

BRITISH GEOLOGICAL SURVEY

Mineral Reconnaissance Programme Report

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A reconnaissance geochemical drainage survey of the Harlech Dome, North Wales

BRITISH GEOLOGICAL SURVEY Natural Environment Research Council

Mineral Reconnaissance Programme

Report 74

A reconnaissance geochemical drainage survey of the Harlech Dome, North Wales

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A report prepared for the Department of Trade and Industry



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On 1 January 1984 the Institute of Geological Sciences was renamed the British Geological Survey. It continues to carry out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects; it also undertakes programmes of British technical aid in geology in developing countries as arranged by the Overseas Development Administration.

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SUMMARY

A geochemical drainage survey was carried out across $1\ 050\ {\rm km}^2$ of the Harlech Dome and adjacent areas at a mean density of 0.85 sample/km². Fine (-100 mesh) stream sediment, panned concentrate and water samples were collected at every site. Cu, Pb, Zn, Mo, As, Ba, Fe, Mn, Co, Ni, Cr, V and Zr were determined in stream sediment samples; Cu, Pb, Zn, Ba, Fe, Mn, Ti, Ni, Ce and Sn in panned concentrates, and Cu, Pb and Zn in water. Gold was determined in panned concentrates from part of the area.

The results show that the area is metalliferous, containing large anomalies for a wide range of metals. Strong regional patterns are displayed by many elements and it is demonstrated that these are caused by bedrock lithology, hydromorphic processes, mineralisation and contamination. Geochemical signatures characteristic of the following metalliferous concentrations were identified:

- disseminated copper 'porphyry-style' mineralisation;
- (ii) 'gold-belt' vein-style mineralisation in Cambrian rocks;
- (iii) mineralisation in Ordovician volcanic and sedimentary rocks;
- (iv) bedded manganese deposits in the Cambrian;
- (v) manganese vein-style mineralisation in Ordovician volcanic rocks;
- (vi) granite-related mineralisation;
- (vii) dark mudstones.

Rhobell Fawr volcanism and possible associated metasomatism may also have generated metal anomalies but the evidence available is inconclusive. Small, bedded iron ore deposits failed to produce distinct anomalies. Despite widespread past mining activity eleven areas or styles of mineralisation have been identified where it is considered that further work might lead to the recognition of deposits of economic or supply significance. These targets include base metal anomalies in Ordovician volcanic rocks where there is some potential for volcanogenic stratiform mineralisation; copper and gold anomalies in Upper Cambrian rocks indicating the presence of further gold-belt vein-style mineralisation; arsenic anomalies over Ordovician acid volcanic rocks whose gold potential merits investigation; manganese and barium anomalies related to manganese-barium vein mineralisation in Arenig volcanic rocks and metalliferous concentrations in dark mudstones marginal to the Rhobell volcanic centre.

A metallogenetic model is proposed for the area involving: syngenetic metalliferous concentration during Cambrian sedimentation; copper and possibly gold mineralisation in an island arc-type setting at the close of the Cambrian; syngenetic and volcanogenic base-metal enrichment during the Lower Ordovician, and deep burial and remobilisation of these metals to form vein-style deposits during or after the main (end Silurian) Caledonian orogenic event.

Strong regional trends displayed by elements not directly involved in mineralisation, such as Zr, Ce and Cr, can be related to the lithostratigraphy and suggest, in conjunction with other evidence, significant palaeogeographic changes at the close of the Middle Cambrian, involving the derivation of sediment from source areas of contrasting geochemical character in Lower Cambrian and Upper Cambrian—Ordovician times. The characteristics of volcanic rocks show less clearly because of the rapid alternation of acid and basic lithologies with respect to the scale of the survey.

INTRODUCTION

This survey covers about 1100 km^2 of western Wales bounded by the towns of Bala in the east, Tywyn in south, Blaenau Ffestiniog in the north, and Cardigan Bay in the west (Figure 1). The area is formed almost entirely of sedimentary, volcanic and intrusive rocks of Lower Palaeozoic age, folded into the structure known as the Harlech Dome. The area lies within the Snowdonia National Park and is mountainous. The most prominent hills are the Cader Idris, Aran, Arenig and Moelwyn groups which rise to 907 m on Aran Fawddwy and form a ring on the periphery of the survey area. The westcentral part of the area is dominated by another range of hills, the most prominent of which is Rhinog Fawr. Drainage is dominated by the catchment of the Afon Mawddach, which drains the central part of the area.

Acid, peaty soils underlain by variable thicknesses of glacial deposits and interspersed locally with extensive areas of rock exposure characterise the high ground. Lower slopes are blanketed in drift deposits and have less acid soils. Streams cut to bedrock except in the lower reaches of the larger rivers. High ground is covered by heather or rough grass and used for sheep grazing; lower ground is mostly grass covered with small areas of deciduous forest. There is little arable farming. Extensive coniferous forest plantations cover all except the highest ground in several areas. Stream contamination is only a problem in the vicinity of farms, villages and a disused military training area to the east of Trawsfynydd.

No detailed geochemical survey data has been published for this area though surveys have been carried out by universities and commercial companies. The area is included in the Wolfson Geochemical Atlas (Imperial College, 1978) and a geochemical study of Wales by Urquidi-Barrau (1973). Both works are based on the same data and provide useful information on a regional scale. Mohr (1959) studied the lithogeochemistry of the Manganese Beds, and more recently geochemical data were included in studies of the Rhobell Fawr Volcanic Group (Kokelaar, 1977) and Aran Volcanic Group in the type area (Dunkley, 1978). The results of airborne geophysical, magnetic, electromagnetic and radiometric surveys of the Harlech Dome and geological, geophysical and geochemical investigations of twenty six anomalies arising from them, as well as various orientation studies carried out in support of these investigations, are described in an earlier MRP report (Allen and others, 1979). The literature on geology and mineralisation in the area is extensive and was summarised in the earlier report (Allen and others, 1979). Recent publications of most relevance to this study include, on the geology, Matley and Wilson (1946), Davies (1958), Lynas (1973), Bassett, Whittington and Williams (1966), Ridgway (1975, 1976) and BGS 1:50 000 map sheet 135; on mineralisation, Rice and Sharp (1976), Allen and others (1979), Cole (1977) and Foster-Smith (1977); and on mining and the environment, Searle (1975).

GEOLOGY

Stratigraphy

The area is underlain almost entirely by Lower Palaeozoic rocks; the Tertiary sediments to the west of the Mochras fault are nowhere exposed and have made no contribution to the drainage samples (Figure 2). The oldest rocks exposed are sedimentary rocks of Cambrian age. The succession is summarised in Table 1.

Harlech Grits Group This group, of Lower and Middle Cambrian age, is exposed in the core of the Harlech Dome. It comprises the lowest seven formations in the classification of Matley and Wilson (1946), modified by Allen and Jackson (on BGS 1:50 000 sheet 135, 1982). The group consists of coarse-grained turbiditic sandstones interbedded with green, grey, or purplish siltstone or muddy siltstone. The base of the lowest formation, the Dolwen, is not exposed but a deep borehole at Bryn-Teg proved underlying interbedded sedimentary and volcaniclastic rocks, tuffites and lavas (Allen and Jackson, 1978). The formational divisions reflect the broad alternations of sandstone-dominated and siltstone-dominated units. The principal siltstone-dominant formations, Llanbedr, Hafotty and Gamlan, however, all contain interbedded sandstones. The succession represents a progressive upward change from a deltaic through pro-



Figure 1: Location of survey area

deltaic to a deep basinal sedimentary environment. The Hafotty Formation contains a bed of manganese ore about 9 m above its base, which is underlain by silty mudstones and overlain by 2 m of manganiferous mudstones followed by a distinct 1 m thick grit band. Mohr (1959) suggested that the ore deposit formed in a basin with restricted access to the ocean. The upper part of the Gamlan Formation is manganiferous, spessartite, quartz and chlorite forming laminae, nodules, lenses, and beds less than 5 cm thick, in most places interbedded with purplish grey mudstones. Woodland (in Matley and Wilson, 1946) described the petrography of the sedimentary rocks. The sandstones are quartzwacke or greywacke in composition, usually with chlorite dominant in the matrix. Quartz is the main coarse clastic component; feldspars are not common. There is a wide variety of rock types among the lithic fragments. Among the heavy minerals, zircon, tourmaline, colourless and brown garnet, sphene, epidote, clinozoisite and magnetite were listed as common, with rare occurrences of anatase, enstatite, diopside, sillimanite, apatite, ilmenite and hematite. Mohr (1959) also recorded very rare barite in

sandstones from the Hafotty Formation. Authigenic pyrite and magnetite are commonly associated with the manganese ore-bed, and in the Hafotty Formation greenbrown tourmaline and spessartite occur throughout the mudstone (Woodland, 1938 a, b).

Mawddach Group This group, predominantly of Upper Cambrian age, conformably overlies the Harlech Grits Group and consists essentially of dark grey to black mudstone and silty mudstone interbedded with coarse quartzose siltstone (Table 1).

The Clogau Formation consists almost entirely of dark grey or black mudstone with up to 4 per cent carbon. It contains many seams, lenses and veinlets of sulphide, mostly pyrite and pyrrhotite with marcasite, minor chalcopyrite, sphalerite and galena (Allen and others, 1979). Mohr (1956) pointed out that this formation was also relatively manganiferous compared with the rocks above it.

The lower part of the Maentwrog Formation consists of thinly interbedded silty mudstone and coarse quartzose siltstone, with fine quartzwacke sandstones near the



Figure 2: Simplified geological map of the survey area

base. The interbedded silty mudstone is mid to dark grey in colour, but in the upper half of the formation, which is dominantly argillaceous, black mudstone units occur. These rocks are commonly pyritic.

The Ffestiniog Flags Formation contains coarse quartzose siltstone thinly interbedded with light grey silty mudstone. Sedimentary characteristics indicate a shallow water, turbulent, depositional environment for this formation, marking a shallowing of the basin. The overlying Cwmhesgen Formation consists of black, carbonaceous mudstone of the Dolgellau Member overlain by the siltier, less carbonaceous Dol-cyn-afon Member. Ponsford (1955) recorded low levels of uranium and thorium in the Dolgellau Member, which is also locally pyritic and metalliferous (Cooper and others, 1983). Thin beds of reworked tuff are recorded near the top of the member and thin beds carrying phosphatic nodules are found within it. Table 1 Cambrian succession in the Harlech Dome

Group	Formation	Lithology			
Rhobell Volcanic		Basaltic lavas and breccias			
	Cwmhesgen	Black siltstone and mudstone (Dolgellau Member) overlain by grey siltstone and mudstone (Dol-cyn-afon Member)			
Mawddach	Ffestiniog Flags	Interbedded guartzose siltstone and silty mudstone			
	Maentwrog	Silty mudstone with thinly interbedded quartzose siltstones and fine grained sandstone			
	Clogau	Black silty mudstone			
	Gamlan	Interbedded siltstone and mudstone			
	Barmouth	Coarse grained greywacke			
	Hafotty	Siltstone and locally greywacke, manganese ore bed near base			
Harlech Grits	Rhin og	Coarse grained greywacke with silt- stones locally			
	Llanbedr	Siltstone and mudstone with locally interbedded fine sandstones			
	Dolwen	Feldspathic sandstone with interbedded pebbly sandstone and siltstone			

Rhobell Volcanic Group The group, which comprises at least 3.9 km of mixed, compound and multiple lava flows and variously reworked blocky lava breccias, unconformably oversteps the two upper formations of the Mawddach Group on the south-eastern side of the Harlech Dome. The rocks are believed to be the product of a single short phase of subaerial eruption in the late Tremadoc (Wells, 1925; Kokelaar, 1977, 1979).

Aran Volcanic Group This group, named by Ridgway (1975, 1976), consists of a complex succession of volcanic and sedimentary rocks of Arenig to early Caradoc (Costonian) age. The group and its correlatives (Table 2) encircle the Harlech Dome and the rocks rest unconformably on both the Rhobell Volcanic and Mawddach groups. The group is thickest, about 2000 m,

around Cader Idris and attenuates both to the south-west and the north. The volcanic succession comprises a bimodal suite of basaltic and acid rocks interstratified throughout with locally tuffitic and pyritic black or dark grey mudstone and siltstone. There are local, thin beds of pisolitic ironstone within these mudstone formations.

At the base of the group the Allt Lwyd Formation and its equivalents mark the progress of the transgressive Arenig sea over the emerged Cambrian rocks. The basal, impersistent, coarse quartzose sandstone (Garth Grit) is overlain by grey volcanic sandstones and black and white, striped siltstone, in places ferruginous. These rocks, laid down in turbulent shallow water, are recognisable all around the Harlech Dome. There is some indication of contemporaneous volcanic activity in the south-eastern area of outcrop, but the main eruptive episode started after this formation was deposited.

An attempt to correlate the various components of the Aran Volcanic Group around the Harlech Dome in shown in Table 2. The correlations depend on the widespread presence of two major and distinctive units; the Upper Basic Volcanic Group of Cader Idris and its equivalents, and the thick, persistent Upper Acid Volcanic Group. There are, however, complications in detail because of the impersistent nature of some units, and there is a major palaeontological problem. Wells (1925) recognised fossils with a Caradocian aspect beneath the Benglog Volcanic Formation east of Rhobell Fawr. Near Arenig, however, Fearnsides (1905) discovered Llanvirn fossils in the Daerfawr Shales which overlie the equivalent of the Benglog Volcanic Formation on Arenig.

The spilitic pillow lavas, hyaloclastites, basic tuffs and tuffites, appear to represent numerous, purely local centres of eruption. The acid rocks, however, mainly ash flow tuffs with subordinate rhyolite flows, form the thickest, most persistent horizons and possibly emanate from an eruptive centre in the south or south-west of the area, where the group is thickest. The basic volcanic rocks were erupted entirely in a submarine environment. The acid ash-flow tuffs, however, though they came to rest in a submarine environment may have been erupted subaerially. Davies (1958) recorded spindle bombs on Cader Idris which might indicate a local subaerial eruptive centre. It is likely that the area of the Aran

Table a received variation and correlation within the Aran roleanic Gro	Table 2	Regional variation	and correlation	within the	Aran Volcanic	Group
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CADER IDRIS	SW ARANS		AFON WNION TO ARENIG	ARENIG		MIGNEINT	
Cox and Wells 1927	Dunkley 1978			Fearnsides 1905		Lynas 1973	
Upper Acid Volcanic or Craig y Llam Group	Aran Fawddwy Formation		Aran Fawddwy Formation	Upper Ashes of Arenig		Llyn Conwy Formation	
Llyn Cau Mudstones	Pistyllion Formation			Daerfawr Sha	les		
	Craig y Ffynnon Forn	nation					
Upper Basic Volcanic or Pen y Gader Group	Basic Lava Member Upper Mudstone M. Basic Volcanic M. Lower Mudstone M. Arenaceous M. Brithion Formation Pont Sel Formation		Benglog Volcanic Formation	Platy Ashes Great Agglomerate	Lower Ashes of Arenig		
Llyn y Gader Mudstone				Olchfa or Bifidus Group		Serw Formation	
Lower Basic Volcanic or Llyn y Gafr Group			Undivided Siltstone				
Cefn-hir Ashes							
Crogenen Slate Bryn Brith Grits Moelyn Slates			Melau Formation				
Lower Acid or Mynydd y Gader Group	Y Foel Formation		Offrwm Volcanic Formation	-			
Pont Kings Slate	Bryn Fawr Formation		Siltstone	Filltirgerig or Hirundo Beds Erwent or Ogygia Limestones Henllan or Calymene Ashes Llyfnant or Extensus Flags Basal Grit			
Basement Group			Allt Lwyd Formation (Garth Grit at base)			Carnedd Iago Formation	

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Volcanic Group exposed here represents a cross section through the submerged flanks of a single volcano whose centre was somewhere east or south-east of Dolgellau.

Moelwyn and Y Glog volcanic formations The Moelwyn (230 m thick) and Y Glog volcanic formations (Bromley, 1965; Shackleton, 1959) are mainly acid tuffs, ash-flows and agglomerates confined within a succession of mudstones of Costonian age. Bromley (1965) suggested that the Moelwyn Volcanic Formation represented a series of pyroclastic cones. Lynas (1973) correlated these formations with his Rhiw Bach Formation in the Migneint and though he considered it to equate to the whole of the Aran Volcanic Group above the Carnedd lago Formation (i.e. co-eval with Serw and Llyn Conwy formations, Table 2) there is some doubt about this point. Sedimentation was strongly controlled by active north-south block faulting during the early Ordovician and the standard succession within the Aran Volcanic Group ends abruptly in the Migneint at such a fault (Ffynnon Eidda Fault). West of it lies the Rhiw Bach, Moelwyn and Y Glog volcanic formations of no certain correlation with the rocks on the east of it.

Glanrafon Group and equivalents The Aran Volcanic Group is overlain conformably by a dominantly argillaceous succession called, in different parts of the area, the Ceiswyn Formation (in the south); Nant Hir Formation (east and north-east) and Glanrafon Group (north). There is no unified or agreed lithostratigraphic nomenclature or classification for this part of the succession and many names other than those given above have been used for parts of it.

An attempt is made in Table 3 to show the subdivisions and correlations within the succession above the Aran Volcanic Group. Modifications to the existing nomenclature for the southern part of the area are also made by Martin, Howells and Reedman (1981). The Ordovician rocks above the Aran Volcanic Group form a succession up to 3 km thick in the southern part of the area, broken by a major unconformity at the Caradoc/Ashgill boundary. The succession below the unconformity is composed mainly of blue-grey silty mudstones with thin beds and laminae of grey silty sandstone. Near the top of the Ceiswyn Beds the mudstones are calcareous. The Nod Glas, a thin unit of black mudstone with limestone ribs and phosphatic nodules, is the topmost division of the Caradoc succession, but is absent about Bala and in the north of the survey area.

Two thin beds of tuff, the Perfeddmant Ashes, occur near the base in the south-western region; but eastwards and northwards thin beds of acid tuff, the Cefn Gwyn, Ffronderw and Gelli Grin ashes are present at higher levels (Schiener, 1970).

In the northern area the thick Snowdon Volcanic Group and all the overlying sedimentary and volcanic rocks equate to the upper part of the Gelli Grin Ash Formation or the top of the Ceiswyn Beds.

The Ashgillian rocks above the unconformity are typically grey silty mudstones interbedded in the upper part (Garnedd-wen Beds) with greywackes. The profound change in sedimentary environment marked by the appearance of turbidite greywackes persists upwards through the Silurian succession which lies outside the survey area.

Intrusions

Small intrusions are common throughout the area. They may be divided into two groups: those associated with the Rhobell volcanic episode and those related to Ordovician volcanism.

Intrusions associated with the Rhobell volcanism are numerous and range from dolerite to microtonalite in composition. With few exceptions they were emplaced within rocks of the Mawddach Group. There are four main areas where these intrusions can be recognised.

