

Natural Environment Research Council

Institute of Geological Sciences

Mineral Reconnaissance Programme Report

This report relates to work carried out by the Institute of Geological Sciences on behalf of the Department of Industry. The information contained herein must not be published without reference to the Director, Institute of Geological Sciences

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

No. 39

**Copper-bearing intrusive rocks at
Cairngarroch Bay, south-west
Scotland**

Mineral Reconnaissance Programme

Report No. 39

**Copper-bearing intrusive rocks at
Cairngarroch Bay, south-west
Scotland**

Geology

P. M. Allen, BSc, PhD

Geochemistry

P. J. Bide, BSc

D. C. Cooper, BSc, PhD

Geophysics

M.E. Parker, BA

Mineralogy

H. W. Haslam, MA, PhD

Mineral Reconnaissance Programme Reports

- 1 The concealed granite roof in south-west Cornwall
- 2 Geochemical and geophysical investigations around Garras Mine, near Truro, Cornwall
- 3 Molybdenite mineralisation in Precambrian rocks near Lairg, Scotland
- 4 Investigation of copper mineralisation at Vidlin, Shetland
- 5 Preliminary mineral reconnaissance of Central Wales
- 6 Report on geophysical surveys at Struy, Inverness-shire
- 7 Investigation of tungsten and other mineralisation associated with the Skiddaw Granite near Carrock Mine, Cumbria
- 8 Investigation of stratiform sulphide mineralisation in parts of central Perthshire
- 9 Investigation of disseminated copper mineralisation near Kilmelford, Argyllshire, Scotland
- 10 Geophysical surveys around Talnotry mine, Kirkcudbrightshire, Scotland
- 11 A study of the space form of the Cornubian granite batholith and its application to detailed gravity surveys in Cornwall
- 12 Mineral investigations in the Teign Valley, Devon. Part 1—Barytes
- 13 Investigation of stratiform sulphide mineralisation at McPhun's Cairn, Argyllshire
- 14 Mineral investigations at Woodhall and Longlands in north Cumbria
- 15 Investigation of stratiform sulphide mineralisation at Meall Mor, South Knapdale, Argyll
- 16 Report on geophysical and geological surveys at Blackmount, Argyllshire
- 17 Lead, zinc and copper mineralisation in basal Carboniferous rocks at Westwater, south Scotland
- 18 A mineral reconnaissance survey of the Doon-Glenkens area, south-west Scotland
- 19 A reconnaissance geochemical drainage survey of the Criffel-Dalbeattie granodiorite complex and its environs
- 20 Geophysical field techniques for mineral exploration
- 21 A geochemical drainage survey of the Fleet granitic complex and its environs
- 22 Geochemical and geophysical investigations north-west of Llanrwst, North Wales
- 23 Disseminated sulphide mineralisation at Garbh Achadh, Argyllshire, Scotland
- 24 Geophysical investigations along parts of the Dent and Augill Faults
- 25 Mineral investigations near Bodmin, Cornwall. Part 1—Airborne and ground geophysical surveys
- 26 Stratabound barium-zinc mineralisation in Dalradian schist near Aberfeldy, Scotland: Preliminary report
- 27 Airborne geophysical survey of part of Anglesey, North Wales
- 28 A mineral reconnaissance survey of the Abington-Biggarr-Moffat area, south-central Scotland
- 29 Mineral exploration in the Harlech Dome, North Wales
- 30 Porphyry style copper mineralisation at Black Stockarton Moor, south-west Scotland
- 31 Geophysical investigations in the Closehouse-Lunedale area
- 32 Investigations at Polyphant, near Launceston, Cornwall
- 33 Mineral investigations at Carrock Fell, Cumbria. Part 1—Geophysical survey
- 34 Results of a gravity survey of the south-west margin of Dartmoor, Devon
- 35 Geophysical investigation of chromite-bearing ultrabasic rocks in the Baltasound-Hagdale area, Unst, Shetland Islands
- 36 An appraisal of the VLF ground resistivity technique as an aid to mineral exploration
- 37 Compilation of stratabound mineralisation in the Scottish Caledonides
- 38 Geophysical evidence for a concealed eastern extension of the Tanygrisiau microgranite and its possible relationship to mineralisation
- 39 Copper-bearing intrusive rocks at Cairngarroch Bay, south-west Scotland

The Institute of Geological Sciences was formed by the incorporation of the Geological Survey of Great Britain and the Geological Museum with Overseas Geological Surveys and is a constituent body of the Natural Environment Research Council

Bibliographical reference

Allen, P. M. and others. 1981. Copper-bearing intrusive rocks at Cairngarroch Bay, south-west Scotland *Mineral Reconnaissance Programme Rep. Inst. Geol. Sci.*, No. 39

Photocopied in England for the Institute of Geological Sciences

CONTENTS

Summary	1
Introduction	1
Geology	1
Sedimentary rocks	1
Igneous rocks	3
Bay Complex	3
Glen Complex	3
Minor intrusions	4
Veining	4
Geophysics	4
Discussion of results	4
Geochemistry	8
Sample collection, preparation and analysis	8
Results	8
Water samples	8
Soil samples	8
Talus samples	12
Rock samples	12
Interpretation	14
Water	14
Soils	14
Talus	14
Rocks	14
Alteration and metasomatism	14
Petrogenesis	16
Conclusions	16
Acknowledgements	19
References	19

FIGURES

1	Geology and some geophysical data for the area adjacent to Cairngarroch Bay	2
2	Geophysical results for traverse line 150W	5
3	Geophysical results for traverse line 00	6
4	Geophysical results for traverse line 400E	7
5	Geochemical sample sites and results for copper	9
6	Geochemical sample sites and results for lead	10
7	Geochemical sample sites and results for zinc	11
8	Plot of TiO_2 versus Zr	15
9	Plot of K versus Rb	15
10	Triangular plot of Rb—Ba—Sr	17
11	Summary of geological, geochemical and geophysical data for Cairngarroch Bay area	18

TABLES

1	Summary of analytical results for soils	8
2	Rock analyses	13
3	Comparison of some geochemical ratios from Cairngarroch with other Southern Uplands intrusions	16

SUMMARY

Two intrusion complexes, the Bay and the Glen, probably representing an early phase of the Devonian magmatic episode, and a number of dykes, are emplaced within a folded succession of Silurian sedimentary rocks at Cairngarroch Bay. Only the roof of the Bay Complex, which consists of microtonalite and granodiorite, is exposed. The Glen Complex, of uncertain form, comprises quartz porphyry, porphyritic quartz-microdiorite and quartz-microdiorite. Exposure is good along the shore line, but much of the area is covered in thick, drumlinised drift.

Local high chargeability zones were identified along three geophysical traverse lines. Soil samples were collected on a 50 m grid over the area of IP anomalies. In addition, water, base of slope talus, and rock samples were chemically analysed.

Both the intrusion complexes and some of the sedimentary rocks show locally intense hydrothermal alteration. In the Bay Complex narrow zones of bleached rock are rich in calcite, chlorite and pyrite and contain minor chalcopryrite and pyrrhotite. The Glen Complex displays network fracturing, brecciation and locally intense alteration to sericite or calcite. There is locally abundant pyrite in veins and disseminated and rare chalcopryrite. Arsenopyrite is present in wall rock adjacent to the Bay Complex.

Rock geochemistry indicates a pervasive but patchy Cu-Fe-As-Mo mineralisation in all rock types, with copper enrichment greatest in the Bay Complex where the highest level recorded is over 600 ppm Cu. The mineralisation is accompanied by irregular barium, potassium and strontium enrichment. The K/Rb ratios suggest that the hydrothermal liquors were not entirely late magmatic. The mineralisation and alteration have some characteristics of a porphyry system and it is conceivable that copper enrichment might increase with depth.

INTRODUCTION

In this area, which is on the North Channel coast of the Rhins of Galloway, south-west Scotland (Figure 1) intrusions of porphyrite and granite of ?Lower Old Red Sandstone age (Scottish 1-inch sheet No. 3, Stranraer) are emplaced within sedimentary rocks of Silurian age. There is no record of mining in this area. Geikie (1873) commented

that all the intrusions in this area were pyritic, which prompted a reconnaissance visit to Cairngarroch Bay where secondary copper minerals, chalcopryrite and locally intense pyritisation were observed in and around the intrusive rocks. Subsequently, geochemical and geophysical surveys were carried out to determine the type and extent of the mineralisation.

The area investigated covers about 1.5 km² mostly of gently undulating farmland on top of 80 m high sea cliffs and cut by a deep glen. The highest point in the area is 133 m above OD.

GEOLOGY

Solid geology is well exposed along the shore line and moderately so in the fields around West Cairngarroch farm. Elsewhere the ground is covered by a locally thick deposit of drumlinised red-brown sandy boulder clay. In places near the cliff edge the soliflucted boulder clay (head) is overlain by up to 1 metre of fine sand. A thin layer of windblown sand, presumably derived from this deposit, is extensively distributed. Scree occurs on the slopes of the glen in the south of the area, whereas the upper part of the sea cliffs is covered with head. There are some small land-slips.

SEDIMENTARY ROCKS

Much of the exposed part of the area is underlain by sedimentary rocks attributable to the Gala Group of Silurian age. They consist of grey, turbiditic greywackes in beds rarely more than 60 cm thick, with interbedded light grey or purplish-blue banded siltstone. Thick units of grey mudstone occur in the southern part of the area. A schistosity is visible locally in the mudstone. The greywacke consists of coarse grains of quartz, feldspar and lithic fragments in a matrix of sericite and clay minerals. Brown biotite is prominent in rocks adjacent to the intrusions. Finely disseminated pyrite, locally associated with chalcopryrite and arsenopyrite, is present abundantly in some of the arenaceous rocks.

The sedimentary rocks strike between NE and ENE and dip steeply northwards and southwards, displaying local overturning. Minor folds were observed with near vertical axes. Minor faults commonly trend NE whereas a major fault along the glen trends about 085°.

