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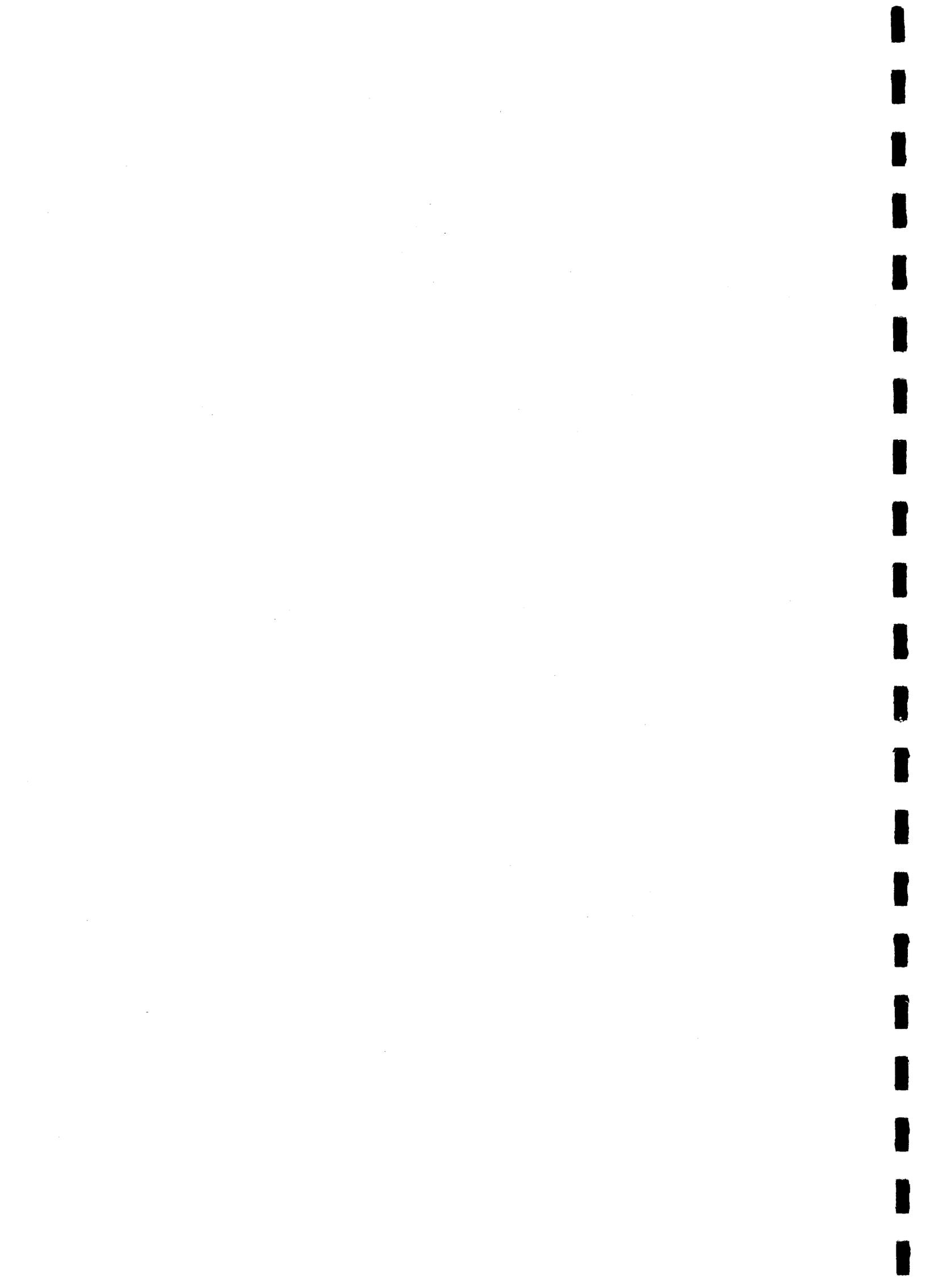
Mineral Reconnaissance Programme Report

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D. Ostle
Programme Manager
Institute of Geological Sciences
Nicker Hill, Keyworth,
Nottingham NG12 5GG

No. 67

Baryte and copper mineralisation in the Renfrewshire Hills, central Scotland



INSTITUTE OF GEOLOGICAL SCIENCES

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Mineral Reconnaissance Programme

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**Baryte and copper mineralisation
in the Renfrewshire Hills, central
Scotland**

D. Stephenson, PhD

J. S. Coats, PhD



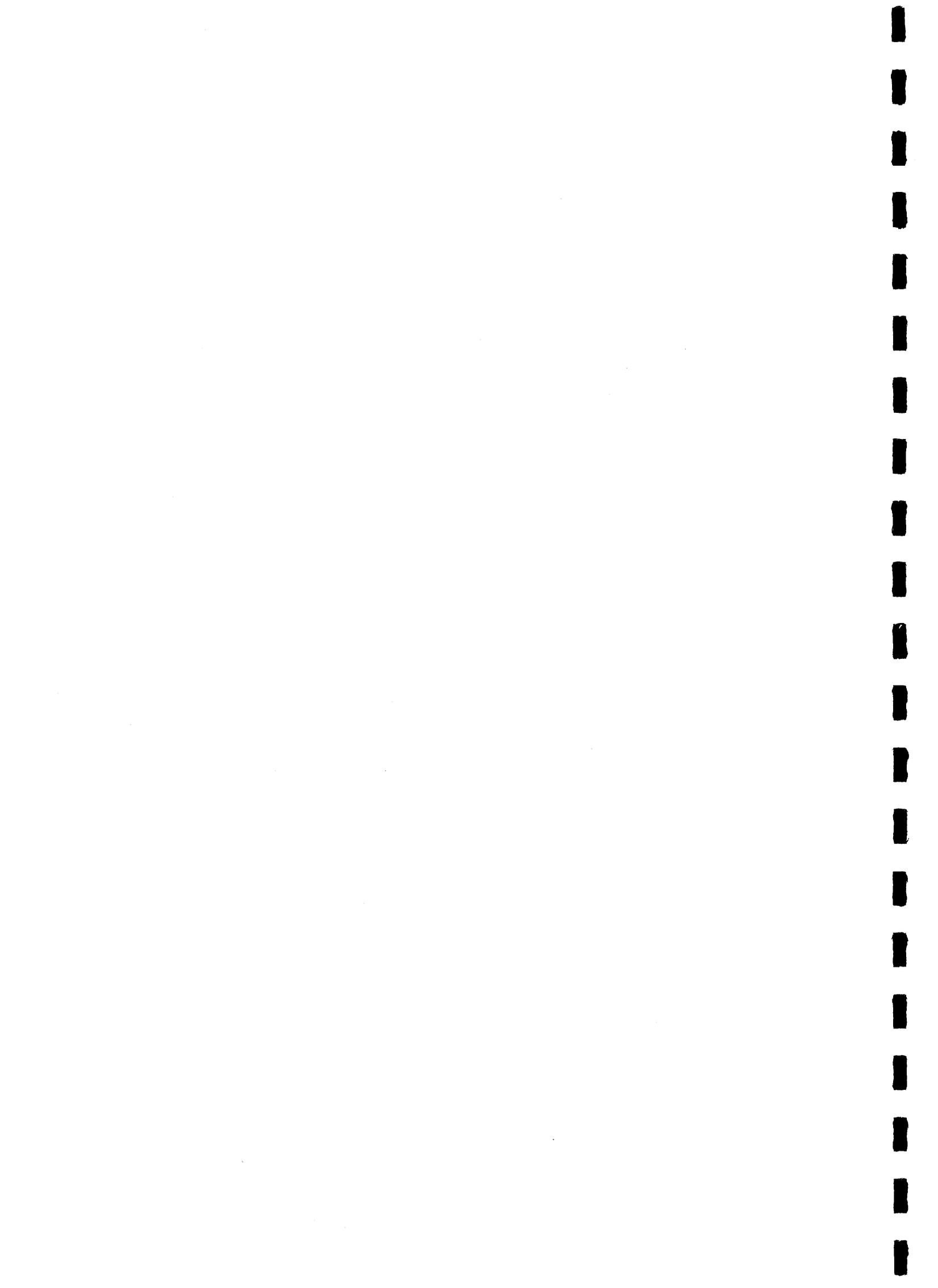
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SUMMARY

Lower Carboniferous volcanics have been mapped and sampled in detail in an attempt to establish the controls, age and genesis of known mineral veins and to locate possible sites of new occurrences. A study of mining records provided additional information on the nature of worked veins and a reconnaissance stream sediment and panned concentrate survey indicated a potential for further geochemical exploration.

Baryte veins are particularly concentrated in massive, open-jointed rocks of the Misty Law trachytic complex where they occupy a variety of fracture directions within the limits of a NW-SE swarm of Tertiary dolerite dykes. K-Ar isotopic dates (Moore, 1979b) on veins which are cut by the dykes indicate a Triassic age. Outside the trachytic complex, in the less massive basaltic sequence, baryte veins are confined to major ESE to ENE-trending fault zones and the margins of ENE-trending late-Carboniferous quartz-dolerite dykes, with which they are probably contemporaneous. Similar baryte vein deposits elsewhere in Scotland are also located on major NW-SE or NE-SW fracture systems. It is suggested that baryte mineralisation occurred at intervals from the late Carboniferous onwards during tensional stress regimes when increased heatflow circulated low-temperature, barium-rich brines, which combined with sulphurous groundwaters in near-surface oxidising conditions. Barium may have been leached from Devonian and Lower Carboniferous clastic sediments, or from trachytic rocks within the volcanic pile.

Copper mineralisation occurs in a wide variety of environments ranging from replacement of plant debris by malachite in sandstones to veins of chalcocite, chalcopyrite and malachite on the margins of quartz-dolerite dykes. Mineralised rocks include basal Carboniferous to Lower Limestone Group sediments and volcanics and late-Carboniferous dykes. Some of the copper has a direct late-stage hydrothermal association with the basaltic magmas and it is suggested that cupriferous veins were deposited by later, possibly late-Carboniferous hydrothermal fluids which leached copper from the basalt pile.

Several new discoveries of isolated, wide veins of pure baryte could be economic if worked on a small scale, and follow-up geochemical work may reveal more extensive deposits. Panned concentrate sampling and analysis is the most sensitive method of detecting outcropping baryte veins near streams, backed-up by stream sediments which may be more effective in detecting finer-grained, more widely-dispersed material. Follow-up in selected upland target areas of relatively thin drift could be possible by overburden sampling and all three methods would benefit from the use of rapid field analysis for barium by portable X-ray fluorescence equipment. Suitable areas for further exploration include extensions of structures with known economic mineralisation, an area of thin drift cover with abundant baryte float, and areas with barium anomalies in drainage samples. Drainage geochemistry is successful

in detecting known copper mineralisation and could reveal further occurrences in regional surveys.

INTRODUCTION

Muirshiel mine in the Renfrewshire Hills was one of three major baryte mines in southern Scotland (Muirshiel, Gasswater and Glen Sannox), all of which are now closed. From 1946 to 1966 the Muirshiel and Gasswater mines collectively accounted for about one third of the annual UK production of baryte, of which up to 17 000 tonnes per annum came from Muirshiel. Total production from Muirshiel is estimated at 300 000 tonnes, prior to closure in 1969. Numerous other small baryte veins are recorded in the Renfrewshire Hills and several small copper prospects were worked in the nineteenth century. In view of the recent increase in demand and price of baryte the area was selected for geological and geochemical investigation to search for further veins, to determine the controls of mineralisation and to assess the potential of the area for further exploration.

SCOPE OF THE PRESENT INVESTIGATION

Field investigation of the mineral veins was combined with a resurvey of the area for the 1:50 000 Geological Sheet 30W (Greenock) during the period June 1979 to October 1982. Conventional field mapping techniques at 1:10 560 scale were augmented by the use of specially-commissioned, black and white, vertical air-photos at 1:10 000 scale (copies may be purchased through IGS). The mapping clarified the field relationships of the mineral veins in general and revealed several hitherto unrecorded veins. Samples of country rock were examined microscopically and representative samples were analysed for major elements and selected trace elements to determine background lithochemical concentrations. An orientation geochemical drainage survey was carried out in the River Calder catchment area in November 1979. The object of this study was to ascertain the effectiveness of drainage geochemistry in the identification of barium and base metal mineralisation in the peaty upland area of the Renfrewshire Hills and in the surrounding farmland at a slightly lower elevation. Other factors examined were length of dispersion from known mineralisation, the extent of contamination from old workings and agricultural activities, and possible geochemical differences between the various volcanic units which constitute the country rock. Factor analysis was used to identify elements which might be of use in prospecting. The area has subsequently been resampled in the course of the systematic regional geochemical reconnaissance programme of the IGS (funded by the Department of Industry) and results will be published in due course as part of the Regional Geochemical Atlas (Clyde Sheet).

This report reviews the baryte and copper mineralisa-

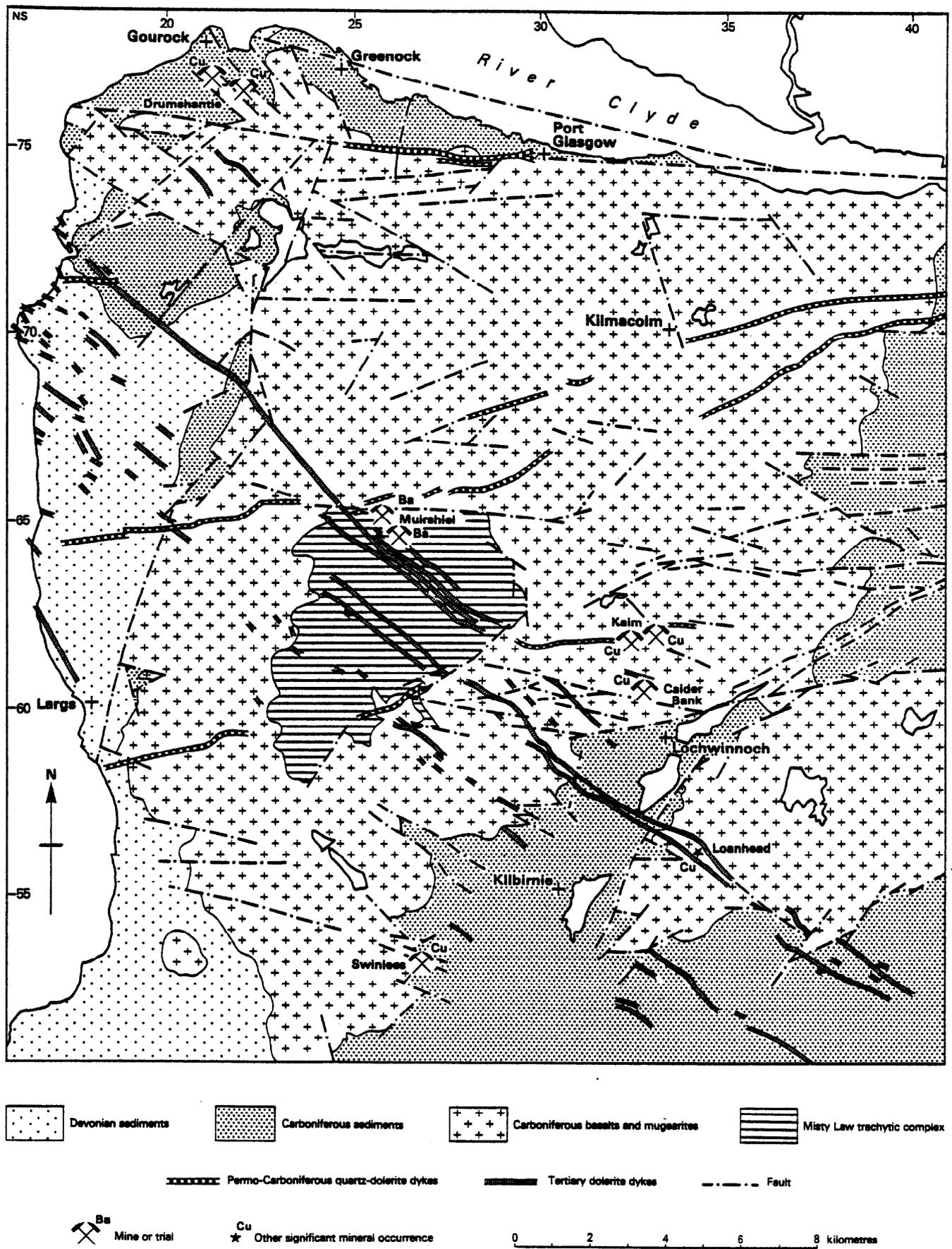


Fig. 1. General geology of the Renfrewshire Hills, west central Scotland, showing sites of known mineralisation

tion of the Renfrewshire Hills in the light of old records and current field investigations. It updates and expands previous Geological Survey accounts of the baryte mineralisation (Wilson and others, 1922; MacGregor, 1944) to take account of the major post-1944 development and extraction at Muirshiel mine, and it expands previous descriptions of the copper deposits (Wilson, 1921). An interpretation of the controls, age and genesis of the mineralisation is presented as a guide to further prospecting and the efficiency of drainage geochemical sampling in the area is assessed. The potential of the area as a source of further economic vein deposits is evaluated, suitable exploration techniques are suggested and some sites worthy of further investigation are identified.

LOCATION AND TOPOGRAPHY

The Renfrewshire Hills occupy a triangular area of some 400 km², bounded to the north and west by the Firth of Clyde and to the south-east by the lowlands of the Garnock valley and Black Cart Water (Figure 1). Steep escarpments rise to over 200 m from the Firth of Clyde but the south-eastern edge is a more gentle dip-slope. Most of the intervening ground consists of undulating, peat-covered moorland of average elevation 400 m, rising to over 500 m in the central Hill of Stake-Misty Law area. Access is difficult, with only two roads and a few tracks penetrating the remote central area. The Hills occur mostly within one-inch New Series Geological Sheets 30 (Glasgow) and 22 (Kilmarnock) with narrow coastal strips in Sheet 29 (Rothesay) and Old Series Sheet 21 (North Arran).

GENERAL GEOLOGY OF THE RENFREWSHIRE HILLS

GENERAL SUCCESSION

The southern part of the Hills is described in Geological Survey memoirs (Geikie and others, 1872; Gunn and others, 1903; Richey and others, 1930) but the northern parts (sheets 29 and 30) have no general description.

The stratigraphic succession ranges from Upper Devonian to topmost Lower Carboniferous, most of which consists of the Clyde Plateau Volcanic Formation (Table 1). The position and nature of the Devonian-Carboniferous boundary is currently under review, so the lithostratigraphic divisions 'Old Red Sandstone' and 'Calciferous Sandstone' are used in Table 1 and throughout this report. Formation names are those which will be used in future editions of Geological Survey maps (I. B. Paterson, oral communication). Contemporaneous, comagmatic intrusions occur within the volcanics and underlying sediments, and the Hills are traversed by two suites of younger dykes: widely-spaced, ENE-trending quartz-dolerites of late-Carboniferous age, and NW-SE Tertiary-age dolerites which are particularly concentrated in a 2.5 km wide swarm through the centre of the Hills. A few Permian volcanic vents are recognised in the south of the Hills. The overall structure is simple, with a general dip of 6 to 10° to the south-east and a superimposed pattern of block faulting. Major fault systems bound the area to the south-east (the 'Paisley Ruck'), the north and west and a major dislocation trends SSW from Greenock to Largs, essentially separating volcanics in the east from older sediments to the west (Figure 1).

