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Mineral Reconnaissance Programme

Reconnaissance drainage survey for base-metal mineralisation in the Lleyn peninsula, North Wales

MRP Report 132 Technical Report WF/94/3

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RC Leake and TR Marshall

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BRITISH GEOLOGICAL SURVEY

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RC Leake and TR Marshall

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SUMMARY

A geochemical drainage survey has been carried out over the Precambrian and Lower Palaeozoic sedimentary and volcanic rocks of the Lleyn peninsula using a combination of minus 100 BSI mesh stream sediment samples and panned concentrates collected from the same site. There is widespread contamination of drainage sediment with metallic material of domestic and, locally, industrial origin. Accordingly, 39 concentrates containing high levels of base metals were examined mineralogically to help distinguish anomalous samples containing natural minerals from those containing metallic contaminants. Chalcopyrite, sphalerite, galena, secondary lead minerals and baryte were the main minerals of hydrothermal origin detected. In some samples weathering of contaminants was seen to have produced secondary copper and lead minerals similar to those of natural origin.

Samples containing high levels of base-metals are widespread throughout the area and those with the largest contents contain contaminants. Anomalies largely of natural origin which probably reflect mineralisation upstream, are concentrated within the outcrop of Lower Ordovician shales towards the western end of the peninsula, mostly between Llanbedrog and Botwnnog. From the spatial distribution of anomalies in this area both structurally-controlled mineralisation and stratabound sulphide enrichment are possible types of source. In addition, there are several Cu and Ba anomalies along the outcrop of the Precambrian Gwna Group, an olistostome containing a variety of igneous and sedimentary rock fragments, which probably reflect minor vein mineralisation.

INTRODUCTION

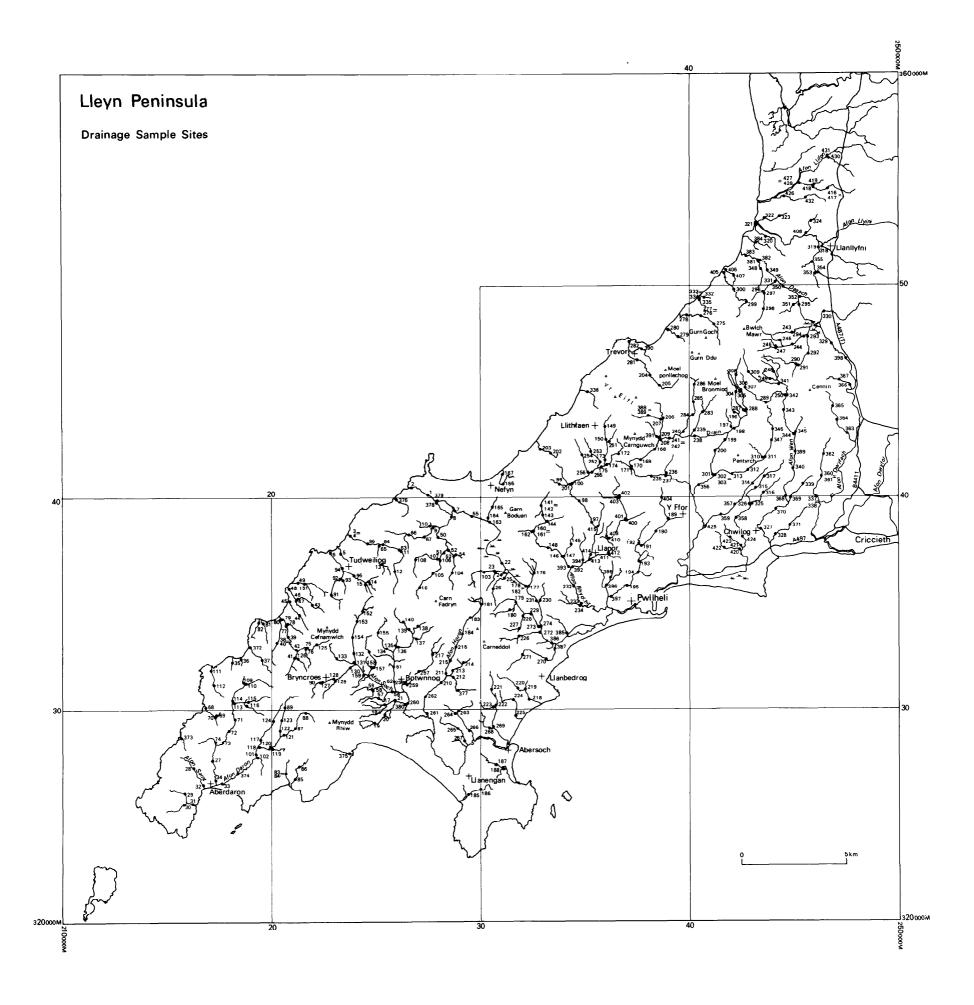
The Lleyn (or Llyn) peninsula is an area of isolated hills protruding from flat drift-covered ground. This report decribes a reconnaissance drainage survey over 415 km² of the peninsula up to an eastern limit defined by the A487 road and the valley of the Afon Dwyfach. Samples were collected from 417 sites (Figure 1) comprising a minus 100 BSI mesh sample and, at all but one site, a panned concentrate. The minus 100 mesh samples were analysed for Co, Ni, Cu, Zn, Ag and Pb by AAS after hot nitric-perchloric acid digestion and for B, Fe, Mo, Sn and Ba by OES. The elements Ca, Ti, Mn, Fe, Ni, Cu, Zn, Sn, Sb, Ba, Ce and Pb were determined in the panned concentrate samples by XRF.

Parts of the Lleyn peninsula are relatively densely populated, and metallic contamination of drainage sediment is widespread. Exploration for base metals using drainage sediment as the reconnaissance sampling medium is thus made very difficult and additional techniques such as mineralogical examination of heavy minerals is required to detect the subordinate component derived from mineralisation. Accordingly 39 panned concentrates containing anomalous concentrations of individual or combinations of the metallic elements Cu, Zn, Pb, Sb and Sn were examined mineralogically to establish to what extent high metal contents were due to natural minerals or contaminants. Anomalies are represented as all but the lowest class on the distribution maps in concentrate samples at > 80 ppm Cu, > 160 ppm Zn, > 100 ppm Sn, > 10 ppm Sb and > 100 ppm Pb respectively.

