THE GEOCHEMISTRY OF THE SEDIMENTARY ROCKS OF THE HARLECH DOME, NORTH WALES.

A thesis submitted for the degree of Doctor of Philosophy in the
Department of Geology, University of Aston in Birmingham.

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Abstract

Bedrock geochemical analysis, coupled with detailed data analysis, was carried out on some 260 samples taken from two areas of the Harlech Dome, near Dolgellau, North Wales. This was done to determine if rocks from mineralised and non-mineralised areas could be distinguished, and to determine mineralisation types and wall rock alterations. The Northern Area, near Talsarnau, has no recorded mineralisation, while the Southern Area, near Bontddu, has been exploited for gold. The rocks sampled, in both areas, were from the Cambrian Gamlan Flags, Clogau Shales, Vigra Flags, later vein materials, and igneous intrusions.

All samples were analysed, using a new rapid, atomic absorption spectrophotometric technique, for Si, Al, Fe, Cu, Ni, Zn, Pb, Sr, Hg, and Ba. In addition 60 samples were analysed by X-ray fluorescence for Mn, Ti, Ca, K, Na, P, Cr, Ce, La, S, Y, Rb, and Th. Total CO_2 was determined, on selected samples, using a combustion technique.

Elemental distributions, for each rock type, in each area, were plotted, and means, standard deviations, and enrichment indices were calculated. Multivariate statistical analysis on the results distinguished a Cu-type mineralisation in the Northern area, and both Cu and Pb/Zn types in the Southern Area. It also showed the Northern Area to be less strongly mineralised than the Southern one in which both mineralisation types are associated with wall rock alteration. Elemental associations and trends due to sedimentary processes were distinguished from those related to mineralisation. Hg is related to mineralisation, and plots of factor scores, on the sampling grid, produced clusters of mineralisation related factors in areas of known mineralisation. A double Fourier Trend Analysis program, with a wavelength search routine, was developed and used to recognise

sedimentary trends for Sr, Y, Rb, and Th. These trends were interpreted to represent areas of low pH and reducing conditions. They also indicate that the supply of sediment remained constant over Gamlan, Clogau, and Vigra times. The trend surface of Hg showed no association with rock type. It is shown that analysis of a small number of samples, for a carefully selected number of elements, with detailed data analysis, can provide more useful information than analysis of a large number of samples for many elements.

The mineralisation is suggested to have been the result of water solutions leaching ore metals from the sedimentary rocks and redepositing them in veins.

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CHAPTER I

INTRODUCTION

1:1 GENERAL GEOLOGY OF THE HARLECH DOME.

The Harlech Dome is a topographic and tectonic dome of Lower Palaeozoic rocks, covering an area of 300 square kilometres in West-Central Wales (Fig.1). Its Northern and Southern boundaries are the Afon Dwynyd and Afon Mawddach respectively. The Eastern boundary approximates the line of the Dolgellau - Trawsfynydd road (A. 487), while to the West it is bounded by the sea.

The area is one of great topographic contrasts with rounded hills rising from the Mawddach Estuary in the South, and the high angular Rhinog Mountains (Y-Llethr, 754.38m) in the centre. Further contrast is afforded by the long sandy beaches along the Western margin from Barmouth to Portmadoc.

The general domical aspect of the topography reflects the underlying geology. Hard resistant grits crop out in the core of the dome, surrounded by younger less resistant shales and sandstones (Fig.2). Major rivers, and the sea cliffs along the coastline, tend to follow the strike of the rocks, though a radial drainage is also present.

Bedrock exposure is generally good though the shale sequences are commonly eroded to form broad valleys, many of which have a cover of glacial debris or alluvium. Excellent sections, in which all rock types are exposed, are present in numerous road cuttings. The section of the A496 between Dyffryn (SH 586223) and the toll bridge to Penmaenpool (SH 690191), and between Talsarnau (SH 706355), have almost continuous fresh exposure along

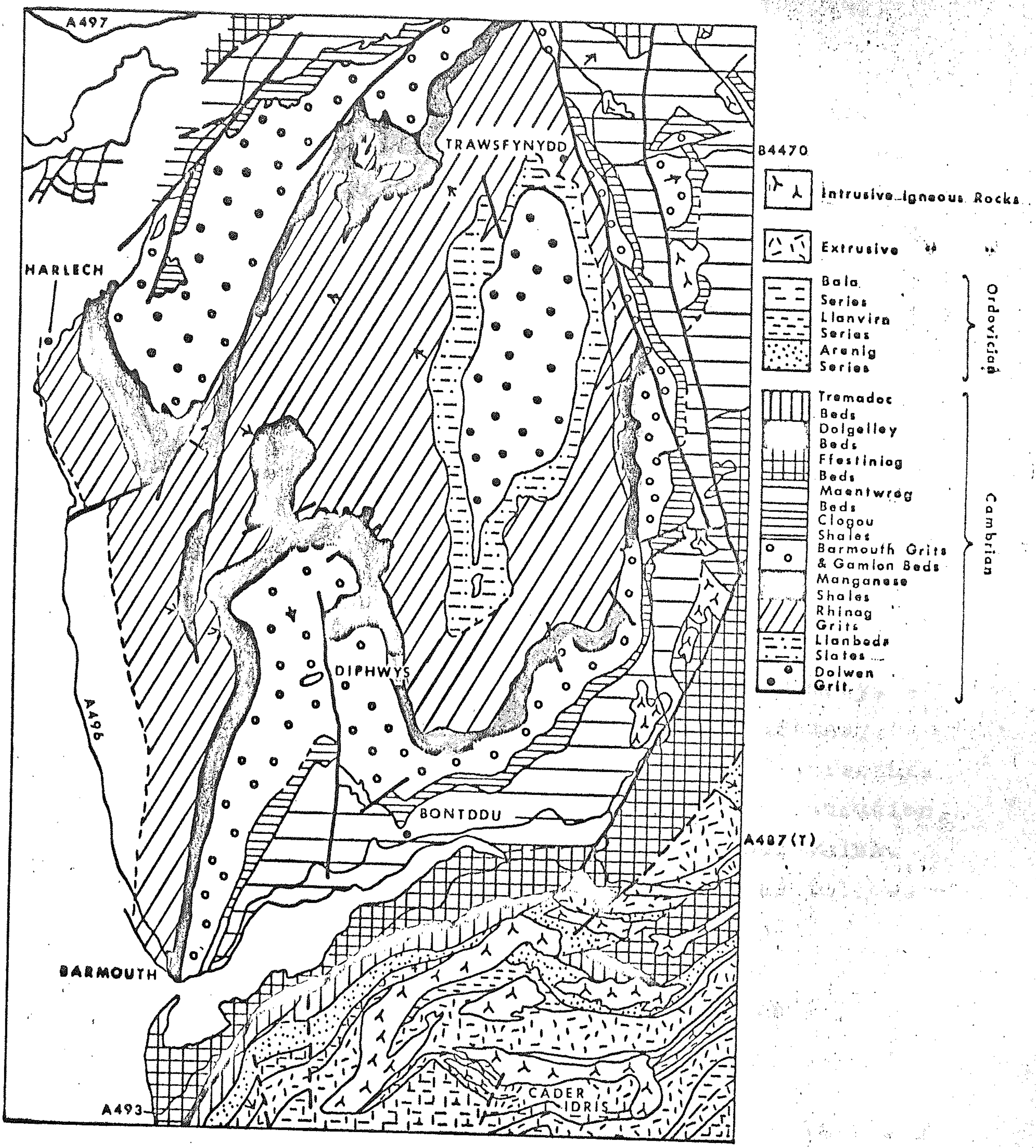


Fig.1. GEOLOGICAL MAP OF THE HARLECH DOME AND THE CADER IDRIS RANGE (after Gilby (1968))

their length. In other parts of the area gritstone boulders have fallen from the outcrop area, and cover the shales and sandstones. These boulders are commonly large enough to be mistaken for bedrock outcrops. The main valleys have a glacial cover which consists largely of stiff blue clay with up to 10% gravel sized fragments of the underlying rocks. This material is in turn commonly covered with a thin peat layer and some rounded boulders. The drift thickness varies from 0 to 8m, with the thickest part in the centre of the valleys.

1: 2 STRATIGRAPHY.

The stratigraphic succession of the area was studied by a number of geologists in the 19th Century, and a Geological Survey Memoir was published in 1866 (Ramsay, 1866), followed by a second edition in 1881 (Ramsay, 1881). These works recognised the main fold structure of the area, the faults, two types of igneous intrusion, and noted the occurrence of some metalliferous veins. The succession at that time was sub-divided as follows:-

Tremadoc Slates - Upper Cambrian
Lingula Flags - Upper Cambrian
Menevian Slates - Middle Cambrian
Cambrian Grits and Flags - Lower Cambrian

Belt (1867) proposed a subdivision of the Lingula Flags into the Dolgellau, Ffestiniog and Maentwrog beds, based solely on lithologies.

The succession in use today is that published by Matley and Wilson (1946). This was derived from previously unpublished maps produced by Lapworth and Wilson between 1900 and 1910. The sequence has been adopted by later workers (Price, 1963; and Gilby, 1968), and is that used in the present work. The succession is quoted in Fig.2.

Fig. 2. Geological sucession of the Harlech Dome (after Matley and Wilson, 1946)

			Thickness in metres
Upper Cambrian	Ffestiniog Flags (upper beds absent)		500
	Maentwrog Flags	(2) Penrhos Shales	333
		(1) Vigra Flags	366
Middle Cambrian	Clogau Shales		93 -100
	Cefn Coch Grit		1 - 166
	Gamlan Flags and Grits		230 - 333
	Barmouth Grits		116 - 200
Lower Cambrian	Manganese Group	Upper Manganese Shales	100 - 200
		Manganese Grit	1 - 66
		Lower or Ore Bed Shales	16 - 20
	Rhinog Grits		400 - 833
	Llanbedr Slates		100 - 233
	Dolwen Grits (base not exposed)		133 - 166

1: 3 IGNEOUS ROCKS.

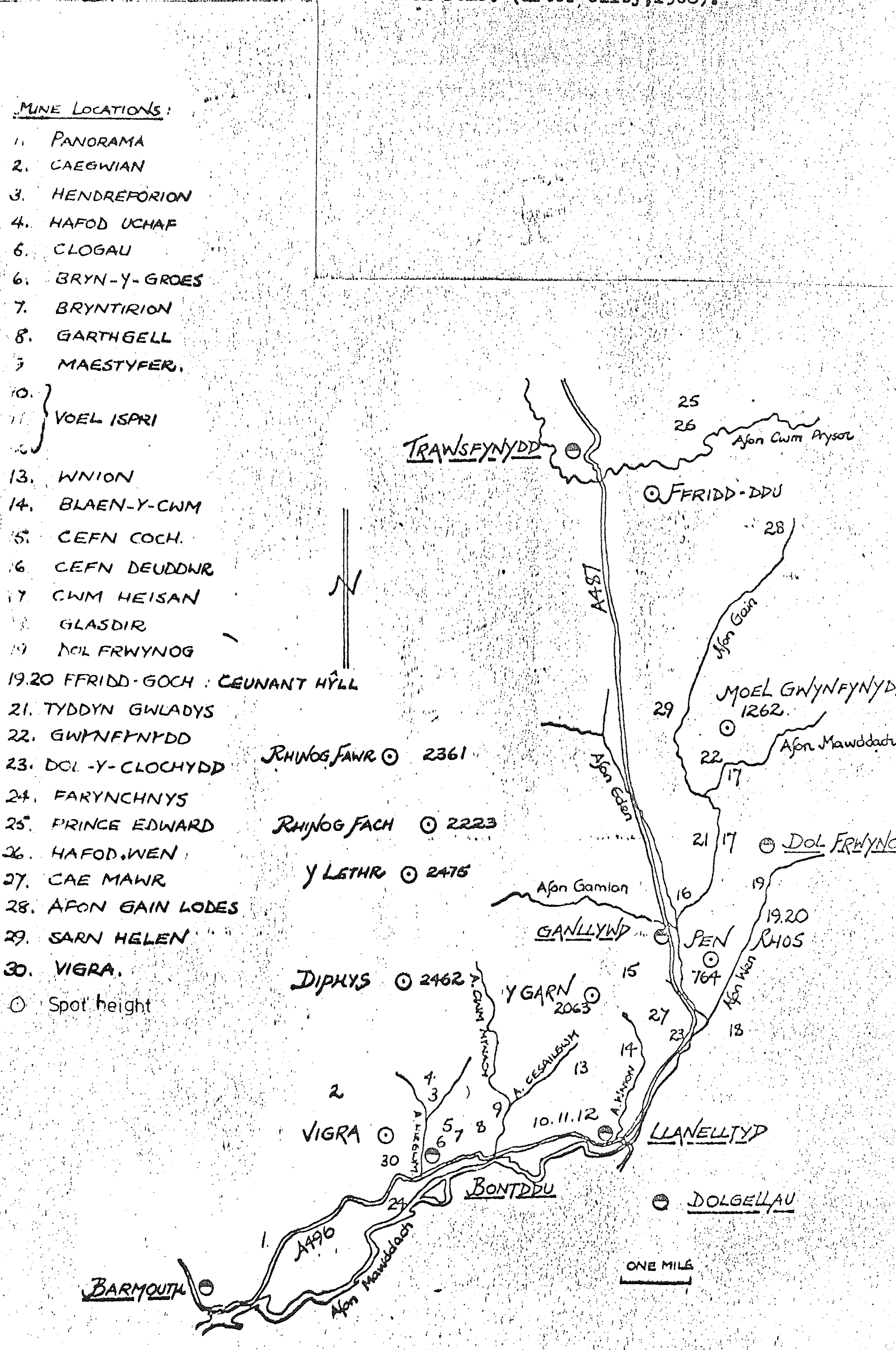
Igneous rocks in the area are all intrusive and consist of a number of dykes and sills of two major types; a dolerite and a hornblende diorite. These intrusions vary in thickness from a few cm to several tens of metres, and may extend for up to 3 km. The effect of low grade regional metamorphism has made positive identification of the rock types difficult and only a detailed petrographic study, as made by Woodland (1938) and Mately and Wilson (1946) reveals the original mineralogy. The relationship of the intrusions to the surrounding sediments has been described by many workers (Salter, 1865; Teal, 1888; Plant and Williamson 1866; Belt, 1867-8). More recent work by Andrew (1910), Mately and Wilson (1946) and Gilby (1968) has confirmed the conclusions of the earlier works and a detailed history of the intrusions has been developed. This is outlined in Chapter 3.

1: 4 MINERALISATION.

The most important mineralisation economically in the area is the gold mineralisation, first reported in the literature by Dean (1844) and Roberts (1844), but possibly worked in the time of Charles I (Readwin, 1888). In addition, copper and lead/zinc mineralisations are present but are economically less important. The mineralisation has the form of quartz vein lodes, and has been worked on a small scale until the mid 1930's. One mine, the St. Davids at Bontddu, is still operated on a part-time basis by its owner, but presently produces only a few ounces of gold per year.

All of the gold bearing mineralisation is on the South and Eastern flanks of the Dome, between Bontddu and Gwynfynydd (Fig.3). Reports on the mineralisation are plentiful (Dewey and Dines, 1923; Dewey and Smith, 1922; Dewey and Eastwood, 1925).

Fig. 3. Mine locations in the Harlech Dome. (after Gilby,1968).



Matley and Wilson (1946) use the interpretation of Andrew (1910) as to the occurrence of the gold ores. Gilby (1968) discusses the wider aspects of the mineralisation in relation to its genesis and type. The conclusions of these works are summarised in Chapter 5.

1: 5 AIMS OF THE PRESENT WORK.

The aim of this study is to investigate, in detail, the relationship between mineralisation and bedrock geochemistry in terms of element distributions derived from bulk samples of the rocks. Major and trace element distributions were determined in both mineralised and non-mineralised areas in order to detect primary or secondary dispersion haloes which might be used as prospecting targets.

The petrography of the rocks was described and interpreted to determine the relationship of lithology and stratigraphy to the elemental distributions obtained.

The structural geology was examined to allow structural factors to be related to mineralisation if applicable.

Chemical analyses were carried out using both X-ray fluorescence and atomic absorption spectroscopy. The techniques used are described in the appendices of this thesis.

Analytical results were subjected to statistical and trend analysis techniques in an attempt to explain the geochemical relationships. A hypothesis for the origin of the mineralisation will be developed and an extension of the above techniques for use as an exploration tool, suggested.

In order to develop the above aims three different areas were investigated, each with very similar stratigraphy, structure and lithologies, but with differing degrees of mineralisation. The overall area of the Harlech Dome was chosen because it is geologically well known, and the economic mineralisation was confined to three rock types (the Gamlan Flags, the Clogau Shales and the Vigra Flags). This made sampling easier and reduced the number of variables to be taken into account in interpretation. In addition, the recorded mineralisation is confined to small well defined areas on the Southern and Eastern flanks of the Dome (Fig.3).

The three areas selected for this study are:-

(a) The area to the North of Bontddu (Fig.4) which was selected as it is the main area of mineralisation in which the overall effects of mineralisation and bedrock chemistry could be studied.

(b) The area to the North of the Harlech Dome (Fig.4) was chosen to act as a control. This will enable the chemistry of the bedrock to be studied in isolation as no economic mineralisation has been recorded in this area.

(c) The Gwynfynydd Mine (Fig.4) was the last of the gold mines of the area to stop production on a commercial scale, and easy access to the workings is possible. The object of the sampling was to determine directly the influence of the mineralisation on the country rock by sampling the mineralisation, country rock, intrusives and included fragments of country rock in the veins, all within the 'zone of mineralisation.'

A detailed literature search revealed sufficient information on the stratigraphy and mineralogy of the lodes, to allow the study to be purely geochemical.

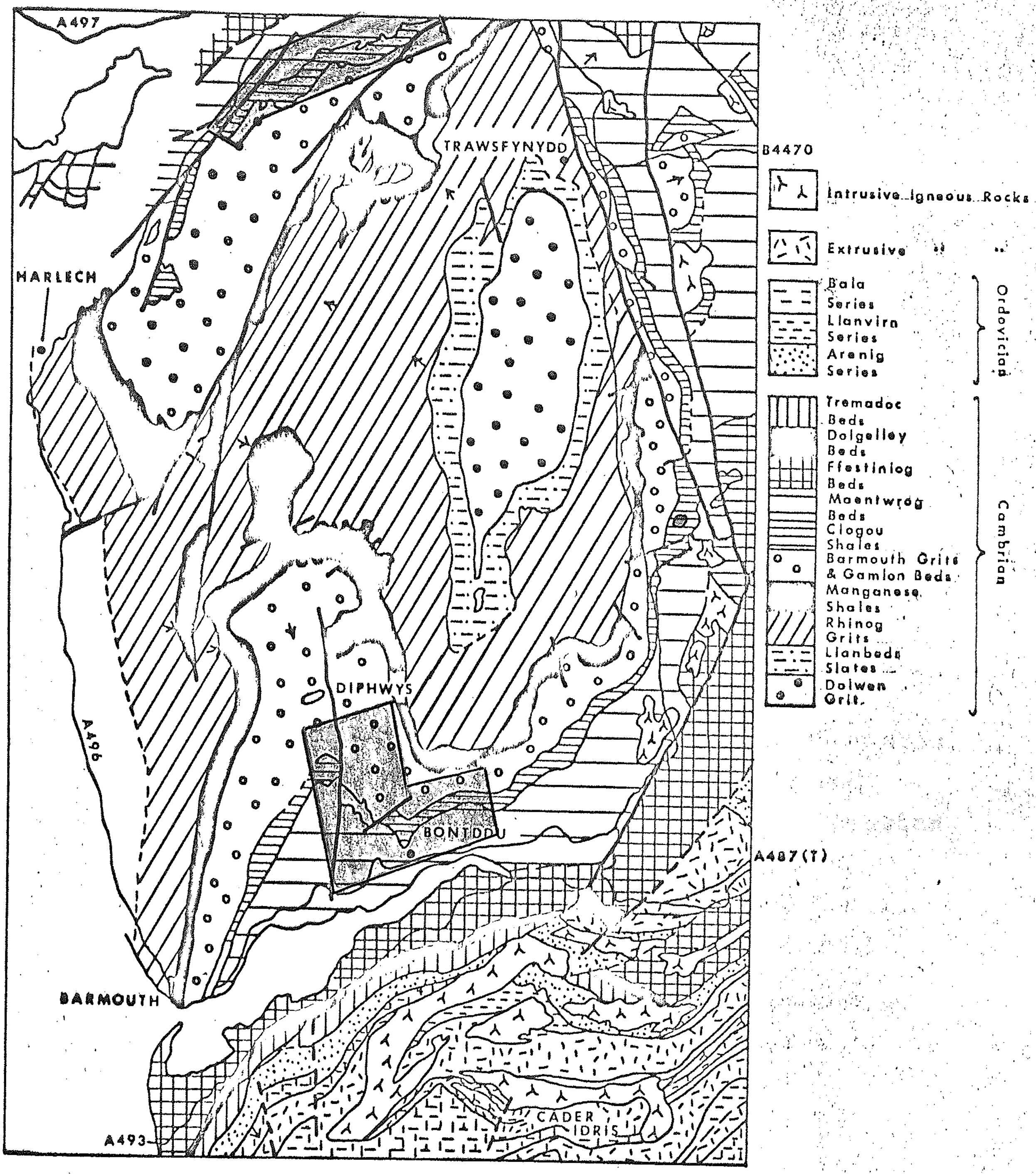


Fig.4. GEOLOGICAL MAP OF THE HARLECH DOME AND THE CADER IDRIS RANGE WITH SAMPLE LOCATIONS

CHAPTER 2.

THE STRATIGRAPHY OF THE HARLECH DOME.

2: 1 INTRODUCTION.

The detailed stratigraphy of the Harlech Dome has been formalised by various authors, as discussed in Chapter 1. Because of this only a brief description of the full stratigraphic column for this area is given. The beds studied in the present work are described in more detail.

2: 2:1 GENERAL STRATIGRAPHY.

The sedimentary rocks of the Harlech Dome are all assigned to the Cambrian system by Matley and Wilson (1946), and their stratigraphic succession is shown in Fig.2. All contacts between the beds in the exposed succession of some 3,000 metres are conformable, and in most instances are sharp. Brachiopods and trilobites are present in the Middle and Upper Cambrian rocks. No fossils, except for some annelids and obscure brachiopods, have been found below the Gamlan Flags making correlation with other areas difficult.

The base of the Cambrian succession is not exposed in this area but is placed at the base of the Dolwen Grits by reference to other areas (Jones, 1936).

2: 2:2 DOLWEN GRITS.

The lower part of this unit is not exposed. The rocks consist of a medium-grained green or greenish-grey feldspar rich arkose with a clay matrix now changed to a mixture of chlorite and sericite.

2: 2:3 LLANBEDR SLATES.

These are conformably above the Dolwen Grits. They consist of blue and purple weathering, well-cleaved, argillaceous slates with some green layers. Arkosic layers 1-5cm thick are also present within the sequence.