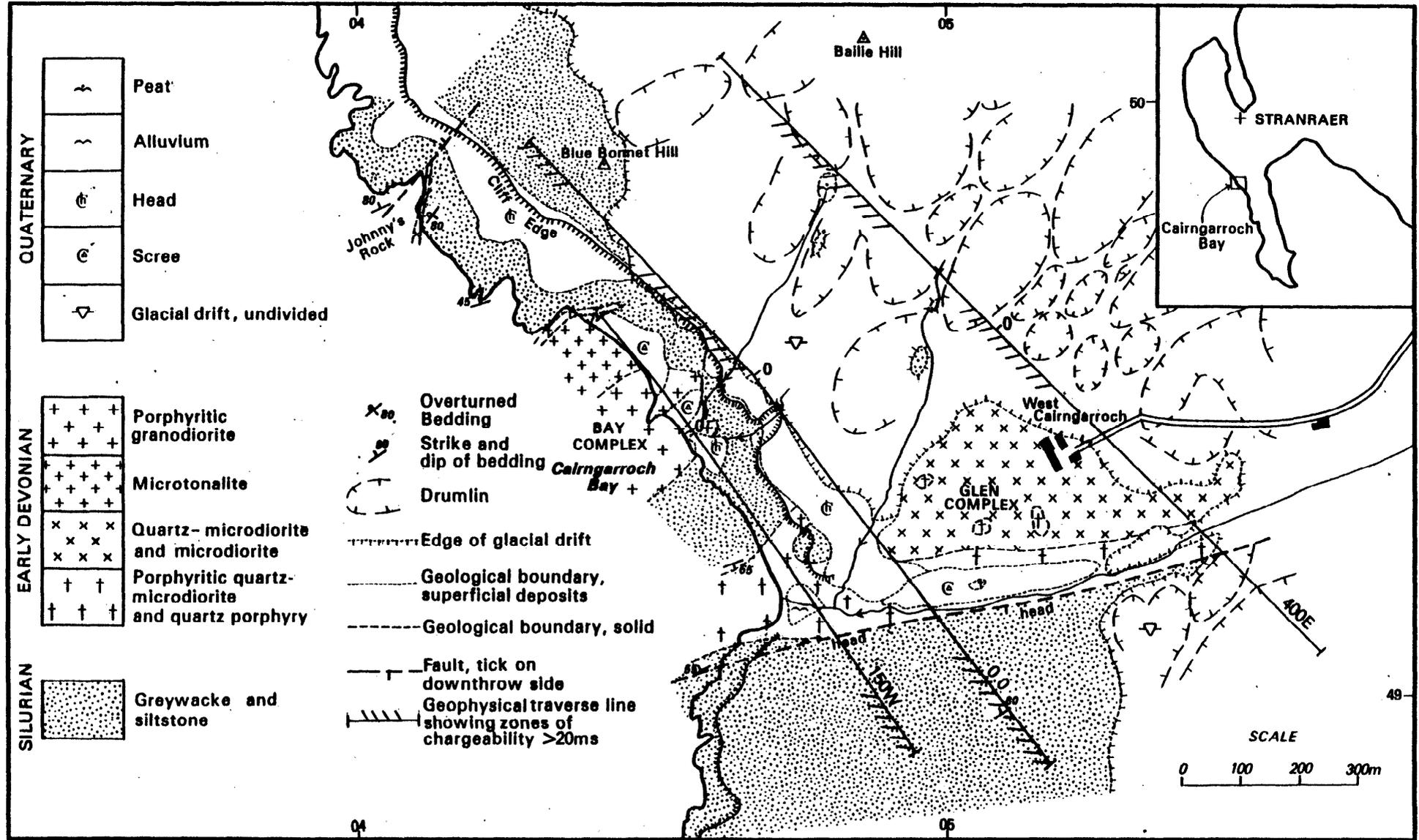


FIG.1. Geology and some geophysical data for the area adjacent to Cairngaroch Bay

IGNEOUS ROCKS

There are two intrusion complexes, named here the Bay and the Glen, and a number of minor intrusions in the area. Compositionally they range from granodioritic to dioritic.

Bay Complex

This complex is exposed (Figure 1) along about 300 m of the sea shore around [NX 045 495]. The cliffs above the outcrop consist of sedimentary rocks, which suggests that the outcrop is part of the roof of an intrusion. The two main components of this complex are dark grey biotite-hornblende-microtonalite and pink, or less commonly grey, porphyritic biotite-hornblende-granodiorite. Microtonalite is the older of the two and comprises the north-western half of the area of outcrop. The south-eastern half consists of porphyritic granodiorite which shows a sharp intrusive contact against the microtonalite and there are numerous veins of it, and dykes up to 3 m thick, cutting the older rock. Thin veins of aplite and pegmatite cut both major rock types and there is one dyke, 2 m thick, of dark grey sparsely porphyritic biotite-microtonalite within the porphyritic granodiorite.

The microtonalite is dark grey and uniformly fine grained. It contains sparse basic xenoliths. The main constituent minerals (S 67007, S 68049) are zoned, randomly orientated oligoclase-andesine, up to 0.6 mm long, clear interstitial quartz, fresh or partly chloritised brown biotite and, roughly in the same proportion as biotite, calcite/chlorite pseudomorphs after green amphibole. The feldspar is usually mildly altered to calcite and sericite. There are accessory magnetite, hematite and apatite. Sulphides include pyrite and rare chalcopyrite and pyrrhotite commonly as blebs in it. Quartz veinlets are locally common, whereas calcite veinlets are ubiquitous. It is usual for chloritisation of biotite to be increased adjacent to calcite veinlets. Throughout the outcrop there are linear zones, from a few cm to 3 m wide, of bleached rock (S 68050) within which the feldspar and amphibole are completely replaced by calcite and the biotite is altered to colourless chlorite and opaque minerals. Accessory minerals include hematite, magnetite and apatite. Disseminated pyrite, traces of chalcopyrite and pyrrhotite are more abundant in the alteration zones than in the unaltered rock. Spots of malachite have been noted.

The porphyritic granodiorite, though apparently uniform in hand specimen, shows some textural diversity and it is likely that there are at least two phases of intrusion, both later than the microtonalite. The southern contact with the country rock is well exposed [NX 0454 4937]. There is intense minor quartz veining of both the country rock, which is baked, and the intrusive. Finely disseminated arsenopyrite is locally abundant along the contact.

The predominant rock type (DAR 240, LA 611, S 68055) consists of closely spaced subhedral and euhedral crystals, up to 3 mm long, of andesine showing both normal and oscillatory zoning and with small exsolved blebs of potash feldspar. The plagioclase is set in a groundmass of median grain size about 0.1 mm composed of a mosaic of quartz, potash feldspar and plagioclase. Brown biotite, in places partly chloritised, slightly exceeds green hornblende in proportion. The latter is commonly represented by pseudomorphs of calcite and chlorite. Pyrite with small inclusions of chalcopyrite, pyrrhotite, and some discrete grains of chalcopyrite, apatite, zircon and sphene are all present in the rock. The principal variation in the rock is in the grain size of the groundmass which may be much coarser or finer than 0.1 mm. A particularly fine-grained variety (S 68051), with a median size about 0.03 mm, forms a small intrusion 2–3 m in diameter within microtonalite [NX 0438 4963], but is itself cut by veins up to 5 cm thick of granodiorite showing different textural characteristics. In the vein (S 68049) the marginal parts resemble the type rock but they pass inwards into a non-porphyritic graphic-textured rock. In another variety, which forms dykes (S 68053–4) up to 3 m thick cutting microtonalite and may be grey in colour, the larger plagioclase crystals are set in a matrix of only slightly smaller quartz, plagioclase and potash feldspar crystals, the latter containing inclusions of all other minerals.

As in the microtonalite the amount and distribution of alteration is variable but calcite veinlets are ubiquitous. Intense alteration (S 68048, 68052) is confined to narrow zones even in the dykes (e.g. S 68052) and the style of alteration in them, including the enhanced sulphide content, is identical to that in the zones in the microtonalite.

Glen Complex

This complex is exposed on the seashore at the mouth of the glen and around West Cairngarroch farm. The principal rock types, in their probable order of emplacement, are quartz porphyry, porphyritic quartz-microdiorite and quartz-microdiorite.

Quartz porphyry, which probably represents the earliest intrusive stage in the formation of the complex, occurs as small xenoliths and enclaves up to 8 m wide in porphyritic quartz-microdiorite. The quartz porphyry (LA 750) is crudely banded, locally brecciated and veined and replaced by calcite. Pyrite is disseminated and in late-stage, undeformed veinlets.

The part of the complex exposed along the coast consists primarily of porphyritic quartz-microdiorite. Its contact with the country rock is irregular in detail, but is generally concordant. Xenoliths of siltstone and greywacke occur locally. The disposition of the intrusion with respect to the

country rock suggests either that it has been folded or that it was emplaced into a synform. The rock (S 67002-3, 67010) contains plagioclase phenocrysts up to 2.5 mm long and muscovite/calcite pseudomorphs after ?biotite in an equigranular or recrystallised matrix of feldspar and quartz. The rock is highly altered. A sample (S 67010) from high up the glen [NX 0545 4925] is strongly sericitised. Those from the shore line, however, are intensely replaced by calcite and contain veins of (a) calcite, (b) quartz and calcite with or without pyrite and (c) pyrite which intersect each other in a complex set of inter-relationships. In places the rock is brecciated and there is network fracturing lined with pyrite, which is also abundantly disseminated.

Quartz-microdiorite is exposed mainly in the fields near the farm. Several small areas of porphyritic quartz-microdiorite in these fields, including varieties (DAR 5031) with fresh hornblende and biotite, are presumed to be large enclaves. The rock (DAR 5032-34) is non-porphyritic. It consists of subhedral, partly intergrown, zoned andesine crystals, ranging in size from 0.15-2.5 mm, patchily developed interstitial quartz, brown biotite and pseudomorphs of yellow ?serpentine and calcite after amphibole. There is much local variation in grain size and quartz content. Alteration in feldspar varies from minor replacement by calcite to intense sericitisation. Biotite, though usually fresh, may be totally chloritised in some rocks. One small body of this rock (DAR 5040) within the margin of the complex on the seashore [NX 0466 4911] and another forming a dyke to the south of it (DAR 5039) are intensely altered to calcite. Pyrite and minor chalcopyrite occur disseminated within the wallrock in this area.

Minor intrusions

There are numerous dykes in the area, some several metres thick and showing both discordant and, in areas of steep dip, concordant relationships with the sedimentary rocks. Dykes of porphyritic microtonalite (DAR 235, 236) occur, among other places, near the edge of and within the Glen Complex. The rock is distinctive in that it contains phenocrysts of quartz in addition to feldspar, biotite and chlorite/calcite pseudomorphs after amphibole. The rock also contains pyrite and chalcopyrite.

Porphyritic hornblende-microdiorite dykes (LA 761) post-date quartz veins in the country rock adjacent to the Glen Complex, as do thin veins of quartz porphyry, which also intrude quartz-microdiorite near West Cairngarroch Farm [NX 0513 4940].

A prominent, highly mineralised dyke of microdiorite (LA 764) containing abundant calcite, pyrite and some chalcopyrite occurs on Johnny's Rock [NX 0411 4982].

Veining

Barren quartz veins and veins with pyrite, chalcopyrite and other minor sulphides occur within the sedimentary rocks in many parts of the area, though there is a preferential development adjacent to the intrusive complexes. On Johnny's Rock and elsewhere pods of pyrite occur up to 40 cm long and 10 cm wide in quartz veins which are intersected by NW-trending barren quartz veins.

GEOPHYSICS

Induced polarisation (IP) and resistivity measurements were made on three traverses as shown on Figure 1. The expanding dipole-dipole array was used with a dipole length of 60 m. Total magnetic field measurements were also made.

The positions and lengths of the lines were constrained by the cliffs, and by crops in the fields.

DISCUSSION OF RESULTS

The chargeability and resistivity pseudosections for the traverses are presented on Figures 2-4 and summarised in Figure 11.

Line 150W shows mostly low resistivities, particularly at the greater dipole separations, due partly to the nearness of the sea. At either end, where the traverse climbs above the beach, values are rather higher. There is a strong narrow low arising from about 300S, where the line crosses the stream from the glen, due perhaps to brackish water-saturated alluvium, or to the fault along the valley. Chargeabilities are also generally low on the beach and higher on the slopes, with the highest values present over the Bay Complex, and the pyritic sedimentary rocks in the south. A strong, narrow IP low lies at about 150S. The magnetic profile is somewhat noisier over intrusive rocks, which contain both magnetite and pyrrhotite, than over sedimentary rocks.

Line 00, at the top of the cliff, has roughly the same pattern as 150W. The fault along the glen gives a resistivity low, and the sedimentary rocks on the south of it have high resistivity and moderately high chargeability. Most of the line gives low to moderate resistivity and chargeability. North-westwards from the baseline rather higher chargeabilities occur, separated by a narrow low from a strong IP high at 420N northwards. This lies on the cliff top above the pyritous rocks at Johnny's Rock. Between 00 and 200S a noisy magnetic zone occurs, which by analogy with line 150W could be ascribed to intrusive rocks. However, in this area sedimentary rocks are thought to underlie the thick drift.