 Table 3
 Correlation of the Ordovician succession above the Aran Volcanic Group

TYWYN	DINAS MAWDDWY	BALA	NORTHERN AREA		
Jehu 1926	Pugh 1928	Bassett and others 1966			
Garnedd-wen Beds			· · · · · · · · · · · · · · · · · · ·		
Narrow Vein	Abercorris Group	Foel y Ddinas Mudstone			
Red Vein					
Broad Vein	Abercwmeiddaw Group	Moelfryn Mudstone			
unco	nformity				
Nod Glas			·		
			Snowdon Volcanic Group		
		Gelli Grin Calcareous Ash			
Ceiswyn Beds or	Hengae Group	Allt-ddu Mudstones	Capel Curig Volcanic Formation		
I al y Liyn Mudstone		Frondderw Ash			
		Glyn Gower Siltstone	Glanrafon Group		
Perfeddnant Ash		Cefn Gwyn Ash			
		Nant Hir Mudstone			
Craig yr Aderyn Group (part of Craig y Llam)	Craig y Llam Group	Upper Ashes of Arenig	Llyn Conwy Formation		

- a) Along the north side of the Mawddach estuary from Barmouth to Ganllwyd there are numerous sills, mostly of dolerite with fewer of microdiorite and microtonalite composition, emplaced within the Clogau and Maentwrog formations.
- b) From Capel Hermon south to Dolgellau, on the west of Rhobell Fawr, there is a complex of intersecting dykes mainly of dolerite which Kokelaar (1977) regards as being in the root zone of the Rhobell Fawr volcano. To the west of these and, therefore, stratigraphically lower are several laccoliths of quartz microdiorite, microdiorite, and microtonalite. All of these rocks are within upper Maentwrcg or higher formations.
- c) A large area centred on Craig Aderyn in Cwm Prysor consists of a complex of probably interconnected microtonalite laccoliths within the Maentwrog and Ffestiniog Flags formations.
- d) The central part of the Harlech Dome is cross cut by a swarm of altered dolerite dykes probably related to this late Tremadoc magmatism.

There are numerous contemporaneous intrusions within the Ordovician succession. They are principally acid (granophyric and rhyolitic rocks) and basic (dolerite and gabbro) in composition reflecting the strong bimodality of the volcanism. Good examples are documented from the Aran Volcanic Group. The thick Crogenen and Cader Idris granophyre sills are believed by Davies (1958) to represent an erupted acid magma, contemporaneous with the Upper Acid Group on Cader Idris. The large Foel Ddu rhyolite intrusion within the Cambrian basement east of Rhydymain passes upwards into the erupted Brithion Formation of rhyolites and acid tuffs. On Arenig Fawr and northwards across the Migneint and into the Manods there are numerous dome-like bodies of quartz latite intruded within the Serw Formation and its equivalents low within the group. Sills and semi-concordant intrusions of dolerite, some of them ilmenite rich (Dunkley, 1978), occur throughout the group. In places there is physical continuity between massive, doleritelike bodies and pillow lavas.

The Tan y Grisiau granite is the only intrusion of its type in the survey area. It is an equigranular microgranite composed of albite-oligoclase, alkali feldspar (microperthite), quartz and chloritised biotite, with a distinct zone of highly vesicular, altered roof rocks. Field relationships suggest that it was emplaced by stoping and that intrusion was contemporaneous with the Snowdon volcanic episode and not a late-Caledonian event (Bromley, 1966).

Structure, tectonic setting and metamorphism

The main direction of folding trends north-south, giving rise to open, major folds with nearly vertical axial planes. The Dolwen pericline, which is the core of the Harlech Dome, and another pericline in the Penaran forest area may reflect the imposition of NE-SW cross folding on the main trend, in evidence on a minor scale elsewhere. It is more likely, however, that the periclines are the end product of a prolonged, complex and not fully clarified history of folding in this area. For example, Kokelaar (1979) recognised periods of northsouth folding both before and immediately after the Rhobell Volcanic Group magmatism, and there is clearly a fold phase along the same trend post-dating Ordovician volcanism.

The major faults trend north-east and roughly northsouth. The latter trend has been active at least since the late Cambrian, and according to Lynas (1973) fault blocks with this trend exercised an important control on sedimentation. Kokelaar (1979) shows that north-south fractures also controlled Rhobell Volcanic Group magmatism. The north-easterly fractures, the most pronounced and best known of which is the Bala fault, have a similar history and influence. Other locally important fault directions are also recognised (see, for example, Bassett, 1958).

The rocks throughout the area have been subjected to low grade regional metamorphism. Dunkley (1978) recognised pumpellyite in volcanic rocks from the Aran Volcanic Group, but in the Cambrian rocks the stable mineral assemblage is characteristic of the low greenschist facies.

It is now generally believed (e.g. Bassett, 1980) that the area evolved in Lower Palaeozoic times as a marginal basin or trough along the south-eastern flank of the lapetus Ocean. A submarine rise or landmass to the north-west appears to have been an active source of detrital sediment, whilst to the south-east the basin margin lay close to and was perhaps controlled by the line of the Towy Anticline. During late Silurian times the final phase of continental collision destroyed the basin and produced the Old Red Sandstone Continent.

Extensive transcurrent faulting during or after continental collision, may have strongly influenced the present disposition of the Lower Palaeozoic rocks on a regional scale (Nutt and Smith, 1981).

MINERALISATION

Mineral deposits in the Harlech Dome may be divided into three broad groups on the basis of age and style: bedded ores, disseminated 'porphyry type' mineralisation and vein deposits. The old mines, which exploited either vein deposits of gold and sulphide minerals or bedded ores, were relatively small-scale operations which flourished in the nineteenth century. Many had crushing plants and tips sited close to streams and these represent a major source of contamination to the stream sampling programme. The sites of all known workings are shown in Figure 3.

Bedded deposits

Situated about 9 m above the base of the Hafotty Formation the manganese ore bed, some 50 cm thick, has been mined at many points (Woodland, 1939; Mohr, 1959; Mohr and Allen, 1965). The ore is of low grade and cherty appearance, and consists of a fine intergrowth of rhodochrosite and spessartite with disseminated hematite, pyrolusite and secondary todorokite (Glasby, 1974). The black manganese oxides in the weathered zone contain 20 to 30 per cent Mn and were mined opencast on a small scale with the total production 1892-1928 quoted as 45 000 tons. Internal structures (Woodland, 1939) suggest that the ore was formed as a colloidal gel, with diagenesis and low grade metamorphism responsible for the present mineralogy. Large amounts of ore remain in the ground but the thinness of the bed, remoteness of outcrop, low grade of the ore, steep dip of the rocks at many localities and National Park considerations all preclude economic exploitation.

Manganese rich horizons also occur within the Gamlan Formation, as thin beds, lenses and nodules of spessartite-quartz-chlorite rock, but individual beds are very thin and they are only known to have been worked at Ffridd-llwyn-gurfal (Dewey and Dines, 1923).

Bedded, pisolitic iron ores outcrop in the north of the survey area near Porthmadog and in an ENE trending belt south of Dolgellau (Pulfrey, 1933). Deposits occur at different horizons; the age of the Cader Idris ores was identified as Llandeilian by Cox (1925) whilst the eastern-most bed in this belt, at Tyllau Mwm, is near the base of the Melau Formation of the Aran Volcanic Group and hence of Llanvirn age. Individual ore bodies are generally small, though some horizons are more persistent than others. The ores consist of chloritic ooliths, variably replaced by siderite, magnetite, pyrite and secondary chlorite, in a chloritic or sideritic mudstone matrix. The ironstones are associated with chloritic mudstones, ferruginous and oolitic mudstones, limestones and sandstones. The complex mineralogy and textures seen in some deposits, such as Tyllau Mwm, indicate a complex history involving chamositic ironstone formation in lagoonal conditions and subsequent reworking under turbulent conditions, followed by recrystallisation and remobilisation to form veins and veinlets during folding and regional metamorphism. The iron content of the ore averages 45 per cent and the ore beds, which are much disturbed by folding and faulting, were exploited by shallow open workings and small levels (Dunham and others, 1982). No details of production are known but the size of the workings indicate that only small amounts of ore were extracted in this area.

Disseminated sulphide ores

Proved but not worked disseminated copper mineralisation is located at Coed y Brenin. It has been described by Rice and Sharp (1976) and interpreted by them as of 'porphyry type'. The mineralisation is believed to be associated with the end-Cambrian Rhobell Fawr volcanic episode. The orebody is situated within a subvolcanic intrusive complex of microtonalitic and microdioritic rocks in the root zone of the Rhobell Fawr volcano. The orebody is characterised by a central zone of copper with associated gold and weak molybdenum mineralisation, surrounded by a strong zone of pyritisation and a very weak outer zone of lead and zinc mineralisation. Phyllic alteration, roughly coincident with the copper mineralisation, is surrounded by a wide propylitic alteration halo. Potassic alteration is absent except for some local development of biotite in the phyllitic rocks (Rice and Sharp, 1976), though weak potassification may have been obscured by a later soda metasomatism overprint (Allen and others, 1976). Allen and others (1979) suggest that within the intrusive complex there are extensions to the proved ore zone or even separate orebodies.

The unusual copper deposit at Glasdir, worked until 1910, has recently been interpreted as a mineralised breccia pipe formed during the same magmatic episode (Allen and Easterbrook, 1978).

Vein mineralisation

Quartz-sulphide veins intersect rocks of all ages in this area. There is a pronounced grouping of gold bearing lodes in the 'Dolgellau gold-belt' which is on the southeast side of the Harlech Dome and extends from Barmouth, through Llanelltyd to Gwynfynydd, roughly coincident with the outcrop of the Clogau Formation. The most prominent mines exploiting these veins were Clogau-St. Davids, Vigra and Gwynfynydd. The latter was the last to close, in 1938. Recently small scale extraction of ore from Clogau- St. Davids has restarted and Gwynfynydd is being rehabilitated.

Detailed studies of the gold-belt veins have been made by Andrew (1910) and Gilbey (1969). In the simplest terms two vein types have been worked for gold:

a) pyrite-pyrrhotite-chalcopyrite with negligible galena and sphalerite,

b) sphalerite-galena-pyrite with minor chalcopyrite.

Among the minor ore minerals identified in the veins are arsenopyrite, mackinawite, cobaltite, tellurobismutite and tetradymite. Native gold occurs either dispersed in quartz or intimately associated with the sulphides. In some places it is present as replacement or exsolution blebs in pyrite or arsenopyrite. Gold analyses by Forbes (1867) show up to 22 per cent silver. In some of the sphalerite-galena-pyrite veins the silver content of galena is high; galena at Cwm Heisian was originally mined for silver. Ineson and Mitchell (1978) reported K/Ar ages in the range 345 to 397 m.y. for potassium rich clay mineral assemblages associated with the mineralisation, which they were unable to relate to a specific geological event. Gilbey (1969) postulated that the gold belt mineralisation was the product of fluids, derived from mixing magmatic and juvenile fluids from a subjacent batholith with connate water, penetrating an open fracture system.

Outside the gold-belt, quartz-sulphide veins have been mined at several localities. At Castell Carn Dochan,

near Llanuwychllyn, a quartz vein cutting the Aran Volcanic Group was worked for gold, lead and silver. The Prince Edward mine near Trawsfynydd is the most northerly in the district at which there is a record of gold mining. The vein cuts Maentwrog Formation rocks and carried gold with galena, sphalerite and minor chalcopyrite. Several veins with a similar sulphide mineralogy were mined or tried in Cwm Prysor and in the Moelwyn Hills where the veins cross-cut both Cambrian and Ordovician rocks. Shepherd (in Allen and others, 1979) demonstrated the feasibility of using fluid inclusions to discriminate between quartz veins associated with vein type and disseminated mineralisation. Details of individual mines, production figures, and the history of mining in the area may be found in a wide range of publications, notably Dewey and Smith (1922). Dewey and Eastwood (1925), Hall (1975), Morrison (1975), Bick (1978) and Foster Smith (1977).

Manganese has been mined from veins in the area around Arenig. Dewey and Bromehead (1915) described the deposits as joints or fissures in volcanic rocks filled with psilomelane and minor pyrolusite. Lynas (1973) however identified the mineral as hollandite, a Ba, K, Na bearing manganese mineral.

SAMPLING AND ANALYSIS

The primary objective of the survey was to identify areas with anomalously high metal levels which might be related to bedrock mineralisation. A second objective was to identify regional geochemical trends. Geological modelling suggested that several types of mineral deposit might be found in the survey area. These included vein, disseminated and massive sulphide deposits as well as stratiform concentrations of ferrous and other metals. Some of these deposits, notably massive sulphide ores, often have a very small surface expression even when not masked by overburden, whilst others yield a weak geochemical dispersion halo, so, ideally, a high sample density was required to aid detection. Limitations imposed by drainage density as well as by cost resulted in a sampling pattern yielding 1 sample per km² in areas of adequate drainage, with a higher density over the Ordovician volcanic rocks where massive sulphide deposits were most likely to occur, and a lower density over the sedimentary rocks of the Harlech Grits Group. The exact position of each site was chosen on the ground to avoid contamination and to optimise the heavy mineral content of the sample. The central part of the stream was sampled to minimise the amount of locally derived bank material in the sample.

Orientation studies in the Harlech Dome and previous surveys elsewhere in North Wales had shown that collection of more than one sample type at each site greatly increased the information which could be gained from the survey. During this survey three sample types were collected at each site: the -0.15 mm fraction of the stream sediment, a heavy mineral concentrate, and a water sample. The heavy mineral concentrate can be examined mineralogically and in conjunction with the analytical results from the other sample types greatly aids the identification of anomalous results caused by contamination, mineralisation, hydrous oxide precipitates and other geochemical processes (e.g. Cooper and others, 1982). Water samples were collected principally as a means of delineating areas of disseminated copper mineralisation similar to Coed y Brenin, which previous study had shown to be most clearly defined by this method (Peachey, Cooper and Vickers, 1980).

Eight hundred and eighty eight sites were sampled, yielding an overall density of 0.85 sample per km². Coverage was poorest in the western coastal belt (<0.5 sample per km²) and greatest in the Lower Ordovician volcanic belt (>1 sample per km²). The samples were collected using methods described in detail elsewhere (Plant, 1971; Leake and Smith, 1975; Allen and others, 1979). Briefly, water samples were collected in 30 ml polyethylene bottles, acidified in the field with 0.3 ml perchloric acid to prevent sorption of metals onto

the container walls, and analysed for copper, lead and zinc by Atomic Absorption Spectrophotometry (AAS) without further sample preparation. Detection limits, were approximately Cu and Zn 0.01 ppm, Pb 0.05 ppm. Stream sediments were wet sieved at site to pass -100 mesh BSS (0.15 mm nominal aperture) using a minimum of water in order to retain the clay and silt fraction. In the laboratory samples were dried and finely ground prior to analysis. Copper, lead and zinc were determined by AAS following digestion of a 0.5 g subsample in boiling concentrated nitric acid for one hour. Arsenic was determined by X-ray fluorescence spectrometry (XRFS) on a pellet prepared by grinding a 12 gsubsample with 3 g of 'elvacite' binder in a 'tema' swing mill and pressing the resulting powder in a die. Other elements were determined by Optical Emission Spectrography (OES). Detection limits were approximately Mo 1 ppm, As 2 ppm, Cu 3 ppm, Pb and Zn 5 ppm, Cr, Co, Ni and V 10 ppm, Zr 20 ppm, Mn 50 ppm, Ba 100 ppm and Fe 0.5 per cent. Panned concentrate samples (approx. 50 g) were made at site from about 4 kg of the -8 mesh BSS (2 mm nominal aperture) fraction of the stream sediment. In the laboratory these were dried and split, and a 12 g subsample was ground in a 'tema' mill for 15 mins with 3 g of 'elvacite' before pelletising and analysis by XRFS for a range of elements. Theoretical detection limits (2σ) were Zn 3 ppm, Ni 5 ppm, Cu and Mn 6 ppm, Sn 9 ppm, Pb 13 ppm, Ce 21 ppm and Ba 27 ppm. Improvements in XRFS prior to the determination of many samples resulted in lower

detection limits than those quoted. Gold was determined on a series of panned concentrates made from twice the normal amount (two panfuls) of -2 mm stream sediment by neutron activation analysis following the method described by Plant, Goode and Herrington (1976). In every case the whole concentrate (c.50 g) was irradiated and counted to minimise the sub-sampling problems associated with gold analysis. The detection limit was 0.02 ppm.

Studies were made of all three sample types to establish sampling and analytical variation by duplicate sampling and replicate analysis. In addition replicate sampling of four contrasting sites was carried out over a fifteen month period to establish seasonal and within site variation. The results form part of a separate study to be . presented in a later report.

RESULTS

Analytical results are given on fiche (Appendix 3, back pocket) with a summary in Table 4. For results below the detection limit the actual value reported was used in all calculations, except in the few cases where this was negative when it was set to zero. The two elements reported for which results are most affected by this truncation are Mo in stream sediments and Sn in panned concentrates. The results for four elements, Cu, Pb and Zn in water and Sb in panned concentrate, were removed from the data matrix prior to computer processing because a very large proportion of the results were below the detection limit, and consequently they are not

 Table 4
 Summary of analytical results for stream sediment and panned concentrate samples.

	Median	Mean	Geometric Mean	Maximum	Minimum	Geo. Mean +2 Geo. Dev.	Skewness
Stream Sedim	ents						
v	112	119	110	749	17	263	3.96
Cr	60	68	59	955	<10	195	8.73
Mn%	0.67	1.35	0.72	14.8	0.04	6.61	3.31
Fe%	6.1	6.4	6.0	19.6	1.25	11.48	1.37
Co	56	85	57	598	<10	347	2.23
Ni	45	56	45	652	<10	162	5.03
Cu	25	64	26	4000	<3	166	10.85
РЬ	60	104	-69	6300	<5	263	15.33
Zn	200	328	229	3400	30	1148	3.66
As	47	80	51	2000	4	282	7.88
Мо	1	2.2	2.3	66	<1	9.8	8.93
Ва	460	530	457	5748	13	1318	5.33
Zr	282	337	295	2020	7	851	2.81
Panned Conc	entrates						
Ti%	0.67	0.74	0.64	4.98	0.12	1.77	3.48
Mn%	0.13	0.20	0.14	6.48	0.01	0.65	10.31
Fe%	7.1	7.0	6.61	23.0	1.26	13.8	1.21
Ni	31	33	28	152	<5	93.3	1.31
Cu	14	54	16.2	3299	<6	224	9.14
Pb	35	94	41	8187	<13	407	15.93
Zn	132	177	135	9659	19	447	19.70
Ba	448	476	417	8444	35	1148	11.62
Sn	<9	32	<9	2389	<9	178	10.70
Ce	352	3750	447	149800	<21	25700	6.59

Results in ppm except where indicated. 888 samples

shown on the computer-generated fiche (Appendix 3). Ba values in panned concentrate are suppressed where Ce levels are very high because of a Ce line overlap onto the Ba background counting position. Consequently, when Ce levels are >c.2000 ppm, Ba values are probably erroneous. Enhanced Pb and Ni levels are also reported from panned concentrates containing very high Ce, due to line overlap from other rare earth elements.

For conciseness in the text, results for sediment, panned concentrate and water samples are differentiated by the subscripts s, p and w after the symbol of the element concerned. For example 'copper in stream sediment' is abbreviated to Cu_s .

INTERPRETATION Introduction

Statistical treatment of the analytical data was restricted by the bimodal or complex form of most element distributions. The complex forms could not be readily sub-divided into geologically meaningful subpopulations of simple form, and it is clear that the complexity of some distributions is due to other factors besides background geology.

The following approach was employed. Distribution analysis using cumulative frequency curves was used to set threshold levels, define anomalous populations and aid identification of sources of element variation. Regional trends were studied by moving average 'greyscale' and isometric plots superimposed on the known geology. Element associations were examined using correlation and factor analysis, following log-trans-formation of all variables where a distribution of more normal form could be obtained, but the presence of some bimodal and complex distributions resulted in a theoretically unsound database for these parametric techniques. The results were therefore treated with caution, but as the more highly significant element associations were geologically sensible and meaningful they were applied in conjunction with field observation and other available information to assess the cause of anomalies, clarify the behaviour of individual elements, assess the causes of regional trends, and identify catchments worthy of further examination.