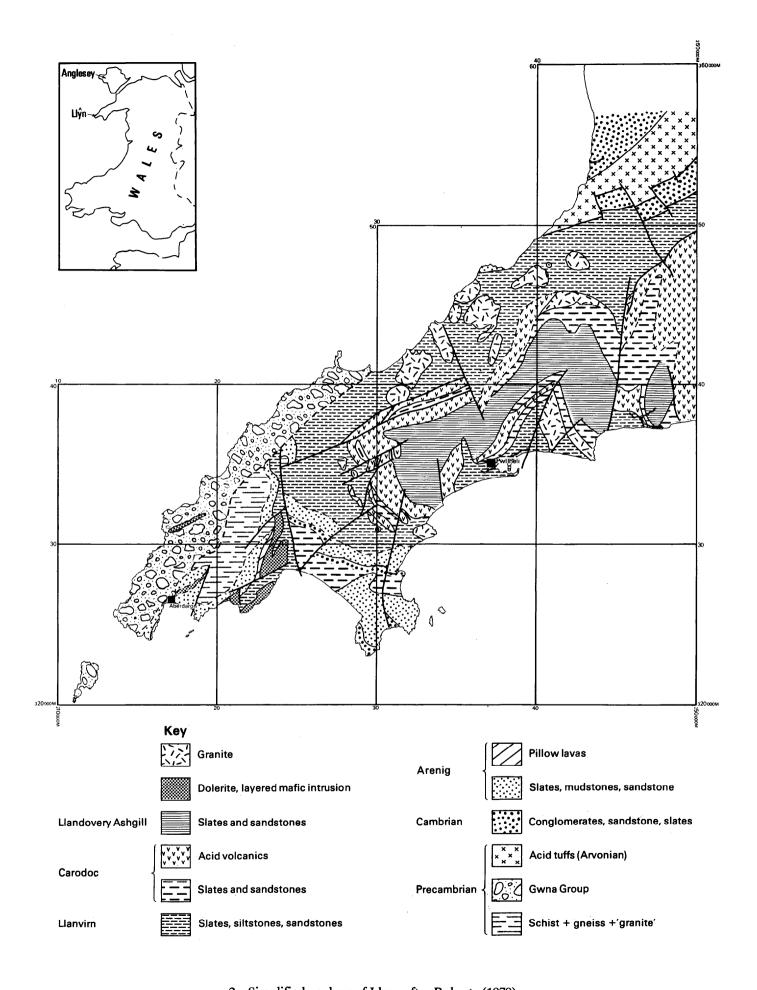
Additional chemical analyses of water and minus 100 mesh sieved sediment samples collected from the Lleyn peninsula form part of the BGS Geochemical Survey Programme data release covering the Liverpool Bay and Anglesey sheets.

GEOLOGY

The Lleyn peninsula is mostly made up of rocks of Ordovician age, with small outcrops of Cambrian rocks and a more extensive area of Precambrian rocks in the west, between Aberdaron and Nefyn (Figure 2). An outline guide to the geology is given by Roberts (1979). The Precambrian rocks comprise the Gwna melange, interpreted as an olistostome containing spilitic pillow lavas, mafic tuffs, cherts, limestone, quartzite, greywacke and pelite, overlain locally by a thin sequence of acid tuffs. There is also a mass of schists and gneisses on the eastern edge of the outcrop of the Gwna group containing a granitoid rock which is thought to have been intruded in the late Precambrian or early Cambrian. A separate unit of Precambrian rocks, the Arvonian Series, consisting mostly of rhyolitic ignimbrites, occurs along with overlying Cambrian rocks in the extreme north of the area. Outcrops of Cambrian rocks on the south coast are very small and of a sequence similar to that occurring some 30 km to the east in the Harlech Dome. The Cambrian rocks comprise greywackes and mudstone (some enriched in phosphate), manganese-rich shales and mudstones, pyritic mudstones, siltstones and shales.



1 Location of drainage sample sites



2 Simplified geology of Lleyn after Roberts (1979)

Ordovician rocks can be separated into two, with a regional stratigraphic or structural break near the base of the Caradoc. The lower Ordovician sequence consists of an alternation of conglomerates, sandstones, siltstones and slates of shallow marine origin followed by the Rhiw Volcanic Group which consists of pillowed spilite and andesite and crystal tuffs. Some of the tuffs are ignimbrites and there is evidence from fragments of contemporaneous basic and acid volcanism. Within the Rhiw Volcanic Group there are bodies of bedded manganese ore. Above the volcanic rocks is a sequence of grey and brown slates and mudstones passing up into dark grey slates and mudstones of Llanvirn age.

The Upper Ordovician sequence in central Lleyn includes two major volcanic suites which are probably lateral equivalents of the Snowdon volcanics to the north-east. They are separated by sandstones, mudstones and shales of Lower Longvillian age. The lower volcanics consist of andesites and spilites, the latter often pillowed. The upper volcanic suite comprises rocks of andesitic to rhyolitic aspect, including a significant development of ignimbrites. Vulcanicity terminated in the area with minor development of basaltic pillow lavas and hyaloclastites. Overlying the volcanics are pyritic black mudstones and black slates.

Dolerites are widespread, but are most conspicuous as intrusions within the the higher levels of the Llanvirn and the Caradoc. Cumulate mafic rocks with rhythmic layering form the Rhiw complex which was probably emplaced during the Llanvirn. Subvolcanic intrusions of quartz latite to rhyolite are associated with the Caradocian volcanic rocks. Stocks, bosses and laccoliths of microgranites and similar rocks are common in the northern part of Lleyn and vary in age from pre-folding to post-folding.

MINERALISATION

Bedded and lensoid manganese mineralisation has been worked in the past in Lleyn. There are three types of occurrence. Manganese-rich shales of Cambrian age, equivalent to the manganese beds of the Harlech Dome outcrop in the small coastal exposures south of Abersoch (Figures 1 and 2). The old manganese mines around Rhiw worked lensoid bodies of silicate/oxide and carbonate ore in mudstone and there has been subsequent MRP exploration in the area (Brown and Evans, 1989). A further minor bedded manganese deposit in later, Ordovician rocks was worked in the northern part of Lleyn (Brown and Evans, 1989). Stratabound ironstone occurs in the same areas as the lensoid manganese mineralisation. Small occurrences of pisolitic and oolitic ironstone also occur in Ordovician rocks.

The Rhiw layered basic igneous complex contains an "ore band" of sulphide-rich rock containing pyrrhotite, pyrite, magnetite and traces of chalcopyrite. This occurrence was the stimulus for exploration using soil sampling by Noranda Kerr Ltd in 1970-72, details of which are available on open file at BGS. This work showed no evidence of nickel mineralisation in association with pyrrhotite, but modest Cu anomalies, up to 120 ppm, were found in an area where some finely disseminated pyrite was observed. Minor carbonate-quartz vein mineralisation containing chalcopyrite and arsenopyrite occurs within coastal exposures of Precambrian rocks along the north coast. Veins carrying lead minerals were worked at various times between 1679 or earlier and 1892 in eight mines situated along 3 km of a roughly east-west fault zone cutting grits, sandstones

and mudstones of Arenig age south of Abersoch (Lewis, 1967; Foster-Smith, 1977). Old records indicate that galena was accompanied by chalcopyrite, sphalerite and baryte.