The third line, 400E, crosses thick drumlinised drift. Resistivity is moderate, with a significant low occurring over the fault along the glen, and a near-surface low lying at the northern end of the line. Two zones of high chargeability occur, at 60-

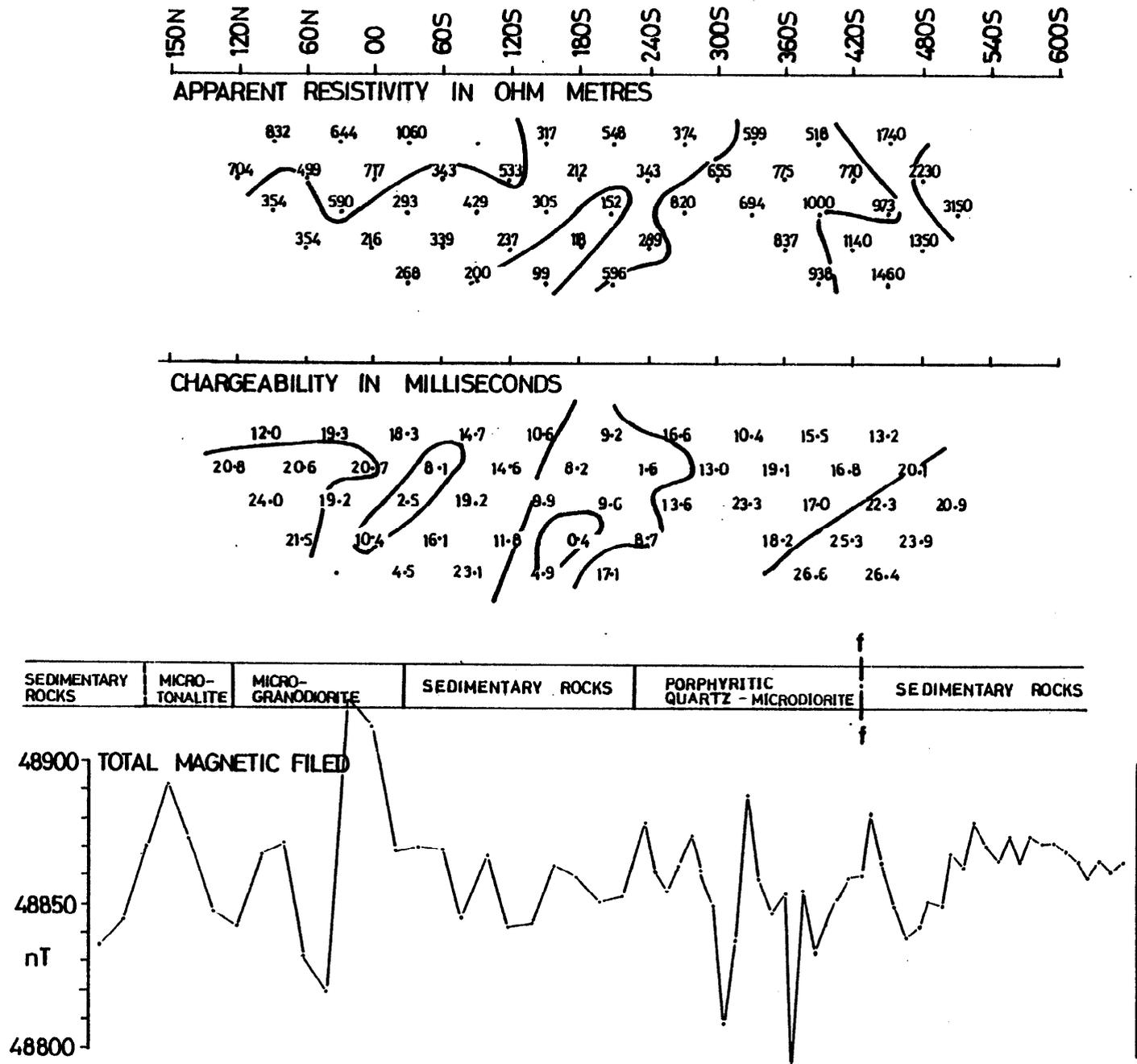


Fig.2. Geophysical results for traverse line 150 W

5

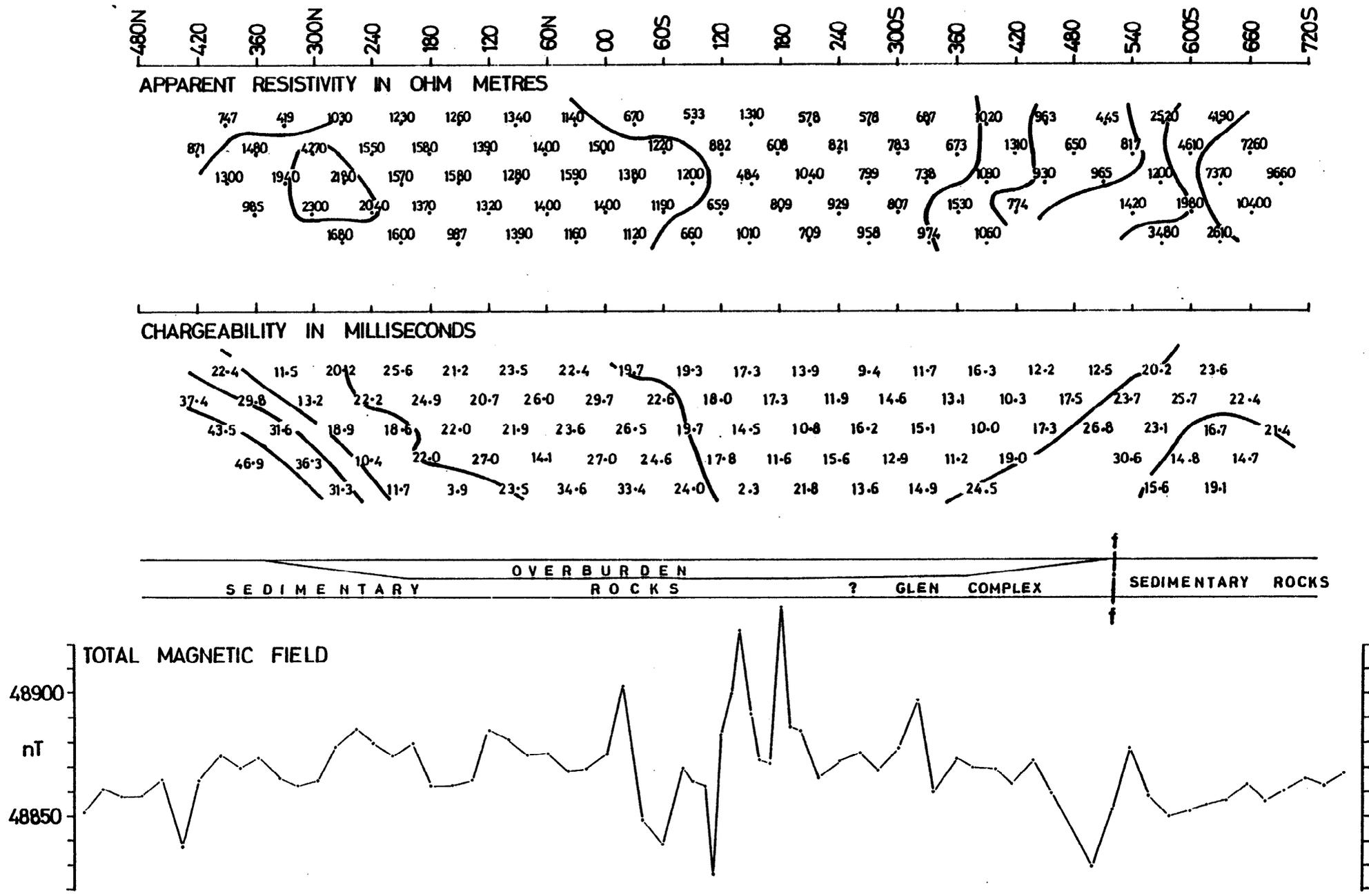
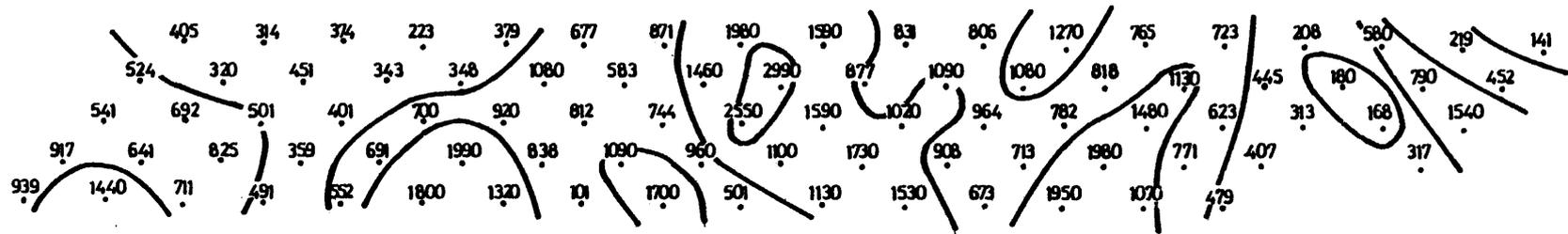


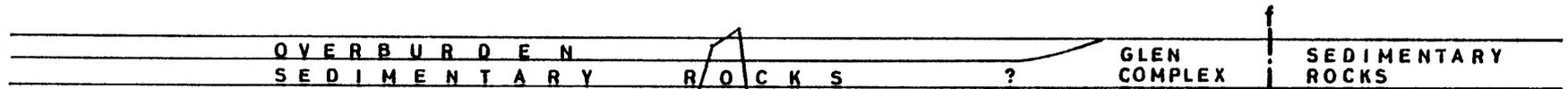
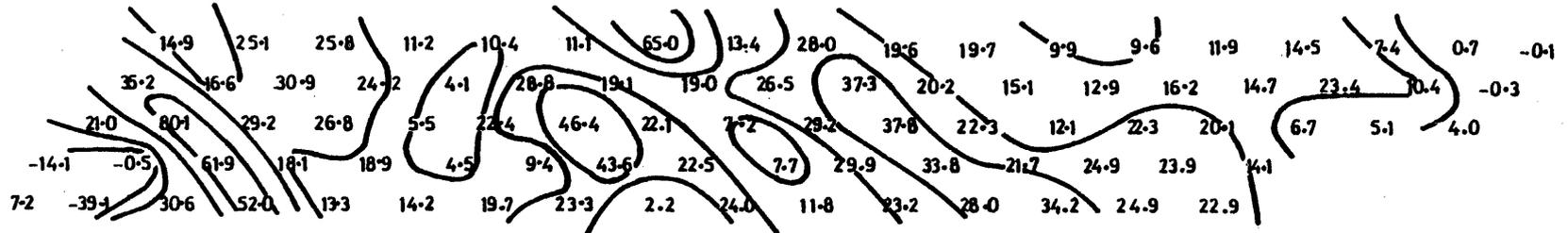
Fig.3. Geophysical results for traverse line 00

480N 420N 360 300N 240 180 120 60N 00 60S 120 180 240 300S 360 420 480 540 600S 660 720S

APPARENT RESISTIVITY IN OHM METRES



CHARGEABILITY IN MILLISECONDS



TOTAL MAGNETIC FIELD

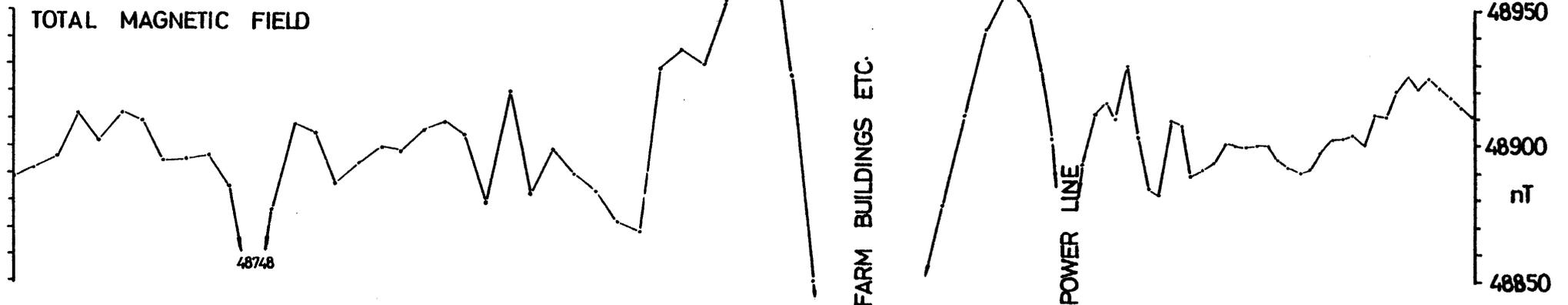


Fig.4. Geophysical results for traverse line 400E

180S and 450N. At the ends of the line, negative IP effects were recorded. Where these have been recorded elsewhere in south Scotland they have been ascribed to sharp conductivity contrasts in the overburden, and the resistivity results on this line indicate that this is probably the cause here too. There is no evidence of artificial conductors in the area of the negative values. The magnetic profile of 1400E is more or less flat, except for two very large peaks due to powerlines.

