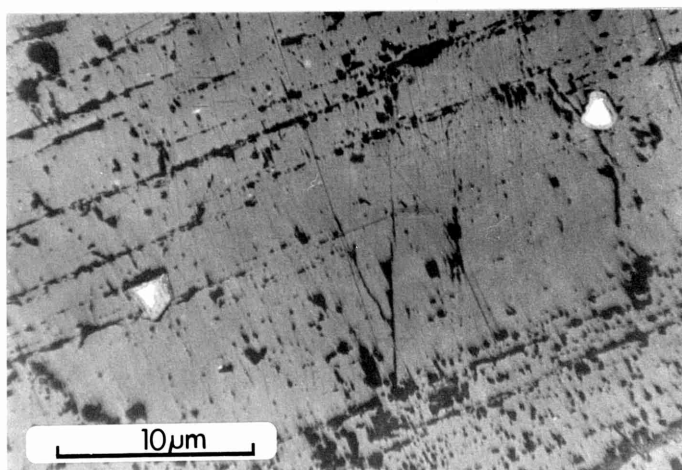
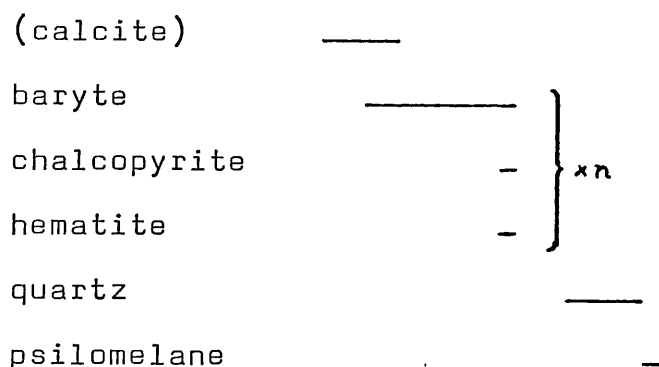


Fig.26 Small 'blebs' of slightly altered chalcopryrite, in tabular baryte (incident light, Gasswater).



Hematite, occasionally a little altered, was present in the pink specimens as usual. Quartz veining was not seen, although subhedral to euhedral crystals sporadically occur within the baryte samples.

The schematic paragenetic sequence is:



The wall rocks appeared little affected by the mineralisation; a minor bleaching of 1.5 cm in some areas of contact with the pale-brown ortho-quartzite expressed the repulsion of ferric iron cementation by the mineralising solutions (Figs. 28 and 29). The quartz grains of the rock developed overgrowths of silica and a small amount of baryte had found its way into interstitial positions between the grains (Figs. 23.v and 27). Brecciated blocks of wallrock, enclosed within the veins, had also suffered similar alteration, appearing grey with a slight greenish tinge.

Glen Sannox (NS007453).

The baryte is medium-grained platy to coarse-grained tabular, with some cockscomb, and is

....generally

Fig.27 Overgrowths on quartz grains at the vein/rock boundary (crossed polarised light, Gasswater).

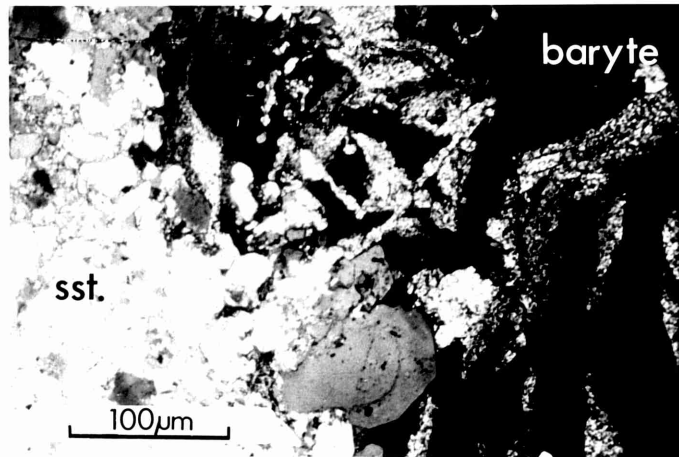


Fig.28 Limit of obvious wall rock alteration of an arenaceous sandstone, depicted by an iron-rich fringe (plane polarised light, Gasswater).

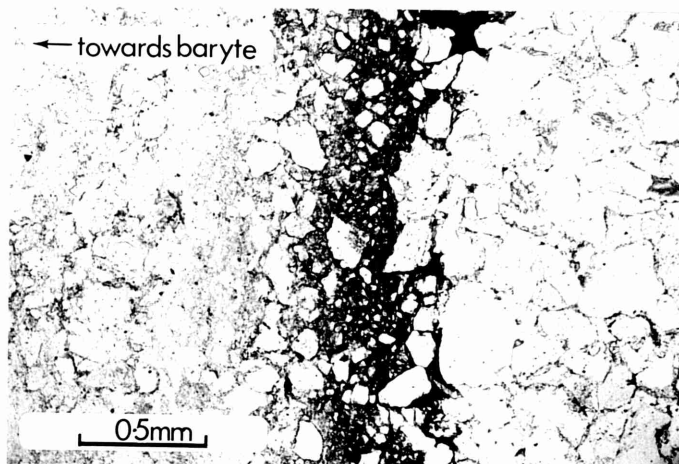
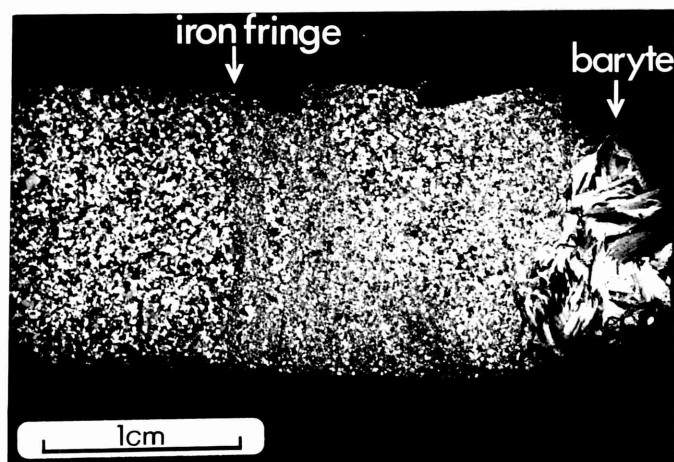


Fig.29 The zone of obvious wall rock alteration, from which figs. and are details (crossed polarised light).



generally white. An exception is the colourless, solitary, tabular prismatic crystals which have grown in a wallrock void. Occasionally the baryte appears pink, but usually due to iron staining rather than the dispersions of finely-divided hematite noted elsewhere.

Hematite does occur as a vein mineral, as interstitial specularite and commonly associated with the dolomite present in part of the vein. Chalcopyrite is also present, associated with the late, fine-grained interstitial quartz (Fig. 23.ii). A few crystals of sphalerite have also been found in one specimen only, apparently associated with the calcite occasionally found.

The schematic paragenetic sequence is:

baryte	_____
dolomite	—
hematite	—
calcite	—
sphalerite	—
chalcopyrite	—
quartz	—

The red and purple-red sandstone and mudstone wallrocks which have been brecciated and veined by the mineralisation, are partially replaced by both baryte and carbonate. The country rocks themselves contain hematite and some chalcopyrite,

....and are

and are possibly the source of their vein counterparts. The staining of the baryte is almost certainly due to groundwaters which have picked up iron from the surrounding country rocks (The baryte close to the vein hematite did not show any pink staining).

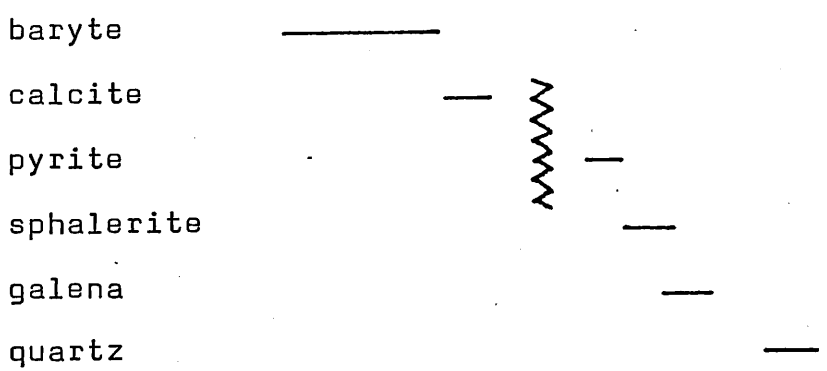
Hangit man (Port Mary, near Barlocco bay, NX754454).

The vein is purely of white, coarse-grained tabular baryte which is occasionally stained pale pink. No other mineral was observed.

Hilderstone (NS955726).

The vein, which contained "good white barytes" (Wilson et al, 1922), is no longer visible; the tips have also been obscured. A lot of calcite is still to be found, and the limestone countryrock contains fine veinlets of white calcite which is accompanied by small amounts of galena, pyrite and sphalerite.

Vein specimens made available by the Hunterian Museum, Glasgow, contained all the above minerals and revealed the following schematic paragenetic sequence:



The mineralisation, as reported by Wilson (1921), was: galena and niccolite (primary ones); annabergite, erythrite and native silver (secondary ores). The gangue was mainly baryte and calcite, the former containing small globules of a black carbonaceous mineral (albertite).

The carbonaceous material was presumably derived from the limestone host. The dolerite dyke, with which the deposit is closely associated, is believed to be a possible source for the ores.

Leadhills and Wanlockhead (NY8814).

The mineralogy of these deposits has been dealt with in detail previous to this study, most notably by Temple (1956) whose published paragenesis is outlined below. Hence a description of the baryte only is given here.

ankerite	_____	
pyrite	_____	_____
chalcopyrite	_____	_____
sphalerite	_____	_____
galena	_____	_____
Ni arsenides	-----	
calcite	-----	-----
baryte	_____	
aragonite		-----
witherite		-----
quartz		_____

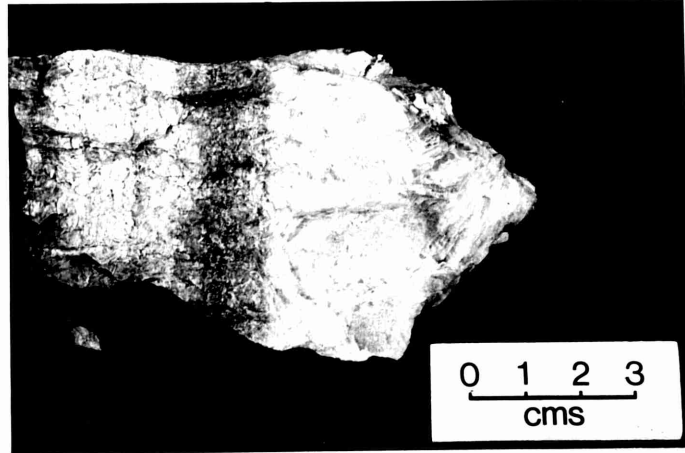
Although a small number of baryte samples were seen in the Leadhills area, Wanlockhead appears to be far richer in the mineral. It usually occurs as white or translucent, coarse-grained platy aggregates, occasionally displaying a good cockscomb texture (Fig. 11). No pink baryte was observed or has previously been recorded (Wilson, 1921; MacGregor et al, 1944; Temple, 1956; Rivera Murillo, 1967).

The only occurrence of witherite to have been discovered in Scotland was in the New Glencrieff vein at Wanlockhead where it is apparently secondary after baryte. The presence of hydrogen sulphide in the mine waters presumably affected a conversion to the soluble barium sulphide, which subsequently reacted with bicarbonate ions to form barium carbonate.

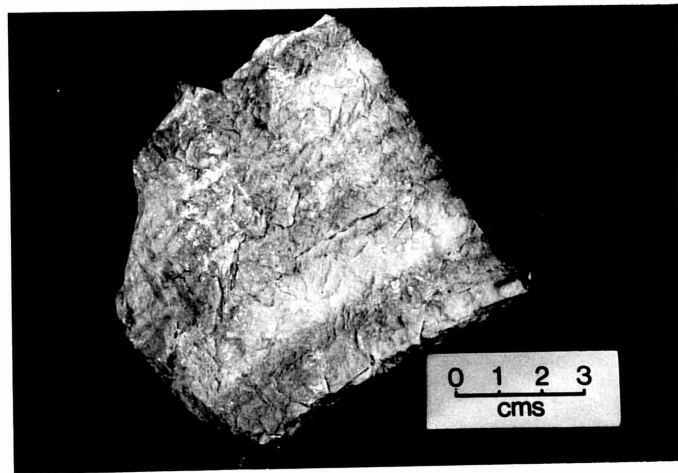
The ankerite is regarded by Temple to have originated from the Upper Ordovician greywackes which form the majority of the wall rocks, having made the observation that they were carbonate rich. Muirshiel (NS283650).

The baryte at Muirshiel commonly shows a very characteristic banding of various shades of pink (Figs. 30 and 31). This in effect proves that the hematite, which causes the pink colouration,

....has



Figs.30 and 31
Examples of the colour
'banding' in the finer-
grained compact-platy
baryte (Muirshiel).

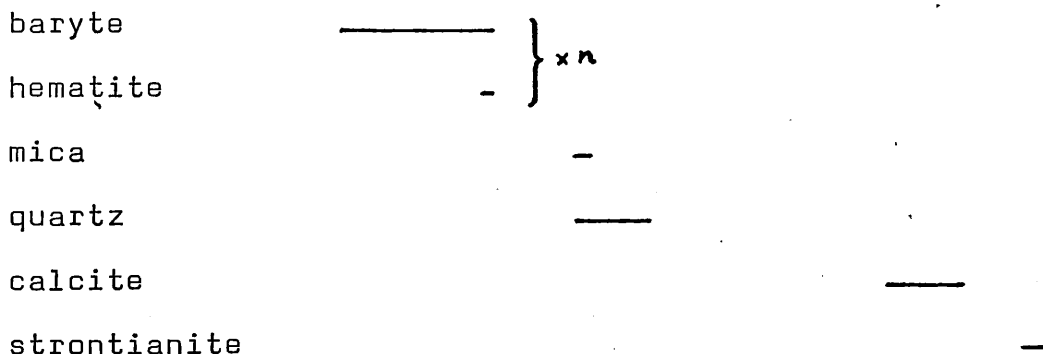


has not simply seeped in after the main mineralising episode.

The baryte is mostly fine to medium-grained compact-platy, and is by far the major mineral of the veins. Only small amounts of quartz are present, and smaller quantities of calcite and (very late) strontianite (see Chapter 8). In one part of the main vein a pod of quartz was found to have crystals of a micaceous mineral within the individual quartz grains (Fig. 23.vi).

Blebs of chalcopryrite ($\sim 5 \mu\text{m}$ in diameter) are only rarely found in polished sections of the baryte, and no evidence of the secondary copper minerals (after chalcocite and bornite) which have been found elsewhere in the surrounding districts, was seen in hand specimen.

The schematic paragenetic sequence is:



The altered trachytic lavas which form the wall rocks to the veins, appear unaffected by the mineralisation, except for the ubiquitous stringers and veinlets which penetrate them in fractures.

....Horses

Horses within the vein have sometimes been broken down to form ferruginous clay gouges by the action of faulting and metasomatism. The clays, montmorillonite and illite, were identified by X-ray powder diffraction.

The Ochil Hills (N08598).

The baryte of this area retains a rather consistent shade of pink throughout the numerous veins which exist. The common habit is medium-grained compact-platy, with occasional coarse-grained tabular or cockscomb varieties found as the latest generation to be deposited.

There appear to be two groups of mineral assemblages: the first in which pink baryte is the dominant mineral and only subordinate copper ores and quartz are associated; the second is where calcite is dominant with lesser baryte and minor quartz. The associated ores comprise various copper, lead, silver, iron, cobalt and arsenic minerals.

In the first group, the copper ores consist of chalcocite, chalcopyrite and rarer tetrahedrite; malachite and chrysocolla being the common alteration products.

The schematic paragenetic sequence is:

baryte	—————	} x n
hematite	-	
copper ores	-	
quartz	—————	

In the second group the calcite occurs in massive anhedral and rhombohedral forms, and in varying shades of pink depending on the amount of hematite present (a vein of dark red calcite occurs in the hillside above Menstrie). The metallic elements form the minerals chalcopyrite, galena, pyrite, argentite, native silver, erythrite and arsenopyrite (Wilson, 1921).

The schematic paragenetic sequence is:

baryte	_____
calcite	_____
metallic ores	_____
quartz	_____

The quartz occurs in both groups either as interstitial vein material (Fig. 23.i), as fine veinlets in the wall rock, or as jasperoid material resulting from the alteration of brecciated lumps of wall rock (the red colour being imparted by the inclusions of finely-divided hematite). The latter two are the only instances in which the mineralisation is observed to affect the already heavily-altered lavas and ashes which comprise the wallrocks to the veins; although a ferruginous gouge is reported in one of the Silver Glen veins (Francis et al, 1970).

....The

The second group of minerals referred to above, bears a strong resemblance to the assemblage at Hilderstone; the spatial association with the Ochil quartz-dolerite intrusive also correlates with a similar dyke at Hilderstone.

Discussion.

From these descriptions it is possible to group together those deposits which have similar mineral assemblages. Three groups are recognised:

Type 1 (or Midland Valley type) comprises the Muirshiel, Gasswater, Aberfoyle, Hangit Man, and Auchencairn veins, some of the Ochil Hills veins, and some of the veins of the Auchenstilloch district.

Here baryte comprises the vast majority of the mineralisation, hematite is a minor but ubiquitous component and accounts for the pink colouration of the veins. Chalcopyrite or chalcocite are rarer accessories which commonly alter to malachite. Quartz is a common late mineral and minor amounts of calcite may also occur.

Type 2 (or Southern Uplands type) comprises the Wanlockhead/Leadhills veins, those at Barlocco, and some of those in the Auchenstilloch district.

Baryte is not the dominant mineral in this group, although it is still a major one. Calcite and ankerite occur in similar quantities. Galena,

....sphalerite

sphalerite and pyrite occur with chalcopyrite in minor amounts. Quartz is present as a late mineral, but hematite is not found.

Type 3, is very similar to Type 2 in that it has galena, pyrite and major calcite in its assemblage. However, the important distinction is the inclusion of silver, cobalt and arsenic minerals. The spatial associations of the veins at Hilderstone and some of the veins of the Ochil hills with quartz-dolerite intrusives is also believed to be of importance (these two locations are the only ones in this group).

The generalised paragenetic sequence for all three 'types' are given in Fig. 32 and cover all but one of the deposits studied. This is the Glen Sannox deposit (Isle of Arran). The mineralogy here is essentially of the Type 1 kind for it has dominant baryte with minor hematite and trace chalcopyrite but a few crystals of sphalerite occurring with carbonates have been noted. Furthermore, unlike the rest of the Type 1 deposits, the hematite is not as dispersed crystals but as interstitial congregations of specularite, or iron glance. Bearing this in mind the deposit will be included in future references to Type 1 deposits.

The hematite which occurs in Type 1 veins was not introduced into the veins after baryte mineralisation had ceased, it is a primary mineral
....having

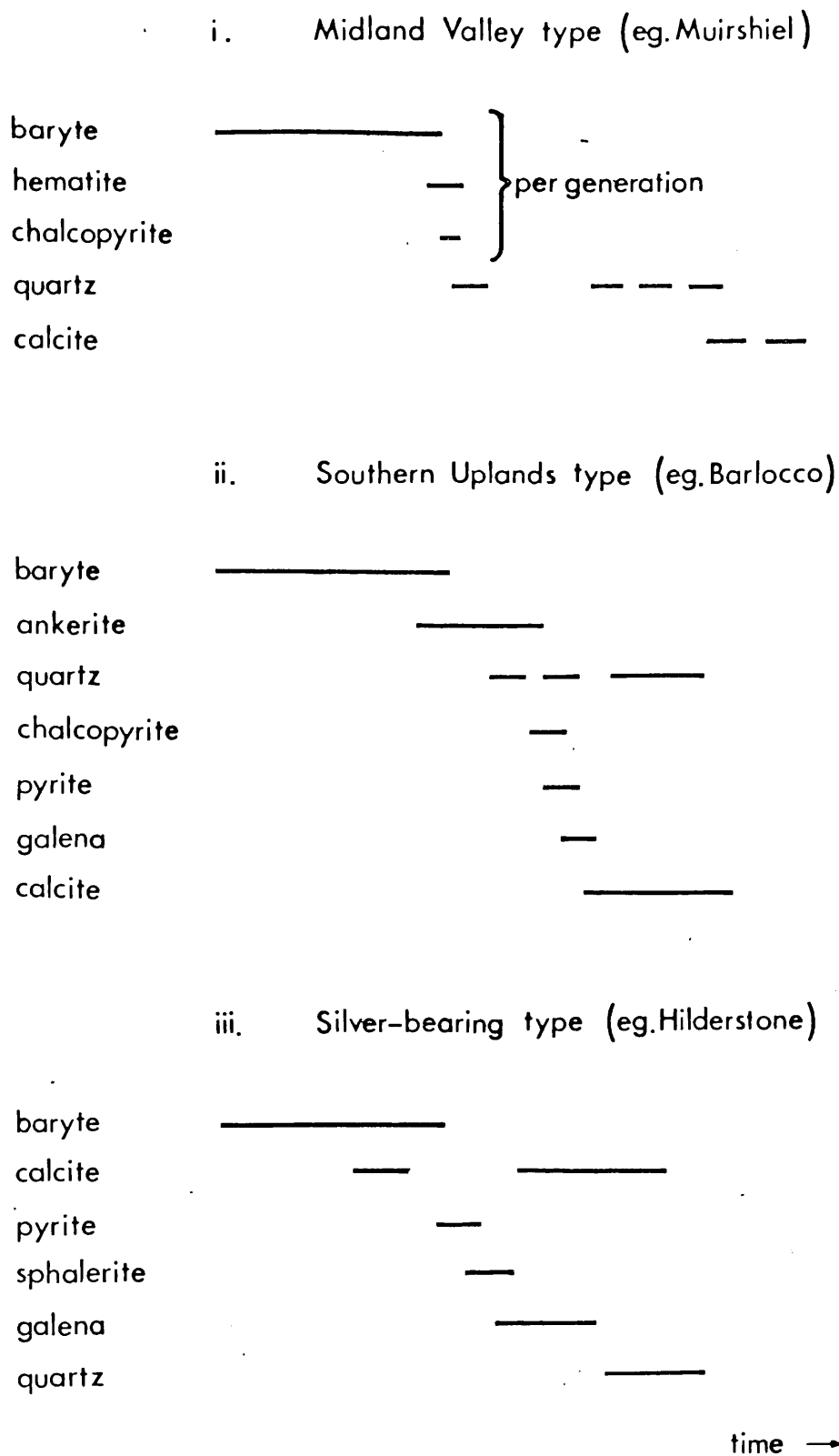


Fig.32 The generalised paragenetic sequences of the three 'types' of baryte occurrences, as typified by the deposits named.

having been precipitated penecontemporaneous with the baryte in each generation of mineralisation. The main evidence for this lies in the pink banded varieties of baryte which show variations in hematite content between successive crystal layers (generations) of baryte. This cannot be demonstrated for the chalcopyrite present, however it is believed that this mineral is also primary. It occurs as rare blebs intimately associated with the baryte, commonly not showing any relationship to the cleavages or crystal boundaries of the latter.

The common occurrence of these minerals, particularly hematite in the surrounding country rocks to the Type 1 veins, and carbonates and pyrite in the country rocks surrounding Type 2 veins leads to the inference that local groundwaters, in equilibrium with the country rocks, made up a significant component of the mineralising fluids. Temple (1956) made the observation that the country rocks surrounding the Leadhills deposit were carbonate rich and postulated that these rocks were the source of the carbonate ions for the ankerite which occurs very early in the paragenetic sequence. This was subsequently endorsed by Rivera Murillo (1967), and supported by the high average concentrations of calcium and iron in the Ordovician and Silurian greywackes of the Southern

....Uplands

Uplands (Alsayegh, 1971).

At Barlocco, ankerite occurs associated with baryte in the replacement of wall rock, but not as a separate vein mineral. In studies of the Silurian greywackes of this area of the Southern Uplands, Rust (1965), Weir (1974), and Floyd (pers. comm., 1978) found large quantities of carbonates (average 36% carbonate minerals) in the matrix of the greywackes. Rust thought that the introduction of the carbonate into the turbidites of south-east Wigtownshire occurred during diagenesis. However, Weir found the minerals to be more secondary in nature in the rocks west of Gatehouse and thought carbonate metasomatism related to the nearby Caledonian granites was likely. In either case the carbonate would have been available in the country rocks well in advance of the baryte mineralisation.

Rust also noted the presence of ore minerals (principally pyrite), in the graptolitic shales of the Riccarton beds. These then provide a possible source for the vein pyrite.

Chapter 3 : The geology of the deposits

Chapter 3. The geology of the deposits.

The veins are of the simple fissure-infill type and are invariably situated in fault planes or crush zones. The mineralisation having occurred either during or after faulting took place. From the evidence of slickensides occurring at various, and varying, angles within the veins, and between generations of baryte, it is concluded that continual faulting brought about a series of generations of mineralisation (e.g. Figs. 24 and 33). The possible mechanisms for this will be discussed later in the chapter.

The mineralisation was not restricted to the main fault zones. It was found that any fractures in the surrounding country rock would contain baryte, even if they were relatively distant from the 'main' vein (e.g. at a distance of 1 km from the Gasswater veins, in a direction perpendicular to the trend of the veins, the Lower Carboniferous sandstones were seen to contain many tiny baryte veinlets).

The above observations were mainly made at Type 1 deposits because few exposures of Type 2 veins remain, as a consequence of lead mining activities. However, previous literature (Wilson, 1921; Wilson, et al, 1922; MacGregor, et al, 1944; Temple, 1956; Rivera Murillo, 1967; Francis, et al, 1970) has given concurring descriptions

....of

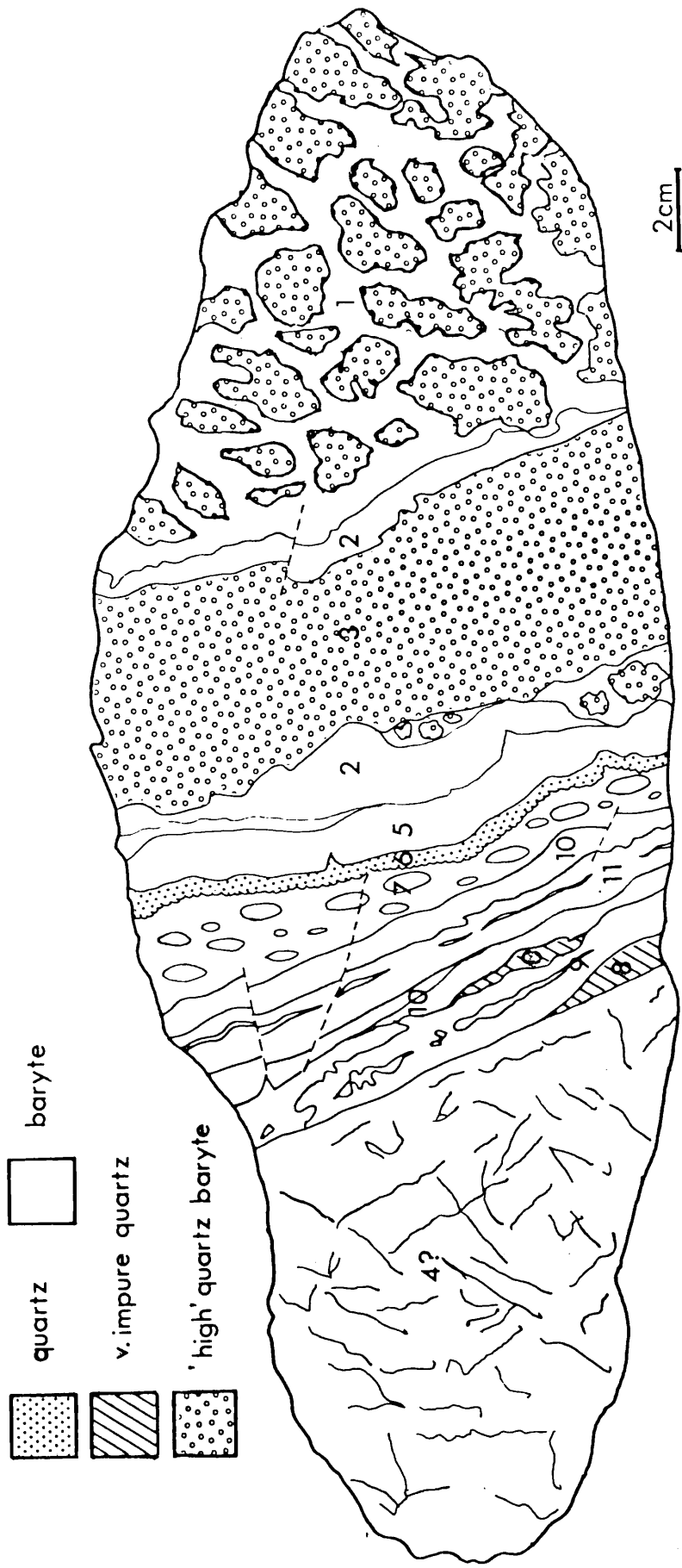


Fig. 33 Sketch of a specimen from Aberfoyle depicting the numerous generations of mineralisation and a possible order of deposition. (n^o. 1 being the earliest.)

of slickensides, fault gouges, etc. from underground exposures.

Details for individual deposits.

Aberfoyle (Type 1 deposit).

The country rocks of the immediate area comprise Lower Old Red Sandstone quartz conglomerates and dark red mudstones. One or more flows of contemporaneous, vesicular, andesitic lava have also been reported (Wilson et al, 1922). The wall rocks at the Arndrum opencasts are conglomerates.

The veins lie on the northern limb of the Strathmore syncline, just south of the Highland Boundary Fault, trending 320-340° and dipping to the south-east at an angle of approximately 80°. The two veins at Arndrum are 70 m apart and are subparallel; the west vein is 4 to 5 m wide at the surface but thins to 1 m at a depth of 10 or 11 m, the larger east vein is 90 m long with a maximum width of 12 m (4 to 6 m at the surface) and extends to a depth of at least 38 m. They cannot be traced to the edge of the Old Red Sandstone area, or into the Highland rocks north of the H.B.F.

Auchencairn (Type 1 deposit).

The vein trends E.N.E., dipping northwards, in hard ferruginous grits of Calciferosus Sandstone age. The surface exposure of the main vein was 0.6 m

....in

width, but this increased in the mine. There are also many stringers and lenses of baryte in the sea cliffs a little to the east.

The country rocks are close to the Criffel granite and also the faulted contact with the contact metamorphosed Silurian greywackes and shales (Fig. 34).

Auchenstilloch area (Type 1 and 2 veins).

The Lesmahagow inlier, in which most of the veins are situated, is an elongate (N.E.-S.W.) dome of Silurian buff and reddish sandstones and grey mudstones. Into these have been intruded a number of pink, Lower Old Red Sandstone felsite sheets and several north-westerly trending dykes of presumed Tertiary age. The folding, according to Walton (1965), took place in Lower Old Red Sandstone times.

The veins occur mainly in the Downtonian strata, but some traverse the Lower Silurian (Fig. 35). They also appear to have a spatial relationship with the felsites, especially the Type 1 variety. Fig. 40 shows the relation of the veins to the domal structure. Scott (1956) considered the mineralisation here, and at Gasswater and Muirkirk, to be related to the "Line of Steep Metals" fault, thought to have been active during the Carboniferous. However, this is the only area along its length with concentrations of mineralisation and the fault

....itself

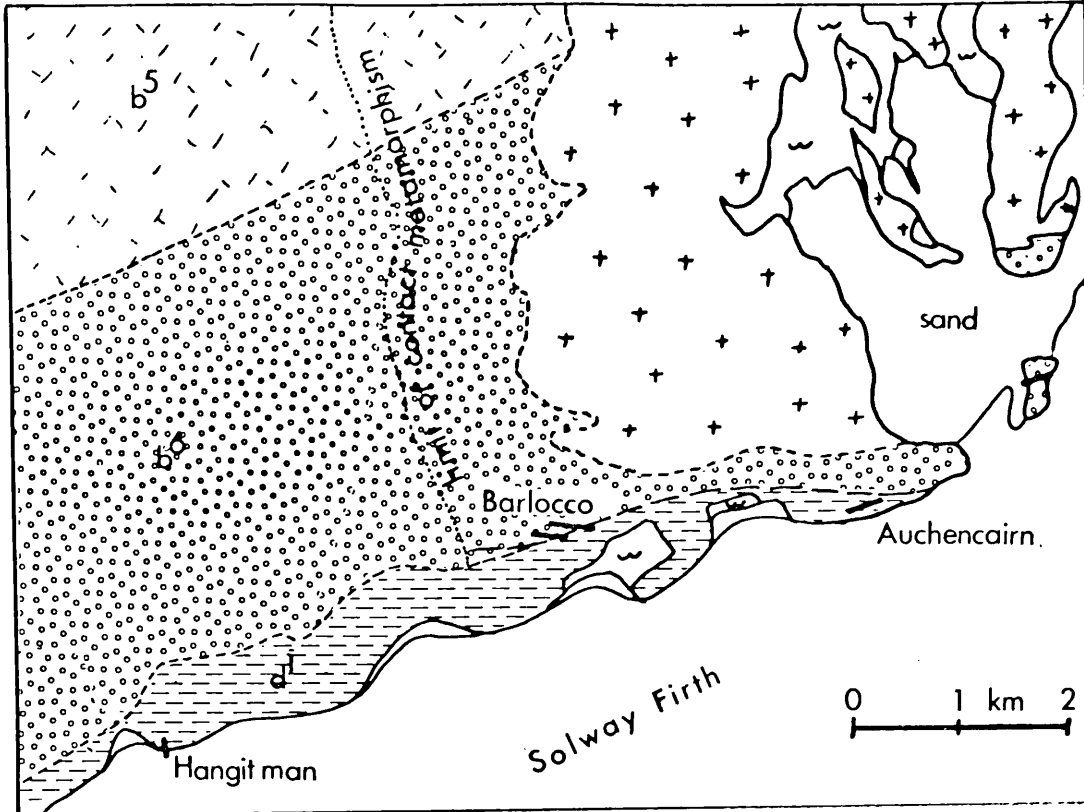


Fig.34 Geological sketch map of the area around the Kirkcudbrightshire veins.

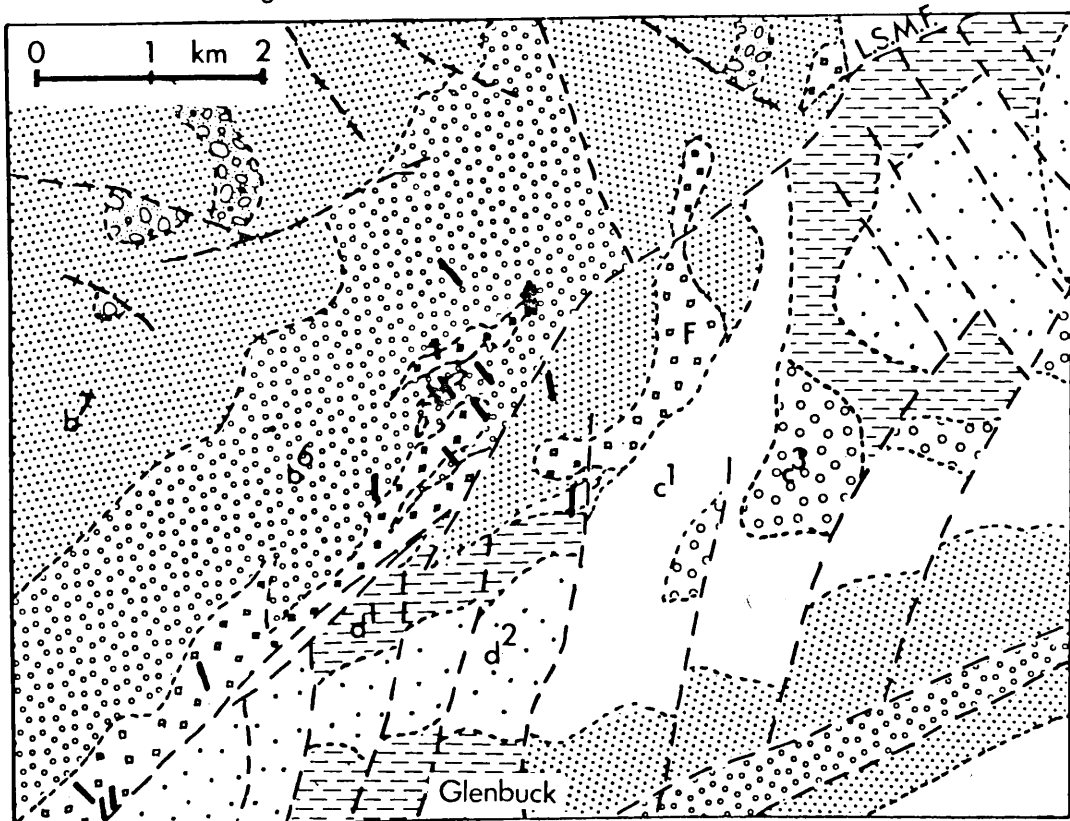


Fig.35 Geological sketch map of the Auchenstillloch district.

(For the key to figs.34 to 41 , see fig.41).

itself is barren of mineralisation.

The veins are individually quite small, only two attaining a width of 2 m and most being less than 1 m wide, but there are at least ten of them within a three kilometer radius of Mannoch Hill. They all have a general N.W. to N.N.W. trend.

Barlocco (Type 2 deposit).

There are two parallel veins of 1 to 2 m thickness trending 100° and dipping steeply to the south. They are situated to the south-west of the Criffel Granite in country rocks of grey-to-brownish greywackes of Wenlock age, close to the junction with the Lower Carboniferous (Fig. 34).

Gasswater (Type 1 deposit).