DRAINAGE GEOCHEMICAL SURVEY

Summary statistics of the geochemical data are shown in Table 1. Mineralogical examination of concentrate samples indicates that contaminants account for at least as much of the base-metal content of concentrate samples as metallic minerals of natural origin. In consequence, simple statistical analysis of the geochemical data is not likely to identify anomalies unequivocally related to mineralisation and cumulative frequency plots were not used to identify class intervals for plotting. Rather, class intervals were chosen more subjectively drawing on previous experience of drainage surveys of less contaminated areas. The distributions of single elements in stream sediment and panned concentrate samples are shown in Figures 3 to 21 and described below in order of atomic number. Maps showing the distribution of Ag, Sn and Ba in the sieved sediment samples were not plotted, as the distribution of these elements shows little of interest.

Table 1. Summary statistics of drainage data

	geometric mean	maximum	minimum
B ppm sediment	70	161	28
Ti% concentrate	0.76	6.35	0.13
Mn% concentrate	0.083	3.640	0.009
Fe% sediment	3.47	10.00	1.12
Fe% concentrate	4.36	19.85	0.81
Co ppm sediment	15	70	<5
Ni ppm sediment	25	80	5
Ni ppm concentrate	17	110	<5
Cu ppm sediment	13	360	5
Cu ppm concentrate	9	5023	<6
Zn ppm sediment	100	640	20
Zn ppm concentrate	63	1493	9
Ag ppm sediment	<1	1	<1
Mo ppm sediment	1	5	<1
Sn ppm sediment	< 5	227	<5
Sn ppm concentrate	13	3532	<9
Sb ppm concentrate	<11	190	<11
Ba ppm sediment	389	1150	172
Ba ppm concentrate	150	16100	<27
Ce ppm concentrate	380	32100	<21
Pb ppm sediment	35	550	10
Pb ppm concentrate	30	10143	<13

Boron in <100 mesh stream sediment

Samples containing the highest levels of boron are concentrated in the west of the area (Figure 3) and occur on rocks of all ages from Precambrian to Upper Ordovician. There is some evidence that boron enrichment may be associated with some of the larger faults shown on the geological map (Figure 2). Some association of higher boron contents with the foliated and unfoliated varieties of the Precambrian Sarn adamellite and the adjacent schists and gneisses of similar age is also evident but there are no corresponding metal enrichments of natural origin in these samples to suggest the presence of mineralisation. There are no samples with high boron contents in the area near Carn Fadryn where outcrops of tourmalinite are associated with feldspathic sandstone and andesitic volcanics in the Upper Ordovician sequence (D Bate, personal communication, 1993). The explanation may lie in the relatively coarse grain-size of the tourmaline and tourmalinite fragments and their mechanical stability, so that they do not contribute significantly to the minus 100 mesh fraction.

Titanium in panned concentrate

Samples with relatively high levels of titanium are grouped particularly in the east of the area (Figure 4) in areas apparently underlain by sedimentary rocks rather than volcanics or doleritic intrusions (Figure 2). The westernmost Ti-rich sample can be explained by its location over a dolerite.

Manganese in panned concentrate

The Mn-rich sample from the west of the area (Figure 5) reflects the manganese mineralisation around Rhiw. The grouping of Mn-rich samples in the east of the area coincides closely with the group of Ti-rich samples. This suggests that both elements could occur together in ilmenite which in turn would imply the existence of mafic rocks not shown on the geological map.

Iron in <100 mesh stream sediment

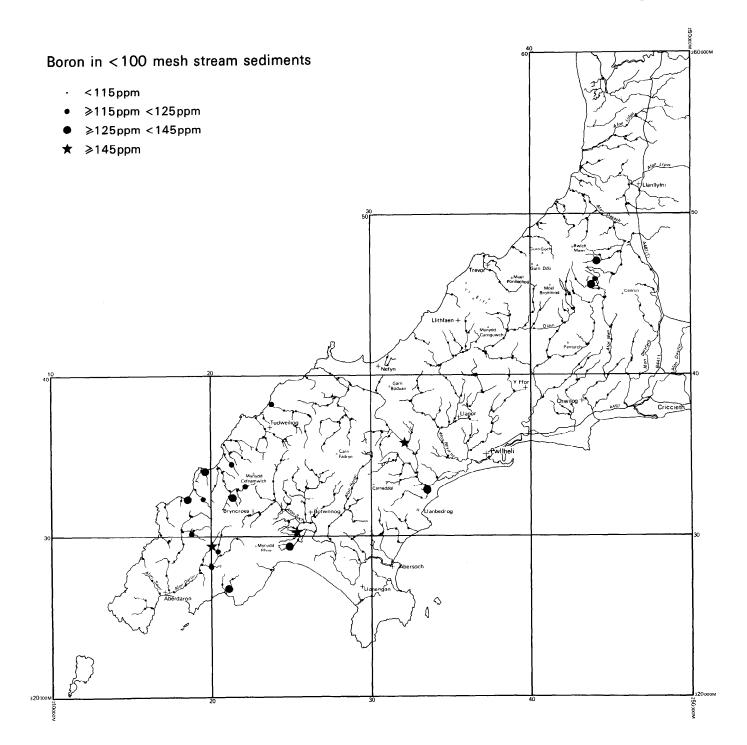
Samples containing the highest levels of iron (Figure 6) are grouped in the east of the area, and particularly within the same general area as the Mn-rich concentrates, the outcrop of the upper Caradoc and Ashgill black mudstones and slates.