The positions of the main IP anomalies are marked on Figure 1. It is possible to interpret them either as forming a partial 'halo' or as a series of linear anomalies following the strike of the sedimentary rocks.

GEOCHEMISTRY

SAMPLE COLLECTION, PREPARATION AND ANALYSIS

Five water samples were collected in 30 ml plastic bottles from streams and a spring (Figures 5–7), acidified with 0.3 ml perchloric acid in the field and subsequently analysed for copper and zinc by AAS (atomic absorption spectrophotometry) without further sample preparation. Detection limits are 0.01 ppm for Cu and Zn.

Three hundred and forty six soil samples were collected at the intersections of a 50 m square grid within the zone of IP chargeability anomalies and at the intersections of a 100 × 50 m grid around the periphery. Samples of about 200 g were taken from as deeply as possible using a 1.2 m long hand auger from two or more holes at each site. They consist of boulder clay, alluvial deposits and weathered bedrock which could be described as B, C and E horizon material (Hodgson, 1976). Samples were dried, sieved and the -85 mesh BSS (0.18 mm) fraction was analysed for copper, lead and zinc by AAS following dissolution in hot, concentrated nitric acid for one hour. Detection limits for soil samples were Cu 3 ppm, Pb and Zn 5 ppm.

Twenty four base-of-slope talus fines samples (Hoffman, 1977) were collected using hand augers at the foot of sea cliffs and along the north side of the glen (Figures 5–7). These were processed and

analysed as soil samples.

Twenty seven samples of igneous and sedimentary rock and mineral veins were collected (Figures 5–7). A minimum of 2 kg was crushed. One split was ground in a Tema Mill with 'elvacite' for 5 minutes before pelletising and analysing for a range of trace elements by XRF (X-ray fluorescence); another was ground and analysed for major elements by Betaprobe. XRF detection limits were 1 ppm for Y, Rb and Sr; 2 ppm for Zr, As, Th and Mo; 3 ppm for Zn; 5 ppm for Ni; 6 ppm for Cu and Mn; 13 ppm for Pb and 21 ppm for Ba and Ce.

RESULTS

Water samples

Levels of copper were at or below the detection limit for all samples except for 0.03 ppm in a spring water sample (Figure 5). Without further results from springs in this area it is impossible to judge whether this result is anomalous. Compared with stream water results from north Wales (Allen and others, 1979) it would be considered mildly anomalous. Three stream samples contained appreciable amounts of zinc (Figure 7), which, when compared with results from elsewhere (e.g. Allen and others, 1979), could be termed anomalous.

Soil samples

Summary data for analytical results on soil samples are given in Table 1.

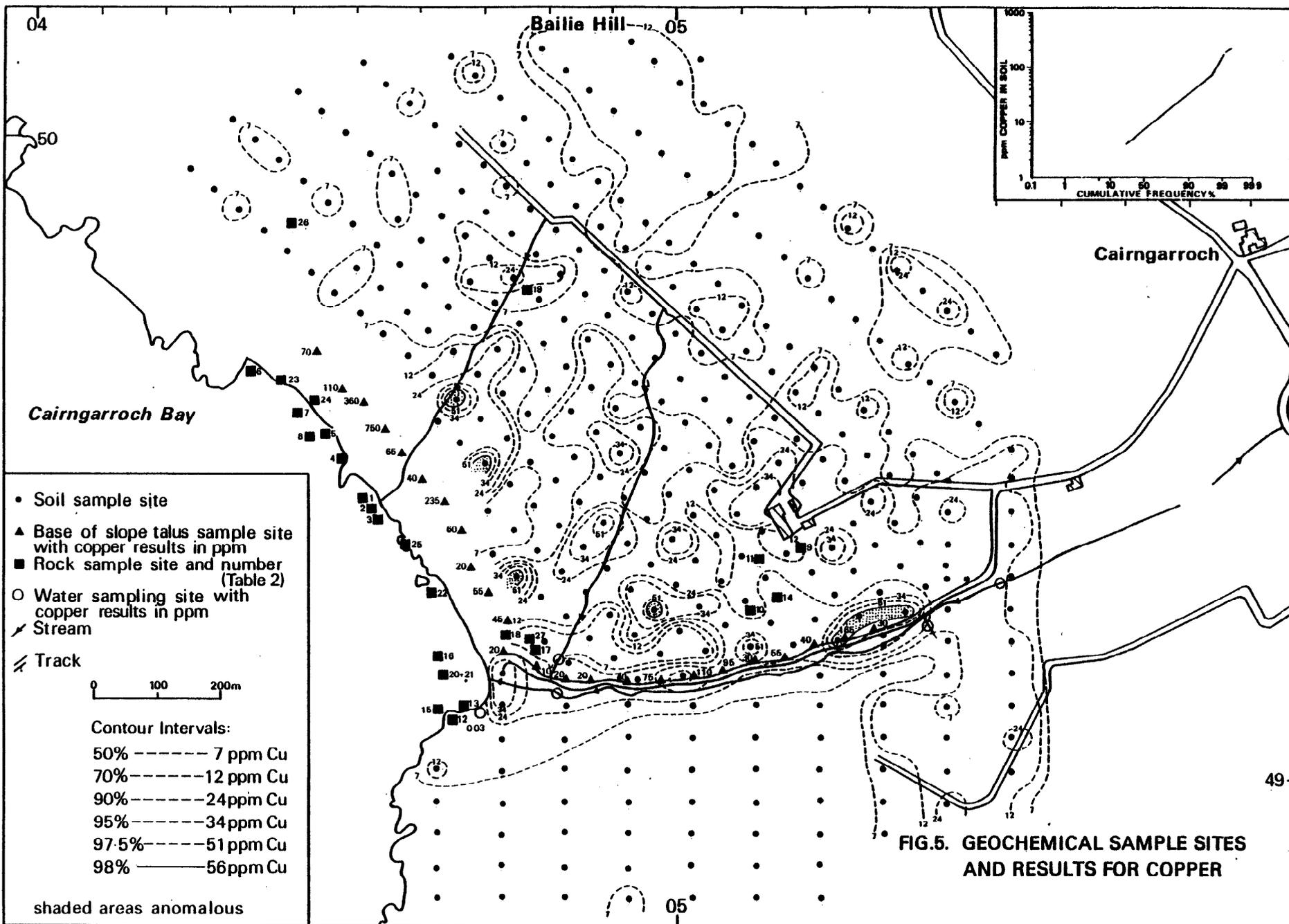
Log cumulative frequency plots of Cu and Pb (Figures 5, 6) approximate to bimodal form with clear inflexion points; but they may represent top-truncated sigmoidal forms (Lepeltier, 1969; Parslow, 1974). The zinc distribution (Figure 7) also shows a clear inflexion point, but is believed to represent a combination of a background population and an upper lognormal population. With the lead and zinc results reported in 10 ppm intervals and a small range of results, both these graphs are imprecise. Threshold levels were set at the inflexion points for all these elements: 31 ppm (95 percentile level) for lead, 51 ppm (97.5 percentile level) for zinc, and 56 ppm (98 percent-

Table 1 Summary of analytical results in ppm for Cu, Pb and Zn on 346 soil samples

	*Median	Mean	Max.	Min.	Geometric Mean	Geo. Mean + geo. dev.	Geo. Mean + 2 geo. dev.
Cu	7	14	250	<3	10	22	52
Pb	17	23	90	10	21	32	48
Zn	22	29	130	<5	24	47	92

*Median levels were determined graphically

Values less than the detection limits for Cu and Zn are set at zero for calculations