Table 1 Generalised stratigraphical succession in the Renfrewshire Hills

	Quaternary	till, late-glacial marine and fluvioglacial sand and gravel deposits, peat, alluvium
	Tertiary	dolerite dykes (NW-SE trend)
	?Permian	volcanic vents with mantle-derived xenoliths
	Late Carboniferous	quartz-dolerite dykes (ENE trend)
	Lower Limestone Group (Lower Carboniferous)	
26-114 m		mudstones with thin sandstones, limestones and few coals
	Calciferous Sandstone Measures (Lower Carboniferous)	
50-330 m	Lawmuir Formation	sandstones with mudstones, few limestones and coals volcaniclastics at base in places
		<i>unconformity</i>
50-1500 m	Clyde Plateau Volcanic Formation	
thins south	Upper mafic lavas (Dunsapie, Craiglockhart and Dalmeny type basalts)	
	Middle lavas (Markle type basalts and mugearites with Misty Law trachytic complex in centre)	
	Lower lavas (Dalmeny with some Jedburgh and Craiglockhart type basalts)	
	Basal tuffs and volcaniclastics	
		<i>unconformity</i>
80-500 m	Clyde Sandstone Formation	mainly white sandstones with few mudstones and cornstones
40-180 m	Ballagan Cementstone Formation	mudstone with thin limestones and some sandstone
	Upper Old Red Sandstone	
70-170 m	Kinnesswood Formation	sandstones with cornstones and few thin mudstones
?1500 m	Upper Old Red Sandstone (undivided)	red-brown sandstones with thin conglomerates and pebble beds

SEDIMENTS BELOW THE VOLCANIC FORMATION

The Upper Old Red Sandstone of the Clyde coast has been the subject of several detailed accounts (Patterson, 1951) and sedimentological studies related to basin development (Bluck, 1978; 1980). Red and brown fluviatile sandstones predominate, with conglomerates and pebble beds abundant in the lower part of the sequence. These are overlain by a series of sandstones, containing nodules and vertical pipes of carbonate (termed 'cornstones'), which constitute the Kinnesswood Formation. The cornstone-bearing beds resemble soil profiles formed in seasonal tropical environments and suggest a mature land surface of low relief with low rates of sedimentation at the close of Upper Old Red Sandstone time.

The cornstone-bearing sandstones grade upwards into marine deposits of the basal Calciferous Sandstone measures, composed of mudstones and sandstones with a few, usually dolomitic, limestones (termed 'cementstones'). In the area around Gourock and Greenock these pass upwards into more persistent, massive, pale-coloured sandstones of the Clyde Sandstone Formation.

The generalised succession described is complicated by the probability that the 'cornstone' and 'cementstone' facies may be developed locally at various horizons, and all the formations are subject to lateral change.

CLYDE PLATEAU VOLCANIC FORMATION

The volcanic rocks are part of a widespread outcrop extending north, west and south of Glasgow from Stirling to Gourock to Strathaven, which are termed the Clyde Plateau Volcanics (Geikie, 1897). Of the general descriptions already mentioned, that of Richey and others (1930) gives details of the volcanics in the south. General observations on the volcanics of the northern Renfrewshire Hills are included in a detailed description of the Misty Law trachytic complex (Johnstone, 1965). The petrology of the southern volcanics is described by A. G. MacGregor (*in* Richey and others, 1930), incorporating earlier publications on the subject.

The formation rests upon the Clyde Sandstone Formation in the north and on cornstone-bearing sandstones in the south. The intervening ground is complicated by faulting. Outside the area the volcanics are seen to rest upon the Ballagan Cementstone Formation (in the Campsie and Kilpatrick Hills), upon cornstone-bearing sandstones (south of Paisley) and upon Upper Old Red Sandstone (on the Isle of Bute). It thus seems likely that the base rests unconformably upon a slightly-folded sequence of older rocks.

Most of the succession consists of basaltic lavas which may be sub-divided according to their field characteristics using the Scottish Carboniferous basalt classification (MacGregor, 1928) (Table 2). Pyroclastic deposits are rare and the lavas are entirely sub-aerial, as is

Table 2 Macroscopic features of principal volcanic rock-types in the Renfrewshire Hills (after MacGregor, 1928)

Rock type	Colour	Phenocrysts	Other features
<i>Macroporphyrritic basaltic rocks</i>			
Markle	blue-grey	plag ± ol	sometimes grades vertically into mugearite
Dunsapie	blue-grey	plag + ol + cpx	
Craiglockhart	blue-grey	ol + cpx	
<i>Microporphyrritic basaltic rocks</i>			
Jedburgh	blue-grey	plag	
Dalmeny	blue-grey	ol	very fresh and massive in upper mafic lavas
<i>Intermediate to acid rocks</i>			
mugearite	blue-grey	none	close-spaced platy joints
trachyte	pink, purple-brown	alk fsp	frequent flaky jointing
rhyolite	pink	alk fsp ± qtz	frequently flowbanded and sphaerulitic

demonstrated by the presence of many reddened flow tops and red-brown clay 'boles' between successive flows. Individual flows are up to 20 m thick (commonly 10 m). A relatively small proportion (10 to 15%) of this thickness is composed of massive lava, as seen in outcrops. The remainder is usually poorly-exposed and consists of amygdaloidal lava, slaggy material and soft, friable zones of intense contemporaneous hydrothermal alteration, frequently exhibiting autobrecciation and convolute flow structure. Trachytic and rhyolitic flows tend to be more massive and although they are almost invariably altered, oxidised and often autobrecciated, they do not in general contain soft or friable material.

The lava sequence may be divided into three sharply-defined stratigraphical units (Table 1). The basal unit is well-developed around Largs where up to 200 m of basalts bearing mafic phenocrysts rest upon basal basaltic tuffs and reworked volcanoclastic beds of variable thickness. The majority of flows are microporphyritic Dalmeny basalts with a few macroporphyritic Craiglockhart basalts. Southwards the unit is represented by a few non-mafic microporphyritic Jedburgh basalt flows. The unit is not present in the north around Gourock and Greenock.

The middle unit may be over 1000 m thick, accounting for most of the outcrops in the centre of the hills and on the eastern dip slopes. The unit thins southwards towards Ardrossan where it is the only representative of the lavas and is probably less than 50 m thick. It is characterised by an alternating sequence of petrologically uniform, macroporphyritic Markle 'basalts' and aphyric, platy-jointed mugearites. The Markle 'basalts' characteristically lack the olivine phenocrysts present in this type elsewhere and sometimes grade vertically into the mugearites suggesting that the flows represent a comagmatic assemblage of intermediate hawaiite-mugearite compositions. The Misty Law trachytic complex occurs approximately in the stratigraphic and geographic centre of this unit.

The upper unit occurs on the eastern flanks of the Hills from Bishopton to Ladyland and consists of up to 200 m of mafic basalts. Lower flows are of macroporphyritic Dunsapie and Craiglockhart type and the top of the unit consists of a distinctive series of massive, fresh, blue Dalmeny basalts which are particularly well-developed around Kilbarchan.

The Misty Law trachytic complex (Figure 2) was recognised and described in parts by Geikie (1897) and G. V. Wilson (*in* Richey and others, 1930) and the whole complex was reviewed by Johnstone (1965). Trachytic lavas form a shallow cone, 6 to 8 km wide, within the basaltic sequence. Rhyolites are concentrated in the central, upper part of the cone. Individual flows are difficult to distinguish owing to the lack of flow top and base features, but irregular slabby jointing parallel to flow banding suggests that the lavas erupted as localised, viscous flows and domes. Trachytic agglomerates are locally abundant as small vents and as bedded deposits, particularly in deeply-eroded valleys where they are commonly welded and probably represent a basal accumulation. More persistent outcrops of pyroclastics occur in the south-west of the complex where they appear to be centred upon the trachytic plugs and vent agglomerates of Irish Law and Knockside Hill. These vents probably post-date the trachytic lava pile. Other trachytic plugs (e.g. Box Law, Slatey Law, Black Law) are numerous in the south-western half of the complex and irregular dolerite intrusions also occur. A zone of basaltic flows extending

from The Tongue to Hill of Stake to Queenside Hill may represent a basic interlude within the trachytic pile, and hill cappings of trachybasalt in the east of the complex (e.g. Misty Law) may be remnants of a cover of intermediate lavas. Contemporaneous, comagmatic dykes are numerous, corresponding in composition to the full range of eruptive rocks in the complex. They occupy a wide range of fracture directions and seem to be concentrated in the lower parts of the complex and in the underlying basaltic sequence.

In addition to the Misty Law complex, trachyte and felsite occur as sills, dykes and small bosses which are widespread in the sediments below the lavas and in the lower parts of the lava succession. Agglomerate-filled volcanic necks of both trachytic and basaltic composition, often with associated basaltic plugs, are particularly abundant in the coastal areas around West Kilbride and Largs. Rock types frequently match those of the eruptive rocks and the suite is considered to be of contemporaneous Lower Carboniferous age. Other vents in the southern part of the hills form a separate suite of probable Permian age.

SEDIMENTS ABOVE THE VOLCANIC FORMATION

The volcanic succession is overlain unconformably by sediments which form overlapping margins to the Carboniferous depositional basins of north Ayrshire and Renfrewshire. The volcanics formed a landmass, on the flanks of which up to 20 m of volcanic detritus were deposited as red-brown marls, often resembling decomposed basalt, and bands of conglomerate or volcanoclastic breccia. In the north of the area, the volcanic detritus is overlain by marls, mudstones and fireclays with coal, sandstones and up to four thin limestones, which comprise the Lawmuir Formation at the top of the Calciferous Sandstone Measures. South of Lochwinnoch this succession is overlapped and the Dockra (= Hurllet) Limestone, which marks the base of the Limestone Coal Group, rests directly upon the volcanic detritus or the volcanics.

INTRUSIONS OF POST LOWER CARBONIFEROUS AGE

Quartz-dolerite dykes are part of a swarm extending E-W throughout central Scotland and generally considered to be of late-Carboniferous age (Walker, 1935; Macdonald and others, 1981). Within the Renfrewshire Hills dykes up to 30 m wide occur in continuous lengths of up to 6 km within pre-existing E to ENE-trending fractures. Alignment of the individual lengths suggests the presence of up to five discontinuous major dykes with a general ENE trend across the Hills (Figure 1). The dolerite is usually fresh, blue-grey, coarse grained and equigranular with pinkish interstitial, quartzo-feldspathic patches visible in places.

In the south of the Hills, several basaltic volcanic vents have a different character to those of Lower Carboniferous age. Agglomeratic material includes basaltic fragments of alkaline affinities, rocks and minerals of possible mantle derivation (e.g. peridotite, spinel, garnet), and sandstones of aeolian New Red Sandstone type. Such vents have thus been assigned a Permian age, contemporaneous with lavas in south Ayrshire (E. M. Bailey *in* Richey and others, 1930).

Tertiary dykes, conventionally assigned to the Mull swarm, trend NW-SE across the Hills, passing through the Misty Law Complex, and continue south-eastwards

through southern Scotland into north-east England. Many individual dykes are up to 15 m wide and may be traced for tens of km. The swarm has a total width of approximately 5 km but dykes are particularly numerous and persistent in the north-eastern half (Figures 1 and 2). The north-eastern margin is sharply-defined throughout the length of the swarm, with an almost total absence of Tertiary dykes in ground to the north-east. The dykes are characteristically very fresh, blue-grey, equigranular dolerites commonly exhibiting horizontal columnar jointing. Some of the more persistent dykes have andesitic tendencies but the majority are tholeiitic dolerites and tholeiitic olivine dolerites. More alkaline types are not recorded in the Renfrewshire Hills (A. G. MacGregor *in* Richey and others, 1930).

STRUCTURE

In general the lavas of the Clyde Plateau Volcanic Formation form rigid blocks around the margins of the Central Coalfield and Ayrshire Coalfield basins. As such they tend to deform by brittle fracture (i.e. faulting), preserving consistent low-angled general dips within blocks in marked contrast to the complex folding of the adjacent sedimentary basins. Lavas of the Renfrewshire Hills dip consistently to the south-east at 6 to 10°, the only significant deviation being in a shallow syncline trending ESE parallel to the Upper Gryfe Reservoirs. South of Largs the sediments also have a general south-easterly dip, broadly conformable with the overlying lavas. North of Largs, the sediments below the lavas are block-faulted into a configuration of broad 'folds' with maximum dips of 15°. Steeply dipping zones occur locally, adjacent to major fault systems.

The area is bounded on three sides by major faults. To the south-east the 'Paisley Ruck', a broad belt of shattering, extends south-westwards from the sedimentary basin at Renfrew to truncate the lava succession between Howwood and Lochwinnoch. Further to the south-west, the 'Ruck' is not identified, but the straight south-westerly course of the north Ayrshire basin margin suggests a deep continuation structure with a few NE-SW faults at higher levels. The northern edge of the Hills is marked by an E-W fault immediately south of Greenock and Port Glasgow which throws lava down to the south, against Lower Carboniferous sediments in a coastal strip to the north. Related faults probably trend ESE along the River Clyde. To the west, a straight N-S coastline and steep local dips in Upper Old Red Sandstone sediments suggest the presence of a major N-S fault offshore.

Within the area a major NNE-SSW fault extending from Greenock to Largs and then offshore to Hunterston and Farland Head is probably a major splay from the Highland Boundary fault system. The fault throws down to the east and separates folded sediments in the west from the more constantly SE-dipping sediments and overlying lavas to the east. In detail the fault is seen to consist of a system of interconnecting NE, NNE and N-S faults, adjacent to which the base of the lava sequence becomes tilted almost vertically in places. Other faults within the lava block occur in a variety of directions, the most significant of which are shown in Figures 1 and 2. Displacements are probably rarely in excess of a few tens of metres except for several persistent E-W faults which are seen to displace the top or base of the lava succession and extend into adjoining sediments. One such fault also forms the northern margin of the Misty Law trachytic complex.

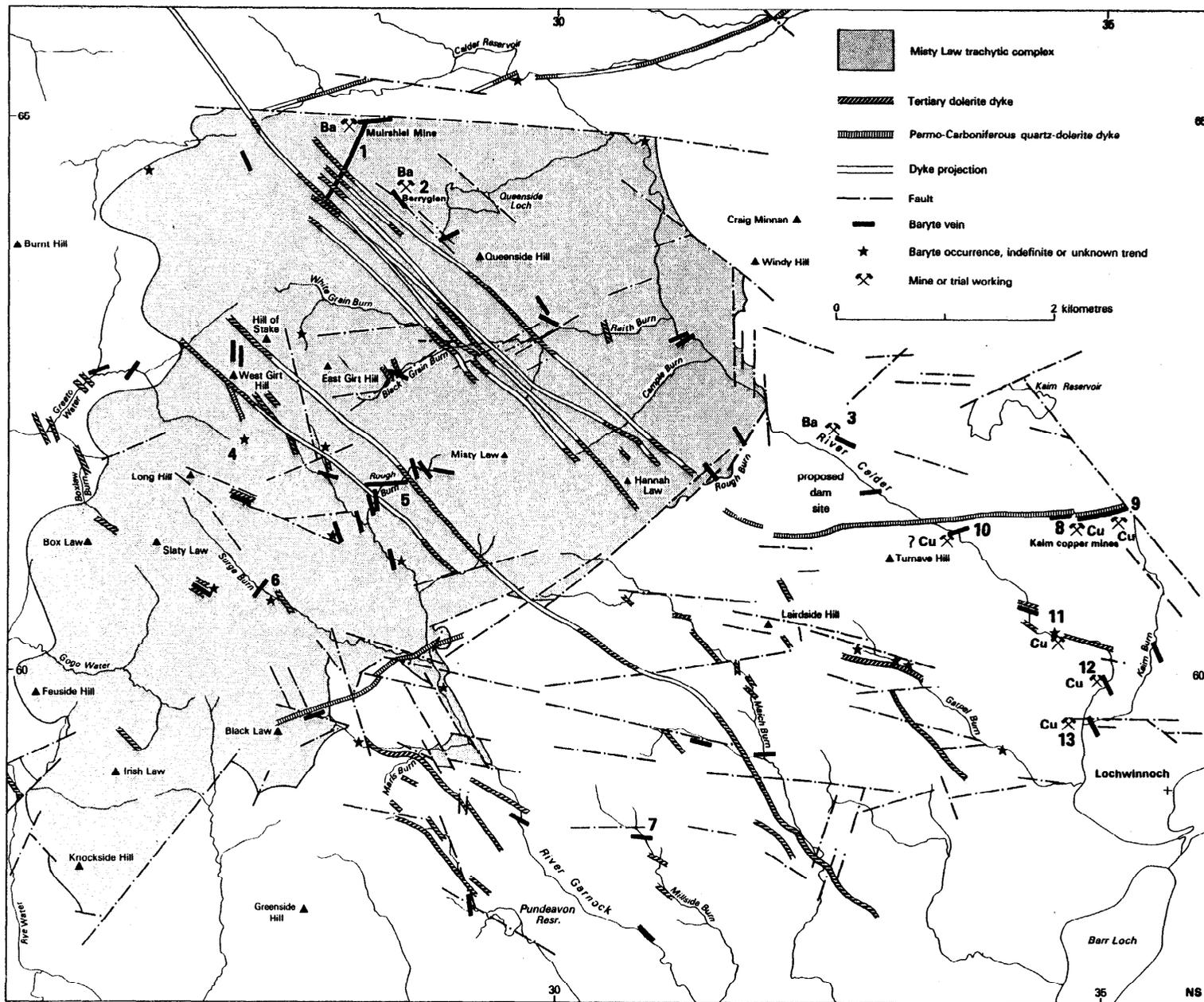


Fig. 2. Baryte veins and workings in the area of the Misty Law trachytic complex. The outline of the complex is shown but contemporaneous plugs, vents and dykes and many faults are omitted. Outside the trachytic complex the sequence consists of alternating flows of aphytic mugearite and porphyritic basalt. Localities: 1, Muirshiel baryte mine; 2, Berriglen baryte mine; 3, Heathfield baryte trial; 4, High Corby Knowe; 5, Rough Burn (Garnock); 6, Surge Burn; 7, Millside Burn; 8, West Kaim copper mine; 9, East Kaim copper mine; 10, Reikan Linn copper trail; 11, Sandy Linn copper trial; 12, Calderbank Bleachfield copper trial; 13, Bridgend copper trial.

QUATERNARY DEPOSITS

Lower slopes of the Renfrewshire Hills are mantled by glacial till (boulder clay) which tends to be thickest in valleys and thin over higher ground. A thin cover of till (less than 1 m) is frequently found beneath peat in the central high ground, which is almost totally mantled by blanket peat up to 2 m thick. As a result of these deposits rock outcrops are rare and only the more massive central parts of lava flows, plugs and vents are seen outside stream sections. This is particularly so in the Misty Law complex, in which the trachytes offer little erosional contrast and provide a topographical and chemical environment conducive to peat development.

In coastal areas marine sand and gravel form raised beach deposits, often spreading over wide areas (e.g. Largs and Hunterston). River valleys contain fluvio-glacial sand and gravel in their lower reaches (e.g. Inverkip) and sporadic glacial moraine mounds in upper reaches (e.g. River Calder). River alluvium occurs in small localised patches except in the valley of the River Gryfe and between Castle Semple Loch and Kilbirnie Loch where wider alluvial flats are developed.