Distribution analysis

Histogram and cumulative frequency plots were used to identify element distributions and set thresholds Parslow, 1974; (Lepeltier, 1969; Sinclair, 1976). Apparently simple lognormal distributions are displayed by two elements, Co_s and Sn_p . The majority of variables (Pb, Zn, Ba, Mo and As in sediment and Zn and Mn in panned concentrate) yield approximately binormal plots on logscale probability graphs (Parslow, 1974). In detail these are top-truncated sigmoidal plots, indicating the presence of two lognormal populations. Complete sigmoidal plots, related to two overlapping lognormal populations, are given by Cu_p , Ce_p and Zr_s results. The distributions of four variables, Fes, Vs, Crs and Nip, are interpreted as a combination of a normally distributed lower population and a lognormal higher population. More complex distributions, related to the presence of three or more sample populations, are displayed by Cu, Ni and Mn in sediment and Pb, Ba, Fe and Ti in panned concentrate. Severely bottom-truncated distributions of uncertain overall form are given by $\mathrm{Cu}_W,\,\mathrm{Pb}_W,\,\mathrm{Zn}_W\,$ and Sbp. Other highly bottom truncated distributions are $M\dot{o}_s$ and Sn_p with 32 per cent and 69 per cent of results below the 2 σ detection limit. For all elements, results below the detection limit tend to a normal distribution.

Most elements displaying bimodal distribution possess a lower sample population which can be related to bedrock lithology and an upper population which is generated by mineralisation. Some complex populations can be ascribed to these two sub-groups plus a third population: Pb_p to an additional population related to

contamination; Cus to an additional population related to disseminated 'porphyry style' mineralisation, and Mn_s to an additional population related to hydrous oxide precipitates. Other bimodal distributions, particularly those with a normal lower population, are displayed by elements concentrated in basic rocks and mudstones (Cr_s, V_s, Ni_p, Fe_s) and can be related to a lower population generated by acid to intermediate volcanics, sandstones and siltstones, and an upper group derived from dark mudstones and basic volcanics. Zrs shows the reverse relationship, with the higher population related to the acid rocks. The complex form of Fe_p is related to these sources with an additonal population generated from sulphide mineralisation. The complex form of Ba_{p} is most probably caused by analytical interference, whilst the bimodal Ce_p distribution is related to the occurrence of monazite (see below). The apparently simple distributions of Co_s and Sn_p are thought to be caused by the dominance of a single source of variation: hydromorphic processes on Cos and contamination on Snp.

Definition of anomalies

Threshold levels were set to isolate the samples in the sub-populations related to mineralisation and other sources of high metal levels. For elements yielding sigmoidal or complex logscale cumulative frequency plots the threshold was set where the line deflects significantly (95 per cent confidence level; Sinclair, 1976) from the well defined lower 'background' population. These points are printed boldly in Table 5. As a result of this definition the anomalous grouping will probably contain more than one sample population when

Table 5Threshold levels and class intervals for anomalousresults.

Variable	Percentile Level (Approx.)							
	<90	90	95	97.5	99			
Sediments								
v	155	174	201	242	290			
Cr	70	114	131	143	173			
Mn%	1.39	3.30	4.81	7.40	10.00			
Fe%	8.00	8.74	9.95	11.40	13.00			
Co				321	405			
Ni		110	126	165	235			
Cu	41	66	116	340	860			
Pb	111	141	221	351	781			
Zn	201	691	951	1451	1801			
As	105	162	199	340	600			
Мо					12			
Ba		951	1065	1405	1910			
Zr	441	557	675	900	1200			
Panned Concer	ntrates							
Ti%	0.90	1.12	1.44	2.11	2.65			
Mn%	0.261	0.376	0.659	0.891	1.387			
Fe%			11.2	12.11	15.61			
Ni		55	63	74	90			
Cu	46	71	168	440	950			
PĎ	125	170	310	488	700			
Zn		305	341	435	800			
Ва			830	1000	1300			
Sn	13	59	126	258	501			
Ce	100	7501	18000	32000	69200			

Results in ppm except where indicated

the distribution is complex. It will also contain a proportion of samples from the lower population, particularly at levels near the threshold. By using this method, however, very few samples belonging to the upper 'anomalous' population will be incorrectly classified. In the case of sigmoidal plots approximating to binormal form the break point of the dog-leg was taken as the threshold which, if they represent incomplete sigmoidal forms, is effectively the same point as that defined for sigmoidal plots. These points are also printed boldly in Table 5. For Co_s the threshold was set at the 97.5 percentile level, equal to the mean plus two standard deviations for a perfect lognormal distribution. Because of its role as an indicator of contamination Sn_D was treated as a special case. Naturally occurring levels of tin in this area would be expected to be below the 3 σ detection limit of 13 ppm, so this was arbitarily taken as the threshold.

Above the threshold anomalous levels were sub-

divided into classes on a percentile basis (Table 5) and these classes used in constructing anomaly maps (Figures 4 to 14).

Major sources of element variation

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From statistical analyses, element distribution maps, a comparison of sediment and panned concentrate results and the known behaviour of the elements, the following major controls on element variation were identified.

Bedrock Geochemically, there is a strong contrast in rock composition between the siliceous acid volcanics, sandstones and granites and the silica-poor mudstones, basic intrusions and volcanics. This provides the major source of variation in the data, clearly displayed in factor analysis models where elements in the first factor (V, Ni, Cr, Fe, Ti and Zr) are those with variation closely related to this lithological and compositional spectrum (Figure 15). Consequently, the factor also reflects the

1

Factor	1	2	3	4	5	6	7	8
Loading								
+9						De		Sn _p
+8	۷ _s				Mnp	Bas		
+7	Ni _p Cr _s					Вар		
+6	Fep				Mns			
+5					J			
+4	Ni _s Ti _{p .}					14	Zn _S	
+3	Fes		Zrs		Zr _S Nis	Mos	Ban	Pbn
	Cu _S	Zr _S	5		Zn _s		Ni _s	۲
-3	Mn _s	Cu _s	Ni _p Mo _s Ba _p	Nip Tip Nis Fep Mos	Tip		Zrs ^{Pb} p Nip	
-4				-			Ρ	
-5	Zrs	Zn _s Ni _s Pbs	Zn _s Fe _p Pb _s					
-6	-		Tip		Mos			
-7		Mns						
-8		Fe _s Co _s	Znp	Cus			Cep	
-9	-			Cup				
% Var	25	13	9	8	7	6	5	4
Σ_% Var	25	38	47	55	62	68	73	77

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Figure 15. Factor loading graph constructed from an R-mode eight factor model of the transformed drainage data

major geochemical contrast between the arenaceous Harlech Grits Group and dominantly argillaceous overlying sediments.

Ba shows quite distinctive behaviour, as demonstrated by the factor analysis model (Figure 15). Spatial distribution plots indicate that the variation is at least in part related to bedrock lithology, highest levels showing an association with known concentrations in mudstones and the Rhobell Volcanic Group (Table 6). The independent behaviour is thought to be produced by the involvement of several other poorly defined sources of variation Ba_p, notably, analytical interference affecting hydromorphic processes affecting Bas, and Mn-Ba mineralisation affecting Ba_s and Ba_p . Additionally, detailed work at a prospect near Rhobell Fawr (Cooper and others, 1983) suggests that Ba metasomatism may be the cause of high Bas locally.

Mo variation is also primarily related to bedrock type though some highly anomalous values are generated by mineralisation. Low levels of Mo_s are severely truncated by the detection limit, affecting spatial distribution plots and probably contributing to the apparent lack of correlation of Mo_s with other elements concentrated in argillaceous sedimentary rocks.

Bedrock lithology is also primarily responsible for Ce_p variation which also shows independent behaviour in factor analysis models. Most of the variation, and all the extremely high Ce_p results, are caused by the presence of an unusual distinctive form of monazite found dispersed in Ordovician and Silurian sedimentary rocks of the Welsh Basin. Details of the occurrence, composition and distribution of the monazite are given in Cooper and

Read (1983), Cooper, Basham and Smith (1983), Read (1983) and in the 'Cerium' section of this report.

Hydromorphic processes The levels of many elements in stream sediments are affected by these well documented processes (e.g. Reedman, 1979). Factor analysis models identify them as the second most important source of element variation and imply that the elements affected are Co, Fe, As, Mn, Pb, Zn and Ni. A brown iron-rich precipitate collected from a stream draining known mineralisation in the area was scanned by XRFS and found to contain, besides major Fe, appreciable amounts of Mn, Cu, Zn, Co, Pb, Ni and Cd as well as minor Cr, Ti, Mo, Nb, U, Ag, Rb and As. The amounts of different elements present in a precipitate will be governed by metal availability as well as the precise physio-chemical conditions, but the above list gives an idea of the range of elements that may be concentrated by these processes in the Harlech Dome. Reedman (1979) lists Ca, Co, Ni and Zn as the elements strongly scavenged by Mn hydrous oxides whilst As is strongly scavenged by Fe oxides; Cu, Mo and Pb are weakly scavenged (Nowlan, 1976). Under certain conditions Ni and Cr are also concentrated (Carlson and others, 1978). Pb may also be concentrated locally by its ability to form organometallic complexes.

Distribution analysis suggests that Co_s is the variable whose distribution is most strongly controlled by hydromorphic processes, but bedrock exercises a strong overall control on hydromorphic concentrations at a regional scale. For example, low levels of the elements affected by these processes are found around the Rhinog

No.	1	2	3	4	5	6	7	8	9	10	11
Ti%	-	0.677	0.729		0.305	1.306		0.669	0.124	0.289	-
v	778	165	123	161	-	-	233	-	-	-	212
Cr	61	76	83	25	-	-	51	-	-	-	37
Mn%	0.013	1.17	0.02	0.076	0.124	0.162	0.116	0.210	0.037	0.031	0.11
Fe%	3.36	6.43	6.62	5.35	4.28	8.74	6.95	7.07	1.31	1.40	21.50
Co	10	27	-	16	-	-	27	-	-	-	15
Ni	105	68	27	29	-	-	69	· _	-	-	31
Cu	110	70	13	640	40	20	70	4	14	12	21
Pb	40	-	14	10	10	10	10	16	16	11	25
Zn	40	-	75	50	70	105	100	172	59	37	90
As	58	-	7	9	10	10	4	11	2	3	50
Mo	43	-	<2	6	1	1	2	<2	2	1	4
Ba	8640	750	1180	275	217	178	1260	1073	244	301	219
Zr	-	230	205	-	80	183	-	401	234	287	-

 Table 6
 Analyses of selected rocks from the Harlech Dome.

1. SH 7897 2414 Dark shale from Dolgellau Member, Cwmhesgen Formation (Cooper and others, 1983).

2. Mean of manganese shale analyses (n=7 - 23; Mohr, 1959).

3. SH 8017 2471 Laminated silty mudstone, Aran Volcanic Group (Cooper and others, 1983).

4. Median of 20 mineralised porphyritic microtonalite samples from Bryn Coch c.SH 739 245 (Allen and others, 1979).

5. Median of 27 unmineralised intermediate intrusive rocks into Cambrian strata (Allen and others, 1976).

6. Median of 8 basic intrusions and lavas (Allen and others, 1976).

7. Mean of 2 basaltic andesites from Rhobell Fawr*.

8. Mean of 5 crystal tuffs from the Benglog Volcanic Formation (Cooper and others, 1983).

9. Mean of 15 rhyolitic rocks from the Foel Ddu rhyolite intrusion, Aran Mountains [SH 83 23]*.

10. Mean of 7 rhyolitic lavas and tuffs from the Brithion Formation, Creigiau Brithion, Aran Mountains [SH 84 21]*.

11. Mean of 4 iron ore samples from tips, Tyllau Mwn, Aran Mountains [SH 844 205]*.

* Hitherto unreported analyses by Optical Emission Spectroscopy (V, Cr, Zr) and X-ray Fluorescence Spectrometry (remaining elements) using compressed powder pellets.

Results in ppm except where indicated.

Mountains where peaty soils are strongly developed but the sandstone bedrocks are believed to contain low levels of the elements most affected, whereas high levels are recorded in catchments to the north of Dolgellau where there is an abundant supply of metals from argillaceous and mineralised rocks. Consequently the most conspicuous hydromorphic concentrations are found where the two factors of metalliferous bedrock and peaty upland occur together, and a more precise definition of factor two (Figure 15) would be: elements susceptible to hydromorphic processes concentrated in basic rocks, mudstones and sulphide mineralisation.

Sulphide mineralisation This is most clearly defined by high levels of Cu, Pb and Zn in panned concentrates. High levels of these and other elements in sediment also reflect mineralisation but additional variation is often introduced by hydromorphic processes. Factor analysis models reflect major features of the regional distribution plots in distinguishing between Pb_D + Zn_D and Cu_S + Cu_D. High Cu shows a strong spatial relationship to the outcrop of the Mawddach and Rhobell Volcanic groups, whereas high levels of Zn_p and Pb_p are associated with Upper Cambrian and particularly Aran Volcanic Group Ordovician rocks. Consequently Pbp and Znp show an association with elements concentrated in basic rocks and mudstones and factor three can be interpreted in part as an Aran Volcanic Group association and factor four as a late-Cambrian mineralisation factor (Figure 15).

Manganese mineralisation Bedded and vein Mn mineralisation is closely correlated with Mn_D and Mn_S results, though Mn_S is also affected by hydromorphic processes. No other element determined appears to be closely associated with the bedded mineralisation and only Ba with the vein mineralisation. The latter affects few samples and does not show in statistical analyses of the complete dataset, the Mn_S and Mn_D grouping showing independent behaviour. The apparent negative relationship with Mo_S in some factor analysis models has no obvious geological basis and may in part be a distortion generated by detection limit truncation of the Mo_S data.

Contamination High levels of Sn_p are related to contamination. Element distribution plots show a concentration of all high values close to farms, roads, towns and villages and no relationship to the geology and mineralisation (Figure 14). Contamination of streams is, however, generally weak in this area and the affects of contamination on the data much less than in many areas, for example, Anglesey (Cooper and others, 1982). No other element determined shows a strong association with Sn. A weak correlation exists with Pbp, and some Pbp variation and anomalies are caused by contamination. For elements such as Cu, Zn and Fe, however, any variation due to contamination is clearly small compared with that from other sources and can be disregarded as a major source of anomalies.

Elements reflecting sulphide mineralisation

Copper Clearly anomalous sample populations related to sulphide mineralisation were identified from Cu results in both sediment and concentrate. Consequently the spatial distribution of anomalies is broadly similar in both sample types (Figures 4 and 5). Cu shows distinctive behaviour: Cu_s and Cu_p are closely correlated but show no close relationship with any other element determined (Figure 15).

The regional variation pattern of Cu is demonstrated by the isometric moving average plot of Cu_p (Figure 16). It shows the strong association of high Cu_p levels with the Mawddach Group. Low to moderate levels, with a few isolated highs are found over Ordovician rocks and the Harlech Grits Group. The Cu_s distribution is very similar except that some moderately high levels are



Figure 16: Isometric moving - average plot of copper in panned concentrate results

reported from catchments draining Ordovician rocks in the north and north-west of the area.

A particular feature of both Cu_S and Cu_D background variation is the change across the Bala faultline from low levels over the Aran Volcanic Group rocks in the Arenig-Arans belt to somewhat higher levels in the Cader Idris block.

Copper anomalies are derived from a variety of sources though the anomaly pattern is dominated by two: the disseminated copper mineralisation at Coed y Brenin and the 'gold belt' vein mineralisation. The Coed y Brenin mineralisation, enhanced by locally exploited vein mineralisation in the same catchments, generates the largest anomalies with long dispersion trains in the catchments of the Afon Wen and Afon Mawddach, for example at SH 7350 2510 (No. 629) and SH 7400 2330 (No. 613). The very large anomalies are promoted by:

- (i) the disseminated form of the mineralisation and hydrothermally altered, fractured, easily weathered, nature of the host rocks;
- (ii) the large area of mineralised rock at surface;
- dispersion of mineralised rock by glaciation processes;
- (iv) acid groundwater, which, promoted by the breakdown of pyrite in and around the mineralisation, aids dissolution of chalcopyrite and brings appreciable Cu into solution.

The precise area of copper mineralisation is poorly defined by Cus and Cup because anomalies are very large, dispersion great, and misleading patterns are produced by the relative proportions of detritial and hydromorphically redistributed Cu in samples (see 'signatures of mineralisation'). Cold extractable Cu in sediment (Rice and Sharp, 1976) or Cu in water (Peachey, Cooper and Vickers, 1980) have much shorter dispersion trains and Cu in water in particular defines the area of Cu mineralisation more precisely. Cu anomalies from the disseminated mineralisation are associated with large Fe_D and Fe_S anomalies, derived mainly from the pyrite halo, and high Mos and Ass. Because Mos and Ass anomalies may be formed from other sources, such as mudstones, the characteristic disseminated copper mineralisation signature here is defined as large Cus and Cup anomalies with high Cuw locally. High Mos, Ass, Fe_s , V_s and Fe_p without high Cr_s , Ni_s and Ni_p are also found. The disseminated mineralisation may be distinguished from the gold-belt vein mineralisation in which it occurs by the absence of Pb and Zn anomalies.

Copper anomalies related to 'gold-belt' style vein mineralisation may be traced in a semi-circular arc coincident with the outcrop of the Mawddach Group from Barmouth, through Llanelltyd, Ganllwyd, east of Trawsfynydd, Maentwrog to north of Harlech (Figures 4 and 5). Typical anomalies include those downstream of Prince Edward Mine (e.g. SH 7388 3830, No. 395) and Voel Ispri (SH 7070 1968, No. 3031). Anomalies in the southern part of the belt are disproportionately few with respect to the known occurrences of mineralisation because of biased sampling away from streams known to be contaminated by old mine workings. Anomalies are characterised by high levels of Cu associated with high or anomalous levels of Pb, Zn, As and, where determined, Au. High levels of V, Cr and Ni derived from the Clogau mudstones may also be present, and some weak Cus anomalies in the southern part of the belt may be derived from the mudstones and not vein mineralisation. An association with Mn anomalies is usually attributable to the outcrop of Hafotty Formation as well as Mawddach Group rocks in the upstream catchment (for example at SH 6666 1988, No. 132). Some Mn anomalies may, however, originate in Clogau Formation mudstones or basic intrusions.

Many Cu anomalies over the Mawddach Group are not attributable to known mineralisation. The existence of Cu and associated anomalies around the northern part of the Dome in the Trawsfynydd-Maentwrog-Talsarnau area suggests a continuation of gold-belt style vein mineralisation into this area which is not evident from known records. Some weak Cu anomalies in this area may be derived from metalliferous sedimentary rocks (see 'Lead and zinc') but Au analyses showed the presence of anomalies in the area and field observation located several poorly documented trials and workings in mineral veins. The largest Cu anomaly in this area is in a panned concentrate from Eisingrug (SH 6148 3438, No. 176). The site is contaminated but an anomalous gold level was reported and resampling revealed further anomalies in the upstream catchment (Figure 17).