2: 2:4 RHINOG GRITS.

These rocks consist of hard, coarse grained (up to 1cm), grey, grey green and blue massive arkoses with argillaceous layers and a few flaggy layers. The overall thickness varies from 600 metres in the East to 370 metres in the West, around Llanbedr. The argillaceous and flaggy layers are usually less than one metre thick with sharp contacts. In the grits quartz is predominant over feldspar. Layers containing well-rounded pebbles, up to 5cm in diameter are present and some may be traced over 2km. The contact with the underlying Llanbedr slates is abrupt in the central area of the Dome, where the lowest grit beds are quartz rich forming an area of quartzites.

2: 2:5 MANGANESE GROUP.

The rocks of this group conformably overlie the Rhinog Grits. They consist of the Lower Ore Bed Shales, the Manganese Grit and the Upper Shales, the Upper Shales forming the main part of the formation. The shales are fine-grained argillaceous rocks with a bluish or greenish colour, the outcrops having a striped appearance.

A more detailed study of these beds was made by Mohr (1959) who concluded that the Manganese Ore Bed, near to the base of the Lower Shales, was deposited in basins with restricted circulation having some connection with the open sea.

2: 2:6 BARMOUTH GRITS.

The rocks of this group overlie the Manganese Group with a sharp but conformable contact. They are between 100 and 250 metres in thickness and resemble the Rhinog Grits, but are generally fine-grained (1cm), less massive (layers generally 1-2m) and have fewer arkosic layers. Pebbly layers are present, some of which can be traced over distances of 5-6 km.

2: 2:7 GAMLAN FLAGS AND GRITS.

This group conformably overlies the Barmouth Grits, and, in this area, consists almost entirely of silicified fine-grained arkosic (flags) and argillaceous layers with a few coarse-grained arkosic layers. In general the grit layers are 3-4m thick with the flags up to 1m thick. The argillaceous layers are usually between 2cm and 2m thick, and may contain numerous fine-grained contorted siliceous layers.

In the North-Eastern part of the Harlech Dome the Gamlan Flags and Grits are approximately 370m thick. To the South-West the beds become thinner giving a total thickness of 230m. Further South-West in the area of Afon Hirgwm (SH 660 205), most of the coarse-grained beds are absent. To the West at Barmouth, the Gamlan Beds consist entirely of flags and shales.

In the North-East, near Afon Gain, (SH 740 320), the Gamlan passes abruptly into the overlying Cefn Coch Grit, which is cosidered by Andrew (1910) to represent the basal unit of the Clogau Shales. It was mapped as a separate unit by Matley and Wilson (1946) because in the Western part of the area, from Blaen-cwm-Mynach (SH 690 232) to Barmouth (SH 610 160), a marked transitional zone is present at the top of this unit. This zone is some 10m thick and in it the grey, purple and green shales of the Gamlan are inter-bedded with dark-coloured Clogau Shales, the Cefn Coch Grit being absent. In most of the area however, the Cefn Coch Grit forms a characteristic upper boundary for the Gamlan Flags.

2: 2:8 CEFN COCH GRIT.

This is a coarse-grained (1cm) commonly quartz-rich arkose, and is the highest of its kind in the Cambrian sequence of the area. It varies in thickness from 1m to a maximum of 15m at Pistyll-y-Cain (SH 735 275). It is present throughout the area, except where represented by the argillaceous passage beds to the East of Barmouth. Variations in thickness of this unit are used to suggest that the source for the grit lay to the North-East of Trawsfynydd (Matley and Wilson (1946).

2: 2:9 CLOGAU SHALES.

In the field the Clogau Shales are poorly exposed except in stream sections. They commonly have a rusty yellow appearance. These are approximately 77m thick, and consist of well-cleaved dark grey-blue to black, fine-grained, shales. They are free from the siliceous layers ('ringers' of Matley and Wilson 1946) which are present in the overlying formations, and, to some extent the underlying ones. The shales have numerous pyrite-rich layers, 5mm to 15mm thick, within individual beds. The pyritic layers are commonly not visible on hillside outcrops but are readily seen in stream sections as lighter coloured layers in the dark shales. Andrew (1910) suggested that these lighter layers are due to the pyrite weathering and being oxidised to ferrous sulphate and sulphuric acid. The sulphuric acid would then bleach some of the dark carbonaceous material to produce the lighter bands.

The dark colour of the shales is probably due to the presence of both pyrite and carbonaceous material. Andrew (1910) quotes an analysis of the shales as follows:-

	wt%
Organic matter	5.78
Iron in the form of sulphide	21.88
Not determined	72.34

This quantity of carbonaceous material would certainly produce a dark coloured rock.

2:2:10 MAENTWROG FLAGS (INCLUDING THE PENRHOS BEDS AND VIGRA FLAGS).

The Clogau Shales pass conformably into a series of alternating slates and flags, which contain numerous fine-grained arenaceous layers from 0.5cm to 1m in thickness. The maximum thickness of the complete sequence is some 650m. In the upper part of the sequence the arenaceous layers form thin, irregular, white-coloured bands from 0.5 to 4cm thick. In the lower part of the succession these layers vary in thickness from 0.5m to 1m and are sufficiently resistant to form surface features. In Bontddu Glen (SH 669 190) they comprise approximately 25% of the formation (Andrew 1910). The presence of the thicker layers was used by Lapworth and Wilson (unpublished map, about 1910) to separate the Maentwrog Flags into the upper, or Penrhos Beds, and the lower Vigra Flags.

THE VIGRA FLAGS.

These consist of dark grey, thinly layered, fine-grained argillaceous beds, with numerous siliceous bands varying in thickness from 0.5cm to 1m. The thicker siliceous bands (above 7cm) have been termed 'ringers' by Matley and Wilson (1946) and used to separate the Maentwrog into the two divisions. The 'ringers' are fine-grained, compact, arenaceous rocks consisting of sub-rounded quartz fragments in a matrix of muscovite, with a little feldspar and pyrites (Andrew 1910). Structures are present in these rocks which indicate shallow water deposition.

The shales in the sequence are similar to those in the overlying Penrhos Beds, but are less well cleaved, probably because of the occurrence of ringers in the lower Vigra Flags. In appearance the shales resemble the Clogau Shales.

The 'ringers' appear to be in groups inter-layered with slatey shales.

The total thickness of the Vigra Flags is 340m (Matley and Wilson 1946).

PENRHOS SHALES.

These were separated from the Vigra Flags by Matley and Wilson (1946) on the arbitrary lithological boundary above which no siliceous band thicker than 7cm occurred.

The shales are very similar to the Clogau Shales, being dark-grey to black, pyritiferous and showing some rusty weathering. The thin siliceous bands also die out completely.

Cubic grains of pyrite up to 1cm across, are present in some of the beds. Andrew (1910) ascribes the dark colour of these shales to the presence of finely disseminated pyrites and organic matter. He quotes the following analysis for the shales:-

	Wt %
Organic matter	3.90
Iron in the form of sulphide	12.48
Not determined	83.62
TOTAL	100.00

From this it can be seen that although carbon-rich, these beds have a lower carbon content than the Clogau Shales.

The top of the Penrhos Shales is put at the horizon where the thin siliceous bands re-appear (MAtley and Wilson, 1946). This makes the sequence thinner than the 490m proposed by Andrew (1910), who used colour and general appearance of the shales as a criterion for distinguishing the different units. The thickness of these beds, estimated by Matley and Wilson (1946), is approximately 280m.

2:2:11 FESTINIOG FLAGS.

These rocks resemble the Vigra Flags in that they contain 'ringers' up to 1m thick. The major part of the beds is made up of argillaceous shaley layers with a few thin arenaceous layers, which vary in thickness from 0.5cm to 4cm. The 'ringers' in this unit are less persistent and more lenticular than those of the Vigra Flags, and less pyrite is present in the shaley layers. Passage from the Penrhos Shales is gradational and they are distinguished largely on the lack of rusty weathering as seen in the Penrhos Shales, (Matley and Wilson, 1946).

The upper beds of the Festiniog Flags are absent in the area studied. However, Matley and Wilson (1946) estimated the total thickness of this unit to be some 450m by reference to equivalent rocks in other areas.

2:3 DESCRIPTION OF THE STRATIGRAPHY OF THE FIELD AREAS.

2:3:1 THE AREA TO THE NORTH OF BONTDDU (SOUTHERN AREA).

This area is shown on Figs. 4, 5 and 6, and its topography is described in Chapter 6.

The rock types in this area are the Gamlan Flags and Grits, the Clogau Shales, and the Vigra Flags.

THE GAMLAN FLAGS AND GRITS.

These rocks are conformable with the underlying Barmouth Grits, and form a lower, somewhat less craggy, topography. The outcrop pattern resembles a 'V' shape, pointing South, the axis of which runs along the gorge behind Bontddu (Fig.6).

The main area of outcrop is marked by high heather-covered moorland, dotted with large boulders and crags, produced by the harder arenaceous layers in the succession.

Exposure is good, especially on the North side of the stream running from Hafod-Uchaf (SH 659 211) to the G.P.O. telephone box at SH 668 198 (Fig.5) where the land rises to the crags of the massive Barmouth Grits. In this area the Gamlan rocks are more massive near their base where they grade into the Barmouth Grits. The Gamlan Flags consist of an alternating sequence of argillaceous and arenaceous layers described by Matley and Wilson (1946) as flags and grits. In the area between SH 640 210 and Hafod-Uchaf (SH 660 210) the rocks are predominantly hard, grey to black, argillaceous rocks, which exhibit both bedding and cleavage. Coarse, green arenaceous layers, 2-3m thick, occur interbedded with thicker argillaceous layers. Bedding is not seen in the arenaceous layers, and a rudimentary cleavage is present only in some exposures.

Two distinct types of argillaceous rocks are present, a black to dark grey thinly bedded rock; and a lighter coloured, harder, more massive rock with few traces of bedding.

The darker member is fine-grained with slightly crenulated bedding ranging from 1 to 40mm in thickness. These weather to expose alternate light and dark layers, making the crenulations stand out. Cleavage planes are present between 1 and 10mm apart, and have a high angle with the bedding.

Parts of the rock appear vuggy with unfilled spaces widely distributed throughout the rock. No mineralisation or evidence of fluid permeation can be found and this phenomenon is explained in terms of the physical process of sedimentation (see below).

The harder, lighter coloured shale is present as thick layers with no obvious bedding or cleavage. The thickness of the beds varies from 25cm up to 3-4m. Less iron staining is noticeable in this rock type than in others (e.g. Vigra and Clogau Shales).

The overall dip of these rocks is 10-20° to the South, the strike varying across the area from 020° in the North West corner to 075-080° in the South East corner.

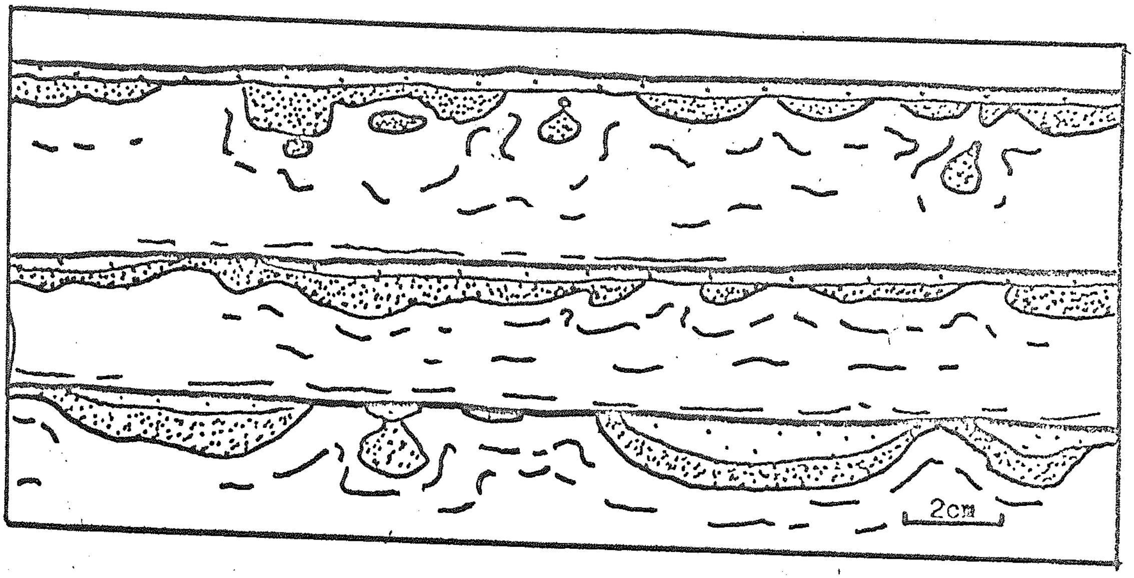
In thin sections three rock types can be distinguished; these are argillaceous; arenaceous; and an intermediate transitional type.

The argillaceous rock type consists of major (in excess of 10%) quantities of chlorite, sericite, muscovite, and quartz, with minor (less than 10%) quantities of apatite, calcite, haematite and some plagioclase feldspars.

The rock has a fine-grained ground mass (5m) of chlorite and sericite with angular quartz grains (0.1mm). Layering is seen in the ground mass; the layers being formed by differing sericite/chlorite ratios, and the quantity of quartz present.

Blebs of aligned chlorites (up to 0.5mm) are present in some instances. In addition some members have a layering produced by alternate calcite-rich and calcite-poor layers. These members have circular structures, up to 1cm in diameter, which, in hand specimens, appear as tubes. These consist of a calcite-rich core surrounded by layers of chlorite, sericite and haematite. Crenulations in the bedding are also more apparent in these members. These tubes are ascribed to the activity of worms by Andrew (1910). However, they may be explained in terms of a theory put forward by Anketell et al (1969). He suggests that where an inverse density gradient occurs, a slight shock may cause the lower, lighter layer, to rise diapirically upwards through the denser layer above. The more dense layers then sink to form an elongate drop shape (Fig.7). In these rocks carbonate-rich layers beneath clay-rich layers may have formed the necessary unstable configuration shortly after deposition. Uprise of these low density, calcite-rich layers through the high density clay layers, would tend to form vug-like tubes consisting of a calcite-rich core surrounded by layers of clay-rich material (now chlorite/sericite). Other structures observed in the rocks (Plate 1) represent the more dense layers below.

Fig. 7. Diagram of 'worm tubes'.



Sequence consists of siliceous 'tubes' set in a shale matrix.

░ Si rich (high density)

▒ Clay rich (high density)

☰ Carbonate rich (low density)-rises

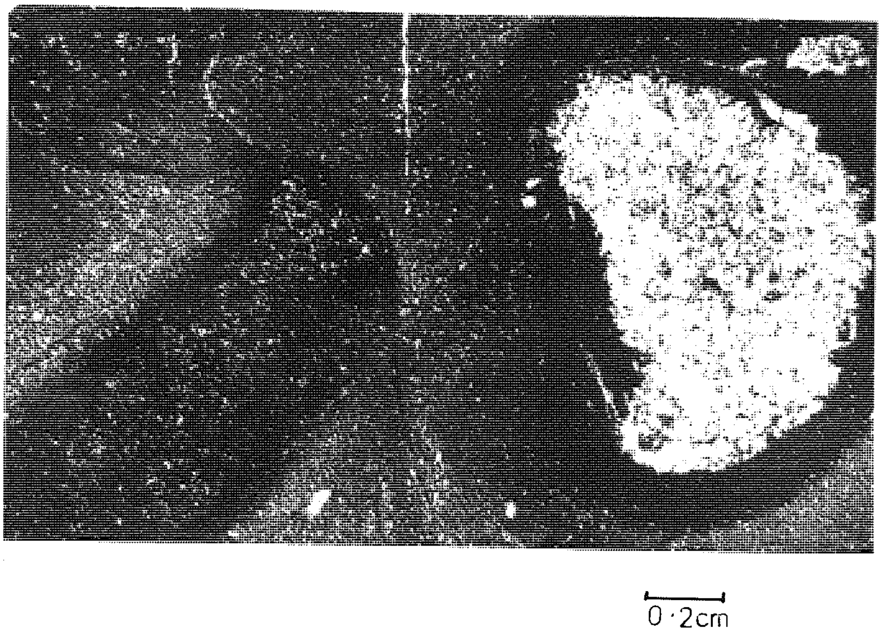


Plate 1. 'Vug' of chlorite and quartz surrounded by fine grained ground mass - specimen GR 1,2. Crossed nicols.

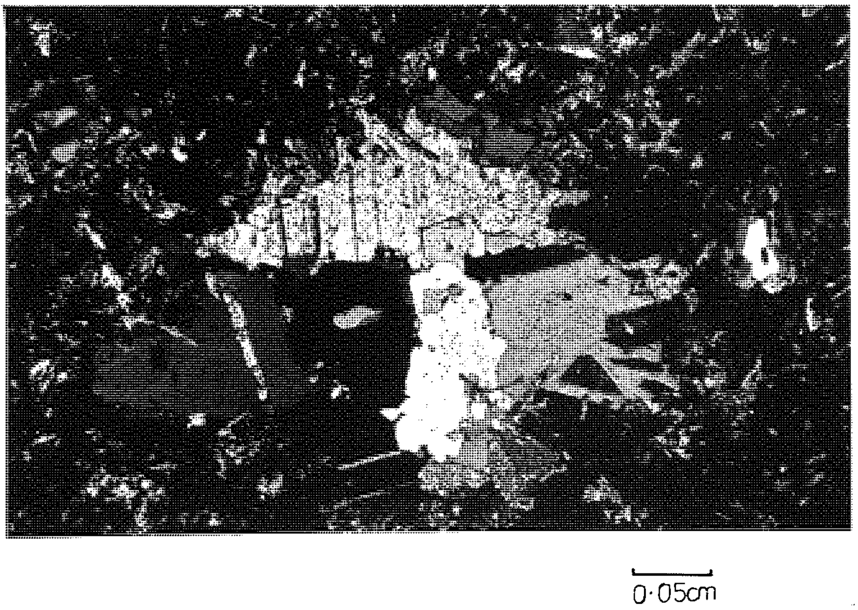


Plate 2. Single grain containing quartz and feldspar crystals - specimen GR 11,6. Crossed nicols.

The arenaceous members of the succession vary from coarse to fine-grain size (0.5cm to 0.5mm) and contain major quantities of quartz, feldspar, chlorite and sericite, with minor quantities of calcite and opaque minerals.

The quartz and feldspar which most commonly occur as separate grains are sub-angular to sub-rounded in shape. A few quartz grains show re-crystallisation.

The feldspars are predominantly plagioclase of An_{30-40} composition with some orthoclase. The relative amounts depend on the section but in each case plagioclase comprises more than 50% of the total feldspar. In all thin sections the feldspar were seen to be fresh with only a few alterations present in the centres, and round the edges of crystals. In some thin sections quartz and feldspar are present in combined grains in the grit (Plates 2 and 3). This suggests that the grits were formed from the rapid weathering and erosion of an acidic igneous mass. Also from the relative amounts of alkali and plagioclase feldspar present and from the composition of the plagioclase feldspar it is inferred that the parent igneous rock was of granodioritic composition. Also the freshness of the feldspar suggests that the source rock was only a few km distant.

The ground mass of the arenaceous member consists of fine-grained (20-50 μm) grains of sericite/chlorite, sometimes showing layering in the bedding direction. Some specimens (GR 17, 13) have a linear arrangement of chlorites (0.1mm diameter) at an acute angle to the bedding direction, which may be a rudimentary cleavage. In members which have an obvious bedding, a few small (0.5mm) muscovite grains are present growing along the bedding planes. The calcite present is almost entirely formed from the alteration of the plagioclase feldspar. Most is found in the area of plagioclase grain pseudomorphs.

The intermediate rock type consists of a mixture of the other two; quartz feldspar, sericite and chlorite being present in major quantities of calcite and opaques. Some few layers rich in carbonaceous material are also present. The angular quartz and feldspar grains (up to 1mm diameter) are set in a fine-grained ground mass (up to 50mm) of chlorite/sericite/muscovite which is dark brown in colour due to the presence of very fine carbonaceous material.

Variations in the proportions of quartz and feldspar to the ground mass form the alternating layers of the bedding.

Some recrystallisation of the muscovite has occurred, however no preferred elongation direction is present in the specimens examined.

The topography of the area in which the Gamlan rocks are exposed is generally rough, which contrasts sharply with the smooth gentle area of the Clogau Shales. In this area the Cefn Coch Grit is absent, and the change from the Gamlan Flags to the Clogau Shales is sharp, the hard, thick grit bands dying out over (approximately) 2m and being replaced by black shales. In the area North of St. David's Hill (about SH 677 204) the junction is marked by a valley cut into the Gamlan Flags. The South side of the valley approximately follows the line of the junction. Intrusions are common in this area, and some of these, together with associated veins and shear zones, cross the junction making detailed mapping difficult.

In the area between SH 668 197, and SH 660 200, the junction is difficult to find since both the Clogau and Gamlan rocks have weathered in a similar way to produce a gently sloping land surface with little change of shape at the junction.

THE CLOGAU SHALES.

These consist of dark-grey to black, fine-grained argillaceous rocks showing bedding and/or cleavage. Abundant pyrite is present much of which occur as large crystals (up to 1cm square). In this area the outcrop width of the shales is never more than 100m.

Excellent exposure of the shales are present on the sides of the river gorge North of Bontddu (SH 668 194). They have a striped appearance due to the presence of large quantities of pyrite crystals along the bedding planes which weather to a lighter colour.

Elsewhere the Clogau Shales are poorly exposed. When they do appear they occur as weathered black shale, some exposures of which show cleavage.

The weathered zone of the Clogau Shales extends up to 0.5m into the outcrop. It has been suggested (Gilby, 1968) that it may extend to depths of 100-200m from the surface due to deep weathering in the shales.

Sampling was made difficult by the necessity for removal of 0.5m from the surface to obtain a relatively fresh specimen.

The bedding in the Clogau Shales has the same general attitude as the underlying Gamlan Flags, except in the vicinity of faults where steep dips are commonly present. However, because bedding is not always obvious, especially where pyrite is absent, reliable dip measurements were impossible to obtain in parts of the area. Where seen, the thickness of the bedding varies from 3mm to 3cm. In places where cleavage is present all traces of the original bedding are generally obliterated and a fissile shale/slate is produced. The cleavage planes are up to 5mm apart, and are at a high angle to the bedding, dips of 50° to 80° to the South being common.

In thin section the Clogau Shales are uniform in character, consisting of a mixture of fine-grained (20 μm) chlorite and sericite with a few small quartz grains. Proportions are difficult to estimate due to the presence of carbonaceous material, however chlorite and sericite make up some 70% of the rocks, with the remainder consisting of carbonaceous material, quartzes and opaque minerals.