BARYTE MINERALISATION

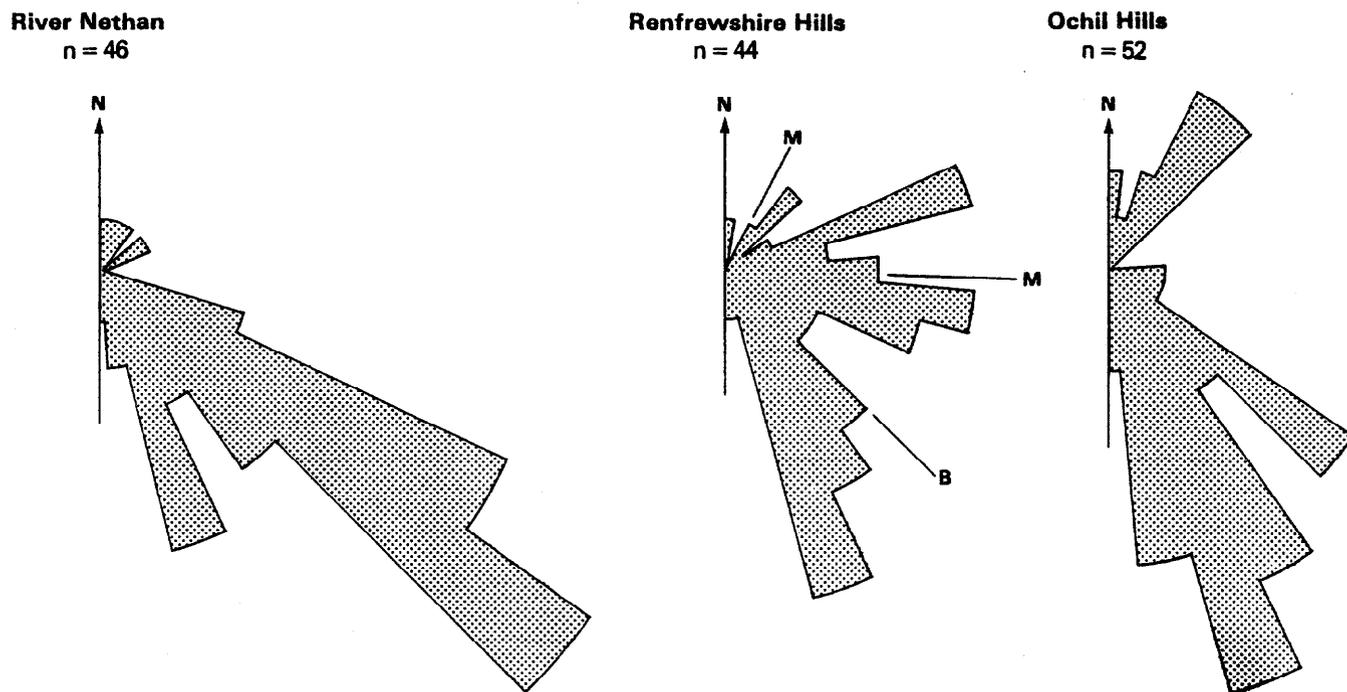
GENERAL DISTRIBUTION AND NATURE OF BARYTE MINERALISATION

Baryte veins in the Renfrewshire Hills are almost entirely confined to the vicinity of the Tertiary dyke swarm. They are particularly abundant within the north-eastern half of the swarm, where the dykes are more numerous, but are also found up to 1 km beyond the north-eastern edge of

the swarm. The majority of veins occur within the Misty Law trachytic complex; several cut the basalt succession above (south-east of) the trachytes, but few are found below (north-west of) them. Almost all of the known veins in the Hills occur within the area shown in Figure 2.

Although the veins occur within and around the NW-SE dyke swarm, they occupy a wide variety of fracture directions, particularly within the trachytic complex, corresponding to most of the common fault trends of the area (Figure 3). Veins trending SE to SSE, parallel to the dykes, are numerous but so also are ENE veins. Other areas of baryte mineralisation in central Scotland (e.g. the River Nethan district and the Ochil Hills) have a much more prevalent SE to ESE distribution of veins (Figure 3), as does the area around Gasswater mine (Scott, 1967). It is worthy of note that the worked NNE and E-W trending veins at Muirshiel mine follow fractures which are not commonly mineralised in the Renfrewshire Hills. Outside the trachytic complex, the majority of veins trend ESE and are closely associated with major faults of the same trend. Some of the veins, particularly those outside the trachytic complex, follow or are close to the margins of E-W to ENE trending late-Carboniferous quartz-dolerite dykes and are frequently associated with copper mineralisation (e.g. Kaim mines). Sporadic, small (20 cm), irregular pods of baryte occur throughout the basalts above the trachytic complex but only become abundant in fault zones.

The general distribution of baryte veins, and in particular their relationship to the Tertiary dykes, has been the subject of much debate (MacGregor, 1944; Scott, 1967; Gallagher, 1968). In the Renfrewshire Hills, in addition to occupying the NW-SE fractures, thin baryte



M = worked veins at Muirshiel Mine; B = Berryglen vein
Fig. 3. Trends of baryte veins in three districts of central Scotland.

veins are commonly found in lavas close to and parallel with the margins of Tertiary dykes, in a similar manner to that described by Gallagher (1968). Such veins are commonly of white baryte. At Muirshiel mine a Tertiary dyke was recorded cutting the main vein (MacGregor, 1944) and further examples revealed in subsequent workings confirm the relationship. In each case the baryte is white for up to 2 m from the dyke margin suggesting that the white veins elsewhere are also contact altered and therefore predate the dykes. Baryte is never present in the dykes and it therefore seems likely that the veins and dykes successively occupied the same fissure system but did not necessarily have a direct genetic connection. In contrast, baryte veins on the margins of late-Carboniferous quartz-dolerite dykes frequently invade both dolerite and country rock and elsewhere in central Scotland baryte mineralisation is demonstrably contemporaneous with such intrusions (Stephenson, 1983).

Veins are usually of a simple fissure-infill type consisting of almost pure, pink and white, banded baryte. Much of the baryte is finely crystalline but coarser aggregates of plates ('cock's comb' type) perpendicular to vein margins are common. Pink colouration is due to minute inclusions of hematite. The most common impurity is quartz, which occurs locally in thin stringers parallel to vein margins, as cavity linings and more rarely as larger lenticular masses. Inclusions of country rock occur sporadically close to vein margins at Muirshiel mine and clay-filled vugs (montmorillonite and illite) are also reported. Calcite is a rare accessory, usually grey to pink, but stained brown when in contact with baryte which it appears to replace. A fluid inclusion study of the Muirshiel vein suggests that the calcite was deposited after the baryte from a boiling aqueous solution of abnormally high temperature (Moore, 1979a). Strontianite has recently been identified in the Muirshiel vein (Moore, 1979b) and also with disseminated baryte in the Dockra Limestone near Beith (S. K. Monro, oral communication). Small specks of galena have been recorded from an old (1865) borehole in the Muirshiel vein (MacGregor, 1944) and traces of chalcopryrite occur sporadically (Moore, 1979b), but it is a general feature of the veins that they are free from sulphides. However, baryte occurring as irregular pods in basalt usually contains small specks of pyrite and chalcopryrite. The following paragenetic sequence has been established for the Muirshiel vein (Moore, 1979b): Baryte plus a small but significant amount of hematite in repeated cycles; minor mica; quartz; much later calcite; followed by strontianite.

Rock alteration on a regional scale in the Renfrewshire Hills is unrelated to the baryte mineralisation and in most cases is probably due to contemporaneous, late-stage, deuteric volcanic processes. The abundance of geotechnically-weak, hydrothermally-altered zones within the basalt flows has been discussed. The trachytic and rhyolitic rocks are affected by a general alteration of feldspars and groundmass but remain geotechnically strong. The overall pink and purple colouration is caused by an almost total oxidation of iron oxides and any iron silicates which may have been present. In some areas (e.g. Rough Burn, Calder valley) the trachytes are locally affected by a diffuse, pale pink alteration, emanating out from spherical spots and spreading along joint planes and other fracture surfaces. Such alteration is commonly accompanied by thin baryte veinlets and is strong along NW-SE fracture zones. Thin sections reveal that the alteration spots are centred upon alkali feldspar microphenocrysts and hence are probably due to a

redistribution of potassium, possibly by hydrothermal fluids associated with the baryte mineralisation. This redistribution could be an early stage in a process of wallrock leaching resulting in a movement of barium from the country rock to the veins. However, wallrock alteration adjacent to the Muirshiel vein is limited to minor increases in barium and possibly zinc over a few centimetres and there is no evidence of wallrock leaching at this level (Moore, 1979b).

MUIRSHIEL MINE AREA

Muirshiel mine is situated in remote moorland, 300 to 400 m above sea level and 12 km by road north-west of Lochwinnoch. Access is by metalled road for 8 km to Muirshiel Country Park (on the site of Muirshiel House). The further 4 km of mine track is in a reasonable state of repair, but the bridge over the River Calder, 0.5 km beyond the park, is now closed to motor vehicles.

In the earliest reference to a mine (Montgomery, 1839) it is stated that unsuccessful trials for lead were made before 1779 and again about 1821. By 1839 the value of baryte had been recognised for paint, paper and porcelain manufacture and for calico printing; the mine was established and a mill had been erected. Baryte veins are recorded in the New Statistical Account for Scotland

Table 3 Baryte production from Muirshiel mine 1895-1969

Year	Production (tonnes)	Year	Production (tonnes)
1780-1894	no records	1942	
1895	610	1943	
1896	711	1944	4700*
1897	1016	1945	
1898	1118	1946	
1899	942	1947	
1900	893	1948	
1901	1087	1949	
1902	610	1950	12000*
1903	705	1951	12000*
1904	528	1952	
1905	891	1953	no extraction
1906	1013	1954	no extraction
1907	914	1955	15000*
1908	883	1956	6000*
1909	1037	1957	no extraction
1910	1085	1958	no extraction
1911	1138	1959	
1912	711	1960	
1913	680	1961	
1914	410	1962	17000
1915	308	1963	17500*
1916	267	1964	
1917	195	1965	17000*
1918	117	1966	
1919	—	1967	
1920	92	1968	
		1969	
Total to 1920	17962	Total 1942-1969	283000

* estimated production

Total production to date of closure in September 1969. approximately 300 000 tonnes

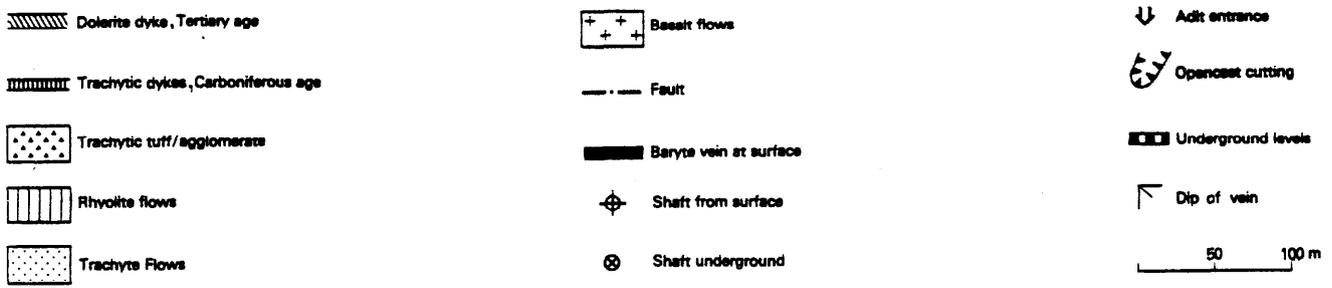
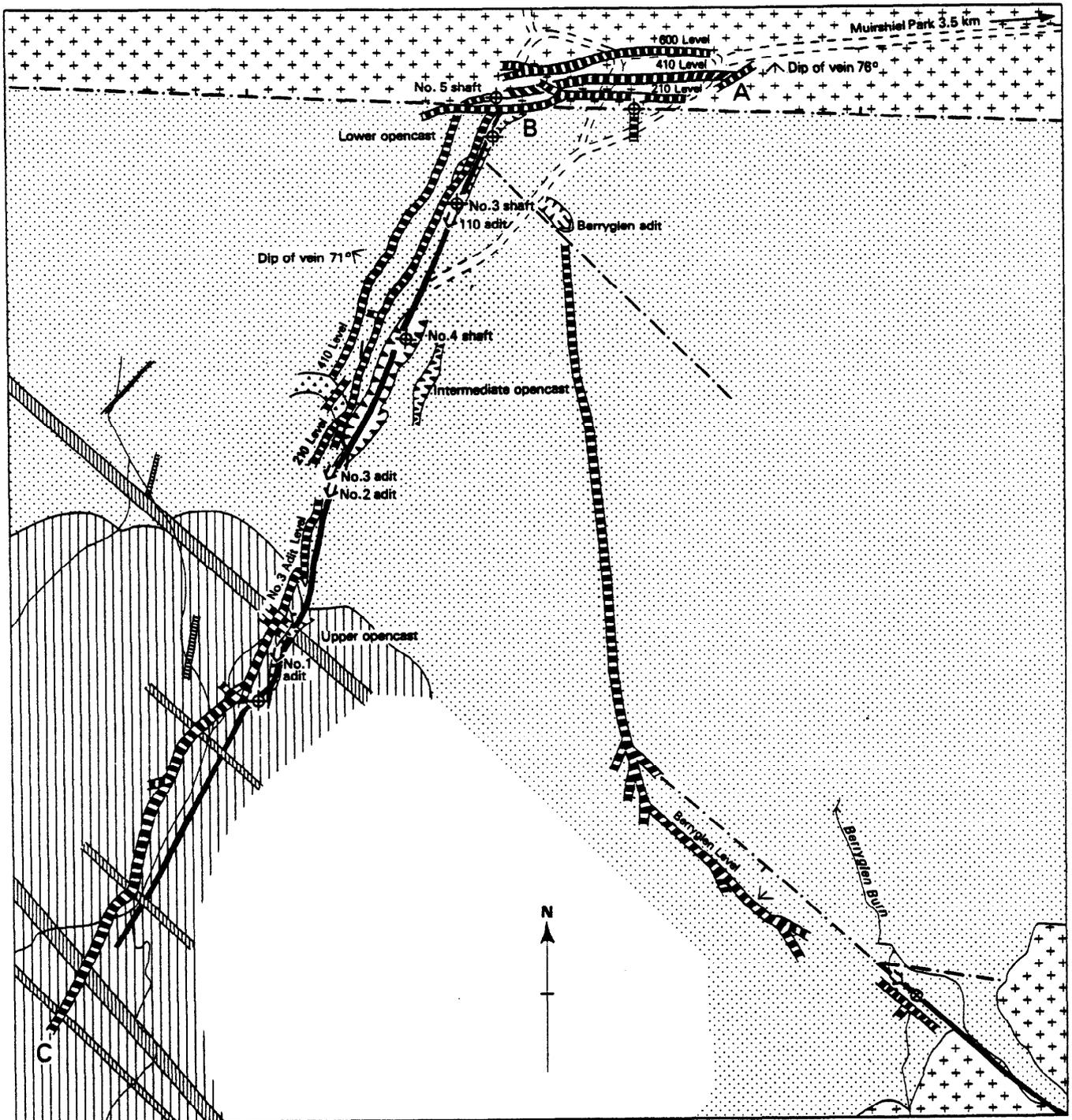


Fig. 4. Plan of workings around Muirshiel baryte mine adapted from the mine abandonment plan 6th September 1969. Only representative mine levels are shown; other levels are shown in the mine sections A—B and B—C (Fig.5). Major geological features are drawn from surface mapping.

(1845) but the mining activity is not recorded. By 1865 the mine was sufficiently established to justify the sinking of a 26 m borehole and by 1900 both opencast and underground mining was in operation (Smith, 1900). Although Wilson and others (1922) refer to mine journals dating back to 1780, official Home Office production statistics only cover the period from 1895 to the closure of the mine in 1920 (Table 3). The mine closure, presumably due to increased difficulty and/or expense of mining with methods available at that time, coincided with the reopening of the Glen Sannox mine, Arran and the opening of Gasswater mine.

In 1942 the Arran Barytes Company wound down their operations in Glen Sannox and reopened Muirshiel mine using many transferred mine personnel. Modern methods of pumping and extraction enabled the underground workings to be extended to a depth of 150 m so that when the mine closed in September 1969, almost all of the workable baryte had been extracted. Some 94% of the mine's total production of 300 000 tonnes came from the period 1942–1969, of which almost half was produced between 1963 and 1969 (Table 3). Further exploration and trials in the mine area were unsuccessful.

Two veins were worked at Muirshiel. The main vein, which was up to 6.5 m wide, could be traced for 800 m in a NNE–SSW direction. Most of the workings were in the northern 450 m of this vein, which pinches and becomes impersistent southwards. The vein dips WNW at 72° with local variations from 35° to 85° . At its northern end the main vein is diverted into an E–W vein up to 4 m thick and dipping north at 76° , which has been worked for about 300 m to the east. Montgomery (1839) indicates that it was this E–W vein which was first tried unsuccessfully for lead. Both veins extend to a depth of 150 m before pinching sufficiently to become uneconomic (Figures 4 and 5). Local pinching of the veins resulted in

temporary interruptions in mining activity. The veins cut massive trachyte and rhyolite flows with interbedded pyroclastics and minor intrusions of the Misty Law Complex (Figure 4). A major E–W fault which forms the northern limit of the complex terminates the NNE baryte vein and acts as a control for the E–W vein. The NNE vein is cut at right angles by at least three NW–SE Tertiary dolerite dykes and an irregular Tertiary dyke follows the E–W fault and vein, impeding the workings in places.

Early Geological Survey publications relate almost entirely to the pre-1920 workings (Wilson and others, 1922; MacGregor, 1944). Initial extraction was from a series of three opencasts, up to 25 m deep, which followed the vein SSW, stepping upwards into the hillside. Five adits were then driven SSW from the floors of the opencasts for up to 100 m and a limited amount of stoping was carried out from these and from two short intermediate levels which were connected by a winze. The relatively insignificant extent of these early underground workings as shown by MacGregor (1944, fig. 7) is indicated in Figure 5. Details of outcrops in the three opencasts are given by MacGregor (1944). Some of this detail has been obscured by subsequent collapse of walls and dumping of waste, but sections of the baryte vein up to 1.2 m wide are still visible in the southern headwalls of both lower and intermediate opencasts. South-south-west of the opencasts, up to 1 m of baryte is also visible close to a later shaft and at a prominent junction of two streams (Figure 4).