Large Cu anomalies unrelated to past mining activity occur in the catchments of the Afon Prysor and Afon Gain, to the south-east and east of Trawsfynydd (Figures 4 and 5). Many of the anomalies contain intermediate intrusions in their catchments which are believed to be broadly co-magmatic with that hosting the Coed y Brenin mineralisation (Allen and others, 1976). The anomalies are, however, not thought to be derived from disseminated mineralisation as most are associated with anomalous Pb or Zn and a range of other metals, but not Mo (Figure 12). The area drained by these anomalies was the subject of follow-up investigations arising from an airborne geophysical survey (Allen and others, 1979). To summarise briefly, at Glanllafar [SH 73 36], Craiglaseithin [SH 73 32] and Dol Haidd [SH 76 36] soil sampling, ground geophysics and geological mapping were carried out. At Mynydd Bach [SH 74 31 and Waun Hir [SH 74 32] very limited follow-up work was carried out because of the danger posed by buried explosives remaining from an old artillery range. In all of these areas weak vein mineralisation was identified as a cause of geochemical anomalies. In addition weak metal sulphide enrichments in mudstones were found at Mynydd Bach and Glanllafar and local, weak disseminated mineralisation in tonalitic intrusions at Craiglaseithin and Dol Haidd. At Waun Hir the presence of mineralisation of uncertain style associated with a poorly exposed intermediate intrusive was also suspected. At Waun Hir and Mynydd Bach contamination from pig bristle drying, cordite burning and ironmongery was identified as a major cause of stream anomalies. Where exposed the intermediate intrusives do not show the alteration characteristic of a porphyry system and the intrusions have a sill-like rather than stock-like form. These features, coupled with the drainage survey results and conclusions from the airborne geophysics follow-up work, suggest that no well developed porphyry style mineralisation is located near surface in association with these intrusions.

Immediately to the north of Coed y Brenin, at Hafod Fraith, a Cu_S anomaly is only accompanied by anomalous Zn_S (SH 7480 2748, No. 3014), and nearby another Cu anomaly draining the same area (SH 7440 2728, No. 3088) is accompanied by high Mo_S and anomalous As_S and Cr_S. Investigations (Allen and others, 1979) suggest that these anomalies are related to disseminated mineralisation in intermediate intrusions and could possibly represent a fault controlled extension of the Coed y Brenin mineralisation. To the south of Coed y Brenin, in the Nannau area, geological parameters suggest a similar favourable area for disseminated mineralisation but stream cover is so poor that a metalliferous concentration here would easily escape detection.

Groups of copper anomalies can be attributed to other sources besides vein or disseminated sulphide mineralisation. Several, generally weak, anomalies in both sediment and concentrate samples are accompanied by a wide range of other metal anomalies, notably Mo, V, Ni and Ba, and have Cwmhesgen Formation rocks in their catchments. Analyses of dark mudstones from this formation (Table 6, No.1; Cooper and others, 1983) show that they are the source. The most prominent anomalies of this type are at Cwmhesgen (SH 7881 2918, No. 3010 and SH 7930 2882, No. 3068). Other anomalies attributed to this source are located in the Dolgellau-Rhydymain area, such as at SH 7204 1763 (No. 2414), SH 7862 2032 (No. 508), SH 7831 2415 (No. 784) and SH 8484 2519 (No. 527). In all these cases basic intrusions or Rhobell Volcanic Group rocks are also found in the catchments and may actively contribute to the anomalies. At most sites Cu anomalies are of small magnitude (<100 ppm Cu) and within concentrations typical of dark mudstones, but the catchments of some of the larger anomalies, for (No. 488), merit SH 7890 2369 further example investigation (see 'Barium and 'Nickel, chromium and vanadium'). Two isolated anomalies in the north of the (SH 7648 4788, No. 2258 and SH 7670 4730, area No. 2246) show similar groupings of anomalous elements and bedrock.

Several Cu anomalies, often accompanied by high levels of V, Ba, Fe and Zn, occur in catchments draining the Rhobell Volcanic Group. The most prominent anomalies in panned concentrate appear to be at least enhanced by contamination: that at Llanfachreth (SH 7559 2258, No. 502) by household waste and that near Hendre (SH 7639 2676, No. 588) by hardcore from the Coed y Brenin mineralised zone in a forest road by the stream. Additional drainage samples and a suite of Rhobell Volcanic Group rocks were collected from the area east of Hendre [SH 77 26] whilst investigating airborne geophysical anomalies (Allen and others, 1979). The drainage anomalies were confirmed and although moderate levels of Cu were reported in the rocks (median 80 ppm, range <3 to 190 pm, 51 samples) they were not exceptional for basaltic andesites and it was not clear whether they represented the source of the Cu anomalies. V, Zn and Fe anomalies in the drainage samples equate with levels typical of basaltic rocks but Ba levels are exceptional and some form of Ba enrichment is suspected (see 'Barium'). Secondary malachite and pyrite are the only indications of mineralisation known in the catchments of these anomalies. It is, therefore, uncertain whether the Cu anomalies $% \left({{{\mathbf{r}}_{i}}} \right)$ reflect a background of basaltic rocks, distinct hitherto undetected mineralisation, a primary weak enrichment in the volcanics reflecting a metallogenetic association with the Coed y Brenin mineralisation, or an outer halo to that mineralisation.

Four groups of anomalies where Cu_S is greater than Cu_p may be due to enhancement by hydromorphic precipitation and scavenging processes. They are:-

- (i) A group of weak Cu_s anomalies in the Afon Artro, for example at SH 6218 2998 (No. 190), where rocks such as 'the Hafotty Formation provide a source of metals, Mohr (1959) reporting 5 to 300 ppm Cu in the Manganese Shales (see 'Lead and zinc').
- (ii) In the extreme north-west of the area, in the Afon Croesor and Afon Maesgwm, Cu_S anomalies are associated with a wide range of high metal values in stream sediments. It is most probable that they are derived from the sheared Glanrafon mudstones or associated volcanics and enhanced by hydromorphic processes, though unknown mineralisation in the catchments is another possible source which deserves further investigation.
- (iii) In a series of streams running south-westwards over Aran Volcanic Group and Mawddach Group rocks to the south and east of Blaenau Ffestiniog Cu_s anomalies are accompanied by a wide range of metal anomalies in sediment and weakly anomalous Cu_p . Anomalies are probably enhanced by hydromorphic processes and mudstone bedrock, but mineralisation is the source of at least some of the anomalies as pyrite was frequently observed in the pan, old Pb-Zn-Cu workings are recorded at Gamallt [SH 7378 4368], (Figure 3) and Lynas (1973) recorded the presence of a brecciated crystal tuff carrying up to 10 per cent chalcopyrite upstream of the anomalies at SH 7324 4462 (No. 2154) as well as quartz vein mineralisation at several localities.

(iv) Streams draining into Cwm Cynfal north of Hafod Fawr contain several weak Cu_s anomalies accompanied by high Cr_s or Zn_s . They are attributed to a high background enhanced by weak vein mineralisation, similar to that containing chalcopyrite tried at SH 7388 4170 (Figure 3), and hydromorphic processes. Some, for example at SH 7348 4112 (No. 2027), may be caused by contamination.

Moderate to large Cu anomalies in sediment and concentrate to the north-east of Penrhyndeudraeth such as at SH 6345 4132 (No. 2071) and SH 6766 4447 (No. 2105) are accompanied by high levels of Pb and Zn and caused by vein mineralisation exploited in the catchments. More detailed sampling would be required to ascertain if there is a contribution from unknown mineralisation.

Isolated anomalies occur at a few sites, particularly the Cader Idris area. Only one of these, at in SH 6254 1241 (No. 2520), is readily explained: it is downstream of an old mine working. Anomalies to the south of Dolgellau show an association with the Ffestiniog Flags Formation, Cwmhesgen Formation, Rhobell Volcanic Group and basic intrusions. Vein mineralisation marginal to the basic intrusions is one of many possible causes of the anomalies. Other isolated anomalies occur over the Llanbedr Group at SH 6918 2502 (No. 73) and Upper Ordovician sedimentary over rocks at SH 7944 4878 (No. 2270), SH 8336 4962 (No. 2182), SH 9045 3892 (No. 2280) and SH 8932 4016 (No. 2005). The latter two anomalies are near a main road and contain high levels of Snp which suggests that contamination may be the cause.

Gold Samples were not routinely analysed for Au; but to test the association of As with Au, and the theory that gold-belt mineralisation extends around the north of the Dome into the Talsarnau-Maentwrog area, a series of panned concentrates were collected and analysed for Au. The results are shown on Figure 17.

Au results greater than the detection limit (0.02 ppm)are considered anomalous. No other elements were determined on the gold samples and comparison with the results of routinely collected samples from the same sites show no strong correlation (Spearman-rank) of gold with any other element determined. Arsenic, the element most likely to show a strong association was not determined in concentrates and As_S results show no significant correlation with Au values, but this does not necessarily preclude an Au-As relationship in the rocks. There are several other possible explanations for this lack of correlation:

- As_s concentrations are strongly influenced by hydromorphic redistribution;
- (ii) a large number of the Au results were below the detection limit, severely limiting comparison of results;
- (iii) gold sampling frequently gives rise to erratic results on small samples because of its occurrence in a small number of discrete grains.

All anomalous gold results are in streams running along north-east or north-west trending faultlines and several are sited close to the intersection of these two directions. Upstream of the highly anomalous site at SH 6430 3678 in the Afon y Glyn extensive old mine workings were located. These apparently exploited a north-west trending vein parallel to the stream and a second vein intersecting it at right angles. Galena, sphalerite, arsenopyrite and pyrite were found in the stream. Upstream of the largest anomaly (1.82 ppm Au at SH 6700 3822) carbonate and quartz veining, locally carrying chalcopyrite, was identified. At none of the other anomalous sites was a plausible source for the gold located, though old mine workings [SH 603 333] are located to the west of anomalies in the Afon Eisingrug. At a few sites individual grains of gold were identified in the pan but it is not known whether most of the Au occurs free or whether some is combined with sulphides.



Figure 17: The location of gold in panned concentrate anomalies in the Maentwrog – Talsarnau area

Also it is not proved, though it appears most likely, that vein mineralisation is the source.

Although Au was not determined in any other samples, known occurrences suggest a widespread distribution in streams eroding Mawddach Group rocks in particular. High values may be predicted for the Afon Wen, as the Coed y Brenin mineralisation contains appreciable Au, and the Afon Mawddach, where Au was recorded in the pan and which contains many Au bearing veins in its catchment. Au was not seen in panned concentrates collected elsewhere in the area, though acid volcanic rocks in the Ordovician are considered a potential host for gold mineralisation and worthy of more detailed study from this viewpoint.

Lead and zinc Lead and zinc in both sediment and concentrate show a broadly similar regional distribution. Pb_W results were invariably below the detection limit except in streams draining some old mines and no regional pattern could be discerned. Znw results also gave no clearly recognisable regional pattern, though locally very high values could be related to old mine workings and moderate levels to peaty upland environments. Very low levels of Pb and Zn in sediments and concentrates are typical of catchments containing rocks of the Harlech Grits Group. The only exception is found in the north and west of the outcrop where moderate to high levels of Zns show an association with Mn anomalies. A moderate to high background with some highly anomalous areas is characteristic of Mawddach and Aran Volcanic group terrain. Zns levels show a relative decrease over the Upper Ordovician and Silurian

sedimentary rocks. The main lithology considered responsible for the high background is mudstone with levels of Zn enhanced by basic and Pb by acid volcanic rocks (Table 6). These major trends, produced by lithological variation, have other sources of variation superimposed on them, generating lows and highly anomalous areas over the Upper Cambrian and Lower Ordovician rocks. A fundamental lack of these metals in much of the Harlech Grits Group is considered responsible for a very low background and any 'superimposed' variation here is, relatively, of much lower magnitude and less obvious. The most prominent of the superimposed sources of variation is redistribution of metals in the weathering zone by hydromorphic processes: both Zns and Pbs are strongly affected. Virtually all areas of high Pbs are in low ground marginal to the principal upland areas of Upper Cambrian-Lower Ordovician rocks, for example in the Vale of Ffestiniog and in the catchments of the Afon Wnion, Afon Mawddach - Afon Gain and Afon Tryweryn (Figure 18). The distribution of Zns is similar except that high values are concentrated over high ground as well as the margins. Some Pb_p and Zn_p anomalies are caused by known mineralisation. Other Pb_p anomalies are caused by contamination. These are characterised by $Pb_p > Pb_s$ and accompanying anomalous Sn_p . They occur in a belt along major roads following the Sn_p distribution (Figure 14). Another source of superimposed variation is analytical interference: several anomalous Pb_p results in the east of the area are generated by the very high concentrations of rare earth elements in the samples. The regional distribution of Pb and Zn is quite



Figure 18: The location of high levels of lead in stream sediment with respect to high ground

distinct from Cu. Levels of all three metals are low over the Harlech Grits Group and increase dramatically over the Mawddach Group, but whereas high levels of copper are virtually confined to outcrops of this group and intrusives into them, high levels of lead and zinc persist across Ordovician rocks. This difference is believed to be of fundamental importance with respect to metallogenesis and, consequently, exploration in the area. High levels of copper (and gold?) have sources related to metalliferous sedimentary rocks and intermediate intrusions in the Cambrian, whilst lead and zinc have an additional, and perhaps their principal, source in Lower Ordovician volcanics and mudstones. This difference may be connected to a change in tectonic setting, late Cambrian magmatism taking place in an island arc environment, whereas Ordovician rocks formed in a marginal basin setting.

The most prominent groups of Pb and Zn anomalies are related to known or suspected mineralisation. Zn_p and Pb_p did not detect areas of worked mineralisation efficiently, sediment data proving more effective. For example sites downstream of Prince Edward Mine [SH 744 386] yield large Pb_S and weaker Zn_S anomalies but no Zn_p or Pb_p anomalies (Figures 6 to 9). This behaviour is considered surprising and the reasons for it uncertain, but they are presumably connected with the rapid breakdown of detrital galena and sphalerite. An Lshaped group of anomalies in the catchment of the Afon Mawddach from SH 7365 2685, downstream of Gwynfynydd Mine, to SH 6512 1818, west of Bontddu, is derived from the mine workings in the 'gold-belt'. The source of a large group of anomalies in the catchment of the Afon Gain was investigated during a previous study (see 'Copper' section and Allen and others, 1979) where it was concluded that Pb-Zn anomalies are derived from known mine workings, hitherto undetected vein mineralisation, contamination and hydromorphic processes. A large group of anomalies to the east of Ffestiniog, mostly in the catchments of the Afon Teigl and Afon Gamallt are partly caused by contamination and worked vein mineralisation, but the extent of the anomalies and favourable nature of the bedrock suggests that further mineralisation, perhaps related to volcanism, may exist and the area is, therefore, worthy

of further study (see also 'Copper'). West of Ffestiniog, in the area between Llanfrothen and Afon Croesor, large anomalies related to old workings are located at SH 6318 4064 (No. 2074) and SH 6345 4132 (No. 2071). Others have no obvious source and are worth further investigation, although some at least are enhanced by contamination (e.g. SH 6174 4140, No. 2046) or by hydromorphic processes (e.g. SH 6250 4411, No. 2066).

Prominent groups of Pb-Zn anomalies accompanied locally by high levels of Mn_s , As_s , Fe_s and Fe_p in the catchment of the Afon Wnion were investigated. Those near Benglog (e.g. SH 8071 2404, No. 649) are caused in part by Pb-Zn vein mineralisation but the possibility of stratabound volcanogenic metalliferous concentrations in the vicinity has not been eliminated (Cooper and others, 1983). Geological mapping, soil sampling and geophysical surveys were carried out in Penaran Forest, in the catchments of the anomalies at SH 8448 2724 (No. 537) and SH 8402 2732 (No. 538), and across a wide area on the north-western slopes of the Aran Mountains between SH 85 23 and SH 82 19 where a large number of Pb and Zn anomalies occur (Figures 6 to 9). In both areas indications of volcanogenic mineralisation were found and drilling targets defined on the basis of geochemical and geophysical anomalies and indications of mineralisation, such as blebs of sphalerite in volcanic rocks, seen at surface. Drainage anomalies in both areas are partly the product of hydromorphic processes and, as at Benglog (Cooper and others, 1983), soil analyses proved difficult to interpret because of the widespread redistribution of metals within the weathering zone. Anomalies in the Dyfnant (SH 8484 2519, No. 527) and Afon Mynach (e.g. SH 8279 2516, No. 599) have not been examined but are most probably derived from similar sources. Anomalies in catchments draining the southern side of the Aran ridge have not been investigated. Some are derived from past mining activity, for example the site at SH 8370 1728 (No. 519) is close to Craigwen mine, but others are either caused by further mineralisation or, as may be the case with weak anomalies in the upper reaches of Nant y Graig-wen (SH 8298 1821, No. 2435), a high background and secondary concentration.

Scattered anomalies in the Arenig area have several different causes. A distinct group of weak Pb_p anomalies accompanied by high Mn_p , Ti_p and Ce_p in the Afon Hesgin may be the product of analytical interference, as may some other scattered weak anomalies in the area, for example at SH 8034 3829 (No. 326). At least one Pb_p anomaly, at SH 8158 3746 (No. 327), may be caused by contamination. Some anomalies are associated with Mn-Ba vein mineralisation, for example Zn_p at SH 8302 4003 (No. 345) and Zn_s at SH 8636 4101 (No. 2002). Others, however, have no obvious source and may be related to base-metal mineralisation in the volcanic pile. They include Pb_s , Zn_p and Zn_s anomalies near Arenig Fawr (SH 8509 3922, No. 645) and Pb_s and Pb_p anomalies at SH 8346 4256 (No. 309) in a catchment draining Arenig Fach. These anomalies merit further study.

Several Pb and Zn anomalies occur marginal to the Rhobell volcanic centre associated with a wide range of other metal anomalies. Anomalous sites include those at SH 7831 2415 (No. 784) and SH 7592 2892 (No. 782). The source of these metal anomalies is uncertain and, though indications are weak, mineralisation cannot be excluded (see 'Copper' and 'Barium').

Many weak Zn_s anomalies occur in the west of the area accompanied by Mn and locally Cu, Pb, As, Ba and Ni anomalies. These are attributed in part to secondary, hydromorphic concentration with the source of metals being either vein mineralisation or, most likely, metal-liferous concentrations in the Hafotty and Gamlan formations. With the exception of the Manganese Bed (Mohr, 1959; Mohr and Allen, 1965; Glasby, 1974), these metalliferous concentrations are poorly documented but they may be closely associated with coticule (spessartite garnet-quartz) rocks and merit further investigation.

Other anomalies do not form coherent groupings and

are related to a variety of causes. In the south, large anomalies at SH 6254 1241 (No. 2520) are caused by the old mine workings at Cyfannedd (Figure 3). All other Pb_p anomalies in the Cader Idris block may be caused by contamination, all the anomalous samples containing appreciable Sn and having a plausible source in the vicinity. Most Pb_{S} and Zn_{S} anomalies in this area can be related either to a background lithology or come from sites showing evidence of secondary concentration. There are few indications of mineralisation in the Cader Idris block. Anomalies at SH 6946 1507 (No. 2394) and SH 6736 0880 (No. 2549) are the most likely exceptions if they are not the product of contamination. Pbp anomalies related to high Cep levels are found in the east of the survey area for example at SH 8206 3042 (No. 461) and SH 7891 3169 (No. 456). Zn_{S} anomalies in the upper reaches of the Afon Lliw, for example at SH 7998 3408 (No. 410), are attributed to hydromorphic concentration aided by basic intrusions and Cwmhesgen Formation rocks in the catchment providing an abundant source of metals. Prominent isolated anomalies in the north of the area at SH 6992 4848 (No. 2203), SH 7944 4878 (No. 2270) and SH 7648 4788 (No. 2258) are most probably caused by contamination and mudstone source rocks, though mineralisation may be an additional source of metals.