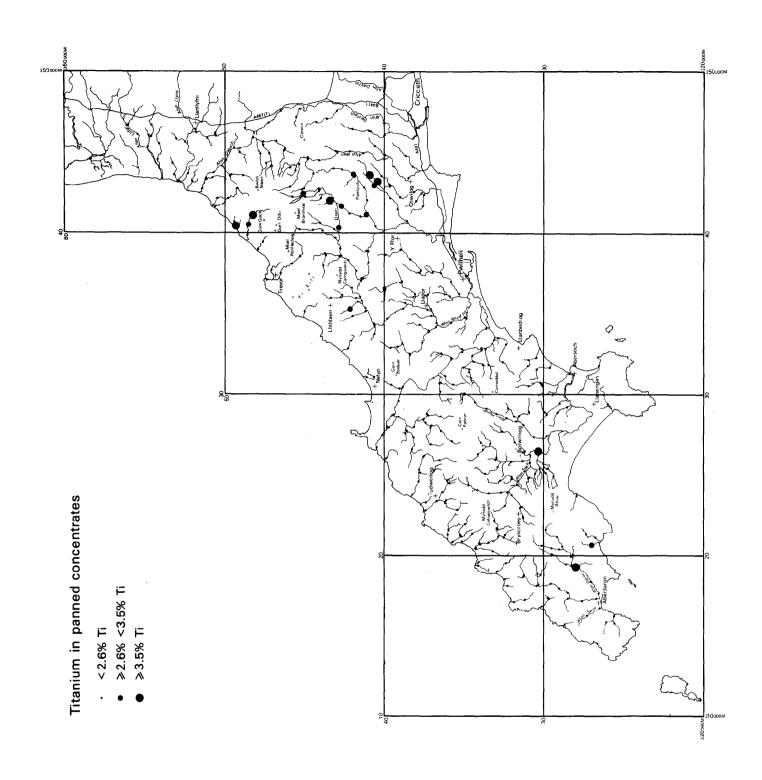
Iron in panned concentrate

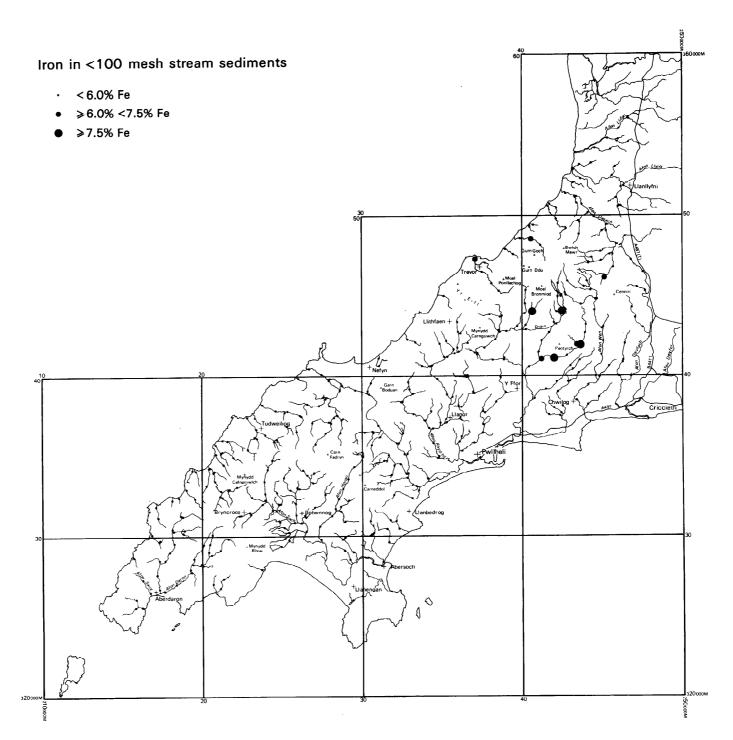
There are considerable differences in the distributions of iron in the two sample types. Concentrate samples with elevated levels of iron occur particularly in the west of the region (Figure 7) over the Precambrian rocks where there are no corresponding high Fe contents in the sieved sediment. This probably reflects upgrading of iron oxide and perhaps pyrite in the concentrate. Only at two sites in the west of the area are there coincident iron anomalies in both sample types.

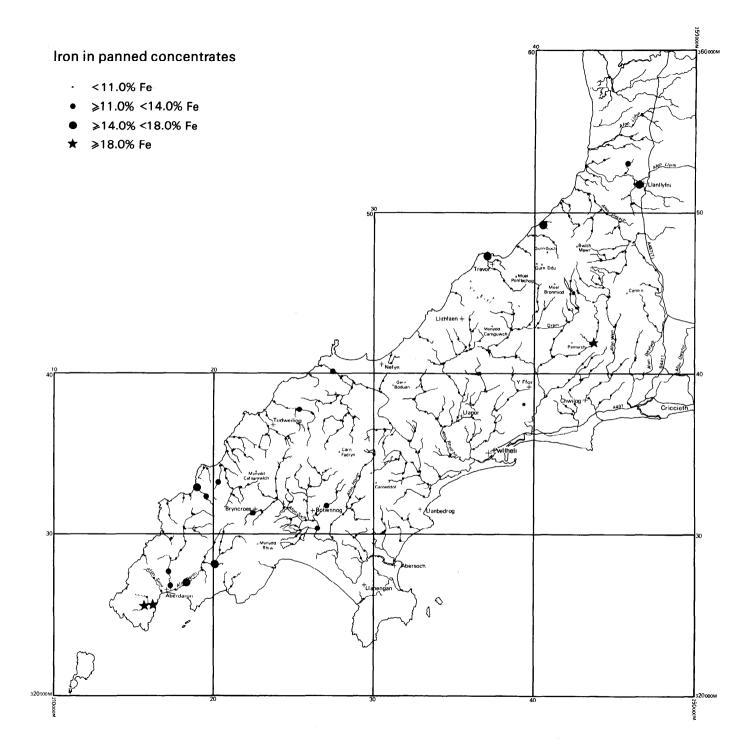
Cobalt in <100 mesh stream sediment

Samples with relatively high cobalt contents are concentrated in the east of the area (Figure 8). There is some degree of correlation with sites containing anomalous amounts of iron in the same sample but lack of corresponding Mn analyses makes it impossible to assess the extent of coprecipitation of Co with hydrous oxides of manganese.









Nickel in <100 mesh stream sediment

Relatively nickel-rich samples are grouped mostly in the east of the area (Figure 9) in the same general area as boron-rich samples. The anomalous streams drain Upper Ordovician volcanics intruded by an elongate granite body.

Nickel in panned concentrate

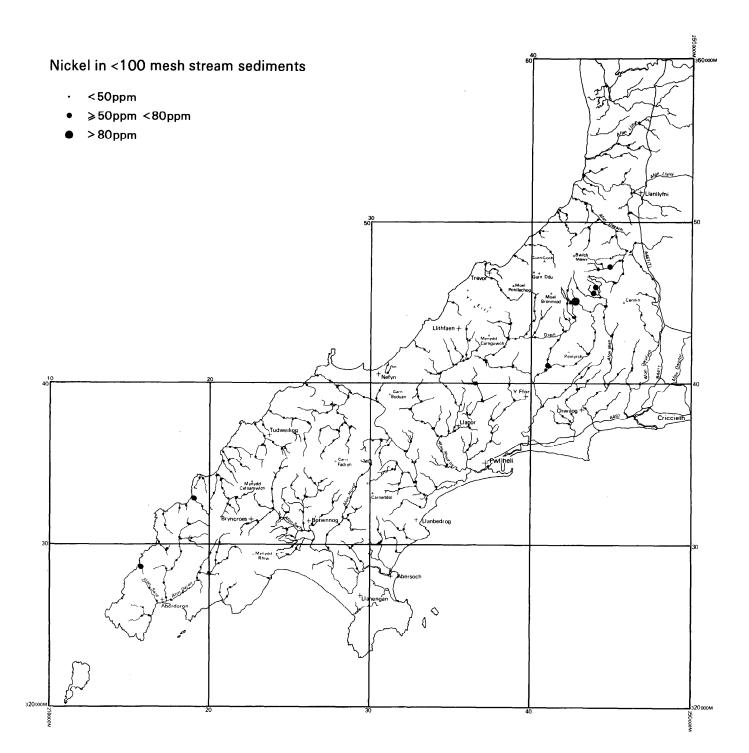
Samples with the highest concentrations of nickel (Figure 10) are grouped in the east of the area but not at sites with high concentrations of nickel in the sieved sediment sample. There is a general correspondence between the nickel-rich concentrate samples and those containing relatively high levels of titanium. This suggests that the source could be basic igneous rock, though the area is apparently underlain only by dark shales (Figure 2). The isolated nickel-rich sample in the west of the area reflects the layered mafic intrusions at Rhiw which were investigated for nickel mineralisation by Noranda Kerr between 1970 and 1972 (Open-file data held by BGS).