During the post 1942 phase of activity the mine was visited at regular intervals by officers of the Geological Survey and a series of internal reports provide a good record of development (1942, 1944, 1950, 1951, 1953, 1957, 1963, 1966). The mine activity of this period is also described by Hobson (1959). Development was centred initially upon the main NNE vein in which three main shafts and six main levels were established eventually to a

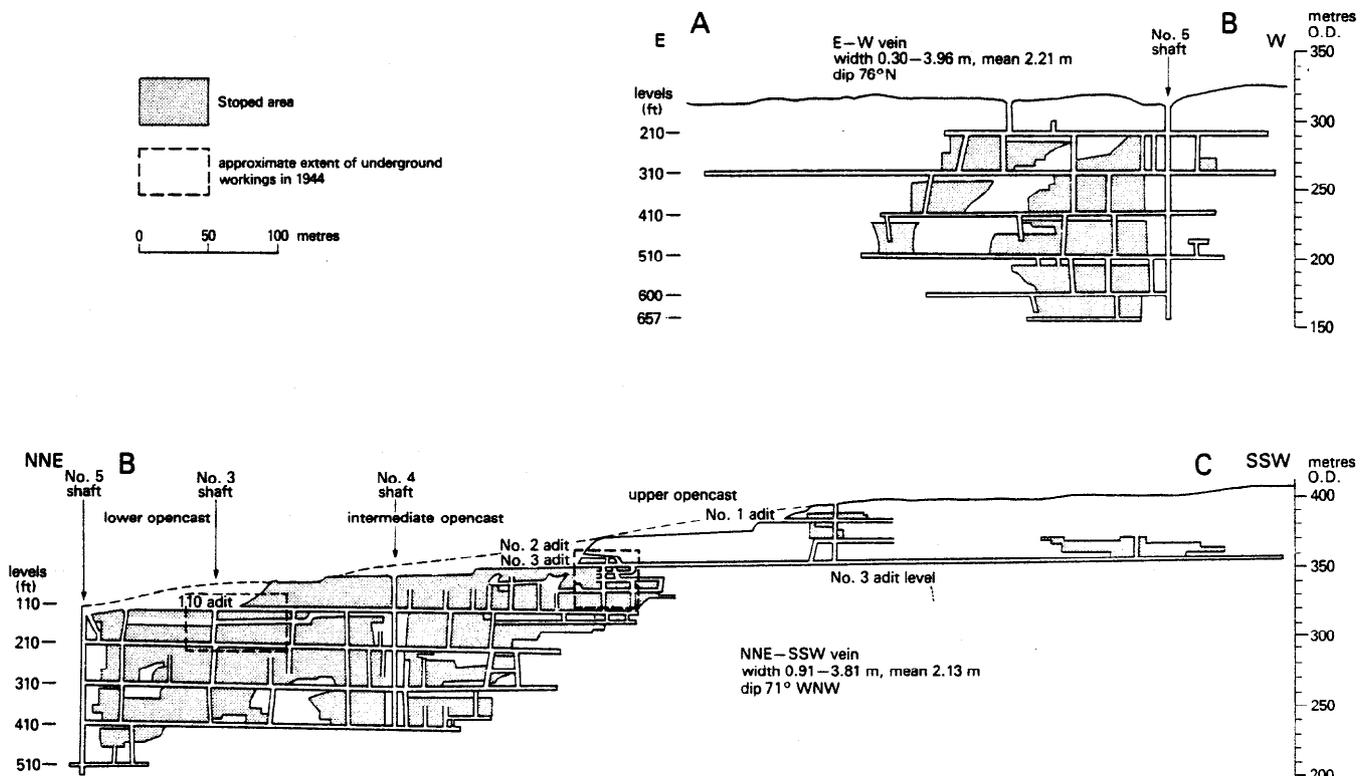


Fig. 5 Sections of worked veins at Muirshiel baryte mine, adapted from the mine abandonment plan of 1969. Names of levels refer to feet below No. 3 adit level.

depth of 150 m. The vein pinches out southwards, 100 m beyond the intermediate opencast in the higher levels and further north in successively lower levels (Figure 5). The vein also became unstable and hazardous to work at greater depths. The SSW extension of the vein beyond the pinching was explored by surface trenching, by boreholes and by extending No. 3 adit level as far as the last observed surface outcrop at the stream junction (Figure 4). There is no record of exploration into the unexposed ground beyond. Development of the vein in the higher levels explored was found to be patchy, with some economic widths separated by long barren stretches (Figure 5). Since the vein is later than the major E-W fault, into which it is deflected at its northern end, a northern extension beyond the fault is considered to be unlikely.

The E-W vein was discovered in underground workings about 1950, but development was hindered by a 5 m-wide Tertiary dolerite dyke which follows the crush zone of the E-W fault for some distance before breaking out into a more normal NW-SE Tertiary trend. Production from the E-W vein was therefore restricted until 1963 by which time the NNE vein was almost worked-out. Six levels were established eastwards for 300 m from No. 5 shaft, which was situated at the junction of the two veins. The vein was found to pinch out rapidly westwards. Despite the presence of more impurities and irregularities than in the NNE vein, almost half of the post-war production came from the E-W vein during the final years 1963 to 1969. It seems likely that production ceased when the impurities became too great to make safe extraction and development profitable without further output from the purer NNE vein. There is no record of any exploration to the east or west of the limits of mining along the E-W fault.

Mining in both veins was by overhead stoping using cut and fill methods. The ore was then passed along the underlying main levels to the shaft base to be hauled to the surface. Prior to 1920 the ore was treated locally at a water-powered mill, close to the bridge at Muirshiel House. A detailed account of the ore treatment during this period is given by Wilson and others (1922). In the post-1942 period some of the ore was taken to Glasgow by road for treatment and an increasing amount (total output by 1966) was sent by rail from Lochwinnoch to Widnes, Lancashire. Analyses of dressed and undressed ore are given by MacGregor (1944). In general the output from the NNE vein was of high purity, 95 to 96% on average, which could usually be increased to 99% simply by mechanical separation. The E-W vein was less pure, falling to 70% in places with a significant iron content. Recent analyses show that the baryte contains 1% to 2.5% SrSO_4 in solid solution (Moore, 1979b).

BERRYGLEN VEIN AREA

A baryte vein of similar characteristics and high purity to the Muirshiel NNE vein is exposed intermittently over a length of 100 m in the Berryglen Burn 600 m south-east of the highest opencast at Muirshiel mine. The vein occurs in a NW-SE fault zone, dips steeply SW and has a maximum width of 1.2 m. In one outcrop the vein splits into two branches of about 0.6 m which coalesce downwards and are separated by 1 m of country rock trachyte.

The remains of about 1 km of light railway run south from the Muirshiel mine road up the Berryglen Burn to the vein. The vein had not been exploited at the time of

the original geological survey in 1875 so the railway must have been built between 1875 and 1920. No further records exist and it is difficult to reconcile the construction of an elaborate railway with the fact that by 1942 there were no signs of the vein every having been worked (MacGregor, 1944). Between 1944 and 1950 trenching along the vein provided an accurate measurement of trend which, if projected NW, would meet the Muirshiel NNE vein in the intermediate opencast. Horizontal underground bores failed to confirm this extension and intersection. In the Berryglen, an adit was driven a short way SE in the exposed vein, from which a 20 m winze gave access to NW and SE drives and a SW cross-cut at a lower level (Figure 4). The vein was found to pinch to less than 0.15 m within 35 m in both directions and the workings were abandoned.

In 1962 work commenced on a drive extending SSE from an adit close to the Muirshiel mine building (Figure 4). This intersected the fault crush in line with the Berryglen vein at 516 m which was then followed for 184 m to the SE. The main drive was completed in 1966 and work continued along small offshoots until 1968. There are no records of mineralisation encountered apart from a few baryte stringers, and it is assumed that no economic concentrations were found since the mine closed soon afterwards in 1969.

OTHER LOCALITIES

Over forty baryte veins and occurrences are shown in Figure 2. Although several of these have widths of 1 m or more, their lateral persistence is unknown and most are in remote areas where the mining of small deposits would not be economic. However, developments at both Muirshiel and Gasswater mines have shown that worked economic veins pinch and swell rapidly both laterally and vertically (Hobson, 1959; Scott, 1967), so that the possibility of workable deposits always exists. Thick deposits of boulder clay and/or peat over much of the area make prospecting difficult unless geochemical and geophysical methods can be developed that at least enable veins to be traced from known outcrops. Such methods were tried with only limited success at Gasswater (Scott, 1967). Electrical resistivity methods are able to trace faults, and gravity surveys will detect thick baryte veins, but complex terrain corrections make the latter method time consuming and therefore costly. Geochemical sampling by auger or portable drill is hampered by a restricted dispersion around baryte veins which necessitates a high sampling density (Scott, 1967), but it is thought that veins and vein systems could be detected by this method, particularly on the peat-covered upland areas. Analysis of the heavy mineral fraction of basal till by portable X-ray fluorescence equipment (Grout and Gallagher, 1980) could make this the best method for detecting unexposed veins. Detailed sampling upstream of anomalous stream sediment samples will also locate further veins, but their lateral persistence would still have to be checked by other more detailed methods such as overburden sampling.

Detailed exploration has taken place only around the Muirshiel and Berryglen veins. Further exploration in this area may be profitable and should concentrate on the E and W projections of the E-W vein and the SSW projection of the NNE-SSW vein beyond the limits of existing workings. Further deposits may exist in the structures beyond the pinches which terminated activity in 1969.

The only other known baryte vein in the area is a small

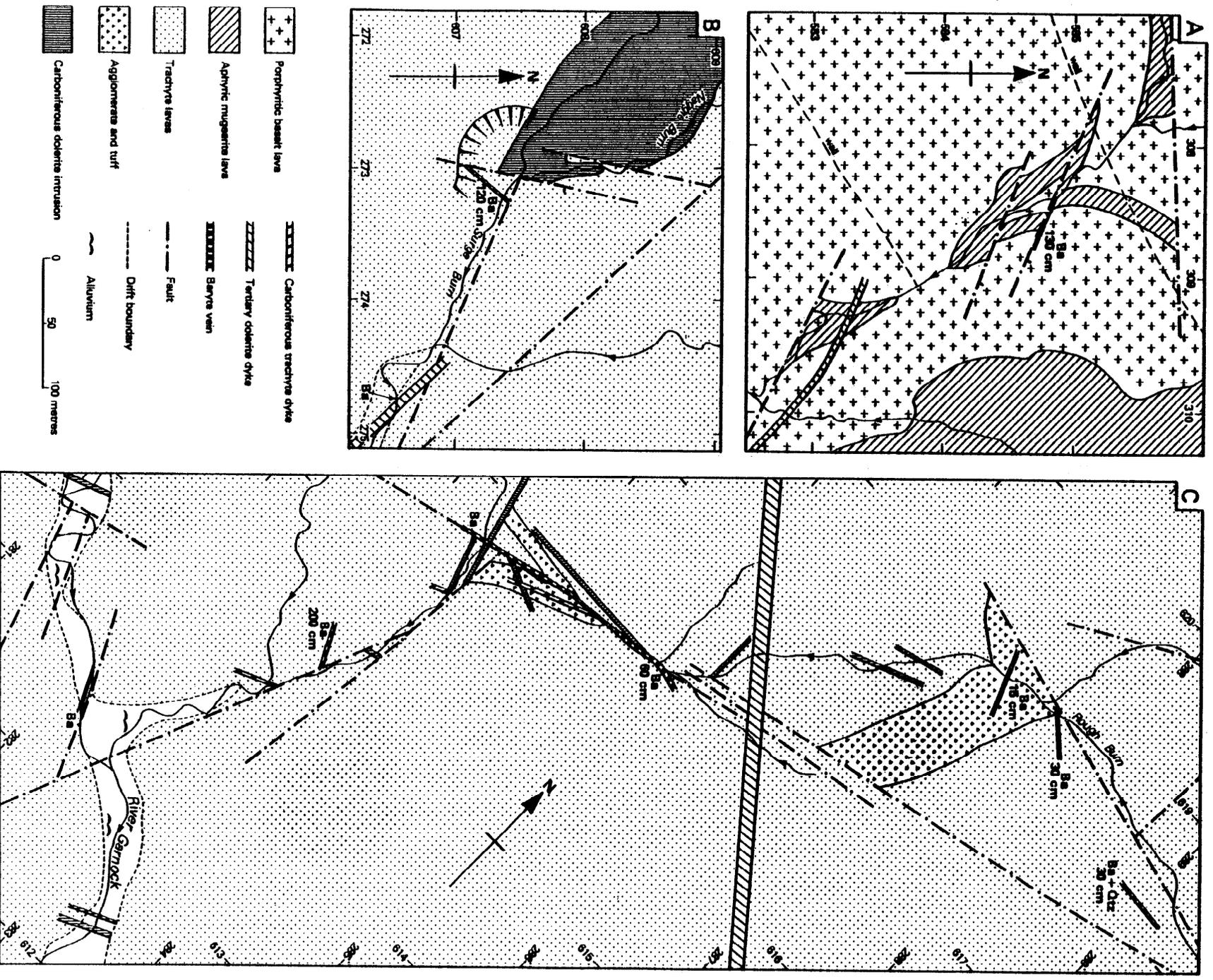


Fig. 6. New discoveries of baryte veins in the Rentfrewshire Hills. A. Millside Burn, Ladyland; B. Surge Burn; C. Rough Burn, upper Garmock Valley. Localities 7, 6 and 5 respectively in Fig. 2.

opencast less than 20 m long 750 m SE of Heathfield Farm in the Calder Valley. The vein is erroneously shown on the original geological survey map of 1870 with a NNE trend (parallel to a drainage cut). In fact the vein trends ESE in a mugearite flow. Some white baryte is seen but the width of the vein is not known. It was probably worked by virtue of the fact that it is only 100 m from the existing road.

Other areas of particular interest, where veins are numerous or of greater than average width, are numbered on Figure 2. Three such localities are shown in detail in Figure 6. MacGregor (1944) records eight veins exceeding 60 cm in width: two 900 m and 1700 m due west of Muirshiel mine; one 350 m WSW of Hill of Stake; and five in the headwaters of the River Garnock (see below). To these may be added the newly-discovered localities in the Surge Burn and Millside Burn (see below).

The presence of numerous loose blocks of banded baryte in the area between High Corby Knowe and West Girt Hill has been long known (Smith, 1900). Further examples were found during the present survey and it is clear that a substantial vein or veins must occur beneath the peat in this immediate area in addition to the vein outcrops shown on Figure 2. This conclusion is also supported by the limited drainage geochemistry. The locality lies on a watershed, where drift cover consists of 1 to 2 m of peat only, and is thus well-suited to an overburden sampling survey. However, the locality is the highest and remotest part of the whole area, being some 4 km from the nearest road across rough moorland.

Several veins of white baryte cut trachytic flows and agglomerate in the Rough Burn tributary of the River Garnock, 600 to 1500 m WSW of Misty Law, and 3.5 km from the nearest road (Figure 6C). The most persistent vein can be traced for 200 m along the stream in a ENE direction with an average width of 60 cm. A NW-SE vein cutting the stream is 2 m wide. Drift cover in this area is likely to be 1 to 2 m of peat on less than 1 m of boulder clay.

A 1.2 m wide vein of pink, banded baryte similar to that of the Muirshiel vein, trends NNE across the Surge burn, 10 m below its confluence with the Naggie Burn (Figure 6B). The vein cuts trachyte flows with agglomerate bands but is close to the highly-faulted margin of an altered dolerite intrusion. It may terminate northwards against a NW-SE fault which controls the stream course, since there is no trace north of the fault despite relatively thin drift cover. To the south the valley is filled with up to 10 m of boulder clay. The locality is 3.5 km from the nearest motorable track across very difficult moorland terrain.

At Millside Burn, 1.1 km W of Cockston Farm, Ladyland (Figure 6A), a 1.3 m wide vein of white baryte trends NW-SE in a fault crush zone cutting mugearite and Markle basalt flows. This is the widest vein recorded in the basalt succession, which does not normally form a suitable host to persistent baryte veins. Drift cover is thin and the locality is relatively close to existing roads and tracks.

COPPER MINERALISATION

Several small copper mines and prospects occur around the periphery of the Renfrewshire Hills where access problems are considerably less than in the baryte localities.

Most of the workings date from the 19th century and records are few. Mine plans appear in the 'Catalogue of Plans of Abandoned Mines' (1931) but attempts to trace them have been unsuccessful. Locations are shown on Figures 1 and 2 and detailed maps of the mine areas are given in Figure 7.

KAIM MINES

The mines are situated 3 km north of Lochwinnoch and are close to a metalled road (Figure 7B).

Montgomery (1839) and the New Statistical Account for Scotland (1845) record the presence of copper carbonate and baryte in surface outcrops associated with a dyke at Kaim but no attempt had been made to work the ore. In places the concentration of copper was so high as to inhibit growth of vegetation. It seems that mining started about 1848, continued intermittently until 1877 (Houston, 1912) and is reputed to have finally ended when the City of Glasgow Banking Company crashed in 1878. A prospectus issued by the West Kaim Copper Mining Co. (Ltd) in 1862 indicates that earlier abandoned workings were cleared out and that considerable development of new shafts, levels and dressing plant was carried out at this time. Over 72 tons of hand-dressed ore were cleared from the old workings and sold at £5 6s to £9 1s per ton in Swansea to help to pay for the operations. Houston (1912) records an output of 800 tons in eight months in 1861.

The copper occurs with baryte, quartz (often amethystine) and calcite in veins extending for 800 m on the southern margin of a 20 m-wide quartz-dolerite dyke trending E10°N through amygdaloidal mugearite. Shaft debris suggests that the mugearite is underlain by a Markle basalt. The dyke is altered and vesicular in the vicinity of the veins, and both dyke and country rock are permeated by the copper mineralisation. Several sub-parallel veins are recorded in places, dipping south at 60 to 70°. The largest vein (No. 2 Lode) was 2 to 3 m wide and was proved horizontally for up to 550 m. Records refer to 'grey sulphuret of copper' and chalcocite (Houston, 1912), but more recent examinations suggest that the main assemblage is malachite with bornite and chalcopyrite. Much malachite is present as green stains on joints, as disseminated irregular patches, as thin veinlets, and as fibrous crystals with quartz or calcite in vugs and amygdaloids.

The veins were worked by two separate companies, Lochwinnoch Consols Co. at East Kaim and from 1861 The West Kaim Copper Mining Co. (Ltd) at West Kaim. At East Kaim, the one main shaft had reached a depth of 58.5 m in 1874, from which levels were driven along the vein, the lowest being at 55 m. In addition, five adits and trial workings are recorded in the side of the Kaim Burn and the site of a smelter is still marked by a pile of glassy, black slag (Figure 7B). At West Kaim, three shafts, two adits and surface workings are recorded. The most easterly shaft was sunk to 20 m, south of the dyke, and cross cuts were driven north for up to 16.5 m to intersect several veins. Other trial adits occur in the base of a mugearite flow, 200 m downstream from East Kaim in the Kaim Burn.

CALDERBANK TRIALS

Five small copper trials are recorded in the steep banks of the River Calder upstream from Lochwinnoch (Figure 7C).

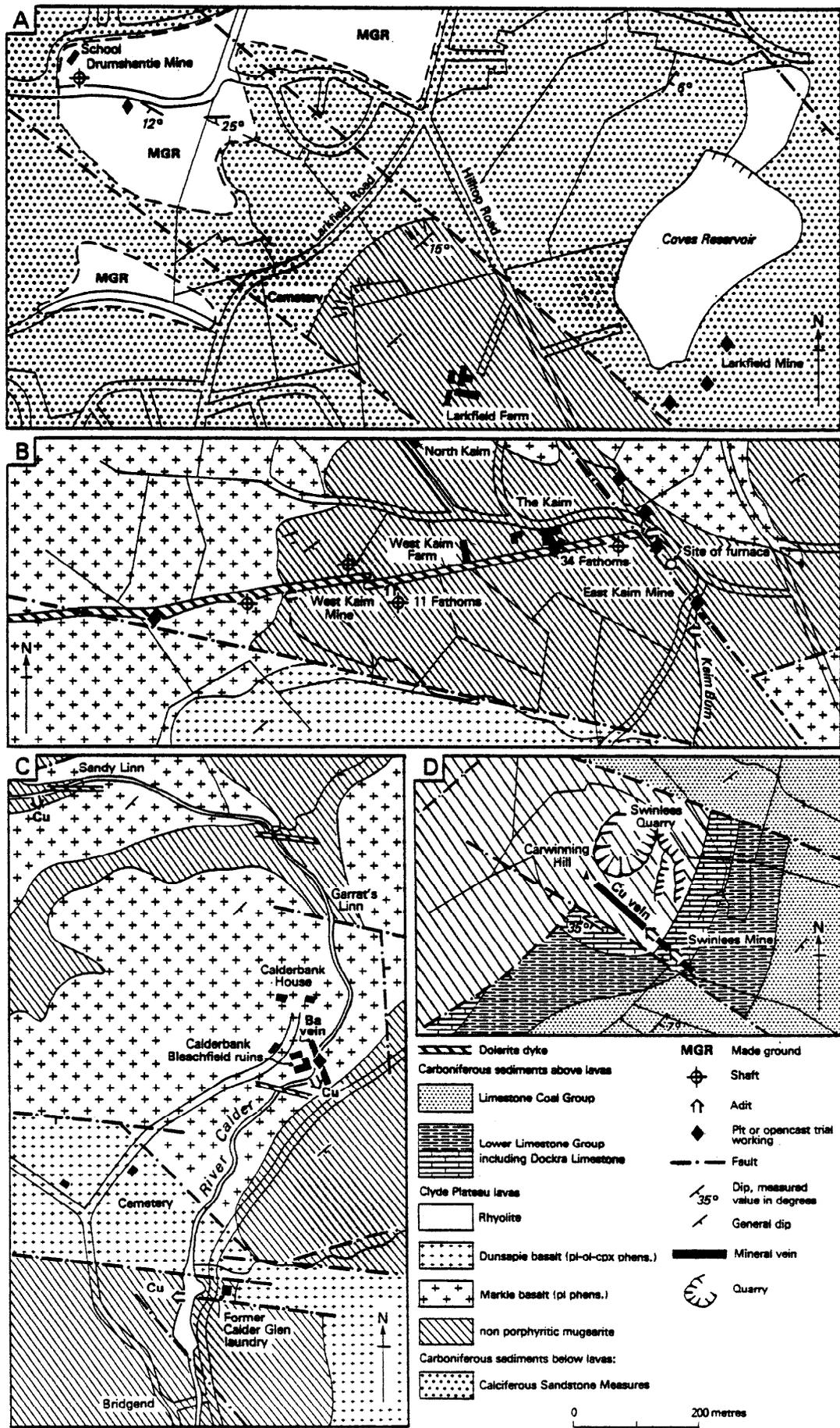


Fig. 7. Old copper mines and prospects in the Renfrewshire Hills. Geology based upon recent mapping at 1: 10 560.