Elements greatly influenced by hydromorphic processes

Arsenic Arsenic levels in the survey area are exceptionally high compared with those from many other areas, for example the Preseli Hills (median 14 ppm, mean 17 ppm; Cameron and others, 1984). The regional distribution pattern of As_s does not show a close relationship to the geology, though a low corresponds roughly with the outcrop of the lowermost Cambrian in the centre of the Dome and the highest levels occur over Mawddach and Aran Volcanic group rocks, with an ill-defined decrease over the Upper Ordovician and Silurian. The imprecise correlation with lithology is partly caused by hydromorphic redistribution and partly by mineralisation.

Major anomalies (Figure 10) are derived from known mineralisation in the 'gold-belt', for example anomalies downstream of Prince Edward (e.g. SH 7388 3830, No. 395), Cae Mawr (SH 7288 2280, No. 3006) and Voel Ispri (SH 7070 1968, No. 3031) mines. The number and magnitude of anomalies in the vicinity of the Coed y Brenin porphyry style mineralisation reflect the presence of arsenic in this deposit (Rice and Sharp, 1976).

In the area between Prince Edward [SH 744 386] and Gwynfynydd [SH 734 280] gold mines several large As_s anomalies are recorded. Some of these can be related to small trials, for example anomalies at SH 7410 3218 (No. 421) and SH 7685 3496 (No. 303), but others, such as at SH 7819 3348 (No. 3043) have no obvious source. Follow up investigations in the area identified known mine workings, hitherto undetected vein mineralisation, hydromorphic processes and weak sulphide enrichments in mudstones as the sources of As anomalies. The size of the As_S anomalies suggests that either appreciable gold bearing vein mineralisation or metalliferous sedimentary rocks remain undetected beneath the extensive overburden in this area.

In the Migneint area, a broad belt of large As_s anomalies is located over Aran Volcanic Group rocks. It is most likely that the anomalies are the product of secondary concentration phenomena, forming from As rich waters either by chelation or other bonding mechanism with the abundant organic matter found in this peaty terrain, or by co-precipitation with hydrous iron oxides (Boyle and Jonasson, 1973). The anomalies are unusual, however, in that other chalcophile elements are rarely anomalous whereas Cr_s levels are often high. A possible source of the As is in the dark pyritous mudstones, such as those within the Serw Formation (Lynas, 1973). This source would explain the Cr association and the high Fe, Mn, Ti and V levels accompanying many of the weaker anomalies in, for example, the Afon Serw (SH 7842 4188, No. 2128; SH 7770 4270, No. 2160). Some anomalies, however, drain catchments containing a large proportion of volcanic rocks and do not show the Cr-V-Fe-Ti association strongly. These include the most highly anomalous sites, which are in the Nanty Pistyll (927 ppm at SH 7530 4370, No. 2093, and 845 ppm at SH 7504 4286, No. 2094). Here either hydromorphic processes have successfully concentrated and separated arsenic from other elements enriched in dark mudstones, or there is another source of As in the vicinity. This is most likely to be pyritised acid volcanic rocks for they are apparently common (Lynas, 1973) and analyses of pyritiferous rhyolitic volcanic rocks from Carreg y Foelgron quarry [SH 7433 4280] showed weak As enrichment (69 pm) but no enrichment in base metals and low levels of Ti, Fe and Mn. Cr, V, Co and Ni were not determined.

In contrast, As_s anomalies in westward flowing streams such as the Afon Gamallt, immediately to the west of the most highly anomalous sites, show a wide range of associated anomalous elements (Pb, Zn, Ti, Cr, Fe, Mn). The Gamallt mine [SH 738 437] worked Pb-Zn-Cu vein mineralisation reported to be auriferous (Foster-Smith, 1977) and the mine or similar vein mineralisation is a source of anomalies. The range of anomalies, however, suggests that metal-rich mudstones may also be contributors to the anomaly grouping and, as in the catchment to the east, pyritised volcanic rocks are another possible source. Further work is required in the Migneint—Ffestiniog area to clarify the sources of this large belt of As anomalies and the possibility of accompanying gold mineralisation.

Scattered relatively low magnitude (<200 ppm) As_{S} anomalies accompanied by high levels of Zns, Mns, Fes and Cos occur over much of the Upper Cambrian and Lower Ordovician outcrop, and are considered to be generated by hydromorphic processes though this does not necessarily preclude the presence of a metalliferous source. Two anomalies near Llanfrothen (SH 6318 4064, No. 2074 and SH 6345 4132, No. 2071) are downstream of old mine workings but other high As_s results to the north of the Vale of Ffestiniog fall into this category. Old trials and workings in the area suggest that mineralisation or the Glanrafon mudstones are the source of metal. Weak anomalies on the eastern side of the survey area show a similar anomaly association and in many cases metals may be derived from the Cwmhesgen Formation, for example at SH 7914 3297 (No. 433). Anomalies at the type locality of the Cwmhesgen Formation are relatively high (194 ppm at SH 7881 2918, No. 3010, and 153 ppm at SH 7930 2882, No. 3068) and an additional surce of metals is suspected in these catchments (see 'Barium') and others to the south of the Rhobell volcanic centre (e.g. SH 7890 2369, No. 488 and SH 7831 2415, No. 784). The source of the large anomaly at SH 8176 3231 (No. 479) is uncertain. The two groups of anomalies on the north western slopes of the Aran Mountains are in an area with mineral potential (see 'Lead and zinc'). One group of anomalies (e.g. SH 8304 2087, No. 532) contain Cwinhesgen Formation rocks as well as pyritic acid volcanics and weak vein mineralisation in their catchments. The Cwmhesgen Formation rocks have not been analysed but the pyritic volcanic rocks and vein mineralisation contain only low levels of As (<14 ppm). The second group of anomalies (SH 8440 2150, No. 545 and SH 8449 2154, No. 546) have catchments containing pyritic, rhyolitic breccias of the Brithion Formation which hereabouts contain elevated levels of As (<136 ppm) and represent the only rocks analysed from this sub-area which show appreciable As enrichment. The cause of the two prominent isolated anomalies (Figure 10) on the Cader Idris range is uncertain.

In the Maentwrog—Talsarnau area there are only two anomalous sites, at SH 6470 3658 (No. 168) and SH 6478 3642 (No. 167). Both are in a catchment which subsequently yielded appreciable Au_D , but with the exception of these two sites there is no evidence from the As_s results for the continuation of the 'gold-belt' into this area (Figure 10) and correlation between Au_p and As_s results is poor. The possible reasons for this are discussed above (see 'Gold'), but the contrast with the Llanelltyd—Prince Edward part of the 'gold-belt', where large As_s anomalies are derived from old mine workings, is striking. The absence of As_s anomalies in the Barmouth—Llanelltyd area can be accounted for largely by biased sampling away from mine workings. The absence of anomalies in both the north and the south part of the 'gold-belt' destroys any close regional pattern between As_s results and known gold mineralisation.

Cobalt and iron in stream sediment The distribution of these elements is controlled by bedrock lithology and hydromorphic processes. Regional scale features are attributable to bedrock whilst anomalies occur where the two factors work in harmony. The distribution of Fe_s is quite distinct from Fe_p whose dispersion pattern is strongly influenced by detrital minerals derived from basic igneous rocks in the Cader Idris area and the pyritic halo of the Coed y Brenin mineralisation.

Both Co_s and Fe_s have a high background and many scattered anomalies are developed over the Mawddach and Aran Volcanic groups, where mudstones, basic volcanics, locally developed sedimentary iron ores and basic intrusions outcropping in peat covered upland areas provide a source of metals.

High or anomalous concentrations are associated with: $\label{eq:concentration}$

- (i) intermediate intrusions, mudstones and vein mineralisation in the Prince Edward—Afon Gain area investigated earlier (Allen and others, 1979);
- Glanrafon Group sedimentary rocks and associated intrusions in the belt north-east of Llanfrothen (Fearnsides and Davies, 1944);
- (iii) Aran Volcanic Group rocks in catchments draining northward from Arenig Fach;
- (iv) Aran Volcanic Group rocks and associated mineralisation, perhaps enhanced downstream by Mawddach Group mudstones, in the Afon Gamallt area, north-east of Ffestiniog;
- Mawddach and Aran Volcanic group rocks on the north-west slopes of the Arans and in Penaran Forest, two areas which have been the subject of further work (see 'Lead and zinc');
- (vi) basic volcanic rocks and intrusions south-west of Cader Idris;
- (vii) oolitic ironstones, notably at Tyllan Mwn.

Both elements are generally low over outcrops of the Harlech Grits Group, which in view of the good conditions for secondary scavenging processes, infers very low levels in bedrock. No anomalous grouping is associated with the Manganese Beds, confirming the results of Mohr (1959) who found no particular Co enrichment in the Manganese Shales (<2-68 ppm Co). Three isolated Co_s or Fe_s anomalies are found over the Harlech Grits Group at SH 6686 3357 (No. 231), SH 6738 2130 (No. 3074) and SH 6218 2998 (No. 190). Their source in uncertain but associated anomalies suggest that the latter two may be derived either from vein mineralisation or metalliferous horizons within the Hafotty Formation.

The distribution of the two elements is dissimilar in a few areas. The most prominent are the high levels of Fe_S in the Afon Serw (Migneint) where Co_S is very low and around Llyn Arenig Fawr (e.g. SH 8530 3762, No. 2305) where a similar situation is found. The contrast may be caused by the differing physico-chemical conditions of precipitation of hydrous Fe and Mn oxides. Both Fe_S and As_S are high over Migneint whilst Zn_S, Ni_S, Co_S and Mn_S are low which fits the observation of Reedman (1979) that Zn, Ni and Co are scavenged primarily by Mn oxides whilst As is taken up by iron oxides. It is possible that Fe and accompanying As are fixed locally, causing anomalies in the peaty area whilst Co and Mn are being removed. Availability of As and Fe from the breakdown

of sulphide may, however, be a contributory or alternative explanation. Co_S also shows a less strong association with Cwmhesgen Formation rocks, which is the source of several Fe_S anomalies to the east of Rhobell Fawr (e.g. SH 7881 2918, No. 3010 and SH 7971 2535, No. 3082).

Known concentrations of these elements in bedrock are restricted to the small locally developed oolitic ironstones in the Aran Volcanic Group (Pulfrey, 1933) and weak Co mineralisation in a few of the gold-belt veins (Gilbey, 1969). Iron concentrations of any economic significance are most unlikely but the possibility of a primary Co enrichment in one of the anomalous areas cannot be eliminated because, although no obvious targets such as ultrabasic rocks are known, few analyses of Co are available. Those that are published suggest no unusual enrichment in mudstones of the Hafotty Formation (Mohr 1956, 1959), Cwmhesgen Formation or Y Fron Formation (Cooper and others, 1983). Follow up investigations found no evidence of substantial Co enrichment in mineralised, pyritic or other rocks, though in several of the areas investigated Co was not determined (Table 6; Allen and others, 1979). Highest results were from a quartz-sphalerite-chalcopyrite-pyritechlorite vein at Blaenau Ffestiniog (250 ppm), a Prince Edward Mine vein sulphide concentrate (236 ppm) and a sphalerite-pyrite vein (105 ppm) in Cwmhesgen Formation rocks in the Aran Mountains [SH 8309 2069]. Therefore, despite the high levels of both elements in some drainage samples, few anomalies are thought to be derived from primary bedrock concentrations with any economic potential. The value of the results lies more in their use as indicators of hydromorphic activity and hence the origin of other metal anomalies.

Elements related to manganese mineralisation

Manganese The distribution of Mn is dominated by the presence of the Manganese Bed in the Hafotty Formation. Mns dispersion is modified by hydromorphic processes, but Mn_p is closely related to the presence of detrital Mn minerals. Consequently, Mnp shows the highest values in catchments draining Hafofty Formation rocks in the west of the area and moderate levels over Aran Volcanic Group rocks where Mn-bearing Fe-oxides are the source, supplemented in the Arenig area by Mn vein mineralisation. Low Mn_{D} levels are a feature of the central part of the area, in catchments draining the greywacke and siltstone formations of the Cambrian. The regional distribution of Mns is similar except for moderate to high values in the central part of the area, some very high levels over the Aran Volcanic Group and a distinct low over Migneint.

Most Mn_p anomalies in the Barmouth-Harlech area (Figure 11) can be related to the crop of the Hafotty Formation and in particular to workings along the Manganese Bed. The remainder, for example at SH 6064 3322 (No. 164) and SH 6542 3756 (No. 151), are probably derived from the Gamlan Formation which also contains manganiferous horizons. At some sites the Clogau Formation may also be a contributing factor, for example the anomaly at SH 6393 1903 (No. 267) and others in the same area.

The only other highly anomalous results are recorded from about Arenig, where some of the anomalies are clearly derived from known vein mineralisation, for example at Pistyll Gwyn (SH 8494 3678, No. 2306) and Nant yr Helfa (SH 8302 4003, No. 345). Anomalous Ba_D accompanies Mnp at these sites, suggesting the presence of hollandite reported by Lynas (1973). A sample of altered volcanic rock carrying vein mineralisation from Nant yr Helfa [SH 8318 4010] was found to contain 1.1 per cent Ba and 5.8 per cent Mn. Other metal levels were low: V 4 ppm, Cr 4 ppm, Co 13 ppm, Ni 11 ppm, As 8 ppm, Cu 5 ppm, Zn 110 ppm, Pb 10 ppm and Fe 3 per cent. Other large Mnp anomalies in the area, such as at SH 8444 3774 (No. 644) and SH 8636 4101 (No. 2002), are probably caused by similar but unrecorded mineralisation. The mineralisation in this area

is poorly documented and merits further examination as results suggest that it is more extensive than the known workings indicate.

A group of weak Mn_p anomalies, associated with high Ba_p , Ti_p and Pb_p , is located to the north-east of Arenig in the Afon Hesgin. The catchment is occupied by the acidic ash flow tuffs of the Llyn Conwy Formation and it is not clear whether the anomalies are reflecting further mineralisation or bedrock lithology. Other high levels in the Arenig area appear to be derived from 'pyroclastic mudstones' (Fearnsides, 1905), and are associated with a wide range of weak metal anomalies. Examples include the sites at SH 8336 3570 (No. 2287) and SH 8158 3746 (No. 327).

The only other distinct group of high Mn_p results are those in the south-west of the area, between Cader Idris and Tywyn, where they are associated with Zn, Cr, Ni and V anomalies. From the distribution of anomalies it is not clear from which particular formation, if any, they are derived. The highest value, from SH 6737 1074 (No. 2470), drains a catchment of mudstones (Tal-y-llyn) and acid volcanics (Upper Acid Volcanic Group; Cox and Wells, 1927). The lack of associated metal anomalies at this site may be indicative of local Mn mineralisation, though most anomalies in this area are attributed to basic igneous rocks.

Only a few scattered Mn_p anomalies lie outside these groups (Figure 11). Some of the isolated anomalies may be derived from the Gamlan Formation, for example at SH 7328 3464 (No. 388) and SH 7032 3806 (No. 407), and at least one, at SH 7800 2728 (No. 3092), is probably the product of hydrous oxide coatings on grains in view of the very high level (13.8 per cent Mn) in sediment. Two anomalies of uncertain origin are those at SH 7878 3507 (No. 401), collected from a stream draining intermediate intrusives, and at SH 6345 4132 (No. 2071), close to the base of the Arenig and old lead workings at Hafod Boeth.

Differences in the distribution of Mn_s compared with Mn_D are largely attributed to hydromorphic processes, though the primary manganese-bearing minerals are also an important factor. This, for example, probably accounts for the anomalies around Cader Idris and Tywyn showing less clearly in the sediment results. The reason for a distinct low over Migneint is not clear, either the bedrocks are deficient in Mn, Mn is locked in a resistant mineral or Mn is being transported in solution across this peaty terrain (see 'Cobalt and iron in stream sediment'). Hydromorphic processes are considered to be the principal cause of Mns anomalies in catchments drainage peaty uplands were Mn_p is not anomalous. The main areas are Penaran (e.g. SH 8384 2653, No. 769), on the northwest slope of the Aran ridge (e.g. SH 8387 2184, No. 2378) and west of Ysbyty Ifan (e.g. SH 8228 4888, No. 2206), where levels are so high (>4 per cent) that a Mn-rich source is probable. In the first two of these areas basic volcanic rocks provide a possible source and further investigation has indicated the possibility of volcanogenic mineralisation, which could also be a source of manganese (see 'Lead and zinc').

Elements principally related to lithology

Nickel The distribution patterns of Ni_S , Ni_D , Cr_S and V_S are broadly similar and governed by bedrock type, locally modified by hydromorphic processes affecting Ni_S . Anomalous populations shown by all three elements are related to mudstones and basic igneous rocks, but with rare exceptions none of the elements is present in amounts to suggest that concentrations of economic significance exist in the area.

 Ni_p levels are generally very low across the whole area whilst Ni_s levels are higher. This suggest an absence of nickeliferous heavy minerals, with Ni concentrated in phases such as chlorite. An association of Ni_s with Co_s , Fe_s and As_s at some sites suggests local concentration by secondary scavenging and precipitation processes. Ni levels are very low in sediment and concentrate over Cambrian rocks below the Hafotty Formation and the

Aran Volcanic Group in the Arenig area. Elsewhere levels over the Aran Volcanic Group are erratic and reflect the proportion of basic rocks and mudstones in the catchments. Relatively high values, particularly in concentrate, are a feature of catchments in the Cader Idris area draining basic intrusions and volcanics of the Llyn y Gafr Spilitic Formation. Other Nip levels above 55 ppm are found over sedimentary rocks statigraphically above the Aran Volcanic Group. As these correlate with high Cep they are attributed to analytical interference. A few high $\rm Ni_{\rm D}$ results are recorded in samples collected downstream of old mines such as at Voel Ispri (SH 7070 1968, No. 3031). They are accompanied by a wide range of other metal anomalies, and an abundance of pyrite containing minor Ni is the most likely source, rather than the rare Ni mineralisation recorded in veins (Gilbey 1969).

High levels of Ni_s are concentrated over the Middle Cambrian, Upper Cambrian and Lower Ordovician rocks. They are attributed to:

- (i) vein mineralisation;
- (ii) basic volcanics in the Cader Idris range;
- (iii) bedded manganese deposits of the Hafotty Formation;
- (iv) Rhobell Volcanic Group;
- (v) dark mudstones.

Of the rocks analysed during follow up investigations those from vein mineralisation returned the highest nickel contents. These included 250 ppm in a quartz-Blaenau sphalerite-pyrite-chalcopyrite vein from Ffestiniog [SH 6932 4406] and 349 ppm in a mineral concentrate from Prince Edward Mine [SH 744 386], downstream of which high Nis and Nip levels were obtained. The Manganese Shales provide a source of Ni with concentrations of 35 to 152 ppm reported by Mohr (1959). In sediments the primary concentration may be enhanced locally by co-precipitation with other metals, for example at SH 6277 2278 (No. 234) and SH 6292 3646 (No. 162). The dark mudstones of the Cwmhesgen Formation also contain relatively high levels of Ni (Table 6, No. 1) compared with other mudstones in the area (Cooper and others, 1983) and contribute to Ni anomalies to the northwest of Rhobell Fawr, for example at SH 7971 2535 (No. 3082). The distribution of high values suggests that the Rhobell Volcanic group is another source of Ni. Available analyses (Table 6) suggest levels typical of basic volcanics. Basic volcanics may also be responsible for Nis anomalies in the Cader Idris area, but the prominent Ni_p feature in that area suggests that a higher proportion of Ni is present in a heavy mineral phase.