Some specimens show 'blebs' of chlorite (up to 100 μm diameter) and coarse sericite (2-30 μm diameter) producing a more coarse grained rock. Bedding appears as alternating light and dark layers, the colour being due to the relative quantities of very fine-grained carbonaceous material (probably .1μ- 1.0μ). In some specimens, layers may have abundant angular quartz grains, surrounded by chlorite and sericite. In specimens showing cleavage (e.g. GR 16, 14) the sericites have a preferred orientation which is at a steep angle to the bedding. 'Blebs' of chlorite are larger than those in specimens without cleavage (e.g. GR 12, 16). Opaque minerals may appear as 'blebs' throughout the thin sections. These appear to have formed by precipitation in amorphous masses, or as cubic crystals in layers following the bedding.

At the top of the Clogau Shales there is a rapid change of lithologies to the Vigra Flags. There are black argillaceous rocks with hard siliceous bands or 'ringers' (Matley and Wilson, 1946) throughout the succession.

THE VIGRA FLAGS.

These rocks are well exposed on the Y-Vigra and St. David's Hills, producing the craggy slopes and irregular tops to these hills. They are also well exposed, together with a number of associated igneous intrusive bodies, along the A 496 road between Caerdeon (SH 651 182) and Rhuddallt (SH 679 188). In the road section the rock sequence is seen to consist of thinly-bedded fine-grained argillaceous and arenaceous rocks. They grade along the outcrop to more massive argillaceous rocks with little evidence of bedding. Near the Bontddu Hall Hotel (SH 671 188) the Vigra Flags consist of a sequence of alternating, crenulated, black and grey argillaceous layers. A few 'ringers' are present. In some parts of the exposure more massive arenaceous beds occur containing pyrite cubes up to 0.5cm diameter, dispersed along the bedding. On St. David's Hill the Vigra Flags show similar lithological variations to the previously described outcrops. The weathered rocks of this locality do not show the same detail, however, as the fresh specimens from the road cuttings. In this area, and on Y-Vigra, the weathered rocks have the appearance of dark grey to black shale, especially where siliceous layers are absent. Cleavage is present in these rocks, the intensity of which varies with the competence of the beds. In general the cleavage has a strike of 060° with dips to the South of between 40° and 80°. In this section the Vigra Flags falls into two broad types. The first type which comprises the majority of the rocks have quartz, chlorite, and sericite, making up approximately 80% of the rock, with opaque minerals making up the balance. Layering is distinguished by the relative abundance of quartzes. Quartz-rich layers consist of sub-angular to angular quartz, up to 0.1mm diameter, set in a matrix consisting predominantly of sericite and chlorite (up to 0.1mm longest dimension). In some specimens layers consisting entirely of very fine-grained (0.1mm diameter) are present. Quartz-poor layers are also present with less sericite, and more chlorite, than the quartz-rich layers. These layers are generally finely-grained. The grain size of the sericite is approximately 100μm and the chlorite is approximately 100μm. The rock is made up of approximately 50% chlorite, 30% sericite and the remainder is mostly quartz and opaque minerals.

The second rock type consists of sericite, chlorite, haematite and fine, dark carbonaceous material. Only a few small (100μm) angular quartz grains are present. Due to the fine grain size (10 - 50μm) proportions are difficult to estimate, especially in the presence of carbonaceous material. Layering in this rock type is delineated by variations in carbon content and the relative proportions of chlorite, with the quantity of sericite remaining constant. Rocks of this type exhibit cleavage both in hand specimens and thin section. Cleavage developed on a microscopic scale has aligned sericite showing buckling typical of strain slip cleavage. Since few new sericite crystals have developed along the cleavage planes it would appear that the cleavage was formed after, or in the late stages of metamorphism.

In both types of Vigra Flags the quartz crystals present show some recrystallisation, especially in the more coarsely-grained members (e.g. GR 14, 17). In these rocks the pyrite grains present vary in size from 1mm to 5mm along the faces, and are present only along bedding planes. In some specimens the pyrite is sufficiently abundant to give the rock a striped appearance.

2:3:2 THE AREA AT THE NORTHERN END OF THE HARLECH DOME (NORTHERN AREA).

The extent of this area is shown in Figs.4 and 8, and its topography is described in Chapter 6. The Gamlan Flags and Grits, the Clogau Shales and the Vigra Flags, are present in this area as in the Bontddu area (Southern Area).

GENERAL DESCRIPTION OF THE ROCKS IN THE NORTHERN AREA.

The Gamlan rocks form the flanks of the high hills of the centre of the Harlech Dome. Exposure is generally good except in drift covered valley bottoms.

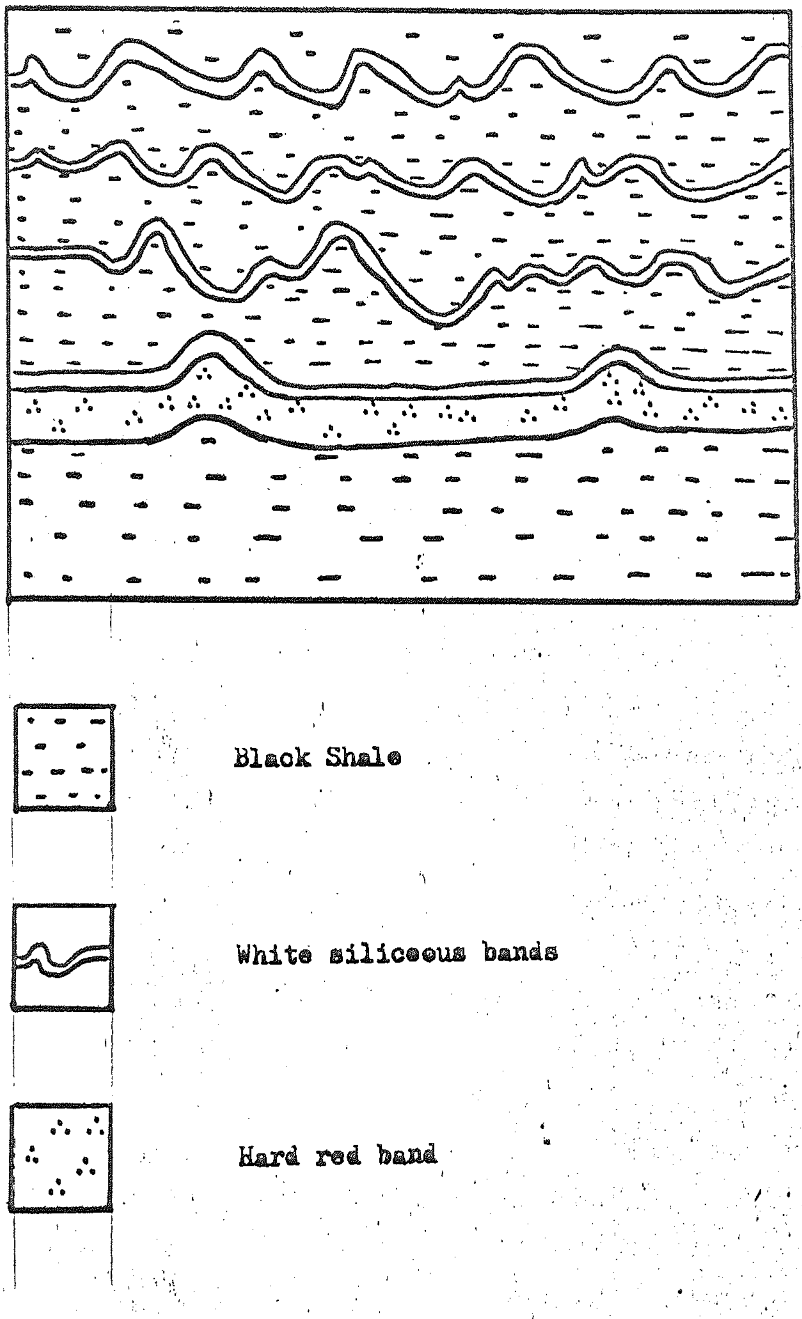
The rocks consist of hard dark grey, argillaceous materials, interbedded with arenaceous layers and siliceous layers ('ringers') similar to those of the Gamlan in the Southern Area. The siliceous layers, up to 2cm thick, have an undulating form and occur within a lithological unit which is overlain by shales or grits without 'ringers' (see Fig.9).

In thin section these rocks are almost identical to the rocks of the Southern Area, the majority of the specimens examined falling into the first category, i.e. the black to dark-grey shales. The only real difference between the rocks of the two areas is the scarcity of 'worm tubes' in the rocks of the Northern Area. Only a limited number of samples were collected from this area hence a statistical treatment of lithologies is not possible; however, from field examination, it seems that both categories of Gamlan rocks are present in the Northern Area.

Following on conformably from the Gamlan rocks the Cefn Coch Grit consists of a layer of coarse grit (up to 1cm) rarely exceeding 10m in outcrop width. Some parts of the grit stand out above the surrounding rocks while other parts weather in a similar manner to the surrounding rocks. The variable exposure of this rock type prevented sampling of this rock type for chemical analysis. This was done so as not to introduce the risk of bias into the final analysis.

Immediately above the Cefn Coch Grit the Clogau Shales form flat or gently sloping fields, which give good exposure due to their very thin soil cover. The main outcrop area of these shales, which were sampled for analysis, occurs on the South Eastern side of a steep valley which follows a major fault. The outcrops follow the valley as it curves to the West, the pattern being modified somewhat by two directions of faulting (N.E.- S.W. and N.W.- S.E.). The Clogau Shales of this area are also practically identical to those of the Southern Area. They consist of light to dark grey, fine-grained argillaceous rocks of varying hardness, with bedding from 0.1 to 2.0cm thick. In suitable exposures (e.g. around FN 14, Fig.4) the Clogau Shales vary in hardness along their strike. This explains

Fig. 9. Gamlan Flags - section next to sample position FN7 (Northern Area).
showing sedimentry structures.



why such a great variation in hardness is noted between one small exposure and the next. The differing hardness causes intensity of cleavage to vary, the softer parts showing more closely spaced cleavage planes than the harder parts. Only one cleavage direction is seen in this area, the strike being about 010°, dipping 80° to the East (e.g. at position FN 13).

In thin section specimens of the Clogau Shales of the two areas are indistinguishable from one another.

Conformably overlying the Clogau Shales are the Vigra Flags and Shales. These rocks form the base and North Western flanks of the valley near to Plas Llandecwym (SH 635 735). Exposure in this area is very good and several good sections are present in which sequences of shales and flags are easily accessible (e.g. FN 25, FN 52). The rocks consist of alternating argillaceous and arenaceous layers, and 'ringers' similar to those of the Vigra Flags of the Southern Area. The argillaceous rocks vary from soft, dark-grey, rusty weathering similar to the Clogau Shales, to harder, lighter-grey, shales with thin (.25-2cm) siliceous layers. The siliceous layers have a wavy bedding suggesting either current action or diapiric structures. In some outcrops, e.g. FN 45, the shales show thin alternating light and dark beds similar to the Clogau Shales, while in others, e.g. FN 43, cleavage removes all trace of bedding. The 'ringers' of Matley and Wilson (1946) occur throughout the succession, varying in thickness from 2cm to 1cm, and in some instances 2m. Some outcrops show surface markings caused by differential weathering which give the impression of layers in the form of cross-bedded structures. This effect is probably formed by the weathering of chlorite-rich layers within the siliceous layer. In thin section the rocks are similar to the two broad types as found in the Southern Area.

Towards the top of the Vigra Flags the 'ringers' die out leaving a dark-grey to black, rusty weathering shale, which marks the start of the Penrhos Shale. Excellent exposures of this rock type occur along the Harlech-Maentwrog road (A 496) in new road cuttings. All of the samples collected were collected from this section (Fig.10).

The Penrhos Shales consist of fine-grained, grey, thinly-bedded argillaceous rocks containing inclusions of black carbonaceous matter. Quartz veining is common in some areas. In thin section these rocks are seen to consist of irregular quartz veins up to 0.1mm diameter surrounded by a ground mass of chlorite and muscovite (up to 0.01mm diameter) with a few larger grains of muscovite, up to 0.1mm diameter. In all specimens the quartz grains are recrystallised. Chlorite and muscovite make up 60-70% of the rock. The remainder of the rock is principally made up of quartzes and opaque minerals. Bedding is outlined by the relative abundance of quartz and chlorite. Darker layers have less quartz, and more chlorite, than the lighter layers. In some specimens bedding shows cut-offs, and other microstructures indicative of current action.

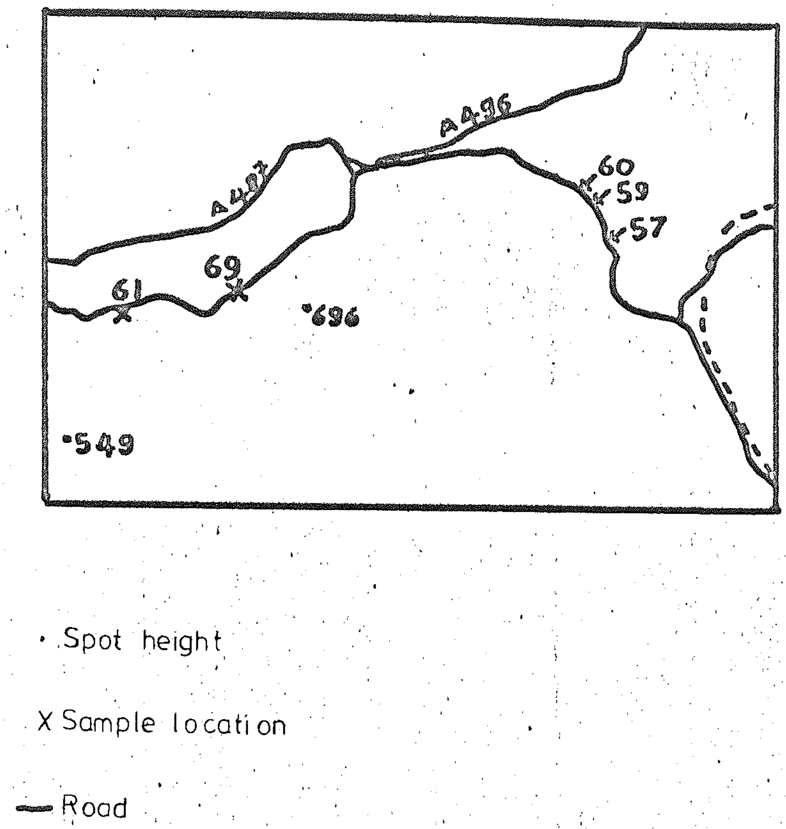


Fig. 10. Sketch map of roadside exposures in Northern Area.

Scale - one inch to one mile.

CHAPTER 3

THE IGNEOUS ROCKS OF THE HARLECH DOME.

3:1 General Description.

In the area of the Harlech Dome a large number of Igneous intrusions may be found, many of these being of considerable size. These rocks may be compared to the Igneous rocks of the Rhobell Fawr district, immediately to the South of the Mawdach Estuary (Wells, 1925). They are related to the Rhobell Fawr volcanism (Cox and Wells, 1927; Cox, 1925) which preceded the major folding and cleavage periods of the Caledonian Orogeny.

The intrusions are of three types; conformable sills; transgressive sills; and dykes.

(1) Conformable Sills.

These are the most common intrusion, and comprise the greater part of the intrusive rocks of the area. They occur more frequently in the softer rocks, being very numerous in the soft Clogau Shales, increasing the thickness of this unit by 50% (Andrew, 1910). They range in thickness from 30cm thick units interlayered with the shales near Bontddu, to 60m thick, almost laccolithic, intrusions, such as that forming the bridge at Llechfraith (SH 670 195) (Andrew, 1910). Generally, however, they are most commonly between 1 and 2m thick.

(2) Transgressive Sills.

These may be confused with the larger sills until mapped in detail. They form the larger igneous masses of Matley and Wilson (1946), and are limited in occurence compared with the other sills.

(3) Dykes.

These are least common intrusions and the most clearly defined ones occur in the hills behind Bontddu (SH 670 190). In thickness they vary from 60cm to 15m; the majority being less than 8m. The trend of the dykes varies a great deal with the most common direction being N.W.-S.E.

Thermal metamorphism of the surrounding rocks for all intrusions is slight, being most noticeable where the intrusions cut shales. These are baked to form hard porcellanites, up to 2m from the intrusions, and some slight decolourisation of the shales is common.

Emplacement of the igneous rocks was before the impression of the cleavage on the enclosing rocks. Some of the sills have a schistosity, and a cleavage is developed on the margins of some of the larger intrusions.

In many places the fissures occupied by the dykes are fault planes, and some evidence of simultaneous faulting and intrusions is present (Matley and Wilson, 1946). However, because some of the dykes are cut by faults a further, later, period of faulting is indicated.

The age relationships of the intrusions to one another is not clear. Matley and Wilson (1946) suggest that "most of the dykes are later than most of the sills"; however some dykes appear to be feeders to the sills and some sills appear connected to two parallel dykes.

The petrography of the rocks is difficult to determine due to alteration caused by the chlorite grade regional metamorphism, in which much of the original mineralogy has been destroyed.

Two main rock types have been recognised; a dolerite, and a hornblende diorite, which is some specimens has sufficient quartz to be classified as a dacite in terms of mineralogy (Gilby, 1968). Both of the rock types have medium and fine-grained members (Matley and Wilson, 1946).

Ramsay (1881) and Andrew (1910), both attempted to map the two types of intrusion, but in some instances each author assigned a particular intrusion to a different rock type. Matley and Wilson (1946) did not differentiate the two types on their map due to the difficulties in field identification.

In thin section positive identification of the rock type depends on the recognition of pseudo-morphic shapes of original amphibole and pyroxene (Gilby, 1968). Gilby (1968) only notes primary amphibole in one thin section out of 50, and in the present work no primary amphibole was recognised in 30 thin sections. These rocks consist essentially of chlorite, calcite, sodic plagioclase (An_{20-30}), epidote-clinozoisite, opaque minerals and quartz. Chlorite is the main mineral in the ground mass, and also occurs in larger masses, associated with calcite, probably replacing the primary mafic minerals. In most specimens the mafic minerals have been completely altered and no pseudo-morphic shapes remain. Most of the plagioclase is secondary, though in several specimens primary, unaltered plagioclase is present with a composition of An_{50-70}.

3:2 Description of the Igneous Rocks of the Field Areas.

The igneous rocks from both the North and Southern areas are similar and no difference was noted in the present work. In the field the igneous rocks were recognised by the fact that they are more resistant to weathering than the sediments. In addition, they have a 'glassy' appearance and, in come outcrops, look like quartzites.

The dykes are mostly between 1cm and 1m thick though several are 8-10m and in some places 15m. The sills are generally between 10cm and 1m thick, with some, in the St. Davids area, reaching 5m thick.

The grain size varies from very fine-grained, flint like on the margins of some small dykes, up to 2-3mm in certain of the larger intrusions.

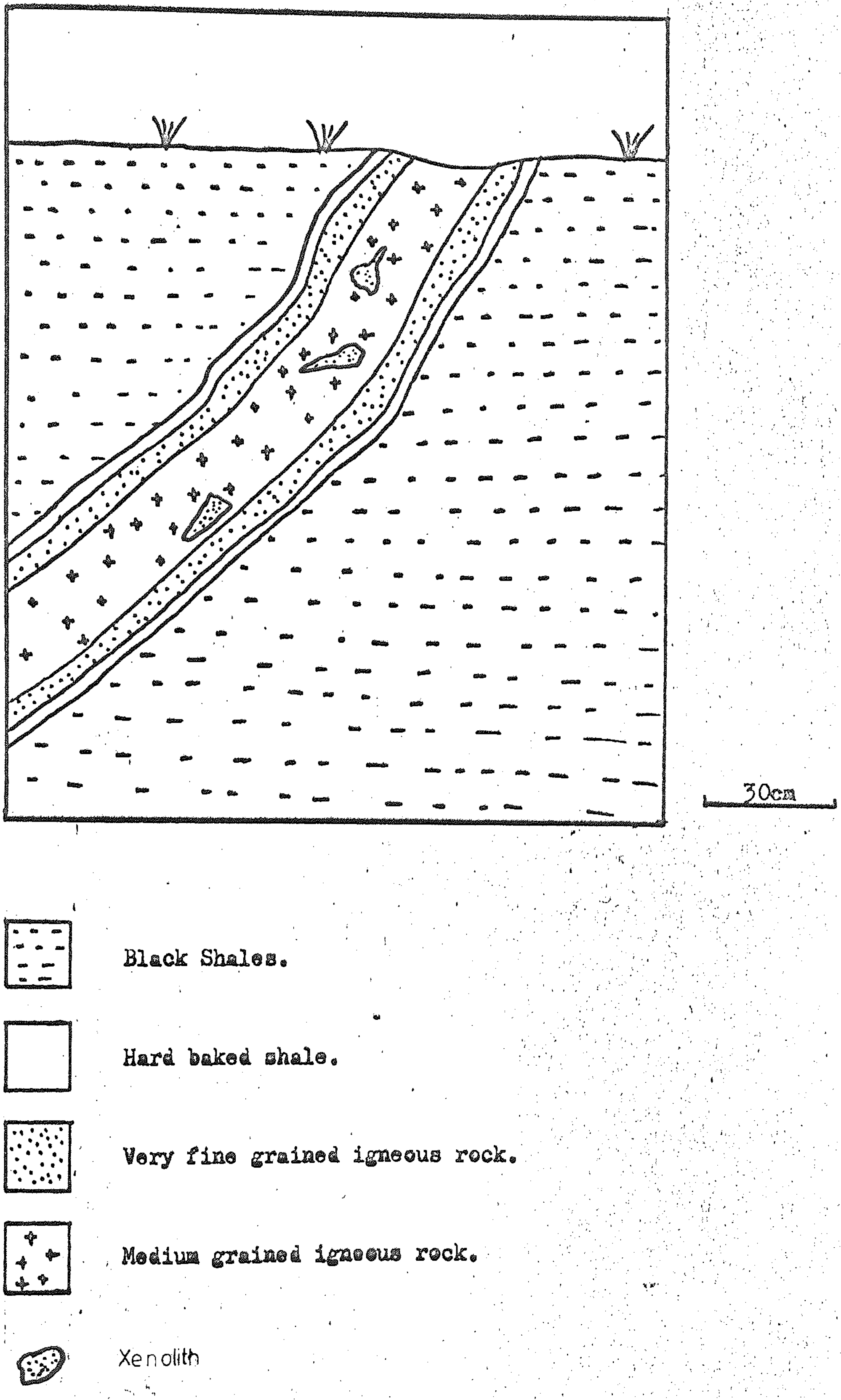
Baking of the country rock may occur up to 10cm from the contact. The Clogau Shales are most affected with hardening and discolouring extending up to 10cm from the contact. The arenaceous layers in the succession show the least change, (e.g. roadside exposure North East of Bontddu, SH 188 680 and South West of Bontddu SH 667 185).