This, the largest deposit in the project area, consists of three major veins running N.W.-S.E. (the Main Vein, the West Vein and the Quarry Vein) connected by several crosscuts (Fig. 36). The veins can be traced for over 2 km, with an average width of around 3 or 4 m and occasionally attaining 10 m. Scott (1956) showed this N.W.-S.E. trend to correspond to the minor of the two regional faulting trends, the major one being north-easterly.

The country rocks of (red) Lower, and (buff) Upper, Old Red Sandstones and (buff) Calciferous Sandstone, are in fact in a highly faulted region

....close-to,

and just north of, the Southern Uplands fault. The folding is quite gentle, producing shallow elongate domes and basins in the above rocks and in the adjacent ones of Silurian, Old Red Sandstone and Carboniferous, igneous and sedimentary strata.

Glen Sannox (Type 1 deposit).

The immediate country rocks are Lower Old Red Sandstone in age and comprise red micaceous sandstones interbedded with coarse red conglomerates and purple mudstones. To the east are brown Upper Old Red Sandstone sandstones, and approximately 1 km to the west the 'Northern Granite'. The intrusion of the granite in Tertiary times had a strong influence on the structure of the northern half of the island, causing the sedimentary strata to be 'draped' about it. Hence the country rocks have a gentle easterly dip. (Fig. 37).

The veins occupy fault zones, and strike generally north or north-west, over a distance of approximately 1 km. However, they exhibit a pod-like or lenticular form, the richest deposits being at the intersection of two veins. The maximum width of vein recorded was approximately 8 m.

To the south-west, in rocks of the same age and lithology, about half way up Glen Rosa, small veinlets of baryte with northerly trends were also found.

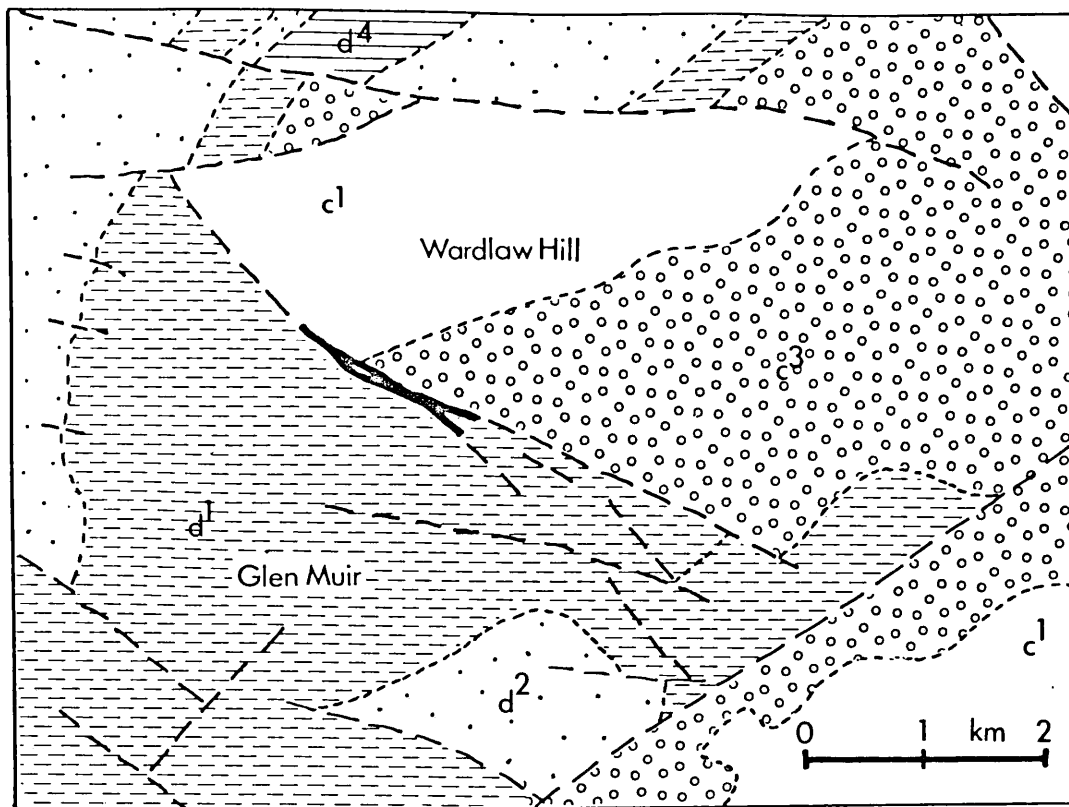


Fig.36 Geological sketch map of the Gasswater area.

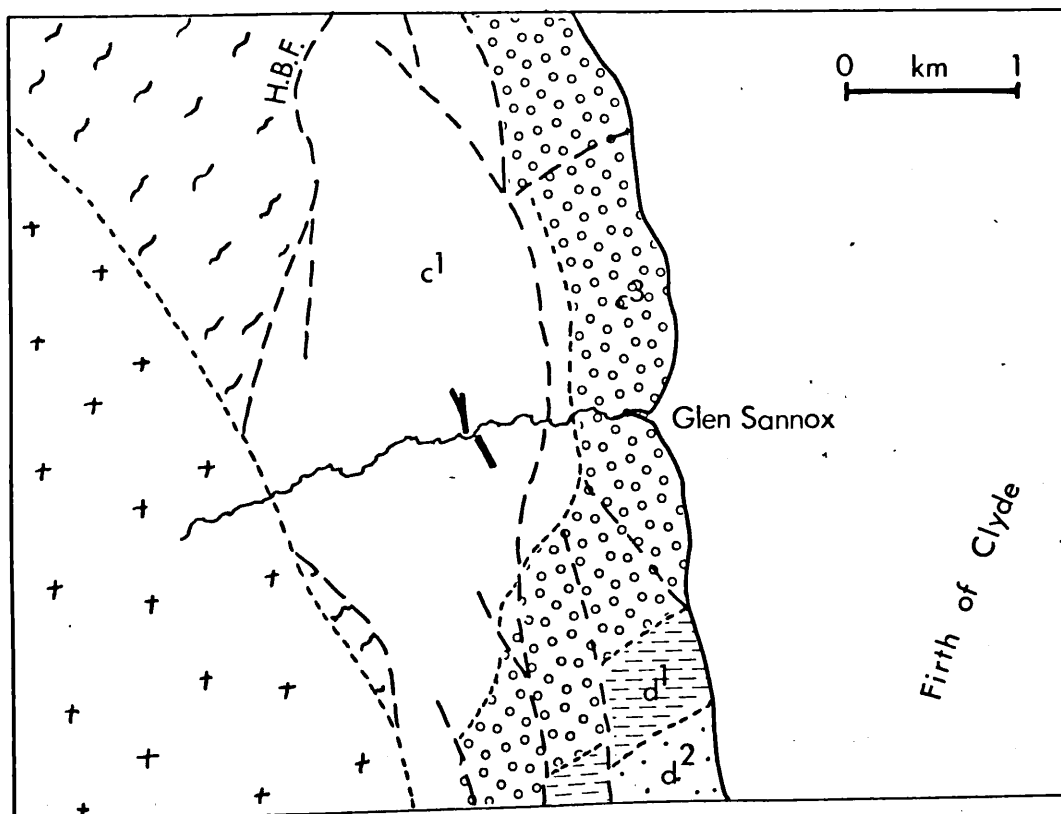


Fig.37 geological sketch map of the Glen Sannox area, Arran.

Hangit Man (Type 1 vein).

This minor vein occurs approximately 10 km to the south-west of Auchencairn mine, (Fig. 34) in identical country rock and with a similar trend. It is in a small coastal promontory and before recent severe erosion took place formed a natural arch of pure baryte. All that remains now is a pod approximately 3 m wide, 5 m high and 5 to 5 m long, accompanied by numerous stringers.

Hilderstone (Type 3 deposit).

The trend of the veins of this very old, and flooded, mine has not been recorded in the literature.

The country rocks to the vein, which contained a 2 m width of pure baryte, are limestones of the Limestone Coal group (Carboniferous Coal Measures), basaltic lavas and ash, and quartz-dolerite intrusives (of probable Permo-Carboniferous age). They are on the eastern limb of the Syncline which extends from the Ochil fault in the north, to Motherwell in the south. A series of east-west trending dykes, associated with the intrusives, cut the area.

Leadhills/Wanlockhead (Type 2 deposit).

The deposit is situated in an area of intensely folded rocks of Ordovician age. The Arenig is represented by various igneous rocks succeeded by cherts; the Llandeilo by an alternating sequence

....of

of black shales and cherts; and the Caradoc by the Lower Hartfell shales and the greywackes and mudstones of the Lowther Group. It is when the veins cut these greywackes that the mineralisation is richest, presumably as a result of the open fracture possible in these hard brittle rocks.

The regional control on mineralisation is believed (Walton, 1965) to be a large reverse fault (the Leadhills Line) which dips at 40° to the north-west. This fault is thought to persist over much of the Southern Uplands and link up with the mineralisation in the Cairnmore of Fleet district (e.g. Newton Stewart, and possibly Barlocco).

There are approximately seventy veins recorded in the area, the majority of which have a N.-S. or N.N.W. trend and dip to the east (Mackay, 1959).

Muirshiel (Type 1 deposit).

Some nine or ten veins, only one of which is large enough to have been mined, occur over a relatively small area around the Hill of Stake. The country rocks are grey and pinkish (hematite rich) trachytic and trachy-andesitic plateau lavas and ashes of Calciferous Sandstone age. They lie to the western edge of a Carboniferous basin and are intruded by trachytic bodies and north-westerly trending doleritic dykes, some of which are seen

....to cut

to cut the main baryte vein (Fig. 38).

The trend of the veins is variable; several have north-westerly trends, but some east-west, and the main vein a north-north-easterly one. The latter, which is up to 9 m wide, is truncated at its northern end by an east-west fault which was also found to be mineralised when mining operations reached it. All the veins are very steeply dipping.

Ochil hills (Type 1 and 3 veins).

This area contains numerous veins which mainly occur in altered andesitic and basaltic, lavas and ashes, around Blairlogie, Menstrie and Alva (Fig. 39). These volcanics lie in an antidual structure immediately to the north of the Ochil fault and on the eastern limb of the Strathmore syncline. The Ochil fault is a major east-west structure containing a quartz dolerite intrusion which outcrops in places along its length. To the south of the fault Carboniferous rocks outcrop in the N.-S. synclinal formation referred to earlier (see 'Hilderstone'). A small number of baryte veins occur outside the volcanics, in the Lower Old Red Sandstone sediments of the Strathmore syncline. No mineralisation, however, has been recorded on the Carboniferous side of the Ochil fault, any which may have occurred having presumably

....been

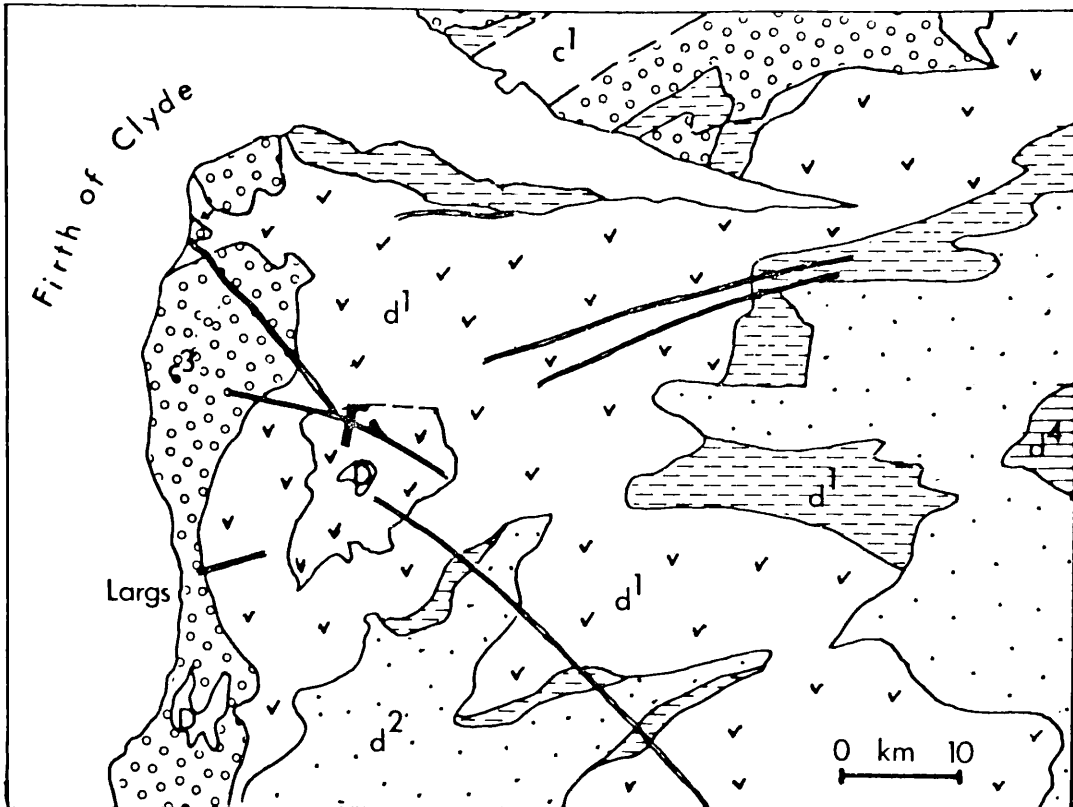


Fig.38 Geological sketch map of the Muirshiel area.

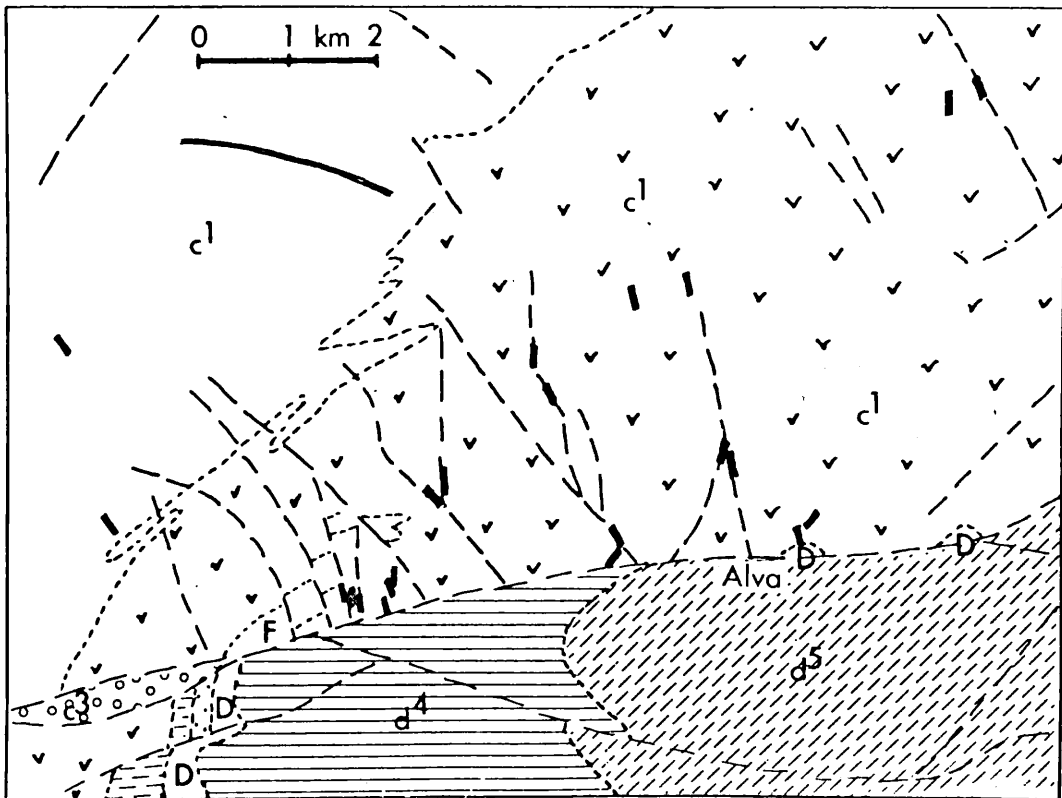


Fig.39 Geological sketch map of the mineralised section of the Ochil Hills.

been downfaulted by the 3000 m displacement estimated by Francis, et al (1970).

Lithological control on the mineralogies.

The above descriptions show a striking correlation between the mineral assemblages of Types 1 and 2, and the lithologies of the surrounding country rocks (Type 3 deposits are not considered with respect to their country rocks, but are thought to bear an association with the intrusives with which they are apparently spatially related): Type 1 assemblages occurring in ferruginous sandstones or lavas of Old Red Sandstone or Calciferous Sandstone age; and Type 2 assemblages in Ordovician or Silurian shales and greywackes.

In Kirkcudbrightshire three baryte veins occur less than 7 km away from each other. The veins at Auchencairn and Hangit Man occurring in the ferruginous grits of the Rascarrel formation (Calciferous Sandstone) have Type 1 mineralogies, whereas the deposit at Barlocco in Wenlock shales and greywackes (but in a fault which extends into the grits), has a Type 2 mineralogy. Another example of this apparent lithological control is seen in the Auchenstilloch district where the Lesmahagow inlier of Silurian rocks is surrounded by minor basins of Carboniferous and Old Red Sandstone sediments, and intruded by Lower Old Red Sandstone felsites. The lack of exposure of some

....of

of the veins is unfortunate, but the tendency is for those carrying white baryte with galena to occur in grey shales and mudstones, whilst those carrying pink baryte (in two instances with major hematite) may be seen in the red and brown Silurian sandstones, the pink felsites and also the Old Red Sandstone sandstones at the southern edge of the inlier. These different veins may occur within a few hundred metres of each other.

One deposit, within the project area, which was not visited was that at Forbidden Cave, on the east coast near Arbroath. Wilson, et al (1922) describe a vein of pink baryte which trends N.E. and dips to the S.E., in the cliffs of Lower Old Red Sandstone sandstone. This therefore fits the Type 1 category. This is also the case for the baryte veins in sandstones of Lower Old Red Sandstone near Nairn in Morayshire (J.G.Fitton, pers. comm.), close to the unconformable junction with the Moine.

This principle is found to hold true for baryte deposits in Ireland, and also the Welsh border district of England. In the latter case two distinct districts are recognised: to the west of the Stiperstones ridge in the old lead mining area of Shelve, the baryte is white, and accompanied by galena and calcite, occurring in the Mytton grits

....and

and shales of the Arenig; to the east of the ridge, the baryte field of the north-west portion of the Longmynd contains only pink baryte and is occasionally accompanied by traces of copper ore. Calcite and galena are rare, and the country rocks are chiefly coarse, red and purple sandstones with subordinate red and green argillaceous, and sandy shales.

In the County of Cork, Ireland, fault fissure veins of baryte with copper ores abound in the slates, grits and red conglomerates of the Upper Old Red Sandstone (e.g. at Deriennalomane, Derryfunshion and Caherolickane, Cashelfean, Mount Gabriel, Letter, Skeagh, Golan, Coolagh More, Ardrah and Dereengreanagh and, Drunmore and Mountain Common), especially when associated with the copper-bearing horizon of these strata. Where hematite is present, it is as the micaceous ore rather than being finely divided and dispersed, but galena and calcite etc. are absent until the fissures cut the overlying Carboniferous rocks. The Old Red Sandstone throughout Ireland has a common association with baryte, as an interstitial cement (J.McM.Moore, pers. comm.).

The veins with mineralogies corresponding with Type 2 deposits are not as easily sorted out, as similar mineralogies occurring in limestones,

....gneisses

gneisses and granites confuse the issue somewhat. However occurrences at Monaghan and at Waterford have Type 2 mineralogies and occur in the grits and states of the Upper Silurian, and Ordovician, respectively.

In Tipperary at the large Silvermines deposit, the veins of pink baryte with associated copper mineralisation tend to be found in the Old Red Sandstone; the Silurian rocks generally containing baryte with galena, sphalerite etc. (Hallissy, 1923). At the Tynagh stratiform ore deposit (Galway), the lead-zinc mineralisation is more or less confined to the Lower Carboniferous whilst the copper has a marked affinity for the adjacent faulted block of Old Red Sandstone. Baryte mineralisation occurs in both lithologies (J. McM. Moore, pers. comm.).

Structural controls on the deposits.

Various regional controls have been suggested in the past for the mineral deposits in Scotland: MacGregor et al, (1944) noted that the Muirshiel, Gasswater, Leadhills, Wanlockhead and Auchenstilloch deposits occurred in a north-westerly 24 km wide belt which stretched from the North Pennine mining district in the south, to the Loch Fyne district in the north. This coincided with the southern trail of the Mull dyke swarm and so a genetic relationship between the two was postulated, and

....hence

hence a Tertiary age thought probable for the mineralisation.

More recently, Russell (1971) postulated the existence of north-south geofractures, in Ireland and Scotland, to which he relates certain base-metal deposits. In Ireland the correlations are more convincing than in Scotland, where fewer base-metal deposits exist, and several other deposits do not show any such correlation. The geofractures suggest a common source for the deposits which lie along their length. However, it is seen that the Leadhills/Wanlockhead and the Ochil Hills deposits both lie on Russell's Number 5 geofracture: these have mineral assemblages of Type 2, and Types 1 with 3 respectively, and are therefore likely to have dissimilar origins.

The author feels that whereas Russell has based his arguments for the existence of these geofractures on reasonable structural evidence, any attempt to draw straight lines through mineral locations usually yields only a fortuitous correlation. For example an excellent straight line may be drawn to connect the baryte deposits of Glen Sannox, Muirshiel, the Ochil hills and Forbidden Cave (Arbroath), all of which are Type 1 deposits, which is coincidentally sub-parallel to both the Southern Upland and Highland Boundary faults.

....If

If a regional influence were sought for the deposits, in the Midland Valley at least, the best relation is to the major synclinal structures of the area, i.e. the Carboniferous trough and the Strathmore syncline (O.R.S.) numbered 1 and 2 respectively in Fig. 42. The deposits occur 'up-structure' spread out along the flanks of the troughs.

On a local scale, the correlation of mineralised faults with anticlinal or domal structures is good: figures 40 and 41 show sections through the Auchinstilloch and Gasswater areas respectively. At the latter deposit it has previously been recognised that a monoclinial fold appeared to exert some control on the localisation of mineralisation (Scott, 1967). Also that, as with most fissure-infill veins in normal faults, the mineralisation was more extensive along steeper sections of the fault, more space being available between the fault sides (Anderson, 1947).

The veins at Blairlogie and Menstie in the Ochil hills occur in lavas which form an anticlinal arch on the southern limb of the Strathmore Syncline (Waterson, 1965; Francis, et al, 1970) continuation of this structure north-eastwards would place the Forbidden Cave deposit in a similar position. The Aberfoyle deposit is located on the opposing limb

....of

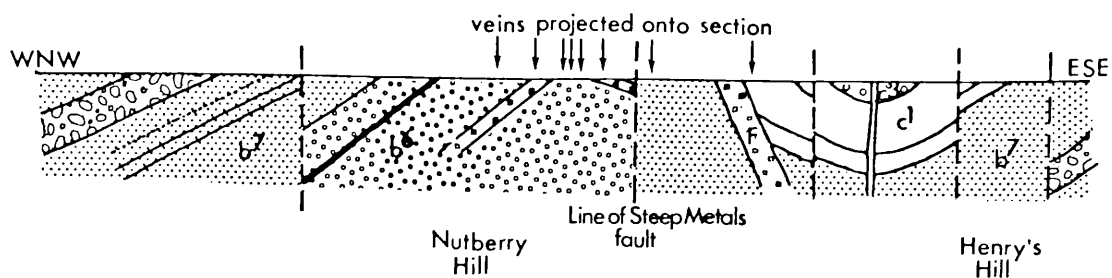


Fig.40 Section across the Auchenstiloch area, showing the association of the veins with the felsite intrusives and anticlinal structure. (horizontal scale 1":1mile)

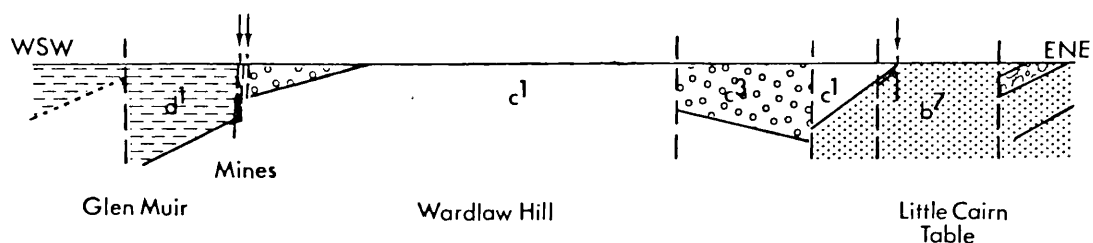























Fig.41 Section across the Gasswater area. (horizontal scale 1":1mile)

Key to figs 34 to 41 .

	raised beach		Upper O.R.S.		Dalradian
	Coal Measures		Lower "		dolerite intrusion
	Millstone Grit		lavas		felsite "
	Carb. Lst. Series		Upper Silurian		granite
	Calciferous Sst.		Lower "		baryte vein
	lavas		Ordovician		geol. boundary
					uncertain "
					fault
					dyke

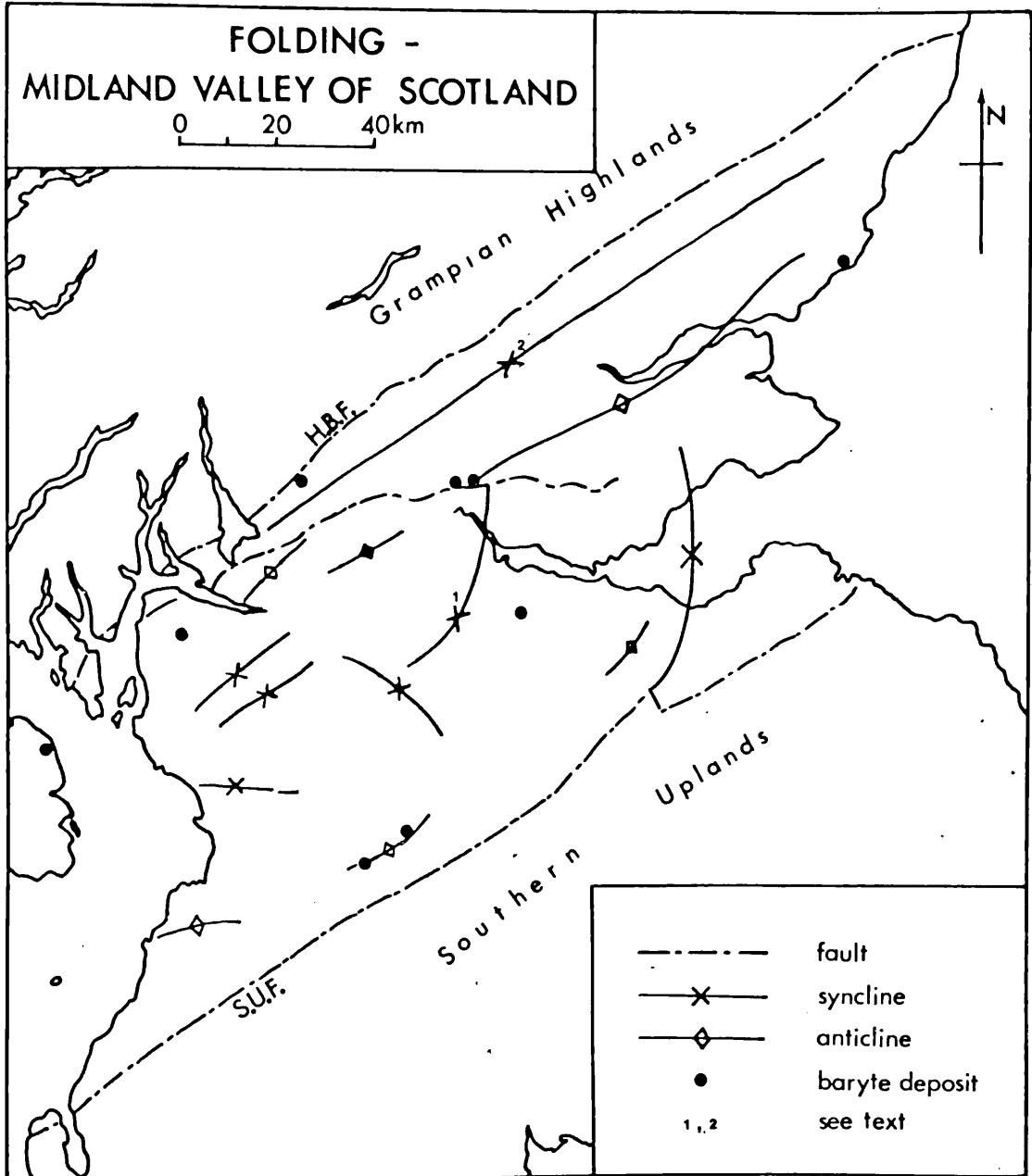


Fig. 42

of the Strathmore syncline, just south of the Highland Boundary fault.

Although there are no marked anticlinal structures in the Muirshiel area, the surrounding areas are markedly synclinal, containing younger strata. In Arran the veins occur in a strip of the Palaeozoic. However, the Highland Boundary fault passes close-by (Fig. 37) and so a similar position to the deposit at Aberfoyle probably existed prior to the Tertiary granitic intrusions on Arran.

Possible mechanisms for deposition of the veins.

The fluid inclusion studies presented in Chapter 5 show that the baryte was deposited by very low-temperature fluids. Consequently, simple temperature reduction as a cause of precipitation is not easily envisaged. The other factors which must be explained by any hypothesis of possible methods of deposition are as follows:

1. the invariable occurrence of the veins in faults;
2. the intimate association of faulting with each generation of baryte, as attested by the occurrence of slickensides between subsequent generations of baryte;
3. the episodic or discontinuous nature of the veins, producing numerous generations of mineralisation;
4. the restriction of the mineralisation to open fractures in the country rocks.

It seems likely that, rather than the migration of mineralising fluids being the initial cause of the faulting, the faulting provided access for the solutions. As pointed out by Sibson et al (1975), seismic faulting is commonly accompanied by dilatancy of the adjacent rocks and fluid diffusion into them, from depth. This occurs to such a degree that not only do the rocks become saturated, but during movement on the fault sizeable outpourings of groundwater occur along the fault traces (the location of easiest pressure relief on partial release of the shear stress).

The brecciation of angular rock fragments in the veins, which for the most part are in faults of very little displacement, suggests perhaps that hydraulic fracturing of the wall rocks has occurred (Phillips, 1972).

In agreement with these authors evidence from the field observations points to the conclusion that the faults played an active part in the mineralisation, rather than a passive one of solely presenting a permeable conduit. Furthermore, the episodic but continual nature of seismic activity provides a good explanation for the countless generations of mineralisation which have occurred.

The above hypotheses would therefore necessitate the mixing of waters drawn from depth with those

....present

present at near-surface levels. This would provide a possible method of precipitation as an alternative to falling temperatures. An argument against the theory of mixing of fluids to produce mineralisation is that the initial precipitation would effectively seal the channelways against further influx of fluid (C.Carlon, pers. comm.). This however, would not be the case where faulting is active and contemporaneous with the mineralisation.

The argument that precipitation by mixing would cause only cryptocrystalline materials to form, as was noted by Clowes (1889) in the Newcastle-upon-Tyne coal mines where barium chloride mine waters had reacted with sulphate-bearing waters, is countered by Hallissy (1923): if sulphate were in excess in the waters of a fissure, the continued introduction of soluble barium salts would lead to the gradual accumulation of barium sulphate, and only when the supersaturation point of the salt had been reached and exceeded would a precipitation take place. Hence megascopic crystals are possible. Furthermore the presence of chlorides in solution would increase the solubility product of baryte (Uchamey~~#~~shvili, et al 1966) and hence also retard precipitation. Actual evidence that a change in chemical conditions can cause an immediate precipitation producing megascopic crystals is provided

....by

by the veins and breccias in the Lower Magnesian Limestone of the English Permian (Harwood, 1978). Here barium-bearing solutions were 'injected' under loading pressure, from unconsolidated calcareous mudstones, into dolomitised limestone and crystallisation of the sulphate occurred rapidly enough to cement and support both clasts and rafts of the dolomite.

The age of the deposits.

The ages of the baryte and lead-zinc deposits of Scotland has been a point of contention for many years. This has been mainly due to the lack of Permian, and absence of Mesozoic strata in the areas concerned: with the exceptions of the dykes of assumed Permo-Carboniferous age reported to be cut by the mineralisation at Black Craig mine, Wanlockhead (Temple, 1956), and the atypical deposit at Hilderstone which occurs in Carboniferous Limestone rocks; the youngest rocks cut by baryte veins are Calciferos Sandstone in age (at: Auchencairn, the continuation of the fault at Barlocco, Hangit Man, and Muirshiel). Hence, Lower Carboniferous must be the lower limit for the possible ages of the veins. The upper limit is ill-defined. At Muirshiel and Glen Sannox, north-westerly trending dolerite dykes and seen to cut the veins and therefore place a probable lower Tertiary upper limit.

MacGregor, et al (1944) attempted to find alternative lines of evidence which would throw some light on the problem. They noted that the veins in Renfrewshire, Ayrshire and Lanarkshire follow the trends of crush-lines of faults of post-Coal Measures age seen in surrounding areas, and which are younger than associated E.N.E. and N.E. faults of Permo-Carboniferous age. Also cited was the coincidence of several deposits being within a 24 km wide belt delineated by the dykes of the Mull dyke swarm and stretching across southern Scotland. From this a probable Tertiary age was assigned to these deposits. However, Speight and Mitchell (1979) have shown many north-westerly trending dykes, in north west Scotland, to be Permo-Carboniferous in age.

For the veins in the southern Ochil hills; the N.N.W. to W.N.W. trending ones of baryte with minor amounts of copper were thought Tertiary (having the "Tertiary trend"), whilst those with roughly E.-W. trends and mineralogies comprising major calcite with subordinate baryte and sulphide ores, were thought to be Permo-Carboniferous in age (the trend being similar to that of the Ochil fault). Francis, et al (1970), endorsed these findings.

Scott (1956) showed both the folding and faulting of the Gasswater/Auchenstilloch area to be

....related

related to the Line of Steep Metals fault which, he proposed, indicated an Hercynian age for these structures. In the Leadhills area, Temple (1956) considered that the veins could not be accounted for by Caledonian movements; this was also supported by the observation that the veins post-dated the Caledonian dykes of the area.

In the present study the deposits have been spatially related to the regional and local folding patterns (Fig. 42). These folds affect the whole of the Carboniferous and occasionally the Permian, and hence it is suggested that a Permo-Carboniferous age must represent the lower limit.

Isotopic age dating.

The lead isotope dates produced by Moor bath (1962) for galenas from three deposits in Central and Southern Scotland are as follows:

Wanlockhead, Dumfriesshire	320 \pm 50 m.a.
Silver Ridge Mine, Kirkcudbrightshire	320 \pm 80 m.a.
Nutberry Hill Mine, Lanarkshire	310 \pm 60 m.a.

The Holmes-Houtermans single-stage model was used in the generation of these dates (ref. Russell and Farquhar, 1960); a model which has come under severe criticism in recent years as its basic assumptions are not now considered credible for epigenetic and syngenetic ore bodies (Richards, 1971).

....Furthermore

Furthermore it can be seen that if revised data for the basic constants used in the model are employed (ref. Slawson and Russell, 1967), the new dates indicated are geologically not plausible, i.e. late Tertiary (Fig. 43). It is however interesting to note that the original isotope ratios measured by Moorbath give almost identical values for Wanlockhead and Silver Ridge Mine. This would seem to lend support to the theory that there is some genetic relationship between the ores of the Leadhills/Wanlockhead district to those of Kirkcudbrightshire and Wigtownshire (viz. the postulated connecting reverse fault referred to earlier).

Recalculation from the same isotope ratios using a two-stage model, that of Stacey and Kramers (1975), yields older ages than those from the single-stage model, i.e. 128 m.a., 128 m.a. and 56 m.a. respectively. It would seem that if lead isotopes are to yield useful data for such deposits, the suggestion of Richards (1971) must be heeded: that what is required is a multistage model allowing more or less complete mixing of leads at each stage.