Copper in <100 mesh stream sediment

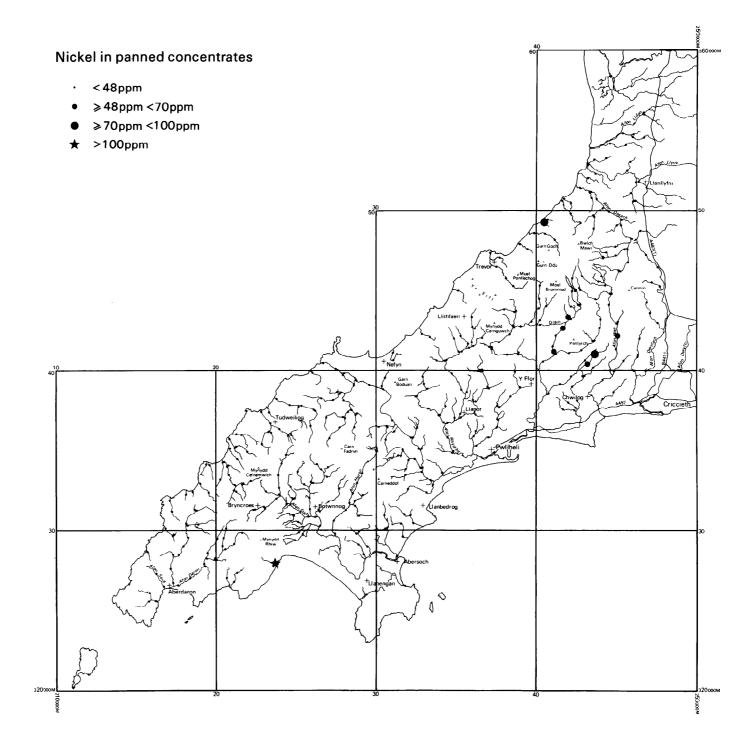
Copper enrichment in the sieved stream sediment sample (Figure 11) is associated with three regions. The highest copper contents are associated with samples adjacent to the north coast of the peninsula downstream of the A499 main road and are most likely to be contaminant-derived. A group of samples with lower amplitude copper enrichment occurs in the north of the area, following the outcrop of the Cambrian rocks and the Ordovician rocks overlying them. A further group of similar samples is associated with a sector of the outcrop of Precambrian Gwna Group and metamorphic rocks in the west of the area.

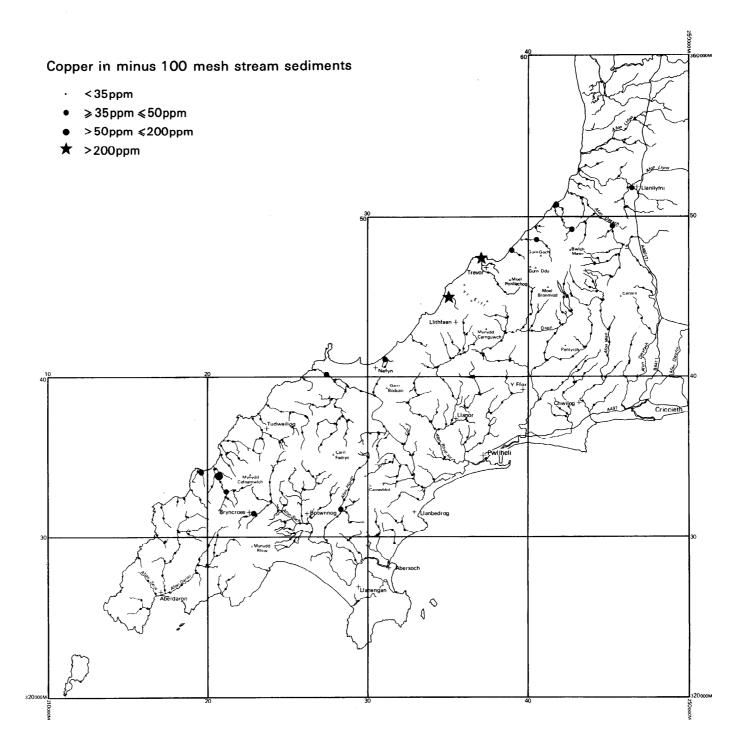
Copper in panned concentrate

Copper enrichment is more widespread in the panned concentrate samples (Figure 12) than the sieved sediment samples. Agreement between the two sample types is poor except where enrichment in the element is greatest. Interpretation of the pattern of distribution of copper in concentrate samples is aided by the mineralogical examination of all but five of the 25 samples classed as anomalous in Figure 12 (< 80 ppm Cu). Copper-rich contaminants were observed in 13 of the 20 samples examined, but in 7 of these chalcopyrite was also present, though subordinate to the contaminants. Sites where natural copper minerals were observed in the samples are also shown in Figure 12 and at 7 of these copper contents are < 80 ppm. In the presence of so much contamination of the drainage sediment the distribution and amplitude of anomalies is mostly unrelated to sources of natural mineralisation. Potentially the most significant enrichment of copper of natural origin is associated with the outcrop of Lower Ordovician shales between Llanbedrog and Botwnnog, towards the west of the peninsula. Copper enrichment of natural origin is also associated with the outcrop of the Precambrian Gwna Group.