Evidence of multiple injection can be seen around GR7, 11 and also in the area of the St. Davids lode (Fig.11). In these exposures shales are intruded by igneous rocks causing baking of the shales for 3-4cm, from the contact. On each side of the dyke, in contact with the shales, is a very fine-grained, almost glassy igneous rock. This zone varies up to 20cm in thickness. Between these, with very sharp irregular contacts, is a medium grained (up to 1mm diameter grains) igneous rock.

Some of the intrusions have a rudimentary cleavage which is approximately parallel to the cleavage developed in the enclosing sediments.

In thin section the rocks consist of chlorite, calcite, quartz and plagioclase feldspar in varying proportions. Muscovite and opaque minerals are present in minor quantities (Plate 4). The ground mass consists of chlorite and sericite, up to 0.01mm diameter, which are generally randomly aligned. Within the ground mass associations

Fig. 11. Sketch of multiple dyke injection near St. Davids lode, near Bontddu.



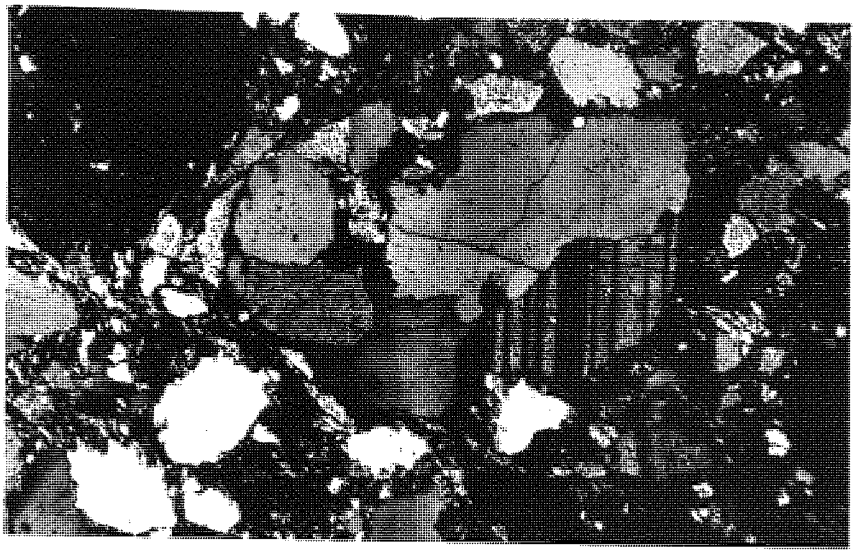


Plate 3. Single grain containing quartz and feldspar crystals - specimen GR 18,13(1). Crossed nicols, Gamlan Flags

Plate 4. Igneous rock, general view - specimen F/71/B. Crossed nicols,

of chlorite and calcite, up to 0.1mm diameter, are present together with individual grains of chlorite, up to 0.1mm diameter. Some of the chlorite/calcite aggregates have definite outlines against feldspars indicating replacements of phenocrysts (e.g. slide F/71/0, F/71/E). These thin sections may therefore belong to the hornblende diorite of Matley and Wilson (1946).

The feldspars, which in some specimens (F/71/A) make up 50% of the rock, have a grain size of up to 0.5mm. Two broad types are present; a fresh plagioclase feldspar (An_{20-30}), which makes up to 70 - 80% of the feldspar present; and a much corroded plagioclase feldspar (An_{50-70}).

The fresh feldspars (Plates 4 and 5) have inclusions of the ground mass inside their grain boundaries, indicating crystal growth. The corroded feldspars which give every indication of being altered primary feldspars, have a composition of up to An_{50-70} suggesting an original basic dolerite composition. Some quartz grains are present as a secondary growth. Muscovites, up to 0.01mm diameter, are present in varying quantities with rare larger grains up to 0.1mm diameter. Some thin sections (Plate 4) have muscovites aligned in one direction indicating a period of stress during crystallisation. In addition aligned 'blebs' of chlorite are present (e.g.specimen 11,8)

Calcite, generally present in minor quantities has three modes of occurrence. The first is associated with chlorite in the pseudomorphs ; the second in single large grains up to 0.5mm diameter; and the third in small veins. The single grains, or groups of grains, show evidence of having grown at a late stage in the ore, examples of calcite surrounding all of the other minerals (Plate 6) being present.

Plate 5. Small feldspar laths - specimen GR 18,14(2). Crossed nicols,
Igneous rock

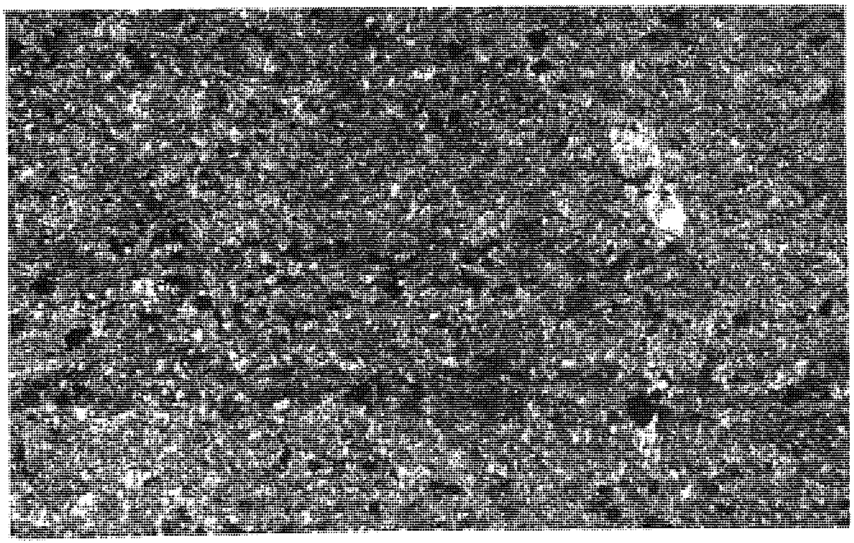
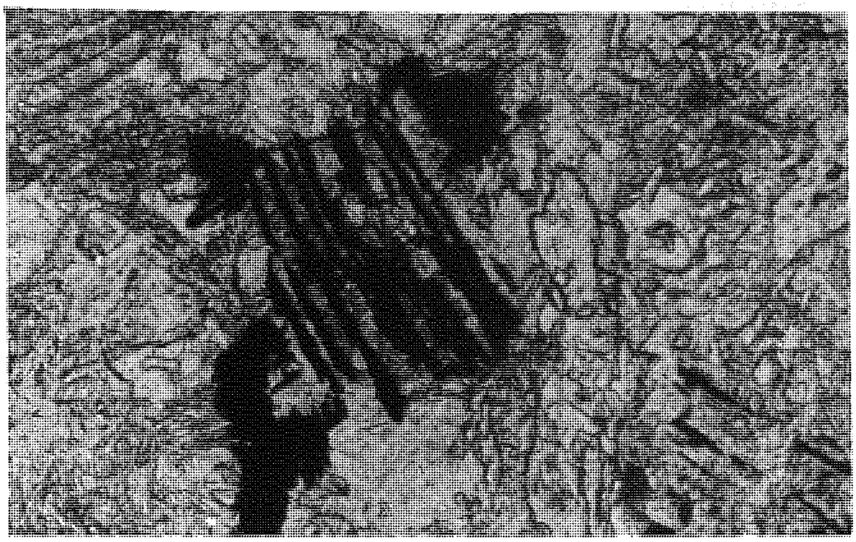


Plate 6. General view of igneous rock showing lineation of opaque minerals - specimen F/71/C. Plain polorised light,

Opaque minerals where present, generally have square outlines. In hand specimens they appear to be pyrite and chalco pyrite. In thin section some of the opaques appear to be skeletal ilmenites (Plate 7). In some thin sections and hand specimens (Plate 6 and 8) the opaque minerals are aligned. This foliation is also noticeable in the roadside exposures of some of the dykes to the North East of Bontddu (SH 679 189). In these exposures the foliation appears to be almost horizontal within a vertical dyke and is present across the full width of the dyke.



0·025cm

Plate 7. Skeletal ilmenite in igneous rock - specimen F/71/B. Plain polorised light.

0·05cm

Plate 8. Igneous rock, general view - specimen F/71/B. Crossed nicols, showing small feldspar laths

CHAPTER 4.

THE STRUCTURAL GEOLOGY OF THE HARLECH DOME.

4:1 Introduction.

The major feature of the area is the dome with its core near to the Rhinog mountains (Chapter 1). From its centre the sediments dip away to form a dome. Superimposed on the dome are a series of folds with N-S axes which modify the outcrop pattern. Two major groups of faults are present, the first consisting of major faults axial to the folds, and the second a series of faults radial to the dome.

4:2 Folding.

The sedimentary rocks dip away from the centre of the dome at angles between 30° and 40°. In a few areas, e.g. road cutting 1 mile East of Bontddu, dips of 60°- 70° occur and in places the beds are overturned due to faulting (Matley and Wilson, 1946).

The two major fold structures of the area (Fig. 12), superimposed on the dome structure, were named by Matley and Wilson, (1946) as the Caerden Syncline in the East, and the Dolwen pericline in the West. Both have their long axes aligned approximately N-S, and have a Southerly plunge of some 5°-15°, The amplitude of the folds is some hundreds of metres. In the Southern part of the dome a small branch anticline breaks away from the Dolwen pericline with a NW-SE trending axis.

4:3 Faulting.

The major series of faults in the area are the 'Meridional' faults of Matley and Wilson (1946), which have a N-S trend (Fig. 12) and are sub-parallel to the main anticlinal axis. These faults indicate that the last movement on them was caused by tension,

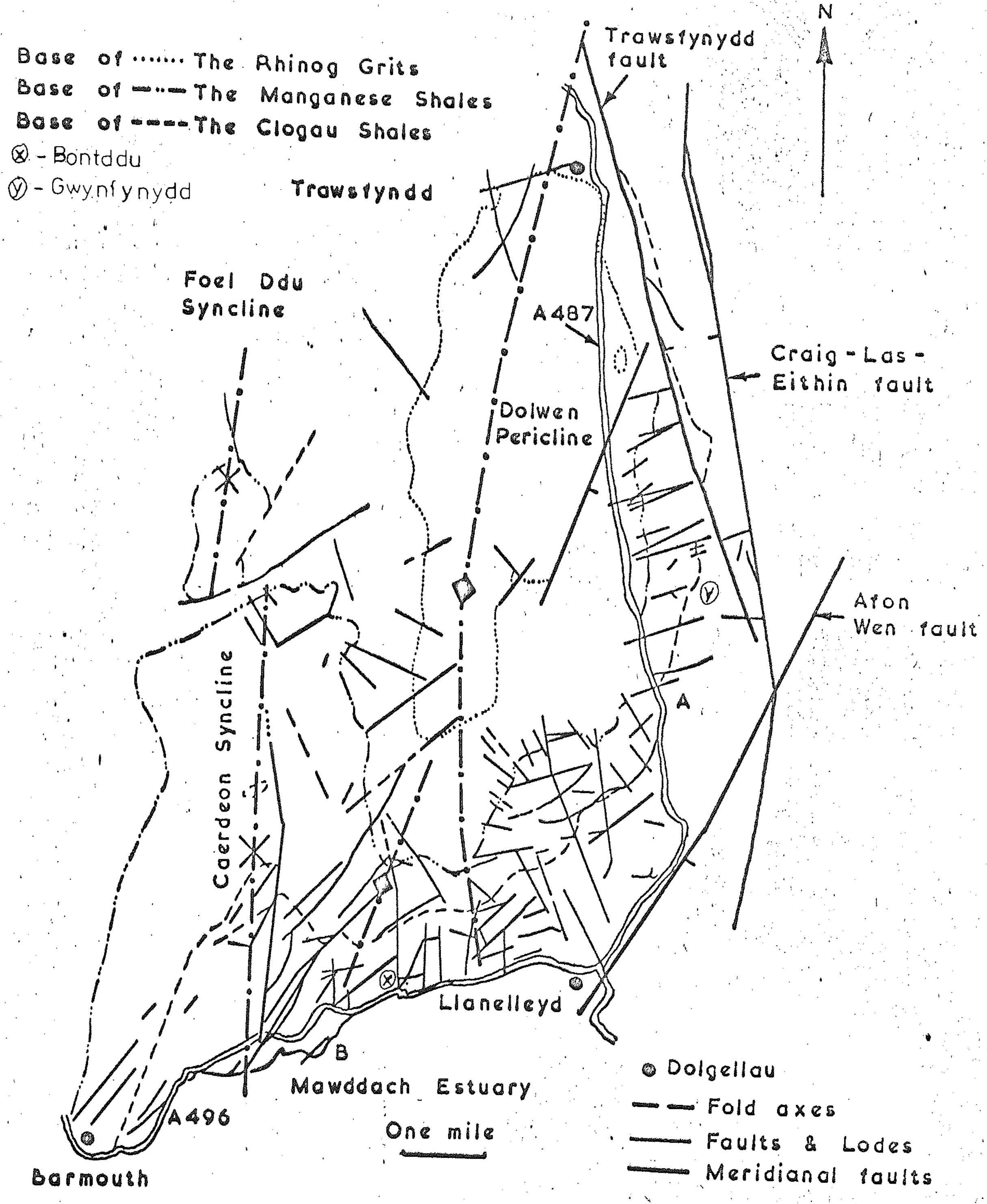


Fig.12. STRUCTURAL MAP OF THE HARLECH DOME

after Gilby 1968

after starting out as compressional features (Andrew, 1910; Matley and Wilson, 1946; Gilby, 1968).

The second series of faults are radial to the dome structure and were formed as a result of the rise of the dome (Gilby, 1968).

The faults vary in the degree of mineralisation asssociated with them. In the Eastern part of the dome, in the Gwynfynydd area, the radial faults are very common, and are generally mineralised. The majority of these faults terminate against a major N-S trending fault, the Trawsfynydd fault (Fig. 12) (Matley and Wilson, 1946).

In the area between Gwynfynydd and Bontddu the radial faults are less heavily mineralised and are difficult to distinguish from the meridional faults, and have only small quantities of mineralisation. Heavy mineralisation of the strike faults occurs in the area of Bontddu.

4:4 Cleavage.

The cleavage in these rocks is generally related to the N-S trending folds, although it swings round to 090° South and West of Gwynfynydd. The dip of the cleavage varies a great deal due to undulations on the cleavage plane, but on average dips at 80° to 85° to the East. It is not clear whether or not the undulations are due to folding of the cleavage plane or refraction due to the differing hardness of the rocks. All of the rocks in the area are affected by the cleavage to some degree. The cleavage is generally later than the regional metamorphism and emplacement of most of the intrusions (Matley and Wilson, 1946). This is seen where crystals of chlorite in the country rock show deformation due to cleavage, and the imposition of a rudimentary cleavage on the igneous rocks.

A detailed description of the structural geology is given by Andrew (1910), Matley and Wilson (1946) and Gilby (1968).

4:5 Geological History of the Harlech Dome.

After deposition of the sediments the area was stable until Post-Tremadoc times when an interruption in deposition produced an unconformity with the overlying Arenig rocks. In adjacent areas the complete sequence is shown which proves the unconformity (Price, 1963). The first folding and faulting was probably associated with the intrusion of sills, and the Rhobell Fawr volcanism (Fig. 13). Faults acted as lines of weakness for the intrusions which followed them.

Towards the end of Silurian times, when a thickness of approximately 9000m of sediment had been deposited above the Penrhos Shales, the main Caledonian Orogeny resulted in compression from the East to form the many folds. The fact that the fold axes trend N-S instead of the common NE-SW Caledonide trend is suggested by Gilby (1968), to be due to a basement warp interfering with the Caledonide trends. This basement uplift of the underlying Precambrian rocks may have been associated with the emplacement of a granite mass. The basement warp of Caledonian age was first postulated by Powell (1955) from gravity and magnetic anomalies (Figs. 14 and 15). The recently published aeromagnetic map of the U.K. supports this idea.

Fig. 13. Tectonic history of the Harlech Dome.

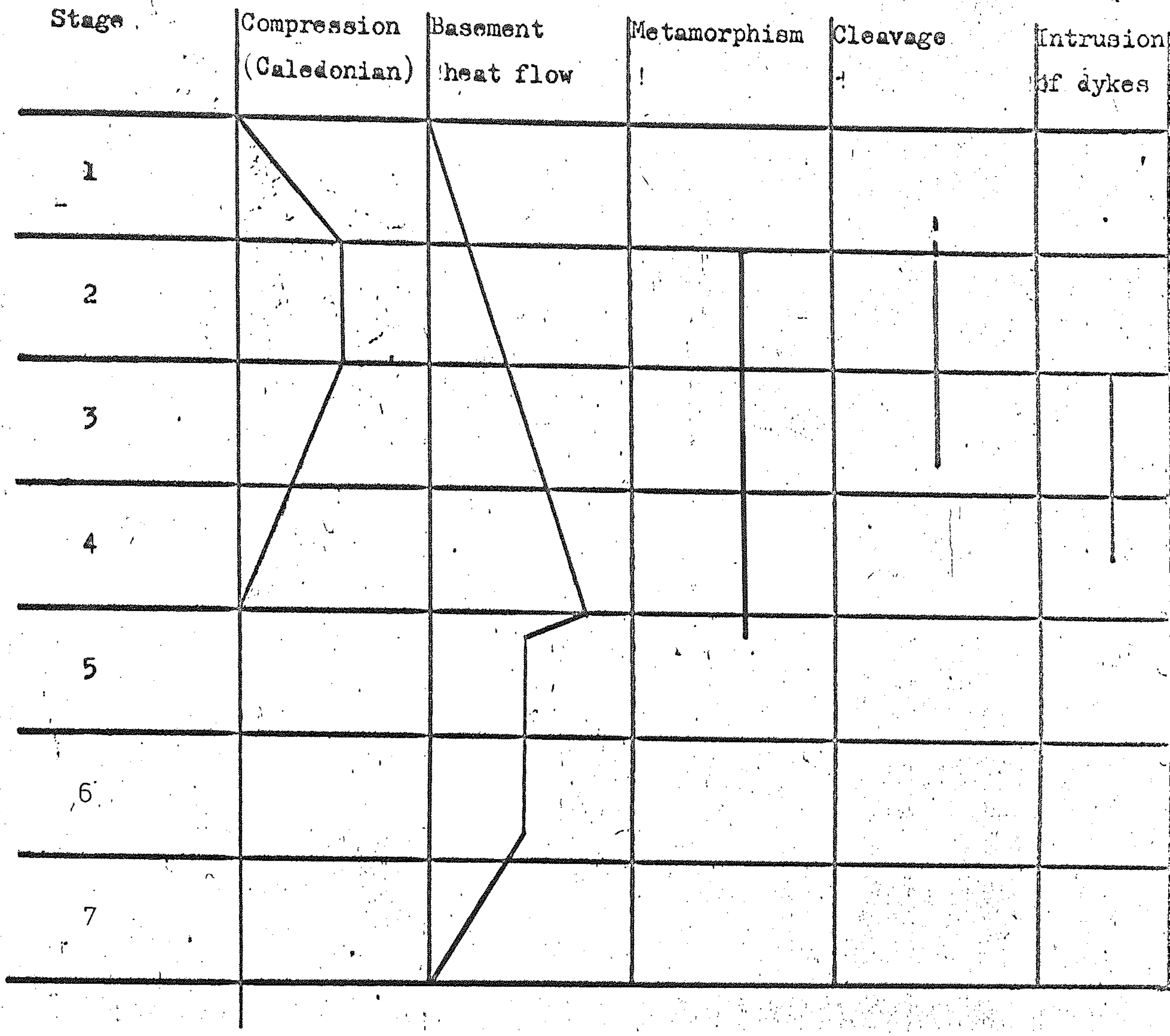
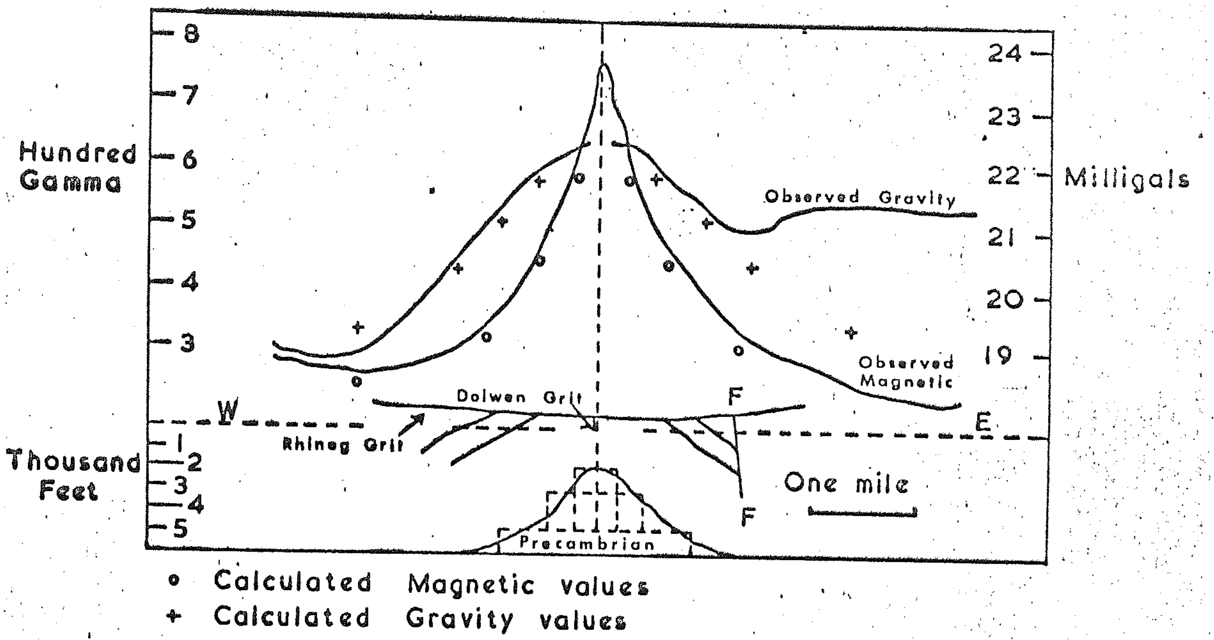


Diagram is a composite taken from the work of Matley and Wilson (1946), Powell (1955), Price (1963) and Gilby (1968).

Sloping lines indicate a build up (from the left) of the episode.