Potassium-Argon isotopic dating as a method for dating ore deposits is one which must be used with care and a full knowledge of the possibilities

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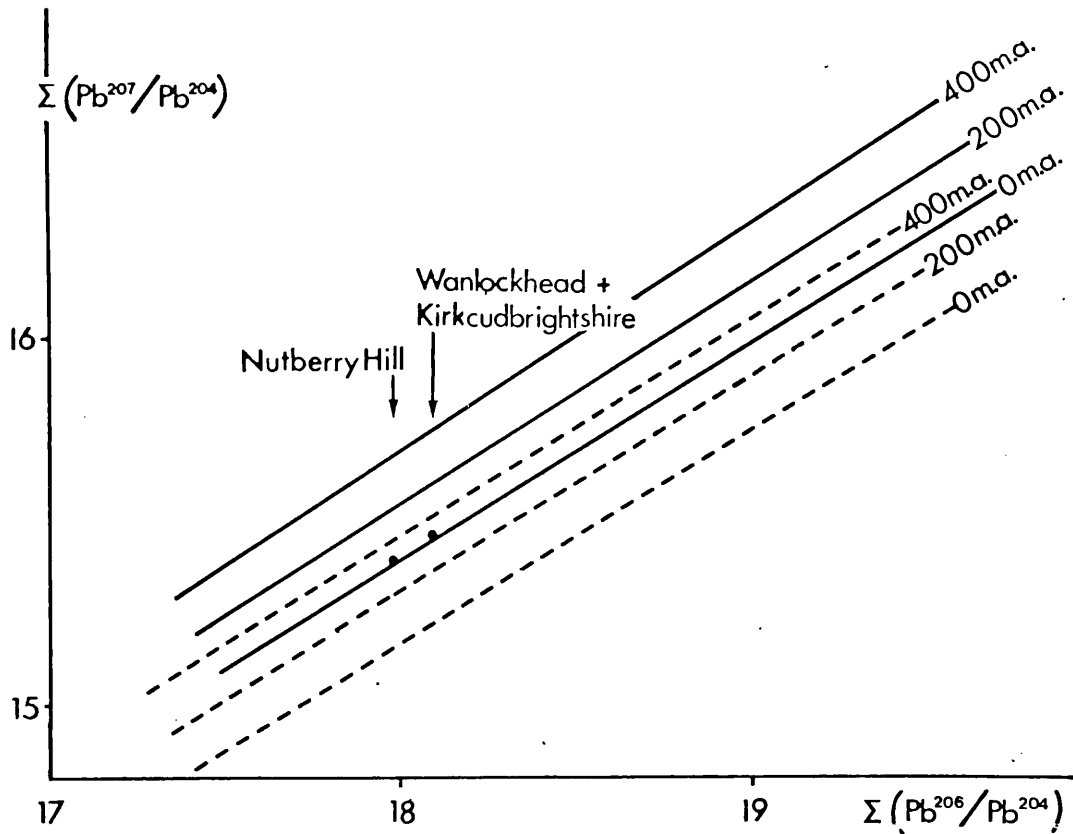


Fig.43 Moorbath's (1962) lead isotope data for Wanlockhead, Kirkcudbrightshire and Nutberry Hill (Auchenstilloch) plotted on the Holmes/Houtermans diagram.
Dotted isochrons - as used by Moorbath; solid isochrons - from revised data for isotope ratios and age of earth.

and limitations governing its use. In particular it was thought until recently that very low temperature deposits, such as those of the present study (see Chapter 5), would not be capable of 'resetting the argon clock' of potassium-bearing minerals in the enclosing wallrocks. The present study, along with several previous ones (e.g. Ineson and Mitchell, 1974 and 1975), have produced data which show that this sort of deposit can indeed lend itself to the above technique: when several samples taken from different parts of the same deposit, and with possibly differing mineralogies and K_2O contents, yield mutually concordant dates then it must be conceded that some significant isotopic event in the evolution of that deposit has been recorded. In the absence of evidence to the contrary this may be taken to be the age of formation of the deposit. The suggestion that purely physical effects i.e. deformation, could be the mechanism causing argon loss (Dalrymple and Lanphere, 1969) is perhaps worth noting in the present circumstances.

The samples chosen for this study ^{were} taken mainly from wall rock or fault gouges which had been completely enclosed within the mineralisation, and which contained minerals that not only contained enough potassium to make potassium and argon determinations feasible, but which were known to retain argon under normal geological conditions. They

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also had to be relatively resistant to alteration and dissolution by groundwater. Illite and muscovite (also sericite) contain high proportions of potassium and have also been found to satisfy these other criteria (Hurley, et al 1963). Doubts have been cast on the validity of ages obtained from chlorites however (Shepherd, et al 1976).

These minerals were concentrated in the samples by allowing settling of the crushed sample material in pyrex beakers of de-ionised water. By virtue of their platy habit these minerals tend to settle on top of the angular grains of the sediment. Hence by sequentially scraping off the top layers and re-sedimenting this material, a "clay-concentrate" is obtained. X-ray diffraction techniques were used to determine the mineralogy of each sample.

The K-Ar isotope data for those deposits selected for the study are presented, as follows:

Potassium and argon measurements were made at the
Univ. of Newcastle-upon-Tyne, by Dr.J.G.Mitchell.

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Table 1.

Sample	details	mineralogy	%K ₂ O	age (m.a.)
Barlocco				
D371	Partially replaced wall rock adjacent to baryte min ⁿ .	Sericite-quartz	4.42	250 [±] 5
D372	Partially replaced wall rock completely enclosed by min ⁿ .	Sericite-quartz-ankerite	4.55	230 [±] 4
D373	Clayey wall rock completely enclosed by baryte.	Sericite-quartz-ankerite	5.58	219 [±] 3
D374	Wall rock adjacent to baryte mineralisation.	Sericite-quartz-ankerite	4.82	250 [±] 3
Gasswater				
[D45	Lwr. O.R.S. sandstone wall rock close to West Vein.	Muscovite	8.91	423 [±] 8
D345	Calcif. Sst. sandstone wall rock adjacent to Main Vein.	Quartz-illite	1.17	305 [±] 6
D346	Clay gouge within Main Vein.	Illite-quartz	7.12	270 [±] 5
D348	Clay gouge within Main Vein.	Illite-quartz	5.55	284 [±] 4
D349	Clay gouge within Main Vein.	Illite-quartz	2.77	275 [±] 4
D350	Clay gouge within Main Vein.	Illite-quartz	7.07	287 [±] 3
D351	Calcif. Sst. shale wall rock adjacent to Main Vein.	Sericite-quartz	4.40	261 [±] 5

Sample	details	mineralogy	%K ₂ O	age (m.a.)
Glen Sannox				
D420	Tip spec ⁿ . of sandstone completely enclosed by min ⁿ .	Muscovite-quartz	5.56	224±4
D421	Tip spec ⁿ . of mudstone completely enclosed by min ⁿ .	Illite-quartz	3.62	213±2
D422	Tip spec ⁿ . of mudstone completely enclosed by min ⁿ .	Illite-quartz	4.84	210±2
D500	Clay gouge from principal vein.	Illite-quartz	5.84	201±3
D501	Upper O.R.S. ⁿ sandstone 150 m from N ⁿ . Granite	Quartz-sericite	4.48	84±2
D502	Upper O.R.S. sandstone 200 m west of veins.	Quartz-sericite	2.46	309±5
D505	Clay gouge from an offshoot to the principal vein.	Quartz-baryte-illite	3.33	209±3
D506	Tip specimen of wall rock completely enclosed by min ⁿ .	Quartz-baryte-illite	3.60	214±3

....Muirshiel

Sample	details	mineralogy	%K ₂ O	age(m.a.)
<u>Muirshiel</u>				
D205	Altered lava adjacent to vein.	Quartz-feldspar-illite	5.31	285 \pm 3
D242	Altered lava adjacent to vein.	Quartz-feldspar-illite	4.38	286 \pm 4
D313	Clay gouge from within vein.	Quartz-illite	7.53	229 \pm 3
D314	Clay gouge from within vein.	Quartz-illite	3.33	213 \pm 3
D315	Clay gouge from within vein.	Quartz-illite	6.12	220 \pm 3
D315A	Clay gouge from within vein.	Quartz-illite	6.25	240 \pm 3
[D337	Dolerite dyke cutting principal vein.	Whole rock	0.07	-]

The data enclosed in parentheses are from samples not expected to reveal the age of mineralisation, but ones which were collected to aid the interpretation of the remaining data:

D45 was collected early in the study, and showed that micas from the wallrock a few centimetres away from the vein had not been affected by the mineralisation; the Silurian age obtained probably reflects the Caledonian granite from which the sediment was derived.

D501 and D502 were collected to establish whether the Tertiary (Macintyre, 1973; Mitchell and Reen, 1973) Northern Granite on Arran had overprinted the mineralisation date, this has apparently not happened as rocks closer to the granite from the veins themselves, yielded pre-mineralisation ages. The sandstones close to the granite were however significantly overprinted.

D337 is from a dyke which displaces the baryte vein at Muirshiel. This is the only definite instance in which a rock post-dates one of the deposits, but unfortunately no age could be calculated as the K_2O content of the dyke was too low.

From the other results, D205 and D242 are samples which were not enclosed within the veins, and also which contain feldspars which may not have

.....been

been totally re-set during mineralisation, a feature of this technique noted by Halliday (1977). Consequently their ages are not concordant with the remaining Muirshiel samples. . Again at Gasswater, the samples (D345 and D351) from only partially affected wall rock yielded discordant ages, and hence, of the four dates for Barlocco those of D371 and D374 must be considered suspect on similar grounds.

Over the four deposits there are then a total of sixteen samples in which confidence may be placed. This is not a sufficient number to establish the respective dates very precisely, however the general periods are outlined and these are shown in Fig. 44, along with previous data for certain other of the deposits (Ineson and Mitchell, 1974).

It should be noted that Ineson and Mitchell found no difference between the ages of the veins of differing mineralogies (and trends) in the Ochil hills, which conflicts with the hypothesis of the existence of two separate mineralising episodes in this area (MacGregor et al, 1944).

Two periods, a Triassic and Permo-Carboniferous one are depicted in Fig. 44, with apparent disregard to the mineralogies or geological settings of the deposits. The Hercynian is a recognised period of important mineralisation in Britain (Dunham, 1952), and Mitchell and Halliday (1976) have established

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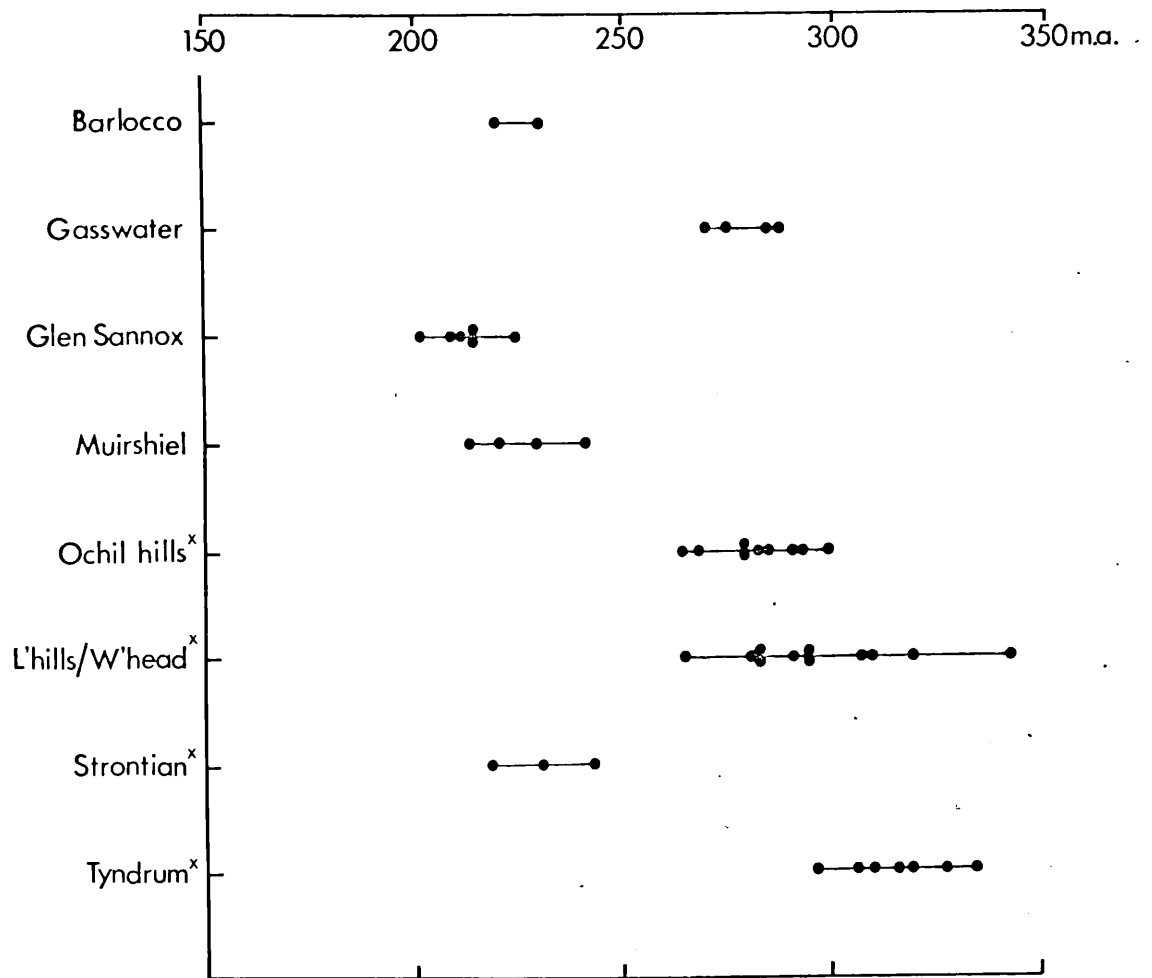


Fig.44 Potassium-argon dates for Scottish baryte deposits
(^x -data from Ineson and Mitchell, 1974).

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the existence of a province of hydrothermal activity of Triassic to early Jurassic age: the deposits span the Atlantic and have been related, by the authors, to the graben subsidence associated with the early opening of the North Atlantic; the tensional features extending north from the zone of active spreading. The dates therefore correspond with those of known hydrothermal episodes and do not contradict any geological evidence at any of the deposits studied.

Chapter 4 : The geochemistry of the deposits

Chapter 4. The geochemistry of the deposits.

a) The Wall rocks.

The observations of limited wall rock alteration at each deposit, as judged by mineralogical changes, were presented in Chapter 2. In this section the chemistry of the wall rocks, at intervals away from the veins, is investigated using the standard analytical techniques of Atomic absorption spectroscopy, X-ray fluorescence spectrography, and u.v. emission spectrography.

Sample selection was biased against material containing visible mineralisation, however it was not possible for this to be totally successful as many fine veinlets ubiquitously infiltrate the country rocks. This fact, together with a natural lack of exposure around many deposits, made it virtually impossible for totally unaffected, but lithologically similar, samples to be taken for chemical comparisons. The normal strict precautions were taken to avoid any contamination of the samples.

Three deposits were selected for this study on the basis of good exposure and the variation in lithologies between them:

Mu 1. is a 1 m traverse into the altered trachytic lavas adjacent to a 1 m wide offshoot to the main vein at Muirshiel.

Mu 2. is a 30 cm traverse away from the same vein but approximately 30 m from the position of the

....Mu 1.

Mu 1. traverse.

Ga 1. is a 30 cm traverse away from the Gasswater West vein into the Calciferous Sandstone sandstones.

Ga 2. traverses 5 m into the same sandstone as Ga 1., but also includes brecciated samples enclosed within the vein and heavily veined wall rock adjacent to the main mineralisation.

Bl 1. is a 1 m traverse into the very altered andesitic lavas adjacent to a 1 m wide vein near Blairlogie.

The results are presented in Figs. 45, 46, 47, 48 and 49. (N.B. The symbols for each element remain constant throughout).

There is no apparent regular variation of the elements, as a function of distance from the vein, with the exception of barium which in three traverses showed a rapid decrease away from the veins. There were however, several individual cases where elements showed apparent increases in concentration towards the veins, i.e.: zinc in Mu 1., Ga 1. and Ga 2; Copper in Mu 2., Ga 1., Ga 2. and Bl 1; iron and manganese in Ga 1. and Ga 2. It is suspected that the majority of the remaining variations in element concentrations are unrelated to the mineralisation, in view of their apparent random nature.

In order to make a systematic check of the observations from the diagrams, correlation coefficients

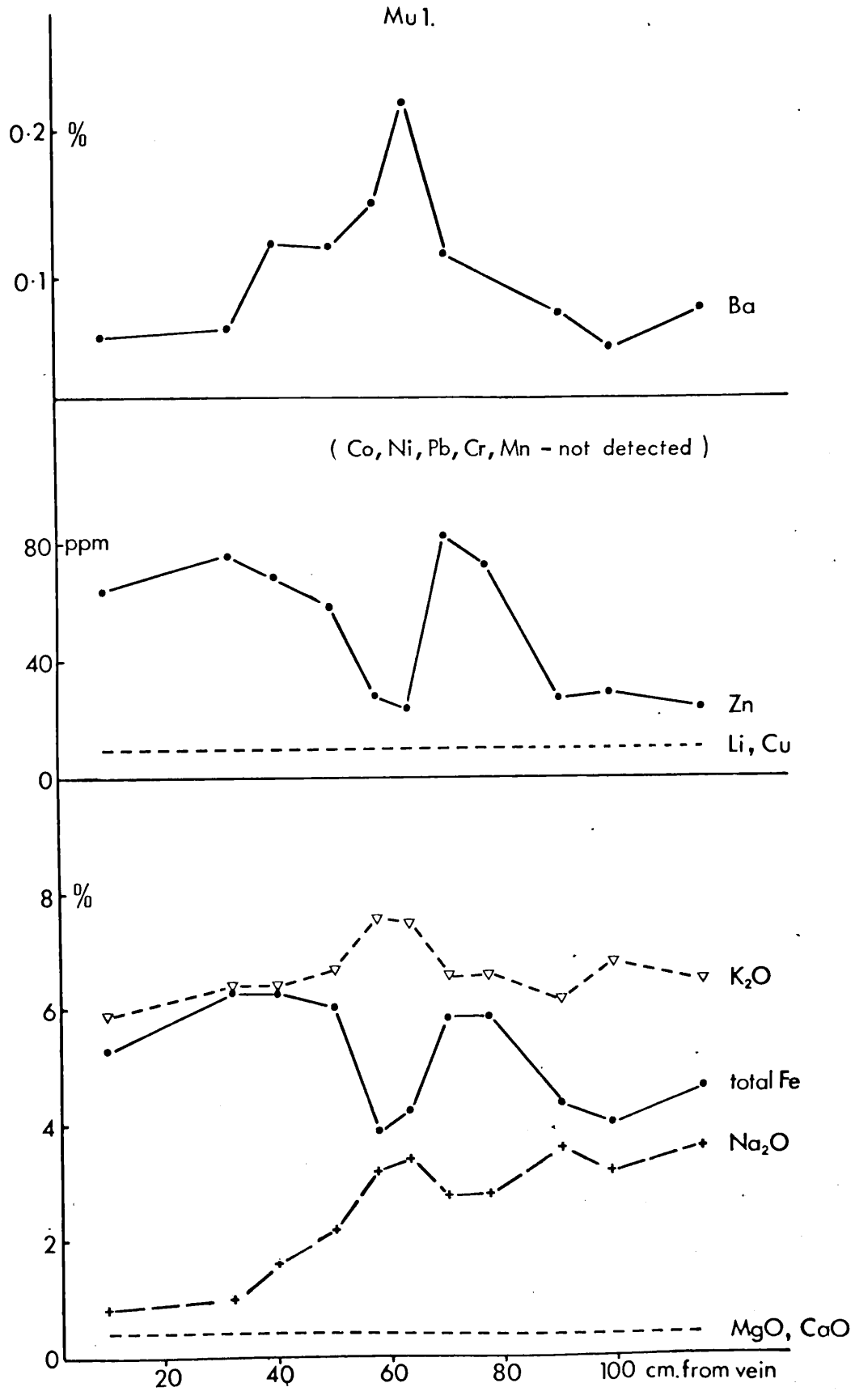


Fig.45 A wallrock traverse in the altered lavas adjacent to the Muirshiel main vein.

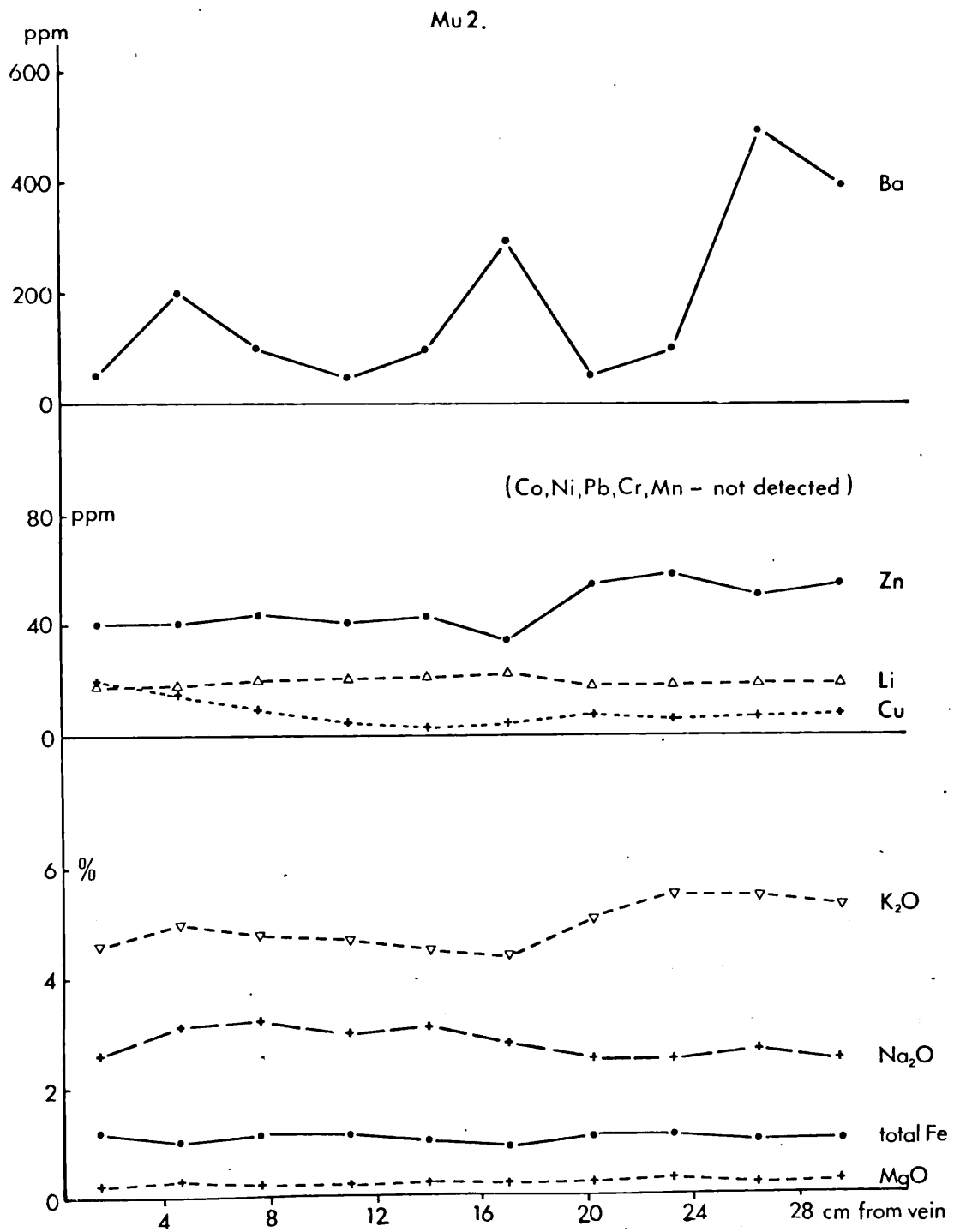


Fig.46 A wallrock traverse on a small scale, in the altered lavas adjacent to the Muirshiel main vein.

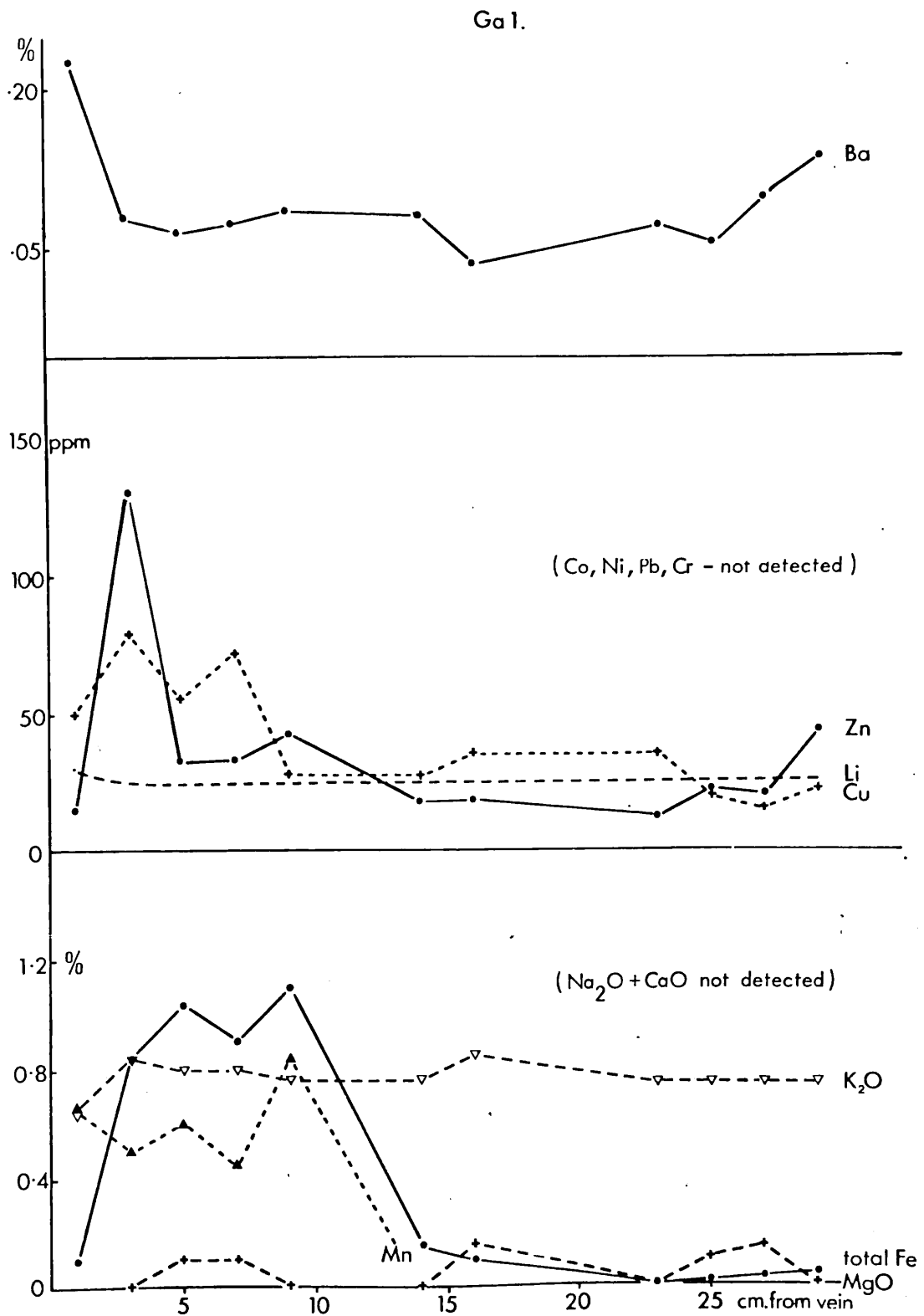


Fig. 47 A traverse on a small scale, in the light brown sandstone of the southern wall of the Casswater West vein.

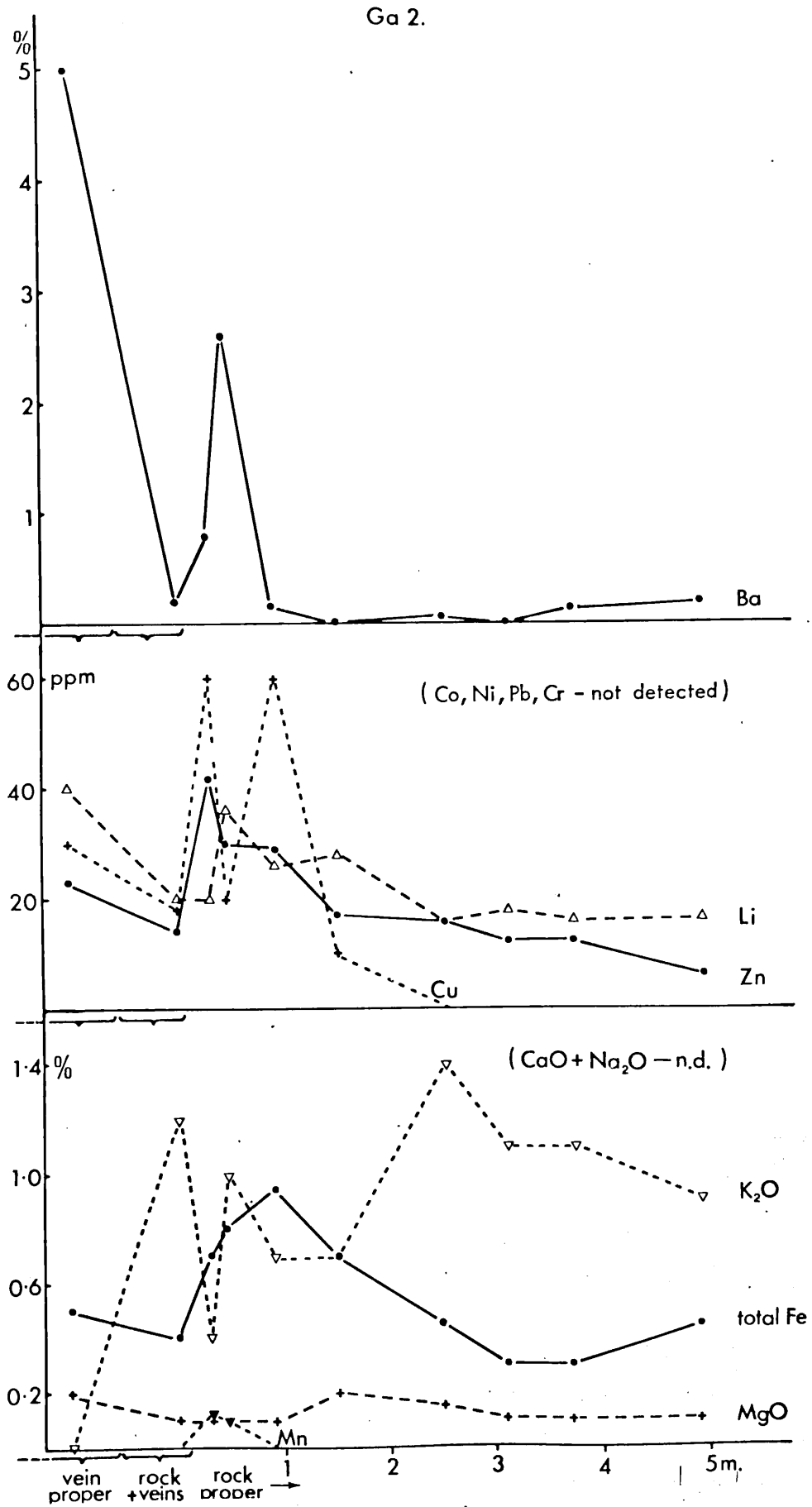


Fig. 48 A wallrock traverse on a medium scale, in the light brown sandstone which forms the southern wall to the Gasswater West vein.

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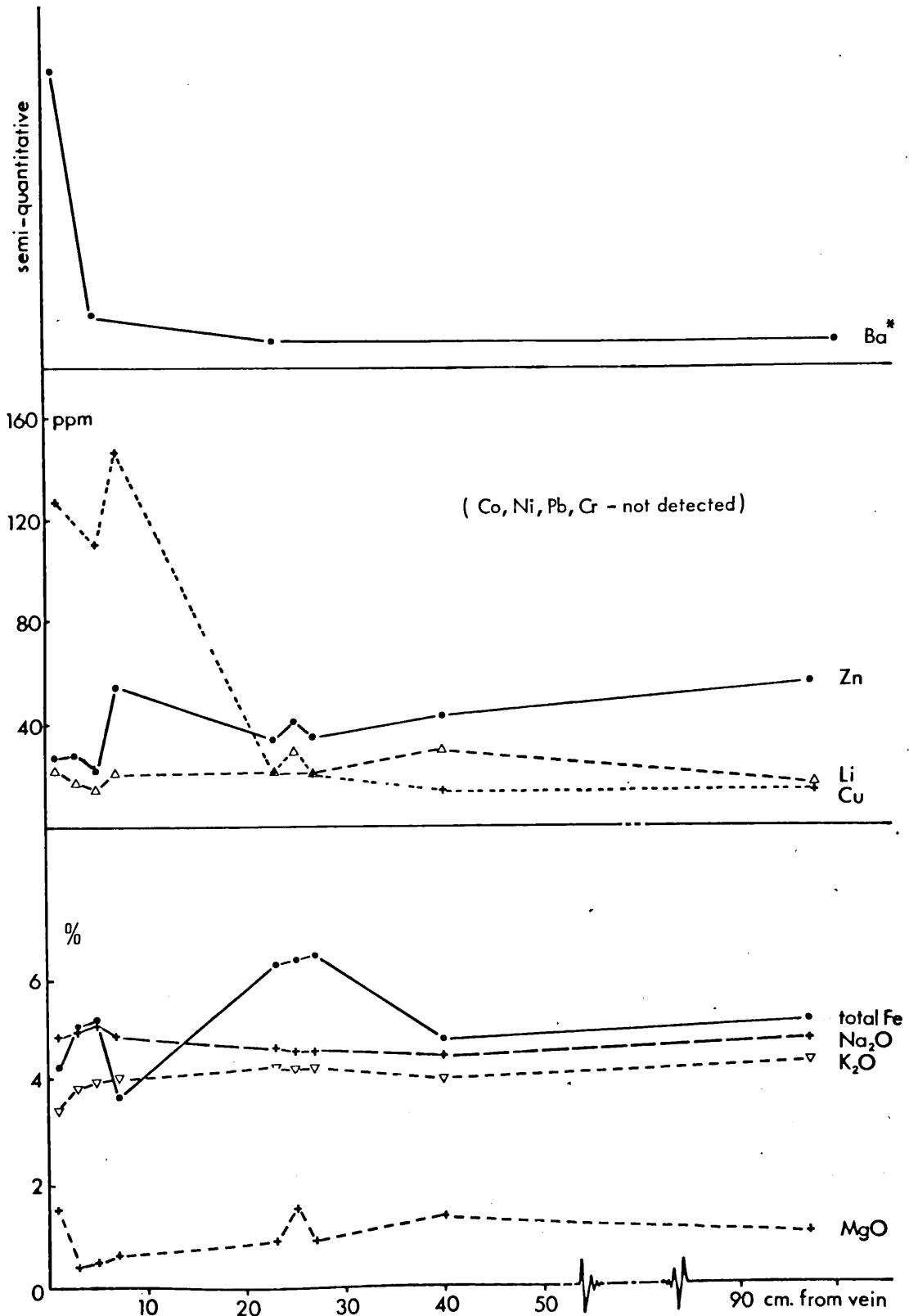


Fig. 49 A wallrock traverse in the altered intermediate lavas adjacent to a 1m. wide vein near Blairlogie, in the Ochil hills.

efficients were computed between all elements in each traverse. A 99% significance level was accepted as being meaningful (This rather high percentage was necessary in order to ensure that no fortuitous correlations were made as a result of the rather limited sample sizes).

The results confirmed the initial observations, the only correlations indicated by the calculations were those between chemically similar elements, such as Cu and Fe, or CaO and MgO. Even these rarely gave coefficients greater than 0.9 and were not consistent between traverses. Hence the variations are interpreted as representing normal chemical (or mineralogical) changes within a lithology.

The veins do apparently affect the wall rock which has been completely, or partially enclosed within the vein or, as in some cases, which occurs within a very short distance from the vein (i.e. One or two centimetres. viz. Figs. 29, 47 and 48). However apart from an influx of baryte, limited silicification is all that can be said to occur.

There is no evidence for a suggestion of derivation of barium from the surrounding wall rocks, by a leaching process. For this to be the case the barium concentrations would have to increase significantly as the traverses stretch away from the
....vein,

vein, as was found at the Zambarak ore deposit, Central Asia (Lur'ye, 1963).

Veins of such simple mineralogy would not however, be expected to produce varied mineralogical changes in their associated wall rocks. Furthermore, fissure infill veins do not give rise to large-scale chemical dispersion patterns such as the ones described by Gwosdz and Krebs (1977) at the Meggen ore deposit (Germany), or by Russell (1974), at the Tynagh Stratiform orebody (Ireland) where a manganese dispersion halo of some 7 km radius was detected. (N.B. It was noted that at Gasswater a manganese halo of approximately 20 cm occurred, probably related to the late manganese minerals recorded at this deposit, it was not found elsewhere). The lithologies of the wall rock would also prove adverse to alteration, sandstones being less amenable to metasomatic changes than say the Waulsortian 'reef' limestones at Tynagh.

The three deposits chosen for the traverses were all Type 1 deposits, due to the lack of exposure of any major Type 2 vein. From tip specimens at Type 2 deposits it is obvious that a more effective, though still weakly metasomatic, alteration of the wall rock has occurred, and may be classed as "propylitic" (Hemley and Jones, 1964).

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Its assemblage including ankerite, calcite, sericite, pyrite, chalcopyrite and quartz.

Although the extent of the alteration cannot be seen, the chemical difference between the metasomatised rock and an unaffected one, may be assessed by comparing the average of six analyses of tip specimens from Barlocco, with the average of a large number of Silurian greywackes from the Kirkudbrightshire area (Alsayegh, 1971):

Table 2. A comparison of partial chemical analyses for Southern Upland greywackes (Silurian).

Element	Ave. compn. of unmineralised greywackes from the Kirkudbrightshire area (Alsayegh).	Ave. compn. of six samples from close to the Barlocco veins.
MgO	4.71%	4.38%
CaO	5.14%	11.03%
tot.Fe	6.27%	5.95%
Na ₂ O	2.18%	0.42%
K ₂ O	2.05%	3.02%
Zn	71 p.p.m.	16 p.p.m.
Cu	20 p.p.m.	87 p.p.m.

What is found is that whereas the calcium content of the Barlocco samples is double that of the general one, the magnesium and iron contents are almost identical. The Na₂O content is less than one quarter of the regional value, but that of

....K₂O

K_2O is 50% higher. In the trace elements, copper is over four times the regional average.

These comparisons therefore argue for the introduction of calcite and chalcopyrite from a vein source, but the derivation of the constituents of ankerite and pyrite from the country rocks: the presence of sedimentary or diagenetic pyrite has been noted in the Riccarton beds (graptolitic shales) of the Silurian (Rust, 1965), and in the Ordovician greywackes (Kelling, 1971) so possible sources of iron for both Barlocco and Leadhills respectively, do exist. The high potassium, relative to sodium, is probably the result of potassium fixation in sericite (and illite), the sodium having apparently been leached from the rocks.

b) The baryte.

The orthorhombic cells of the baryte crystal structure comprise sulphate ions, as tetrahedra, linked by barium ions, each barium ion coordinated by twelve oxygens from seven different sulphate groups. The minerals celestine and anglesite, have similar cell dimensions and have been shown to be isostructural with baryte (James and Wood, 1925). They have also been shown to form complete solid solution series with baryte, although their natural occurrences are limited essentially to end-members of the series (Hanor, 1968; Boström, et al, 1968).