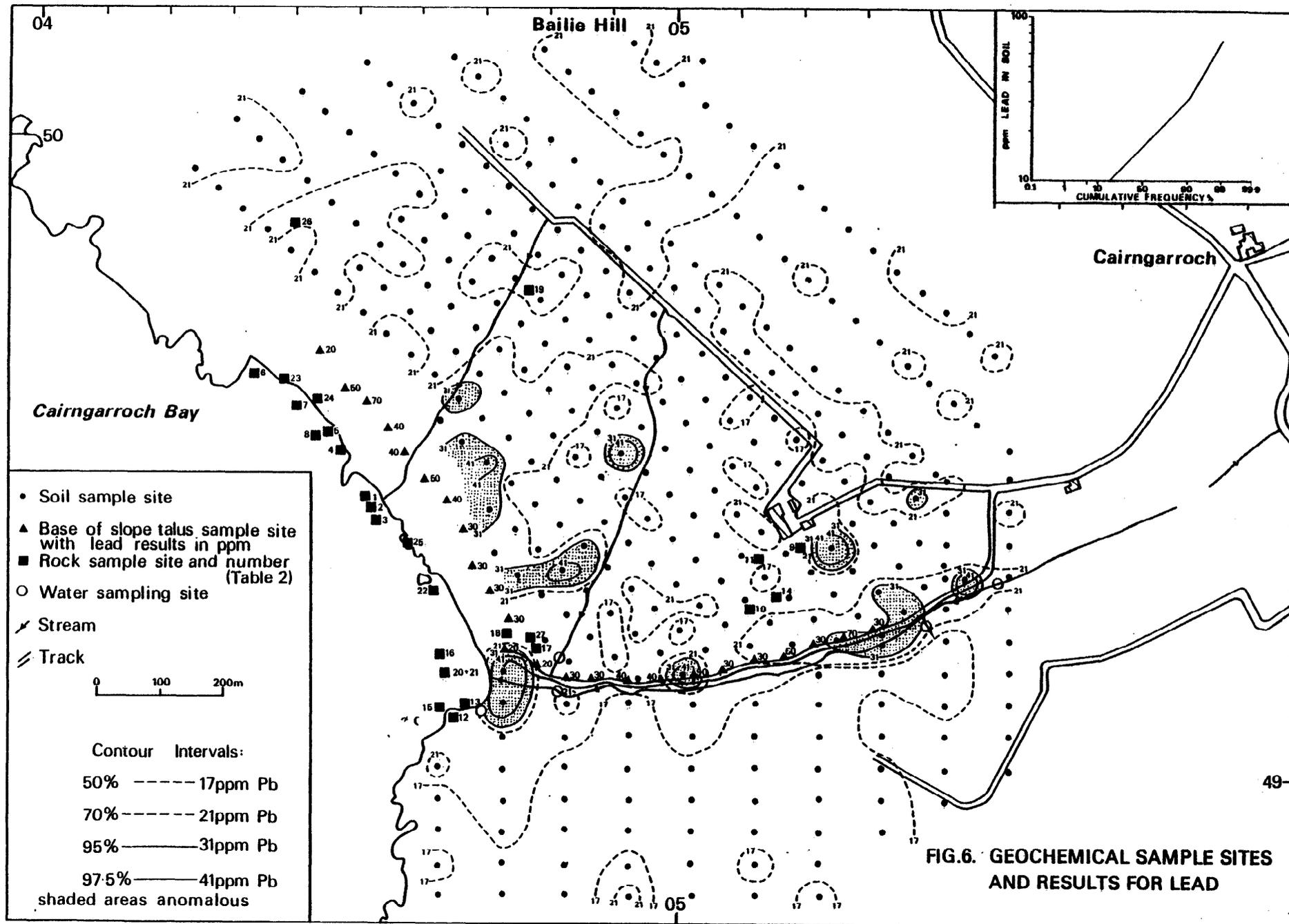


FIG. 6. GEOCHEMICAL SAMPLE SITES AND RESULTS FOR LEAD

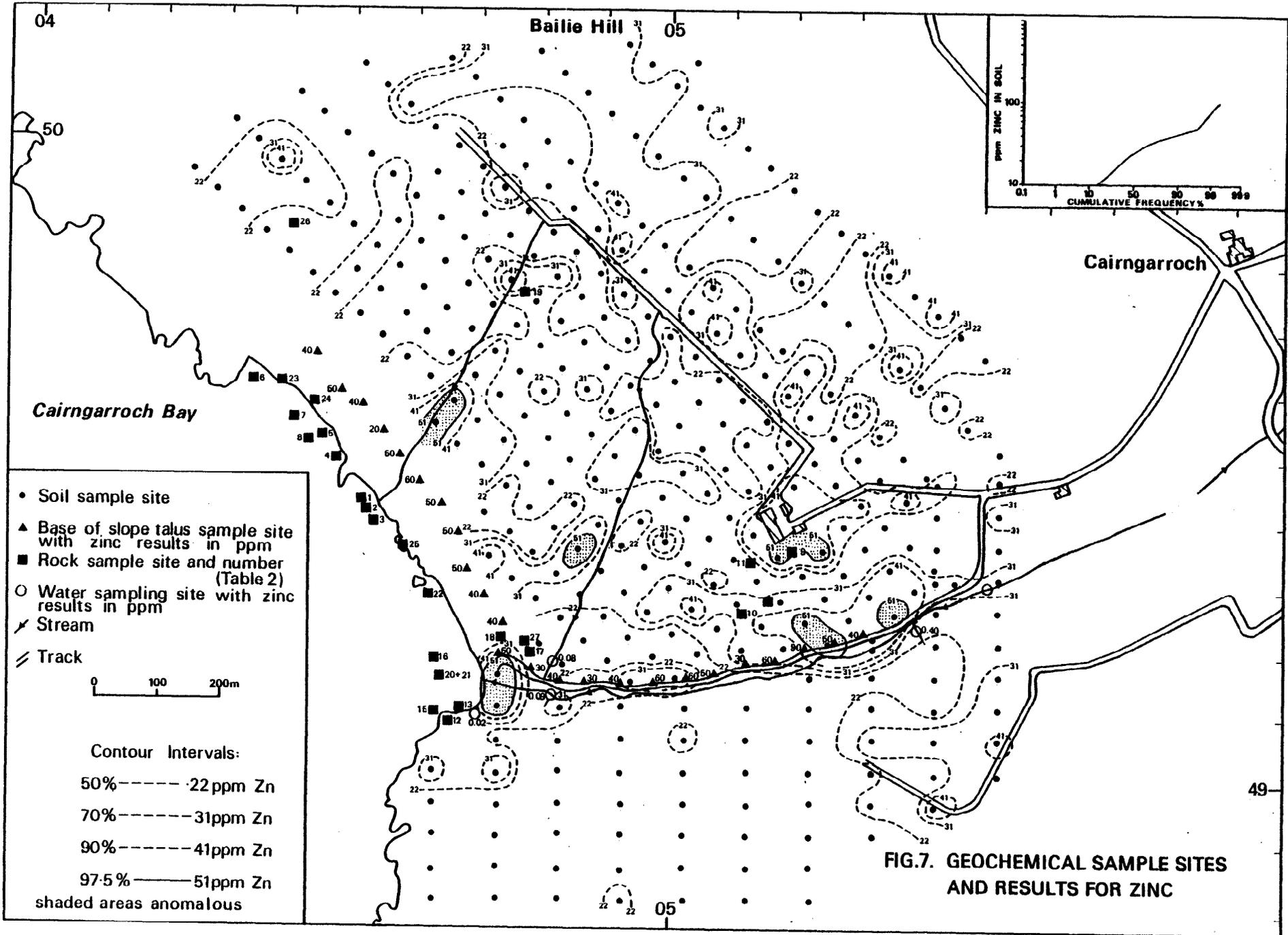


FIG.7. GEOCHEMICAL SAMPLE SITES AND RESULTS FOR ZINC

ile level) for copper. The level for copper is the most precisely set, representing the 95% confidence level point of departure from the log-normal line (Sinclair, 1976). If the binormal plots are top-truncated sigmoidal forms then the anomalous samples will also contain a proportion of the background sample population.

Hand-contoured plots of the Cu, Pb and Zn results are shown in Figures 5, 6 and 7 respectively. Contour levels for copper were set arbitrarily at the 50, 70, 90, 95, 97.5 and 98 percentile levels of the sample population distributions. Because of the stepped data, the small range of results and the different threshold levels the percentile-based contour levels for lead and zinc are slightly different (see Figures 8 and 9). On the diagrams contours at and above threshold are emphasised by solid lines.

Talus samples

The analytical results are shown on Figures 5–7. The small number of samples prevented detailed statistical analysis of the data. Threshold levels could not, therefore, be determined from the data, but where this sample type has been collected over similar lithologies elsewhere in Britain (e.g. Allen and others, 1979) levels are broadly similar to those found in boulder clay soils. Evidence from Hoffman (1977) suggests that base metal levels in talus fines are somewhat higher than in stream sediments from the same area. Therefore, Cu results above 100 ppm in talus fines can be taken as anomalous with confidence and somewhat lower values (50–100 ppm) may also be significant in terms of mineralisation. Levels of lead in talus fines are similar to soils here whilst zinc results are generally slightly higher but on the above criteria none of the results can be described as clearly anomalous.

Rock samples

The variety of rock types and the small number of samples precluded meaningful statistical analysis of the results. Except for very high arsenic and low barium and copper contents, the baked mudstone (Table 2) has a composition similar to the average slate of Turekian and Wedepohl (1961) and shale, quoted from various sources by Reedman (1979).

Among the greywackes only sample 26 (Table 2) shows typical greywacke major element chemistry (Pettijohn and others, 1972). Two of the samples (23 and 24) fall outside the greywacke range as defined by a plot of $\log(\text{Na}_2\text{O}/\text{K}_2\text{O})$ v $\log(\text{SiO}_2/\text{Al}_2\text{O}_3)$ because of their abnormally high potash and low soda contents, probably indicating potash metasomatism or soda depletion. Silica levels generally are rather low. Iron and calcium are high, which reflects a high argillaceous content and the effects of pyritisation and carbonate veining. Less data are available for comparison of trace element contents. However, compared with average sandstones of Turekian and Wedepohl (1961) the

Cairngaroch rocks contain higher levels of several elements, most of which can be attributed to the argillaceous component in the greywacke. The exceptionally high level of arsenic in sample 23 is probably caused by arsenopyrite and the high level of nickel reported in all samples may be partly caused by pyritisation. The minor chalcopyrite noted in sample 25 is confirmed by a relatively high copper content.

The Bay Complex granodiorite shows a broadly similar major element composition to quoted analyses of granodiorites except for low SiO_2 and high MgO . In view of the low major element totals (mean 96.97) the former may be an analytical error, whilst the latter may be related to the presence of carbonate veinlets. The outstanding feature of the analysis is the copper content of the rocks, four of the five samples containing more than four times the average level for this lithology. There are no corresponding strong enrichments in any of the other elements determined, although one sample is enriched in Mo, another in As and the sample with the highest copper content also contains a large amount of Sr.

The three microtonalite samples are of similar composition, which is quite distinct from that of the granodiorite. The microtonalite has a more basic composition, containing lower SiO_2 , K_2O , Rb, Zr, Y, Ce and Th, and higher Al_2O_3 , TiO_2 , Fe_2O_3 , Mn and Zn. In terms of magmatic differentiation this agrees with the order of emplacement indicated by field relations. However, some features which may be the result of later alteration contravene this pattern; the microtonalite samples contain more Ba and less nickel, and yield lower K/Rb ratios than the granodiorite. Except for the high levels of Cu, Mo and As, the composition of these microtonalites is broadly similar to quoted analyses from elsewhere. The Cu enrichment is apparently not so pronounced as in the granodiorite but As and Mo levels are generally higher and more uniform.

The dioritic rocks of the Glen Complex and the dykes are chemically unclassifiable on the available data. They show a wide range of compositions, the result in part of alteration and mineralisation. Comparison of the two least altered rocks (9 and 10, Table 2) with average analyses of diorites (Vinogradov, 1962) and 9 Cambrian microdiorites from the Harlech Dome (Allen and others, 1976) suggest that these rocks are fairly typical in composition. The altered rocks show erratic enrichment in Cu, Ni, As, Mo and Ba, but only small deviations from quoted averages in major element geochemistry. There is a suggestion of a reduction in the silica content and increases in K_2O , P_2O_5 , Fe_2O_3 , MgO and CaO . The heavy alteration to carbonate, observed petrographically in several samples, is reflected only in the analysis of sample 5 where Mg and Ca are high. Although comparisons are difficult because of the alteration, the microdiorites of the Glen Complex are