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Zinc in <100 mesh stream sediment

It is difficult to interpret the distribution of zinc in sieved sediment anomalies in the absence of corresponding manganese data. A few samples have been analysed for manganese and these show a wide range of contents, up to a maximum of 1.35%. As zinc is relatively high in the most manganiferous samples, it is probable that several of the samples showing low amplitude zinc enrichment (Figure 13) are associated with secondary enrichment of manganese. Most of the samples in this group are derived from areas consisting predominantly of Upper Ordovician slate. The group of samples showing low amplitude enrichment in Zn in the area between Llanbedrog and Bottwnnog probably reflect mineralisation, at least in part, in view of the spectrum of other elements enriched and the presence of sulphide minerals including sphalerite in several concentrates from the area. At only ten sites is there correspondence between zinc enrichment in concentrate samples and in the sieved sediment samples, and three of these are found in this belt. Further higher amplitude zinc enrichment, probably reflecting mineralisation, is present to the north-west of Criccieth and east of Moel Bronmiod.

Zinc in panned concentrate

Zinc-containing contaminants have been noted in concentrates from several sites including six classified as anomalous (> 160 ppm, Figure 14). Platy grains of metal seem to be the commonest zinc-rich material in these samples. In contrast, sphalerite has been observed in concentrates from seven sites (Figure 14) but in none of these is zinc present in anomalous amounts. Six of these sites are on the Lower Ordovician shales in the west of the area where there are several other indications of material derived from mineralisation. Two areas where both sample types are enriched in zinc, ie north-west of Criccieth and east of Moel Bronmiod, also probaly reflect mineralisation. Outside these areas the majority of the enhanced zinc in concentrate samples is derived from contamination. At a few other sites elevated zinc contents could be natural in origin, eg at Chilwog and the two sites south of Llithfaen (Figure 14)

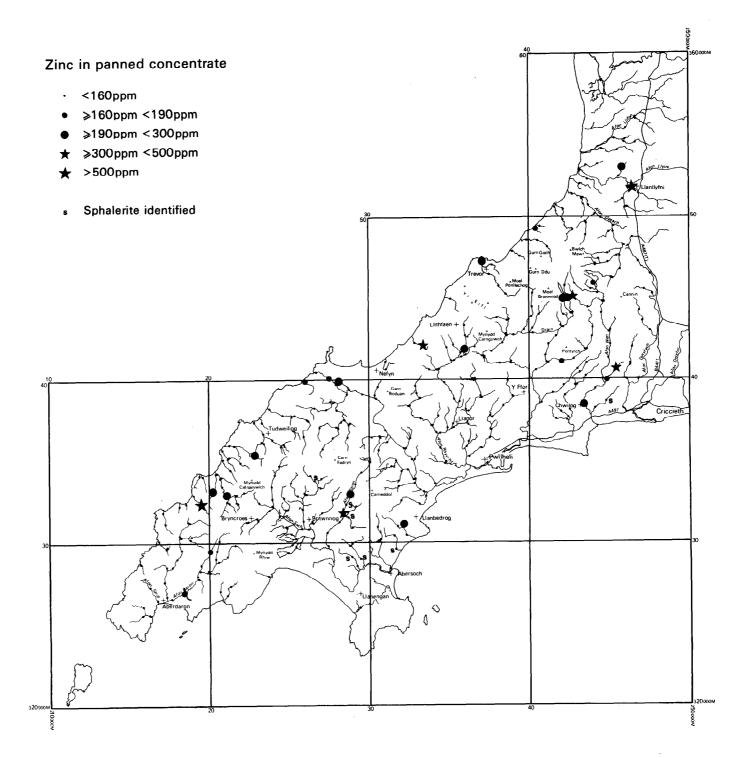
Molybdenum in <100 mesh stream sediment

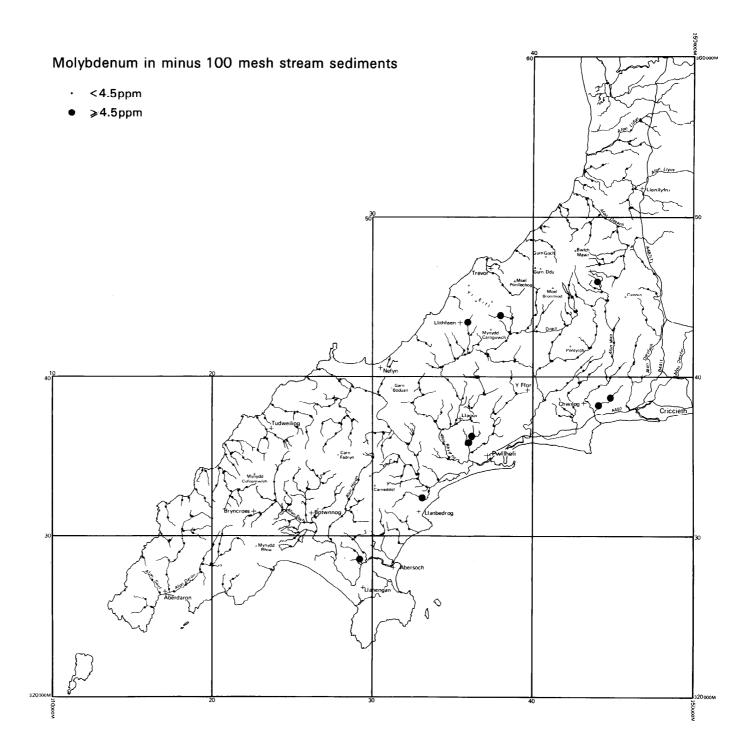
Molybdenum concentrations in the sieved sediments reach a maximum of 5.7 ppm. The scattered low amplitude Mo enrichment in the south of the peninsula (Figure 15) probably reflect local enhancement of the relatively high background level in slates. The three Mo-rich samples in the north of the area could be derived from molybdenum enrichment in the aureole of granite bodies.

Tin in panned concentrate

In areas devoid of tin-rich mineralisation the tin content of panned concentrates is a useful monitor of metallic contamination. Lead is very frequently associated with tin in contaminants followed in decreasing order of frequency by copper and zinc. Highly contaminated sites are likely to contain lead, copper and zinc, and other metals, together with high concentrations of tin. Fragments of tin can and solder may account for much of the tin contamination which is often present in association with human habitation in rural areas of Britain. Samples with tin enrichment (Figure 16) are widely scattered over much of the area and indicate the scale of contamination of drainage sediment with base metals.

Zinc in <100 mesh stream sediments





Antimony in panned concentrate

Antimony is often used as a hardener of lead metal and most of the anomalies (Figure 17) are associated with high levels of lead and tin (maximum 190 ppm Sb associated with 1.0% Pb and 0.3% Sn). Only four anomalies as defined in Figure 17 are not associated with clear indications of contamination but as Sb levels in these are low compared with other anomalies their significance is doubtful.