Several other compounds have the general structure of baryte: $(\text{NH}_4)\text{ClO}_4$, KClO_4 , RbClO_4 , CsClO_4 , TlClO_4 , KMnO_4 , BaSeO_4 , PbSeO_4 (kersterite), BaCrO_4 , SrCrO_4 and $(\text{K,Cs})\text{BF}_4$ (avogadroite). (Bragg, 1937; Deer, et al, 1962). The structure of anhydrite is dissimilar to that of baryte as a result of the smaller calcium ion, however, a partial solid solution is found to exist, up to approximately 6% CaSO_4 being able to substitute (Grahmann, in Deer, et al, 1962).

Many previous bulk analyses of baryte have included significant levels of silicon, aluminium, iron, magnesium, zinc, manganese, copper, silver, titanium, and mercury (e.g. Boyle and Jambor, 1966; El Sokkary and Monem, 1977; Kowalski, 1976; Maher and Fagan, 1970; Scott, 1956; and various sources compiled in Deer, et al, 1962). Several of these authors recognised the probability of such constituents being present as contaminants from alien minerals, such substitutions being highly unlikely from a theoretical point of view.

With all the above in mind, the analysis of baryte samples to a high degree of accuracy and confidence was proposed in order that a general knowledge of the chemistry of Scottish baryte could be obtained and any changes in chemistry that possibly exists between various types of baryte could be distinguished.

Analysis of baryte.

Barium sulphate is insoluble in all normal solvents, with the exception of highly concentrated sulphuric acid. This, however, is of no consolation as any attempts to convert the resulting solution to one which lends itself to the technique of atomic absorption spectroscopy, caused the immediate re-precipitation of the sulphate. Sodium carbonate fusions were not performed as this method invokes serious consequences as regards final detection limits and also introduces an added possibility of contamination.

Utilisation of the facility of X-ray fluorescence spectrography (X.R.F) allows analysis of the samples in the solid state. However, other problems arise: barium is approximately ten times more absorbent than silicon and hence causes the curves plotted for detector count-rate against concentration in a baryte matrix to have a correspondingly shallower slope than those for a silicate matrix. As a result much larger uncertainties in the final analysis are involved, and also the detection limits are five to ten times worse. These points were all confirmed by the study of spiked standards ('Specpure' BaSO_4 spiked with 'Specpure' compounds), and effectively mean that trace element analysis

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by X.R.F. (Siemens 60 kV apparatus) is not feasible, although analysis for 'minor' elements is (>1000ppm).

An electron probe microanalyser was used on polished samples of baryte in order to assess the minor elements possibly present in the baryte, more conveniently. The detection limits of the 'probe' were approximately 500 p.p.m. for quantitative analysis. The instrument has the advantage of precluding the possibility that other minerals could contribute to the analyses, as a very precise area may be selected in order to avoid such material. The facility to study the distribution of minor elements within crystals is also available (on a micro-scale if required).

The results, for 55 generations of baryte from 49 varied specimens (approximately 170 'spot' analyses), are as follows:

1. strontium was detected in varying amounts in all specimens;
 2. the elements lead, calcium, iron, aluminium and silicon were not detected in any analysis.
- Furthermore even within 5 μm distance of co-existing crystals of calcite and galena, the baryte did not contain detectable quantities of calcium or lead.

To determine the actual bulk concentrations of strontium in a larger number of samples, specimens

....were

were prepared for analysis by X.R.F. It was found that with specimens of such a high degree of purity the best method of mineral separation was that of hand-picking. The selected samples were hand-ground in an agate mortar to less than 350 mesh (38 μm), and subsequently 2 g of each were pressed into tablets (1:1 with cellulose powder) prior to analysis.

Attempts to remove hematite from the pink specimens by magnetic separation were made in vain, and hence it was necessary to tolerate this impurity: later analysis for iron on a sample containing the most dispersed hematite of all the samples collected showed only 0.10% Fe_2O_3 (as total iron) to be present. This quantity would not be able to cause any detectable difference in the measured strontium content.

To check the purity of the samples each was qualitatively analysed for calcium and silicon, calcite and various silicates being the most likely contaminants. Any sample containing either or both of these elements was rejected.

The weight percents of strontium was then determined by comparison of the sample analyses with those of artificial standards ('Specpure' BaSO_4 spiked with various amounts of 'specpure' SrSO_4 : the mixing of these two components was thorough in order to ensure complete homogeneity, an important factor in dealing with highly absorbent substances).

The results of the 244 analyses are presented as percentages of SrSO_4 , in Fig. 50.

It is seen that the samples from the deposits of central and southern Scotland show large ranges of strontium compositions, and that no distinction can reasonably be made between pink and white baryte (see lines c.i, c.ii, and h.i, h.ii, h.iii), types of deposit, or individual deposits, on the basis of strontium content. The latter of these three observations is contrary to data presented by Carlon (1975), who found the compositional ranges from two English deposits to be significantly different and hence characteristic. The data also conflicts with the observation made by Scott (1967) that the baryte from Gasswater contains more strontium than that at Muirshiel.

The data from the North Pennine samples has a similar but slightly larger range (0.13 to 8.82% SrSO_4) to those of the Scottish deposits (0.80 to 6.27% SrSO_4). However, that from the two Highland deposits (Strontian and Tyndrum) show restricted ranges, which may or may not be representative of each deposit as a whole as only six and five samples (respectively) were taken (even though the samples were from different parts of each deposit). The Strontian deposit is generally known for its overall

....strontium

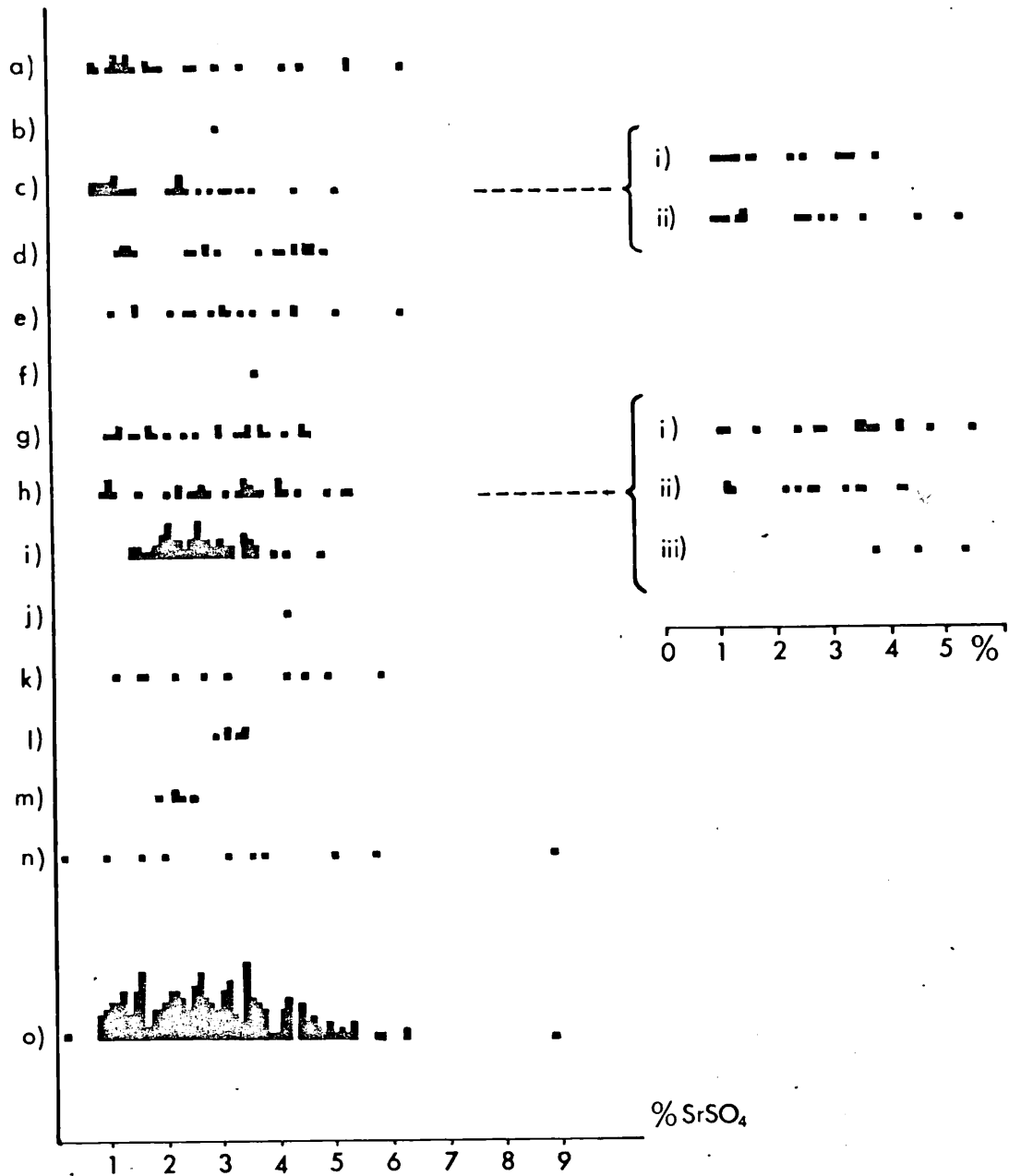


Fig. 50 Frequency histograms for the strontium content of pure baryte from each deposit investigated, (plus three others), and a cumulative histogram for the total population of samples (=244).

index: a) Muirshiel; b) Old Cumnock; c) Auchenstilloch- i) white, ii) pink; d) Arran; e) Leadhills/Wanlockhead; f) Nairn; g) Ochil hills; h) Kirkcudbrightshire- i) Barlocco, ii) Auchencairn, iii) Hangit man; i) Gasswater; j) Elie; k) Aberfoyle; l) Strontian; m) Tyndrum; n) Nth. Pennines.

strontium enrichment (the occurrence of strontianite being fairly common etc.), however this enrichment is not reflected in the baryte compositions. It may be inferred from this that the availability of strontium is not the controlling factor for its substitution into baryte.

A break-down of the data for the various groups of deposits is tabulated below:

Table 3.

Population	Sample size	Arithmetic mean	Standard deviation	Range (% SrSO ₄)
Type 1 baryte	162	2.68	1.27	0.82 to 6.27
Type 2 baryte	61	2.90	1.27	0.80 to 6.14
Highland baryte	11	2.70	0.54	1.84 to 3.44
N. Pennine baryte	10	2.81	1.75	0.13 to 5.66 (8.82)
Scottish baryte	234	2.68	1.22	0.80 to 6.27
(cen. + Sthn. baryte)	223	2.68	1.24	0.80 to 6.27)
All samples	244	2.69	1.24	0.13 to 6.27 (8.82)

The results concur with previous analyses of baryte, notably the compilation made by Starke (1964) whose average SrSO₄ content from 2293 analyses was 2.13% with the majority of the compositions ranging between 0.1 and 3.0% and only a few exceeding 8.0%.

The value of 8.82%, in brackets above, is suspected of containing some celestine, although this has been unable to be confirmed by X-ray powder diffraction. One other sample from the N. Pennines which contained approximately 35% SrSO₄ was, later, found to contain celestine when 'diffracted'.

This phenomenon of the compositions of (Ba, Sr) SO₄ to cluster around the end members of what has been shown to be a complete solid solution series (Starke, 1964; Boström, 1968) is well-known. Hanor (1968), in explaining this, postulated that 'inert precipitation' occurs, i.e. at each stage of the process of precipitation from solution, the precipitated solid does not react or equilibrate, in terms of Ba and Sr, with the remaining solution. The mathematical model constructed on this postulate agrees well with the observed frequency of the compositions of baryte and celestine.

In order to investigate the possible occurrence of trace elements in baryte, preliminary analyses of several samples were made by ultra-violet emission spectrography. The results were encouraging, not only in the way that the baryte behaved during the vaporisation, but also in the very low limits of detection able to be obtained. The preliminary

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work also showed the sensitivity of the technique to any possible contamination and subsequent steps to avoid this were taken.

The final total of analyses carried out are presented in Fig. 51 (with the relevant detection limits indicated). Calibration was against artificially prepared standards.

The iron contents recorded, are due to the hematite dispersed within certain samples (it was confirmed that the depth of colour correlated with the iron content determined). The copper content may presumably be attributed to the minute blebs of chalcopyrite found associated with many samples (see Chapter 2), and the aluminium and silicon, to silicate contamination. The remaining elements: Ti, V, and Mg, remain unexplained although they may also be associated with silicate contamination. Microprobe analyses of both the hematite and the chalcopyrite inclusions did not reveal the presence of these elements.

The elements sought but not detected in any specimen, were Li, K, Na, Rb, Ca, Co, Cr, Mn, Ni, Be, Ag, Bi, Cd, Sb, Zn, Sn, Rb, Eu, Ge, Mo, Ta, Tl, Rh, Pt, Ir, Ur, Th, W, Zn, Y, and Sc. These analyses show clearly the great purity of the baryte from these veins, to within approximately 100 p.p.m. the mineral is 'pure' $(\text{Ba, Sr})\text{SO}_4$.

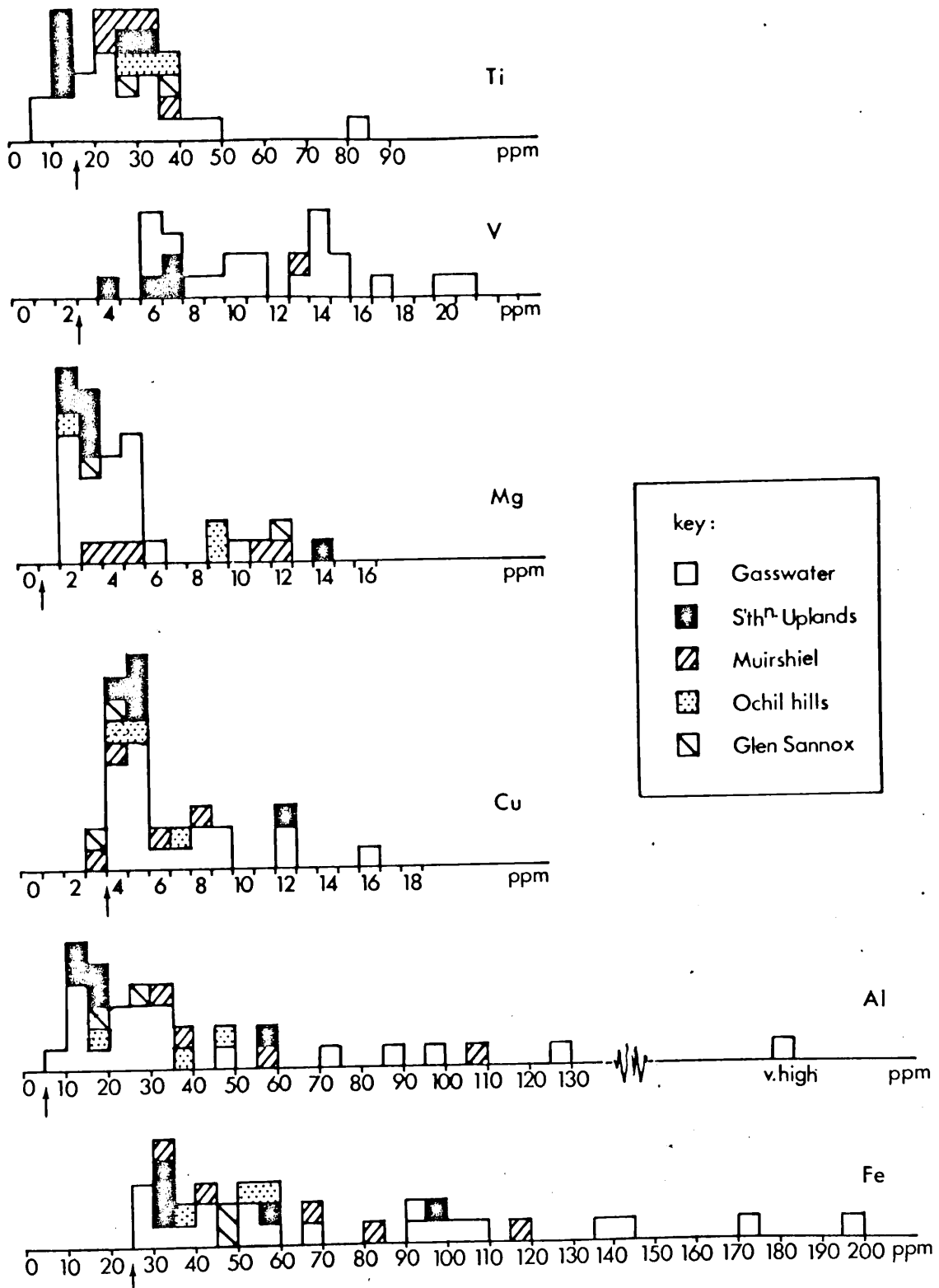


Fig. 51 The trace element contents of selected baryte samples, as determined by emission spectrography. (the arrows denote the approximate lower limits of confidence in fully quantitative analysis)

Fig. 51 also shows the lack of correlation, for any element, between composition and the location of a deposit.

It is of particular interest that neither calcium nor lead was detected in any of the samples (the detection limits for these elements were approximately 5 p.p.m. and less than 1 p.p.m., respectively). One of the samples of baryte was taken from within a few millimetres of a co-existing galena crystal, and similarly another associated with calcite. It may therefore be confidently stated that, in the Scottish baryte samples, no substitution of lead or calcium occurred even though the mineralising fluids obviously contained these elements. Furthermore the observations of microscopic blebs of sulphide (chalcopyrite) in several specimens may cast doubt on previously published analyses of baryte which show significant lead (and calcium) contents. If the samples have not been examined for such inclusions the results cannot be justified by merely pointing to the fact that the relevant solid solutions have been shown to exist (by, Boström et al, 1968).

To establish whether certain rare earths and other elements exist in baryte in very small quantities, one sample of visually pure (white) baryte (from Gasswater) was subjected to neutron activation

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instrumental analysis. The spectrum was recorded over the range 800 to 1400 keV and compared with U.S.G.S. and Open University standards. The analysis showed that no iron, scandium, tantalum or terbium could be detected (limits of detection: 40.0, 0.05, 0.06 and 0.062 p.p.m. respectively). The remaining elements; europium, cobalt and rubidium were not convincingly detected either (limits of detection: 0.033, 0.071, 0.033 p.p.m. respectively); the hints to their presence being considered due to interference from satellitic barium peaks (pers. comm. P.J.Potts).

Uranium was detected at levels of approximately 0.4 p.p.m. in the three samples which were analysed by the uranium fission-track method. (Two samples were from Glen Sannox and one from Barlocco). The method also allows the distribution, of the uranium present within the crystals, to be studied; no zoning was found however, the particle tracks appeared quite evenly distributed.

Strontium distribution.

i) Within the veins.

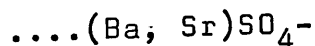
The X.R.F. analyses for strontium (Fig. 50) contain sequences of analyses from samples taken across a whole width of a vein (Fig. 52), and also sections of veins. Field notes on relative paragenetic positions of smaller sets of samples are

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also presented in Appendix 1. These analyses show that in all the recorded cases, those samples which were paragenetically later than others, contained less strontium than their respective earlier counterparts. This paragenetic control appeared to override any lateral variations in strontium along the veins. Sampling with respect to depth below the surface exposure of the veins was not possible, but was undertaken in a previous study at Gasswater (Scott, 1956): the conclusion reached was that no discernable variation with depth existed.

Carlson (1975), pointed out that the rate of crystallisation of baryte could affect the amount of strontium incorporated. This however was not apparently an important factor in determining the chemistry of the Scottish deposits, as the paragenetic variation is still seen when samples of approximately the same crystal size are taken (Fig. 52). A further qualitative check was made by selecting 40 samples from Gasswater and comparing their strontium contents with their crystal sizes and habit (as defined in Chapter 2). No systematic variation was able to be discerned.

Several theoretical explanations for the behaviour of strontium in baryte exist. Firstly, the role of changing temperature in the system



(Ba, Sr)SO₄-H₂O is shown in Fig. 53 (as presented by Carlon, 1975): the assumptions must be made that the bulk composition of the aqueous phase is constant and that there are no separate reactions which would compete for strontium. The initial situation illustrated is one in which the mineralising fluid has a strontium mole fraction (N) of 0.4, which is transmitted to the solid after complete precipitation has occurred. It can be seen that under isothermal conditions (by following any one curve) the strontium content increases with increasing precipitation.

The systems BaSO₄-NaCl-H₂O and SrSO₄-NaCl-H₂O are investigated by Scherp and Strübel (1974). Fig. 54 depicts the retrograde solubility of strontium-bearing solutions and hence it is inferred that the strontium content of baryte will increase as temperatures decline during precipitation.

The above situations will result, therefore, in an increase in strontium levels as precipitation proceeds: this is contrary to the decrease found in successive generations of baryte during this study. It may therefore be inferred that one or both of the initial assumptions made did not hold true for these deposits: as no other strontium-bearing minerals are present, it may be concluded that the bulk composition of the fluids did not remain constant during the mineralisation.

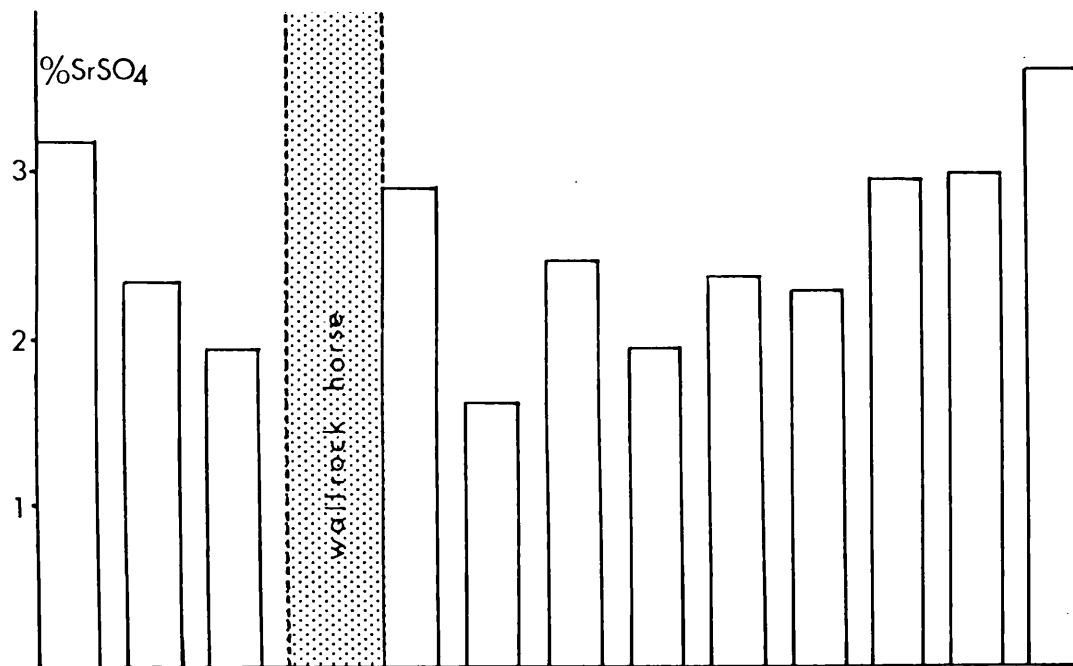


Fig.52 variation in Sr content across the Gasswater West vein (as determined by X.R.F.). The vein width is 2m.

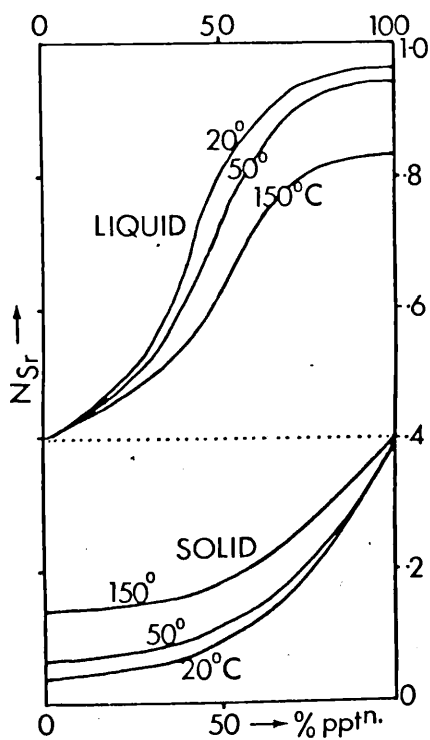


Fig.53 Compositions of the $(Ba, Sr)SO_4$ precipitate as a function of $\%(Ba+Sr)$ precipitated (after Carlon, 1975).

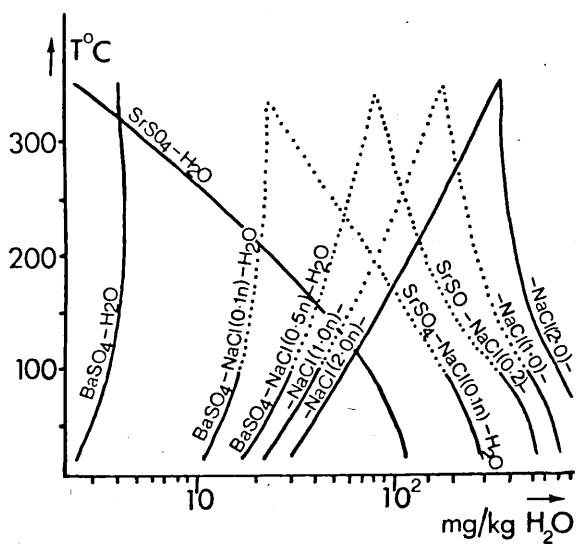


Fig.54 Solubilities for the system $BaSO_4-NaCl-H_2O$ and $SrSO_4-NaCl-H_2O$ (after Scherp and Strübel, 1974).

Fig. 54 also indicates that variations in salinity of the fluids could be an important factor controlling the amount of strontium allowed in the baryte.

Alternatively, it is suggested that the baryte did not precipitate from $BaSO_4$ solutions in response to temperature changes etc., but from the mixing of solutions and in response to the changed chemical environment upon mixing. In this situation variable salinity and variable mineralising fluid composition, with respect to barium and strontium, would be expected.

ii) Within baryte crystals.

The strontium variation found in the bulk sample analyses is also present within single crystals. No visible zoning exists but differing strontium levels were found over quite small distances. Fig. 56 shows a continuous trace of the variation along a baryte crystal from the Auchenstilloch district (as detected by the electron probe microanalyser; calibration was against an homogeneous celestine crystal with subsequent correction for absorption effects etc.). Numerous crystals were examined using this technique, and also by making 'spot' analyses at frequent intervals, along crystallographic directions (Fig. 55).

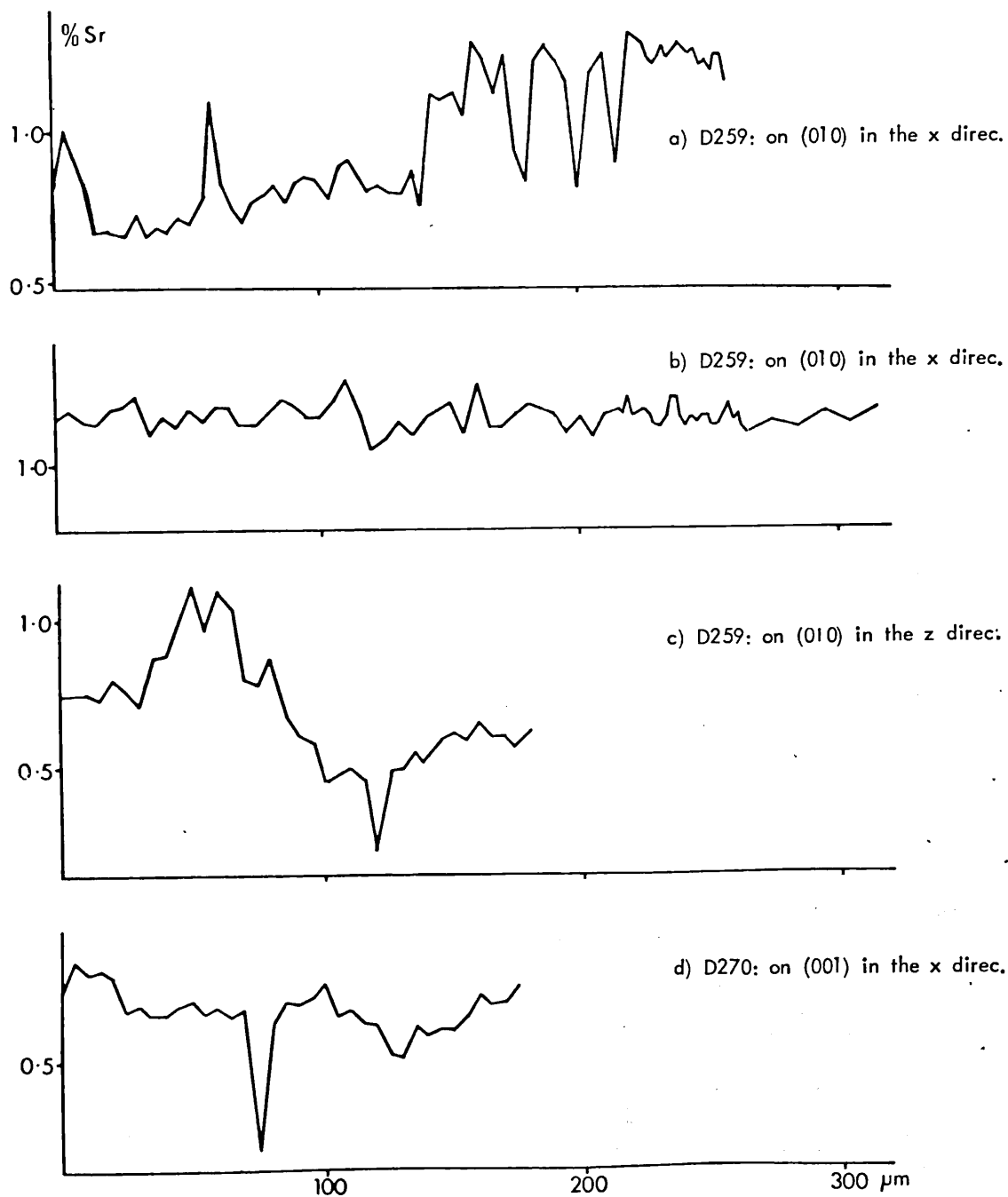


Fig.55 variation of Sr in various crystallographic planes and directions (as determined by electron microprobe).

The value of the continuous trace is immediately obvious, the strontium variation can occur on a very small scale; an observation which has also been made by Roedder (1969) and Leach (1973). Previous work in which spot analyses were made only every half millimeter or so (e.g. Morrow, et al, 1976; 1978) must be criticised in this respect and their conclusions, from such results, questioned.

The crystals examined by Leach (1973) occasionally exhibited a visible zoning, interpreted as growth zoning by relation to crystal planes and to trails of primary fluid inclusions. The very fine zoning, which was nearly always observed to be present, occurred parallel to the visible zones. Roedder (1969) had made similar observations in celestine, from Ohio, where variations in barium levels correlated with visible and cryptic zoning. The strontium levels in the Scottish baryte do not always vary as frequently as is shown by Fig. 56, but it is a very common feature. Parallel analysis traces were made in the direction of crystal growth but these could not be reconciled with a systematic zoning pattern; the peaks occurring quite haphazardly. By making a grid of spot analyses on a crystal face and drawing compositional contours by interpolation of the data, a patchy rather than a zonal pattern was indicated (Fig. 57). This was confirmed by

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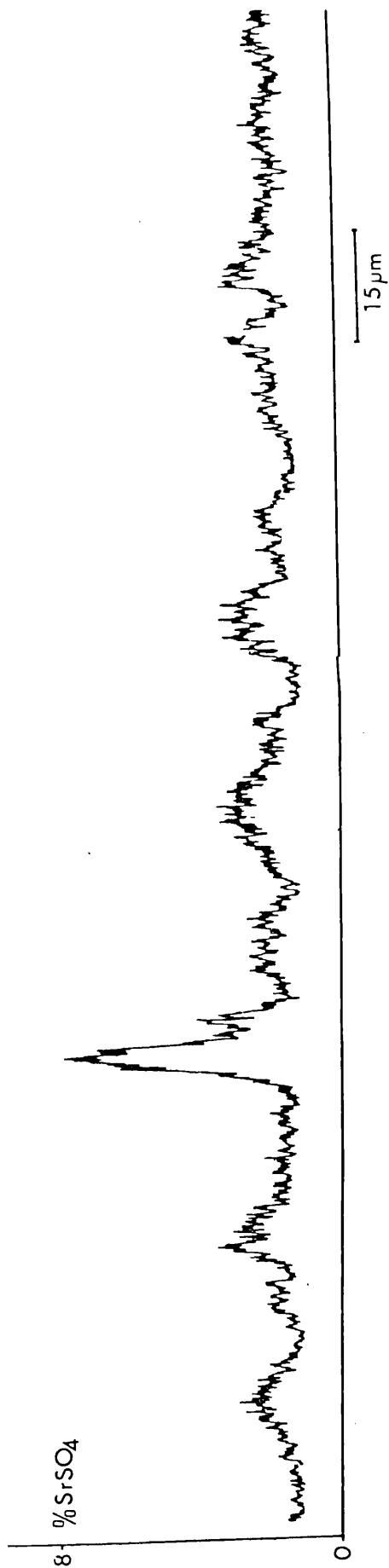


Fig.56 above: a continuous trace showing Sr variation along a baryte blade.



Fig.57 left : a contour 'map' of Sr in baryte, on (010) spot readings recorded on a 15 μ m grid were interpolated to show the distribution pattern. (100 contour units are equivalent to 0.2 wt. percent Sr.)

subsequent X-ray distribution photographs (Fig. 58).

Both Roedder and Leach favoured the hypothesis of annual (seasonal) variations in the Sr/Ba ratio to account for the zoning found, which in view of the geological settings of solution cavities in limestones, is probably a correct one. However, crystals from the fault controlled veins of the Scottish deposits, for which a mechanism associated with seismic activity is postulated to cause mineralisation, would not be expected to contain such zones. The origin of the "patchy" composition observed can only be attributed to the existence of a continually changing chemical environment during mineralisation. In all these cases however, the hypothesis suggested by Hanor (1968), that baryte acts as an "inert" precipitate" (i.e. equilibrium between the fluid and the last-formed precipitate does not occur), is supported.

c) The galena and sphalerite.

Trace element substitution for lead in galena is not thought to occur extensively (Deer, et al, 1962), the majority of elements reported probably occurring in mineral impurities. Bismuth and silver may occur in solid solution, but could also occur as exsolved maltidite (AgBiS_2) and acanthite (Ag_2S). Antimony and manganese are also widely reported (El Shazly, et al, 1957; Marshall and

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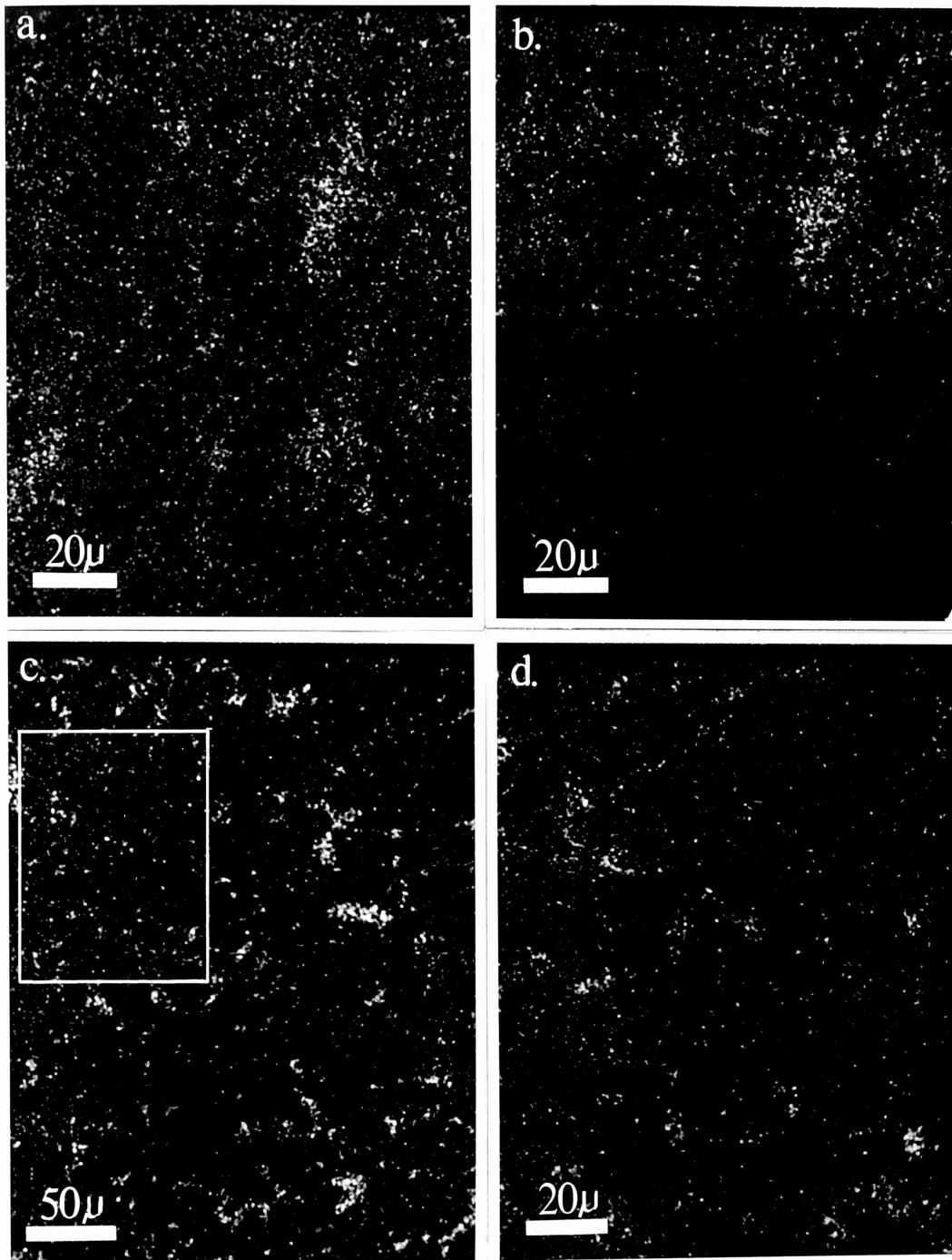


Fig. 58 X-ray distribution micrographs for strontium in baryte: a) Sample from the Ochil Hills, on (010). b) identical area to 'a'; showing the inherent background radiation (lower portion) to be insignificant relative to the characteristic X-rays (upper portion). c) sample from the Auchenstilloch district, on (010). d) the detail outlined in 'c', showing what had previously looked a relatively homogeneous area to contain a comparable variation.