Table 2 Rock analyses

Rock type	Sample No.	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Rb	Sr	Ba	Mn	Ni	Cu	Zn	Pb	As	Y	Zr	Mo	Ce	Th	
<i>INTRUSIVES</i>																									
<i>Bay Complex</i>																									
porphyritic granodiorite	1	63.70	15.52	0.62	4.44	2.71	4.04	4.16	3.49	0.17	104	1265	973	350	21	608	23	<13	6	20	230	2	53	15	
	2	61.17	15.52	0.64	4.49	2.60	4.22	4.05	3.33	0.17	79	666	860	310	23	38	26	<13	9	19	219	3	40	14	
	3	60.32	15.45	0.68	4.68	2.57	4.30	4.21	3.37	0.17	101	601	947	250	25	201	24	<13	8	19	232	<2	63	12	
	4	59.54	15.84	0.74	5.91	3.06	3.30	4.11	2.73	0.19	98	543	810	280	24	144	27	<13	20	19	217	4	52	12	
microtonalite	5	61.33	15.53	0.67	4.89	2.55	4.21	4.06	2.98	0.17	112	576	824	200	21	241	25	<13	7	16	205	23	49	11	
	6	57.51	16.78	0.81	6.57	3.30	5.51	4.02	2.12	0.19	82	869	672	580	11	110	47	<13	89	18	152	8	34	5	
	7	57.55	17.83	0.78	6.84	2.99	2.58	4.47	1.86	0.18	65	656	945	460	12	150	49	<13	49	18	153	9	35	6	
	8	58.98	17.15	0.81	5.61	2.68	5.28	4.53	1.87	0.21	62	717	625	570	10	42	67	<14	21	17	145	3	41	7	
<i>Glen Complex</i>																									
quartz microdiorite	9	57.04	17.30	0.93	6.95	3.62	5.21	4.44	1.98	0.22	60	676	763	620	12	54	63	<13	5	20	122	4	25	5	
	10	53.76	15.18	0.93	7.82	5.57	6.46	3.88	1.39	0.20	50	590	413	720	77	26	76	19	6	21	158	2	30	4	
porphyritic quartz microdiorite	11†	58.22	16.49	0.80	6.02	3.04	5.11	4.56	1.98	0.23	65	838	718	650	9	41	61	16	8	19	143	<2	29	4	
	12*	46.23	13.25	0.83	7.87	5.05	8.51	3.14	1.94	0.12	63	641	565	930	120	71	62	14	123	16	100	<2	<21	4	
	13*	56.07	15.68	0.67	6.32	2.39	5.17	3.34	3.41	0.34	63	531	1039	700	15	18	49	24	54	22	265	<2	87	13	
	14†	60.60	15.53	0.71	5.99	3.18	4.10	4.18	2.89	0.21	92	716	960	390	22	124	34	14	12	20	211	17	53	12	
	15†	68.20	16.70	0.15	1.97	0.96	1.76	5.10	2.88	0.17	78	185	723	410	26	<6	27	<13	24	15	179	<2	36	10	
	16*	57.41	17.49	0.71	5.58	2.95	3.85	2.52	1.14	0.20	52	199	106	410	26	101	32	23	494	18	220	2	49	14	
<i>Dykes</i>																									
porphyritic quartz microdiorite	17*	60.82	15.34	0.54	4.84	2.46	4.48	3.75	1.94	0.16	70	400	640	350	17	70	16	<13	25	20	249	2	51	14	
	18*	61.69	15.52	0.58	5.22	3.00	2.95	3.67	2.35	0.16	67	369	4348	370	19	101	40	<13	<2	22	268	<2	46	16	
<i>MINERAL VEINS</i>																									
quartz/sulphide vein	19	63.22	5.30	0.30	23.97	0.40	0.21	<0.10	0.61	0.09	26	22	642	350	117	1443	6	26	190	6	52	14	<21	7	
quartz/sulphide vein	20	57.42	2.66	0.15	21.60	0.89	0.74	<0.10	0.75	0.08	42	36	54	370	51	3611	580	2649	>1000	<2	<3	10	<21	269	
Qtz./S. vein and wall rock	21	61.96	14.46	0.82	6.62	3.22	1.66	1.55	3.31	0.16	141	162	115	460	118	103	64	73	>1000	18	192	51	36	15	
quartz/sulphide vein	22										19	33	41	190	46	967	18	17	30	2	16	9	<21	3	
<i>SEDIMENTARY ROCKS</i>																									
Greywacke, mineralised	23	64.57	13.35	0.72	6.14	2.54	3.26	<0.10	3.32	0.17	124	200	216	490	74	63	32	<13	531	22	199	<2	39	9	
	24	60.99	13.98	0.81	6.47	2.93	3.67	0.90	1.85	0.14	71	143	100	500	84	59	51	<13	25	21	195	<2	44	7	
	25	61.44	14.80	0.97	8.17	4.44	2.12	2.89	2.56	0.17	108	184	287	460	122	97	48	<13	9	20	206	15	43	9	
Greywacke	26	62.62	13.97	0.93	7.93	5.13	1.94	3.28	1.82	0.17	61	261	454	510	122	52	80	19	15	20	199	3	31	8	
Baked mudstone	27	59.54	15.63	0.78	8.10	2.79	2.30	1.76	3.33	0.10	141	183	317	970	103	17	79	16	63	21	167	3	53	9	

F, U, Ag, Sn and Sb were also analysed but all determinations were less than the detection limits except No. 19, Sb=33 ppm, No. 20, Sb=299 ppm, Ag=17 ppm, F=0.21% and No. 21, Sb=32 ppm

*Heavily altered
†Moderately altered

apparently more basic in composition than those of the Bay Complex rocks and copper enrichment is less regular and weaker.

The samples of vein material show Cu, As, Mo, Sb and Fe sulphide mineralisation and, in a lens of massive sulphide within a vein, Ag, Pb, Zn, Th and F were also detected.

INTERPRETATION

Water

The high copper-in-water result comes from a spring presumably fed by groundwater from within the Glen Complex or along the fault down the glen. It may indicate sub-surface mineralisation. All the zinc anomalies are most likely to be caused by contamination.

Soils

Contoured plots of Cu, Pb and Zn in soil (Figures 5–7) show many features in common, and indicate sources of variation, for all three elements, one of which may be contamination. High and anomalous levels of all three elements around the farm, by the stream to the south, and at [NX 053 492], where there is a rubbish tip, are either caused or enhanced by contamination. Two samples collected over alluvium at the entrance to the glen [NX 047 491] form a high which may represent a transported anomaly enhanced by contamination. All the highest (>51 ppm) lead results may be related to either contamination, or poorly drained sites by streams, or a combination of these factors. Anomalous and high values of Cu and Zn remain, however, which can be related to bedrock chemistry. It should be noted, however, that the Zn values, with a maximum of only 130 ppm, are generally very low and are unlikely to be related to appreciable zinc mineralisation.

Much of the area is underlain by drumlinised drift deposits (Figure 1) with low metal contents, but in the drift-free parts a broad pattern of metal enrichment can be discerned. All the high metal values are in soils from an area extending from the glen fault northwestwards to the Bay Complex and it is clear from the contoured maps that the fault abruptly terminates base-metal mineralisation in a southerly direction. To the north-west of the Bay Complex, low and uniform results are located over sedimentary rocks, an example of which is the sample of unmineralised greywacke (No. 26) in Table 2.

The copper anomaly over the Glen Complex at [NX 0495 4927] and a north-easterly-trending line of anomalies and high values to the north-west of here [NX 0475 4932–NX 0492 4950] probably relate to underlying mineralisation along the north-western margin of the Glen Complex now concealed beneath drift. A copper low separated this area of high values from another group of anomalies extending from the cliff tops above the Bay Complex to NX 0475 4975, where

high values in soil are found by a window in drumlinised drift deposits exposing chalcopyrite-bearing vein mineralisation (Table 2, No. 19) in greywacke. These anomalies are apparently over the roof zone of the Bay Complex. The limits of their eastward extension are not known because of the drift deposits.

Talus

The pattern of talus sample results agrees with the contoured soil results. The most anomalous copper results occur immediately above the outcrop of the Bay Complex and can be directly linked with soil anomalies inland. High values are also found along the glen although the highest result here (165 ppm, NX 0528 4920) may be enhanced by contamination. Pb and Zn generally show slight increases with Cu, as in the soils, but this relationship breaks down over the Bay Complex.

Rocks

Rock samples indicate the presence of mineralisation in the Bay Complex, Glen Complex, dykes and adjacent sedimentary rocks. Appreciable enrichment in Pb, Ag, Zn, Sb, Th and F is restricted to a single specimen of massive sulphide from the largest vein sampled, although weak enrichment in some of these elements in other rocks would have escaped detection. Patchy As, Cu, Mo, (?Ni) and Fe enrichment is more widespread, occurring in intrusive rocks and the adjacent wall rocks. The majority of Bay Complex rocks are enriched in copper and all the microtonalites in Cu, As and Mo. Petrographic examination indicates that sulphides are a secondary feature associated with alteration, not primary magmatic minerals. Inter-element relationships in the intrusive rocks, as demonstrated by Spearman Rank Order correlation coefficients (Downie and Heath, 1974), indicate an erratic form of mineralisation, with no highly significant correlations generated between chalcophile elements.

ALTERATION AND METASOMATISM

Chemical and petrographic data show that all the rock types here have suffered alteration. Two samples of greywacke taken close to the Bay Complex show unusual Na₂O/K₂O ratios which may be ascribed to metasomatism. The minimal variation in the K/Rb ratios (196–247), coupled with very low soda contents, suggest that there may be an element of soda depletion rather than strong potash enrichment in the metasomatism.

Considering the igneous rocks (Figure 9) the least altered samples from the Glen Complex and all the Bay Complex microtonalite samples give K/Rb ratios which fall on the 'main igneous trend' of Shaw (1968). Several altered samples from the Glen Complex show relative enrichment in potash and follow no clear igneous trend whilst only one shows a slight relative increase in Rb.

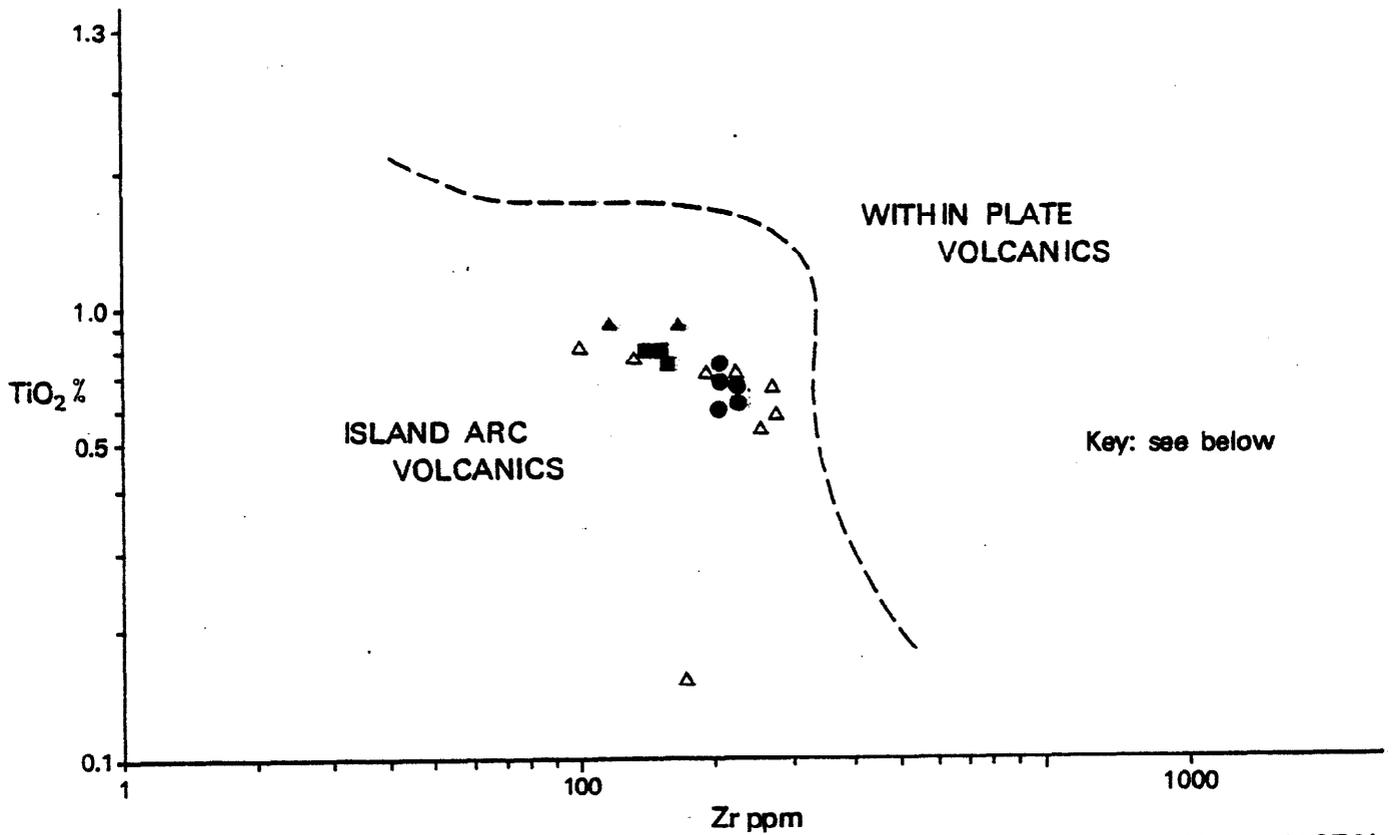


FIG.8. Plot of TiO_2 v Zr with fields devised from data in Pearce & Norry (1979)