Chromium Chromium levels increase over progressively younger rocks, except for variability in the Aran Volcanic Group. The highest levels, therefore, are characteristic of sedimentary rocks of Upper Ordovician and Silurian age and are in marked contrast to the low values generated by the Harlech Grits Group. This feature, viewed in the light of evidence from sedimentary structure analysis (Crimes, 1970) and other geochemical data (Cooper and Read, 1983), suggests that the Ordovician-Silurian sedimentary rocks and Harlech Grits Group were derived from quite distinct sources.

Three other distinct groups of high Cr_S results are recorded. Firstly, high levels are found in the Cader Idris area associated with anomalous levels of Ti_D and V_S and spatially related to basic intrusions and the Llyn y Gafr Spilitic Formation of Ridgway (1976). Anomalous sites include those at SH 7375 1476 (No. 2522), SH 6878 1486 (No. 2396) and SH 7240 1256 (No. 2496). In contrast Cr_S levels over acid volcanics of the Llyn Conwy Formation in the north Arenig area are very low whilst Ti_D remains high (e.g. SH 8724 4314, No. 2015), reflecting the distinct difference in lithology dominating the two areas. A second area of high Cr_S results is located over the Glanrafon Group in the extreme north-west of the area, with the highest values recorded from the Afon Croesor

(e.g. SH 6250 4411, No. 2066 and SH 6528 4604, No. 2061) in association with anomalous Cu_s , Pb_s and Zn_s . The cause of these anomalies is uncertain but Cr_S may be enhanced by the sheared rocks in this area (Fearnsides and Davies, 1944) containing a high proportion of Cr in chlorite group minerals. The third area of high Cr_s is located in the Cwm Cynfal-Migneint area and shows no obvious relationship to the stratigraphy. High values in streams draining Hafod Fawr into Cwm Cynfal and eroding Ffestiniog Flags Formation rocks show an association with weak Cu anomalies (e.g. SH 7369 4031, No. 2021 and SH 7452 4018, No. 2023) whilst those to the east show a strong correlation with As_S and have source rocks covering a wide stratigraphic range in the Mawddach and Aran Volcanic groups. The anomalies are, perhaps, derived from mudstones at various horizons in this succession (see 'Arsenic'). Examples include the sites at SH 8128 4394 (No. 2108) and SH 7770 4270 (No. 2160).

There are few published analyses of Cr in rocks from the Harlech Dome and none from the areas producing high Cr_s results. None of the Cr_s results, however, with one exception, is of such a magnitude as likely to be derived from a source with economic potential. The exceptional result of 955 ppm comes from a small stream in the Migneint area at SH 7642 4442 (No. 2095), draining a catchment of Nant Hir Formation mudstones and adjacent to the catchment containing the largest As_s anomalies. No other element is anomalous and the result is so much larger than any other reported (nearest neighbour 277 ppm) that it may be spurious, but as the cause is uncertain further investigation is recommended.

Vanadium The spatial distribution of V_S is dominated by two clearly defined areas of high values: one related to the outcrop of the Aran Volcanic Group in the Cader Idris block and the other to the Rhobell Fawr volcanic centre and associated mineralised intrusives to the west (Figure 19). In both areas levels of V_S are enhanced by the outcrop of the Cwmhesgen Formation, though the absence of pronounced anomalies associated with this formation across most of the survey area suggests that V levels in the mudstones are typically much lower than those reported in Table 6. Moderately high V_S results are reported from the extreme north-west of the area in catchments draining the Glanrafon Group (e.g. SH 6567 4708, No. 2059), whilst low levels characterise the outcrop of the Harlech Grits Group and Aran Volcanic Group in the Arenig area. In these respects the pattern is similar to Cr_s and Ni_p . High values in the Cader Idris area are associated

High values in the Cader Idris area are associated with Cr_s and Ti_p in particular (e.g. SH 7375 1476, No. 2522 and SH 7109 1451, No. 2402) and are apparently derived from the Llyn y Gafr Spilitic Formation (Ridgway, 1976) for which only major element analyses are published (Davies, 1958). The drainage results suggest that these rocks may have a distinctive trace element chemistry, though the major element composition shows no particular features. The origin of V_S anomalies on the north-side of Cader Idris, such as at SH 7204 1763 (No. 2414), is confused by contributions from Cwmhesgen Formation and Rhobell Volcanic Group rocks which are both vanadiferous sources.

In the main outcrop of the Rhobell Volcanic Group there is a strong association of V_S with Cu_S , Cu_p and, less stongly, with Fe_p and Ba_S anomalies. V_S levels are not exceptional for catchments comprised of basaltic rocks and are similar to levels recorded in the rocks by Kokelaar (1977) and in this study (Table 6, No. 7). The V content of the rocks falls withing the range commonly recorded from elsewhere and the association of V_S with disseminated Cu mineralisation is therefore considered to be a characteristic of the primary lithology associated with the mineralisation. Consequently, a grouping of anomalous Cu with relatively high V elsewhere in the area would be of significance, but no such grouping is recorded. Sites in catchments on the eastern side of Rhobell Fawr, which cross Cwmhesgen Formation rocks but may also contain Rhobell Volcanic Group rocks and basic intrusions, yield the highest V_S levels recorded in the area. These are associated with a wide range of other metal anomalies (see for example 'Barium'). The most anomalous values are 749 ppm at SH 7930 2882 (No. 3068), 715 ppm at SH 7831 2415 (No. 784) and 560 ppm at SH 7881 2918 (No. 3010). A Cwmhesgen Formation dark mudstone sample from this area contained 778 ppm V (Table 6, No. 1), so the source of the

anomalies is evident. The lack of such strong drainage anomalies elsewhere indicates that, for reasons which are not clear, metalliferous concentrations associated with the Cwmhesgen Formation are apparently restricted to the Rhobell Fawr area (see also Barium'). In this area the Cwmhesgen Formation rocks may represent a low grade V resource which requires more detailed assessment.



Figure 19: The location of high levels of vanadium in stream sediment with respect to major rock groups

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Titanium and iron in panned concentrate The distribution of both elements is controlled by bedrock lithology, with high levels associated with basic intrusions and volcanics of the Aran Volcanic Group and the presence of heavy detrital minerals such as ilmenite and magnetite. Additionally, high levels of Fep are derived from mineralisation where pyrite is abundant. Consequently, very low levels of both elements characterise the Harlech Grits Group outcrop, moderate levels occur over the Mawddach Group, high and anomalous values are dominant over the Aran Volcanic Group, and moderate levels are found over the Upper Ordovician and Silurian succession. High and anomalous levels of both elements are a feature of the Tywyn-Cader Idris-Aran Mountains outcrops of the Aran Volcanic Group, associated with nigh levels, of Zr, V, Cr and Ni in the Cader Idris area. Some of the highest results are a feature of the extreme south-west of the outcrop near Tywyn, for example at SH 6250 0918 (No. 2512) and SH 5855 0885 (No. 2488). The highest Fe_{p} levels show a close connection with the outcrop of the Lyn y Gafr Spilitic Formation (Ridgway, 1976) which is also the source of some of the highest Ti_D results. Some high Fep results are derived from outcrops and workings in the oblitic ironstone beds, for example downstream of Tyllau Mwn (SH 8430 2150, No. 2377), but Fen levels are not as high as those derived from some basic igneous rocks and at Tyllau Mwn Fe_s >Fe_p. The volcanics of the Arenig area again show differences. Fep levels are moderate (5 to 8 per cent) though Fes is locally anomalous, whilst Ti_{D} levels are generally high and in the northern part of the outcrop occupied by the Llyn Conwy Formation of acidic ash flow tuffs, where Cr_s and V_s are very low, very high Ti_p is recorded (<3.02 per cent Ti_p). Ti_p also yields some high values over volcanics in the Flestiniog area whilst Fe_p levels are moderate. Consequently Ti_p is the single variable determined most characteristic of the Aran Volcanic Group, with relatively high levels occurring in catchments dominated by both acid and basic rocks.

The distribution of Ti_p in particular is believed to reflect differences between the end-Cambrian igneous event, which is thought to be characterised by low-Ti rocks (basalts, diorites, tonalites; Allen and others, 1976; Kokelaar, 1977) and the bimodal Ordovician volcanism and associated intrusions (basalt, dolerite, rhyolite granophyre; Davies, 1958; Dunkley, 1978) in which Ti is higher for comparable compositions. Dunkley (1978) considered dolerites associated with volcanics in the Aran Mountains to be of tholeitic affinity. It may be speculated that such a chemical pattern would be consistent with a change from an island arc setting for end Cambrian volcanism to a marginal basin situation for the Ordovician events.

High levels of Fe_p and particularly Tip, associated with high levels of many other elements, are a feature of the area north-east of Llanfrothen occupied by the Glanrafon Group and a variety of igneous rocks. The precise source of the high values is uncertain, though some Fe_p anomalies are attributed to either pyrite from old mine workings or bedded iron ore deposits, for example downstream of Pen yr Allt at SH 6318 4064 (No. 2074).

High levels of both elements are also attributed to the Cwmhesgen Formation with, as in the case of many other transition elements, prominent anomalies at sites in the vicinity of Rhobell Fawr. The highest levels of Tio recorded in the survey come from two sites closely associated with these rocks, 4.98 per cent at SH 7967 3760 4.71 per (No. 322) and cent at SH 8034 3829 (No. 326). Ffestiniog Flags Formation occupies much of the catchment of the former and a dolerite intrusion is close to the latter sample site. The anomalies have no other exceptional metal levels associated with them and form a small isolated group whose origin is uncertain.

High $\tilde{F}e_{\rm D}$ results are found in samples with sulphide mineralisation in their catchments. The largest

anomalies are recorded at sites in streams eroding the pyritic halo of the Coed y Brenin disseminated copper deposit, for example in the Afon Wen catchment where Fe_D reaches 23 per cent (SH 7465 2450, No. 617). These anomalies merge with a zone of moderate to high values to the east generated by the basic rocks of the Rhobell Volcanic Group, producing a broadscale high on regional distribution plots defining both the disseminated mineralisation and associated volcanism similar to that of V_s . Tip levels are only moderate over the Rhobell Volcanic Group, reflecting the relatively low levels of 0.51 to 1.18 per cent TiO2 reported in the basaltic rocks by Kokelaar (1977). Fep derived from vein mineralisation aids the production of moderate to high values coincident with the 'gold-belt' and particularly clear in the Maentwrog-Talsarnau section, where contamination may contribute to the anomalies. Examples include sites at SH 6148 3438 (No. 176), where gold, base metals, Sn and Mn as well as Fe are anomalous in the concentrate, SH 6542 3756 (No. 151) and SH 6256 3424 (No. 119).

Molybdenum Molybdenum behaviour is not closely related to that of any other element and the definition of regional patterns is restricted by the large number of samples below the detection limit. Low results (<1 ppm) delineate the outcrop of the Harlech Grits Group and sedimentary rocks younger than the Aran Volcanic Group. Moderate levels with small areas of anomalous results characterise the Mawddach, Rhobell Volcanic and Aran Volcanic groups.

With one exception each Mo_s anomaly can be related to one of the following three sources:

- (i) Porphyry style copper mineralisation. Weak molybdenum mineralisation accompanying disseminated copper mineralisation (Rice and Sharp, 1976) is responsible for anomalies in the Coed y Brenin area (Figure 12). Anomalies are recorded in tributaries to the Afon Mawddach and Afon Wen at SH 7362 2540 (No. 626), SH 7350 2510 (No. 629) and SH 7390 2395 (No. 615) associated with very high Cu_S, weakly anomalous Cu_D and low Fep, suggesting a strong hydromorphic contribution to the anomalies.
- (ii) Dark mudstones. High and anomalous levels of Mo_S occur in catchments containing Dolgellau Member rocks of the Cwmhesgen Formation, which locally show strong enrichment in Mo (Table 6, No. 1). A wide range of other metals concentrated in mudstones are high or anomalous at these sites (SH 7930 2882, No. 3068). As is the case with several other elements anomalous sites are all peripheral to Rhobell Fawr (see 'Barium').
- (iii) Granitic intrusions. The only site covering the outcrop of the Tan y Grisiau Granite (SH 6762-4329, No. 2102) is anomalous for many elements in sediment including Mo. Two other sites marginal to granite (SH 6673 4252, No. 2101 the and SH 6959 4382, No. 2148) also contain high Mos (11 ppm and 7 ppm respectively) and other metal anomalies including $\mathrm{Cu}_S,\,\mathrm{Pb}_S$ and $\mathrm{Zn}_S.$ Late stage hydrothermal activity associated with the granitic intrusion has produced veins containing pyrophyllite, allanite and rarely molybdenite (Bromley, 1969), which is probably the source of the ${\rm Mo}_{\rm S}$ anomalies. The associated anomalies also suggest the presence of base metal mineralisation which may have a separate source, such as the Zn-Pb-Cu vein mineralisation exploited in Moelwyn Mine.

Two anomalies occur in streams draining part of the Crogenen Granophyre crop on the flanks of Cader Idris (Cox and Wells, 1927). Both anomalies are accompanied by high Zn_s and the eastern by high levels of Ti_p , V_s and Cr_s as well. No mineralisation is known to be associated with this intrusion but these anomalies suggest that an examination of the area is merited. The only other Mo_S anomaly occurs at SH 8174 4431 (No. 2106) and has an immediate catchment of Nant Hir Formation Upper Ordovician mudstones. No other high Mo values are reported in the vicinity, but the anomaly is accompanied by high levels of Cr_S , Fe_S and As_S which suggests, a dark mudstone source.

Barium Barium shows very similar distribution in stream sediment and panned concentrate results and independent behaviour from other elements determined. Spatial distribution patterns can be related to lithological variations, manganese vein mineralisation and, in the case of Ba_s , hydromorphic processes. The regional distribution patterns are complex; in the case of Ba_p distortion is caused by analytical interference and the Ba_s pattern is confused by hydromorphic redistribution. In very general terms, low levels are located over the Harlech Grits Group with the exception of the Hafotty Formation, and high levels found locally over the Mawddach and Aran Volcanic groups, whilst high levels are a feature of the Rhobell Volcanic Group.

 B_{a_S} results are generally similar or higher than those in concentrates from the same site where levels are not distorted by high C_{e_p} , indicating that Ba-carrying heavy mineral phases such as baryte are rare or absent in most of the area. The only exception is around Arenig where anomalous B_{a_p} is accompanied by anomalous Mn_p and related to manganese vein mineralisation carrying hollandite (see 'Manganese'). Typical anomalous samples include those collected at SH 8302 4003 (No. 345) and SH 8636 4101 (No. 2002).

The majority of Ba_s and Ba_p anomalies are related to the crop of the Cwmhesgen Formation where they are associated with anomalous levels of a wide range of metals including V, Mo, Cu, Fe, As, Ni, Zn and Pb. Ba_S is typically slightly higher than Ba_p. There is a distinct variation along the crop with the strongest anomalies developed over rocks adjacent to the Rhobell Fawr volcanic centre (Figure 13), reaching a maximum of 5700 ppm Bas at SH 7930 2882 (No. 3068). Other anomalies attributed to the Cwmhesgen Formation are scattered along the outcrop, such as those south of Dolgellau at SH 7204 1763 (No. 2414), near Rhydymain at SH $8055\ 2145$ (No. 2383), and north of Cwmhesgen at SH $8003\ 3427$ (No. 404). A negative feature is the absence of anomalies related to outcrops around Cwm Prysor and the contrast is particularly strong with respect to the high levels about Rhobell Fawr (Figure 13). It is not known whether this contrast is caused by a change in sedimentary facies, sampled streams not eroding the metalliferous horizons in the Prysor area, or volcanic activity in the Rhobell Fawr area. Detailed investigation of the Rhobell Fawr anomalies in the vicinity of Benglog [SH 80 24] showed that the Ba anomalies might be derived from the Rhobell Volcanic Group, dark mudstones of the Cwmhesgen Formation or mudstones of the Y Fron Formation, part of the Aran Volcanic Group. All these rocks contain exceptional levels of Ba: amphibole basalts 132 to 2182 ppm, dolerites from minor sills 132 to 21 000 ppm (Kokelaar, 1977), Dolgellau Member mudstones 2680 to 9100 ppm and Y Fron Formation mudstones 1105 to 4825 ppm (Cooper and others, 1983). The spatial distribution of barium and other metal (e.g. V, Mo) anomalies suggests a genetic relationship to the Rhobell volcanism, but if this is correct another phase of barium enrichment is required to account for the concentration in the Y Fron Formation.

Other Ba_S and Ba_D anomalies in the Rhobell Fawr area are associated with high levels of Cu_S , V_S , Zn_S , Zn_D and Fe_D and have catchments consisting entirely of Rhobell Volcanic Group rocks. The anomalies, for example at SH 7639 2676 (No. 588) and SH 7800 2728 (No. 3092), are attributed to the exceptionally high level of Ba recorded in these rocks. At all sites $Ba_D < Ba_S$, suggesting that Ba is contained in a light mineral such as feldspar.

In the west of the area a belt of Bas anomalies

(Figure 13) is associated with Mnp anomalies and, locally, high levels of Cu_S , Pb_S , Zn_S , As_S , and Ni_S . The anomalous catchments contain Gamlan, Hafotty and in one case, Maentwrog Formation rocks. One site (SH 6336 3134, No. 111) is downstream of workings in the Manganese Bed. Mohr (1959) records high levels of Ba in some of the Manganese Shales from the Hafotty Formation (190 to 2240 ppm) and, as Bas is consistently higher than Ba_D, the anomalies are probably formed from relatively metal-rich horizons outcropping in the catchments, enhanced by hydromorphic processes. To the anomalies in the Afon Hirgwm south, three (e.g. SH 6566 2126, No. 125) are thought to be of similar origin. The possibility of metalliferous concentrations in these formations merits further investigation.

Some Ba_S anomalies are attributed primarily to promorphic concentration, for example those at hydromorphic (No. 255) and SH 6907 2840 (No. 256) SH 6997 3390 where Zn_s and Fe_s are also anomalous and the catchment consists of Dolwen Formation sandstones. To the south, three small Bas anomalies in catchments of Rhinog and Llanbedr formation rocks (e.g. SH 6792 2603, No. 85) probably have a similar origin. The absence of high Mn, Zn or Fe in the stream sediment at these sites is an unusual feature which perhaps reflects a lack of mafic minerals in the rocks whilst feldspar provides the Ba source. A fourth, larger, anomaly in this area (Figure 13) at SH 6918 2502 (No. 73) is accompanied by anomalous Cus and Cup. The association is unusual in this area and the cause uncertain.

A few weak Ba_s anomalies are related to outcrops of acid igneous rocks, such as the Tan y Grisiau granite (SH 6762 4329, No. 2102) and the Aran Fawddwy Formation acid ash flow tuffs (SH 8298 1821, No. 2435). In both cases $Ba_s > Ba_p$, Pb_s is also anomalous, feldspar is the likely source, and the anomalies are probably accentuated by hydromorphic concentration. Analyses of acid volcanic rocks from the Aran Mountains has confirmed that Aran Volcanic Group rocks are locally rich in Ba, samples from the Brithion Formation containing up to 4400 ppm Ba and five crystal tuffs from the Benglog Formation average 1073 ppm Ba (Table 6, No. 8).