Joensuu, 1961; Urabe, 1977; Small, 1978). Barium and strontium have similar ionic radii to that of lead and might be expected to occur, but cadmium, iron, nickel, copper and tin are almost certainly not able to substitute and must therefore, if present, be the result of mineral contamination.

Selenium may substitute for the sulphide ion in galena; a complete solid solution has been shown to exist between clausthalite (PbSe) and galena (Coleman, 1959). PbTe is also isostructural with both minerals.

In sphalerite however, substitution for zinc is common with iron, cadmium and manganese often attaining percentage proportions. Other elements thought able to substitute include cobalt, mercury, gallium, germanium and indium.

In the present study 88 samples comprising galenas, sphalerites, and mixtures of galena and sphalente (from nine locations in Scotland and two in England) were analysed for silver, nickel, copper, lead, zinc, cadmium, cobalt, iron, chromium and manganese by the methods described by Batchelor (1976, a and b). The aim was to establish whether or not any variation in levels of the trace elements exists between deposits.

Mineral separation was by standard dense liquid and magnetic separation techniques: the samples being examined in transmitted and reflected light both prior to separation, and after it, by mounting a representative sample of the grains and then polishing them. The analyses are tabulated in Appendix 2.

For galena, it was found that the quantities of iron (20 p.p.m. to 0.27%), zinc (20 p.p.m. to 4.0%), copper (40 p.p.m. to 4424 p.p.m.) and cadmium (40 to 202 p.p.m.), occasionally detected could be explained in terms of contamination by other minerals. Cobalt and chromium were not detected, and nickel and manganese only on one occasion each (110 and 80 p.p.m. respectively). Silver was almost always present (up to 900 p.p.m.).

In the sphalerites, chromium was always absent and nickel only quantitatively detected in four samples (range: 35 to 105 p.p.m.). The presence of copper (ranging from 1260 p.p.m. to 0.28%) usually corresponded with observations of chalcopyrite contamination. Silver (5 p.p.m. to 0.15%), iron (0.02 to 1.67%), manganese (20 to 276 p.p.m.), cadmium (1040 to 8357 p.p.m.), cobalt (25 to 200 p.p.m.) and lead (41 p.p.m. to 9%) were found to be regularly present, although it is not likely that the lead is contained within the sphalerite lattice.

The minerals were examined for microscopic inclusions of minerals and exsolved phases, none were found. Four samples of galena were also examined using the electron probe microanalyser, in search for exsolutions of silver-bearing phases, again none were found.

The data for the silver content of the sulphides are presented in Fig. 59. The manganese and iron data for the sphalerites are shown in Fig. 60, and the cobalt and cadmium data in Fig. 61 (as ratios with respect to zinc to take into account the mixed ore specimens). The levels of silver found at Leadhills, the North Pennines and Kirkcudbrightshire areas agree roughly with those of previous work (El Shazly, et al, 1957; Cook, 1976; Small, 1978). There are no general differences in the silver contents from one deposit to another, however it is notable that the average silver content of the Hilderstone samples is no greater than the general average, even though significant quantities of silver ores occurred at this locality (Wilson, 1921). The silver contents of the sphalerites are generally lower than those of the galenas, but no correlation exists with the amount of lead present (in the sphalerite analyses) and therefore the levels of silver cannot be attributed to galena contamination.

The data for the sphalerites are also similar from deposit to deposit, with a possible exception

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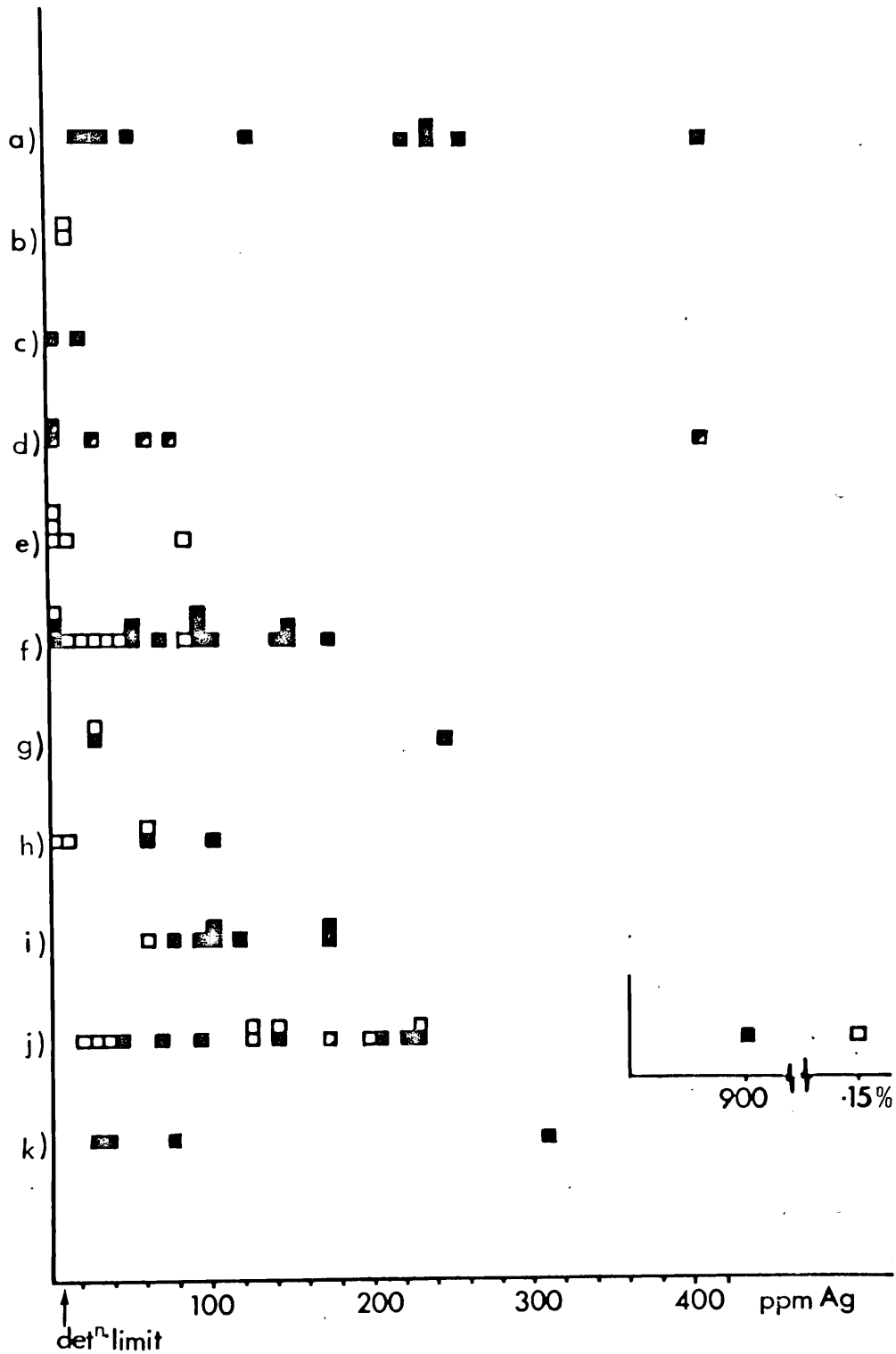


Fig.59 The variation in silver content of galenas (■), sphalerites (□) and mixtures of these two (◐), for the following deposits: a) Auchenstilloch area, b) Glen Sannox, c) E.Calder, d) Hilderstone, e) Leadhills, f) Wanlockhead, g) Kirkudbrightshire, h) Tyndrum, i) Strontian, j) Nth. Pennines. k) Derbyshire. (tot. popⁿ. = 83)

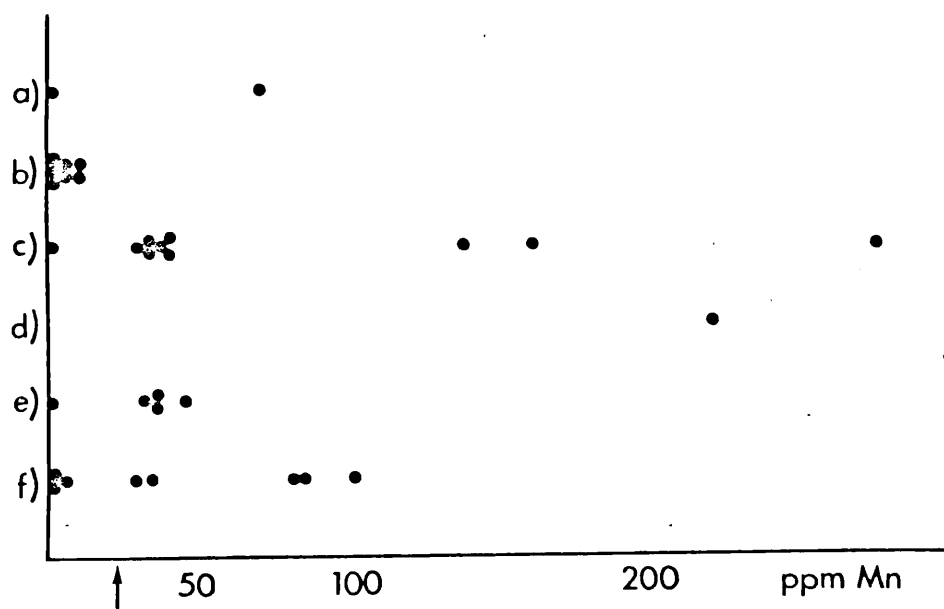
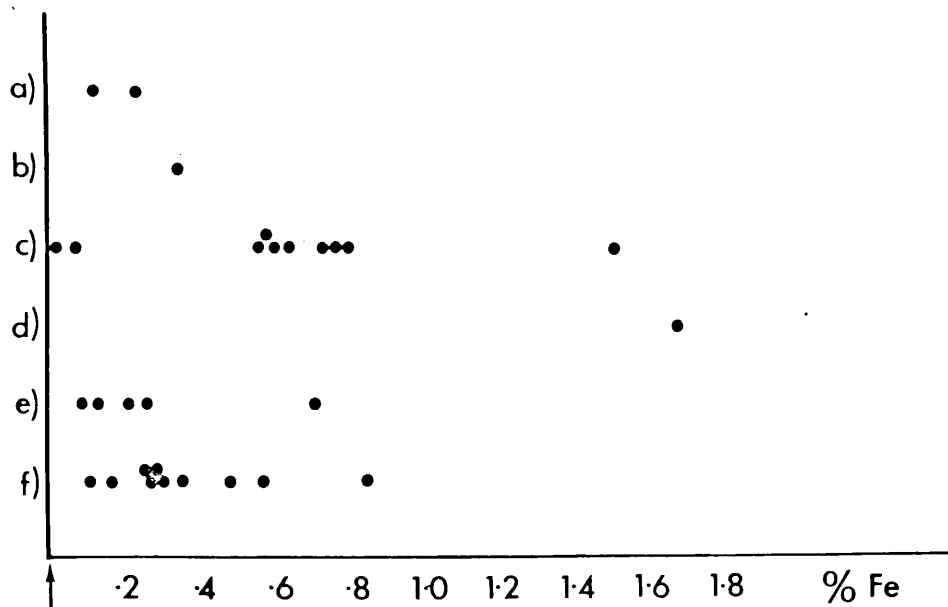


Fig. 60 Iron and manganese contents of sphalerites from :
 a) Glen Sannox, b) Hilderstone, c) L'hills+W'head,
 d) Kirkcudbrightshire, e) Strontian+Tynarum,
 f) N. Pennines. (detection limit indicated by \uparrow)

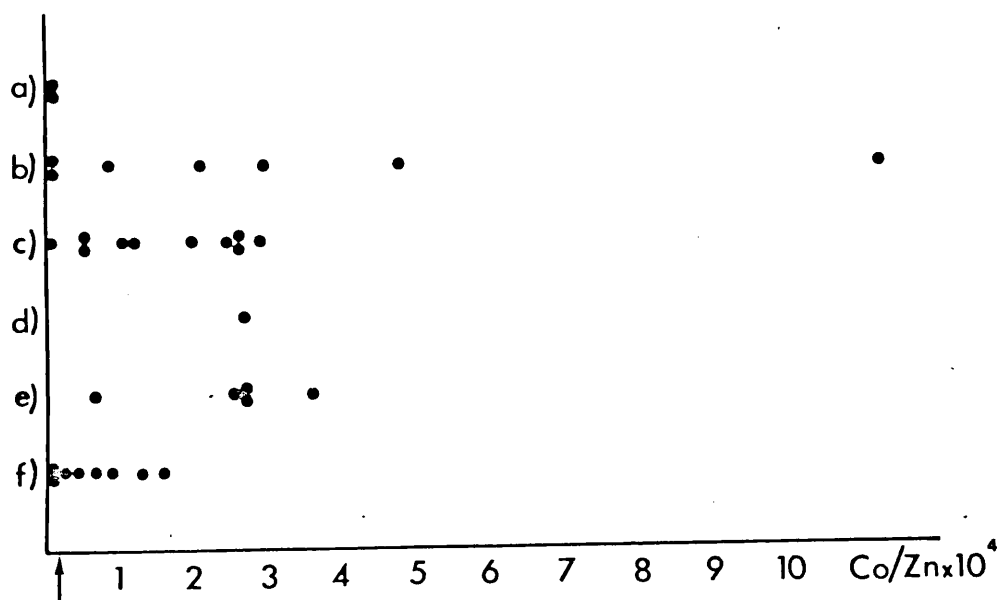
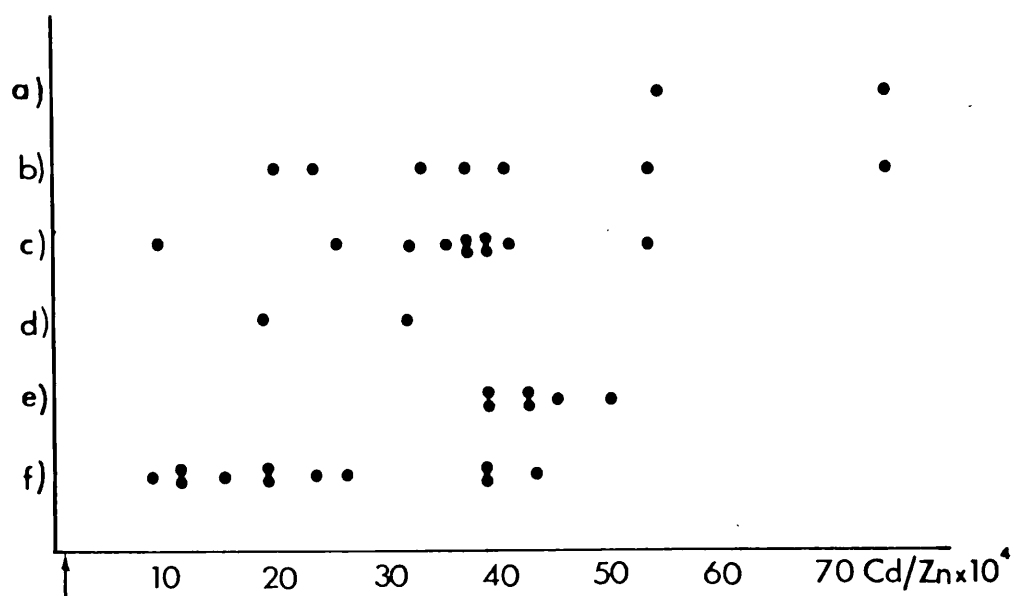


Fig. 61 Cd/Zn and Co/Zn ratios for sphalerites from :
 a) Glen Sannox, b) Hilderstone, c) L'hills+W'head,
 d) Kirkcudbrightshire, e) Strontian+Tyndrum,
 f) N. Pennines. (detection limit indicated by \uparrow)

provided by the noticeable lack of manganese in the Hilderstone samples.

Qualitative analysis of two galenas, by U.V. spectrography, confirmed the absence of manganese, cadmium, chromium and tellurium, and also barium and strontium (approximate detection limits were 5 p.p.m.). Quantities of silver, antimony and bismuth (very low) were found, along with traces of vanadium, copper, iron and aluminium. The latter three elements were presumably from contamination by other minerals.

Chapter 5 : Fluid inclusion studies

Chapter 5. Fluid inclusion studies.

General description.

The inclusions observed in the numerous doubly-polished thin sections prepared, were generally small in size and contained a liquid phase only. Occasionally two-phase, liquid-vapour inclusions occurred, but the proportion of liquid to vapour was variable within a sample, or obvious 'necking' had taken place. Hence no significance could be attached to them. No solid phases were seen within the inclusions, but on surfaces of freshly-broken crystals, isotropic cubes (presumably of halite) could be detected in rare instances. These crystals were presumably precipitated as the fluid evaporated in contact with the atmosphere. Inclusions in baryte have on occasion been found to contain liquid carbon dioxide or hydrogen sulphide (Palache, et al, 1951; Dekate, 1961; Deer, et al, 1962; Rankin and Shepherd, 1978). These compounds were not detected in the present study.

In the coarse-grained samples of baryte, the population density of inclusions was generally considered less than in the finer-grained and platy baryte. The inclusions were, on occasion, able to attain greater dimensions in the coarser material: up to approximately 30 or 40 μm , as compared with an average of 10 μm in the finer. However, in all

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cases there were often considerable numbers of inclusions in the size range of 1 μm or less.

To decide which of the inclusions were primary was virtually impossible. With no euhedral crystals to work with, and in the absence of visible growth zones, the only criterion on which to base assumptions of primary origin was to select those inclusions of a solitary nature. Inclusions in planes parallel to any cleavage or in close proximity to cracks or healed cracks in the crystals, were avoided. In the case of the finer grained baryte, deposited in sequential layers, an added feature of the inclusions was their existence in trails at right angles to the direction of growth of the crystal blades (Fig. 62). It seems likely that these were not primary with respect to the crystals they cross, but are pseudosecondary and were induced by later generations of mineralisation (baryte). Hence these inclusions were also used in the heating and freezing studies.

The shape of inclusions has been shown by Roedder (1968) to bear no positive relation to their origin. However, it was noticeable that the inclusions in baryte rarely attained good 'negative crystal' shapes.

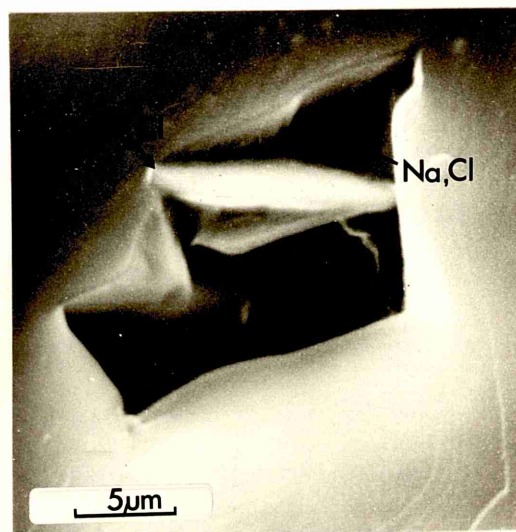
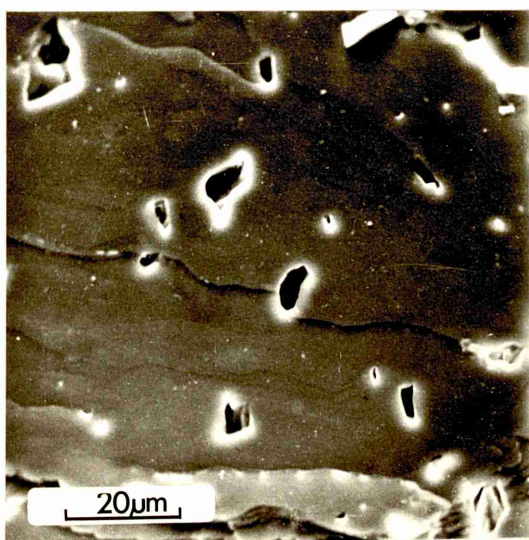
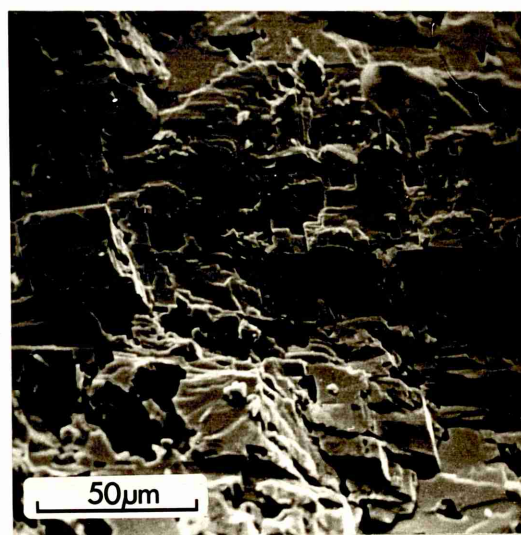
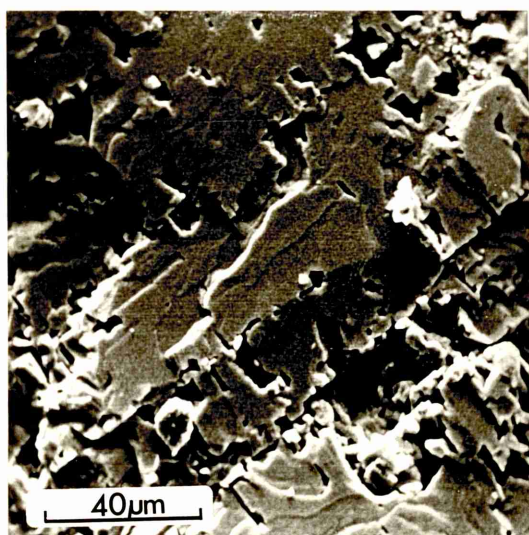
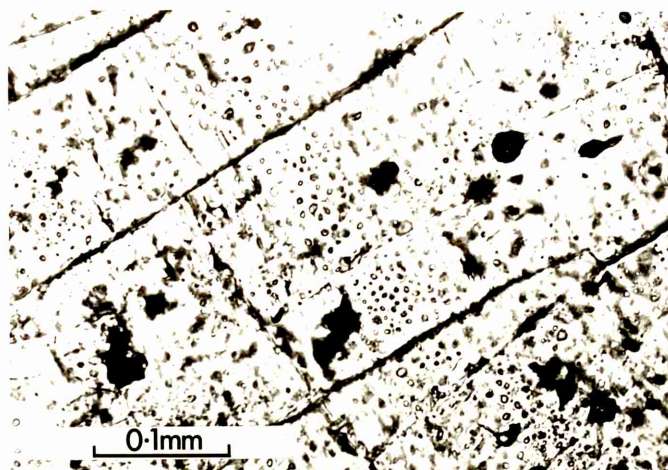
Figs. 63 and 64 are (scanning) electron photomicrographs showing the pronounced effect the

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well-developed cleavage commonly has on the inclusions. It is only when viewing the inclusions via this facility that one realises that the percentage of unaffected inclusions is very low. Calcite suffers from the same problem, but to a lesser extent, being generally a very late mineral it has not been subjected to as much stress and hence many of the cavities have reasonable shapes (Fig. 65). This is also the case with galena, chalcocite and sphalerite. The quartz studied was very poor in primary inclusions, but good negative crystal shapes were commonly exhibited by many of the secondaries.

"Necking down" of the inclusions in baryte to produce distorted shapes is an expected feature in minerals which have been subjected to episodic stressing resultant from fault activity during, and subsequent to, precipitation. Unusually shaped inclusions resulting from the partial healing of the (001) cleavage planes, in particular, were occasionally observed in the coarser specimens. These inclusions are relatively large, planar and dendritic in shape, and bear no relationship to the actual mineralising fluids, but to post-mineralisation groundwaters.

Fig.62 Trails of pseudosecondary fluid inclusions oriented in planes perpendicular to the crystal growth direction (plane polarised light).



Figs. 63 and 64 Effect of the strong cleavages on baryte fluid inclusions (scanning electron micrographs).

Fig.65 Typical fluid inclusion cavities in calcite (S.E.M.).

Fig.66 Daughter phases in a calcite secondary fluid inclusion cavity (S.E.M.).

Microthermometry. a) homogenisation temperatures.

The temperature of homogenisation of a two-phase liquid-vapour inclusion is that temperature at which, on heating up the inclusion, the liquid just expands enough to fill the space occupied by the vapour bubble. The vapour bubble initially formed within the inclusion due to differing coefficients of thermal expansion/contraction of the mineral and trapped fluid. However, it does not form immediately the temperature starts to decrease, a certain amount of strain within the inclusion is able to be tolerated. This tolerance is commonly of the order of 40°C , depending to some extent on the rate of cooling. Hence, it follows that mineralising fluids of temperatures less than approximately 70°C , may not nucleate bubbles at all when trapped and cooled. If the temperature of deposition happened to be identical to "room temperature" the inclusion would be stable and in equilibrium, otherwise a "metastable" situation prevails. The behaviour of inclusions in such a state is not fully understood, however it is sometimes possible to cause the nucleation of vapour bubbles by freezing the samples (in liquid nitrogen for example) and then thawing them. Attempts can then be made at homogenisation, so that a more precise idea of the temperature of deposition may be obtained.

The inclusions in the baryte samples (and also in the associated quartz, calcite and sphalerite) were monophasic, and so the nucleation procedure was followed. The result was that in some samples no 'bubbles' could be nucleated, and in others a tiny percentage only. Subsequent homogenisation temperatures were very varied and often substantially in excess of 70°C:

Table 4.

Sample	T _H range (°C)	No. of inclusions
D46A (baryte)	70 to 90	15
D242 (baryte)	65 to 88	3
D431 (baryte)	86 to 96	4
D227 (baryte)	82	1
D241 (baryte)	60	1
DTY (sphalerite)	96 to 127	20
D433 (sphalerite)	74 to 102	6
D165 (calcite)	72 to 100	6

These data are not thought to be representative of the temperatures of the depositional fluids, as they are from a small minority of the inclusions. It is likely that they have been subject to one or more of the many distortions to which inclusions are prone.

The above observations are consistent with those of many other authors concerned with hydro-

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thermal baryte (e.g. Leach, 1973; Sawkins, 1966; Small, 1977) and the inference is that the occurrence of low-temperature baryte is very common.

b) Freezing studies.

The last-ice-melting temperatures for inclusion fluids in baryte from several localities is presented in Figs. 67 and 68.

The depression of freezing point of inclusion liquids is often translated into an equivalent weight percent of sodium chloride which, if dissolved in pure water, would effect the same depression. The present data has been left in degrees centigrade because evidence from the inclusion leachates (see below), and the knowledge that the mineralising fluids would have to contain considerable quantities of sulphate, make the translation inapplicable. If the overall range of salinities were expressed as equivalent weight percent NaCl, it would be approximately 8 to 25%.

The broad spread of values could mean that secondary and pseudosecondary inclusions have been measured along with primary ones, the problems of distinguishing one type from another were discussed earlier. If it is assumed, for the moment, that the data is from primary inclusions only then the inference may be drawn that fluids of varying

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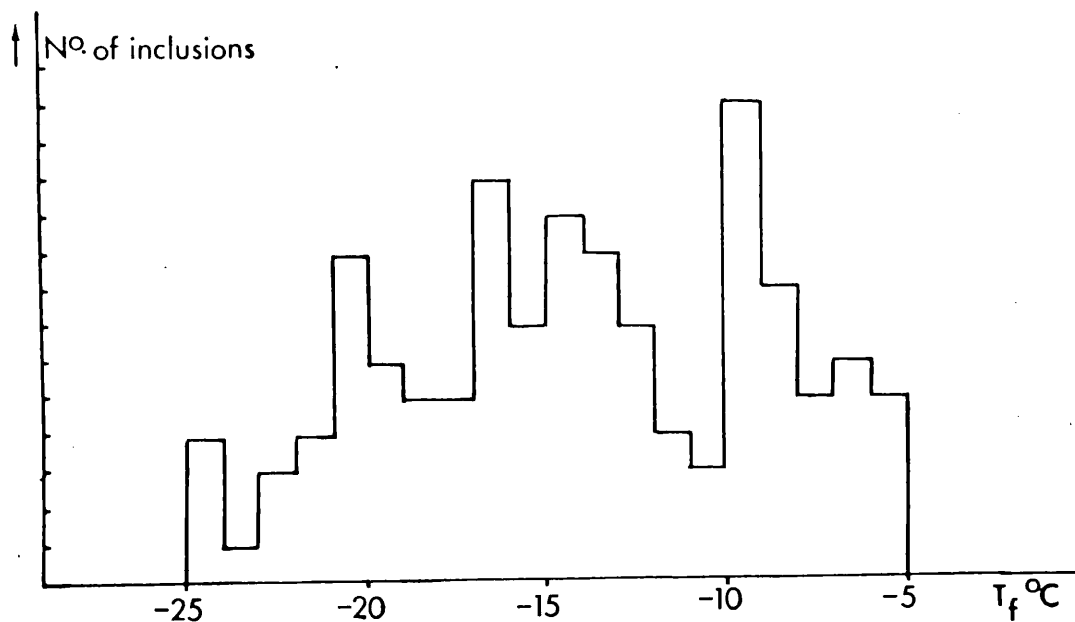


Fig.67 Frequency histogram of the last-ice-melting temperatures of the fluid inclusion liquids (baryte).

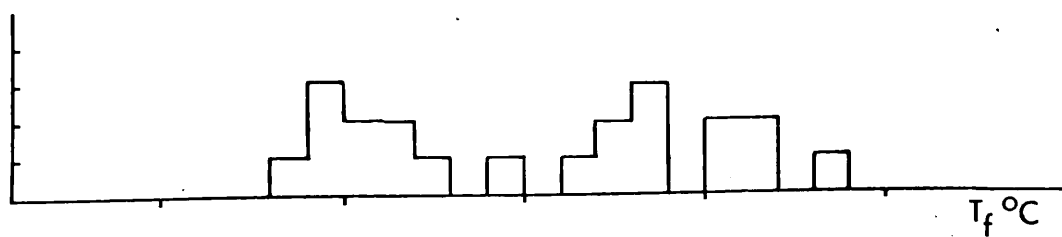


Fig.68 Range of last-ice-melting temperatures of the inclusion fluids from three Muirshiel samples.

salinity were involved in the mineralisation. This would probably be the case where a mixing of fluids occurred, causing precipitation of the baryte. As secondary inclusion data would have to be present on a large scale to totally obscure that of the primaries it is thought that the data is a valid representation of the situation.

The histogram (Fig. 67) is a compilation of data for samples from several deposits, but similar ranges of last-ice-melting temperatures were recorded within each deposit (e.g. Fig. 68) and even within one sample.

Table 5.

location	range °C	No. of inclusions	No. of samples
Gasswater	-6.6 to -25.0	27	6
Muirshiel	-6.6 to -21.7	21	3
Aberfoyle	-8.0 to -13.5	4	1
L'hills/W'head	-5.5 to -17.0	14	4
Glen Sannox	-5.8 to -20.5	22	2
Barlocco	-8.1 to -24.7	20	3
Ochil hills	-8.4 to -24.8	17	3

The relatively small amount of data obtained is due to the problems of working with such a difficult mineral. Although a small number of specimens of calcite, quartz and sphalerite were also studied, the inclusions in the calcite were too small to be

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used and none of the limited number seen in the quartz or sphalerite showed any evidence of being primary.

The depression of freezing point of solvents depends not on the weight of salts dissolved but on the number of molecules or ions. As sodium chloride is a relatively light molecule, to obtain the same, or greater, depression by heavier molecules a greater weight of the compound has to be dissolved. It therefore follows that if the sulphate ion accounts for a significant proportion of the dissolved species the relevant brines must have been quite concentrated. This, according to Roedder (1972, discussion on Rife 1971), is not only possible but quite probable in many cases.

It was found that many inclusions were extremely difficult to freeze. Temperatures lower than -100°C were commonly necessary to effect this change, a phenomenon also noted by Leach (1973). This is interpreted as evidence that these inclusions were completely sealed and not susceptible to cryptic leakage: it is known that liquids under negative pressures will remain in the liquid state at temperatures below their theoretical 'freezing points'.

Inclusion leachates.

The results for the Na/K ratios are given in Fig. 69 and Appendix 3. The majority of the data are for baryte, but some samples of calcite and

....galena

galena associated with baryte, were also leached. All the data obtained is presented, even that where the total salinities are rather low. Small (1977, and pers. comm.) found that low Na/K ratios for baryte from North Yorkshire corresponded with low total salinities, usually from fine-grained baryte, and hence omitted this data assuming that it indicated that the percentage of primary inclusions extracted was low. This was not found consistently in the present study although it could be argued for two or three of the results.

Apart from calcium, which was only sporadically detected and in low concentrations, the other elements which were looked for in the leachates were: iron, magnesium, manganese, lead, copper and zinc. Zinc was qualitatively detected in low concentrations in several of the samples, but the rest were not detected at all. These elements have been detected previously in various inclusion fluids (Czamanske, et al, 1963), however the procedure followed here was not really designed with such low concentrations in mind and so the detection limits are probably in excess of any of the element levels.

The determination of barium and strontium in the leachates was not attempted, as possible contamination by the host mineral would effectively

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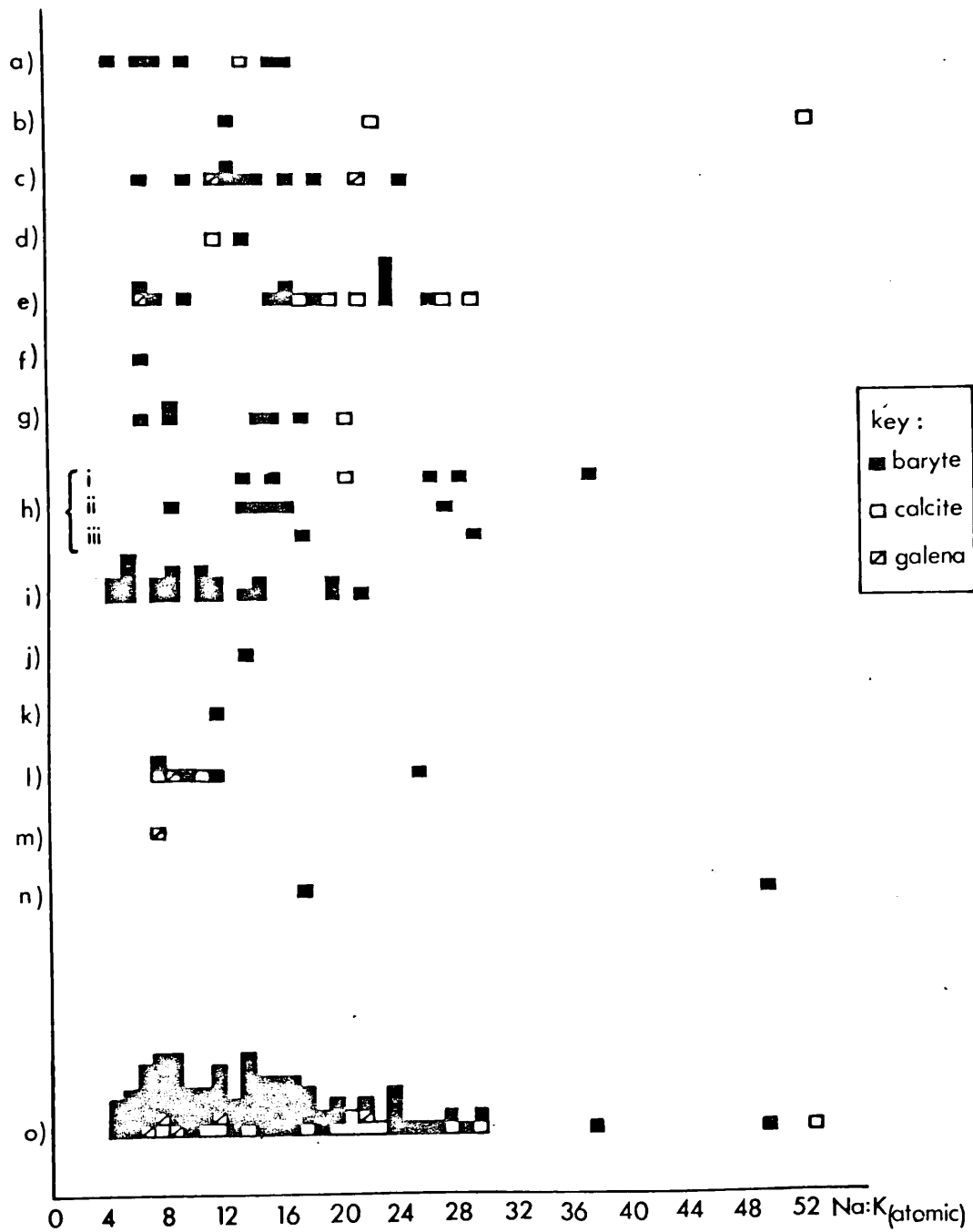


Fig. 69 Histograms showing the range of sodium:potassium ratios for each deposit, and for the total population.
 index: a) Muirshiel; b) Hilderstone; c) Auchenstillloch;
 d) G. Sannox; e) L'hills/W'head; f) Nairn; g) Ochil hills;
 h) -i. Barlocco, -ii. Auchencairn, -iii. Hangit man; i) G'water;
 j) Elie; k) Aberfoyle; l) Strontian; m) Tyndrum; n) Nth. Pennines.

invalidate the results. Also, calcium was obviously high in the calcite fluid inclusions, as demonstrated by the Ca-Cl daughter phase in a leaked secondary inclusion (Fig.66).