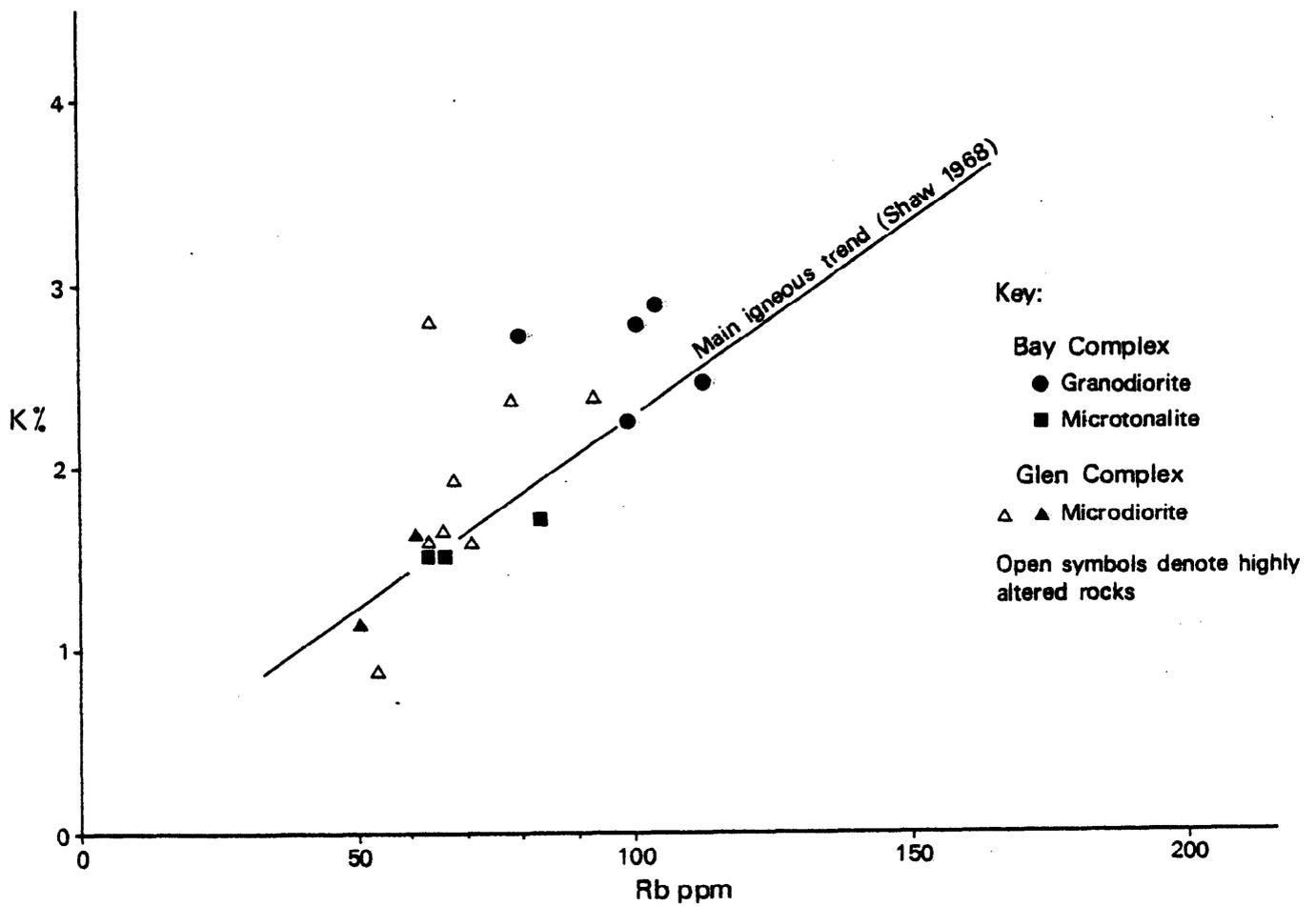


FIG.9. Plot of K v Rb

This can be interpreted in terms of the agency causing the alteration having a very high K/Rb ratio which makes it unlikely that it was a late stage magmatic fluid (Armbrust and Gannicott, 1980). Perhaps the most unusual feature of the K/Rb ratios is the high values given by three of the granodiorite samples. The reason, particularly for the contrast in values with the microtonalite, is uncertain but may be mineralogical; both rock types contain chloritised biotite but only the granodiorite has appreciable K-feldspar.

A triangular plot of the Ba, Sr and Rb (El Bouseily and El Sökkary, 1976) shows a wide spread of points (Figure 10). The limited petrographic variation in the primary constituents of these rocks and the close grouping of the plots of least altered samples indicate a limited range in original composition. The full spread of points, therefore, is more likely to indicate Ba enrichment than a differentiation trend. Again, only in one microdiorite sample is there a suggestion of Rb enrichment. As with the mineralisation the plots and correlation coefficients indicate that metasomatism is patchy and erratic.

PETROGENESIS

Ti and Zr show a significant (99.5% confidence level) inverse relationship in the intrusive rocks. A plot of TiO_2 v Zr for the intrusive rocks suggests, by extrapolating the criteria (Figure 8) of Pearce and Norry (1979), that they were not emplaced in a within-plate environment. Plots of other HFS (high field strength) elements conform to this pattern. For instance the Zr/Y results, although only covering a small part of the overall trend, show a clear similarity to some volcanic arc suites, such as Tonga. In addition, the K_2O , Cu, Pb and Zn abundances and the Rb/Sr ratios compare with those given by Kesler and others (1975) for unmineralised intrusions associated with porphyry copper deposits in an island arc rather than within a craton.

Brown (1979) quotes mean K_2O/Na_2O , Rb/Sr and K/Rb ratios for the major intrusions of the Southern Uplands and some other Caledonian granites in Britain which are quite different from the majority of values obtained on both fresh and altered rocks of Cairngaroch (Table 3). It emphasises the relatively low Rb and K content of the Cairngaroch rocks with respect to Na and Sr, and the high K/Rb ratios of the Cairngaroch intrusives except for the Bay Complex microtonalite. The reasons for these differences are not clear and may be no more than a function of sampling, for when the Cairngaroch rocks are compared with petrographically similar types from other regions they do not show any obvious K or Rb deficiency. However, within the Southern Uplands it appears, on the basis of limited sampling, that differences do exist between the major intrusions and the Cairngaroch rocks, which may indicate that they belong to two separate intrusive episodes; or, most likely, the Cairngaroch rocks represent an early phase within the early Devonian magmatic cycle. The latter interpretation agrees with the observations of Leake (personal communication), and Leake and Cooper (in press) that early representatives of the intrusive magmatic cycle in south-west Scotland are associated with mineralisation.

CONCLUSIONS

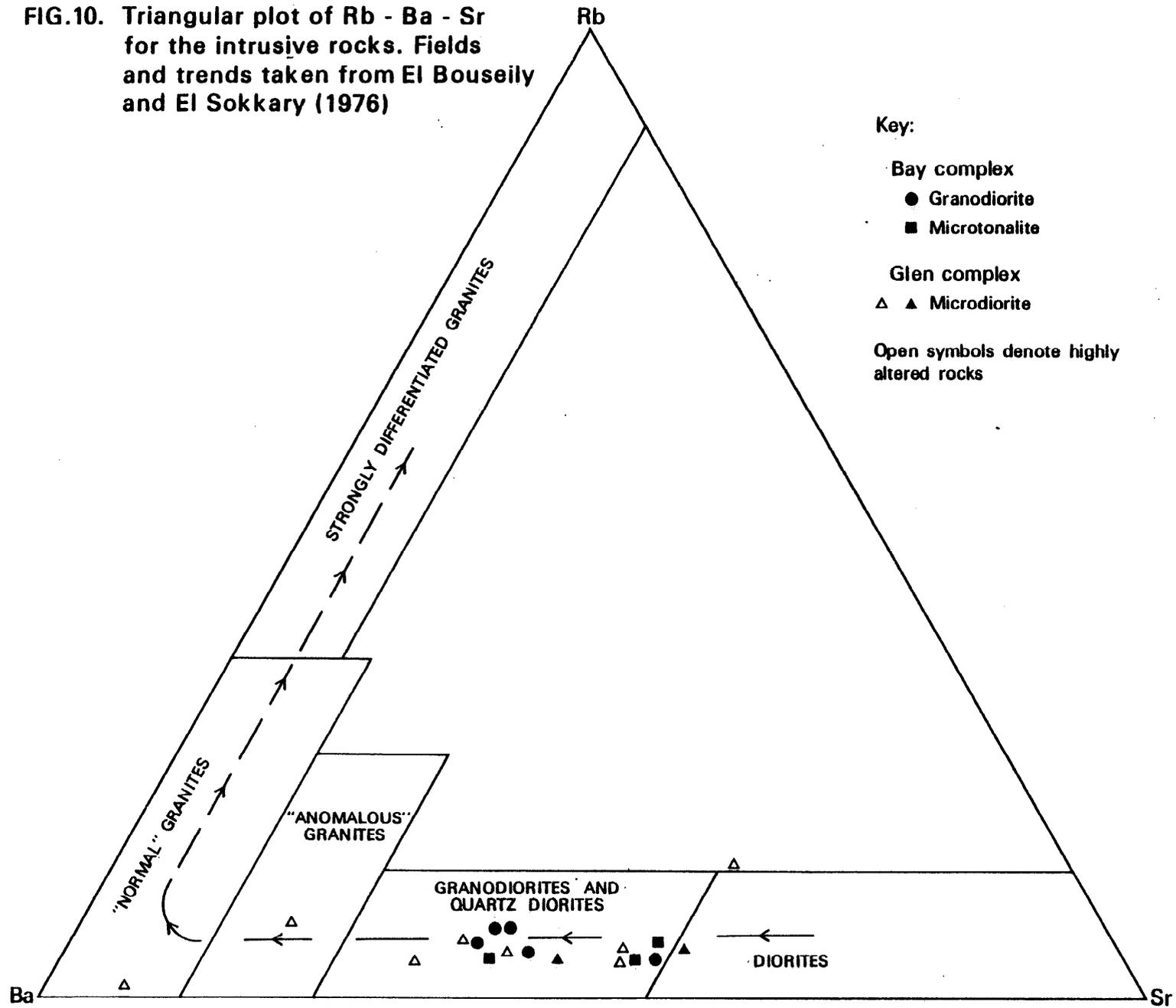
1. Assuming, on the basis of the available evidence, that the Bay and Glen intrusive complexes do not have different magmatic sources, it is possible to erect a tentative chronology for the events that followed the folding and regional metamorphism of the Silurian sedimentary country rock:-

- 5 Second dyke phase
- 4 Barren quartz veins
- 3 Mineralisation and alteration
- 2 First dyke phase
- 1 Intrusion of Glen and Bay complexes

Table 3 Comparison of some geochemical ratios from Cairngaroch with other Southern Upland Intrusions (from Brown, 1979)

	K_2O/Na_2O	Rb/Sr	K/Rb	n
Bay Complex granodiorite (1-5)	0.77	0.15	271	5
Bay Complex microtonalite (6-8)	0.45	0.09	233	3
Glen Complex least altered rocks (2 and 3)	0.81	0.09	252	2
All Glen Complex rocks (2-9)	0.57	0.12	276	8
Dykes (10-11)	0.58	0.18	261	2
Loch Doon tonalite	1.26	0.29	234	21
Criffel Granodiorite	1.01	0.31	198	24
Cairnsmore of Carsphairn tonalite	0.84	0.24	228	5

FIG.10. Triangular plot of Rb - Ba - Sr for the intrusive rocks. Fields and trends taken from El Bouseily and El Sokkary (1976)