A = Drumshantie and Larkfield mines, Gourrock. B = Kaim mines, Lochwinnoch. C = trial workings around Calder Bank, Lochwinnoch. D = Swinlees mine, Dalry. See Fig. 1 for locations.

Some 150 m upstream from Bridgend, opposite the former Calder Glen laundry, an adit extends westwards into the base of an amygdaloidal mugearite flow. The original geological survey field map (about 1869) merely records 'cupreous amygdaloid' but the resurvey (1914–1921) marks the adit as an 'old copper mine', which is thus assumed to be of late 19th century origin.

At Calderbank Bleachfield, 1 km north of Lochwinnoch, a 30 cm baryte vein trends NNW–SSE across the river and an adit (now collapsed) on the eastern bank is a well documented copper trial. It was opened about 1860 with offices, a smithy and a pumping engine, but did not encounter enough ore to pay for the operations and had been closed for several years by 1869. The vein occupied a vertical fault in the altered, slaggy base of a mugearite flow and probably consisted of baryte and quartz with some malachite, although the New Statistical Account for Scotland (1845) records 'copper pyritous' at this locality.

Further trials which are no longer visible were recorded during the 1869 survey at Sandy Linn, Reikan Linn and between Clovenstone and Glenward Hill. At Sandy Linn a trial was made on the south bank in 'soft, decomposed, amygdaloid with flakes of baryte' at the base of a Markle basalt flow. At Reikan Linn, 100 m below the waterfall, levels were driven a short way north through 'cupreous-looking' decomposed Markle basalt to an ENE-trending vein of unknown character on the southern margin of the Kaim quartz-dolerite dyke. Some 500 m upstream from Reikan Linn a well-constructed mine in massive mugearite on the north bank followed a well defined baryte vein trending E–W with a dip of 68° to the south.

GOUROCK MINES

Drumshantie mine was situated by the Gourock Burn in hills 1 km south-east of Gourock. The site is now totally obscured by housing development and made ground, 100 m west of Drumshantie Park (Figure 7A).

Opencast workings were in existence before 1810 (Wilson, 1921) but were long-abandoned in 1839 (Montgomery, 1839). Work was resumed on a larger scale in 1873 when a shaft was sunk to at least 20 m and engines were erected for pumping, crushing and washing. The mine was abandoned in 1875 and has not been worked since.

The copper occurred in the Clyde Sandstone Formation as disseminations of malachite in pink and white, well-bedded quartzose sandstones with pebbly bands of quartz and jasper, dipping south at 10 to 15°. Carbonised plant remains were a distinctive feature of the sandstones and in many cases the malachite was segregated around fragments of 'anthracite'. Malachite was also seen as botryoidal encrustations on weathered surfaces and Heddle (1901) recorded a little bornite.

Small opencast workings, still visible near Larkfield, 1 km ESE of Drumshantie, are also recorded as 'old copper mines'. The workings were long-abandoned in 1873 and were probably worked at the same time as the early Drumshantie excavations. Grey sandstone with pebbly bands and plant debris contains segregations and thin veins of malachite and 'grey oxide of copper'. Recent revision mapping indicates that the Drumshantie and Larkfield deposits occupy a similar stratigraphical position relative to the base of the overlying lava sequence and may form a cupriferous band in the Clyde Sandstone Formation displaced by a NW–SE fault (Figures 1 and 7A).

SWINLEES MINE

The mine is situated on the south side of Carwinning Hill, 3 km north of Dalry close to the current limits of a working rhyolite quarry (Figures 1 and 7D). Wilson (1921) suggests that the mine may have been worked around 1830, though no mention is made by Montgomery (1839) or by the New Statistical Account for Scotland (1845). By the time of the first geological survey (about 1870) the mine was abandoned. Wilson (1921) records that two levels were driven along the vein, but only the entrance to the upper level is now visible and very little dump material remains.

Mineralisation occurred in a 60 to 100 cm wide NW–SE trending vein at the top of the Clyde Plateau Volcanic Formation. The vein cuts both flow-banded rhyolite and the Dockra Limestone (base of the Lower Limestone Group) which are in faulted contact. A fault breccia of limestone and rhyolite is cemented by baryte with calcite, quartz, malachite, azurite and chalcopyrite. Away from the vein both rhyolite and limestone are impregnated with malachite as a fine vein network and as a general staining which is well-seen in the working quarry. Djurleite ($\text{Cu}_{1.96}\text{S}$) has recently been identified from the mine (S. K. Monro, oral communication).

GEOCHEMICAL INVESTIGATIONS

DRAINAGE SAMPLING

Thirty seven stream sediment and panned concentrate samples were collected in the River Calder catchment and the results are tabulated in Table 4. The samples were collected from first or, rarely, second order tributaries of the River Calder, the Kaim Burn and the headwaters of Locher Water above the B786 road (Figure 9). The sample density was chosen at about 1 sample per km^2 and experience in the Highlands of Scotland (Coats and others, 1981), which may not necessarily be applicable at the lower elevations of the Midland Valley, suggests that this is the optimum sample density for the detection of baryte and base metal deposits. The sampling methods are the standard IGS procedure (*op. cit.*) and the $-150\ \mu\text{m}$ stream sediment sample was analysed for Cu, Pb, Zn, Ag, Co and Ni by atomic absorption spectrophotometry (AAS); for B, Sn, Cr, V, Mo, Mn, Zr, Nb, Ba and Fe by optical emission spectrography (OES) (Tait and Coats, 1976); and for As by X-ray fluorescence (XRF). A heavy mineral concentrate, prepared by on-site panning, was analysed by XRF for Ce, Ba, Sb, Sn, Pb, Zn, Cu, Ca, Ni, Fe, Mn, Ti and As.

Cumulative-frequency-probability graphs were used to determine populations within the data (Lepeltier, 1969; Sinclair, 1974), and those for barium in panned concentrates and stream sediments are given in Figure 8. Barium in panned concentrates provides the best indicator of baryte mineralisation, and the cumulative frequency distribution shows a sharp break at 700 ppm Ba and a steep climb to over 50% Ba indicating nearly pure baryte in the concentrate (pure BaSO_4 contains approximately 58% Ba). The background population has a median of 500 ppm Ba and the geochemical contrast (peak/background ratio) exceeds 1000, showing that the panned concentrate is a very sensitive indicator of baryte mineralisation. A similar conclusion was reached in the discovery of the bedded baryte deposit at Aberfeldy (Coats and others, 1981). The peak barium concentrate (Figure 9) was collected from the stream draining the

Table 4A Analyses of stream sediment samples from the Renfrewshire Hills

	N.G.R	Cu	Pb	Zn	Ni	Co	Ag	As	B	V	Cr	Mn	Fe	Zr	Nb	MoSn	Ba	LOI		
MLC 1	22612	66475	20	60	220	30	15	2	19	12	188	27	3110	76800	177	32	0	6	2730	8
MLC 2	22730	66480	20	80	200	20	15	1	11	22	120	8	691	60700	194	33	1	3	536	8
MLC 3	22788	66526	20	100	230	25	15	2	20	27	170	21	3460	73700	234	41	1	8	2030	12
MLC 4	22785	66524	25	70	250	25	25	2	13	17	141	36	2190	66700	211	39	0	5	823	7
MLC 5	22834	66518	25	70	250	25	15	2	11	18	133	16	2330	69900	256	40	1	0	566	10
MLC 6	22858	66502	15	90	170	20	10	1	15	11	81	16	3560	52800	422	72	0	6	33800	7
MLC 7	22884	66537	20	70	250	25	25	1	13	24	134	37	3430	59700	262	48	0	4	35800	8
MLC 8	22895	66563	20	140	280	25	20	1	34	15	207	3	4170	88600	228	39	0	7	573	33
MLC 9	23004	66462	40	100	240	25	30	1	15	14	160	170	7750	63000	234	39	0	4	62200	15
MLC 10	23060	66405	25	170	140	45	25	2	60	13	144	20	22000	98400	272	43	1	7	737	19
MLC 11	23102	66413	10	70	250	25	15	1	28	19	159	12	3050	78700	246	35	1	0	1070	10
MLC 12	23093	66315	20	100	280	30	15	1	31	8	95	2	7900	71800	423	78	0	5	1030	11
MLC 13	23110	66271	15	90	220	30	15	1	37	6	122	20	7020	83600	365	62	1	4	1280	19
MLC 14	22808	66329	15	60	190	25	20	1	24	18	132	14	2670	72000	260	46	0	0	871	9
MLC 15	22900	66300	15	110	230	40	15	1	29	10	126	25	5770	74400	353	75	1	6	686	9
MLC 16	22907	66292	25	160	640	40	25	1	37	12	138	17	13300	64500	359	72	1	7	18700	14
MLC 17	23239	66247	20	120	950	65	40	2	37	8	190	43	21800	94900	256	43	0	6	830	22
MLC 18	23520	66432	10	60	260	25	10	2	19	23	149	11	2230	71800	428	36	0	0	502	11
MLC 19	23526	66411	20	70	400	40	30	2	17	6	194	25	2620	75000	238	41	0	0	505	8
MLC 20	23526	66412	20	70	370	40	30	2	17	12	159	17	2550	69200	213	34	0	0	738	11
MLC 21	23540	66312	20	70	360	40	40	2	11	5	154	38	4920	83200	184	33	1	0	626	11
MLC 22	23521	66153	125	90	620	30	20	2	17	19	150	0	4440	85400	269	36	0	8	641	15
MLC 23	23516	66114	70	70	450	30	40	2	14	18	152	16	2920	79700	252	47	0	0	680	14
MLC 24	23552	66211	20	60	300	30	15	2	13	8	197	0	2240	81100	212	36	0	0	464	21
MLC 25	23552	66088	110	80	430	30	30	2	14	8	181	26	3580	86000	304	43	0	8	706	17
MLC 26	22988	66298	25	140	290	40	20	2	43	4	124	14	12600	76800	342	60	1	8	730	15
MLC 27	22941	66289	20	60	240	20	10	1	13	3	67	0	4300	58100	812	77	0	6	643	9
MLC 28	23191	66227	10	310	630	55	30	2	57	7	97	0	21300	77800	785	87	0	7	10600	11
MLC 29	23304	66143	25	100	1600	70	40	1	38	6	182	7	22000	95300	208	35	0	5	3990	16
MLC 30	23291	66155	25	150	1620	55	40	2	46	7	22	4	949	37400	847	96	4	4	465	16
MLC 31	23394	66085	20	130	1000	60	20	2	32	10	156	15	10300	105000	225	43	0	10	541	18
MLC 32	23435	66328	15	80	350	45	15	1	22	13	209	0	4200	105000	197	38	0	11	593	8
MLC 33	23385	66250	20	120	1030	60	30	2	46	32	234	3	17900	104000	203	39	0	8	570	12
MLC 34	23378	65929	25	120	720	30	20	2	16	10	311	3	4390	113000	232	40	1	10	564	14
MLC 35	23389	65935	30	100	850	30	30	2	21	9	139	3	8080	95000	225	39	1	7	560	14
MLC 36	23422	65926	25	60	350	30	25	2	8	1	22	2	827	41800	862	103	4	6	434	12
MLC 37	23334	65994	30	70	1050	45	55	2	21	6	178	49	12300	94800	222	36	0	10	1330	9

Note All element concentrations in ppm, loss on ignition (LOI) in %.

Berryglen vein, along which substantial trenching and excavation has taken place (see earlier), and this extreme value probably reflects contamination from these activities. The next highest barium content (49% Ba) was collected from the stream draining Queenside Loch, 8 m above the track to Muirshiel mine. Contamination due to dumping from the track should not be significant at this distance and a further source of baryte is indicated upstream. A small vein is shown to the south-west of Queenside Hill (Figure 2), but this seems inadequate to explain the large anomaly and further detailed study of this stream catchment is merited. Other sites above the threshold of 700 ppm Ba are: the upper tributaries of Raith Burn—Black Grain Burn draining East Girt Hill and White Grain Burn draining the Hill of Stake; the next four lower west bank tributaries of the River Calder; and Kaim Burn. The Raith Burn tributaries drain an area of the trachyte complex to the south-west of the main Tertiary dyke swarm and, although one baryte vein is recorded in Black Grain Burn, further investigation of this area is warranted as the recorded vein (Figure 2) is not considered large enough to have produced an anomaly of this size. The next two anomalous tributaries of the River Calder — Cample Burn and Rough Burn — drain the trachyte complex around Misty Law and Hannah Law (Figure 2) and cross the main Tertiary dyke swarm. Two

small veins are recorded in Rough Burn which may account for that anomaly but unexposed veins in Cample Burn are indicated. The next two anomalous tributaries to the south drain basalts and the western end of the Kaim late-Carboniferous quartz-dolerite dyke. Baryte mineralisation may be restricted to the margins of this dyke in a continuation of the baryte-copper veins of Kaim mine or could be explained by mineralisation along the line of the NW-SE trending Tertiary dyke swarm. The former hypothesis is supported by the anomalous barium value (3.62% Ba) in the sample collected from Kaim Burn but the latter hypothesis is suggested by the less anomalous value (0.52% Ba) from Garpel Burn which has recorded baryte float (Figure 2).

Barium in stream sediments has a similar cumulative frequency distribution to that in panned concentrates (Figure 8) but the threshold is at a higher level of 900 ppm Ba and the geochemical contrast is reduced by a factor of 10. The background population has a median of 573 ppm Ba which closely agrees with the median of the analysed volcanic rocks (559 ppm Ba, see Table 6). Because the stream sediment sample has a finer grain size than the panned concentrate sample it is less sensitive to coarse grained baryte, which may be derived from old mine workings or dumps, and more sensitive to finer-grained sources of baryte such as the overburden which may be

Table 4B Analyses of panned concentrate samples from the Renfrewshire Hills

	N.G.R	Ce	Ba	Sb	Sn	Pb	Zn	Cu	Ca	Ni	Fe	Mn	Ti	As
MLP 1	22612 66475	13	24700	4	8	101	271	25	16700	33	169930	2210	32460	7
MLP 2	22730 66480	40	623	0	3	81	198	13	10070	19	131890	1100	26800	7
MLP 3	22788 66526	62	334	0	4	150	257	21	13210	39	260190	3130	48820	12
MLP 4	22785 66524	84	2108	6	9	96	282	17	16940	26	186850	2090	29600	5
MLP 5	22834 66518	70	2172	0	0	94	228	16	11620	32	201400	2310	40730	5
MLP 6	22858 66502	-1	516100	0	0	3	11	74	730	18	4250	170	2110	0
MLP 7	22884 66537	-1	373800	0	0	25	85	70	3950	23	29720	840	9080	3
MLP 8	22895 66563	35	499	1	4	99	257	26	7460	14	134940	1200	20050	5
MLP 9	23004 66462	-1	495300	9	5	3	31	88	1760	29	6940	260	2220	2
MLP 10	23060 66405	103	2032	0	0	49	147	12	8970	13	108990	1210	12920	9
MLP 11	23102 66413	81	8033	7	3	167	257	20	11720	31	276220	3640	48080	13
MLP 12	23093 66315	125	4768	6	13	72	245	27	12580	25	226990	2660	22360	23
MLP 13	23110 66271	70	22000	3	12	95	231	21	11190	24	212950	2320	26020	20
MLP 14	22808 66329	57	10400	3	4	52	184	20	13210	23	108930	980	16410	9
MLP 15	22900 66300	78	1790	1	0	62	214	21	9900	15	105270	1200	14920	7
MLP 16	22907 66292	-1	273200	0	0	54	160	59	5420	24	62720	1790	7460	11
MLP 17	23239 66247	53	1450	6	10	69	335	18	35920	26	127190	2310	18190	10
MLP 18	23520 66432	61	350	5	12	49	138	9	6950	8	91350	690	16240	6
MLP 19	23526 66411	38	575	1	2	73	198	12	9590	24	146410	1290	28050	10
MLP 20	23526 66412	44	591	0	0	57	227	11	8910	18	99770	840	17390	8
MLP 21	23540 66312	56	348	5	5	88	186	15	15770	34	198230	1480	18290	9
MLP 22	23521 66153	24	36200	0	226	189	364	94	4970	22	262350	1970	23380	14
MLP 23	23516 66114	90	3149	0	24	129	443	29	9380	32	273200	3070	46200	22
MLP 24	23552 66211	28	505	6	10	54	219	17	5360	11	111480	840	16550	4
MLP 25	23552 66088	43	2885	1	29	99	369	111	9180	23	198240	1710	21870	7
MLP 26	22988 66298	97	526	1	19	67	182	14	13760	31	188150	1470	13850	18
MLP 27	22941 66289	76	7392	0	8	87	280	41	10550	21	175240	1770	20780	15
MLP 28	23191 66227	-1	178700	-1	0	91	182	47	4140	19	96910	1870	10150	12
MLP 29	23304 66143	-1	39200	0	0	81	376	37	8660	18	120970	1820	18580	4
MLP 30	23291 66155	17	24800	5	14	98	469	23	9660	24	203750	4360	27020	19
MLP 31	23394 66085	39	3083	6	20	99	559	14	7590	15	190650	2460	21260	16
MLP 32	23435 66328	41	412	0	5	117	286	14	5980	18	202420	1920	24900	23
MLP 33	23385 66250	54	408	7	12	122	350	15	6090	17	228380	2810	24690	28
MLP 34	23378 65929	45	792	8	5	101	483	90	10490	12	137160	1800	18010	6
MLP 35	23389 65935	67	538	2	9	69	261	24	9190	53	253440	2980	47890	3
MLP 36	23422 65926	56	928	7	12	105	403	14	14290	31	229140	2830	30120	10
MLP 37	23334 65994	55	5159	1	4	92	489	19	19170	48	203150	3160	18430	17

Notes

- 1 -1 means negative results because of overlap of Ba peak on background.
- 2 All element concentrations in ppm.

derived by glacial action or subsequent soil formation. The stream draining Queenside Loch has the highest barium content (Figure 10), rather than those draining old mine areas such as the Berryglen vein, and this indicates that an overburden source is more likely to be responsible. This stream catchment is therefore worthy of further detailed investigation. Other strongly anomalous sources (>1% Ba) are Black Grain Burn draining East Girt Hill (Figure 2) and Rough Burn (Calder valley). Lesser anomalies (>900 ppm Ba) are found along a belt NW-SE paralleling the Tertiary dyke swarm. The Kaim dyke does not give a stream sediment anomaly, indicating that baryte mineralisation is very limited along its length and old mine dump material may be responsible for the panned concentrate anomaly.