To extract the inclusion fluids into a medium of pure water requires great care. A meticulous and uniform schedule is necessary to ensure that meaningful results are obtained. A brief summary of the procedure is as follows: handpicking of suitable samples and the removal of alien minerals; crushing to between 6 and 8 (B.S.) mesh; further removal of contaminants; weighing out approximately 10 g (for baryte); initial washing; continuous electrolytic cleaning over a period of several days (110 v D.C., platinum electrodes); crushing under distilled water (minimal amount) to a fine powder; filtration of the slurry into cleaned and pre-leached plastic containers, and finally the determination of relative element concentrations by flame emission photometry. The preparation of 'process blanks' are necessary as it was found, for example, that folding of filter papers contributed to the Na, Ca and K readings.

Strictly speaking the measurements are on vastly diluted mixtures of trapped inclusion fluids and 'other waters'. For them to have any significance the proportion of the mineralising fluid to 'other
.....waters'

waters' must be high, or alternatively the salinity of the latter must be insignificant in comparison with the former. Descriptions of the numerous generations of mineralisation occurring, have already been given and it follows that one particular generation will be subjected to the mineralising fluids of all subsequent generations. Hence its proportion of pseudosecondaries may be high but they will still be representative of the baryte mineralising fluids of that deposit.

All but two of the ratios show potassium enrichment with respect to present-day sea-water, and the majority of present-day (non-evaporitic) connate brines (Fig. 70), especially as the data is skewed to the low-ratio end of the abscissa. The evolution of groundwaters is normally to the sodium rich varieties, potassium being preferentially fixed in clays. If evaporites are present then the reverse happens because the solubility of potassium salts is greater than those of sodium. Potassium-rich solutions could also be derived from deep brines, or from contributions from juvenile waters.

Discussion of results.

It may be inferred from the results as a whole that the baryte was deposited by very low-temperature aqueous fluids of variable, and often high, salinity. The ratios of sodium to potassium obtained for the

....inclusion

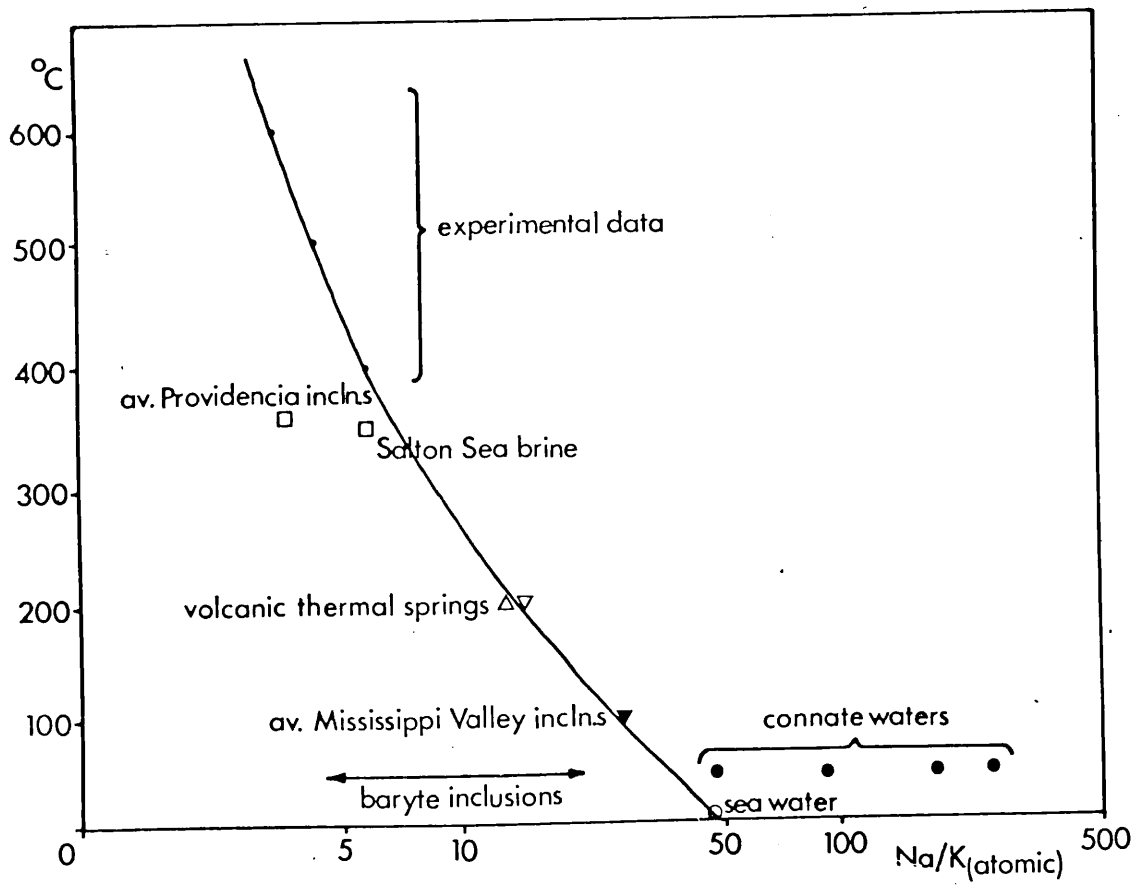


Fig.70 Relationship between temperature and Na/K ratios,
and various waters (after Sawkins, 1968)

inclusion leachates show a principal range of 4 to 30; which is potassium enriched compared with present-day sea-water and connate brines (White, et al, 1963; Sawkins, 1968).

The brines of deeper basins are sometimes potassium-enriched as a result of contact with alkali silicates at some time in their history. Whilst a contribution by such brines could decrease the Na/K ratio of the mineralising fluids, an inherent problem arises from the fact that the geothermal gradient would cause the brines to be heated, which would contradict the fluid-inclusion evidence.

Juvenile waters, although potassium-enriched are unlikely to be capable of producing the sort of volumes required for the mineralising fluids. Nevertheless Sawkins (1968) cited the mafic alkaline rocks, spatially associated with the Mississippi Valley deposits of the United States, as probable sources of potassium-rich waters for these deposits. In the Midland Valley of Scotland a similar, though less pronounced, association exists. A mafic alkaline period of eruption during Middle to Upper Coal Measures Times is described by Francis (1967), examples of which are seen at Loudon Hill, Lugar, etc. These rocks may have affected the chemistry of their local groundwaters.

Davidson (1966) drew attention to the fairly common coincidence of the occurrences of evaporites and telethermal ore deposits, and demonstrated that mineralising fluids showing potassium enrichment could be obtained from these strata.

The K/Ar isotopic dating results (Chapter 3) show the mineralisation of most deposits to have occurred around Permo-Triassic (New Red Sandstone) times. The palaeo-climate was obviously arid, and it is known that groundwaters attain their highest salinity under such conditions. Whether or not any evaporite deposits were formed is unknown, no evidence of any are seen in the sparse remaining outcrops of Permian strata. However, the conditions would have been conducive to their formation. According to George (1960) it is conceivable that a tongue of the Zechstein sea reached up into the Midland Valley, although again no evidence of this remains.

In some of the older strata of the region, evaporitic environments did exist: the cornstones of the Upper Old Red Sandstone, as seen in south Ayrshire, have been described by Burgess (1960) as limestone horizons in fossil calcareous soils which resemble the caliche deposits of the Pliocene in central U.S.A. Having been formed in a semi-arid environment, the cornstones could have been a source

....of

of evaporitic salts which would cause waters percolating through them to be potassium enriched. Similar horizons are also found in the Upper Old Red Sandstone of the Scottish Border area (Leeder, 1976). There are also evaporitic desiccation beds with associated layers of gypsum and salt pseudomorphs, resulting from conditions likened to the present-day playa lakes, occurring at the very base of the Carboniferous.

Chapter 6 : The mineralising fluids

Chapter 6. The Mineralising fluids.

It is probably not possible to determine the precise composition of the fluids which led to the deposition of the various baryte veins, and so emphasis has been placed, in this chapter, on a comparison between 'Type 1' and 'Type 2' deposits, assuming epithermal deposition.

The temperature at which the fluids deposited the minerals has already been shown to be very low ($<50^{\circ}\text{C}$), and so unless otherwise stated all the data used here are those determined at 25°C . The actual values in most instances are unimportant as far as the comparisons are concerned.

From transmitted and reflected light microscopy (Chapter 2) the following suites of minerals (accompanied by rough volume percentages) were assumed to have precipitated from solution at approximately the same time, and hence are the assemblages from which the data have been drawn:

- | | | |
|-----------------|---|------------------------------------|
| Type 1 deposits | - | baryte (>99%) |
| | | hematite (<1%) |
| | | chalcopyrite or chalcocite (<0.1%) |
| Type 2 deposits | - | baryte (45%) |
| | | ankerite (30%) |
| | | pyrite (1%) |
| | | with sphalerite (<5%) |
| | | galena (5%) |
| | | calcite (20%) |

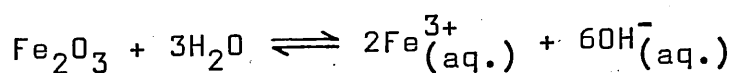
Those minerals which are relatively minor in quantity impose little effect on the overall characteristics of the fluid, but play a valuable rôle as indicators of fluid chemistry.

The phenomenon of complexing of ions in solution is not necessary to invoke as barium, calcium, manganese, strontium and magnesium all form soluble sulphides. The position of iron however, is a little less certain, its minerals being intermediate on the solubility scale.

Type 1 deposits.

To establish what the pH and Eh of the solutions were likely to have been, there are four sources of evidence: i) the minerals which have been precipitated; ii) the nature of the solvent containing the dissolved minerals, as determined from the fluid inclusion evidence; iii) the type of wall rock alteration caused by the solutions; iv) the evidence from analyses of present-day 'groundwaters'.

Barium sulphate is the salt of a strong acid and a fairly strong base and so a fairly neutral dilute solution would be expected. Concerning the small amount of hematite present, the reaction:



would give rise to a slightly alkaline component. However, according to Garrels and Christ (1965) the ferrous ion must predominate for iron to remain in

....solution,

solution, and for this to be the case the pH would have to be acidic, and/or the Eh be reduced. The 'bleached' wall rock close to the vein (in places) at Gasswater, with its outer ferruginous fringe (Fig. 28), also indicates that the fluids contained iron initially in the reduced state.

The solvent has been shown to be a saline one (Chapter 5), and as such would probably have a neutral pH of 7. The solubility of NaCl and KCl being far in excess of BaSO_4 or Fe_2O_3 would mean that the chlorides would have the major influence on the solution chemistry.

The concentration of carbon dioxide in the solution is discussed below, and is suggested to be very low. Consequently it will have had little effect on the pH.

The wall rock alteration caused by these veins was very limited, which also supports the suggestion of a neutral pH solution. Silicification such as that seen at Gasswater involves the least hydrogen metasomatism of all types of hydrothermal alteration (Meyer and Hemley, 1967).

At the present-day, groundwaters in country rocks of a similar lithology to those in which the Scottish baryte deposits occur (as compiled by White, et al, 1963) show pH values varying by plus or minus one unit around neutral. Furthermore, the analyses

.....carried

carried out by Baas Becking, et al (1960) show a similar range for the majority of shallow groundwaters, mine waters (from primary ores only), fresh waters, fresh water sediments, and marginal marine sediments.

Having established a reasonable value of 7 for the pH of the fluids, theoretically the Eh may be calculated by the relation:

$$Eh = E_0 - \frac{0.059}{8} \log \frac{a_{SO_4^{2-}}}{a_{S^{2-}}} - 0.059.pH$$

(where $a_{SO_4^{2-}}$ and $a_{S^{2-}}$ denote the activities of sulphate and sulphide in solution, respectively. E_0 is the potential when all constituents are at unit activity).

Barton⁽¹⁹⁵⁷⁾ used this equation to define a 'hydrothermal region' which encompasses limiting values expected in most hydrothermal ore deposits: a maximum reasonable range for the ratio of the activity of the sulphate ion to that of the sulphide was taken to be 10^4 to 10^{15} (Fig. 71). However for baryte deposits this ratio is likely to be higher than 10^{15} . So the diagram, whilst giving some indication of the Eh, is probably inadequate for the present purpose. (There is considerable difficulty in calculating $a_{SO_4^{2-}}/a_{S^{2-}}$, as most elements which form insoluble sulphates form soluble sulphides, e.g. barium).

Fig. 72 shows the stability fields of baryte, hematite and chalcocite, in terms of pH and Eh, to coincide within the triangular dotted area, assuming a total dissolved sulphur species concentration of 10^{-4} moles. This can be seen to be a reasonable value for ΣS if the following ideal situation is considered, in which $BaSO_4$ exists in solution in a completely ionised form and sulphate is the only sulphur species (i.e. $[SO_4^{=}] = [\Sigma S]$). If the solvent is a reasonably concentrated brine, as is indicated by the fluid inclusion study, then according to the data of Templeton (1960) and Uchameyshvili, et al (1966), the solubility of baryte (and hence $[SO_4^{=}]$) is approximately $2.5 \times 10^{-4} m$ (data for a 2N.NaCl solution, which is approximately equivalent to a 11.7 wt.% solution).

It is also found that if $[\Sigma S]$ is increased, the stability field of sulphur (see Fig. 73) extends to higher values of pH. Hence in the extreme case of $[\Sigma S] = 0.1m$, native sulphur would precipitate prior to baryte at all pH values less than 7.8. As no sulphur has ever been noted it must be concluded that $[\Sigma S] \ll 0.1m$.

The corresponding part of the stability field of chalcopyrite is also crucial in Fig. 72, it is too small to represent adequately on the diagram

....but

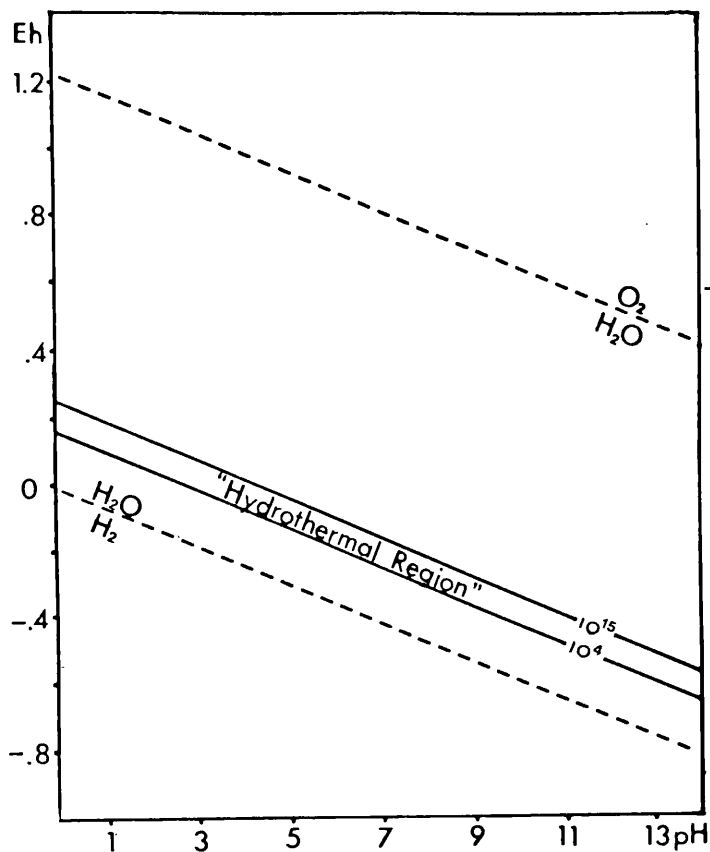
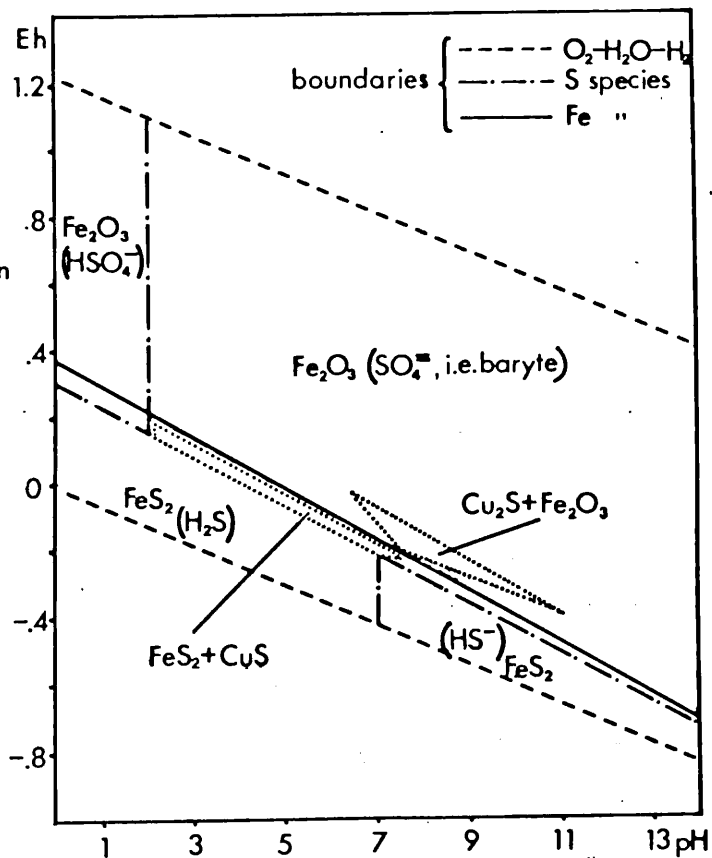


Fig. 71 Limiting $a_{SO_4^{2-}}/a_{S^{2-}}$ ratios, in terms of Eh and pH, for the majority of hydrothermal environments. (Barton 1957, 25°C data.)

Fig. 72 Stability fields at 25°C for the aqueous species of sulphur and iron with those of chalcocite with hematite, and pyrite with covellite (at $[\Sigma S] = 10^{-4} m$), superimposed. (modified from Garrels and Christ, 1965)



but it lies close to the shortest edge of the dotted triangle. Hence at a pH of 7 the corresponding Eh would be approximately -0.1v, which when replotted on Fig. 71 would indeed correspond with a higher $a_{\text{SO}_4^{2-}}/a_{\text{S}^{2-}}$ ratio than 10^{15} .

The Eh measurements on various natural waters, carried out by White, et al (1963) and Baas Becking (1960), show ranges of values the majority of which are greater than zero. This is not surprising however, because not only were the measurements not all taken in situ, but as the data are compilations of the work of various authors the time lag between collection and analysis has varied. According to Garrels and Christ (1965) only surface waters with good opportunity for circulation will be oxidising. Garrels (1960) presents a diagram (Fig. 75) in which various natural environments have been sub-classified with respect to Eh and pH. The environment corresponding to Eh = -0.1v and pH = 7, is that of 'groundwaters'.

Information about other parameters may be obtained by reference to other mineral stability diagrams, for example the system Cu-Fe-O-S in Fig. 74 (the parameter P_{O_2} refers to the partial pressure of oxygen, the values of which result from theoretical calculations. It is analogous to Eh as it

....reflects

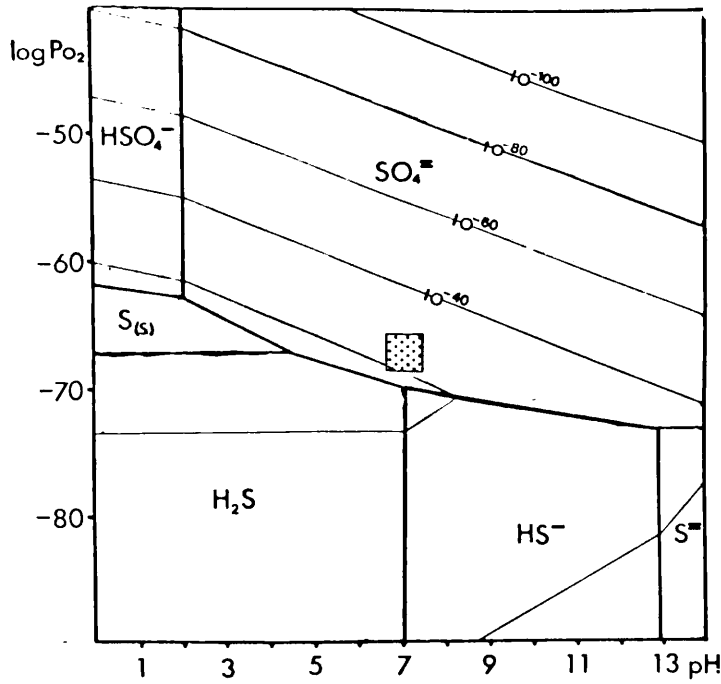
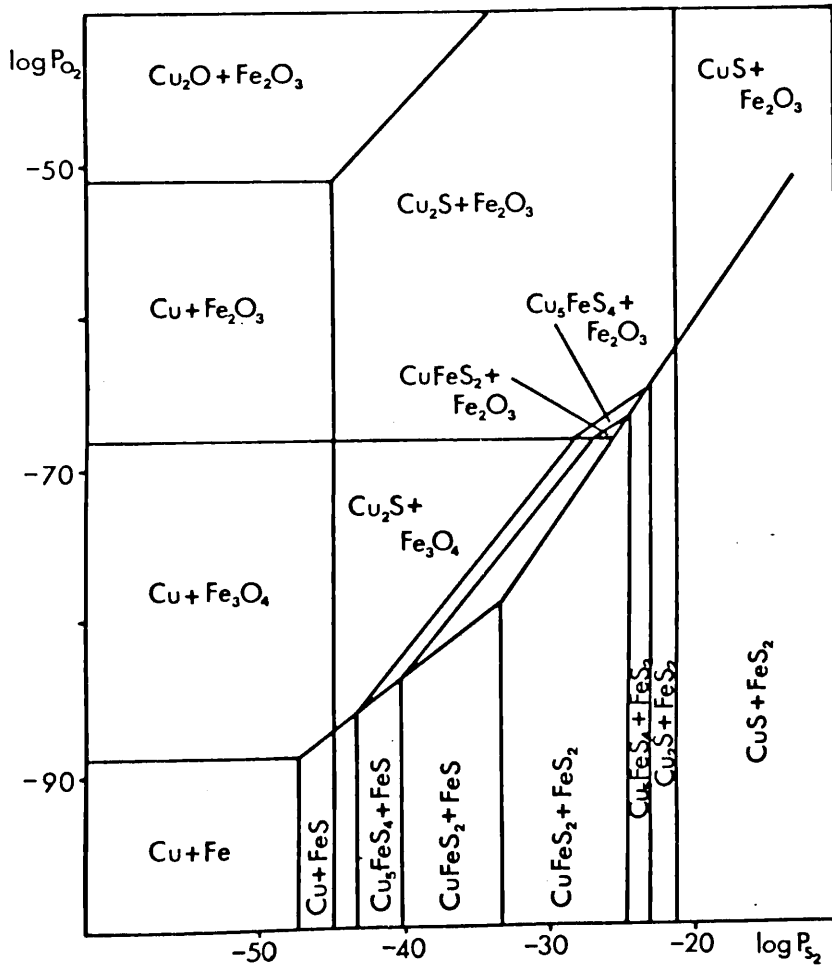


Fig. 73 (left) Distribution of predominant aqueous species at $[\Sigma S]=0.001m$ and $25^{\circ}C$. P_{S_2} contours are superimposed. (from Barnes and Kullerud, 1961)

Fig. 74 (below) Cu-Fe-O-S system stability relations diagram at $25^{\circ}C$. (adapted from Garrels and Christ 1965)



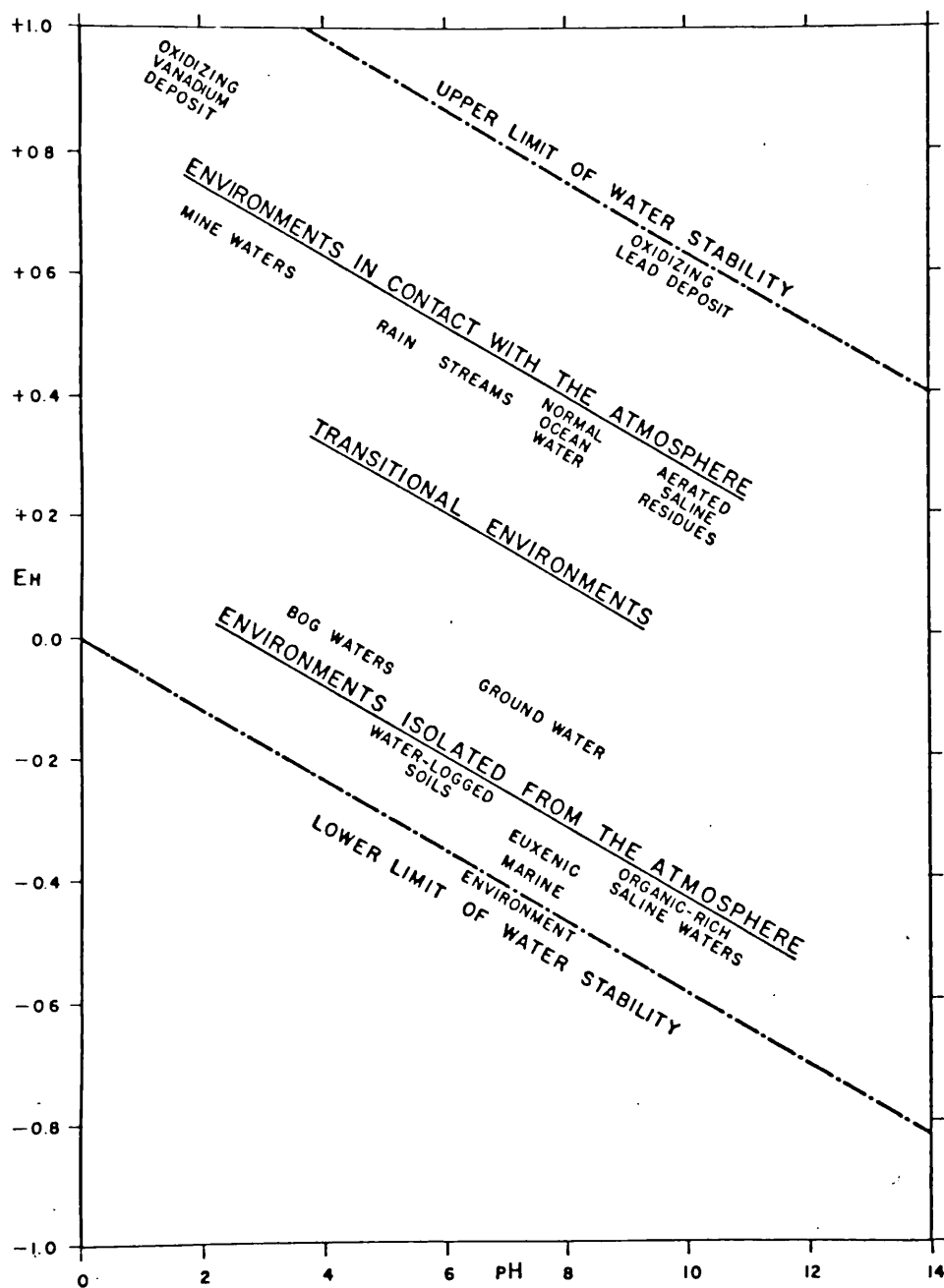


Fig. 75 Approximate positions of several natural environments in terms of Eh and pH (after Garrels, 1960).

reflects the degree of oxidation). From this the values $\log P_{S_2} \approx -26$ and $\log P_{O_2} \approx -67$ are reasonably closely defined by the small field in which both hematite and chalcopyrite are stable. Plotting on Fig.73 confirms that this is in the sulphate stability field and at a pH of 7 (stippled area).

Limits may be placed on the partial pressure of hydrogen sulphide (P_{H_2S}) by the relation:

$$P_{H_2S} = 10^{-6.0} \times a_s = /a_{OH^-}^2 \text{ (see Barton, 1957)}$$

which is derived from equations concerning the dissociation of hydrogen sulphide in water.

Taking a limiting value of $a_s = /a_{OH^-}^2 = 10^{-3.7}$ resultant from the boundary at which hematite becomes the stable iron compound, rather than pyrite (from Barton, 1957 using data from Latimer, 1952), P_{H_2S} must be less than $10^{-9.7}$.

A similar relationship of $P_{CO_2} = 10^{-9.8} \times a_{CO_3} = /a_{OH^-}^2$ is obtained from the dissolution of carbon dioxide in water. Again using iron (as BaO does not occur naturally) $a_{CO_2} = /a_{OH^-}^2$ must be less than $10^{+4.1}$ for hematite rather than siderite to be stable. Hence $P_{CO_2} < 10^{-5.7}$.

Comparisons between Type 1 and Type 2 deposits.

The pH for the Type 2 deposits is unlikely to be very different from that of Type 1. An acid component due to the solution of sulphides, or a basic component resulting from dissolved carbonate

....ions

ions, would probably cancel each other. The area where the stability fields of baryte, pyrite (and covellite) overlap is shown in Fig. 72. The Eh within this field, corresponding to a pH of 7, is therefore -0.2v. This is a small change from the value of -0.1v found for Type 1 mineralogies. The differences in P_{S_2} and P_{O_2} needed to cross from the hematite to the pyrite field are also small (Fig. 74).

It can be seen that now the mineralogy (Type 2 deposits) is more typical of low-temperature hydrothermal sulphide deposits (in contrast to the simpler mineralogies of Type 1 deposits), it plots within Barton's general "hydrothermal region" mentioned earlier.

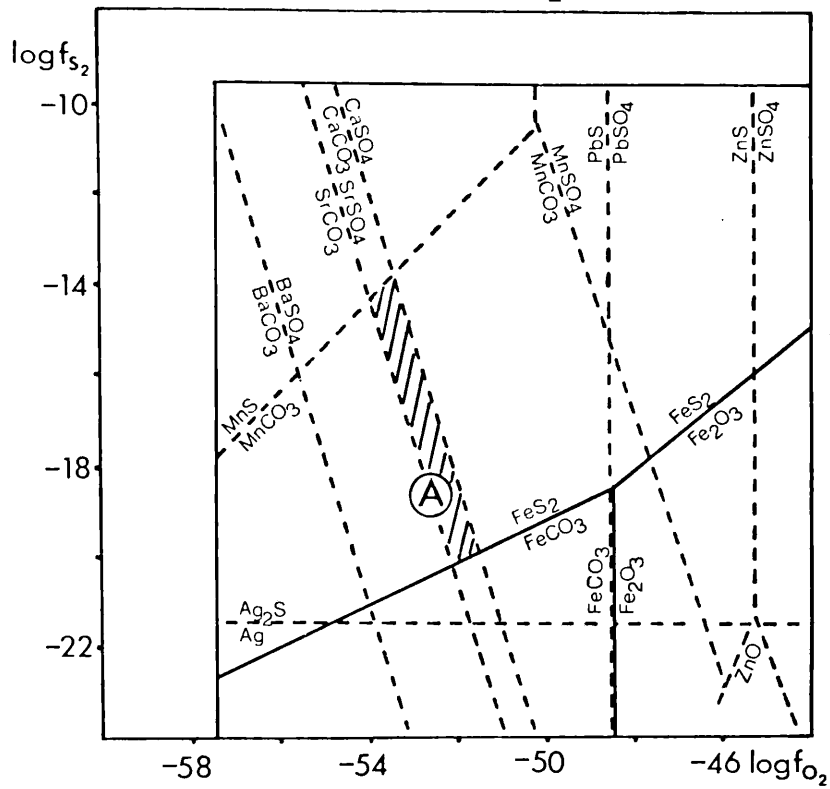
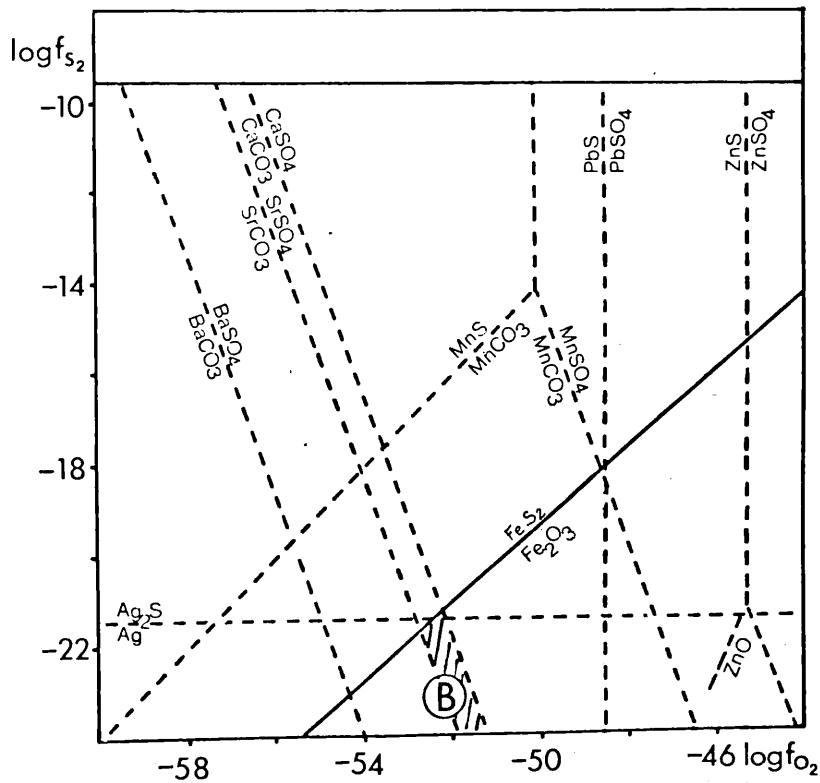
It seems reasonable to assume that deposits containing a dominance of carbonate minerals were deposited by solutions of a high P_{CO_2} relative to those where carbonates are minor constituents. Unfortunately, this parameter is ill defined for Type 2 deposits, the best limit on $a_{CO_3^{2-}}/a_{OH^-}^2$ (where $P_{CO_2} = 10^{-9.8} \times a_{CO_3^{2-}}/a_{OH^-}^2$) is provided by manganese at $10^{+2.6}$, giving P_{CO_2} to be greater than $10^{-7.2}$ (this results from $MnCO_3$ being present, as a component of ankerite, rather than MnO). This does not in itself directly contradict the data for Type 1 deposits (c.f. $P_{CO_2} < 10^{-5.7}$).

Fig. 76 illustrates, that at $P_{\text{CO}_2} = 10^{-2}$ atmospheres, the stability fields of pyrite, strontian baryte and 'ankerite', along with those of galena and sphalerite (i.e. the Type 2 assemblage) overlap in the region denoted by 'A'. That of hematite is excluded, in fact if P_{CO_2} were to be increased any further, hematite would be outside the diagram altogether (Holland, 1965). A reduction in P_{CO_2} to around 10^{-4} atmospheres would modify phase relations to those shown in Fig. 77. Here, region 'B' depicts the overlap of the stability fields of strontian baryte and hematite, whilst that of pyrite is excluded (i.e. a Type 1 assemblage). The diagrams are drawn for data at 100°C , however a reduction in temperature has no net effect on the relative positions of the boundaries. It is seen then that this parameter is the one which exerts the major control on the deposit mineralogies.

It may be noted in passing that the diagrams show quite clearly that a possibility exists for the substitution of calcium in baryte, but lead would not be expected to substitute as the stability field of PbSO_4 is quite distant from that of BaSO_4 (unless very low partial pressures of sulphur prevail).

To summarise, it must be stressed that no absolute values for the concentrations of the species

....in

Mineral Equilibria and CO₂ FugacitiesFig. 76 - modified from Holland, 1965. $T=100^{\circ}\text{C}$ $f_{\text{CO}_2}=10^{-2}$ atmos.Fig. 77 - extrapolated position when f_{CO_2} is reduced to approximately 10^{-4} atmos.

in the fluids have been sought from this study, because many of the controlling factors are incompletely defined. It was also necessary to make the simplifying assumption that the suites of minerals were precipitated in equilibrium and under relatively stable conditions.

The above observations are further evidence supporting the hypothesis of a lithological control of the mineralogy of the deposits. Temple (1956) postulated that the country rocks at Leadhills were the most probable source of the carbonate for the ankerite mineralisation, and this was endorsed by Rivera Murillo (1967). The mode of occurrence of ankerite at Barlocco (Chapter 2), together with the observations and analyses of Rust (1965), Weir (1974) and Floyd (pers. comm., 1978), which confirm the presence of an average of approximately 36% carbonate minerals in nearby Silurian greywackes, led to the conclusion that this was also the case at Barlocco.

The hypothesis of precipitation due to mixing of mineralising fluids with oxidising groundwaters is also supported. The value of $P_{O_2} = 10^{-6.7}$ estimated, is vastly different from that of meteoric water (10^{-2}), and such an increase in $P_{O_2}^{\text{on mixing}}$ would cause an abrupt oxidation of reduced sulphur species, to sulphate, causing precipitation of baryte. (Plummer (1971) says that the increase would also cause $a_{Ba^{++}}$ to decrease sharply and hence cause baryte to precipitate).

Chapter 7 : Summary

Chapter 7. Summary.

The research presented in the preceding chapters describes an attempt to investigate the baryte veins, and the baryte itself, of the central and southern Scottish mineral province, from several approaches.

The baryte-bearing deposits of the area have been divided up into three 'types' on the basis of their constituent mineralogies: Type 1 veins containing mainly baryte with minor to trace quantities of hematite, chalcopryrite and quartz; Type 2 veins containing major carbonate minerals with subordinate, though still major, baryte, and minor galena, pyrite, chalcopryrite etc.; Type 3 assemblages again contain dominant carbonates and minor sulphides, but in addition minerals containing the elements silver, cobalt and nickel.