Barium in panned concentrate

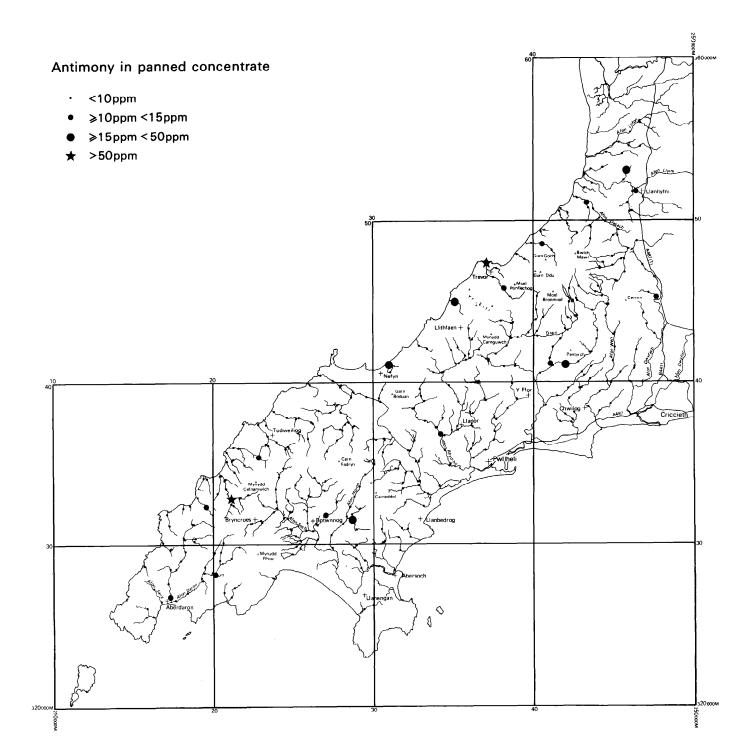
The presence of baryte in concentrates from a highly contaminated area is often a good guide to the presence of base-metal mineralisation. Figure 18 shows that the incidence of baryte is wider than samples considered to contain anomalous concentrations of barium. There is a group of samples with high barium contents along the south coast (Figure 18) associated with outcrops of Arenig sediments and intrusive greenstones, including one probably derived from the vein mineralisation previously worked along the east-west zone to the south of Abersoch. Several sites between Llanbedrog and Botwnnog contain small amounts of baryte, suggesting the widespread occurrence of mineralisation in this region. The presence of baryte in samples from west and north-west of Bryncroes, derived from the Precambrian rocks, indicates that though contamination of these sites is strong, a component of the anomalies is also derived from mineralisation. This is also the case for the highly contaminated site near Trevor on the north coast. Comparison of the distribution of barium with that of the base metals suggests that barium is associated with two mineralisation signatures. Firstly, there is a weak association of baryte with Pb + Zn + Cu, typified by the samples from the Llanbedrog-Botwnnog area. In the second type, barium is associated more with copper than the other metals, as in the anomalous samples west of Bryncroes and Criccieth respectively (Figure 18).

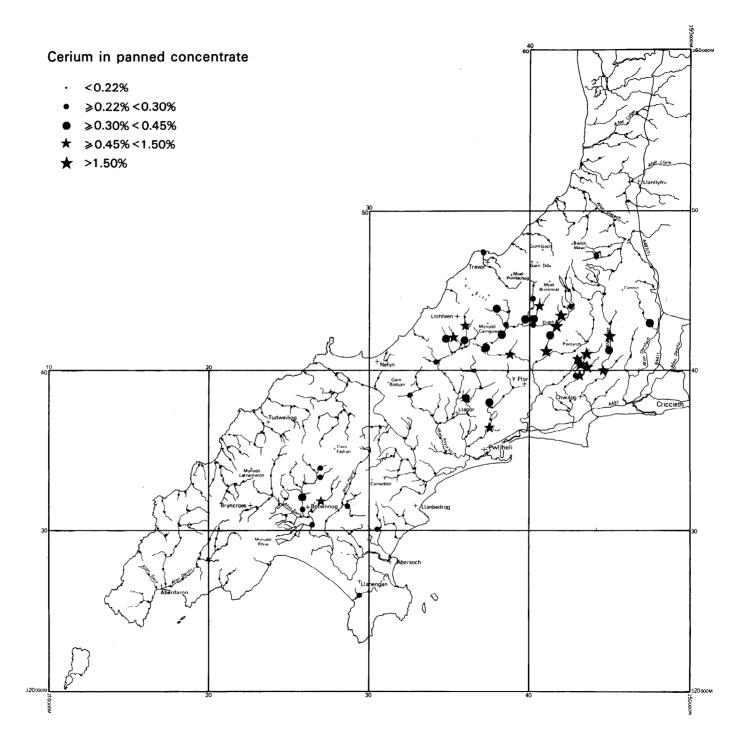
Cerium in panned concentrate

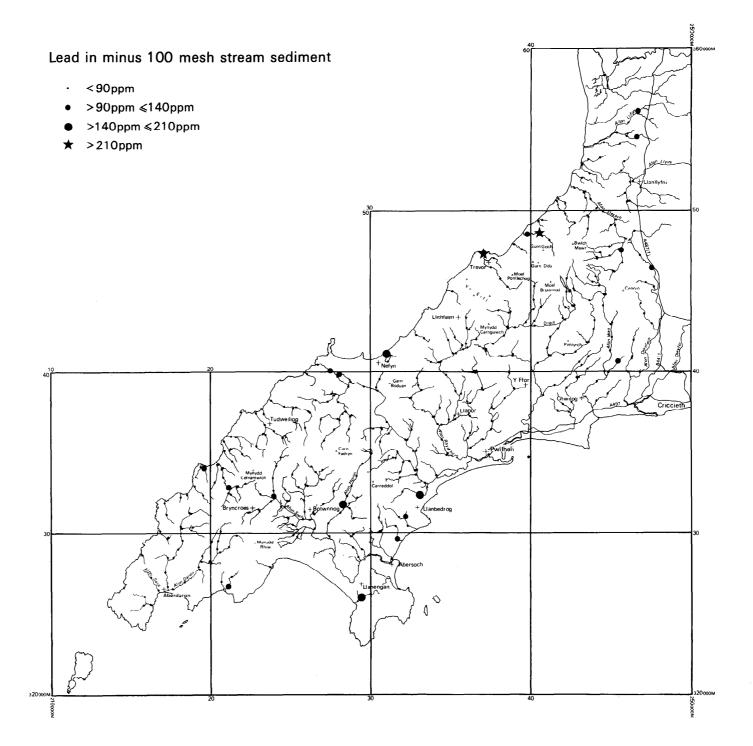
The cerium content of the panned concentrates (Figure 19) reflects the abundance of monazite nodules that have been found to be widepread in drainage in Wales (Cooper et al 1983) and also in Llandovery turbidites (Milodowski and Zalasiewicz 1991). Cerium-rich samples are associated particularly with the outcrop of the Upper Ordovician argillaceous rocks in the east of the area and, to a lesser extent, some parts of the outcrop of the Lower Ordovician slates.