Cerium $Ce_{\rm p}$ reaches very high levels, with three samples, from SH 5966 0548 (No 2492), SH 8570 3026 (No. 2318) and SH 9045 3892 (No. 2280), containing more than 10 per cent Ce and 66 samples containing more than 1 per cent Ce. There is a strong regional relationship between geology and Ce_p levels (Figure 20). Low values (median 53 ppm, range <21 to 490 ppm, n=141) characterise samples collected over the outcrop of the Harlech Grits Group, moderate levels the Mawddach Group (median 692 ppm, range 22 to 8500 ppm, n=177) and some very high levels the Ordovician rocks (median 695 ppm, range <21 ppm to 14 per cent, n=516). Within the Ordovician very erratic levels are found over the Aran Volcanic Group with low values in the Cader Idris area. Catchments which include sedimentary rocks younger than the Aran Volcanic Group contain the highest values (median 2990 ppm, range 44 ppm to 14 per cent, n=121). Low levels (median 250 ppm, range 30 to 1267 ppm, n=16) are found over the Rhobell Volcanic Group. All the high levels over the Mawddach Group are located in the upper reaches of the Afon Mawddach - Afon Gain catchment, for example 8470 ppm at SH 7698 3266 (No. 414).

All high Cep results are related to the presence of a distinctive form of nodular monazite, termed 'monazite grise' by Donnot and others (1973). Panned concentrate results from several surveys suggest that the nodules occur commonly in Ordovician and Silurian rocks of the Welsh Basin but not elsewhere (Cooper and Read, 1983). In several parts of Wales, notably the Berwyn Hills (Cooper and others, 1984) there is an apparent relationship between the distribution of Cep and topography, with the highest values occurring marginal to peaty uplands. This relationship is unexplained as detailed mineralogical studies showed no evidence of nodule

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Figure 20: Isometric moving - average plot of cerium in panned concentrate results

growth related to the current weathering cycle (Cooper, Basham and Smith, 1983; Read, 1983). The nodules have been the subject of intensive study in Central Wales where it was concluded that they are derived from weathered granitic rocks and associated pegmatites and were recrystallised in situ during low grade metamorphism of the enclosing sediments (Read, 1983). The distribution of nodules ascertained from a study of panned concentrate results from many parts of Britain has been used to make speculative deductions on the source of the nodule bearing sediments by Cooper and Read (1983). It was concluded, partly from the evidence of this survey, that the Ordovician and Silurian sedimentary rocks in this area were largely derived from a southerly source containing granitic rocks and pegmatites, and that this source first become available during the Upper Cambrian.

In Central Wales the nodules are not concentrated at any particular horizon but dispersed throughout the sedimentary sequence. Three 15 kg samples of shale and siltstone of Bala and Llandovery age were all found to contain nodules at a concentration of 25 to 50 grains per kg, roughly equivalent to 18 to 27 ppm Ce in a whole rock analysis (Read, 1983). The nodules do not, therefore, assert a strong influence on the bulk chemistry of the rocks and do not represent an economic resource. Also, where analysed in Central Wales, stream sediments contained only weakly elevated levels of Ce (22 to 155 ppm, n=45) although Ce_p was often highly anomalous (136 to >10 000 ppm). This was caused partly by the size distribution of the nodules and partly by upgrading during panning (Read, 1983). There is no reason to suggest that the mode of occurrence or concentration in the Harlech Dome differs from that of Central Wales and therefore the high Ce_p results here are of scientific rather than economic interest.

Zirconium Zr shows a strong regional variation pattern related to bedrock lithology. The pattern is the reverse of that for most elements determined, with high levels characteristic of the Harlech Grits Group and low levels over the Mawddach Group. Levels over Ordovician rocks are erratic. In detail, high levels can be related to sandstones and acid igneous rocks. Conversely, low levels are characteristic of catchments dominated by mudstones and basic igneous rocks. Low levels may also be caused by a paucity of detrital material in the sample and consequently Zr shows a negative relationship to elements concentrated in hydrous oxide precipitates.

The highest Zr values in the area are derived from Aran Volcanic Group rocks to the north-east of Ffestiniog, the most anomalous sites being in Cwm Teigl at SH 7340 4466 (No. 2153) and SH 7272 4396 (No. 2155). Other very high values are derived from the Rhinog Formation greywackes, for example 1376 ppm at SH 6070 2689 (No. 3077), 1290 ppm at SH 6672 2970 (No. 249) and 1336 ppm at SH 6767 3062 (No. 239). Low results partly induced by a lack of detrital material include 127 ppm Zr with 11.8% Fe_S and 5.1% Mn_S at SH 7685 3496 (No. 303). The Rhobell Volcanic Group and coeval intermediate intrusives form catchments with very low Zr_S levels, for example 59 ppm Zr_S at SH 7666 2342 (No. 500) and 46 ppm Zr_s at SH 7432 2260 (No. 504). This agrees with the conclusions of Allen and others (1976) that these are low-Zr igneous rocks showing similarities to those emplaced in island-arc environments.

Elements related to contamination

Tin Greyscale moving average plots and tin anomalies (Figure 14) show no relationship to geology but can be closely correlated with roads, towns and villages. No high levels of Sn_p are associated with granitic or acid volcanic rocks and it was concluded that all Snp anomalies are caused by contamination. Despite the collection of samples well above roads, linear groupings of anomalies follow the main roads whilst uninhabited upland areas, such as about Rhinog Fawr and Rhobell Fawr, are free of anomalies (Figure 14). Several groups of anomalies coincide with towns and villages such as Barmouth, Llanfachreth and Dolgellau. Ffestiniog and Blaenau Ffestiniog do not show prominently because of a lack of samples in their vicinity. Isolated anomalies can usually be traced to farms, old mine workings (e.g SH 7138 2129, No. 281), or activities on the old military range (e.g. SH 7506 3192, No. 417). A particularly strong group of anomalies occurs near Rhyd in an area containing acid volcanics and vein mineralisation, for example at SH 6248 4190 (No. 2047) and SH 6160 4318 (No. 2081), but stream contamination was reported at all anomalous sites.

At anomalous sites throughout the area Pb_p anomalies accompany Sn_p (see 'Lead and zinc') and occasionally high and anomalous levels of Zn_p and Cu_p are also recorded. In these cases mineralogical examination is required to determine whether the anomaly is caused entirely by contamination or whether base metal mineralisation is also present. Prominent anomalies requiring clarification in this respect include those near Rhyd, on the old artillery range in the Afon Gain catchment (e.g. SH 7512 3190, No. 415), draining Rhobell Volcanic Group rocks near Llanfachreth (SH 7559 2258, No. 502), near Talsarnau (SH 6148 3438, No. 176) and near Blaenau Ffestiniog (SH 7024 4377, No. 2147 and SH 6992 4848, No. 2203).

CONCLUSIONS AND METALLOGENESIS

- 1. The survey area is metalliferous and has considerable mineral potential. It is unfortunate that it lies entirely within the Snowdonia National Park and has a history of local opposition to mineral prospecting and development.
- 2. Most elements determined show distinct regional variation patterns which can be related to either mineralisation or lithostratigraphy. Anomaly associations characteristic of the different styles of mineralisation found within the area have been identified and are detailed in Appendix 1. The main features are:-
 - (i) Copper porphyry style mineralisation in the Coed y Brenin area produces strong Cu, Mo and As anomalies in sediment, Cu and Fe anomalies in panned concentrate and Cu in water anomalies. The absence of a similar anomaly association elsewhere suggests that no other deposit of similar style is exposed in the survey area, though poor sample cover invalidates this conclusion in the Nannau area.
 - (ii) Cu, Au and Fe anomalies in panned concentrates, frequently accompanied by anomalous As, Pb and Zn and high Cr, Ni, Co and V in sediments or concentrates, reflect the presence of 'gold-belt' style vein mineralisation and suggest that the belt, albeit in weakened form, continues from the northernmost documented working at Prince Edward across the Maentwrog-Talsarnau area of the Dome.

- (iii) Strong Pb and Zn anomalies, often accompanied by weak Cu, As and Fe anomalies as well as relatively high levels of Ba, Mn, Ti, V, Cr, Ni and Co, indicate the presence of known veinstyle base metal mineralisation in Lower Ordovician rocks and may also locally reflect the presence of unproven stratiform volcanogenic concentrations. Arsenic anomalies in the same areas may be related to hydrothermal alteration and pyritisation of the volcanic rocks.
- (iv) Bedded manganese deposits are effectively delineated by Mn in panned concentrate anomalies, whilst Mn vein mineralisation in the Arenig area is distinguished by associated Mn and Ba anomalies. The vein mineralisation, though exploited, is poorly documented and anomalies suggest that it is more widespread than is suggested in the literature.
- (v) Drainage anomalies suggest that other metals besides Mn may be concentrated locally in sedimentary rocks of the Hafotty and Gamlan formations. Petrographic descriptions suggest that coticule (spessartite garnet and quartz) rocks, which may show a regional association with Caledonian mineral deposits, are present within these formations.
- (vi) Metalliferous concentrations in dark mudstones of the Cwmhesgen Formation produce particularly strong drainage anomalies in the vicinity of Rhobell Fawr. They are characterised by very high levels of V, Ba and Mo, often accompanied by lesser anomalies of Cu, As, Ni, Fe, Zn and Pb in sediment. It is not certain whether, as the drainage patterns suggest, strong metal enrichment is restricted to the Rhobell Fawr area and, if so, whether the concentrations are entirely syngenetic or enhanced by some other process.
- (vii) The cause of Cu, Ba and V anomalies over the Rhobell Volcanic Group and associated intrusions in the Rhobell Fawr area is also uncertain. It is considered most likely that the V is derived from a relatively high background typical of basic volcanic rocks but that Cu and Ba may be related to a halo of metasomatism above the porphyry style mineralisation associated with this volcanic episode.
- (viii) Mo anomalies over the Tany Grisiau granite are ascribed to granite-related mineralisation. Similar anomalies over the Crogenen Granophyre (Cader Idris) most probably have a similar source though no mineralisation is recorded in the area.
- 3. Several areas were delineated where anomalous results suggest that hitherto unknown mineralisation of one or more of the types listed may exist. The most prominent of these, which are considered to merit further investigation, are listed under 'Recommendations'.
- 4. Dramatic regional variations in the background levels of many elements have been related to the lithostratigraphy (see Appendix 2) and probably have palaeogeographical implications. The main features are:-
 - (i) Low levels of most elements determined, except Zr, characterise the Harlech Grits Group. A source area consisting of acid volcanics, sandstones or acid gneisses is postulated. Manganese and other metal concentrations at some horizons within the Hafotty and Gamlan formations indicate that exceptional conditions prevailed when these deposits formed.

- (ii) The greatest regional geochemical contrast in the survey area is between the dominantly arenaceous Harlech Grits Group and the argillaceous Mawddach Group. It is suggested that the contrast is due not only to a change in the dominant type of sedimentary rock, but also to a change in the main sediment source, other evidence showing that there was a palaeogeographical change at the close of Middle Cambrian times with a switch from a northerly to a southerly source area.
- (iii) High levels of Ce in panned concentrate and Cr in sediment over Upper Ordovician and Silurian greywackes suggest that their source area also differed from that of the Harlech Grits Group. Evidence from sedimentary structures and monazite nodules indicates that, in common with at least some of the Upper Cambrian rocks, sediment was derived from a southerly direction and the source area contained granitic rocks.
- (iv) Low levels of Zr are a feature of the end-Cambrian intermediate intrusions and associated volcanism which can be related to magmatism in an island-arc type setting.
- (v) Relatively high levels of Ti are the only consistent feature of the Aran Volcanic Group. The extreme variability of most other elements determined reflects the bimodality of the volcanism.
- (vi) A high background level of Cu is a particular feature of the Mawddach Group, Ba and Cu of the Rhobell Volcanic Group and erratically high levels of Pb and Zn of the Mawddach and Aran Volcanic groups. This pattern is caused by syngenetic and primary igneous metalliferous concentrations and subsequent mineralisation.
- 5. The distribution patterns of chalcophile elements are believed to reflect the metallogeny of the area and the following model is proposed:-
 - (i) Harlech Grits Group deposited, probably in a fault-controlled marginal trough or basin along the south-east flank of Iapetus (Bassett, 1980). Metalliferous concentrations developed in restricted shallow basins (Mohr, 1959; Glasby, 1974) in Hafotty and Gamlan formation times. Sediment source-rocks contained low levels of most metals (e.g. acid gneisses) and lay to the north.
 - (ii) Mawddach Group deposited, some sediment at least being derived from a southerly direction and containing a granitic component. Metalliferous concentrations formed in mudstone horizons, particularly in the Cwmhesgen Formation. It is speculated that these may have been enhanced locally by high heat flow or sulphurous emanations along deep-seated fault lines that controlled the sedimentary basins and location of the Rhobell volcanic episode.
 - (iii) Rhobell Volcanic Group erupted sub-aerially and associated intermediate intrusions emplaced in an island-arc type setting (thin continental crust). Cu-Au porphyry-style mineralisation emplaced under the volcanic centre, perhaps accompained by Ba metasomatism in and about the volcanic pile. Veinstyle Cu and breccia pipe mineralisation probably accompanied this event.
 - (iv) Lower Ordovician bimodal volcanism and sedimentation took place, perhaps in a spreading marginal basin. Metalliferous concentrations, principally of Pb, Zn and Ba of volcanogenic origin probably formed. Other syngenetic metalliferous concentrations, such as oolitic ironstones, developed in restricted basins adjacent

- to the Volcanism. Weak Mo mineralisation accompanied some small granitic intrusions associated with the volcanism. It is apparent, for reasons that are not clear but are probably related to the palaeotectonic environment, that Caradoc volcanism in Snowdonia is dominantly associated with Cu mineralisation whilst the older volcanic activity in the Harlech Dome to the south shows a Pb-Zn association.
- (v) Upper Ordovician and Silurian sedimentation filled the basin and buried the underlying rocks to a depth of 3 to 5 km (Bassett, 1980).
- (vi) End-Caledonian earth movements and low grade metamorphism affected the rocks of the area. Vein mineralisation followed the main deformation. No deep source of metals was required. The veins are most probably derived from the metalliferous Cambro-Ordovician succession, fairly local redistribution of metals into veins accounting for the observed regional zonation. The large aeromagnetic anomaly in the Dolgellau area may be reflecting the presence of a heat source which stimulated the redistribution of metals.

RECOMMENDATIONS

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It is considered that the following areas and metals, in no particular order of priority, merit further investigation to clarify the source of drainage anomalies or the extent and style of mineralisation causing them.

- 1. The upper catchment of the Afon Wnion. Anomalous levels of Pb and Zn, accompanied by locally anomalous Cu, Ba, As, Mn, Fe, V and Ti are found on the north-west slopes of the Aran Mountains [SH 82 20-SH 85 25] and between Penaran Forest [SH 84 27] and Benglog [SH 80 23]. Geological modelling suggests that the conditions suitable for volcanogenic sulphide mineralisation are fulfilled in these areas and they have been the subject of further investigation. Some indications of volcanogenic sulphide mineralisation have been found and drilling targets defined in two sub-areas. An inconclusive report on a third sub-area has been published (Cooper and others, 1983).
- 2. West of Ffestiniog, in the Llanfrothen [SH 62 41] -Moelwyn Hills [SH 68 48] area. Anomalies of Cu, Pb, Zn and As are accompanied by high or anomalous levels of Cr, V, Ti, Co and Ni, in an area formed principally of Tremadocian and Lower Ordovician mudstones, acid volcanic rocks and basic intrusions. The majority of the anomalies are in sediment and although many are no doubt enhanced by secondary precipitates and some caused by high background levels and exploited vein mineralisation, the possibility of metal concentrations related to volcanism as well as further vein mineralisation require investigation.
- 3. North-east of Ffestiniog. Anomalies for Cu, Pb, Zn As, Fe, Mn, Cr and Co are found in streams such as the Afon Gamallt, draining Aran Volcanic Group (Moelwyn Volcanic Formation) and Mawddach Group rocks. The majority of anomalies are in sediment and many are most probably enhanced by secondary precipitates. Vein mineralisation, some exploited, is known in the area and is the cause of at least some anomalies but, as in the area to the west of Ffestiniog to which it is similar in many respects, the extent of the anomalies and type of rocks suggest that unknown mineralisation, perhaps of different style, also exists in the area.
- 4. Migneint. In the area immediately to the east of 3 (above) a wide belt of As anomalies is accompanied

by weak Cr anomalies and, in the catchment of the Afon Serw, by high levels of Fe and V [SH 75 43– SH 80 42]. The source of the arsenic anomalies, many of which are at least in part hydromorphic concentrations, requires clarification. The possibility of associated auriferous concentrations should also be investigated, as sulphides in the volcanic rocks or mudstones appear to be the most probable source of the arsenic. Another anomaly requiring explanation in this area is the isolated but very high Cr value recorded in a small stream draining Gamallt [SH 7642 4442].

- 5. Afon Gain. Anomalies of Cu, Pb, Zn and As in the upper catchment of the Afon Gain, which covers a large area between Dol Gain [SH 729 303], Moel y Feidiog [SH 782 324] and the Trawsfynydd-Bala road, most probably indicate the presence of gold-belt vein-style mineralisation. Follow-up investigations of airborne geophysical anomalies (Allen and others, 1979) did not locate the source of many drainage anomalies and, if vein-style gold mineralisation is of interest, this area merits further investigation. The anomalies are of sufficient magnitude to suggest that appreciable mineralisation is present, but locating it beneath the extensive drift cover in an area once used as an artillery range could pose considerable problems.
- Talsarnau-Maentwrog. Gold anomalies in this area [SH 61 34 - SH 67 40], possibly related to quartz veins tried at various points, require further investigation to determine the extent, magnitude and style of the mineralisation.
- 7. Rhobell Fawr. Concentrations of several metals (V, Mo, Ba, Cu) in Cwmhesgen Formation rocks adjacent to Rhobell Fawr should be examined to ascertain if, as the drainage results indicate, they are unique to this area and, if so, to determine the origin of the concentrations and whether they reach levels of economic significance.
- 8. In the Arenig area two targets merit attention:-
 - (i) Base metal anomalies, particularly the prominent anomaly below Llyn Arenig Fach. The source of the anomalies needs to be identified and, if related to mineralisation, the style of the mineralisation.
 - (ii) Mn-Ba anomalies believed to be derived from poorly documented Mn-Ba mineralisation. The extent, magnitude and style of this mineralisation should be ascertained.
- 9. Mo anomalies associated with the Tan y Grisiau Granite [SH 68 43] and Crogenen Granophyre [SH 67 15] require investigation. Those at Tan y Grisiau are believed to be derived from hydrothermal molybdenite-bearing veins associated with the granitic intrusion but no source is known for the Crogenen anomalies.
- 10. The possibility of gold mineralisation in acid volcanic rocks and associated high level intrusions of the Aran Volcanic Group should be examined. Arsenic anomalies occur over these volcanic rocks at several places, most notably north-east of Ffestiniog, and extensive pyritisation and hydrothermal alteration of the volcanics has been noted in the field and recorded in the literature. Auriferous concentrations may also be developed in pyritiferous dark mudstones which are common in the Upper Cambrian and Lower Ordovician succession.
- 11. Generally weak Cu, Pb, Zn, Ba, As and Ni anomalies associated with the Hafotty and Gamlan formations

and Mn concentrations within them, merit investigation, to ascertain if they are related to appreciable stratabound concentrations of metals other than Mn. The presence, association and role of coticule rocks should be examined in this context.