In the case of Types 1 and 2 this grouping can subsequently be correlated, in general terms, with the lithology of the surrounding country rocks. Type 1 deposits occur in the sandstones and lavas of the Old Red Sandstone and Calciferous Sandstone (Visean), and Type 2 deposits in the Ordovician and Silurian of the Southern Uplands and Midland Valley inliers. Type 3 deposits may have derived part of their chemistry from the quartz-dolerite

.....intrusives

intrusives with which they are apparently spatially related, and consequently the lithology of adjacent country rock is of secondary importance.

The initial aim of using trace element assemblages to distinguish between different deposits was not realised. Firstly considerable problems were encountered in the analysis of baryte for trace elements, and then it was discovered that they did not in any case occur in significant quantities, the majority being easily explained in terms of contributions from contaminant minerals. The levels of strontium present in the baryte structure were not found to be characteristic of individual deposits, or of groups of deposits. This was also found to be the case for the minor and trace elements in the associated sulphides which were analysed.

It has been suggested by MacGregor et al (1944) that the baryte mineralisation had occurred in two distinct periods, associated either with the alkaline-basaltic magmatism of the Permian or the tholeiitic variety of the Tertiary, the deposits being distinguished on the basis of the general trends of the veins (as discussed in Chapter 3). As Scott (1967) pointed out, if this was the case then it might be expected that different trace element assemblages would occur. In comparing

....baryte

baryte analyses from Gasswater and Muirshiel, Scott found no general differences in trace element contents, and subsequently argued against the hypothesis. In the present study, again no general differences were observed, but doubts are cast on the validity of this criteria as it is unlikely that any of the trace element concentrations detected occur with the baryte itself.

Concerning the strontium content of baryte, it has been shown in this and previous studies (Scott, 1956; Gundlach and Weisser, 1964; Starke, 1964; Leach, 1973; Carlon, 1975; Morrow, et al, 1976; 1978, etc.) that naturally occurring baryte is rarely, if ever, pure barium sulphate, the substitution of strontium being ubiquitous. However, as mentioned above, the purity of this strontian baryte is very high. The author, therefore, would like to point out that the presence of strontium should become implicit in the term 'baryte'.

It is generally known that baryte has a very low solubility, and as a result straightforward precipitation from a barium sulphate bearing fluid has not been favoured as a process for the formation of the mineral, in quantity. This is not really a valid argument, barium sulphate has a greatly increased solubility in chloride solutions

....(Templeton,

(Templeton, 1960; Uchameyshvili, 1966; Gundlach et al, 1972; Blount, 1977) and such brines could contain adequate quantities of the compound to provide for the veins. This process is however not advocated here, for two reasons: 1. a change in temperature would have to be invoked to cause precipitation, something which is difficult to envisage in the light of the estimates of the temperature of deposition of the mineral given by fluid inclusion microthermometry. (Evidence from the fluid inclusions does however indicate that the fluid was a very saline one). Furthermore, the strontium distribution across the veins is contrary to what would be expected if precipitation took place from a $BaSO_4$ fluid in response to falling temperatures. 2. the strontium distribution within individual crystals is patchy, or random, and not systematic as might be expected if the crystals were deposited from a fluid of relatively constant composition.

A 'mixing' process as a method of deposition of the veins seems to fit the evidence best, providing a cause of precipitation and an explanation for the variability in both the "salinity" of the inclusion fluids and the strontium levels within crystals. The hypothesis of the direct mixing of a barium brine with a separate sulphate-bearing

....fluid

fluid is not envisaged, as this process requires that the two fluids only make contact at the exact location of the vein, and this is clearly beyond the realms of credibility in view of the coincidence of numerous generations of baryte found in any vein. The preferred process is one where barium and sulphide ions coexist in the same saline solution (barium sulphide being a highly soluble compound) and precipitation occurs when, on reaching the oxidised groundwater zone, the sulphide ions are oxidised to sulphate. In these circumstances a variation in salinity and strontium content of the mixed fluid would be expected.

There are several other characters of the deposits for which the above would also offer explanation. It has often been noted in British mines that baryte gives way in depth to other minerals, e.g. galena in the mining district of Shelve, or calcite at Gasswater (Scott, 1956). A parallel with the oxidising palaeo-groundwater zone could be made. Lastly, the predominance of the closely-packed platy variety of crystals in the veins is evidence in support of the mixing hypothesis insofar as the formation of such crystals would be compatible with a reasonably fast rate of crystallisation taking place in open fissures.

The mechanism proposed for transporting the potentially mineralising fluids to surface environments is the one described as 'seismic pumping' by Sibson et al (1975). This mechanism does not rely on thermal gradients for the impetus for fluid migration, but on pressure variation in areas of seismic activity, and so no contradiction of the low-temperature data from fluid inclusion studies is encountered.

As to the age of the mineralisation, in the absence of direct, closely-defining geological evidence, potassium-argon isotopic dating of the deposits was attempted. It was found that the deposits did not lend themselves to other isotopic dating methods, however the alternative approach of palaeomagnetic dating was considered and samples of the botryoidal hematite from the Auchenstilloch district were taken in order that comparisons with the known polar wanderings during the Upper Palaeozoic and Mesozoic could be made. The results are not yet available.

The K-Ar method records the last significant isotopic event to occur at the deposit. This in effect places the younger limit on the ages of mineralisation and can be taken as the actual age if certain criteria can be satisfied. The dates

....obtained

for several deposits group in Hercynian and Permo-Trias times and show no correlation with the mineralogical 'type' groups. In agreement with the hypothesis concerning the mechanisms which emplaced the veins, these two periods are ones of significant seismic activity.

The author suggests that the theory of a Tertiary episode of baryte mineralisation in Scotland must finally be abandoned, especially as no other isotopically dated deposits have yielded Tertiary ages either.

A problem for which only speculative suggestions can be proffered concerns the origin of the barium, and other cations, involved in the mineralisation. In some cases there is evidence to suggest that the country rocks have contributed to the mineralogy of the deposits, e.g. the ankerite of Type 2 veins, however the data from chemical investigations of the wall rocks precludes the derivation of barium from this source.

It is known that barium and strontium are expelled from the carbonate structure when aragonite converts to calcite and during dolomitisation (Lipmann, 1973; Shearman and Shirinohammadi, 1969), it is therefore a possibility that the diagenesis

....of limestones

of limestones could have been responsible for the release of these elements. Muir, et al (1956) produced numerous chemical analyses of Scottish limestones (together with cornstones, cementstones and marls) ranging in age from Dalradian to Recent. The range of barium levels in the limestones of most periods was zero to 400 p.p.m. however, in the strata of the Carboniferous Limestone, Calciferous Sandstone, Middle and Upper Old Red Sandstone, and Dalradian, the concentrations reached 1500 p.p.m. or more (some samples containing over 0.3% Ba). Hence the sort of concentrations needed to supply mineralising solutions, were available. Indeed strata of these ages have been found to contain quantities of authigenic baryte e.g. the cornstones of the Upper Old Red Sandstone in south Ayrshire (Burgess, 1960). Also, recent work by the Institute of Geological Sciences has also led to the discovery of a large stratiform baryte-sulphide orebody in graphitic schists of the central Dalradian sequence in Perthshire (N.J.Fortey, pers. comm.).

Should future studies of these deposits be considered, the author feels that, apart from further investigation of the uranium contents of the baryte, the fields of isotope geochemistry should be explored. Strontium isotopes have not been used extensively

....in economic

in economic geology but are potentially useful in tracing the source of the vein strontium. The stable isotopes, sulphur and oxygen, could also be useful in this respect and possibly in testing the theory of mixing proposed.

In the North Pennines, Solomon et al (1971) found the isotopic composition of sulphate oxygen and sulphur, in baryte to be very uniform. This was thought to indicate that the source of the sulphate was isotopically homogeneous at all localities, i.e. the source was probably connate waters. In the case of the Scottish deposits the isotopic compositions of the three 'types' of baryte could be compared in the light of interpretations placed on them here. Also, the compositions could be compared between deposits which have, by various authors, been genetically linked, e.g. the correlations made (in Chapter 3) between sedimentary basins etc. and the location of deposits.

Ohmoto (1972) showed the pronounced effect that physico-chemical parameters such as pH, the fugacity of oxygen and temperature have on the sulphur isotopic ratios measured. Although these effects would not be of prime importance in comparing similar deposits, they would be critical in other cases. Hence the investigations into these parameters made

....in Chapter

in Chapter 6 would need to be reassessed for the individual deposits concerned.

In view of the fact that vast areas of Scotland are blanketed with glacial morain and peat it is probable that there are economic veins yet to be discovered. The chemical dispersion of elements in the wall rock adjacent to the veins is not a useful tool for geochemical prospecting, however other characters of the deposits could prove helpful. This research has shown the affinity of the veins for structurally positive areas around sedimentary basins, and has outlined the kind of country rocks in which the high-percentage baryte veins occur.

Having selected a likely region, stream sediment surveys appear capable of picking up barium anomalies (Leake and Haslam, 1978), and a follow-up of soil sampling would more closely define a possible mineralised area. The latter technique proved fruitful in the Teign Valley, Devon (Merefield, 1975; Beer and Ball, 1977) where the 'A' soil horizon was used as it contained the highest barium levels. In Scotland however the peat cover would be a hindrance, Scott (1967) noted barium levels to decay to background values within a couple of metres of the outcrop.

An alternative approach, in view of the profuse minor veining noted around known deposits, would be

.....to use

to use geophysical techniques to locate hidden faults which parallel exposed veins, or are possible extensions of veins. Some success in locating such faults (which turned out not to contain economic mineralisation) was met using an electrical method, at Gasswater (Scott, 1967), but not the gravitational one also tried. Often in the search for coal seams, and subsequently the faults which offset them, seismological methods are used with frequent success (C.Irons, pers. comm.), and so the method could perhaps be applied to baryte veins. Surface trenching over areas indicated by this method would be a relatively inexpensive precursor to possible exploratory drilling, although some of the uncertainty of guidance of the latter will have been removed by the indications of dip, depth etc. from the seismic data (Parasnis, 1979).

Chapter 8 : An occurrence of calcite at Muirshiel

Chapter 8. An Occurrence of Calcite at Muirshiel.

General description.

The mineral described below merits individual description not because calcite has previously not been found at Muirshiel, but because this specimen is believed to have a different origin from the baryte with which it occurs.

Only one specimen was found, and unfortunately it was not in situ. However, the specimen did contain barytes typical of the Muirshiel type, and it appears that both minerals were deposited in a similar plane (as judged by their respective crystal growth directions).

The calcite is pearly-grey in colour, with some pinkish areas due to inclusions of finely divided hematite. The rhombohedral crystals are commonly 1 cm across and appear to replace the pink banded baryte which is partially brecciated and enclosed within the calcite. At the junction of the main masses of the two minerals the calcite becomes very impure and is a dirty-brown colour. In thin section this is seen to be due to a high concentration of hematite and/or goethite. White strontianite was also observed, occurring as a late mineral and occupying interstices between crystals. Strontianite has previously been found at Muirshiel (R.Colvine,pers. comm.)

pers. comm.), again as a late mineral, but colourless and in larger, vuggy crystals.

Thin section description.

The baryte is of the fine to medium-grained, compact-platy type, typical of the Muqdishiel veins. Small hematite inclusions give rise to the pink colour seen in hand specimen. The calcite also contains hematite inclusions in similar quantities to the baryte, except in certain areas, notably those close to the baryte. Here the population density of iron oxides/hydroxides increases markedly, and the crystal size of the calcite decreases. This is thought to be due to the fact that these were the first crystals of calcite to form and the increase in size outwards is that which normally occurs in crystal growth sequences.

The calcite has replaced the baryte along crystal boundaries and cleavages (Fig. 78), and has also veined it along cracks. As the calcite in these veinlets lacks the fluid inclusions which are present in the main mass of calcite (see below) it is assumed that it is secondary.

The fluid inclusions in the baryte (Fig. 62) are noticeably different from those of the calcite. Those of the baryte are small monophasic-liquid inclusions, typical of the normal low-temperature variety

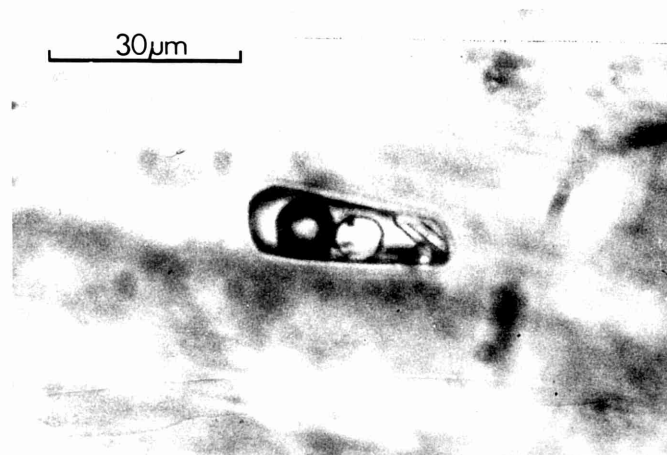
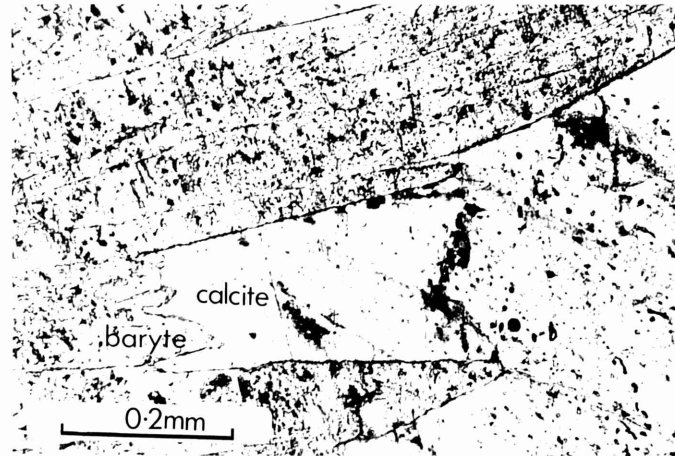
....common

to all the other baryte samples described in Chapter 5. Those of the calcite are multi-phase, high-temperature inclusions of various types (Figs. 79 to 82 incl.). There are two-phase liquid-vapour inclusions, three-phase solid-liquid-vapour inclusions (in which the number of solid phases was seen to vary between one and seven), and monophasic vapour inclusions (Fig. 83). The occurrence of the latter, co-existing with the others, is evidence of boiling of the precipitating fluids having taken place. Furthermore, it appears that boiling continued, episodically at least, after crystallisation of the calcite. This is attested by the occurrence of vapour inclusions in trails of secondaries throughout the specimen. An unusual type of inclusion observed in the calcite is sketched in Fig. 84. These 'coronas' of numerous small liquid inclusions are fairly common. An explanation of their existence is that they are the results of partial leakage due to decrepitation, followed by healing (A. Rankin, pers. comm.).

The orientation of the main trails of inclusions in both minerals were studied in order that further information on their mutual relationship could be obtained. The main pseudosecondary trails (those perpendicular to the direction of crystal growth)

....of

Fig. 78 High-temperature calcite replacing baryte (plane polarised light). The inclusion trails in the baryte are not seen to extend into the calcite.



Figs. 79 and 80
Examples of the multiphase inclusions common in the calcite (plane polarised light).

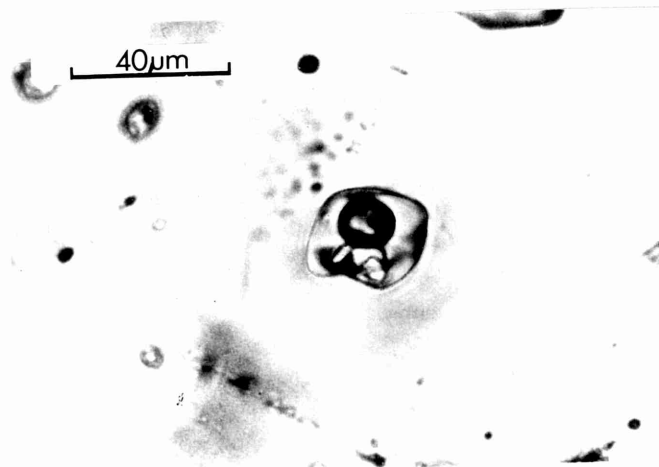


Fig.81 (as figs.79 and 80)

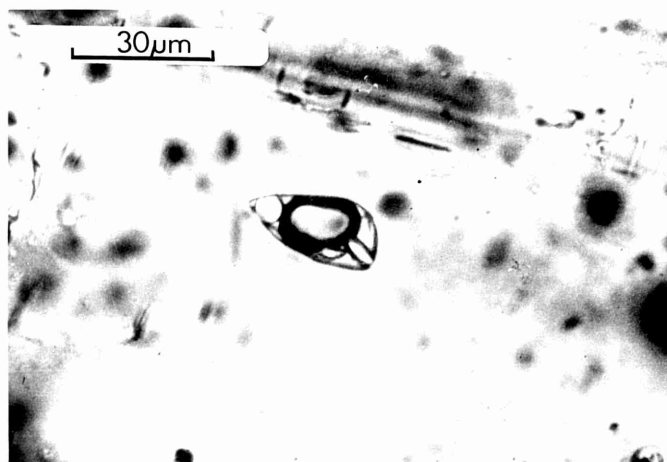


Fig.82 An area of similar inclusions in the calcite, each containing at least seven daughter crystals (plane polarised light).

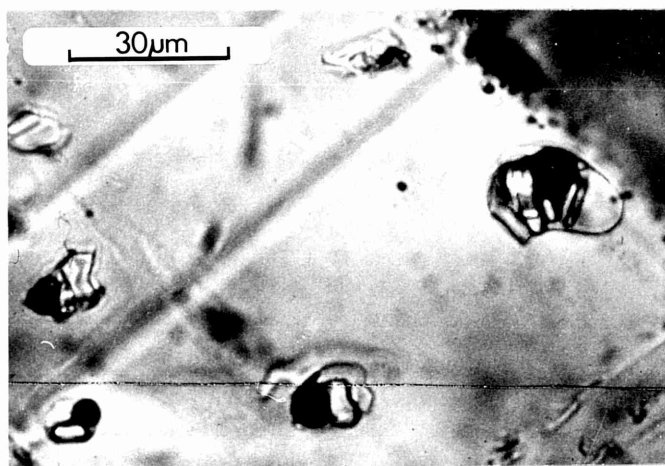
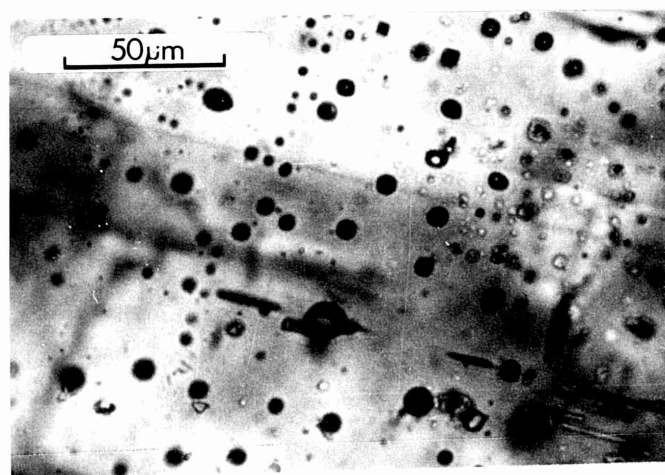


Fig.83 Monophase vapour inclusions in the calcite (plane polarised light).



of the baryte were found not to be reflected in the calcite (e.g. Fig. 78). The orientations of numerous trails of secondary inclusions occurring in the calcite, the majority of which are apparently the results of healed cleavages, were absent in the baryte. (The primary inclusions in the calcite did not show any linear trends, and so none could be correlated in the baryte).

This information seems to confirm that the baryte was deposited before the calcite. However, two points which are not easy to reconcile are:

- i) there are no high-temperature secondaries in the baryte, even close to the baryte-calcite boundary.
- ii) the inclusions in the baryte have apparently remained intact when it might be expected that they would have decrepitated due to the action of the hot carbonate fluids. Nevertheless Fig. 88 shows some "healing" of the baryte to have occurred, close to the carbonate, i.e. the fluid cavities appear less angular and crystal boundaries less distinct. Mono-phase vapour inclusions have also been tentatively identified in the baryte close to the calcite.

Microthermometry.

The histogram in Fig. 86 shows that the main range of homogenisation temperatures is approximately
.....440°C to

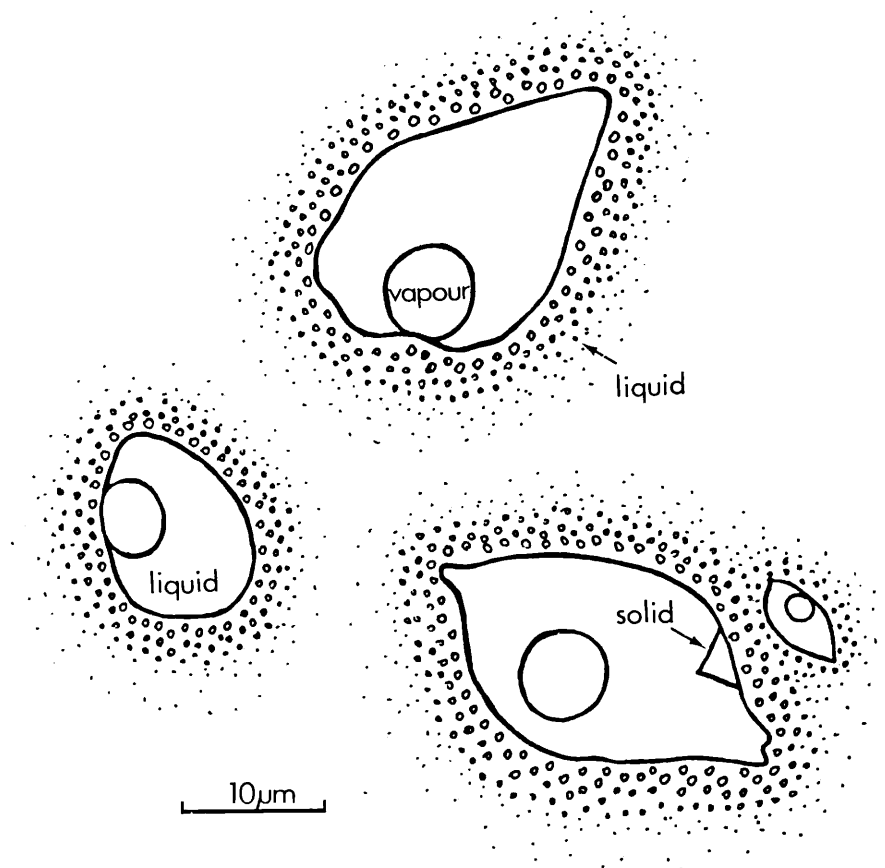
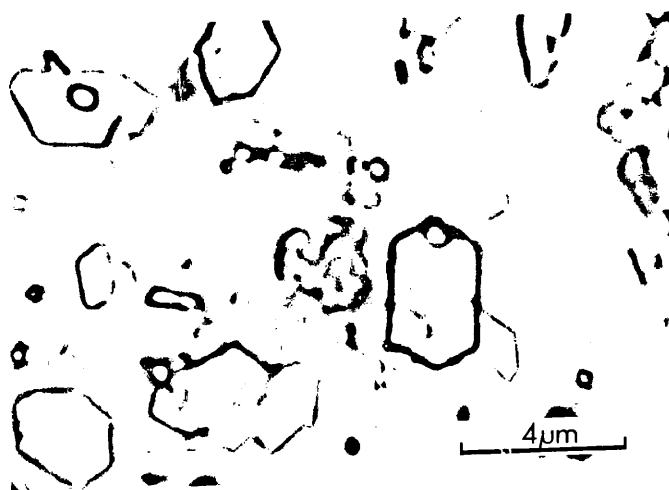


Fig.84 Corona, or aureole effect displayed by some partially leaked inclusions.

Fig.85 Acid insoluble daughter crystals (baryte) from the calcite (plane polarised light, in oil).



440^oC to 480^oC. These temperatures were obtained from both two-phase and multi-phase inclusions. The criterion for assuming a primary origin was the selection of inclusions of a solitary nature, apparently unrelated to trails of inclusions which could have resulted from the healing of a crack or cleavage. Those which appeared distorted in shape were also avoided, as they may have been subject to leakage.

The daughter minerals of the inclusions were generally observed to dissolve before homogenisation occurred. On three occasions the temperature at which this happened, was noted: 312^oC, 365^oC and 370^oC. This was the general range for most of the daughters.

The range of homogenisation temperatures is thought to be representative of the true temperatures of precipitation, no pressure correction being necessary, as the liquid was known to be boiling at the time.

At temperatures in the region of 350^oC and above it was common for violent decrepitations of some of the inclusions to occur. It was possible that the presence of carbon dioxide could have been responsible for these decrepitations. Mass spectrometric analyses for this compound, during step heating of a sample of the calcite, revealed that only when decomposition of the calcite occurred

....(at

(at temperatures $> 600^{\circ}\text{C}$), and no water loss was detected (i.e. all the inclusions had been evacuated), could significant quantities of CO_2 be detected. Hence the possibility was refuted.

The concentration of salts in a boiling aqueous solution would be expected to vary during precipitation from the solution. This is in fact what was found, as the histogram of last-ice-melting temperatures of the inclusion fluids illustrates (Fig. 87). The total range was -6.5 to -43.0°C . It was observed that large variations in "salinity" were possible over small distances within the crystals.

Inclusion leachates.

Leaching the inclusion fluids with pure water (by the method outlined in Chapter 5), yields a sodium to potassium (atomic) ratio of 13.0. This is potassium enriched with respect to present day sea water and normal groundwaters. The baryte samples from Muirshiel also showed a similar potassium enrichment in the range 4.7 to 16.5. However, unlike the case of the baryte, an argument for a juvenile component for the mineralising fluids may be made in view of the temperature of homogenisation. The alternatives of contributions from evaporitic waters or deep circulating brines (see Chapter 5) are not thought likely, but that of
groundwaters

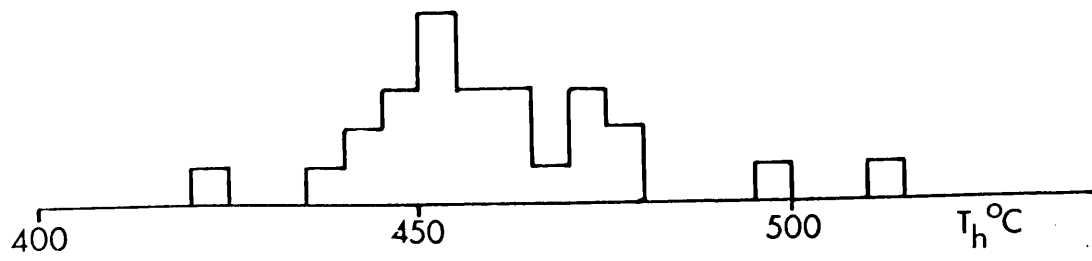


Fig. 86 Homogenisation temperatures for calcite D344.

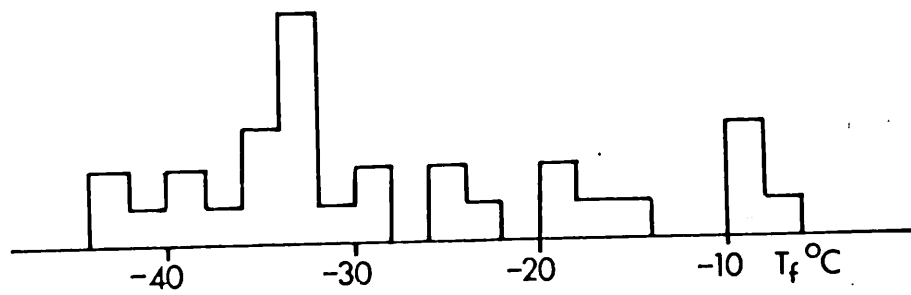


Fig. 87 Last-ice-melting temperatures of the inclusion fluids in calcite D344.

groundwaters in equilibrium with alkalic rocks is favoured: the average K_2O and Na_2O values for the immediate wallrocks are approximately 6.0% and 2.5% respectively (Chapter 4a).

The daughter minerals.

In thin section the number of daughter minerals per inclusion is seen to vary between one and seven. Their shapes are variable but tabular ones seem to dominate. Except in one instance, there does not seem to be a general relationship between the type of daughter and the shape and size of the inclusion. This exception is the case of the 'shallow', very rounded, oval-shaped inclusions which only have one, very small daughter.

None of the daughters were isotropic, but whatever interference colours they may have shown were masked by those of the calcite host. This shows that they were not simple chlorides (e.g. halite), as have commonly been found in hydrothermal ore deposits. This is further supported by the freezing data, because daughters were noted in inclusions whose liquids showed last-ice-melting temperatures inconsistent with those of a saturated chloride solution (i.e. temperatures well above $-22^{\circ}C$).

An attempt was made to extract some of the daughter minerals from the host: by selecting several grams of the purest of the crystals it was hoped that, apart from the ubiquitous hematite, no other contamination would be present. This sample was then dissolved in 10% hydrochloric acid. The resulting solution was decanted off the sparse insoluble residue, which remained at the bottom of the beaker. After washing and drying, this residue was studied under oil, in transmitted light.

Hematite, as expected, was present in sizeable quantities. However, many transparent, tabular, hexagonal-shaped crystals also remained along with a few rather irregularly-shaped ones (Fig. 85). All the crystals appeared colourless and non-pleochroic, and displayed first-order black interference colour. This latter observation is to be expected as the crystals were only, an estimated, 1 μm thick. One rare exception observed was that of lamellar twinning (first order colours).

Great difficulties were encountered in attempts to determine the refractive indices of the minerals by the Becke line test in various oils. It was found that a thin film of, what was presumed to be, moisture, coated the crystals even after lengthy drying. This had the effect of yielding erroneous refractive indices. The problem was partially

....solved

solved by a rapid transfer of the residue from oven to oil. Even so only a few of the crystals were found suitable; these gave a fairly constant, approximate result of 1.65.

An X-ray powder diffraction photograph was taken using a second residue prepared in a similar manner to the first. The pattern corresponded with that of a mixture of baryte and hematite, and hence was in agreement with the refractive index determinations (c.f. baryte, refractive index 1.636 - 1.649). The thin sections of the calcite were re-examined for solid inclusions of baryte but none were found, and so it is believed that the residue was indeed a sample of the acid insoluble daughter minerals contained within the fluid inclusions of the calcite.

The above procedures have served to indicate the major component of the acid insolubles, but the X-ray diffraction did not reveal any of the possible minor quantities of other minerals. In an attempt to detect such occurrences a rather crude use of an electron probe microanalyser was made: some of the residue was "sprinkled" on an adhesive-coated glass slide which was left unpolished. This was then coated with carbon prior to the probe analysis. The incident beam of electrons was concentrated to a "spot" of less than 1 μm diameter in order to reduce the (high) possibility of simultaneously
....analysing

analysing two (or more) crystals. It was found that visual location of the beam onto a particular grain was very difficult, and so the spectrometer was set to detect silicon and the beam scanned "blind" until a positive response was observed. At this point a final adjustment was made to maximise the response and then a full element scan was made at that particular location.

Although the ensuing analyses performed in this way were not expected to be fully quantitative, a few are held to be significant. About ten spots were analysed, of which one yielded a composition corresponding with epidote, and two others with alkali feldspars. The remaining spots showed only silicon, and as no solid quartz inclusions were observed in thin section, it must be concluded that either some of the daughter minerals were quartz, or that the analyses were being performed on the glass slide!

To study the daughter minerals "in-situ" a scanning electron microscope coupled with a multi-channel energy-dispersive analyser, was used. The sample preparation for this technique necessitates fixing the specimen onto a metal stub, and then evaporating on, a carbon coating. During this procedure care was taken not to touch the freshly broken surface of the mineral (the one to be studied) or dissolution

....of the

of the daughters may have ensued. Cutting or polishing of the surface for examination was obviously impossible for the same reason.

The study was successful, and several of the inclusions observed are shown in Figs. 89 to 103 incl. Previous work using this relatively new technique is scarce, however a notable example is that of Le Bel (1976), who worked with multi-phase inclusions in quartz from the Corro Verde/Santa Rosa porphyry copper.

The partial, qualitative analyses of the daughters observed revealed the following, in order of decreasing abundance:

i) calcium-iron-manganese minerals (according to Roedder (1972), only in rare instances does the host mineral form daughter minerals, and so it must be concluded that these calcium minerals are not carbonates).

ii) calcium compounds containing various quantities of one or more of the elements; cerium, lanthanum, neodymium and occasionally titanium. The rare earths of this list are from the light-element end of the lanthanide group of rare earth elements. The minerals they form which could fit the observations made are: Saham^alite $(\text{Ce,La,Nd})_2(\text{Mg,Fe})(\text{CO}_3)_4$;
bastnaesite

100

bastnaesite $Ce[F/CO_3]$; parisite, röntgenite and
synchysite — Ca,Ce, fluorocarbonates; huanghoite
 $Ba Ce[F/(CO_3)_2]$; cordylite $Ba (Ce,La,Nd)_2[F_2/(CO_3)_3]$;
calkinsite $(Ce,La\dots)_2[CO_3]_3 \cdot 4H_2O$; marignacite
 $(Ce,Ca)_2(Nb,Ti)_2O_7$.

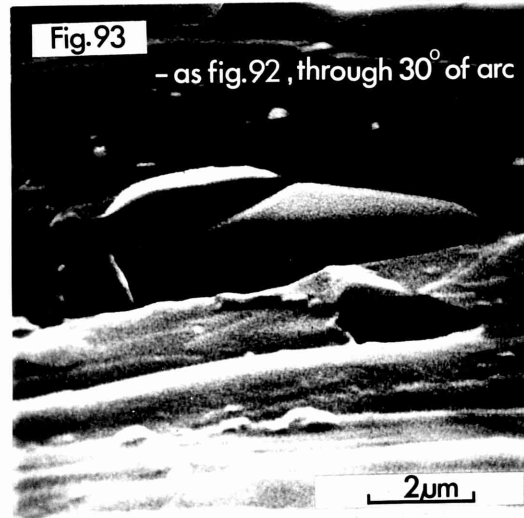
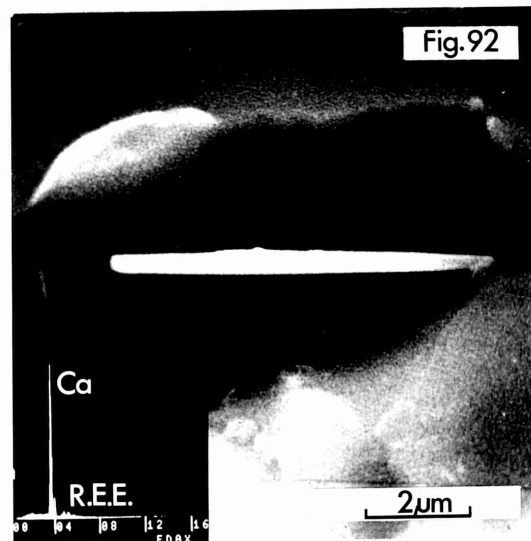
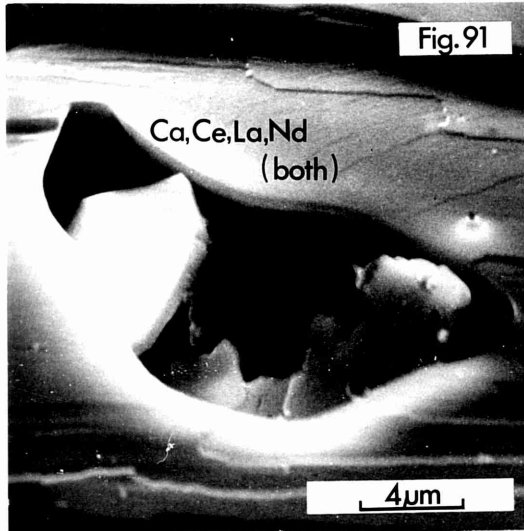
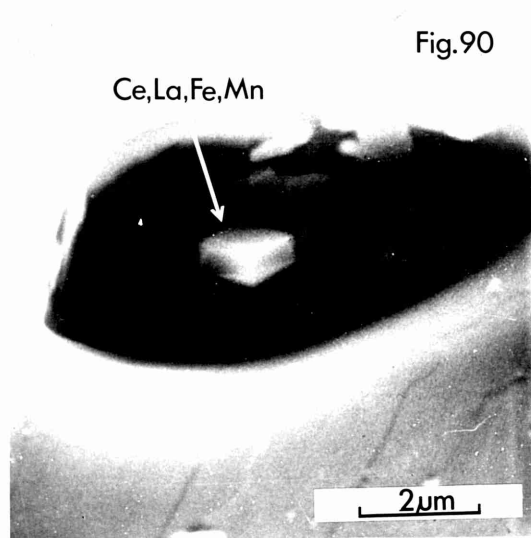
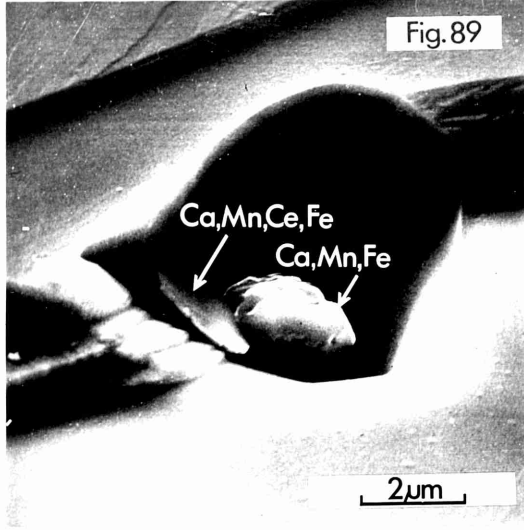
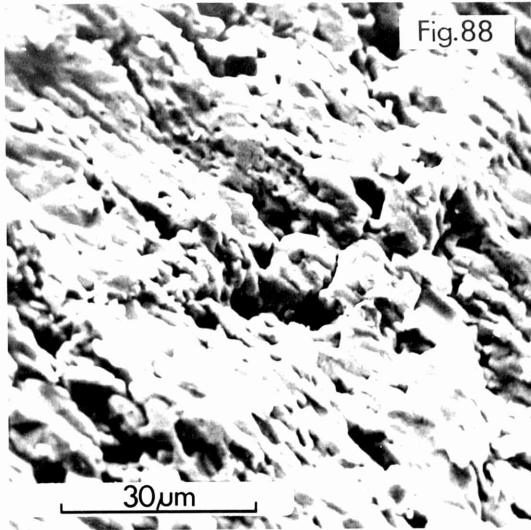
iii) barium-sulphur minerals, presumably baryte

iv) silicates of various compositions.