Profile is one mile south of Trawsfynydd lake. The magnetic anomaly is a better guide to basement relief than the gravity anomaly

Fig.14. <u>GRAVITY AND MAGNETIC ANOMALIES ON A PROFILE ACROSS THE DOLWEN PERICLINE (After Powell, 1955)</u>

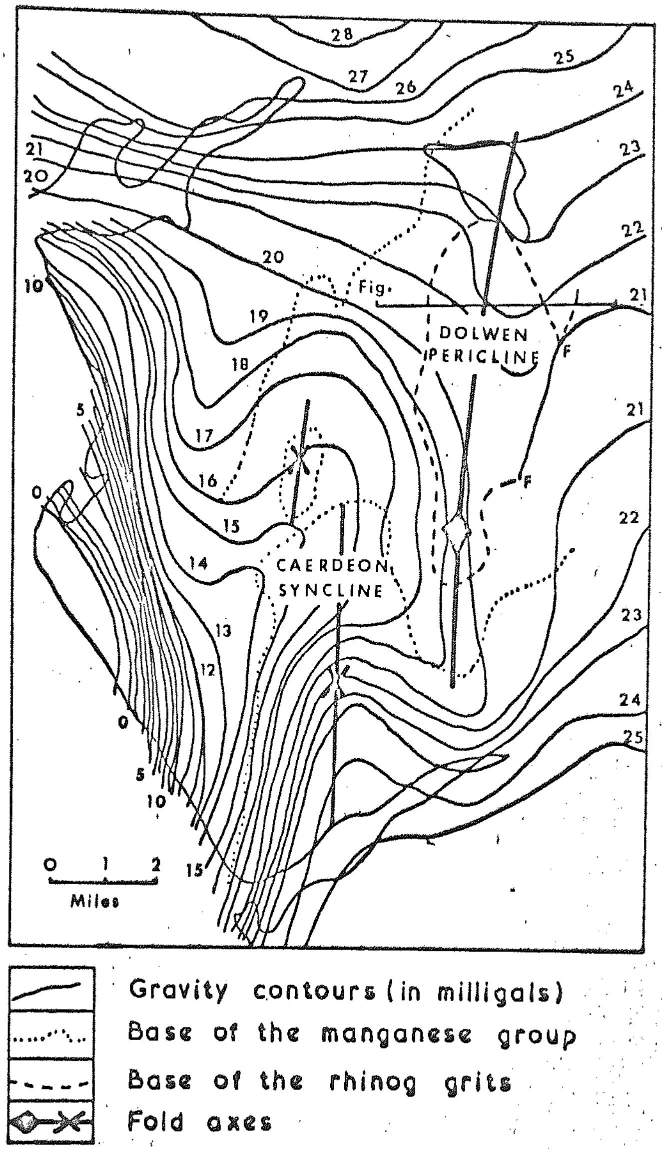


Fig.15. GRAVITY ANOMALY CONTOURS OF THE HARLECH DOME. (AFTER POWELL, 1955)

The contours follow the structures in the Palaeozoic.

The interaction of these two major forces created the Harlech Dome. Initially strong compression resulting from the Caledonian forces produced high angle reverse faults as the start of the meridional faulting. As the Caledonian pressure declined and the dome was uplifted then the former compressional faults became areas of tension and at this time were invaded by mineralising solutions. Later faults are poorly mineralised (Gilby, 1968) and this is taken to indicate that when the pressure finally was released the period of ore formation was past.

CHAPTER 5

MINERALISATION

5:1

The major mineralisation in the area of the Harlech Dome is epigenetic vein type, and provides a geochemical pattern superimposed on the normal pattern of chemical variation. The detailed reporting of mineral occurrences in this area by Readwin (1888) allowed Matley and Wilson (1968) to develop their theories on the origin of mineralisation. The mineralogy identified and paragenetic sequences determined by Gilby (1968) are used for the purposes of this thesis, and are outlined below.

5:2 Physical Occurrence.

The veins are emplaced along fault fissures, many of which are also occupied by igneous intrusions. Generally in this area the emplacement of the igneous intrusions preceded mineralisation. Generally the fissures are the controlling factor in mineralisation as opposed to igneous activity. Both strike-slip and dip-slip faults are present with a displacement of the order of a few metres. Structures present in the veins include 'domino breccias' of "unsupported" inclusions and book and ribbon structures. Vugs, and other open space filling structures are also present.

5:3 Mineralogy.

Three main types of mineralisation are recognised based on the elemental abundances of Gilby (1968). These are :-

Type 1 - Major copper, iron, sulphur, and quartz; minor cobalt, arsenic, and carbonate.

Type 2 - Major lead, zinc, and sulphur, with accompanying carbonate, copper and iron. Later heavy metals depend on the mode of occurrence of the veins.

(a) In the Vigra Flags Cu, Ag, Sb, and S with rare As, Te, and Bi.

(b) In the Clogau Shales and Vigra Shales, and the Ffestiniog and Penrhos Shales, Au, Ag, Bi, Te, Pb, and S.

Type 3 - Major zinc, iron and carbonate; minor copper and lead.

Copper is common in Types 1 and 2, but is more important in the former. The heavy elements of Type 2 were probably exhausted before Type 3 was emplaced. Type 1 occurs mainly to the south-west, and was gradually superceded eastwards by the lower temperature Type 2. Type 3 with crustification banding was emplaced in minor stretches of the more extensive fissures at Clogau, Gwynfynydd and Tyddyn Gwladys.

The location of the various mines in the area are shown in Fig. 16. The minerals found in each of the lode types are indicated on Fig. 17 (after Gilby, 1968) and the geographical distribution of the vein sulphides is shown on Fig. 18.

The different mineralisation types appear to be related to the wall rocks. Type 1 is associated with the Clogau Shales, Gamlan Flags, Penrhos Shales and igneous rocks; Type 2 occurs in the Vigra Flags. Type 3 occurs in the Clogau and Vigra Shales and Vigra Flags. From Fig. 18 it can be seen that the lower temperature, Type 2, assemblage, replaces Type 1 to the east.

The general order of deposition as described by Gilby (1968)

Fig. 16. Mine locations in the Harlech Dome. (after Gilby, 1968).

MINE LOCATIONS:

1. PANORAMA
2. CAEGWIAN
3. HENDREFORION
4. HAFOD UCHAF
5. CLOGAU
6. BRYN-Y-GROES
7. BRYNTIRION
8. GARTHGELL
9. MAESTYFER.
10. 11. 12. } VOEL ISPRI
13. WNION
14. BLAEN-Y-CWM
15. CEFN COCH.
16. CEFN DEUDDWR
17. CWM HEISAN
18. GLASDIR
19. DOL FRWYNOG
19.20 FFRIDD-GOCH : CEUNANT HŶLL
21. TYDDYN GWLADYS
22. GWYNFYNYDD
23. DOL-Y-CLOCHYDD
24. FARYNCHNYS
25. PRINCE EDWARD
26. HAFOD.WEN
27. CAE MAWR
28. AFON GAIN LODES
29. SARN HELEN
30. VIGRA.

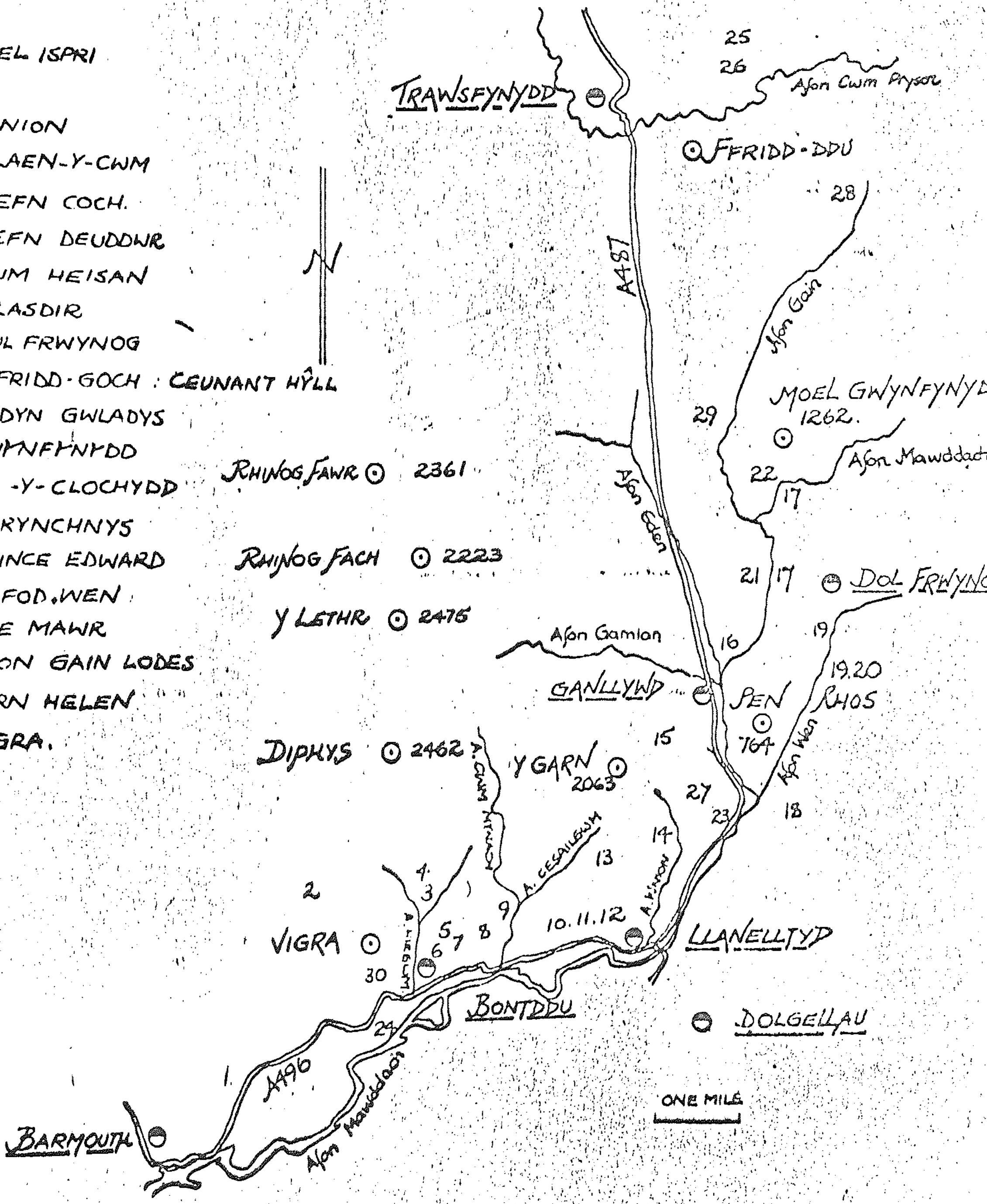
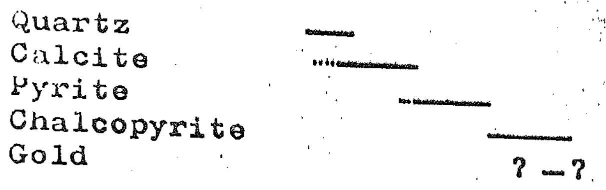


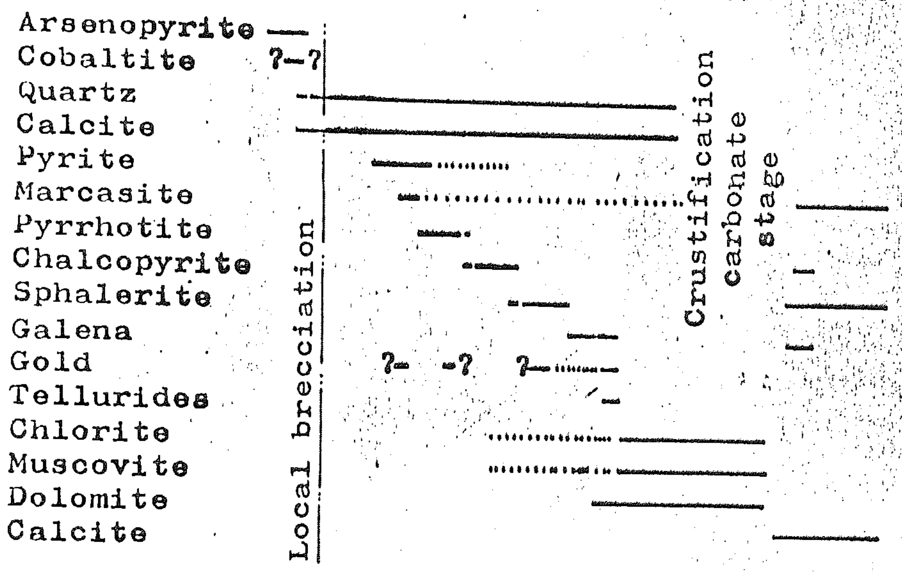
Fig. 17. Paragenesis tables (after Gilby, 1968).

Table No. 1: Cae-mawr type Mineral type 1



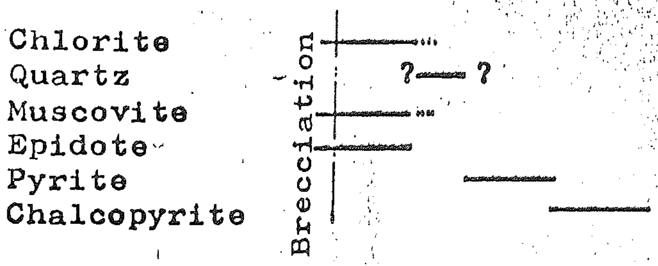
Supergene alteration - covellite, lepidocrocite, goethite.
Surface weathering - malachite, azurite.
Wall-rock alteration - chlorite, clinozoisite - epidote, orthoclase, albite, pyrite.

Table No. 2 : Panorama-Clogau type Mineral type 1 and 3



Supergene alteration - covellite, lepidocrocite, goethite, hematite, erythrite
Surface weathering - malachite, azurite, cerussite, anglesite.
Wall-rock alteration - epidote, muscovite, chlorite, sulphide addition, spessartine.

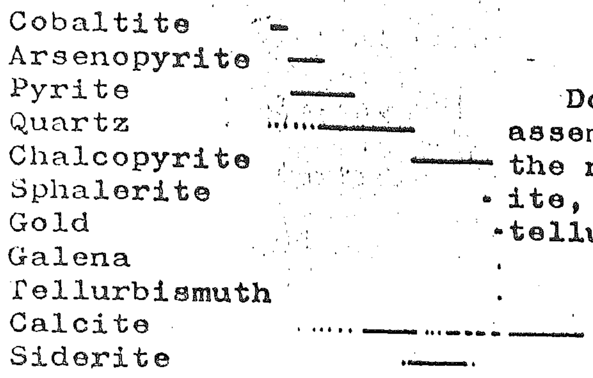
Table No. 3: Glasdir type



Supergene alteration - lepidocrocite, goethite, covellite.
Wall-rock alteration - epidote, chlorite, muscovite.

Fig. 17. (cont'd)

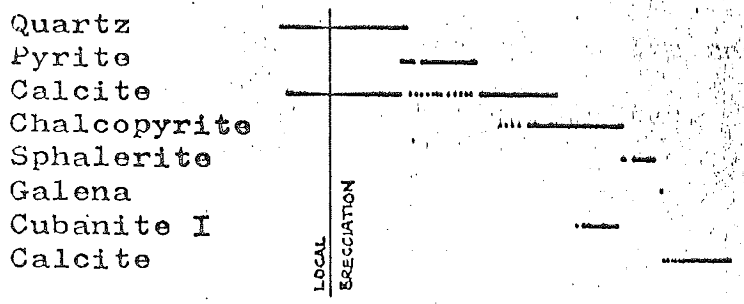
Table No.4 : Ffridd goch types.



Dol Frywnog type: A similar assemblage to Ffridd goch, with the notable absence of arsenopyrite, cobaltite, sphalerite and tellurbismuth.

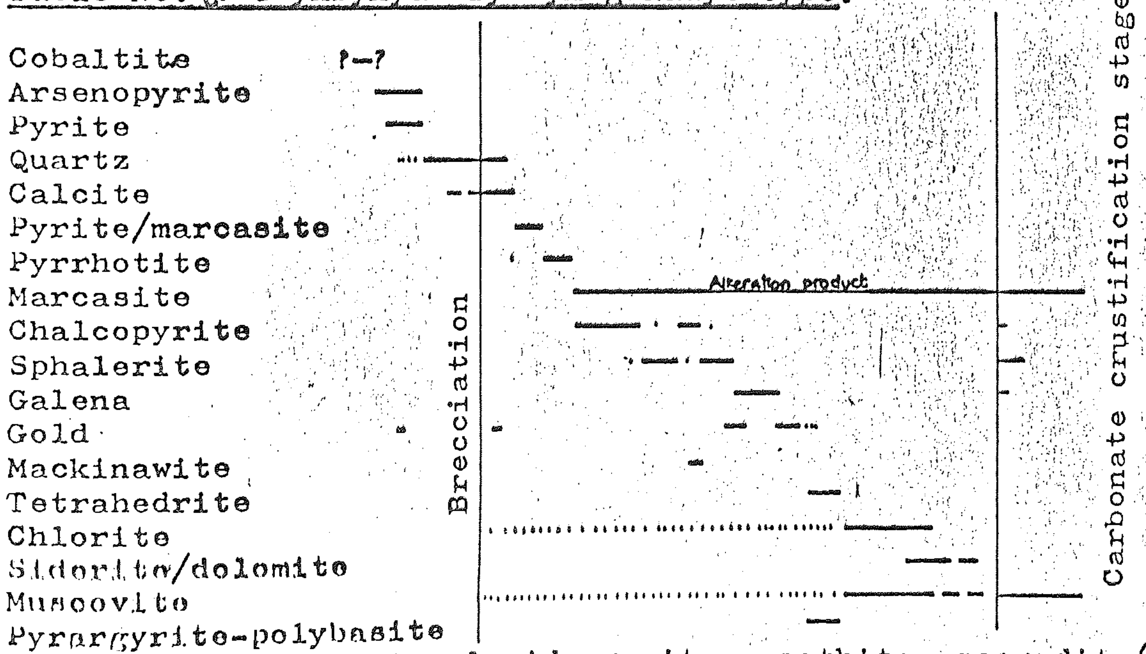
Surface weathering - malachite, azurite.
Wall rock alteration - dolomite, chlorite, albite, epidote.

Table No. 5 : Hendreforion type.



Supergene - goethite, lepidocrocite, pyrite, covellite.
Surface weathering - malachite.
Wall rock alteration - chlorite, epidote, muscovite, spessartine

Table No. 6: Gwynfynydd-Tyddyn gwladys type.



Supergene - covellite, lepidocrocite, goethite, scorodite(?).
Surface weathering - cerussite, anglesite, malachite, azurite.
Wall rock alteration - epidote, chlorite, albite, orthoclase, spessar

Fig. 18. Geographical distribution of vein-sulphides (after Gilby, 1968).

	SW	Panorama	Vigra	Clogau	Wnion	Voel Ispri	Cefn coch	Cefn deuddwr	Tyddyn gwladys	Ffridd goch	Gwynfynydd	Prince Edward	NE
Cobaltite		O	O	O	O	o				o		o	
Arsenopyrite		O	O	O	O		o						
Arsenopyrite+ pyrite						O	O	O	O	O	O	O	
Pyrite+ marcasite		O	O	O	O	o							
Chalcopyrite+ pyrrhotite		O	O	O	O							o	
Sphalerite with chalcopyrite					o	O	O	O	O		O	O	
Mackinawite					o	o	o	o	o		o	o	
Chalcopyrite (late + Au)					O	O	O	O	O	O	O	O	
Sphalerite		o	o	o									
Galena		o	o	o	O	O	O	O	O		O	O	
Gold + tellurides		?	O	O						O	o	?	
Galena + gold/ tetrahedrite								o	O		O		
Marcasite + sphalerite + carbonate assemblage				o					O		O		

KEY

O - common to abundant

o - rare to accessory

? - possible occurrence

is as follows :- (Fig. 18).

(1) Deformation along fissures, with accompanying brecciation and gouging, was accompanied by arsenopyrite deposition, with lesser quantities of pyrite, commonly in the wall rock.

(2) The fissures now opening were occupied by quartz and calcite. Arsenopyrite assemblages were deposited in the eastern part of the area, accompanied by cobaltite in the west. This preceded or accompanied the quartz-calcite emplacement.

(3) Chalcopyrite/pyrrhotite with lesser, earlier pyrite-marcasite were introduced, replacing the gangue minerals, especially the carbonates of (2) above. To the east, pyrite and marcasite superceded the paragenetically later pyrrhotite, (Gilby, 1968).

(4) New spaces were occupied by galena sphalerite, rare pyrite, second generation chalcopyrite, and calcite, which replaced earlier assemblages. This commonly shows crustification banding. Calcite emplacement was accompanied by both dolomite and siderite.

(5) The last stage was the infilling of minor openings (on three lodes only) with calcite-marcasite-sphalerite crustification assemblages. In some instances galena and chalcopyrites are present in the assemblages.

5:3 Vein Emplacement.

The "book and ribbon" structures found in the veins are similar to those produced by vein growth by accretion (McKinstry and Ohle, 1949). The vein is presumed to grow by successive re-openings of the fissure and, since the quartz vein material is stronger than the wall rock, the wall rocks split into sheets or "books". Continued fault movement of the vein walls relative to one another may distort the "books" and structures found, as shown in Fig. 19.

Inclusions of wall rock, ranging in size from several millimetres up to 3m, are present. These are postulated to have formed as a result of cataclasis accompanying successive re-openings of fissures. The inclusions in most cases have only slight contact alteration.

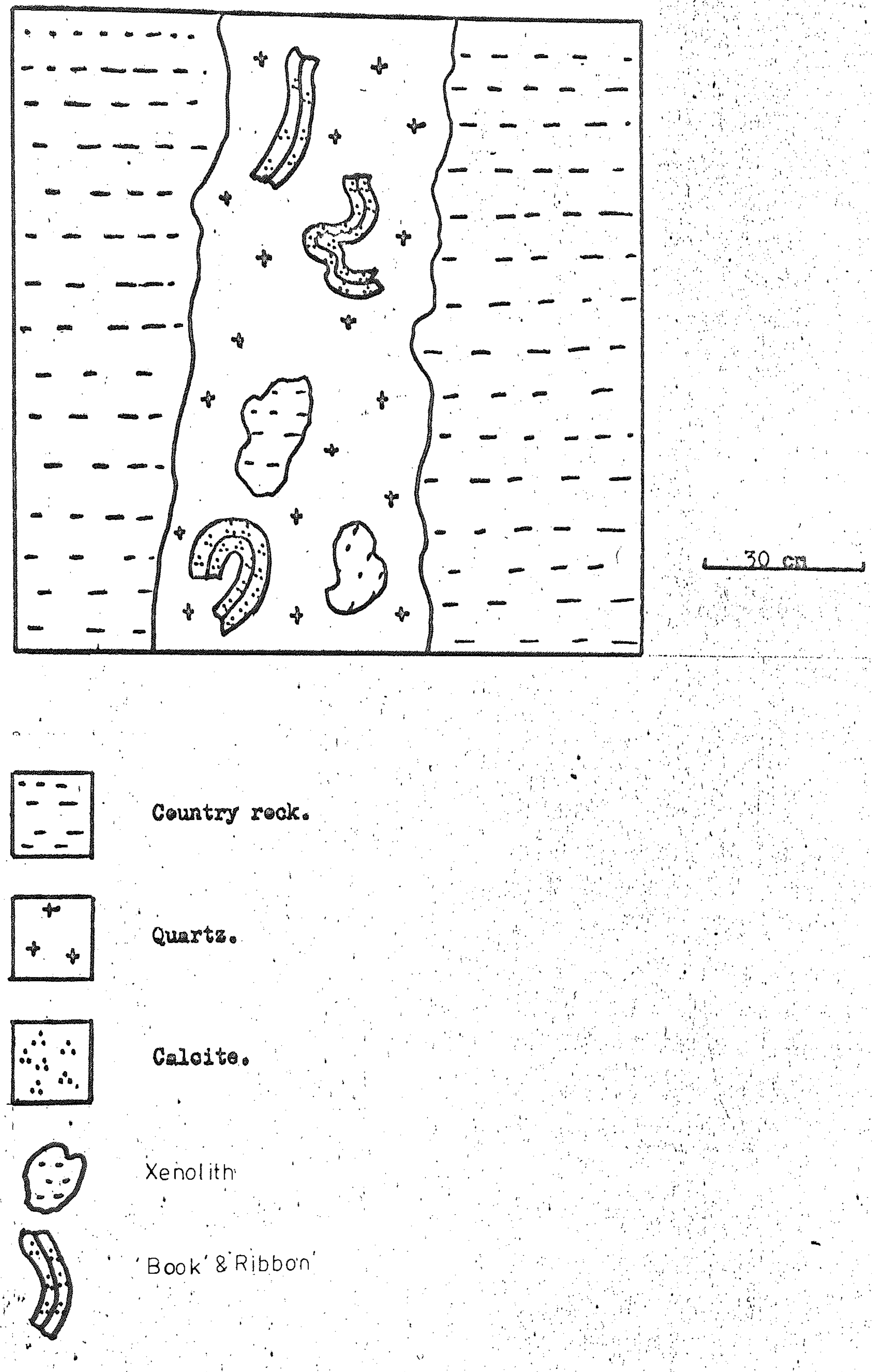
The continual movement necessary to explain these structures occurred on a minor scale, because the fault planes show no evidence for a single movement direction, and many orientations of slickensides may be found (Gilby, 1968).