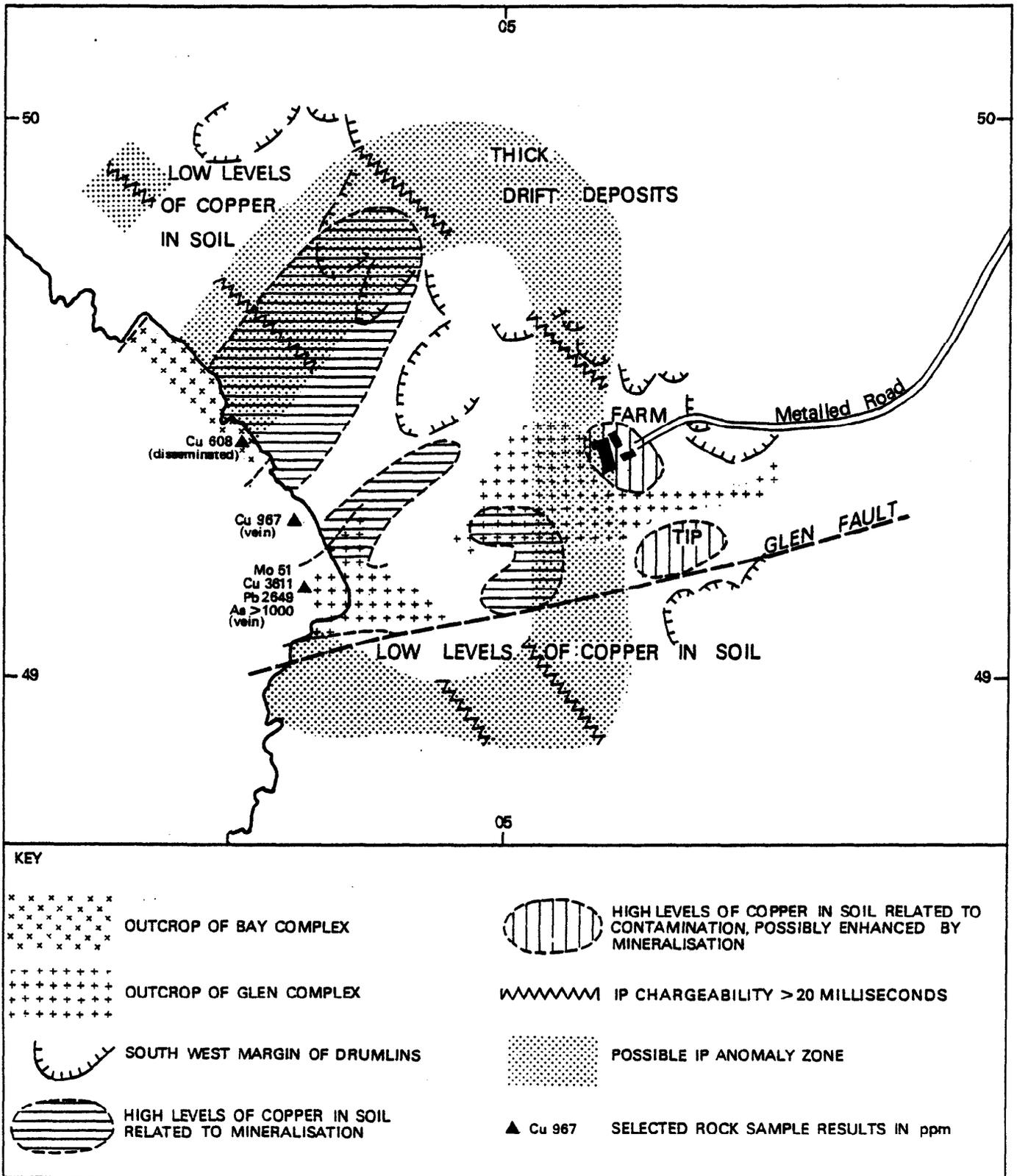


FIG.11. Summary of geological, geochemical and geophysical data for Cairngaroch Bay area

If these rocks can be interpreted as comprising a subvolcanic complex, the rock geochemistry indicates that emplacement was not in a within-plate environment. There is some evidence that they may represent an early phase in the early Devonian magmatic cycle of the Southern Uplands.

2. The rock geochemistry indicates a pervasive but patchy Cu-Fe-As-Mo enrichment in all rock types. In the Bay Complex the granodiorite shows the greatest degree of copper enrichment, whereas the microtonalite shows less erratic Cu, Mo and As enrichment. Enrichment in the Glen Complex is erratic. The source of the iron/copper and arsenic can be traced to pyrite, chalcopyrite and arsenopyrite, both disseminated and in veinlets in these rocks. Mo-bearing phases have not been found.
3. There is geochemical evidence to show that the mineralisation was probably accompanied by a patchy metasomatism involving irregular Ba, K and, perhaps, Sr enrichment. There is only a little geochemical support for Ca enrichment, though alteration to calcite is widespread in the Glen Complex. Within the Bay Complex alteration is confined to narrow linear zones and on the whole this complex is less altered than the immediate wall rock and the Glen Complex exposed on the shore line. In the latter there is abundant fracturing, veining, network fracturing and minor brecciation all of types characteristic of alteration zones around porphyry copper deposits. The K/Rb ratios also indicate that the fluids causing alteration may not have been entirely composed of late magmatic differentiates.
4. In addition to the widespread Fe-As-Cu-Mo mineralisation one sample indicated the local development of Pb-Ag-Sb-Zn-F-Th mineralisation in veins.
5. In the soil survey an area of metal enrichment was defined north of the glen and west of a curved line through West Cairngarroch farm to the coast near Blue Bonnet [NS 042 497]. Anomalous and high values of Cu, Pb and Zn, where they coincide, and all high Pb values are attributed to contamination. Some remaining anomalous Zn values, though probably reflecting bedrock chemistry, are too low to be connected with any appreciable mineralisation. Several small areas of high copper values are considered to indicate disseminated copper mineralisation. It is uncertain whether the mineralisation fades eastwards or is concealed beneath thick drift.
6. The IP anomalies can be interpreted as forming either linear, roughly north-east trending zones of high chargeability or a halo. In the case of the latter interpretation most of the high copper values fall inside the halo. Disseminated pyrite in sufficient quantity to cause high chargeability has been observed at outcrop south of the glen fault and in the cliffs above the Bay Complex.
7. As a model for mineralisation in this area it is suggested that the Glen Complex was intruded before the Bay Complex; that after or during the

emplacement of the Bay granodiorite a broad zone to the east and south of the Bay Complex and narrow linear zones locally within it were subjected to hydrothermal alteration and accompanying Cu-Mo-As-Fe disseminated mineralisation. The arrangement of a zone of high chargeability around an inner Cu-Mo zone and the potassic alteration conforms to the classical model of a porphyry mineralisation (Lowell and Guilbert, 1970; Pelton and Smith, 1976), but there are other factors which do not: the alteration zonation is incomplete, alteration is not pervasive, there is evidence of Ca enrichment, and the Cu-Mo values are very low. It is suggested that this mineralisation may represent a 'failed' porphyry system.

8. The level of metal enrichment here is too low to be considered economically workable. If the model proposed above is tenable it is likely that the mineralised body extends downwards and out to sea. However, a landward extension cannot be ruled out until the form of the high IP chargeability zone is resolved and the absence of copper enrichment beneath the drift is demonstrated.

ACKNOWLEDGEMENTS

Thanks are due to staff of ACU of IGS, particularly T. K. Smith and A. Davies for the rock analyses and M. F. Quinn and P. Joseph for the soil analyses, and to Mr T. Robinson who helped to collect the soil samples.

REFERENCES

- Allen, P. M., Cooper, D. C., Fuge, R. and Rea, J. 1976. Geochemistry and relationships to mineralisation of some igneous rocks from the Harlech Dome, Wales. *Trans. Inst. Min. Metall. Sect B.*, Vol. 85, pp.100-118.
- — and Smith, I. F. 1979. Mineral exploration in the Harlech Dome, North Wales. *Mineral Reconnaissance Programme Rep. Inst. Geol. Sci.*, No. 29.
- Armbrust, G. A. and Gannicott, R. A. 1980. K/Rb ratios as a source indicator for hydrothermal fluids at the Seneca volcanogenic massive sulphide deposit, British Columbia. *Econ. Geol.*, Vol. 75, pp. 466-477.
- Brown, G. C. 1979. Geochemical and geophysical constraints on the origin and evolution of Caledonian granites. In Harris, A. L., Holland, C. H. and Leake, B. E. (Eds.): *The Caledonian of the British Isles reviewed. Spec. Publ. Geol. Soc. London*, No. 8, pp. 645-652.
- Downie, N. M. and Heath, R. W. 1974. *Basic statistical methods*. (New York: Harper and Row.) 355 pp.
- El Bouseily, A. M. and El Sakkary, A. A. 1976. The relation between Rb, Ba and Sr in granite rocks. *Q. J. Geol. Min. Metall. Soc. India*, Vol. 47, pp. 103-116.
- Geikie, A. 1873. Explanation of Sheet 3, Western Wigtownshire. *Mem. Geol. Surv. Scotland*, 34 pp.
- Hodgson, J. M. 1976. Soil Survey field handbook. *Tech. Monogr. Soil Surv. G.B.*, No. 5.
- Hoffman, S. J. 1977. Talus fine sampling as a regional geochemical exploration technique in mountainous

- regions. *J. Geochem. Chem. Explor.*, Vol. 7, pp. 349–360.
- Kesler, S. E., Jones, L. M. and Walker, R. L. 1975. Intrusive rocks associated with porphyry copper mineralisation in island arc areas. *Econ. Geol.*, Vol. 70, pp. 515–526.
- Leake, R. C. and Cooper, C. *In press*. The Black Stockarton Moor Subvolcanic Complex, Galloway, Scotland. *Scot. J. Geol.*
- Lepeltier, C. 1969. A simplified statistical treatment of geochemical data by graphical representation. *Econ. Geol.*, Vol. 64, pp. 538–550.
- Lowell, J. D. and Guilbert, J. M. 1970. Lateral and vertical alteration–mineralisation zoning in porphyry copper deposits. *Econ. Geol.*, Vol. 65, pp. 373–408.
- Paralow, G. R. 1974. Determination of background and threshold in exploration geochemistry. *J. Geochem. Explor.*, Vol. 3, pp. 319–336.
- Pelton, W. H. and Smith, K. 1976. Mapping porphyry copper deposits in the Philippines with IP. *Geophys.*, Vol. 41, pp. 106–122.
- Pearce, J. A. and Norry, M. J. 1979. Petrographic implications of Ti, Zr, Y and Nb variations in volcanic rocks. *Contrib. Miner. Petrol.*, Vol. 69, pp. 33–47.
- Pettijohn, F. J., Potter, P. E. and Seiver, R. 1972. *Sand and sandstones*. (Berlin: Springer Verlag.)
- Reedman, J. H. 1979. *Techniques in mineral exploration*. (London: Applied Science.)
- Shaw, D. M. 1968. A review of K/Rb fractionation trends by covariance analysis. *Geochem. Cosmochim. Acta.*, Vol. 32, pp. 573–601.
- Sinclair, A. S. 1976. Applications of probability graphs in mineral exploration. *Assoc. Explor. Geochem. Spec.* Vol. 4.
- Turekian, K. K. and Wedepohl, K. H. 1961. Distribution of the elements in some units of the earth's crust. *Geol. Soc. Am. Bull.*, Vol. 72, pp. 175–192.
- Vinogradov, A. P. 1962. The average content of chemical elements in the main types of igneous rocks of the earth. *Geochem.*, Vol. 7, pp. 641–664.