In some cases two daughters coexisted with apparently identical analyses (Fig. 91). It is not normally an 'allowed' phenomenon for fluid inclusions to have two daughter crystals of the same mineral. Normally there has been sufficient time for minimum surface energy to have been reached, especially as the distances involved are so small (Roedder, 1972). However, in this case, as the minerals involved are only slightly water soluble (especially baryte), and a reasonably fast rate of precipitation of the host would have occurred during boiling, these occurrences are acceptable. Alternatively it must be remembered that similar element responses are possible from different minerals, as the elements fluorine, oxygen and carbon are not detected by this technique.

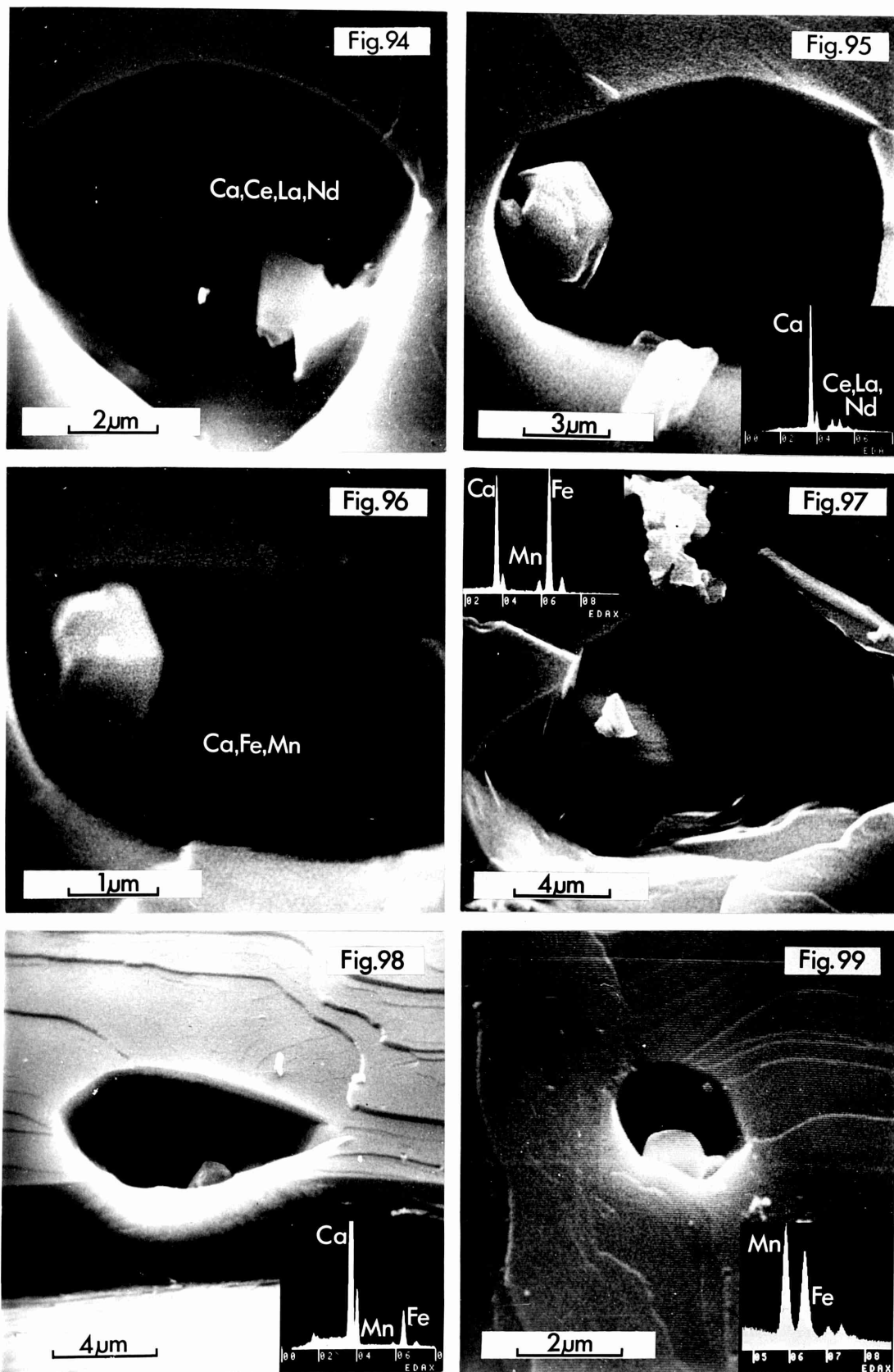
Occasionally a precipitate was observed to have developed from the evaporated fluid of the inclusion. These appeared either as congregations of small roughly equant crystals (Fig.104) which were found to be barium-sulphur minerals, or as

....numerous

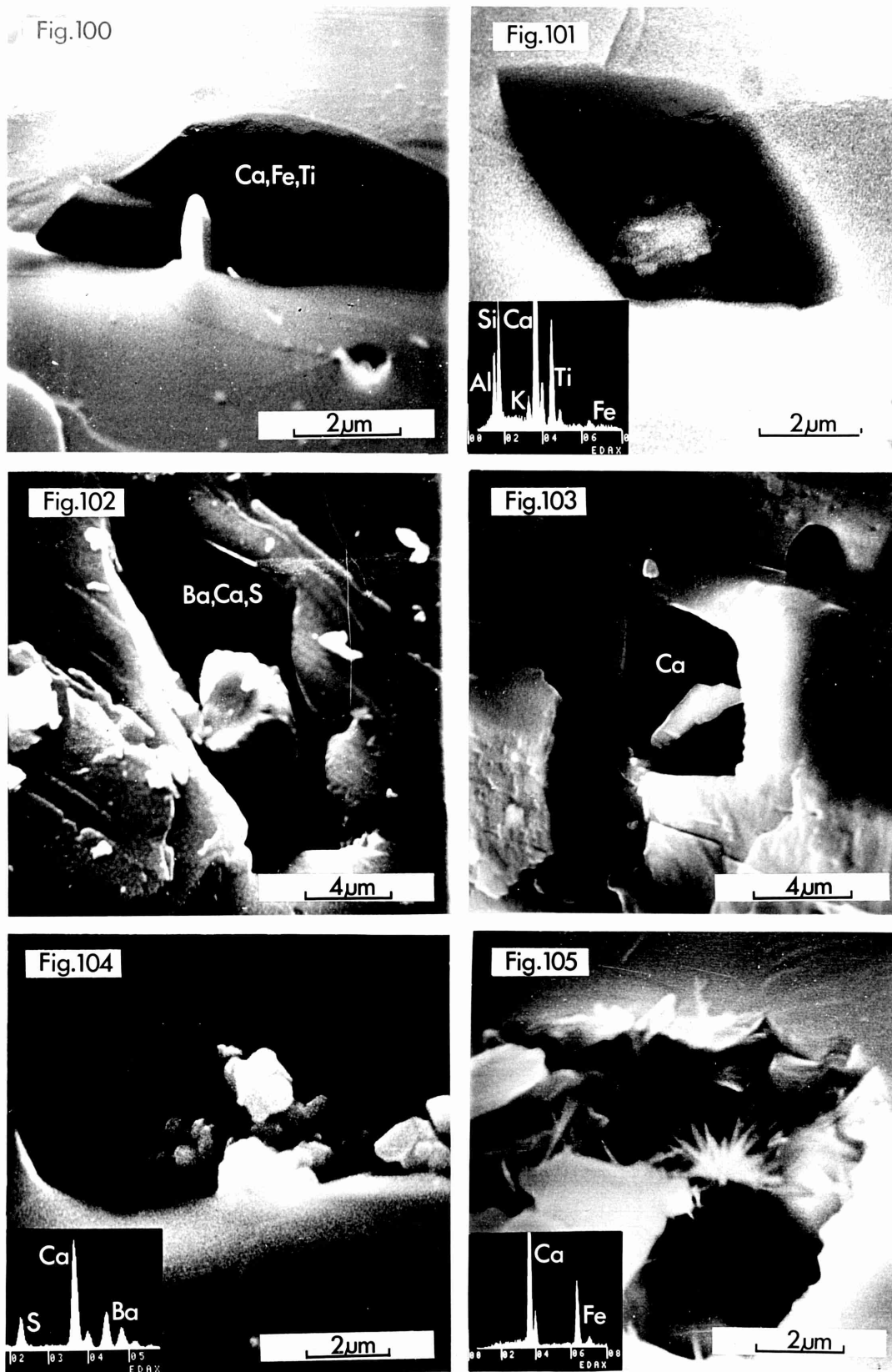


Figs.88 Baryte from close to the high-temperature calcite, the crystals appearing somewhat rounded, or 'healed' (S.E.M.).

Figs.89 to 93 Various, 'in situ' daughter crystals together with their respective partial, qualitative analyses (S.E.M.).



Figs. 94 to 99 Various 'in situ' daughter crystals (S.E.M.).



Figs.100 to 103 Various 'in situ' daughter crystals (S.E.M.).

Figs.104 and 105 Fluid precipitates from opened inclusions within the calcite (S.E.M.).

numerous acicular crystals radiating outwards from parts of the inclusion walls (Fig. 105), giving positive responses for calcium, iron and manganese.

It should be noted that the analytical spectra obtained for these minerals (as presented with some of the scanning photomicrographs) always contain a major calcium component. This is due to the fact that the beam of electrons incident on the daughter, is energetic enough for a large portion to pass through the daughter and reach the host mineral, hence the calcite host is represented in the emergent X-ray analyses.

The detection limit for the instruments used in these analyses is of the order of one percent. Therefore, bearing in mind that the targets for the analyses are located in energy-absorbing cavities, even the minor peaks represent very significant concentrations.

The final observation made was that the calcite host, in random checks at locations close to inclusion cavities, never contained detectable quantities of any of the elements found in the daughter minerals. The only positive response obtained was for calcium.

A drawback in the use of this technique is that a distinction between primary and secondary inclusions is almost impossible. Exceptions being the
....recognisable

recognisable secondaries in distinct trails.

Partial chemical analysis of calcite.

Using plasma-source emission spectrometry two samples of the calcite were analysed for some rare earth elements. The first was untreated, but the second had been leached with distilled water. It was hoped that the leaching would dissolve away the daughter salts etc. and so a comparison between the host and daughters could be made.

It was found however, that the analyses were virtually identical, indicative that the daughters were not easily water soluble. The overall concentrations of the elements which were measured are: yttrium 165 p.p.m; cerium 120 p.p.m; europium 63 p.p.m; ytterbium 34 p.p.m.

Summary and conclusions

The evidence presented above leads to the conclusion that the calcite was precipitated from a boiling aqueous fluid at a temperature of 440 to 480°C. The salinity of the fluid prior to boiling cannot be determined as the salinities of the inclusion fluids vary appreciably. There is evidence that further boiling solutions were in contact with the calcite after initial deposition took place, and also that the temperature of these solutions was in excess of that of the mineralising

....solution

solution (viz. the monophasic vapour secondary inclusions and the partially decrepitated inclusions, respectively).

In the area, the only obvious sources capable of providing the necessary heat for the fluids are the igneous intrusions. Any attempt to date the calcite on the basis of this supposition would necessitate specific isotopic dating of likely intrusions, coupled with isotopic comparisons between the calcite and suspected intrusion. The calcite was deposited after the baryte but how long after is unknown. K/Ar isotopic dating on the gouge clays from the main baryte vein at Muirshiel yielded Permo-Triassic ages (Chapter 3).

The chemistry of the fluids, as attested by the daughter minerals and fluid precipitates, is highly unusual. Although it might be expected that iron and manganese could be associated with carbonate solutions, the occurrence of silicate minerals and rare earth elements in such high concentrations is rather exceptional. It is the opinion of the author, however, that with a more widespread use of the S.E.M. analysis technique, that such suites of elements will prove to be more commonplace than hitherto expected.

The similarity of the ionic radii of some of the rare earths, particularly cerium (1.02\AA) and
....yttrium

yttrium ($1.06\overset{0}{\text{Å}}$) with that of calcium ($1.06\overset{0}{\text{Å}}$), enable the former to substitute for the latter (data from Bragg, 1937). Their occurrence in calcite is therefore no surprise, Müller, et al (1974) analysed calcites and dolomites from regionally metamorphosed marble, for rare earth elements, and found cerium and lanthanum to be by far the most abundant, especially in the calcites (concentrations were of the order of 10 p.p.m.).

Kosterin (1959) suggested, in a study on the possible modes of transport of rare earths in hydrothermal solution, that most lanthanides are transported in alkaline solution as carbonate, fluoride or sulphate complexes and that precipitation could be brought about by a decrease of pressure, fixation of carbonate ions, or a change in alkalinity. Also that the heavy lanthanides form more stable complexes than the lighter ones do, and therefore remain in solution longer. All these points are consistent with the data obtained in the present study.

An analysis of the calcite host, by itself, could not be made as it was found impossible to leach or dissolve away the daughters without also dissolving the calcite. The overall analysis showed the rare earths to be present in relatively high concentrations.

Yttrium and the lanthanides are, on average, more abundant in granitic rocks (ave. total ~290 p.p.m.) than intermediate ones (ave. total ~196 p.p.m.), or basalts (ave. total ~99 p.p.m.). However, the highest concentrations are to be found in alkalic rocks (~310 to 2213 p.p.m.) and carbonatites (~687 to 2250 p.p.m.). The average concentrations of sediments are generally low (~25 to 285 p.p.m.) (data from Hermann, 1970).

The country rocks in the immediate area of Muirshiel mine comprise trachytic and trachy-andesitic agglomerates and ashes, intruded by plugs of trachyte, and various dykes. The chemistry of the rocks is therefore tending to the alkalic varieties and so the probability of reasonable amounts of rare earths being available is good (analysis of the wall rocks for yttrium only, gave values ranging from 50 to 80 p.p.m.).

The barium-sulphur component of the calcite fluids could have been derived from one (or both) of two sources. Either the fluids picked up these elements from the same source which provided for the baryte mineralisation, or they may have dissolved some of the pre-existing baryte itself. There is some evidence for the latter, in that the calcite is seen to have replaced the baryte to some degree.

A sodium to potassium ratio of 13.0 was determined on a leachate of the inclusion fluids. In view of the high homogenisation temperatures, a juvenile source for the potassium enrichment is possible. However, because of the potassic-alkali chemistry of the surrounding country rocks, the most obvious origin for a major component of the fluids (at least) is the groundwater in equilibrium with these rocks.

Holland (1967) shows that the solubility of calcite decreases with temperature, and that at atmospheric pressure and 450°C it is extremely low. Therefore, it would have been necessary for the solutions to have been under a high pressure (and also have been very saline) for them to have been able to hold the carbonate in solution. The release of this pressure in the fault zone caused boiling to occur and the carbonate precipitated out.

The waters in the area, after this mineralisation had taken place, must have been severely depleted in calcium, because strontianite was later precipitated and that is only possible in a calcium poor environment.

Appendix 1

Appendix 1. Baryte analyses.

a) complete major element analyses

Sample	%BaO	%SO ₃	%SrO	total
D239A	65.50	34.27	1.12	100.89
D239B	64.58	34.13	1.14	99.85
D239C	64.85	33.96	0.98	99.79
D239D	65.70	34.30	0.88	100.88
D239E	65.24	34.27	1.20	100.71
D239F	65.78	33.96	1.19	98.81
D248	64.65	33.96	1.76	100.37
D249	65.31	34.30	1.46	100.07
D250	65.24	34.23	1.43	100.90
D251	65.70	34.13	1.10	100.93
D252	64.42	33.61	1.15	99.18
D253	65.63	34.30	0.94	100.87
D255	64.06	33.61	1.18	98.85
D256	64.71	33.96	0.77	99.44
D257	64.78	33.82	1.40	100.00
D258	64.26	33.61	0.94	98.81
D259	64.39	33.61	1.48	99.48
D260	63.40	33.61	1.52	98.54

b) Partial analysis for Sr only (wt.%).

Sample	%Sr	notes	Sample	%Sr	notes
i) Muirshiel, Renfrewshire					
DMu.e	0.88	} ↓ time	D200B	0.58	} vein section
DMu.1	0.60		D200C	0.55	
M11072	0.61		D200D	0.65	

.....

Sample	%Sr	notes	Sample	%Sr	notes
D14	0.80		D200E	0.69	
D14K	0.80		D201	0.73	earlier than D200's
D15K	0.40		D204A	2.52	} edge of vein ↓ centre of vein
D15C	0.36		D204B	2.52	
D15D	0.38		D204C	2.99	
D20	0.59	} - edge of vein	D204D	2.11	
D21	0.91		D204E	0.51	
D22	1.60		D343	1.71	
D200A	0.65		D344	1.91	

ii) Old Cumnock, Ayrshire

BM1957,137 1.41

iii) Auchestilloch, Lanarkshire

DSt1a	1.38		D29	2.09
DSt1b	0.39		D30	0.58
DSt2	0.47		D31B	0.66
DSt3	0.41		D32	1.08
DSt4	0.56		D33	1.12
M225	0.43		D34	0.62
M225A	0.57		D39	0.62
D23	2.4		D207	0.38
D24	0.54	} vein centre	D207W	1.00
D25	1.14		} vein edge	D208
D26	0.74		D209	1.28
D27A	1.45		D210	1.16
D27B	1.54		D215	1.61
D28	1.72			

Sample	%Sr	notes	Sample	%Sr	notes
iv) Glen Sannox, Arran					
BM56303	2.16		D1121	1.95	v.late crystals
DGuy	0.66		D113	2.20	
DAN	1.19		D114	1.91	
D100	0.57		D115	0.59	
D101	2.20		D116	2.07	
D102	2.16		D117	0.63	
D103	1.34		D118	0.63	
D109	1.41		D419	2.06	
D111	1.22		D420	1.78	
D112e	2.33	(see D1121)	D424	1.31	
v) Leadhills/Wanlochead area					
BM1937,74	0.72		D432(ii)	0.72	
DL1	1.70		D432(iii)	1.62	
DL2	1.15		D432(iv)	1.20	
DL3	1.54		D432(v)	0.76	
DL6	0.51		D432(vi)	2.06	
DL7	1.48		D433(i)	1.94	
D276	1.39		D433(ii)	2.96	
D277	1.48		D433(iii)	2.09	
D431	2.40		D433(iv)	1.03	
D431(i)	1.94				
vi) Nairn, Nairnshire					
DNairn	1.82				

Sample	%Sr	notes	Sample	%Sr	notes
vii) Ochil hills, Clackmannanshire					
D1	0.86		D175	1.99	} vein edge
D2	0.59		D176	1.10	
D2K	0.51		D177	1.66	} centre
D4	1.75		D178	2.17	
D11A	0.58	} ↑ time	D179	1.21	} D180 is post D179 or D181
D11B	0.82				
D12	1.42		D181	1.63	
D13B	0.69		D182	0.84	
D156	1.77		D183	0.74	
D158	1.55		D184	1.80	
D159A	2.10	} main vein	D185	2.18	
D159B	0.45		} late crystals	D186	1.67
D160	1.44				
viii) Barlocco, Kirkcudbrightshire					
D58	2.51		D284	1.90	
D58K	1.94		D285	1.69	
D60	0.49		D286	1.62	
D61	0.43		D374	2.18	
D62	1.57		D415	1.78	
D63	1.60		D416	0.73	
D64	1.24		D417	1.28	
D282	1.69		D418	1.06	

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Sample	%Sr	notes	Sample	%Sr	notes
ix) Auchencairn, Kirkcudbrightshire					
D40	1.63		D59	1.94	
D42	0.46		D270	0.50	
D54	1.95		D271	1.05	
D55	1.25		D272	0.99	
D56	1.17		D274	1.47	
D57	1.55		D275	0.48	
x) Hangit Man, Kirkcudbrightshire					
D413	2.05		D413ws	2.45	
D413ps	1.07		D414	2.33	
xi) Gasswater, Ayrshire					
N.B. also see section a).					
D44	1.98		D232	1.66	
D45	1.07		D233	1.50	
D46A	0.89	} younger gen ⁿ .	D234	0.95	late stringer
D46B	1.72		D235	2.27	
D46C	1.60		D236	1.60	
D50	0.86	} v.late gen ⁿ .	D237	1.87	
D216	0.92	late stringer	D238	1.70	centre of a vein
D217	1.28		D240	1.10	
D218	0.98	late stringer	D241	1.23	
D219	1.33		D242	1.18	
D220	0.69		D243	1.69	
D221	1.29		D244	1.37	} edge of vein ↓

Sample	%Sr	notes	Sample	%Sr	notes	
D222	1.18		D245	1.32		
D223	0.73	prob. v.late ↑	D246(i)	1.60	} ↓	
D224	1.31		D246(ii)	1.66		
D225	1.35		D247	1.40		
D226	1.02		D247(i)	1.40		
D227	1.45	D247(ii)	1.51			
D228	1.20	D247(iii)	1.08			
D230	1.60	prob. quite early	D248(i)	1.06		
D231	1.49		D248(ii)	0.98		} centre of vein
D231A	1.41					

xii) Elie, Fife

Elie	1.97
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xiii) Aberfoyle, Perthshire

D302	2.77		D309B	2.14	(see D309A)
D305	0.50	v.late	D310	1.48	
D306	2.30		D311	0.78	
D308	1.98	vein edge	D312/4	1.28	} ↓ time
D309A	0.70	late w.r.t. D309B	D312/11	1.04	

xiv) Strontian, Inverness-shire

D427(iv)	1.64		D428(ii)	1.47
D427(v)	1.58		D428(iv)	1.38
D427(vi)	1.49		D428(v)	1.51

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Sample	%Sr	notes	Sample	%Sr	notes
xv) Tyndrum, Perthshire					
D425(i)	1.05		D426(iii)	0.88	
D425(ii)	1.00		D426(iv)	1.18	
D425(iii)	1.00				
xvi) North Pennines, England					
DFCa	1.68		D411(iii)	0.72	
DFCc	19.50	Celestine cont ^{mn} .	D411(iv)	0.92	
DPG	2.70		D412(i)	0.40	
D400	1.77		D412(ii)	2.35	
D411(i)	0.66		D421(iii)	4.20	
D411(ii)	1.47				

Appendix 2

Appendix 2.

Sulphide analyses - by atomic absorption spectroscopy.

(all quantities expressed as parts per million unless otherwise indicated;
 g. - galena, s. - sphalerite, m. - mixed sphalerite and galena).

Sample	Pb	Zn	Fe	Cu	Ag	Mn	Co	Ni	Cd	Cr	Cd/Zn (at) x10 ⁻⁴	Co/Zn (at) x10 ⁻⁴	Contaminations noted
1) Auchenstilloch area													
g.M225	-	28	n.d.	n.d.	33	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.M225A	-	32	n.d.	40	30	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.D208Y	-	572	18	4424	216	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	ccp.
g.D207X	-	364	23	1335	239	n.d.	n.d.	n.d.	tr.	n.d.	-	-	ccp., cov.
g.D207W	-	205	24	1410	402	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.D207V	-	169	11	1020	21	n.d.	n.d.	n.d.	tr.	n.d.	-	-	ccp., cov.
g.D207Y	-	52	10	690	235	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	traces ccp., cov., sph.
g.D208Z	-	n.d.	tr.	512	49	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.D207Z	-	64	12	707	253	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	traces cov., ccp.
g.DNH	-	tr.	50	220	127	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
2) Glen Sannox													
s.D100	1518	-	0.23%	527	13	tr.	n.d.	n.d.	8357	n.d.	74.35	-	traces py., ccp.
s.DGuy	1740	-	0.12%	470	13	71	tr.	n.d.	8073	n.d.	54.03	-	

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Sample	Pb	Zn	Fe	Cu	Ag	Mn	Co	Ni	Cd	Cr	Cd/Zn (at) x10 ⁻⁴	Co/Zn (at) x10 ⁻⁴	Contaminations noted
3) East Calder (Edinb'shire)													
9.BM88074	-	n.d.	20	40	n.d.	n.d.	n.d.	tr.	n.d.	n.d.	-	-	slight trace ccp.
9.BM88073	-	n.d.	30	40	17	n.d.	n.d.	110	n.d.	n.d.	-	-	
4) Hilderstone													
m.R13038/1	-	22.0%	0.42%	260	402	n.d.	40	n.d.	1960	n.d.	53.18	2.07	sph., traces py.
m.R13038/2	-	13.0%	0.30%	1180	28	n.d.	n.d.	n.d.	880	n.d.	40.41	-	sph.
m.R13038/3	-	3.46%	960	96	tr.	n.d.	tr.	n.d.	213	n.d.	36.75	-	sph., traces py.
m.R13039/1	-	36.6%	969	635	75	n.d.	26	tr.	2068	n.d.	33.73	0.81	sph., traces ccp.
m.R13039/2	-	16.4%	189	447	n.d.	n.d.	42	tr.	1935	n.d.	70.43	2.92	sph., traces ccp.
m.R13040	-	14.9%	255	378	56	n.d.	147	61	578	n.d.	23.16	11.23	sph.
m.R13040	2.58%	-	0.34%	780	-	n.d.	258	n.d.	2113	n.d.	19.56	4.74	
5) Leadhills													
9.BM1935,25	-	tr.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.BM57344	-	140	tr.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.BM57345	-	n.d.	n.d.	n.d.	83	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
s.DL2	41	-	0.75%	445	10	40	152	n.d.	4209	n.d.	37.44	2.58	
s.DCB	120	-	1.5%	270	4	276	60	n.d.	1040	n.d.	9.25	1.02	
s.BM 1957,551	86	-	0.63%	425	4	34	152	n.d.	3960	n.d.	35.23	2.58	traces py., ccp.

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Sample	Pb	Zn	Fe	Cu	Ag	Mn	Co	Ni	Cd	Cr	Cd/Zn (at) x10 ⁻⁴	Co/Zn (at) x10 ⁻⁴	Contaminations noted
6) Wanlockhead													
9.DW2	-	36	n.d.	n.d.	71	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.DW3	-	28	tr.	tr.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D432T	-	160	tr.	n.d.	143	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	sl. trace sph.
9.D432V	-	28	10	43	99	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D432W	-	32	90	35	92	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D432X	-	280	10	43	148	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D432Y	-	280	10	43	148	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D433Y	-	n.d.	tr.	100	172	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D433Z	-	112	21	77	147	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	sl. trace Fe-0
9.D433ZA	-	60	tr.	290		n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.BM1914,16	-	n.d.	n.d.	45	93	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.BM 1920,470	-	n.d.	n.d.	n.d.	94	n.d.	n.d.	n.d.	tr.	n.d.	-	-	
9.BM 1920,471	-	n.d.	n.d.	n.d.	n.d.	tr.	n.d.	n.d.	n.d.	n.d.	-	-	
9.BM 1920,466	-	n.d.	n.d.	n.d.	48	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
s.DW1*	160	-	0.72%	600	32	162	34	n.d.	4570	n.d.	40.66	0.58	(*mean of 5 analys.)
s.D432S	165	-	0.57%	431	13	138	30	n.d.	4406	n.d.	39.20	0.51	
s.D432U	181	-	0.59%	882	28	34	143	n.d.	4133	n.d.	36.77	2.43	
s.D432Z	282	-	0.55%	378	n.d.	34	117	n.d.	3589	n.d.	31.93	1.98	

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Sample	Pb	Zn	Fe	Cu	Ag	Mn	Co	Ni	Cd	Cr	Cd/Zn (at) x10 ⁻⁴	Co/Zn (at) x10 ⁻⁴	Contaminations noted
s.D433W	340	-	0.07%	410	16	36	166	tr.	4300	n.d.	38.26	2.82	
s.BM 1938,1336	1180	-	0.02%	545	42	n.d.	n.d.	n.d.	6000	n.d.	53.38	-	
s.BM 1952,162	716	-	0.79%	525	82	40	76	n.d.	2880	n.d.	25.62	1.29	
7) Kirkudbrightshire													
g.DB'co	-	224	tr.	tr.	244	n.d.	n.d.	n.d.	n.d.	n.d.			
g.D417W	-	4.0%	385	56	24	80	n.d.	n.d.	202	n.d.	(30.15)	-	sph.
s.BM 1961,409	1.31%	-	1.67%	470	31	222	156	n.d.	2077	n.d.	18.84	2.67	gal.
8) Tyndrum													
g.D425V	-	568	10	130	96	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.D425X	-	60	tr.	125		n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.D425Y	-	1.56%	0.27%	1.00%	59	n.d.	tr.	n.d.	112	n.d.	(42.86)	-	sph., ccp.
s.D425U	high	-	0.09%	380		36	75	n.d.	2822	n.d.	50.0	2.5	gal.
s.425T	7220	-	0.13%	0.15%	n.d.	36	156	n.d.	4800	n.d.	42.70	2.65	gal., ccp.
s.D425V	84	-	0.70%	440	57	34	160	n.d.	4420	n.d.	39.32	2.71	
s.D425W	3.0%	-	0.21%	0.28%	13	46	200	n.d.	4200	n.d.	39.18	3.56	gal., ccp.
9) Strontian													
g.D427X	-	52	n.d.	n.d.	119	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	

Sample	Pb	Zn	Fe	Cu	Ag	Mn	Co	Ni	Cd	Cr	Cd/Zn (at) x10 ⁻⁴	Co/Zn (at) x10 ⁻⁴	Contaminations noted
9.D427Y	-	4320	10	tr.	81	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D427Z	-	n.d.	tr.	45	171	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D428U	-	100	n.d.	n.d.	105	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D428V	-	60	tr.	tr.	97	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D428Y	-	40	tr.	n.d.	78	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D428Z	-	36	tr.	35	175	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
s.D428W	9.28%	-	0.26%	371	62	tr.	31	n.d.	4392	n.d.	45.20	0.61	
10) North Pennines													
9.DNent	-	312	n.d.	tr.	139	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.DHit	-	100	40	n.d.	68	tr.	n.d.	n.d.	n.d.	n.d.	-	-	
9.DDrig	-	140	tr.	495	900	n.d.	n.d.	n.d.	65	n.d.	-	-	traces spp.
9.D4087	-	64	30	60	220	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	sl. trace py.
9.D408Z	-	n.d.	20	70	225	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D409	-	60	60	tr.	206	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
9.D412V*	-	814	tr.	n.d.	43	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	(*mean of 5 analys.
9.D412Z	-	0.45%	20	35	91	n.d.	n.d.	n.d.	30	n.d.	(39)	-	sph. ccp.
s.DNent	164	-	0.56%	260	126	30	n.d.	n.d.	1140	n.d.	10.14	-	traces ccp
s.DBG	242	-	0.30%	907	138	n.d.	52	n.d.	1710	n.d.	15.21	0.88	
s.DFCB	726	-	0.35%	550	35	tr.	n.d.	n.d.	5000	n.d.	44.48	-	
s.D409	745	-	0.27%	0.18%	198	tr.	40	n.d.	2134	n.d.	18.99	0.68	traces ccp., py.

Sample	Pb	Zn	Fe	Cu	Ag	Mn	Co	Ni	Cd	Cr	Cd/Zn (at) x10 ⁻⁴	Co/Zn (at) x10 ⁻⁴	Contaminations noted
s.D411Z	1754	-	0.29%	410	172	79	n.d.	105	2945	n.d.	26.20	-	
s.D412X	42	-	0.11%	442	230	n.d.	tr.	35	4366	n.d.	38.84	-	sl.traces py.,ccp.
s.D412Y	2036	-	0.16%	368	127	101	n.d.	n.d.	2661	n.d.	23.67	-	traces py.
s.D412Z	729	-	0.84%	643	0.15%	84	75	n.d.	964	n.d.	8.58	1.27	sl.traces gal.,ccf
s.BM 1907,426	704	-	0.44%	585	24	34	24	n.d.	1220	n.d.	10.85	0.41	traces py., ccp.
s.BM69126	1.8%	-	0.26%	510	18	n.d.	90	79	2060	n.d.	18.83	1.57	gal.
11) Moss Rake (Derbyshire)													
g.DMR1	-	n.d.	tr.	n.d.	39	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.DMR2	-	n.d.	n.d.	n.d.	310	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
g.DMR3	-	tr.	tr.	40	28	n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
12) Ladywash (Derbyshire)													
g.DLW1	-	832	10	tr.	74	n.d.	n.d.	n.d.	30	n.d.	-	-	
g.DLW2	-	68	n.d.	n.d.		n.d.	n.d.	n.d.	n.d.	n.d.	-	-	
Detection limits (fully quantitative):													
g.	40	20	20	40	10	40	50	40	40	n.d.	-	-	
s.	40	10	10	20	5	20	25	20	20	n.d.	-	-	

Key: n.d. - not detected; tr. - qualitatively detected;

ccp. - chalcopyrite; py. - pyrite; sph. - sphalerite; cov. - covellite; gal. - galena

* - two instances where several analyses were made from the same specimen and the average calculated (reproducibility was good).

Appendix 3

Appendix 3.

Partial analysis of baryte, calcite* and galena[†]
fluid inclusion leachates.

Sample	Na ppm	K ppm	Na/K (atom- ic)	Sample	Na ppm	K ppm	Na/K (atom- ic)
i) Muirshiel							
D15d	0.70	0.15	7.9	D343	0.95	0.10	16.5
D200	6.72	0.50	6.3	D344	0.85	0.31	4.7
D201	8.27	0.62	9.3	(D344*	11.90	1.56	13.0)
D204	2.72	0.30	15.4				
ii) Hilderstone							
D277*	13.45	0.83	27.5	D288*	13.20	0.43	52.2
D287	6.00		0.79				
iii) Auchenstilloch area							
DNH [†]	5.10	0.40	21.8	D209	5.60	0.52	18.4
D30	3.75	0.65	9.9	D210	2.90	0.20	24.6
D34	3.20	0.40	13.6	D215	4.45	1.15	6.6
D39	0.32	2.30	12.2	M225 [†]	3.65	0.51	11.9
D207v	4.00	0.48	14.1	M225A	3.20	0.43	12.6
D208	4.15	0.42	16.8				
iv) Glen Sannox							
DAr	9.10	1.15	13.4	D107*	10.90	1.55	11.9
v) L'hills/W'head							
DL2	4.70	0.43	18.7	D68	3.30	0.58	9.7
DL3	5.00	0.90	7.6	D69*	13.45	0.83	27.5
DL6	2.80	0.31	15.4	D431*	14.70	0.85	29.4
DL7	0.95	0.10	16.1	D431	4.13	0.30	23.5
DL8	3.48	0.22	26.9	D433(ii)	2.80	0.20	23.8

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Sample	Na ppm	K ppm	Na/K (atom- ic)	Sample	Na ppm	K ppm	Na/K (atom- ic)
DL9	3.00	0.22	23.2	D433p	9.60	0.70	23.8
DL10	4.35	1.10	6.8	D433W*	14.50	1.40	17.7
DL11*	17.00	1.45	19.9	D433(xx)	2.90	0.30	16.5
DW1*	15.20	1.18	21.9	D433Y†	3.70	1.00	6.3
vi) Nairn							
DNairn	3.05	0.90	6.1				
vii) Ochil hills							
D2	4.29	1.11	6.6	D159e	5.40	1.14	8.0
D4	3.65	0.40	15.5	D1591	3.16	0.31	17.3
D11A	3.20	0.65	8.4	D167*	9.00	0.75	20.4
D156	5.25	0.6	14.8				
viii) Kirkcudbrightshire							
a) Barlocco							
DBco†	8.75	0.73	20.4	D61a	9.45	0.60	26.7
D58(i)	2.00	0.22	15.5	D61b	2.82	0.23	13.5
D58(ii)	7.10	0.32	37.7	D286	5.80	0.35	28.2
b) Auchencairn							
D40A	3.22	0.20	27.4	D59A	9.00	0.95	16.1
D40B	4.15	0.50	14.1	D59B	4.63	0.58	13.6
D54	3.54	0.40	15.1	D55	0.96	0.20	8.2
c) Hangit man							
D413	11.45	0.65	29.9	D414	6.05	0.60	17.2
ix) Gasswater							
D44	4.95	0.44	19.1	D238	2.08	0.30	11.8
D46A	2.60	0.40	11.0	D240	1.85	0.22	14.3

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Sample	Na ppm	K ppm	Na/K (atom- ic)	Sample	Na ppm	K ppm	Na/K (atom- ic)
D46C	1.80	0.58	5.3	D241	2.95	0.38	13.2
D50	1.95	0.4	8.3	D242	2.42	0.27	8.2
D216	3.10	0.50	10.5	D243	1.90	0.58	5.6
D217	3.25	0.98	5.6	D245	1.90	0.15	21.5
D222	0.40	0.15	4.5	D248	3.10	0.53	9.9
D225	4.45	1.05	7.1	D249	3.15	0.30	17.8
D231	5.50	2.00	4.8	D251	5.50	0.65	14.4
D235a	0.96	0.15	10.9	D253	3.60	0.60	10.2
D235b	2.80	0.80	5.9	D257	5.70	1.30	7.5
x) Elie							
Elie	13.9	1.7	13.9				
xi) Aberfoyle							
D308	3.15	0.45	11.9				
xii) Strontian							
D427(i)	3.60	0.55	11.0	D427M*	9.9	1.60	10.5
D427(ii)	4.50	0.30	25.5	D428(i)	4.20	0.93	7.6
D427(vi)	2.50	0.43	9.9	D428V [†]	3.65	0.73	8.5
D427G*	6.30	1.45	7.3				
xiii) Tyndrum							
D425V [†]	3.15	0.70	7.6				
xiv) Nth. Pennines							
DPG	3.65	0.35	17.7	D411(iv)	23.0	0.80	49.0

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