Copper in panned concentrates shows a sharp break in the cumulative frequency distribution at 30 ppm and 10 samples exceed this threshold level (Figure 11). The highest copper value (111 ppm) is downstream of the old Kaim Copper mine workings (Figure 12). Another group of high values is found near the Berryglen and Queenside Loch area and reflects the minor occurrence of chalcopyrite recorded from the main baryte veins (Moore, 1979b). Moderately anomalous values are found

in Black Grain Burn (59 ppm) and Rough Burn (47 ppm), and similar occurrences of chalcopyrite are expected. The southernmost sample, collected at NGR 23378 65929 just north of Gillsyard from a stream draining basalts has a relatively high level of copper (90 ppm) and probably reflects a small copper vein similar to those recorded at Calderbank. A small local source is indicated by the lack of a stream sediment anomaly at the same site.

Copper in stream sediments (Figure 13) shows a similar frequency distribution to that in panned concentrates and the threshold is identical at 30 ppm. Only four samples exceed this threshold, showing that the stream sediment is only picking up the larger copper sources produced by dominantly secondary dispersion (Figure 13). The Kaim area is strongly anomalous reflecting the abundance of secondary copper minerals in the old mine dump material. The other sample exceeding the threshold is from the stream draining Queenside Loch and this again indicates a secondary source for the copper within the overburden rather than dumped material from recent workings which would have shown up only as a panned concentrate anomaly (as illustrated by the Berryglen copper panned concentrate anomaly).

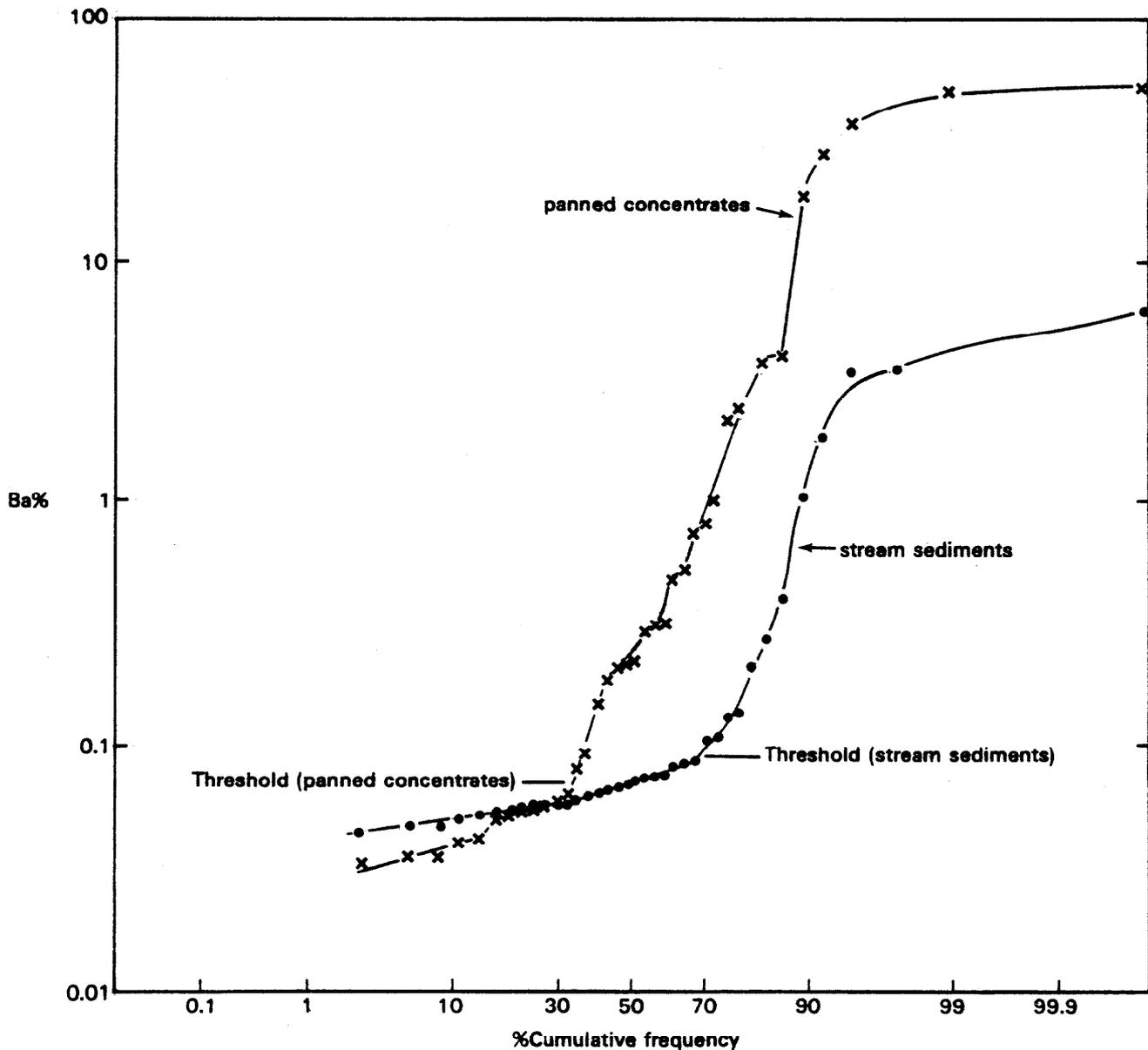


Figure 8 Cumulative frequency distribution of barium in panned concentrates and stream sediments

The distribution of barium and copper are described above in some detail because these are the elements with the greatest economic potential. However, the other elements are also important in view of the orientation nature of this drainage survey. A multivariate statistical method is used to summarise their geochemical variation in order to find out if any other element would be useful in exploration of the area. Factor analysis has been used extensively in geochemistry (Chapman, 1978) to group elements so that underlying geochemical 'causes' or factors can be isolated from large data matrices and to provide a simplification of an often confusing array of data. It was successfully used at Aberfeldy (Coats and others, 1981) to isolate a baryte and base metal factor from the drainage geochemistry and it was hoped that a similar factor could be isolated here.

The first factor (Table 5) has positive loadings of those elements which occur in Fe-oxides in the panned concentrate, such as Fe, Ti, Zn and Mn, and also elements, such as Ca and Ce, which probably occur in clinopyroxenes along with these elements. The negative loadings of barium and copper express the strong negative correlation between baryte and Fe-oxides in the panned concentrate.

The association of copper in the panned concentrate with barium has been noted above and suggests the possible presence of chalcopyrite in the baryte veins.

The second factor includes loss-on-ignition and manganese which are closely related to the organic content of the stream sediment and its pH and eH. This secondary environmental factor is known (Butt and Nichol, 1979) to have a strong influence on the levels of several trace elements by adsorption on secondary manganese oxides and by complex formation with organic molecules. Arsenic, lead, nickel and zinc in stream sediments are commonly influenced in this manner.

Iron is also strongly affected by the surface environment but in this instance behaves slightly differently to manganese and is more dominant in the third factor. This factor has positive loadings for vanadium, iron and boron and negative loadings for zirconium, niobium and molybdenum. The latter elements have high values over the trachyte complex and low values over the basalts and mugearites reflecting the rock compositions (Table 6) which show a general rise in zirconium with differentiation as illustrated by the Rb/Sr ratio. The northern part of

Table 5 Rotated factor matrix, Renfrewshire Hills drainage geochemistry

Factor I (+) Fe _p , Ti _p , Pb _p , Zn _p , Ce _p , Mn _p , Ca _p , As _p , Sn _p , Ag _c	- Cu _p - Ba _c - Ba _p	(-)
28% of trace		
Factor II (+) As _c , Pb _c , Ni _c , Mn _c , Zn _c , LOI _c , Sn _c , Fe _c , Co _c		
15% of trace		
Factor III (+) V _c , Fe _c , B _c	- Mo _c - Nb _c - Zr _c	(-)
13% of trace		
Factor IV (+) Cu _c , Cu _p , Sn _p		
8% of trace		
Factor V (+) Co _c , Cr _c , Ni _p		
6% of trace		

Notes

- 1 c = stream sediment; p = panned concentrate.
- 2 LOI = loss on ignition.
- 3 Factor loadings in order of importance, most positive loading on the left, negative on the right. Only elements with factor loadings greater than 0.4 shown.

Table 6 Analyses of volcanic rocks from the Renfrewshire Hills

	SiO ₂	Ba	Sr	Rb	Sb	Pb	Zn	Cu	Ni	Nb	Zr	Y	Mo	Rb/Sr	Nb/Y
<i>Basalts</i>															
67938	49.32	471	500	43	2	10	314	10	3	47	287	33	4	0.086	1.424
67955	45.45	427	544	37	3	15	1296	25	5	52	285	30	3	0.068	1.733
67964	49.38	621	629	57	0	11	111	8	2	65	320	36	4	0.058	1.806
67974	44.96	675	282	75	3	9	253	30	37	52	263	28	1	0.266	1.857
68012	49.81	706	531	67	4	10	204	8	1	93	488	39	2	0.126	2.385
68014	48.00	585	671	43	3	9	121	27	21	59	298	33	5	0.064	1.788
68016	45.98	319	639	26	1	23	105	7	6	29	181	21	2	0.041	1.381
68027	46.91	259	444	19	4	11	130	15	27	28	182	21	2	0.043	1.333
68028	45.32	421	529	11	1	21	203	109	22	44	264	29	2	0.021	1.517
68029	46.21	277	512	11	1	4	105	61	29	29	194	24	4	0.021	1.208
68030	—	544	507	40	4	10	1642	53	31	35	222	28	2	0.079	1.250
<i>Mugearites & trachyandesites</i>															
67954	53.85	578	497	60	5	15	139	7	2	64	380	40	4	0.121	1.600
67986	56.18	972	399	133	0	13	163	6	2	115	650	41	8	0.333	2.805
68013	58.90	1255	346	113	5	15	309	8	2	94	560	45	4	0.327	2.089
68023	58.67	559	312	64	3	15	212	1	1	72	519	39	5	0.205	1.846
<i>Trachytes</i>															
67968	59.25	1488	115	121	4	10	80	5	2	56	370	32	4	1.052	1.750
67997	68.79	344	66	162	4	10	135	3	1	116	1089	64	1	2.455	1.813

Notes

- 1 All analyses by X-ray fluorescence (XRF) methods using pressed powdered material.
- 2 SiO₂ in per cent, remaining elements in ppm.
- 3 Sample numbers refer to IGS sliced rock collection.

- 67938 Markle flow, Pundeavon Reservoir NGR 2912 5867
 67955 Markle flow, Calder Dam site, BH 81 NGR 3266 6170
 67964 Markle flow, Feuside Hill NGR 2527 5937
 67974 Altered Markle, Boxlaw Burn NGR 2570 6196
 68012 Jedburgh flow, Rye Water NGR 2544 5780
 68014 Markle flow, Rye Water NGR 2515 5834
 68016 Markle flow, Greenside Hill NGR 2736 5832
 68027 Markle flow, Calder Dam site, BH C/10 NGR 3303 6199
 68028 Jedburgh flow, Calder Dam site, BH C/10 NGR 3303 6199
 68029 Markle flow, Calder Dam site, BH C/12 NGR 3245 6166
 68030 Jedburgh flow, Calder Dam site, BH C/12 NGR 3245 6166
 67954 Mugearite flow, Calder Dam site, BH S1 NGR 3266 6170
 67986 Trachyandesite ? plug, East Girt Hill NGR 2793 6283
 68013 Mugearite flow, Rye Water NGR 2522 5841
 68023 Porphyritic mugearite flow, Pundeavon Reservoir NGR 2925 5785
 67968 Trachyte ? plug, Marls Burn NGR 2812 5888
 67997 Altered trachyte flow, Hannah Law NGR 3127 6218