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APPENDIX 1:

Geochemical signatures of mineralisation

The different types of mineralisation recorded in the Harlech Dome produce anomalies in drainage samples distinguishable from each other by their element associations. These associations are described below and summarised in Table 7.

- 1. Disseminated copper 'porphyry-style' mineralisation. Anomalies caused by this mineralisation in the Coed y Brenin area are characterised by very high levels of Cu_s and Cu_p and moderate to high levels of As_s, Fe_s, Fe_p and Mo_s. Pb and Zn anomalies are not recorded. Au_p is probably anomalous but was not determined. Dispersion trains are long and the anomalous Cu values so large and confused by contributions from worked vein mineralisation and the interplay of detrital and hydromorphic contributions, that the precise area of the deposit is not well defined by them. Close to the deposit Cuw anomalies are well developed and provide a more precise definition of the highly mineralised area (Peachey, Cooper and Vickers, 1980). There is a contrast between anomalies with a hydromorphic component in tributaries draining the central part of the deposit, including the 'Turf Copper' area, and those with a very high detrital component eroding the pyrite halo and typified by sites in the Afon Wen. The former have $Cu_s > Cu_p$ and high Mos, whilst in the latter Fe_p is highly anomalous, $Cu_p > Cu_s$ and Mo_s is relatively low. As_s anomalies show an erratic association with other metal anomalies and it is not certain if the As is derived from disseminated or vein-style 'gold-belt' mineralisation. Associated features related to the igneous host rocks are 'gold-belt' mineralisation. moderate to high V_S and low Zr_S, Tip, Cr_S, Nis and Nip.
- 2. 'Gold-belt' vein mineralisation. This mineralisation also generates Cu_s , Cu_p and Fe_p anomalies, often accompanied by high levels of As_s and Au_p where determined. In contrast to the disseminated mineralisation, Mos is never anomalous whereas Pbs, Pb_p , Zn_s or Zn_p anomalies are usually present. Also high or anomalous values of V, Cr, Co and Ni are commonly found. These are usually derived from basic intrusions and mudstones associated with the mineralisation rather than the mineralisation itself. Because of the high detrital component in stream sediments below old workings, metal levels in concentrates are usually much higher than in sediment samples, though below some mines it was found that Pb_p <Pbs. Pb_p is also produced by contaminants, so it proved a most unreliable guide to this style of mineralisation. Dispersion trains in sediment are typically larger than those in concentrate and, if mine waters enter the stream, Cu_W , Pb_W or Zn_W may be highly anomalous close to the source.
- 3. Mineralisation in Ordovician rocks. Vein mineralisation in Ordovician rocks is dominated by Pb and Zn sulphides, with Cu subordinate or absent except in the north-west of the area. Anomalies related to this mineralisation are, therefore, identified by high levels of Pb_S, Pb_p, Zn_S and Zn_p with Cu_S and Cu_p anomalies weak or absent. Elements concentrated in basic volcanic rocks and mudstones, such as Ba, Ti, Mn, Fe, Cr, Co, Ni, and V, are also frequently high or anomalous. Locally As_S is anomalous though it is suspected that often this is derived from the hydrothermal alteration and pyritisation of volcanic rocks and not the vein mineralisation. Similarly, from evidence gained in areas subjected to detailed investigation, it is believed that some metals in this group may be derived locally from stratiform volcanogenic concentrations rather than vein mineralisation.

Table 7 Summary of drainage anomalies associated with different styles of mineralisation.

Mi	neralisation Type	Drainage Anomaly Association						
1.	Disseminated copper porphyry type	$\overline{Cu_{spw} \pm Me_s \pm As_s \pm Fe_{sp}}$						
2.	'Gold belt' (Cambrian) vein mineralisation	$Au_p + Cu_{sp} + Fe_p \pm As_s \pm Pb_{sp} \pm Zn_{sp} (\pm Cr_s \pm Co_s \pm V_s \pm Ni_{sp})$						
3.	Mineralisation in Ordovician rocks	$\frac{Pb_{sp} + Zn_{sp} \pm Cu_{sp} \pm As_s + \pm Fe_{sp} (\pm Mn_{sp} \pm Ti_p \pm V_s \pm Cr_s \pm Ni_{sp}}{\pm Ba_s \pm Co_s}$						
4.	Bedded manganese deposits	Mn_{sp} ($\pm Zn_s \pm Ni_s \pm Cu_s \pm Ba_s \pm Fe_s$)						
5.	Manganese vein mineralisation	$Mn_{sp} + Ba_{sp} ?(+ Pb_s + Zn_{sp})$						
6.	Granite related	Mo_{s} ? (<u>+</u> Pb _s + Zn _s)						
7.	Metalliferous concentrations in dark mud- stones of the Cwmhesgen Formation	$V_s + Mo_s + Ba_{sp} + Cu_{sp} + As_s + Ni_{sp} \pm Fe_{sp} \pm Zn_{sp} \pm Pb_{sp}$						

- 4. Bedded manganese deposits. Large Mnp anomalies are derived from the Manganese Bed in the Hafotty Formation. Many Mn_S anomalies also come from this bed but wider dispersion involving redistribution by hydromorphic processes results in poor definition of the source. Weak anomalies may be derived from other manganiferous horizons in the Hafotty and Gamlan formations. No other anomalies are characteristic of the deposit, though high Zns and, particularly in the north of the crop, weak Fes, Cus, Nis and Bas anomalies accompany Mn anomalies. These are most probably derived from weak metal enrichments in shales and mudstones of the Hafotty and Gamlan formations enhanced by hydromorphic concentration. For example Mohr (1959) reported 36 to 152 ppm Ni, 5 to 300 ppm Cu and 210 to 2240 Ba in the Manganese Shales and all these elements may be affected by scavenging and co-precipitation processes. In some cases vein mineralisation may have contributed to the anomalies.
- 5. Manganese vein mineralisation. This occurs in the Arenig area and produces high levels of Ba_S and Ba_p as well as Mn_S and Mn_p , presumably because of the presence of hollandite (Lynas, 1973). Weak Pb_S anomalies are also invariably present, probably derived from feldspar in the acid volcanic host rocks. The cause of weak Zn_S and Zn_p anomalies at some sites is uncertain. If veins occur without hollandite or other barium-carrying mineral, then only Mn anomalies might be obtained. These would be indistinguishable from anomalies derived from the bedded mineralisation.
- 6. Granite-related mineralisation. Weak Mo mineralisation associated with the Tany Grisiau granite generates distinct Mo_S anomalies. It is uncertain whether other metal anomalies associated with Mo_S here are derived from the same source or elsewhere. For example, Pb_S anomalies could come from feldspar in the granite, Pb-Zn vein mineralisation, or mudstones into which the granite is intruded. Anomalous Mo_S is, therefore, taken as the only definite characteristic of this mineralisation. Mo_S anomalies from the Crogenen Granophyre may be of similar style.
- 7. Metalliferous concentrations in dark mudstone of the Cwmhesgen Formation. Drainage results indicate that these rocks contain anomalous concentrations of many metals in the Rhobell Fawr area. It is not certain if the enrichment is confined to the Rhobell Fawr area or, through chance, whether sampled

streams are not cutting the metalliferous rocks elsewhere. Neither is it clear whether the metal concentrations are wholly syngenetic or if they reach levels of economic interest. Anomalies are characterised by an association of metals commonly concentrated in dark shales and, a slightly unusual feature in this area, very high levels of Ba. Typically metal values in sediment are similar to those in panned concentrates, indicating the absence of heavy minerals. Very high V_s , M_o_s and Ba_s is the most consistent association in the Rhobell Fawr area, often accompanied by anomalous levels of As_s , Cu_p , Ni_s and Ni_p and locally by high or anomalous Fes, Fep, Zns, Znp, Pbs and Pbp. Zrs is predictably low.

A broadly similar metal association is recorded over Tremadoc and Glanrafon Group mudstones, but there is an absence of large V_S and Ba_S anomalies and Mo_S is generally lower whilst Cr_S is higher.

It is difficult to distinguish the dark mudstone association at many sites in the Rhobell Fawr area from high levels of $Cu_S + Ba_S + V_S \pm Ba_D \pm Cu_D$ and low Zr_S which show a spatial association with the Rhobell Volcanic Group. It is uncertain whether this grouping is reflecting a high background characteristic of the Rhobell Volcanic Group, a halo effect in the upper reaches of the Coed y Brenin porphyry style mineralisation system or some discrete undetected mineralisation. A high background generated by basic rocks coupled with a metasomatic/halo effect is considered most likely.

8. Bedded Iron Deposits. These show no geochemical characteristics discernible in the drainage data. The iron ores, for example at Tyllau Mwn, generate Fe_{s} and Fe_{p} anomalies but these are indistinguishable from those produced by basic rocks which outcrop in the same area. High levels of Mn_{s} , Mn_{p} and Zn_{s} are associated with the Fe anomalies but it is not certain whether these are derived from the iron ores, which at Tyllau Mwn do not contain very high levels of these elements (Table 6, No. 11), or basic rocks.

APPENDIX 2:

1.

Geochemical characteristics of major lithologies

The spatial distribution plots of many elements show strong patterns related to bedrock lithology and mineralisation. These variations have been studied using hand contoured 'greyscale' moving average plots covering a window of nine cells, each of 0.65 km^2 . The scale of catchments, sampling interval and cell size are such that small areas of a particular lithology, such as the

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Table 8	Inferred bulk g	eochemical cha	racteristics of	f major lithol	ogical units.	¢.,		

Lithology	Low	High				
Harlech Grits Group	All elements determined	$\overline{\mathrm{Zr}_{\mathrm{S}}}$, (Mn _S)				
	except 2r _s					
Mn beds in Hafotty and Gamlan formations	Ti _p , V _s , Pb _p , Mo _s , Ce _p	<u>Mn</u> p, Mn _s , Ni _s , Ni _p , Cu _s , Zn _s , Ba _s				
Mawddach Group	Zr _s , Mnp	$\frac{Cu_s}{Mo_s}$, $\frac{Cu_p}{Co_s}$, Pb_s , Pb_p , Zn_s , Zn_p , Ba_s , Ba_p , As_s , Fe_s , Fe_p , Ni_s , Mo_s , Co_s				
Dark mudstone of Cwmhesgen Formation	Zr _S	V _S , <u>Bas, Mos</u> , Cu _s , Cu _p , Pbs, Zn _s , As _s , Mo _s , Fe _s , Fe _p , Ni _s , Co _s , Ba _p				
Rhobell Volcanic Group	Zr _s , Ce _p	V_s , (<u>Ba</u> s, <u>Cu</u> s), Zn _s , Zn _p , Fe _s , Fe _p , Mn _s , Ni _s , (Cu _p)				
Aran Volcanic Group		Ti_{D} , Fe_{s} , (Pb_{s}, Zn_{s}, Zn_{p}) ,				
Ffestiniog area		Zr_s , Pb_s , $(As_s, ? Cu_s)$, $?Fe_s$, $?Cr_s$				
North Arenig (acid volcanics)	$\frac{\text{Ni}_{s}}{\text{Cu}_{s}}, \frac{\text{Ni}_{p}}{\text{Cu}_{p}}, \frac{\text{Cr}_{s}}{\text{Fe}_{p}}, \text{V}_{s}$	$\frac{\text{Tip}}{\text{Zr}_{S}}, \frac{\text{Pb}_{S}}{\text{Pb}_{p}}, \text{Zn}_{S}, \text{Zn}_{p}, (\text{Ba}_{S}, \text{Ba}_{p}, \text{Mn}_{S}, \text{Mn}_{p}),$				
South Arenig - Aran ridge	Cu _s , Cu _p , Cr _s	Mn _s , Fe _s , Ba _s , Co _s , Ti _p , (Pb _s , Pb _p , Zn _s , Zn _p)				
Cader Idris (basic volcanics)	Zr _s , Ce _p	V_s , \underline{Ti}_p , \underline{Cr}_s , Fe _p , Mn _p , Ni _p , Ni _s , Co ₃				
Sedimentary rocks shove		n an				
the Aran Volcanic Group	Mo _s	<u>Crs</u> , <u>Cep</u> , Nip, Zr _s , V _s				
Intermediate intrusions	$2 - \epsilon_{\rm e} = -\epsilon_{\rm e} + \epsilon_{\rm e} = -\epsilon_{\rm e}$	$\gamma = 1.6\epsilon^{-1}$				
into Cambrian	<u>Zr</u> s, Mnp	(Cu _s , Cu _p , As _s , Zn _p , Fe _s , Fe _p , Ni _s)				
Granite intrusions		(Mo _s), Ba _s				

Parentheses denote elements whose association is probably caused by a secondary factor such as mineralisation Underlining identifies most characteristic elements

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Italics denote high variability

Tan y Grisiau granite, or ribbon-like outcrops are not distinguished unless they show a very strong geochemical signature.

Patterns generated by each element are described in the text and are summarised in terms of the rock groups whose composition they are believed to reflect in Table 8. The rock groups differentiated in the table are those whose geochemical character can be defined from the drainage data and, for the reasons outlined, there are some notable omissions. For example it was not possible to readily define any specific geochemical characteris-tics of the Clogau Formation. The reasons for this are threefold, firstly, the sinuous outcrop, secondly, confusion introduced by associated mineralisation and thirdly a composition, it is suspected, with no particular strong geochemical characteristics. The geochemical characteristics of the components of the Aran Volcanic Group are not well defined either. This is partly because of the relationship between outcrop and drainage pattern, but mostly because of the rapid alternation of acid and basic volcanics and intrusives within the succession. At the scale studied four sub-areas were disinguished but only two were geochemically reasonably well defined: the north Arenig and Cader Idris sub-areas. Elements whose patterns most clearly define a particular rock group are underlined in Table 8. These are usually elements from factor one of the factor analysis model (Figure 15) which consists of variation related to bedrock type. Some other elements which apparently define a particular lithology may do so, not because they are concentrated in the rock but because of a secondary relationship. For example it is suspected that intermediate intrusions into the Cambrian have high levels of Cu, As, Fe Ni and Zn associated with them, not

because the tonalites and diorites forming the intrusions are particularly rich in these elements, but because mineralisation associated with the intrusions contains these elements. The same argument may possibly be applicable to high levels of many elements associated with the Mawddach Group and the high level of Mn_D associated with volcanic rocks about Arenig. Hydromorphic dispersion may also create false characteristics. For example, moderately high levels of Mns occur over wide areas of the Harlech Grits Group outcrop, but it is suspected that most of the rocks within the group have a low manganese content. The high values are probably derived from a relatively few horizons in the Gamlan and Hafotty formations and concentrated elsewhere by precipitation. Where these secondary features are known to be the cause of a characteristic, the elements concerned are placed in brackets in Table 8.

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The geochemical signatures of the main rock groups reflect the conditions under which they were formed. The drainage samples indicate that the Harlech Grits Group, with the exception of horizons within the Hafotty and Gamlan formations, contain low levels of many elements, particularly Ni, Ti, V and Mo. The only element determined present in relatively large amounts is Zr. It is suggested that this pattern not only reflects the dominant greywacke lithology but infers that the greywackes were derived from a source area which was also low in these elements, and, therefore, might have been composed of acid volcanics, sandstones or acid gneisses. Upper Ordovician and Silurian greywackes apparently show different characteristics (Cooper and others, 1984), drainage samples derived from them containing much higher levels of metals such as Cr, Ce

and As. These differences are most easily explained by the rooks having different source areas and is consistent with the palaeogeographic work of Crimes (1970), Cummins (1969) and others who suggest that the younger rocks are derived largely from a southerly source whilst the Harlech Grits Group have a north westerly source. The lack of metals in the Harlech Grits Group as a whole is in contrast to the Mn and other metal concentrations found in the Hafotty and Gamlan formations. Assuming that there was no great change in sediment source, it suggests that exceptional conditions were responsible for these deposits. Formation in a shallow marine basin by remobilisation of manganese from the sediment column and deposition at the sediment-water interface under reducing conditions as suggested by Glasby (1974) does not require a manganese-rich provenance and is therefore consistent with the drainage data.

The Mawddach Group displays characteristics in drainage samples which are in sharp contrast to those of the Harlech Grits Group and related primarily to the dominantly argillaceous sucession. The Clogau Formation does not generate strong drainage anomalies and it probably does not contain the high metal concentrations found in some other mudstones in the area. Mohr (1956) reports that the Clogau Formation is Mn rich compared with rocks above and it may have geochemical features in common with the Harlech Grits Group. These features may be significant in terms of the profound palaeogeographic changes proposed for the close of the Middle Cambrian (St. Davids Series) by Crimes (1970), sediments of Upper Cambrian age containing material from the south, which may have been a more abundant source of metals than the northern area. Metalliferous concentrations are developed in the Cwmhesgen Formation in particular, but it is not always evident from the drainage data whether high levels of elements such as copper and zinc in the Mawddach Group are related to syngenetic concentrations or subsequent mineralisation. The Rhobell Volcanic Group generates a diagnostic V, Cu and Ba association, but again it is uncertain if this is a primary feature or the product of associated mineralisation.

In contrast the Aran Volcanic Group yields low to moderate levels of Cu in drainage samples whilst Pb and Zn display erratically high levels, similar to the Mawddach Group. Low Cu_s and Cu_p are particularly strong features of the Arenig - Arans sector, and there appears to be a significant change to higher Cu levels in a south-westwards direction coincident with the line of the Bala Fault. The strong bimodality of the volcanism is reflected in the highly variable results for most elements across the outerop of the Aran Volcanic Group. Ti and, to a lesser extent, Fe are the only elements to show consistently high levels associated with this group. Only two geochemically reasonably homogeneous and distinct sub-arces can be defined, where a group of adjacent sample catchments is dominated by a single lithology. In the Cader Idris area, high Cr, Mn, Ti, V, Fe, Mn and Ni form a distinct grouping and are apparently derived from basic volcanics and intrusions, particularly the Llyn y Gafr Spilitic Formation. The second area is centred on the catchment of the Afon Hesgin, north of Arenig, which drains acidic ash flow tuffs of the Llyn Conwy Formation. The characteristic features are high Pb, Ti, Mn, Zn and Ba and low Cr, Ni, V, Fe and Cu. Lithological descriptions suggest that these groupings cannot be considered diagnostic of all acid and basic formations in the group and they may even represent compound characteristics of more than one lithology, for example basic lava - tuff -mudstone. Other formations and finer lithological divisions cannot, however, be resolved at the density of this survey.

Sedimentary rocks above the Aran Volcanic Group are defined by high Cr_s and extremely high levels of Ce_p . Cooper and Read (1983) propose a source area to the south containing granitic rocks and associated pegmatites for the monazite-bearing sedimentary rocks causing the Ce_D anomalies.

Intrusions show few distinctive features because of their small size with respect to the sampling density. The only notable features discerned and attributed to the primary igneous geochemistry are the low Zr_s and Ti_p levels associated with the end Cambrian igneous event compared with the Ordovician volcanism and associated intrusions. These features can be ascribed to the probable island arc setting of the end-Cambrian episode and marginal basin environment of the later volcanism.





Fig.4. Location of copper in stream sediment anomalies



Fig.5. Location of copper in panned concentrate anomalies

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Fig.8. Location of zinc in stream sediment anomalies

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Fig.11. Location of manganese in panned concentrate anomalies











Fig.14. Location of tin in panned concentrate anomalies

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