The successive re-openings of the fissures is likely to form open-spaces, and these are represented by 'vugs', and crustification banding, in some of the vein material Since mineralogical evidence indicates that at the time of vein formation the area was covered by some 9000m of sediment (a hydrostatic head of 2,400 bars)(Gilby, 1968) any open spaces must have been formed by a tensional episode. This fits the structural evidence described in Chapter 4. There it was suggested that at the time of mineralisation the dome was rising and creating tension in areas which had previously been compressed.

5:4 Age of Mineralisation.

Radiometric dates on ore leads from the Cefn Coch mine (Moorbath, 1962) indicate an age of 470±60 m.y. and 430±80 m.y. for a galena sample from the Manod Bach mine (to the north of the Harlech Dome but of the same mineralisation type). This generally confirms the Caledonian age of mineralisation.

Fig. 19. Contorted structures found in veins - diagrammatic only



CHAPTER 6.

GEOCHEMICAL TECHNIQUES.

6:1 INTRODUCTION.

The techniques used for sampling, sample preparation, chemical analysis and data analysis were all examined in detail before the work was started. This was done in an attempt to eliminate systematic errors. The sampling plan was designed to produce results which would allow treatment by statistical and trend surface analysis techniques. Sample preparation was carried out using techniques which ensured that no outside or cross contamination occurred.

Reproduceability of results is more important than absolute accuracy in a study of this kind, and the analytical techniques were varied for different elements to ensure the best overall result. All data handling was computerised to facilitate analysis and minimise handling errors.

6:2 DESCRIPTION OF THE AREAS.

6:2:1 THE AREA NORTH OF BONTDDU (SOUTHERN AREA).

This area is that with mineralisation as opposed to the control area in the North. The area sampled is roughly 'L' shaped (Fig.5). The long arm of the 'L' is 3.6km long and 2.2km wide, and the short arm 1.2km long and 1.2km wide. It is broadly bounded by the A496 Barmouth-Dolgellau road to the South, and the main outcrops of the Gamlan Flags and Grits to the North. The boundaries to the East and West are arbitrary and were fixed with reference to exposure and accessibility.

The twin hills of Y-Vigra in the West and St. David's Hill to the East dominate the topography of the area. Between the two hills is the deep gorge of the Afon Cwm-Llechen in which there are excellent exposures of the Clogau Shales and some intrusive rocks. The Southern end of the hills is covered by a Forestry Commission conifer plantation, making accurate grid sampling impossible. Extensive mineral workings are present on St. David's Hill, extending from the brow of the hill Northward to the edge of the area. In this part of the area exposure is excellent (84% on grid points). Fewer smaller workings are present on Y-Vigra. Exposure is good around the summit of the hill and along the ridge extending to the North.

To the North of Y-Vigra are two broad valleys, separated by a ridge. These valleys become very steep at their Northern ends where crags of Gamlan Flags and Barmouth Grits are present. Exposure is good on both the sides and upper reaches of these valleys. The main valley floors are covered with waterlogged drift making bedrock sampling impossible. Seismic investigation of the Eastern valley, in preparation for diamond drilling, indicated a bedrock drift cover of 4m. Rock types present at the Gamlan Flags and Grits, the Clogau Shales, and the Vigra Flags, together with a few small, basic to intermediate intrusions, and some associated quartz veins. The outcrop pattern has a broad 'V' shape pointing South; the centre line of which passes just West of Bontddu (SH 670 187) (Fig.6).

6:2:2 THE CONTROL AREA IN THE NORTHERN PART OF THE HARLECH DOME (NORTHERN AREA).

This area is just South of Maentwrog on the Northern flank of the Harlech Dome. It has high ground in the South falling away Northwards to the estuary (Figs.4 and 8). It is bounded on the East, North and West sides by the main road which encircles the Harlech Dome. The Southern boundary follows the outcrop of the Clogau Shales along a line from Talsarnau, in the East (SH 360 613), to the road junctions, at SH 396 692, South West of the village of Gellilydan. The Eastern part of the area has a deep valley, running N.E.- S.W. along a fault line. This valley separates the high craggy hills which are towards the centre of the Dome from the lower country along the coast. In the North the craggy hills die away to the steep cliffs on the banks of the estuary.

The hills in the West fall away to the flat, drift covered valley which extends from Llyn Trawsfynydd (SH 370 690) to the start of the Coed Brenin Forest (SH 290 720).

Outcrops in this area follow a N.E.- S.W. trend formed by the Gamlan rocks in the South East and the Penrhos Shales in the North West (Fig.8). There are fewer intrusive rocks present in this area compared with the large number of small sills in the Southern Area, around Bontddu. Because of this exposure is generally poorer.

6:2:3 THE GWYNFYNYDD MINE.

This mine (Figs.4 and 20) was the last mine worked commercially. It is easy and safe to enter and to sample. The main entrance is next to the spoil heaps and engine sheds and about 200m uphill and upstream from the old crushing and processing area. The main level of the mine extends into the hillside for approximately 137m, where it meets a series of inclined stopes. Some of the stopes extend to the surface and link other working levels both above and below the main one.

Samples of the lode material and both sedimentary and igneous country rocks were sampled. The relationship of the faulting to the vein formation was determined, (Chapter 4).

6:3 SAMPLING.

6:3:1 GENERAL CONSIDERATIONS.

The overall geochemistry of the rocks varies a great deal due to the superposition of the mineralisation (Mohr, 1959; Price, 1963). To study the relationship between the mineralisation and bedrock geochemistries detailed sampling of the rocks was necessary. The size of the area sampled was determined largely by the number of sample analyses that could be carried out, and the subsequent data handling, in the time available.

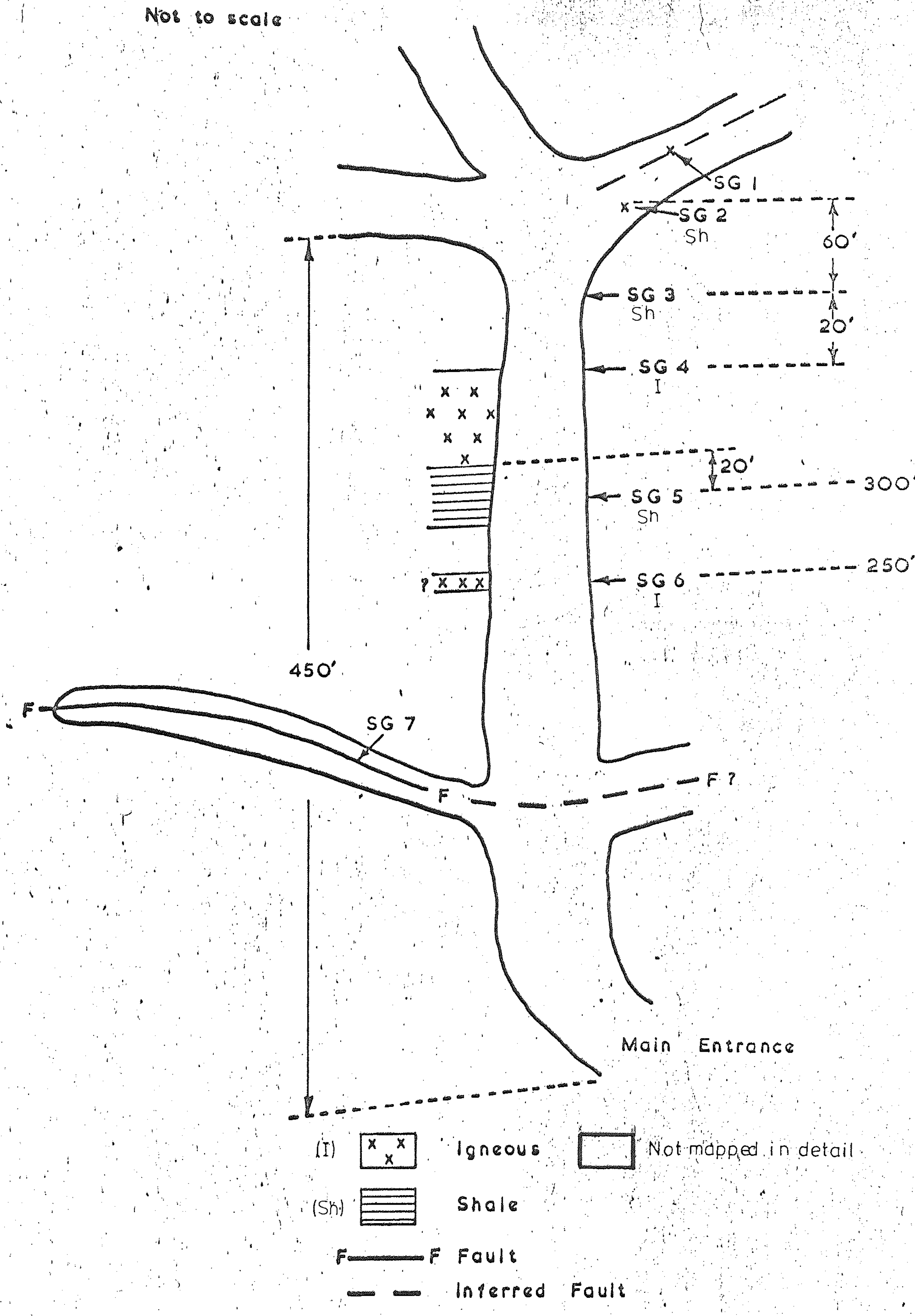


Fig.20. SKETCH MAP OF THE GWYNDYNYDD MINE - MAIN LEVEL TO SHOW SAMPLE LOCATIONS.

The Southern area was chosen for initial sampling because it is the most heavily mineralised and best known geologically. The mineralisation is largely confined to the Clogau Shales and the Vigra Flags, with a small quantity in the Gamlan Flags. Sampling was confined to the outcrop area of these rock types.

The Northern Area was selected as a control because it has little mineralisation. This allowed the variations in bedrock geochemistry to be studied in isolation and the determination of large scale trends in the bedrock geochemistry between the two areas.

The Gwynfynydd Mine was sampled to allow the geochemistry of the lodes and associated wall rocks to be studied and to directly determine the effects of the mineralisation on the enclosing rocks.

Because two variables affect the trace element concentrations in the rocks multivariate statistics, coupled with trend analysis, were considered to be the best techniques readily available for analysis of the geochemical data. Use of these techniques required that the sampling pattern was statistically viable.

To give adequate coverage of the area a 200m grid was constructed, using a 1:10560 O.S. map as a base map. The grid was arranged to run along the strike of the Gamlan, Clogau and Vigra Formations. The grid was placed on the base map with reference to aerial photographs, in such a way as to ensure that the maximum number of exposures were sampled.

Samples were taken at as many points as possible, rather than using a statistical approach in which only a percentage of the grid points are sampled to give a theoretically predictable percentage coverage (De Geffroy and Wu, 1970). This was done because trend analysis was to be used which required the maximum data possible in order to provide reliable trends. The control area has numerous outcrops of Vigra Flags and Clogau Shales and little recorded mineralisation. The outcrops are narrower in this area, and the exposure is less than in the Southern Area. Because of this grid sampling was difficult and trend analysis unreliable. Sampling in this area was therefore carried out on a random basis.

6:3:2 SAMPLE COLLECTION.

Field sampling varied according to the area being sampled. In Bontddu (Southern) area location of the grid points was found to be relatively simple. The majority of points could be located to within 4m, although in some cases the position could only be fixed to within 10m.

Where a grid point fell in an area of varied geology a representative sample was difficult to obtain. At points such as these the rock sampled was selected randomly by throwing a hammer into the air and taking the sample from where it fell. In places where a rapid alternation of shales and flags was present a composite sample of these rocks was taken. In general however the shaley parts of the succession were sampled for analysis because these rocks have potentially more value (Chapter 1).

In any sampling programme involving a fixed grid, lack of exposure is a problem. In the area sampled approximately 50% of the grid points fell on, or near, to outcrops. In detail however, the quantity of exposure varied greatly over the area from 85% in the area behind Bryntirian Wood (SH 676 203) to 10% in some of the upland valleys (SH 658 226). In instances where the grid intersections fell on an area of no outcrop, the nearest outcrop within a 50m radius was sampled, and its exact position plotted.

Reasons for the non-exposure of the bedrock were analysed to discover if they would introduce a systematic bias into the sampling. In the selected area it appears that outcrop occurrence is controlled by two factors. The first is the rock type, and the second is the physical form of the topography produced by glacial erosion and deposition. Rock types in the area are flags, shales, grits, basaltic intrusives and quartz veins. Shales tend not to form outcrops because of their soft nature; however where they are interlayered with flags and grits in the Gamlan and Vigra, and sills as in the Clogau Shales, the overall effect is to produce a hard rock with good exposure. All rock types in the area around the old St. David's goldmine (around SH 676 203) (Fig.3) are well exposed. In the area of the broad valleys, from around SH 658 226 down to Llechfraith (SH 669 205) all rock types, irrespective of hardness, are covered with drift. The valley floors were tested by drilling and some core samples were taken (Appendix 4).

Results of this drilling indicated that the bedrock below the valley floors differs very little from that exposed on the hillsides. (See Chapter 8). As a result of the above considerations it was assumed that there is no significant systematic bias to the exposure of rock types in the area under investigation, assuming a 200m sampling grid.

A brief examination of the Northern (control) Area indicated that this assumption was not true there. In particular the Clogau Shales are very poorly exposed in relation to other rock types for sampling on the 200m grid. Sufficient exposure was available,however, to allow regular sampling of the individual rock types both along and across the outcrops. In this area the sample positions were recorded on a 1:10,560 O.S. map and spacing of the sample points was selected with reference to the available outcrop.

During sampling all relevant geological information was recorded for each sample point. This information, together with aerial photographs enabled a 1:10,560 geological map to be prepared for both areas (Figs.6 and 8). These were used as base maps for relating geology to geochemistry and are not meant to be definitive detailed geological maps of the area.

Sampling in the Gwynfynydd Mine was restricted to collecting specimens of the different rock types at points selected with reference to the structure (e.g. proximity of shear zones). Sample positions were recorded relative to the distance from the mine entrance.

The method of sampling used in the Northern and Southern Areas, was to clear away any soil etc., and to remove as much weathered rock as possible before collecting a fresh rock sample. Fresh samples were not always obtainable due to the depth of weathering. The Clogau Shales for example have a recorded weathered zone extending to a depth of 76m in some instances (Matley and Wilson, 1946). The sample taken was as representative as possible. Between 1 and 2kg of rock were removed from the exposure from which some 500g were selected. The sample was packed into a 'seal top' polythene bag, previously marked in triplicate with the sample reference number. Details of the sample were recorded in a field notebook together with all other geological data available. As a safeguard, a slip of paper with the sample reference number on it was placed in each bag before sealing, and sample details were entered onto duplicated sheets of standard format.

Samples from the Gwynfynydd Mine had little surface weathering. Rock samples of 500g were taken from 1 and 2kg specimens removed from the walls of the passage, and were stored as described above.

6:4 ANALYTICAL TECHNIQUES.

6:4:1 INTRODUCTION.

A geochemical study of this nature involving trend and factor analysis requires analysis of a large number of rock samples, by as precise a method as possible, for a selected number of elements. The analytical methods used in this study were designed to produce large quantities of precise data rapidly. Sample pre-treatment was kept to a minimum in order to minimise the possibility of introducing a systematic error.

The main analytical method used was atomic absorption spectrophotometry with X-ray fluorescence spectroscopy and for those elements not readily determined by atomic absorption. Mineralogical data was provided by thin and polished sections. Carbon analysis was carried out by a combustion method.

6:4:2 PREPARATION OF ROCKS FOR ANALYSIS.

When received into the laboratory each sample was checked against the collecting list to ensure that no labelling mistakes had occurred. The samples were then inspected, dried and cleaned. Weathered material was removed from the sample surfaces by dry grinding on a carborundum wheel. Any resulting rock powder on the surface was removed by a compressed air jet. Both these operations were carried out under a dust removal hood with sufficient air flow to remove all dust particles. At this stage random samples were selected, together with additional specially selected samples, for thin and polished section study.

The remainder of the sample, apart from a small hand specimen, was then reduced to a 200 mesh powder. This operation was carried out in such a way that any systematic error produced by cross contamination or contamination from the crushing and grinding machinery was minimised. A detailed description of the process is given in Appendix 9.

6:4:3 ELEMENTAL ANALYSIS.

6:4:3:1 SAMPLE DISSOLUTION AND ATOMIC ABSORPTION ANALYSIS.

Numerous methods are described in the literature for dissolution of rocks. Most methods require a great deal of time and manipulation making them open to operator error. Because of this a modified technique for silicate dissolution and analysis was developed which gave rapid analysis with a high degree of precision. Details of this method, its development, and comparison with other methods may be found in Appendix 1. Elements determined by this method are Si, Al, Fe, Cu, Ni, Zn, Pb, Sr, Ba.

Mercury was determined, with extremely high precision at the low levels encountered in the rocks, using a modification of existing cold vapour atomic absorption techniques, (Appendix 2).

Absorption readings produced by the instrument were converted to element concentrations in the rock sample using a small computer program. Details of the data handling and program are given in Appendix 5.

6:4:3:2 X-RAY FLUORESCENCE ANALYSIS.

64 samples from the main area were selected at random and analysed by X-ray fluorescence spectroscopy for up to 24 elements. 200 mesh powders were mixed with a polyvinyl alcohol binder and compressed into a pellet. Analysis was carried out on a Phillips PW 1212 sequential X-ray fluorescence spectrometer at the Department of Geology, University of Birmingham. Instrumental parameters were the pre-programmed standard settings used at the Department of Geology. The X-ray intensities were recorded on punched tape by the instrument, and these were converted to elemental concentrations using the Birmingham University KDF9 computer and standard program used by the Department of Geology. Elements determined by this method were Yt, Sn, Rb, Th, Mg, Pb, Na, Ni, Fe, Mn, Cr, Ce, La, Ti, Ca, K, S, Si, Al, P.

Some elements were determined using both methods to check the performance of the X-ray fluorescence calibrations, which were set up for slightly different rock types. In general differences were slight for minor and trace elements. The major elements showed some discrepancies. Generally the atomic absorption results were used for the elements determined by both methods.

6:4:3:3 CARBON ANALYSIS.

To determine the carbon content of the rock samples, a carbon train was constructed. Samples ground to 200 mesh were used and the quantity of CO_2 given off at high temperature determined. This was then expressed as a percentage of the original sample. Details of the constructions and method are given in Appendix 3.

6:5 DATA HANDLING TECHNIQUES.

6:5:1 INTRODUCTION.

To obtain the maximum amount of information from the geochemical analyses three major techniques were used:-

The first of these was to plot histograms of element concentration against number of samples with an element concentration lying in a particular class interval. This was done for all rock types together, and then for individual rock types separately for the Northern Area and Southern Areas. These plots show up differences in means and shapes of distributions. They also show high or anomalous values.

The second method was the used of multivariate statistical analysis on the data to determine associations of elements, and to plot these associations on the sampling grid. This was done to determine the likely causes and distributions of these associations.

Finally, selected elements were put through a Double Fourier trend surface program to discover any trends and residual or anomalous values which may be present.

To carry out the second and third types of analysis required the raw data to be pre-sorted and presented to the computer programs in a set way. To do this two computer programs were written to sort and abstract the raw data, and produce a final output which could be used as input for both statistical and trend surface analysis programs.

6:5:2 COMPUTER SYSTEM.

The computer system in current operation at the University of Aston is an I.C.L. 1905 E processor with 60K of available core, operating under the GEORGE 3 operating system. Input to the computer was via cards and punched paper tape, directly into the core or onto magnetic disc for storage. Compiled programs were also stored on magnetic disc. Output from the programs was either to the line printer, or onto magnetic disc storage. In addition an editor was used which allowed separate data files to be combined to form one new file.

6:5:3 DATA INPUT.

The analytical data consisted of element concentrations, for up to 25 elements for each rock sample, either in percent or ppm. In addition the sample grid co-ordinates were required for the trend surface program. Because all elements were not determined at the same time it was necessary to be able to update the data files. To facilitate this each rock sample was allocated a unique five digit identification number. The first two digits identified the user while the last three identified the rock sample. All searches and data manipulations were performed using this number as a reference. All other identification data, such as grid reference, or XRF pellet number (University of Birmingham), were treated in the same way as the analytical data.

The data was input on either punched cards, or punched paper tape, in the following format:-
1st card or line
Identification number, X.R.F. pellet number, grid reference.

2nd card or line
Atomic number of element, element concentration, control digit.

The second card format is repeated for each element concentration. When a new sample was to be input the first card format was repeated. The control digit was used to identify the type of information for each element analysis, e.g.
Control Digit
0 - new rock identification number
1 - further element concentration
9 - end of data set.

The data was read onto magnetic tape and stored. Program SORT took this data and if existing data was already stored, it either added the new data to the end of the data file, or combined new element analysis with existing ones. A new data file is then stored on magnetic disc (Fig.21A).

6:5:4 DATA MANIPULATION.