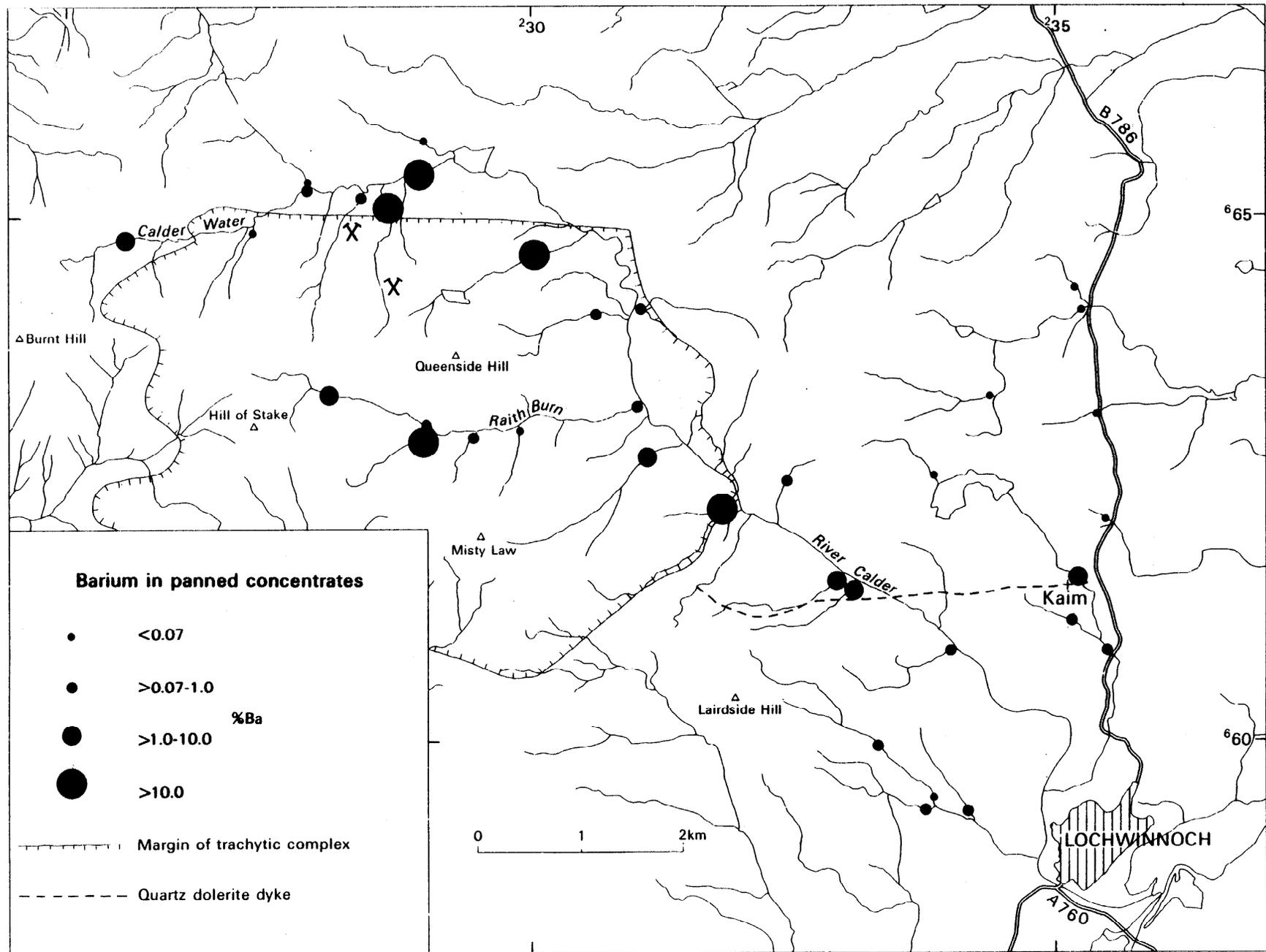


Figure 9 Distribution of barium in panned concentrates

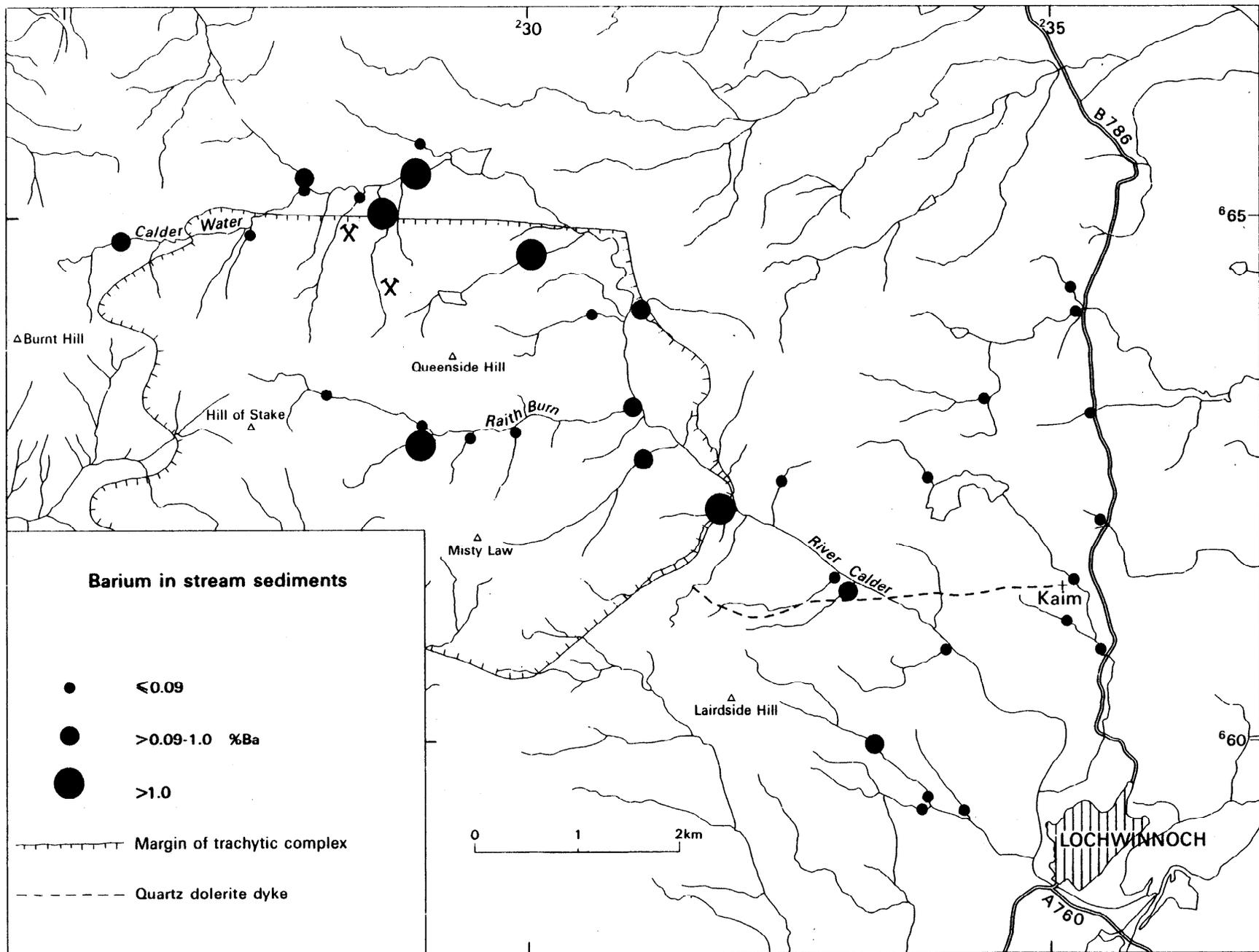


Figure 10 Distribution of barium in stream sediments

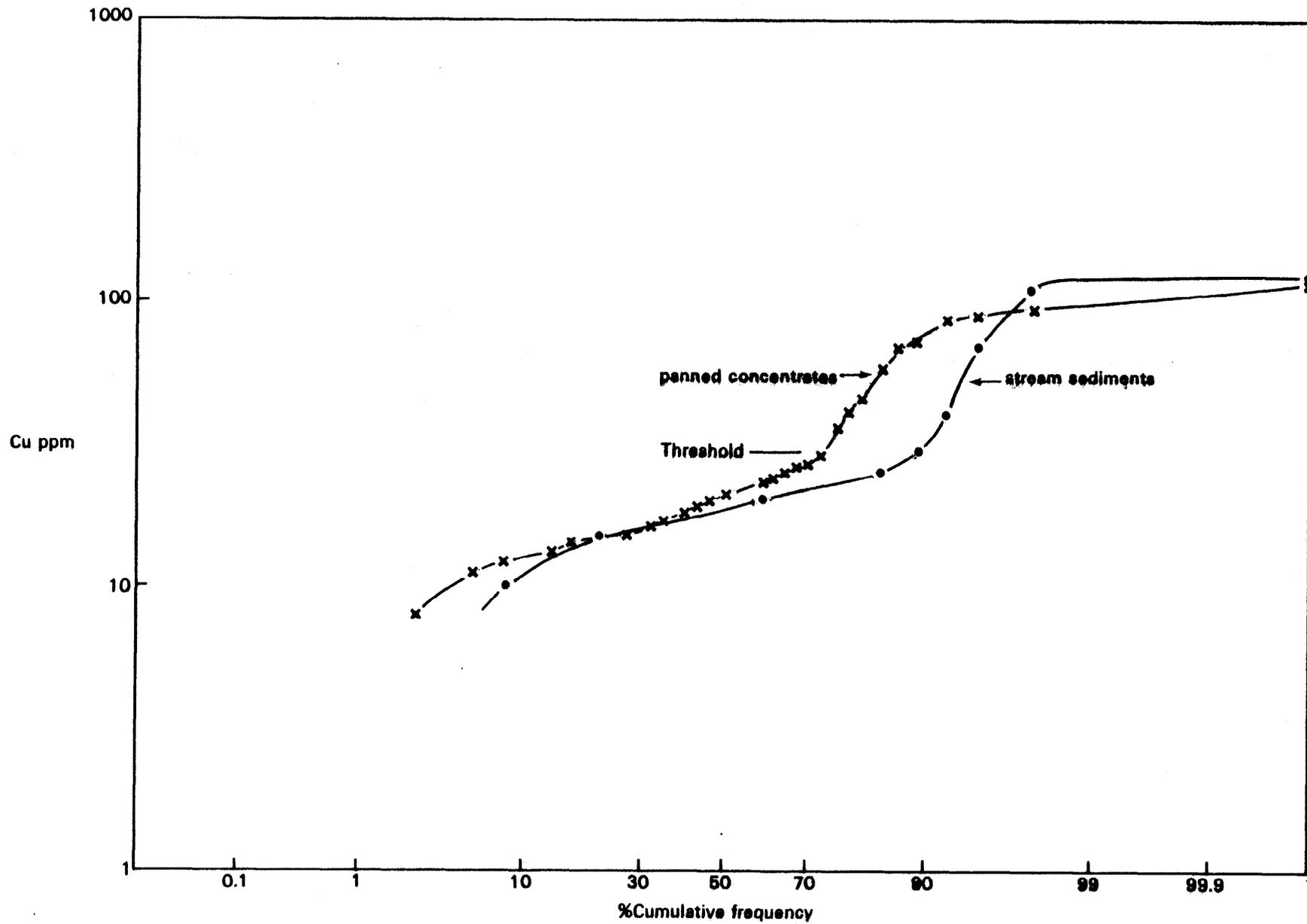


Figure 11 Cumulative frequency distribution of copper in panned concentrates and stream sediments

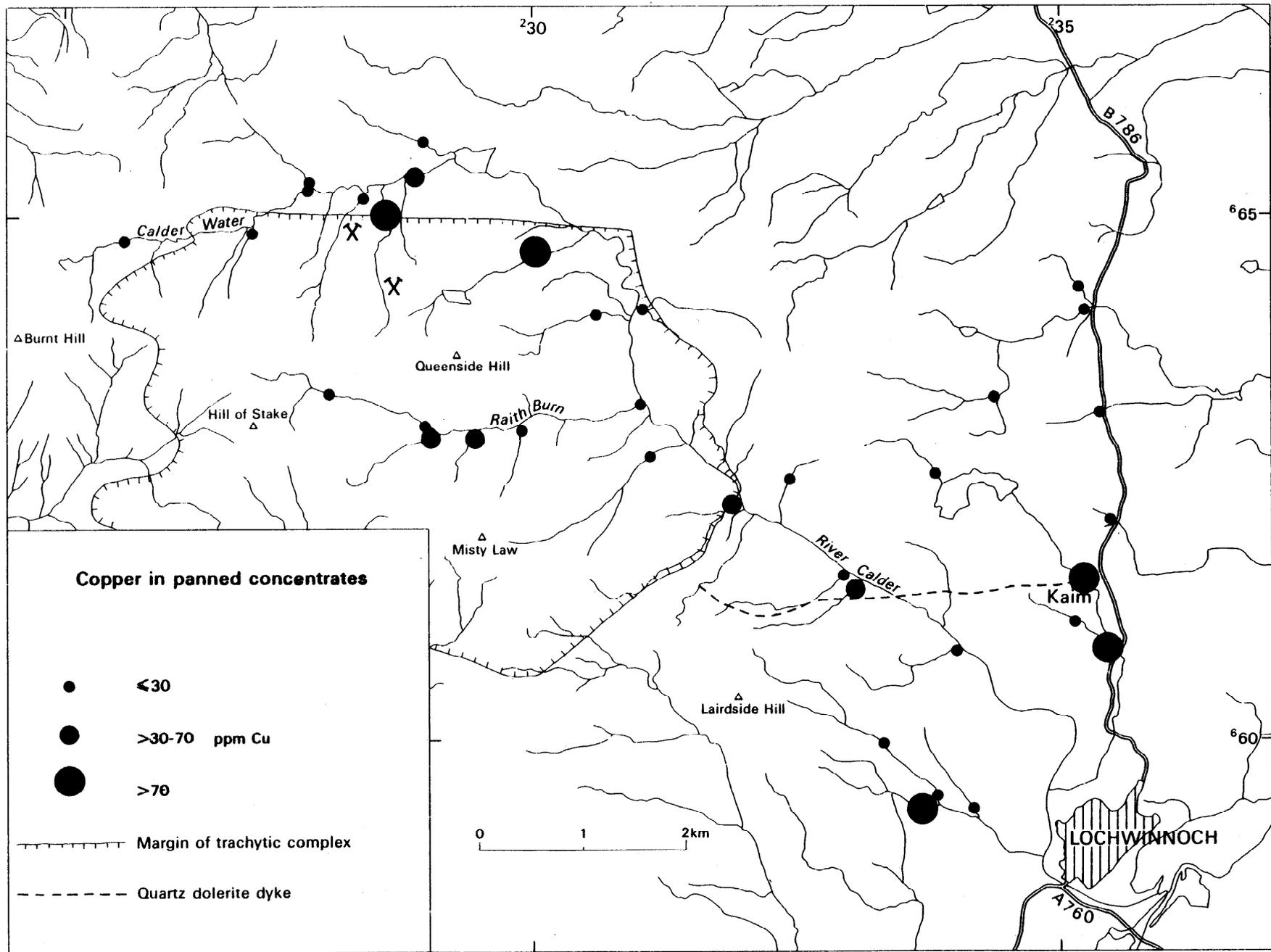


Figure 12 Distribution of copper in panned concentrates

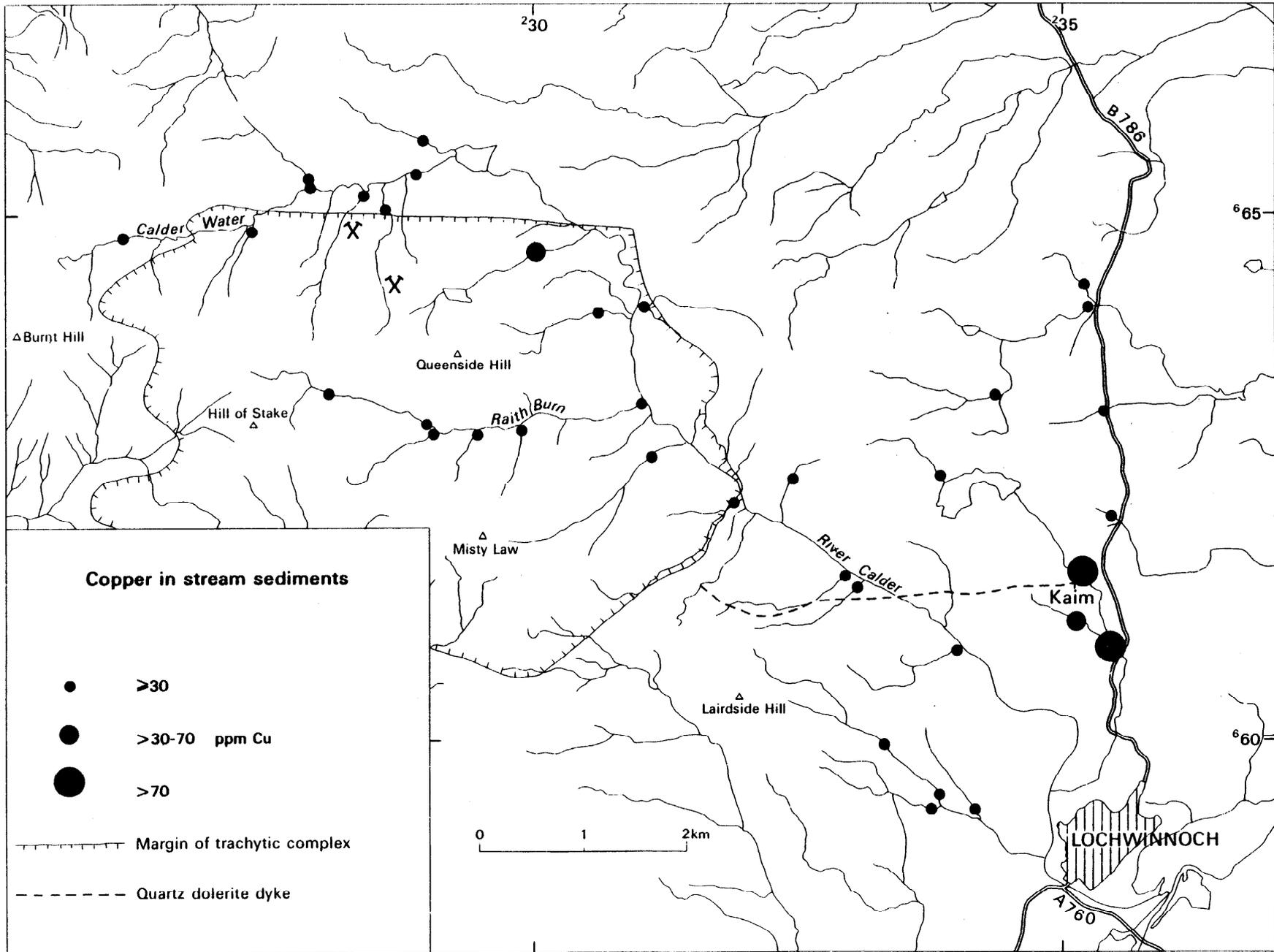


Figure 13 Distribution of copper in stream sediments

the trachyte complex (the tributaries of Calder Water) does not show such high levels of zirconium and niobium as the southern half and there is a slight spillover to the south, which possibly indicates glacial dispersion. Corroboration of this dispersion direction comes from glacial striae which run dominantly south but with some ESE directions (one-inch Geological Sheet 30). The association of vanadium and iron is to be expected as the elements are geochemically similar in the trivalent state. The iron content of the stream sediment is largely controlled by the pH and eH conditions; amorphous iron hydroxides being precipitated where acid, reducing groundwater (containing dissolved Fe^{2+}) is oxidised when it reaches the surface or within the stream sediment. Vanadium is probably coprecipitated with the iron hydroxides and boron is possibly adsorbed on the surface of this reactive material. These three elements are only high over the basaltic rocks around the trachyte complex giving the antipathetic relationship with Zr, Nb and Mo.

Factor four is clearly related to copper mineralisation and samples from the Kaim mines area have the highest scores on this factor. The stream draining Queenside Loch and those draining Lairdside Hill are the next significant groupings. The association of tin in concentrates is somewhat puzzling until it is seen that one of the Kaim samples has high tin (226 ppm) and is obviously contaminated by dumped material such as tin cans. Other samples with tin above background tend to be scattered over the lower, inhabited ground.

Factor five, with high loadings of cobalt, chromium and nickel, is clearly related to the occurrence of these elements in basic rocks, as opposed to elements such as manganese and iron which are more related to secondary environmental factors. However, this factor cannot be positively assigned to one part of the volcanic sequence.

LITHOGEOCHEMISTRY

Trace element analyses of a representative suite of igneous rocks from the Renfrewshire Hills are shown in Table 6. The rocks were selected for their freshness in hand specimen, although all the trachytes in the area are oxidised to a certain extent and several of the basalts and mugearites have a carbonate-enriched matrix. The trace element determinations were carried out at the IGS Gray's Inn Road laboratories using an X-ray fluorescence method.

The trace element concentrations of the basalts are typical of those found in comparable suites of within-plate alkali olivine-basalts (Pearce, 1982). Compared to average mid-ocean ridge basalts (MORB) such basalts are strongly enriched in Rb, Ba and Nb but Y is not comparably higher. The Nb/Y ratio, in particular, is always greater than 1.0 demonstrating the alkaline nature of the parental magma.

With differentiation from basalt to trachyte the levels of the 'incompatible' elements such as Rb, Ba, Nb, Zr and Y rise and there is a good correlation between these elements and SiO_2 . Strontium, which is slightly enriched in alkali olivine-basalts (Ratio Sr Renfrew basalts/MORB = 4.41), shows a slight fall between the basalts (Median = 529 ppm Sr) and the intermediate mugearites and trachyandesites (Median = 449 ppm Sr) and a greater drop to the trachytes (Median = 91 ppm Sr). Strontium normally increases in the melt as a basaltic magma crystallises because of the marked preference of clinopyroxene for Ca over Sr (Wedepohl, 1978). However, it is incorporated into plagioclase feldspar so

that roughly equal concentrations are found in basalts and mugearites and only when significant plagioclase crystallisation has taken place does the strontium content of the melt drop significantly. The final differentiates such as the trachytes then have a much lower strontium content. Rubidium and barium on the other hand do not readily enter either the clinopyroxene or the plagioclase lattice and increase in the residual liquid. The Rb/Sr ratio is therefore quite an accurate indicator of differentiation (Figure 14). The basalts, with only a single exception, have a Rb/Sr ratio of less than 0.1 with higher ratios in the mugearites and trachyandesites. The Ba-Sr pattern (Figure 14) should be similar to the Rb-Sr variation and this is true for the basic and intermediate rocks. One trachyte 67997, however, has a very low barium content relative to its high Rb/Sr ratio of 2.455. The low barium content of this sample can be explained in two ways. Either the melt had crystallised sufficient K-feldspar to deplete the final liquid fraction in barium (which is concentrated in early formed K-feldspars), or barium has been removed from the rock by later alteration. The latter explanation is very attractive in that it provides a source of barium within the trachyte complex which can be precipitated out within the veins by reaction with sulphate-bearing groundwater. Whilst wallrock leaching has not been detected at the present level of exposure (Moore, 1979b) the presence of trachyte with an unusually low barium level relative to rubidium and strontium is an indication that this process could have taken place. Some redistribution of alkalis is recorded in trachytes from the Rough Burn area (page 8) and therefore on geochemical evidence the localisation of the major baryte veins within the complex could be due to the composition of the trachyte wallrock.

Other 'incompatible' elements such as Zr, Nb and Y increase in the more fractionated rocks and the Zr/Nb and Nb/Y ratios increase from the basalts to the intermediate rocks with a maximum in the trachyte flow (67997). The trachyte plug (67968) has low values possibly because of the crystallisation of a zirconium enriched phase, such as zircon.

Zinc varies between wide limits and as it is located predominantly in the magnetite fraction of mafic rocks (Wedepohl, 1978) it is presumably controlled by the crystallisation and settling of magnetite. Without information on ferric and ferrous iron this supposition is difficult to prove. Copper falls with differentiation from a median of 27 ppm in the basalts, to 7.5 ppm in the intermediate rocks, and finally, to 4 ppm in the trachytes. The element is probably located in a very minor sulphide phase, as is the case for most mafic rocks (Wedepohl, 1978). The higher content of the basalts probably explains the distribution of the copper vein occurrences which are confined to the basalt part of the succession or the margins of dolerite dykes. Lead occurs at low levels and appears to have little significant geological variation. Nickel is probably present in olivine which explains the much higher median in the basalts (21 ppm Ni) and its rapid removal from the melt so that intermediate and acid members have very low concentrations (medians 2 and 1.5 ppm Ni respectively).