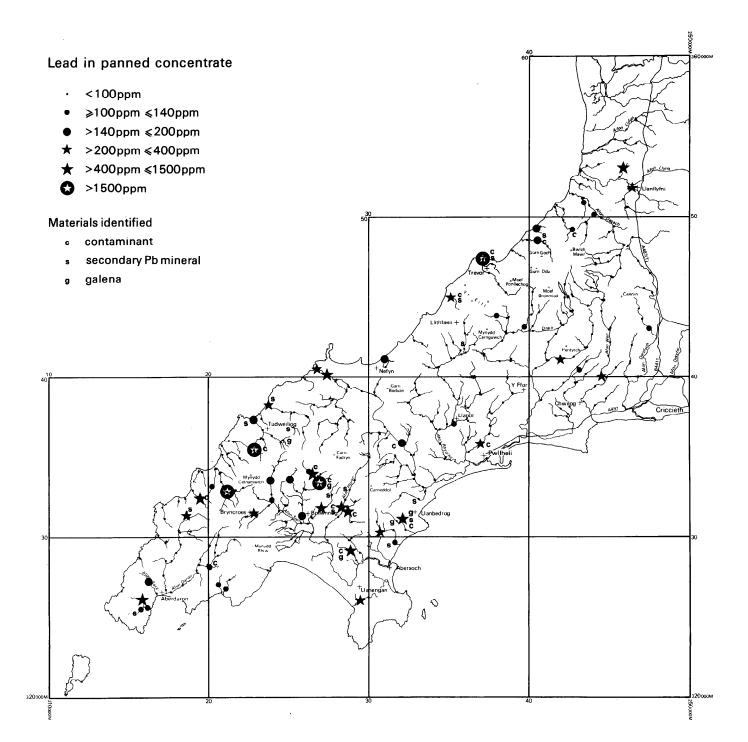
Lead in <100 mesh stream sediment

The interpretation of lead anomalies in sieved sediment samples is difficult in areas with considerable metallic contamination. Though typical lead-rich metallic contamination is relatively coarse-grained and tends to appear predominantly in the concentrate sample, soft secondary lead minerals formed by the alteration of contaminants can be fine enough to pass into the minus 100 mesh samples. Comparison with the lead content of the corresponding concentrate sample is the best means of establishing whether an anomaly is likely to be of natural origin. Lead-rich material of natural origin often appears as an enrichment of roughly similar amounts in each sample type. Four of the lead-rich samples along the south coast as far as Llanbedrog (Figure 20) fit into this category as does the sample from east of Bryncroes. Three samples from the east of the area with slightly elevated lead contents do not show any corresponding enrichment in lead in the concentrate samples and may reflect enrichment in organic material.









Lead in panned concentrate

Many samples contain high concentrations of lead (Figure 21), particularly in the west of the peninsula. All of the samples in the top three classes in Figure 21 probably reflect contamination. However, there are several sites where contaminated samples also contain lead minerals of natural origin. Galena has been identified in 6 of the 39 samples examined mineralogically, four of which show major metallic contamination. White secondary lead minerals occur in 18 samples and in significant amounts in 14 of these. In three highly anomalous samples the secondary minerals are likely to be derived from the alteration of metallic contaminants. In 9 of the samples containing lead secondary minerals no lead-rich metallic contaminants have been identified and it is probable that the lead is of natural origin. On the basis of the mineralogical information and the elements enriched in parallel with lead, sites thought to reflect lead-bearing mineralisation are concentrated firstly in the area west from Llanbedrog to Botwnnog and north-west towards Tudweiliog and secondly along the outcrop of the Gwna Group. Close to one of these sites at [SH287315] there is an old level and small stope roughly parallel to the local strike of the dark grey silty slates (D Bate, personal communication, 1993) but no obvious sulphide mineralisation. Other small groups of sites where slight enrichment in lead may reflect mineralisation are present to the north-east of Chwilog and in tributaries of the Afon Desach in the north of the area. Lead is also enriched (Figure 21) in the sample derived from the western end of the mineralisation structure running east-west to the south of Abersoch.

CONCLUSIONS AND RECOMMENDATIONS

The survey has demonstrated that it is possible to detect base-metals of natural origin in drainage samples in an area in which metallic contamination is widespread, using a combination of diagnostic element associations and mineralogical examination of panned concentrate samples.

The largest grouping of base-metal anomalies of natural origin occurs to the west of Llanbedrog. In detail, the anomalies follow the outcrop of the Llanvirnian shales as far to the north-west as Tudweiliog but are absent from the region underlain by similar rocks to the north-east. Within this zone most, but not all, adjacent and parallel streams contain ore minerals but there is no evidence of significant dispersion of the base-metals downstream. This suggests that sources of the mineralisation are relatively narrow and cut by most streams approximately at right angles. The adit and small stope at [SH287315] possibly worked the source mineralisation.

One possible explanation of the source of base metals in drainage within this zone is a northwest-trending mineralised structure cutting across the oucrop of the Llanvirn shales, together with separate sources along a structure trending west-south-west from Llanbedrog. The combination of minerals derived from the mineralisation is similar to those extracted from the vein mineralisation in the east-west zone to the south of Abersoch. The distribution of base metals does not seem to be related to the distribution of small granitic bodies within the outcrop of Llanvirnian slates or to the volcanic sequence further to the north and east. However, the ore minerals in drainage do appear to follow the local strike as it curves round in the nose of the syncline (Figure 2). It is therefore possible that the anomalies are derived from stratabound mineralisation within the shale sequence and therefore potentially of greater importance. This explanation is supported by the orientation of the old stope at [SH287315] which is parallel to the local strike. Furthermore, there is no evidence in the old adit of veining or a dislocation. On this model two separate sources are required to

account for all the occurrences of base metals in drainage in the area, one at the base of the sequence and another higher up.

The area of Llanvirn shales between Llanbedrog and Tudweilog forming the potential source of Cu, Zn, Ba and Pb minerals should be investigated further in view of the possible occurrence of stratabound mineralisation over a wide area. Overburden sampling and geophysical surveying are required along a series of traverses at right angles to the strike of the shales and the presumed trend of postulated structures to establish unequivocally whether the source of the base metals in this zone is stratabound or structurally controlled.

The scattered anomalies within the Gwna group are derived from a different style of mineralisation which is dominated by Cu and Ba and is likely to be of minor significance. All the other sites containing base metals of natural origin are scattered and isolated. More detailed drainage sampling should be carried out in the area to the east of Chilwog, as the present sampling is insufficient to establish whether the chalcopyrite, sphalerite and baryte in this sample reflects isolated and minor mineralisation or a wider area of mineralisation at the top of the Llanvirn slates or in the overlying volcanic sequence.

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