To provide input to the statistical or trend analysis programs it was necessary to abstract the whole or part of the element analyses for selected samples. To do this Program ABST was written. This program read the stored data file from the magnetic disc and, acting on information read in from punched cards, produced input data in the correct format for either the statistical or trend surface program. This input data for the two programs was stored on magnetic disc (Fig.21B).

A detailed description of these programs is given in Appendix 6. The statistical analysis program required a number of control cards to be read in before and after the analytical data, which consisted of a table of element analyses and rock identification numbers. To simplify the data manipulation the control cards were read in and stored on magnetic disc in two blocks; those required by the program before the analytical data;

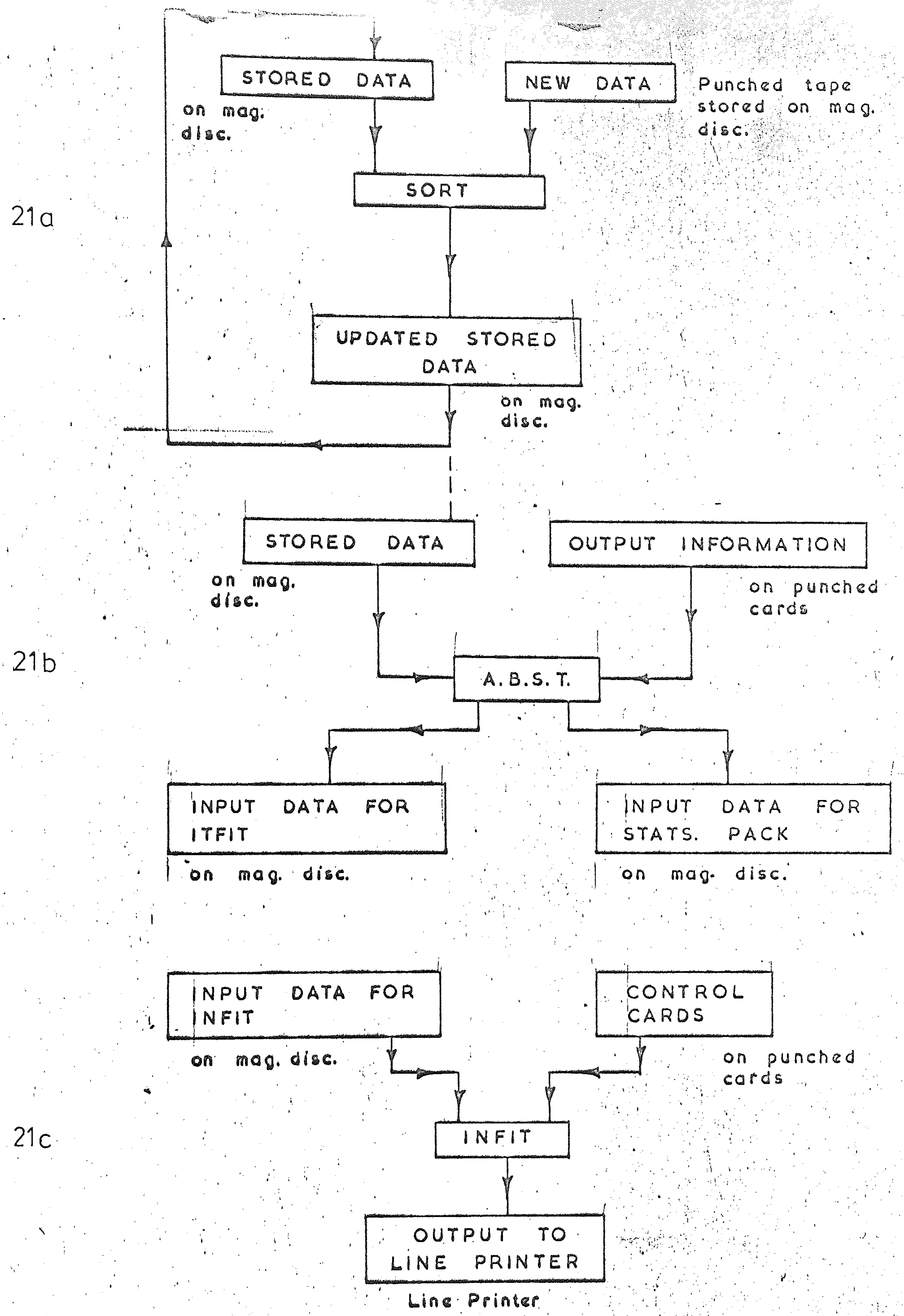
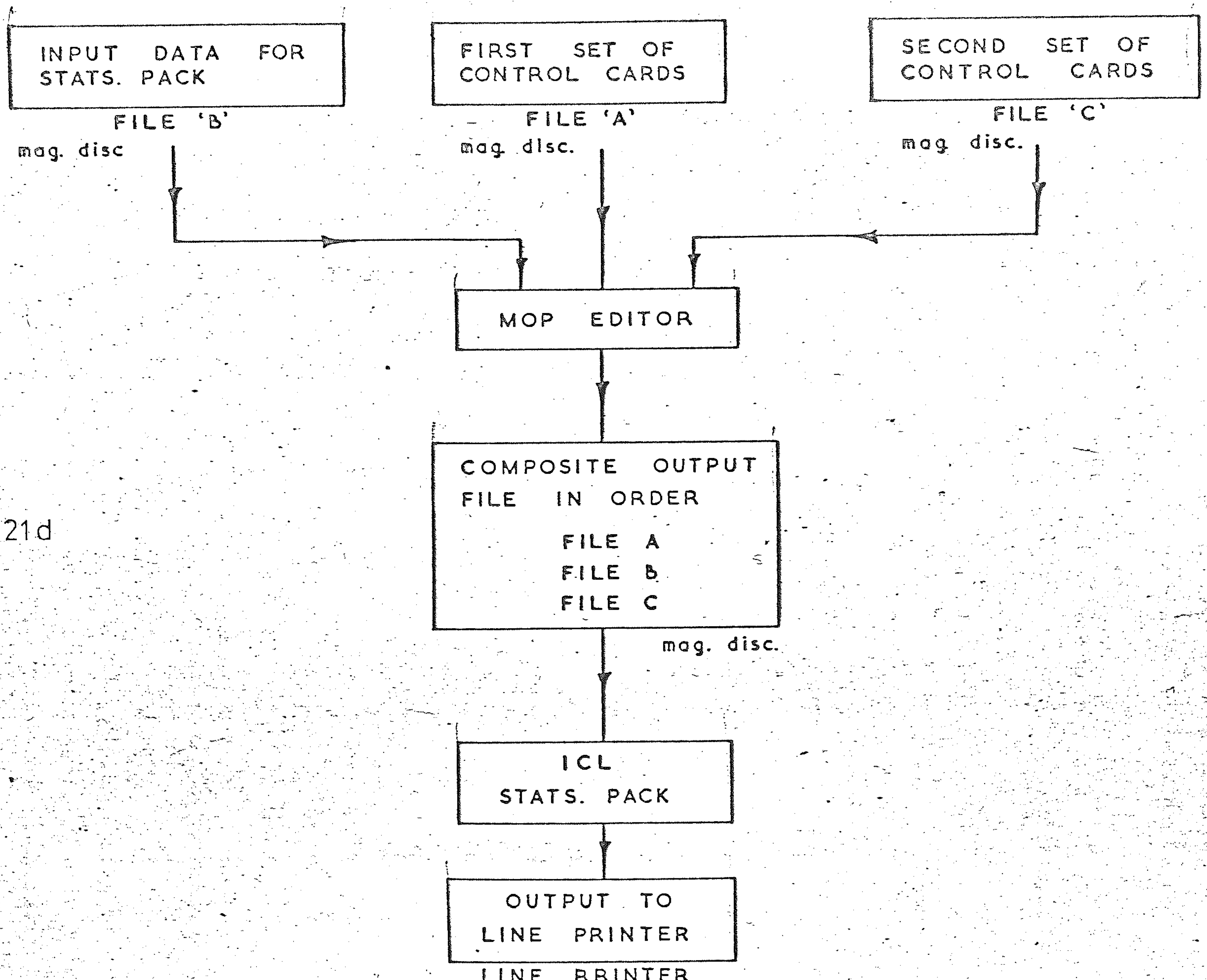


Fig.21 . Computer programs flow sheet.


INPUT DATA FOR STATS. PACK
FILE 'B'
mag. disc
FIRST SET OF CONTROL CARDS
FILE 'A'
mag. disc.
SECOND SET OF CONTROL CARDS
FILE 'C'
mag disc.
MOP EDITOR
COMPOSITE OUTPUT FILE IN ORDER
FILE A
FILE B
FILE C
mag. disc.
ICL STATS. PACK
OUTPUT TO LINE PRINTER
LINE PRINTER

21d

and those required after. These were then combined with the analytical data in the correct order, using the system editor and a single output file stored on magnetic disc. This file was then run through the statistical analysis program (Fig.21d).

Input to the trend surface program (Program FOURFIT) required a maximum of twelve control cards, in addition to the analytical data in the form of a table of concentrations of a particular element with the rock identification number and grid reference. Because of this the control cards were read directly in from the card reader, the compiled program, and the analytical data, being read in from magnetic disc storage (Fig. 21C).

6:5:5 STATISTICAL ANALYSIS.

The statistical analyses used in this work were correlation analysis, principal component analysis, and principal factor analysis. The reason for performing these analyses was to determine associations of particular elements and to plot the distribution of these associations as a geological map. The correlation analysis determined the degree with which the linear distribution of one element was related to the linear distribution of another element. In terms of the present work this type of analysis was useful on a very broad scale, because, as there are a number of different causes of element variations, it was unlikely that a linear relationship would exist between any two elements.

Principal factor and principal component analysis examined the relationship between all of the elements simultaneously and determined which elements were associated. This attempt to find the association of elements which caused the maximum variation in the analyses, and to quantify this variation. This figure was then subtracted from the total variation, and the analysis repeated. In this way a whole series of associations and their relative importances were found. These associations, components or factors, depending on the type of analysis, were related to physical processes, such as sedimentation or mineralisation, by information gained about these processes in this and previous works. The difference between principal component analysis and principal factor analysis is that in the case of principal factor analysis the possible field of variation is narrowed down by neglecting some less important factors, and assigning all of the variation to a small number of factors. This has the advantage of making the associations within the factors clearer. The disadvantage is that a subjective decision must be made as to the relative importance of the factors. A detailed description of the statistical methods used together with the computer program is given in Appendix 7.

6:5:6 TREND SURFACE ANALYSIS.

The method of trend surface analysis used in the present work was Double Fourier analysis. The program for this technique used in the present work accepted irregularly spaced data. It took the analysis for a particular element at a series of grid points and calculated the mathematical function, in three dimensions, that would approximate to the mean surface of the data. This was printed out in the form of a contour map. The mathematical function for the complete fit was then calculated. This function was such that at each point where there was data available, the calculated value was equal to the actual value. The mean, or trend surface data was then subtracted from the complete fit data to produce a map of residual values. This map indicated points where the actual value was higher or lower than the mean or trend value. This therefore indicated points or areas of depletion, or enrichment, in trace elements, as well as showing the underlying trends in element concentrations.

A detailed description of the method and computer program is given in Appendix 8.

CHAPTER 7.

GEOCHEMISTRY OF THE ELEMENTS.

7:1

The major cause of variation in the element concentrations in the rocks of the Harlech Dome is the basic geochemistry of the rock type. Superimposed on this 'regional' geochemistry are the effects of mineralisation which introduced or re-distributed various elements. Because the aim of the present work was to examine each of these effects in isolation, a knowledge of the likely variations was necessary, and these are discussed in this Chapter. Mercury is treated in a separate section since its behaviour is completely different from all of the other elements studied.

7:2 STRATIGRAPHIC CONTROL OF ELEMENTAL VARIATION.

The stratigraphic control of the element distributions provides a broad 'background' variation. The concentrations of elements in the rock are influenced by the source of supply of the sediment, the distance of transport, and conditions of deposition. In addition, subsequent diagenetic changes may have modified the distributions, and caused enrichment or depletion of some elements. To help in the prediction and understanding of large scale trends a knowledge of the Cambrian palaeogeography of the Harlech Dome is of use.

Price (1963) produced a map showing the palaeogeography and sedimentary characteristics for the Clogau Shales (Fig.22). He stated that at that time, the Harlech Dome consisted of an elongated basin with its major axis aligned N.N.W.- S.S.E. Sediment entered the basin from each end along the major axis (Keunen, 1953; Kopstein, 1954). At the end of Gamlan times the marginal flow of sediment from the North West, South West and East South-East, which had occurred throughout Lower and Middle Cambrian times, became the dominant factor.

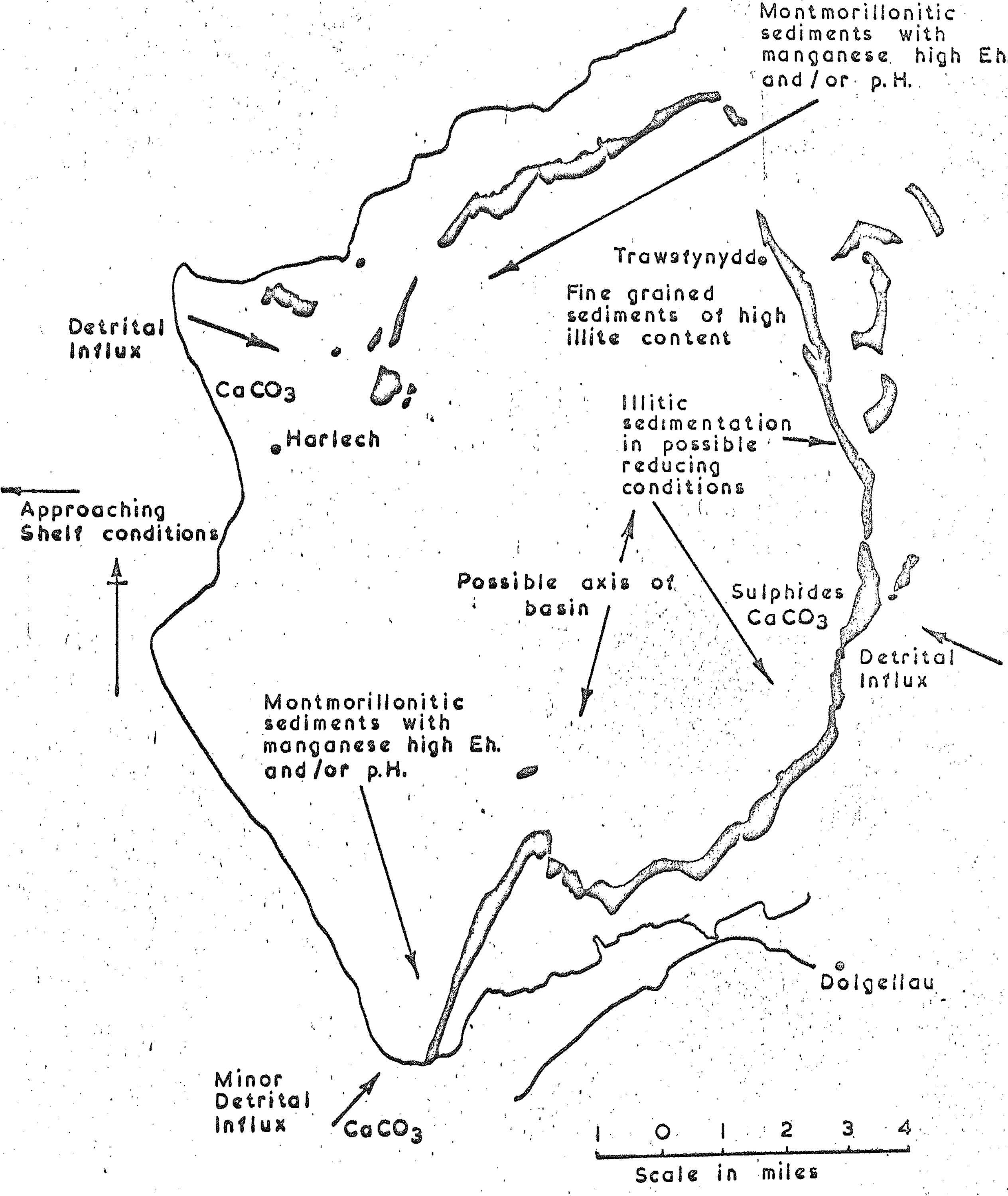


Fig.22. PALAEOGEOGRAPHY AND SEDIMENTARY CHARACTISTICS OF THE CLOGAU SHALES (After Price, 1963).

Woodland (1939) and Mohr (1959) have suggested that the Harlech Dome was an enclosed, or partially enclosed basin during the time of the deposition of the Manganese Shale. Price (1963) suggested that a similar condition could also have occurred in Menevian times. Jones (1938) invoked the presence of a land mass in the North Irish Sea area which could have acted as a source of supply of sediment from both the North West and South West. The source of the sediment from the East South East is unknown (Price, 1963), however the equivalent rocks in the Welsh borderland indicate that shelf conditions existed there at this time (Stubblefield, 1956). This suggests that the same conditions may have existed in the Harlech Dome. The types of sediments deposited in the Clogau Shales unit are shown in Fig.22. This indicates the variation present across the area. Influx of detritus generally produces lower contents of barium and chromium, and higher aluminium, titanium and gallium, than an influx of clay, which would have higher barium, boron, sodium potassium and iron (Price, 1963; Vine and Tourtelot, 1970). The conditions of deposition also affect the element distributions. Under reducing conditions (Fig.22) a concentration of copper and zinc can occur due to a process suggested by Brongersma - Sanders (1968), in which trace metals are concentrated by the life processes of plankton living in surface waters. On death the plankton are carried away by surface countercurrents and accumulated in large numbers. Decay causes a high oxygen consumption, produces hydrogen sulphide, and results in bituminous deposits enriched in the trace metals.

The Clogau Shales, in the vicinity of Bontddu, contain large quantities of pyrite crystals which indicate the possibility of a reducing environment at the time of deposition. This, together with their high carbon content indicates a possible enrichment in trace metals. Due to the presence of large, well formed pyrite crystals (Chapter 2) it is likely that diagenetic changes have taken place in these rocks (Vine and Tourtelot, 1970).

The erosion and local re-deposition of a particular source rock (Chapter 2) may result in the local concentration of relatively unweathered fragments of that source rock (e.g. Plate 3). This may locally produce whole rock analysis close to the original source rock composition.

The variation that is produced by the above processes means that any average or mean value of element concentration will not be representative of the rocks of the whole area, and that element distributions must be used instead to compare rocks. In addition, associations of elements will be useful in determining the more predominant effect, be it of sedimentary or mineralisation origins.

As stated, introduction of clay minerals produces an association of Ba,Sr,Al and Fe, while fragmental detritus produces an association of Al and Si. Thus a sedimentary association of Al, Si, Ba, Sr and Fe is likely in addition to the individual associations of the predominant rock constituents. Combined with these are the likely associates of Cu and Zn in the shales, i.e. with Ba and Sr. This latter association is difficult to distinguish from associations produced by mineralisation (see below).

7:3 MINERALISATION AND ITS EFFECT ON BEDROCK GEOCHEMISTRY.

The effect of mineralisation on the distribution of the elements is twofold. Some elements, e.g. Cu, Zn, Pb, and Hg, are introduced and form anomalous concentrations in veins and their wall rocks. Others, e.g. Si and Al, may be depleted in zones of contact metasomatism. In addition some elements, notably mercury, may permeate the country rocks around areas of input and form a 'halo'.

To predict which elements are more likely to indicate the presence of mineralisation, it is necessary to make assumptions about the nature of the mineralising fluids, and their effects on the country rock. From a study of the mineralisation and geochemistry of the veins and associated wall rocks, Gilby (1968) concluded that the vein mineralisation was produced by hydrothermal fluids, at a maximum hydrostatic pressure of 2,400 bars. The solutions themselves probably had a pH between 6 and 8, with local variations caused by reactions with the wall rocks. In three instances the pH of the solutions is suggested to have been between 4 and 5 resulting in a different mineral assemblage.

The temperature of deposition was deduced, by Gilby (1968), as varying between 100°C and 450°C according to the assemblage. The ore-bearing fluids are considered to have been hot aqueous solutions containing ore elements complexed with alkali halides. This conclusion is supported by the work of Helgeson and Garrels (1968) who were able to show that gold and quartz may be carried in acid solutions as a chloride complex. Precipitation may have been caused by a decrease in temperature or an increase in pH, or a change from an oxidising to a reducing environment. Radtke and Scheiner (1970) showed that gold can be removed from a hydrothermal solution by chelation with carbonaceous matter.

In the Dolgellau Gold Belt the fluids were introduced along fractures and subsequently diffused through the rock changing their composition and increasing their pH (Gilby, 1968). He also concluded that an equilibrium existed between wall rock alterations and the vein mineral assemblage.

The importance of the wall rock for vein information, particularly those containing gold, is demonstrated by the fact that gold is not found in strata other than the Gamlan Flags, Clogau Shales and Vigra Flags. Variations occur between these three rock types, particularly in the extent of wall rock alteration (and the deposition of vein material). Local alteration (up to 1cm) is present in the Clogau Shales, while the Vigra Flags are altered up to 6m from their contacts. The extent of the alteration in the Gamlan Flags lies somewhere between the two. In all the rocks the early deposition of silica from the ore fluids had the effect of sealing the country rocks from further permeation by the ore fluids and stopped wall rock alteration. Because of this it is unlikely that a widespread 'halo' of the ore minerals or elements would be formed. All the elements transported in aqueous solutions were confined to a narrow zone around the veins. This means that any anomalous values will indicate the close proximity of mineralisation. Conversely the absence of large scale 'haloes' means that the regional bedrock geochemistry, due to sedimentary causes, will not be greatly influenced, and can therefore be treated in isolation.

Elemental associations expected to be produced by mineralisation are as follows:-

a) SiO_2, Pb and Zn - due to vein Pb/Zn in quartz.

b) Sr, Ba and SiO_2 associated with various metals indicates that quartz and carbonates are present in the mineral veins.

c) Ba, Pb, Zn and possibly Sr, are indicative of Pb/Zn mineralisation with carbonate gangue.

d) Cu, Fe_2O_3, SiO_2 and possibly Ba and Sr, indicates chalcopyrite mineralisation.

e) Al_2O_3, Pb, Zn and Cu, are indicative of wall rock alteration because this is always associated with an increase in Al_2O_3. In addition SiO_2 would be expected to show a negative association since SiO_2 decreases in the alteration zone (Gilby, 1968).

All the above associations were found by Gilby (1968). They are shown in his Fig.17.

From Gilbey's (1968) work on mineralisation, associations of Pb and Zn indicate a 'type 3' mineralisation, while Cu indicates a high temperature 'type 1' mineralisation (Chapter 5).

7:4 THE GEOCHEMISTRY OF MERCURY.

Analysis of the rocks in the study areas revealed varying concentrations of mercury throughout each of the areas. The behaviour of mercury during igneous, hydrothermal, and weathering processes is controlled by the insolubility of most of its compounds, and its high vapour pressure (Fig.23).