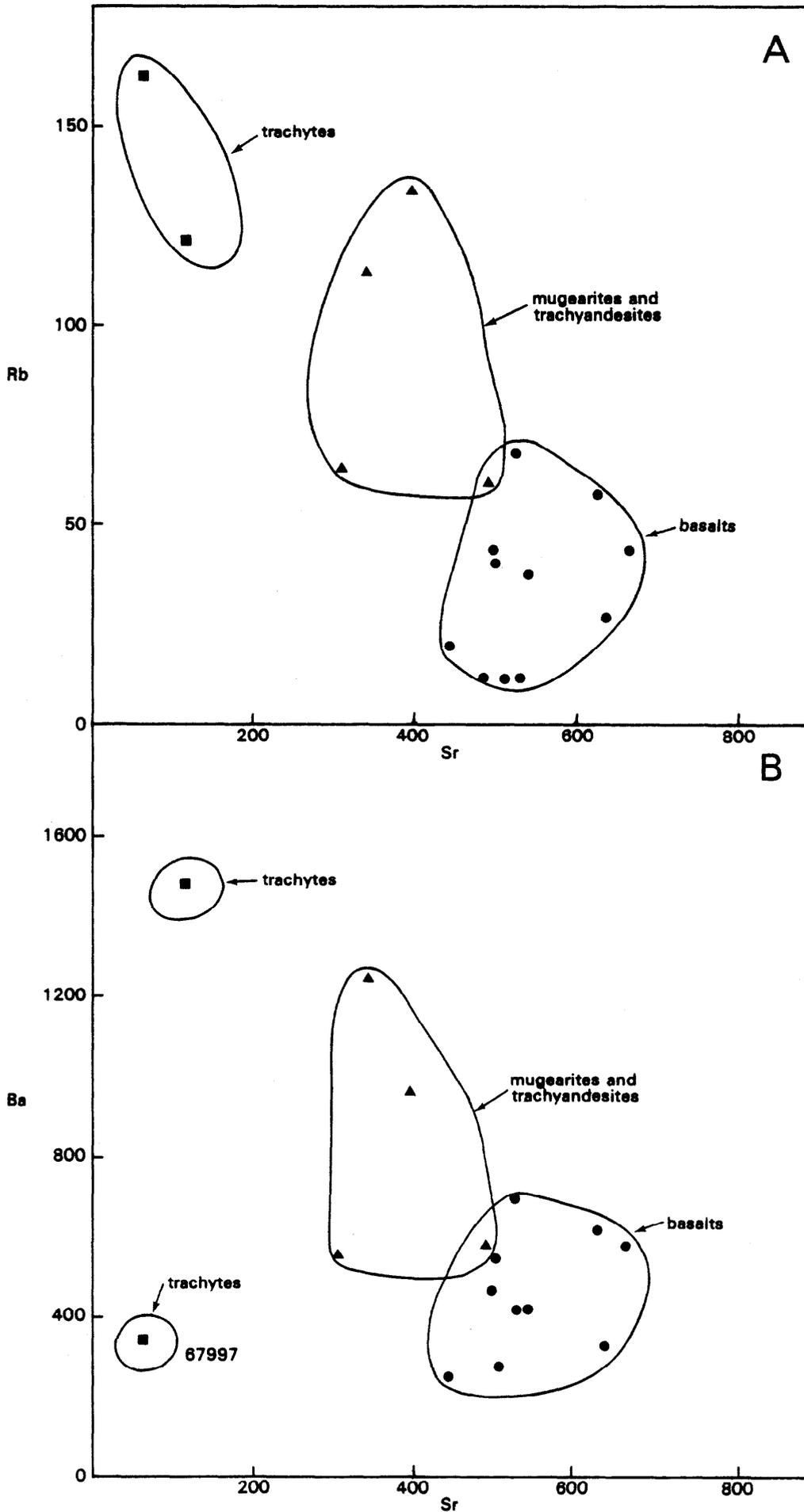


Figure 14 A Rubidium – strontium variation in volcanic rocks
 B Barium – strontium variation in volcanic rocks

CONTROLS, AGE AND GENESIS OF THE MINERALISATION

BARYTE

The most obvious structural control of baryte mineralisation in the Renfrewshire Hills is the close association with the NW-SE Tertiary dyke swarm. Mineralisation is more or less confined to the limits of this swarm and many veins occupy NW-SE fractures, some of which are 'shared' by dykes. Baryte deposits at Myres Burn, Eaglesham and in the River Nethan district are within the same swarm which continues SE through the mineral deposits of Leadhills and the north Pennines. Elsewhere in central and southern Scotland, baryte mineralisation is concentrated along major NE-SW faults and in the River Nethan district occurs at the intersection of one such fault with the NW-SE Tertiary dyke swarm (Scott, 1967; Gallagher and others, 1982). The most obvious NE-SW structure in the Renfrewshire Hills is the 'Paisley Ruck' fault system which forms the SE margin. There is no regional NE-SW structure visible in the mineralised area, although the SE margin of the Misty Law Complex is a discontinuous fault system with an overall NE-SW trend and there is a suggestion (Johnstone, 1965) that eruptive centres in the complex have a NE-SW alignment. Moore (1979b) has pointed out the possibly coincidental alignment of baryte deposits at Glen Sannox, Muirshiel, Ochil Hills and Arbroath along a NE-SW line parallel to the Highland Boundary Fault and the axis of the Midland Valley. This line assumes more significance as the axis of almost all the Devonian and Carboniferous volcanicity in the northern Midland Valley, i.e. Ballycastle, Macrihanish, north Arran, south Bute, Renfrewshire Hills, Kilpatrick Hills, Campsie Fells, Ochil Hills, Sidlaw Hills (Gallagher and others, 1982, fig. 1; MacGregor, 1948). It also coincides with a major aeromagnetic lineament and would seem to be a fundamental deep structure. The Misty Law Complex and baryte field lies at the intersection of this structure with the NE-SE Tertiary dyke swarm.

The concentration of veins within the Misty Law trachytic complex need not imply a direct genetic connection between the baryte and the trachytes since the veins occupy later faults, although the trachytes do constitute a potential source of barium, capable of being redistributed by later circulating solutions (see later discussion). It is likely that the massive trachytes also provided more open fissures than the surrounding basalt sequence in which relatively thin massive parts of flows are interspersed with a greater proportion of soft, incompetent, altered material. A similar effect is observed at Gasswater and in the River Nethan district where veins are best developed in hard sandstone units or microgranodiorite sills in preference to softer sandstones and shales (Scott, 1967; Gallagher and others, 1982). Lithology and competence differences may locally affect the inclination of fault planes, which has shown to affect vein development at both Muirshiel and Gasswater mines where veins are usually wider in the steeper fractures.

The reasons for the precise location of the Muirshiel deposit and for the somewhat abnormal NNE and E-W trends of the worked veins are not clear. It may be that the veins occupy tensional fractures on the margin of the competent trachytic pile, associated with the major E-W fault. The mine is also very close to the intersection of this fault with the maximum Tertiary dyke development on the NE edge of the swarm.

MacGregor (1944) discussed the possibility that baryte

mineralisation was restricted in depth, relative to the present sea level, and concluded that economic veins were unlikely below 250 m OD. This suggestion was disproved by subsequent developments at Muirshiel and Gasswater mines which reached much lower levels (Hobson, 1959). Baryte is a low temperature mineral and the lack of any associated higher-temperature phases in most of the veins suggests that they did originate at a high structural level and that they possibly pass into veins carrying other phases (e.g. calcite) at depth. However, the concentration of known baryte veins in high moorland areas of central and southern Scotland is probably merely a function of exposure in that the lithologies more favourable to baryte deposition are massive and resistant and therefore tend to form high ground.

Direct field evidence for the age of the veins is imprecise. Baryte-bearing veins in the area cut strata up to and including the Lower Limestone Group, which is also the upper limit elsewhere in central Scotland. They occupy ENE to ESE trending faults which extend eastwards into the sedimentary basins and displace Coal Measure strata. Some veins follow and impregnate the margins of late-Carboniferous quartz-dolerite dykes and others are cut by non-mineralised Tertiary dykes. The possible age range for the mineralisation is thus late Carboniferous to Eocene.

Elsewhere in Scotland a late-Carboniferous age for baryte mineralisation is well established. In the Bathgate Hills a recent borehole has proved baryte mineralisation occurring between two successive pulses of an E-W quartz-dolerite dyke (Stephenson, 1983). K-Ar isotopic ages have been obtained from vein gouge clays associated with baryte mineralisation in the Ochil Hills (264 to 299 Ma; Ineson and Mitchell, 1974) and at Gasswater (270 to 287 Ma; Moore, 1979b). It therefore seems likely that some of the Renfrewshire Hills veins are of similar Permo-Carboniferous age. Such veins commonly occupy ENE to ESE trending faults in the basalts overlying the Misty Law Complex. They have a subtly different character to veins within the complex, often with associated copper mineralisation, and several are intimately associated with quartz-dolerite dykes.

The strong association of baryte mineralisation with the Tertiary dyke swarm has led MacGregor (1944) and others to conclude that some of the veins must be of early Tertiary age. If this is so then the veins and dykes must have occupied the same fissure system in rapid succession since in all known associations the dykes post-date the veins.

The Tertiary Period is not renowned for its mineral deposits in the British Isles and so far no Tertiary isotopic ages have been obtained on vein constituents. It would seem more reasonable to propose that the veins predate the dykes by some considerable period, although to do so would necessarily imply that the NW-SE fractures were an old-established system which was later followed by Tertiary magmas. Evidence for the existence of NW-SE structural control in the area dating back to the Lower Carboniferous has been summarised by Hall (1974) who proposed that the Clyde Plateau Volcanics between Greenock and Strathaven have their thickest development along a NW-SE axis, despite the fact that NE-SW faults were also demonstrably active at this time. Further evidence is provided by NW-SE synclinal troughs with fault-controlled Permo-Triassic sedimentation and Hall (op. cit.) considers that Carboniferous and Tertiary igneous centres in the west of Scotland are controlled by the same NW-SE deep fracture system.

More direct evidence comes from recent K–Ar isotopic ages from vein gouge clays (Moore, 1979b) which give Triassic ages for both the Muirshiel (213 to 240 ± 3 Ma) and Glen Sannox (201 to 224 ± 4 Ma) veins (Gasswater yielded an older, Permo–Carboniferous age of 270 to 287 Ma in the same study). The Muirshiel and Sannox ages are comparable with ages of 218 to 242 Ma obtained by the same method for baryte-bearing veins at Strontian in the western Scottish Highlands (Ineson and Mitchell, 1974). A palaeomagnetic pole for a baryte-hematite vein in the River Nethan district suggests a Lower to Middle Jurassic age (Evans and El-Nikhely, 1982). Conditions for the production of baryte veins clearly existed over a long period of time.

Hydrothermal mineralisation of Triassic to mid-Jurassic age has been identified in the Lake District, the north Pennines and the south Pennines where baryte is a common constituent. These deposits have been correlated with others around the North Atlantic margins to form a single early Mesozoic province of hydrothermal ore deposition related to the early opening of the North Atlantic (Mitchell and Halliday, 1976). With this model, the NW–SE deep fractures suggested by the pattern of mineralisation and later dyke intrusion could have formed as early as the late–Carboniferous, parallel to the initial opening along the Labrador–Biscay rift. The fractures controlled the mineralisation in the Mesozoic and also the Eocene dykes, even though the main opening by this time was NE–SW along the Norwegian Sea rift.

The scope of the present work does not enable many definite conclusions to be reached concerning the genesis of the mineralisation. In view of the age relationships it is unlikely that the baryte mineralisation occurred as a hydrothermal event, directly connected with the trachytic magmatism. Possible contemporaneous baryte is restricted to small pods in the basaltic sequences and none of the analysed volcanic rocks have more than average barium contents for their respective compositions. One analysed trachyte has an anomalously low barium content, indicating that it is possible for barium to be leached out of the country rock, possibly associated with the local redistribution of potash which is an observed effect, particularly in close proximity to the line of the Tertiary dyke swarm. Convection cells of meteoric water, with the upward-moving 'hydrothermal' fluid being concentrated along the line occupied by the later dyke swarm, offer a possible mechanism, although geochemical traverses across major veins failed to detect wallrock leaching at present exposure levels (Moore, 1979b). Many of the veins, including the Muirshiel deposit, are relatively close to the base of the trachytic pile, so that derivation of barium from trachytic rocks at depth is less likely, unless the latter also occur in deeper, unexposed, subvolcanic intrusions. Alternatively, the barium may have a more distant source related to a regional hydrothermal system.

Most of the major baryte veins in central and southern Scotland share striking similarities and are characterised by: high baryte content; minor but ubiquitous amounts of hematite; very rare chalcopyrite but no other sulphides; common late-stage quartz; and in some cases late calcite (Moore, 1979b). No significant differences in trace element concentrations have been observed between such veins (Scott, 1967; Moore, 1979b), although K–Ar isotopic ages cover a wide range (Moore, 1979b).

It therefore seems likely that hydrothermal solutions capable of carrying barium were widespread in central Scotland from the late–Carboniferous through the Mesozoic and possibly into the early Tertiary.

In addition to the veins, baryte of diagenetic origin is known to occur in Lower Old Red Sandstone sandstones near Arbroath and at Auchenstilloch; in Upper Old Red Sandstone concretionary sandstones of south Ayrshire; and in the Dockra Limestone of north Ayrshire. Analyses of Old Red Sandstone and Lower Carboniferous age limestones in the area commonly contain over 0.3% Ba (Muir and others, 1956). Gallagher and others (1982) postulate that the Devonian and succeeding reworked Carboniferous clastic sediments constitute a potential source of barium for the later hydrothermal vein occurrences.

The source of the sulphur is unclear. Low values of δS^{34} of +7.3 to +9.7 ‰ sulphate sulphur in central Scotland baryte veins (R. A. D. Patrick, written communication) are similar to those found in intraformational waters, suggesting that Ba-bearing brines mix with sulphate-bearing waters at a high level, causing baryte to precipitate, and this is thought to be the most likely explanation. However, Moore (1979b) proposes an alternative model in which barium and sulphur are carried as complex ions in the same solution and combine to precipitate baryte in the oxidised groundwater zone. Both models imply that the veins were formed at relatively high, oxidised levels by mixing of brines with groundwaters bearing iron from the country rocks (c.f. the presence of hematite in veins). Carboniferous sediments in Ayrshire are reddened by oxidising groundwaters to depths of up to 600 m below the basal Permian unconformity, and fibrous gypsum ($CaSO_4$) is recorded between 100 m and 300 m below the unconformity (Mykura, 1960). Baryte precipitation may have occurred beneath the same land surface or under similar conditions at a later date. Temperatures of formation were therefore low, less than 50°C according to fluid inclusions at Muirshiel (Moore, 1979b), which probably accounts for the lack of metallic impurities in the veins other than iron.

Moore (1979b) explains the emplacement of the veins in terms of 'seismic pumping' of fluids during periods of earthquake activity. This he claims is best able to account for the brecciated textures found in some veins and also keeps the fractures open throughout multiple injections to produce the banded veins. However, the close association in both space and time between veins and various phases of igneous intrusion suggests that they were formed in tensional regimes wherever and whenever geothermal gradients were high, facilitating groundwater circulation (Gallagher and others, 1982). High temperatures of formation (440° to 480°C) obtained from fluid inclusions in late calcite from the Muirshiel vein may be attributable to increased temperatures near to Tertiary dykes (Moore, 1979a).

COPPER

The most significant feature of copper mineralisation in the Renfrewshire Hills is its diversity. Disseminated malachite in sandstones below the volcanic sequence is possibly syngenetic or late diagenetic, whereas epigenetic cupriferous baryte veins cut basic volcanics in the middle of the volcanic sequence and rhyolites at the top, extending up into overlying limestone. Cupriferous veins are not found in the Misty Law Complex, where the numerous baryte veins are characteristically free from impurities with only rare traces of chalcopyrite. Some veins occur on the margins of quartz-dolerite dykes but others have no association with intrusions.

Most of the recorded mineralisation is secondary malachite but primary chalcocite and possibly

chalcopyrite were extracted from mine workings at Kaim and Swinlees, and bornite is recorded from Drumshantie. It would seem that the occurrences are essentially high level manifestations of the mineralisation, but, unfortunately, it is not known what happened to the mined veins in depth.

The mineralisation is widespread laterally. In addition to the worked occurrences already described, there are several other known localities within and around the area of study. Near the Cloch Lighthouse 4 km SW of Gourrock, a fossiliferous shale within the Ballagan Cementstone Formation contains carbonised wood fragments impregnated with pyrite and malachite (Scott, 1885). North of the River Clyde disseminated copper and copper staining occurs at several localities in Calciferous Sandstone Measures below the lavas (I. H. S. Hall, oral communication). Within the basic volcanics native copper is recorded from Erskine, from Neilston and with malachite and cuprite from Boyleston Quarry, Barrhead to the east of the study area (Heddle, 1901; Allan, 1973). Veins of chalcocite with malachite have recently been discovered in volcanics at Loanhead Quarry, Beith (R. J. Gillanders, oral communication).

There are indications that the mineralisation occurred throughout the Carboniferous period. The preferential impregnation of plant fragments in the lower Calciferous Sandstone Measures suggests that mineralisation was active at, or soon after, the time of deposition. At Boyleston Quarry and Loanhead Quarry, copper minerals are closely associated with calcite and prehnite of late-magmatic hydrothermal origin and therefore must be near-contemporaneous with the lava sequence. Veins cut strata up to the base of the Lower Limestone Group and impregnate late-Carboniferous quartz-dolerites. Elsewhere in central Scotland cupriferous baryte veins are commonly associated with late-Carboniferous intrusions (Hall and Gallagher, 1982) and have been shown to be contemporaneous (Stephenson, 1983). K-Ar isotopic ages of 264 to 299 Ma have been obtained from such veins in the Ochil Hills (Ineson and Mitchell, 1974). It is therefore concluded that minor disseminated copper mineralisation took place in the Renfrewshire Hills from the start of the Carboniferous until at least the end of the Clyde Plateau Volcanic Formation. Veins could be penecontemporaneous with the volcanic activity, but some, and possibly all, are the products of later hydrothermal activity.

Copper values in analysed volcanics (Table 6) and in similar analyses from fresh volcanics of the Beith-Barrhead block (c.f. Boyleston and Loanhead) are not anomalously high. However, values in the basalts are high enough to constitute a source for the cupriferous mineralisation, given a sufficiently efficient leaching mechanism. Some mineralisation was derived directly from the volcanics in a late-magmatic hydrothermal stage (Boyleston and Loanhead). Cupriferous veins (Swinlees, Kaim) could have been deposited by any later hydrothermal fluids which had the potential to leach copper from the volcanics. The most likely hydrothermal system is that associated with the late-Carboniferous dyke swarm (c.f. Kaim), which could also have acted as a source of copper, but later events such as that responsible for the main baryte mineralisation may also have resulted in some leaching and redistribution of copper. Disseminated, possibly syn-sedimentary, copper in sediments below the lavas (Drumshantie, Larkfield) is difficult to account for by this model. The lack of associated lead, zinc and other metal occurrences in this area is significant. It may in-

dicating the compositionally restricted source of the basalt lava pile and the tightly bonded nature of the zinc in the magnetites of the basalts, in contrast to other areas of mineralisation in central and southern Scotland where a wide range of potential source rocks provide scope for polymetallic deposits (e.g. Ochil Hills, Hall and Gallagher, 1982; Bathgate Hills, Stephenson, 1983; Wanlockhead-Leadhills, Dunham and others, 1978).

CONCLUSIONS AND RECOMMENDATIONS

- 1 The strongest control on barium distribution seems to be the distribution of trachytic rocks and the line of the Tertiary dykes. Baryte along the late-Carboniferous Kaim dyke is of limited local extent.
- 2 Some of the thicker, newly-discovered veins of pure baryte such as Millside Burn, Surge Burn and Rough Burn (Garnock) (p. 13, Figure 6) may be economic to work on a small scale, provided that access difficulties can be overcome and that the market value of untreated baryte remains high.
- 3 Previous exploration of the Muirshiel mine and Berryglen areas has been extensive. To the best of our knowledge, however, exploration ceased where the main veins pinched out and became uneconomic, and did not continue far beyond the known surface outcrops or underground workings. The veins may 'swell' to economic widths beyond the limits of exploration in the same structures. Further southward extension of the main Muirshiel vein may be traceable by overburden sampling or shallow drilling. The E-W Muirshiel vein follows a persistent major fault which may be worthy of exploration, although deep drift deposits may present a problem in places at the base of the fault scarp. One possible site is where the fault is intersected by the main component of the Tertiary dyke swarm, 0.5 km to 1 km west of the present workings.
- 4 The area between High Corby Knowe and West Girt Hill contains abundant float of banded baryte, has a relatively thin peat cover and would be amenable to overburden sampling. It is, however, the most remote part of the Hills (p. 13).
- 5 Drainage geochemistry indicates that unexposed baryte veins may exist in the Queenside Loch and Black Grain Burn areas (pp. 16-17).
- 6 Panned concentrate sampling is the most sensitive method detecting further outcropping or suboutcropping baryte veins near streams but is sensitive to mining contamination. It is probably the best technique for locating unworked veins by detailed follow-up drainage sampling, in conjunction with a portable X-ray fluorescence analyser for rapid analysis of barium (Grout and Gallagher, 1980).
- 7 Stream sediments may be slightly more effective than panned concentrates in detecting suboutcropping baryte mineralisation, but it is not known how efficient this method may be in locating individual veins during follow-up work.
- 8 Detailed overburden sampling could be employed in selected upland target areas where peat and lodgement till cover is not too thick. An auger or portable drill could be used in conjunction with portable X-ray fluorescence equipment to analyse the heavy mineral fraction of basal till.
- 9 Zirconium and niobium in stream sediments can be used to define the trachyte distribution and the extent of

glacial dispersion.

10 Drainage geochemistry is able to detect the known copper mineralisation within the limited area investigated, where it is restricted to Kaim and the south-east of the area where Tertiary dykes cross the basalts. Minor copper may occur in baryte veins at Berryglen and Queenside Loch. It is likely that further occurrences exist in poorly-exposed parts of the Hills. Any anomalous copper concentrations which may be detected in the regional geochemical survey should therefore be investigated.

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