The principal deposits of mercury in the world are associated with zones of instability, or dislocation, of the Earth's crust. Mercury concentrations are most commonly associated with hot springs or other expressions of high level volcanic activity (Fig.24). The mineralogy of these deposits is generally simple, consisting entirely of cinnabar, or meta-cinnabar, with varying quantities of native mercury. Pyrite, stibnite, realgar, native sulphur, quartz, flourite, and carbonates, (Ozerova, 1962) in the form of veins, stockworks, impregnations or replacement lodes, are commonly present along with the mercury minerals. Mercury is also present in some deposits associated with other hydrothermally transported metals. Saukov (1940) showed that the majority of polymetallic sulphide deposits contain mercury in quantities several times their "clarke" values. He further suggested that the mercury content of such bodies increases with a decrease in temperature of formation of the deposit, reaching a maximum in epithermal deposits (80-100°C). Individual minerals may contain many times the background concentration of mercury: at Boliden, gold, selenokobellite, and tetrahedrite are all strongly enriched in mercury (Grip, 1948). Sphalerite may also have irregular mercury concentrations. These have been suggested to be a function of the temperature of deposition (Ginzburg, 1960, Furzov, 1958).

The mercury content of ores indicates that this element is present in many hydrothermal ore deposits (Furzov, 1958). Correlations with other elements in the deposit may indicate the mode of transport of the mercury. An example of this is given by Webber and Newbury (1971) in

Fig. 23. Comparison of vapour pressure of magnesium, zinc, cadmium and mercury at 200°C and 600°C (after James,1962).

	Vapour pressure in mm Hg.			
Temp. °C.	Mg	Zn	Cd	Hg
200	ca 10^{-5}mm	2 x 10^{-5}mm	3 x 10^{-4}mm	18 mm
600	7 mm	12 mm	80 mm	16,500 mm

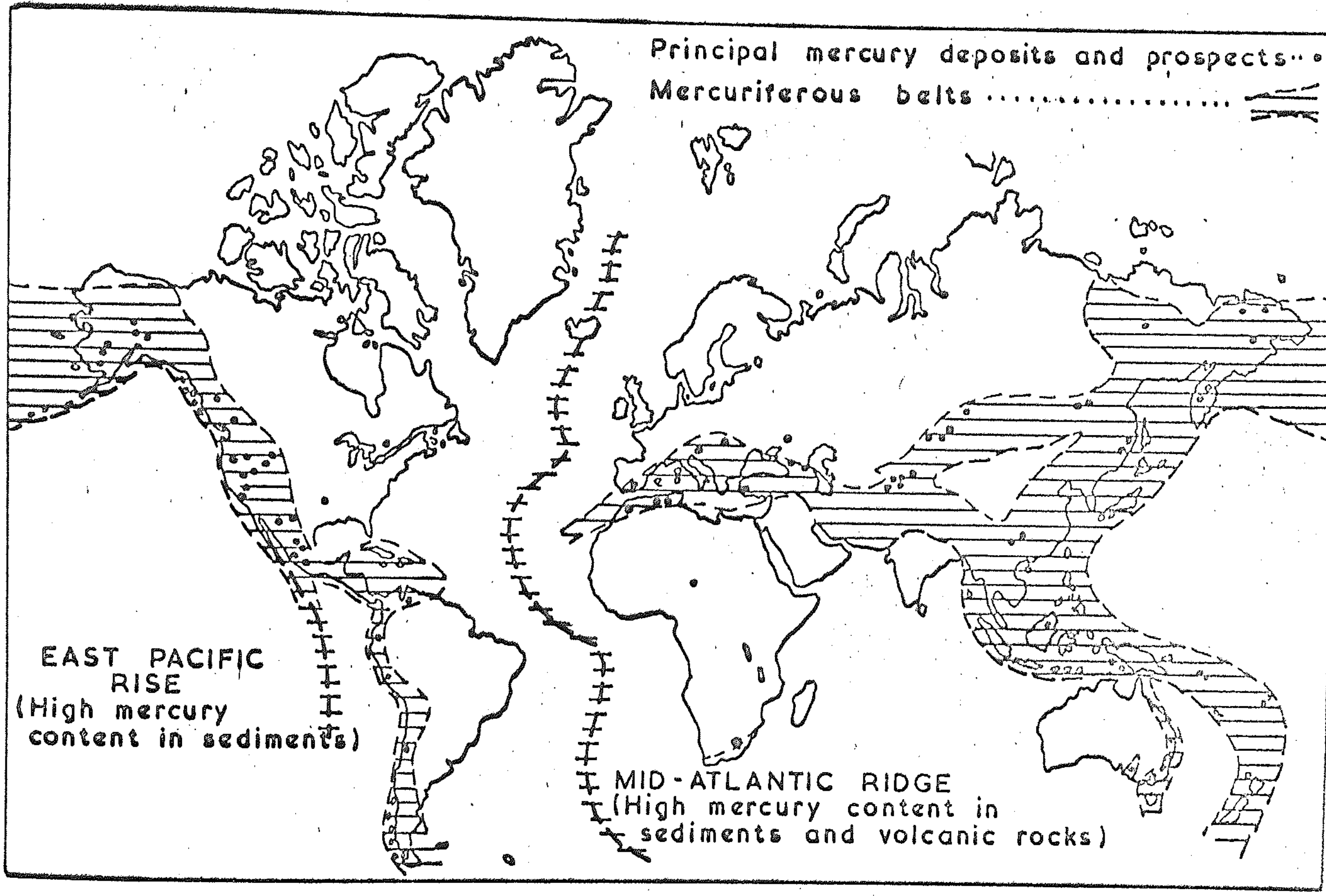


Fig.24. GENERALIZED MAP SHOWING THE MERCURIFEROUS BELTS OF THE EARTH (After Jonason and Boyle, 1972)

which he describes a correlation of mercury and copper in an ore. From this he concludes that the mercury and copper were transported by the same fluid and deposited at about the same time. If the mercury is transported in the vapour phase no such correlations will exist.

The mercury content of an ore body and that in the surrounding country rock may also be affected by the structure of the area. Because mercury is commonly associated with late stage, low temperature, processes, the degree of fracturing of both the ore body and country rock will affect the final concentration of mercury. If the ore body is relatively massive very little mercury may penetrate it, and the majority would go into the country rock (assuming that this is permeable) and produce a primary dispersion halo. The reverse situation, where most of the mercury is concentrated in a highly fractured ore body, may also occur.

Weathering of mercury minerals, and the subsequent redistribution of the element as a secondary dispersion halo, is important where mercury is to be used as an indicator of mineralisation. Cinnabar and native mercury are virtually inert in the normal environment, however, some mine waters contain more mercury than the theoretical quantity soluble under the prevailing conditions (Ginzburg, 1960).

A number of suggestions have been made to explain the solubility of mercury. Garrels (1953) suggested, from thermodynamic calculations that a pH less than 1, and a highly oxidising environment is necessary for the reaction

$$HgS + 2O_2 + (h\nu) \quad HgSO_4$$

$$3HgSO_4 + 2\,H_2O \rightleftharpoons HgSO_4 \cdot 2HgO + 2H_2SO_4$$

These conditions may be found where pyrite, or H_2S, are oxidising rapidly. This has been shown to be possible by the experimental work of Saukov and Aidon'yan (1940). Once in solution the migration and precipitation of the element is controlled by the stability of the solution in relation to its environment. Reducing conditions, with the presence of metal sulphides, and H_2S, will cause rapid precipitation of the mercury as the sulphate. Co-precipitation with other minerals can also occur as a result of sorption and occlusion. Sorption of mercury can occur on both positively and negatively charged particles. Ferric hydroxide (Krauskopf, 1956; Perellman and Saukov, 1957), and hydrated manganese oxides (Ginzburg, 1960; Perellman and Saukov, 1957) both have strong absorptive effects on mercury. Clay minerals may absorb mercury, either outside the lattice, or within the lattice (chemosorption) (James, 1962). The presence of organic material will also inhibit the movement of mercury in solution, removing it by sorption, and possibly by the formation of covalent bonds with the organic carbon (James, 1962).

Application of the geochemical properties of mercury to prospecting was initiated almost entirely by workers in the U.S.S.R.

It has since been used successfully in a number of different situations (Sears, 1971; Ozerova and Aidinlyan, 1966; Sutherland Brown, 1967). The technique relies on the association of mercury with hydrothermal base metal deposits. The mercury permeates the country rock at the time of deposition causing a primary 'halo'. Subsequent weathering of these rocks may partially redistribute the mercury, and create a secondary dispersion pattern or 'halo'. (Dvornikov, et al, 1963; Furzov, 1958; Ginzburg, 1960).
In the study area the distribution of mercury shows definite patterns and associations with other elements. This, taking into account the above information, yields valuable information regarding the mineralisation.

7:5 ELEMENTS DETERMINED IN THE PRESENT WORK.

The elements determined and their methods of analysis are listed in Fig.25. Some elements were determined by both atomic absorption (A.A.) spectrophotometry, and X-ray fluorescence spectroscopy (X.R.F.) but only the

Fig. 25. Elements determined in the present work.

Element	Method
Hg	CV
Zn	AA
Ba	AA
Cu	AA
Sr	AA
CO2	CT
S	XRF
Pb	AA
Si	AA
Al	AA
Fe	AA
Ni	AA
Mg	XRF
Ca	XRF
Na	XRF
K	XRF
P	XRF
Ti	XRF
Y	XRF
Th	XRF
Rb	XRF
Mn	XRF

KEY.

CV = Cold vapour Atomic Absorption

AA = Atomic absorption

CT = Carbon train

XRF = X-ray fluorescence

atomic absorption value was used to ensure consistency. The elements determined by A.A. spectrophotometry on all of the rocks were selected to give as much information as possible consistent with the ease of determination using the equipment available. Nickel, copper, lead, zinc and mercury were determined to show up the mineralisation, and also to determine the enrichment factors for the rocks. Silicon, aluminium, and iron were determined to reflect the major element composition of the rocks, and to examine the effects of wall rock alteration. Barium and strontium were used to detect carbonate associations, and total carbon was used in relation to barium and strontium to determine the effects of organic carbon and carbonate.

Additional elements were determined in the Gamlan Flags of the Southern Area by X.R.F. These were used to examine the detailed geochemistry of this variable rock type. The major elements, magnesium, calcium, sodium, potassium and phosphorous, were determined to give a picture of the variation in the bulk chemistry across the Southern Area.

The trace elements, manganese, titanium, yttrium, thorium, uranium and rubidium were used to study the effect of the variation in rock type on the analyses without any possible mineralisation effects.

CHAPTER 8.

RESULTS.

8:1 INTRODUCTION.

For ease of presentation this chapter is divided into two parts. Part 1 includes the tables of analytical results. Part 2 lists the figures, in numerical order referred to in Chapter 9.

The main atomic absorption and carbon analysis results are shown in Fig. 26. The XRF analyses for the sedimentary rocks of the Southern Area are shown in Fig. 27. In each of these tables the analytical accuracy is inferred from the number of significant figures quoted, this being arrived at with reference to standard rocks (Appendices 1 and 3). In general the atomic absorption results, for elements determined using flame techniques, are accurate to within 4% on the final concentration. The carbon analyses are within 8% (using artificial standards). The accuracy of the mercury determination is difficult to assess since standard rocks of the correct composition are difficult to find. In this case the precision figures are used (Appendix 2) to give a figure of 2%. In the case of the XRF results the accuracy of the determination tended to vary with the silica concentration, falling off as the silica concentration increased, to an overall 12% at high (86-90% SiO_2) concentrations. However, in the present work, absolute accuracy was not essential so long as the results were precise. A precision of better than 2% was obtained in this case.

The statistical analysis tables and trend maps (part 2), are taken directly from the computer printouts. The originals are stored in the Library, The University of Aston in Birmingham.

8:2 ANALYTICAL RESULTS.

The oxide concentrations are quoted in percent, and the metal concentrations quoted in parts per million (ppm). BD indicates that the concentration was below detectable limits for the technique employed. A dash (-) indicates that the element was not determined.

8:3 DATA ANALYSIS.

The tables referred to in Chapter 9 are listed below in numerical order. In the case of the statistical analysis the tables quoted are extracts from the original computer printout, re-arranged in some cases so as to present the data in a clear form. The trend maps are traced directly from the contoured computer printouts, but are reduced in size so as to fit on a single page.

PART 1 ANALYTICAL RESULTS

The Grid Ref. refers to the artificial grid, with its origin in the North West corner, constructed for sampling purposes, and shown in Fig.5.

Fig.26 Atomic Absorption and Carbon Analyses.

Rock Code	Grid Ref.	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba	CO2
1006	1,2	49.	17.3	8.9	58	57	54	BD	BD	.0050	BD	.5
1005	1,3	61.	14.0	10.2	49	BD	105	85	76	.2674	BD	.2
1004	1,4	66.	15.3	6.7	BD	51	94	40	74	.0043	832	.4
1003	1,5	62.	12.8	6.9	17	14	93	72	53	.0868	2001	.6
1002	1,6	87.	6.7	3.1	11	BD	58	BD	83	.0295	8	.2
1001	1,7	64.	14.0	5.5	22	36	75	42	67	.1121	2076	.6
1007	2,2	71.	9.0	7.2	74	53	165	67	64	.0306	5725	.2
1009	2,3	50.	4.4	6.6	16	309	94	54	154	.3380	BD	8.5
1008	3,2	-	-	-	-	-	-	-	-	.0112	-	6.2
1010	4,2	54.	10.3	7.8	62	201	100	44	307	.4735	51	-
1015	4,6	56.	18.7	6.5	7	BD	130	18	70	.0255	1441	-
1017	4,7	54.	14.4	8.5	46	22	79	21	288	.0418	66	4.2
1018	4,8	55.	11.5	8.6	2	BD	76	85	338	.2050	87	3.0
1019	4,9	54.	22.3	7.6	36	17	41	BD	BD	.0075	371	-
1125	4,11	40.	26.3	16.6	13	BD	741	-	107	.0464	BD	-
1126	4,12	60.	15.8	5.3	27	11	52	BD	64	.0111	443	-
1011	5,2	55.	19.0	5.3	32	69	785	BD	244	.0070	329	-
1012	5,3	85.	5.9	3.0	BD	BD	53	29	74	.0821	388	-
1014	5,5	67.	20.4	8.6	14	25	171	114	56	.0290	3187	-
1016	5,7	56.	12.2	8.9	23	BD	91	63	439	.3309	64	-
1020	5,9	59.	17.3	5.8	4	5	67	31	83	.0106	744	-
1239	5,10	61.	22.1	6.1	6	14	59	23	69	.0057	1614	-
1127	5,11	59.	16.1	3.4	15	3	36	BD	61	.0106	756	-
1128	5,12	50.	13.6	9.5	64	74	111	-	249	.0025	57	-
0124	6,5	60.	18.3	7.6	BD	24	65	BD	39	.0235	303	-
1023	6,6	47.	11.8	8.4	11	195	87	15	243	.0165	662	-
1022	6,7	57.	19.4	6.0	14	22	84	39	93	.0110	763	-
1021	6,8	74.	9.3	5.3	19	BD	65	25	62	.1329	447	-
1139	6,11	59.	12.2	6.6	67	92	120	10	160	.0020	25	-
1141	6,12	57.	24.0	7.6	32	138	195	88	286	.0063	322	-
1158	6,13	53.	19.9	9.8	BD	66	186	121	354	.0044	689	-
1129	6,14	57.	11.2	12.9	60	11	156	40	BD	.0020	120	-
1130	6,15	72.	10.2	4.9	BD	BD	61	36	12	.0045	202	-
1157	6,15(2)	102	.4	1.7	3	BD	163	125	BD	.0011	403	-
1140	6,16	62.	6.9	6.5	14	BD	193	107	49	.0054	4327	-
1131	6,17	55.	18.4	4.8	13	9	50	BD	78	.0093	545	-
1034	7,3	63.	12.7	7.3	49	33	82	132	97	.1405	BD	-
1035	7,4	66.	19.6	8.0	38	62	158	74	44	.0334	57	1.0
1036	7,5	62.	14.1	7.4	8	101	94	53	136	.2362	1210	-
1037	7,6	65.	10.6	6.1	29	18	75	51	102	.1377	522	-

Fig.26(continued)

Rock Code	Grid Ref.	Si02	Al203	Fe203	Cu	Ni	Zn	Pb	Sr	Hg	Ba	C02
1123	7,7	57.	17.2	8.4	2	77	94	10	51	.0060	886	.6
1038	7,8	63.	15.1	10.7	8	54	143	27	90	.0110	1140	.4
1039	7,9	63.	15.3	7.9	45	81	102	-	88	.0127	BD	.9
1154	7,11	57.	3.7	9.4	70	132	137	74	276	.0084	99	-
1132	7,13	47.	18.6	10.5	88	66	145	BD	151	.0012	96	-
1133	7,14	42.	11.9	7.9	103	275	65	58	88	.0000	115	-
1134	7,15	54.	14.1	8.9	76	322	87	-	253	.0083	BD	-
1135	7,16	59.	15.9	6.1	21	10	40	BD	43	.0085	600	-
1136	7,17	53.	19.4	6.5	27	23	53	BD	74	.0065	665	-
1121	8,1(2)	63.	10.9	10.8	7	25	74	13	100	.3473	1829	.9
1033	8,2	57.	18.8	5.7	9	56	265	47	112	.1833	2112	2.1
1137	8,12	45.	16.2	14.0	10	15	41	-	352	.0186	BD	3.8
1146	9,7	79.	14.0	6.8	37	36	102	70	113	.0113	1421	-
1031	10,1	83.	10.3	4.2	BD	3	57	8	53	.0079	260	.9
1032	10,2	58.	15.6	8.2	6	61	75	57	83	.0963	1548	.51
1144	10,6	76.	13.6	7.5	16	4	89	BD	22	.0193	1364	-
1143	10,7	72.	15.3	8.1	5	43	100	BD	102	.0164	1305	-
1142	10,8	63.	18.1	6.6	BD	62	96	76	189	.0127	2429	-
1048	11,2	61.	18.7	8.6	16	14	-	BD	27	.0076	456	1.29
1046	11,4	83.	6.2	5.2	BD	BD	30	-	BD	.0117	105	.45
1045	11,5	85.	6.6	3.4	8	BD	41	-	26	.0041	590	1.79
1044	11,6	79.	7.1	3.3	25	21	73	BD	BD	.0088	59	.36
1043	11,7	54.	19.2	6.7	20	38	54	BD	BD	.0302	522	-
1042	11,8	43.	23.2	14.7	61	14	27	-	247	.0032	BD	-
1041	11,9	58.	15.6	8.6	51	-	101	12	99	.0131	1983	-
1040	11,10	58.	14.0	9.7	34	81	110	12	92	.0110	1690	-
1138	11,13	38.	23.4	8.6	37	14	120	43	33	.0050	683	-
1049	12,2	60.	15.5	10.1	14	60	126	BD	19	.0018	498	.93
1050	12,3	57.	22.9	14.3	0.6	15	215	-	46	.0116	308	-
1051	12,4	54.	19.2	7.2	39	36	39	BD	BD	.0139	504	.3
1052	12,5	54.	21.7	7.9	39	BD	49	BD	91	.0276	382	-
1053	12,6	65.	13.2	3.7	12	BD	21	BD	BD	.0088	94	-
1054	12,7	62.	35.3	5.6	27	BD	240	782	45	.0099	5469	1.18
1055	12.8	49.	12.1	8.0	207	71	90	74	721	.0677	115	-
1056	12,9	42.	14.4	7.2	102	83	83	BD	226	.0135	247	-
1057	12,10	68.	15.5	6.0	29	48	120	42	101	.0172	1567	-
1058	12,11	67.	13.6	2.9	BD	20	71	28	39	.0088	899	.26
1059	12,12	64.	14.6	10.1	BD	43	85	4	73	.0163	2083	-
1061	12,13	64.	17.8	8.5	47	93	168	47	69	.0148	6052	.5
1087	12,14	58.	18.1	8.1	27	44	58	BD	BD	.0288	178	-

Fig.26(continued)

Rock Code	Grid Ref.	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba	CO2
1088	12,15	74.	11.6	6.0	37	12	57	75	78	.0411	525	-
1104	12,16	41.	15.3	5.7	2	22	42	BD	BD	.0052	BD	.6
1062	13,13	71.	13.2	5.3	1	BD	51	BD	57	.0139	116	-
1086	13,14	66.	18.7	7.3	BD	126	143	11	65	.0044	1025	-
1102	13,16	45.	5.9	6.3	40	234	95	BD	20	.0136	BD	.3
1103	13,17	63.	15.5	7.0	3	55	156	104	23	.0202	4406	-
1063	14,13	63.	21.3	6.0	1	54	88	15	133	.0054	825	-
1085	14,14	61.	21.7	6.0	BD	51	211	100	54	.0084	5473	-
1089	14,15	43.	11.6	7.2	67	179	67	BD	190	.0099	7	.06
1100	14,16	45.	15.7	9.1	BD	150	65	BD	189	.0022	88	1.78
1099	14,17	56.	19.0	6.0	BD	28	69	4	31	.0109	763	.71
1064	15,13	71.	16.8	8.0	59	35	44	BD	BD	.0076	295	-
1084	15,14	67.	20.2	8.4	21	53	166	72	61	.0121	4652	1.92
1090	15,15	46.	15.4	8.6	40	158	136	BD	85	.0111	276	2.47
1101	15,16	79.	12.5	3.8	BD	4	45	5	68	.0134	381	1.96
1098	15,17	41.	10.5	8.7	45	348	123	13	46	.0068	17	-
1096	15,19	53.	21.8	5.7	22	BD	50	BD	202	.0337	753	.86
1065	16,13	76.	15.9	5.9	18	82	129	47	49	.0414	731	-
1102	13,16	63.	14.5	9.1	27	BD	112	76	90	.0293	1349	-
1083	16,14	55.	21.7	16.3	16	74	131	-	26	.0000	496	.28
1091	16,15	55.	12.3	8.6	64	81	97	157	366	.0812	47	-
1234	16,15(1)	83.	27.0	3.2	BD	BD	212	49	50	.0055	1994	.5
1092	16,16	46.	15.1	12.0	BD	29	136	BD	52	.0034	134	-
1093	16,17	77.	9.9	3.9	BD	BD	58	57	48	.2439	427	-
1094	16,18	58.	17.3	6.1	4	BD	65	81	81	.5349	1529	.87
1095	16,19	67.	16.0	5.9	6	BD	65	90	102	.2692	829	-
1067	17,13	60.	18.9	0.6	8	7	10	BD	151	.0118	1330	.62
1082	17,14	53.	10.6	9.3	BD	187	87	-	66	.0052	BD	-
1080	17,15	54.	15.6	9.0	75	77	119	-	193	.001	525	2.06
1079	17,16	62.	16.2	6.7	BD	BD	75	42	82	.0145	1419	-
1077	17,18	67.	20.9	5.7	22	9	67	18	149	.0045	886	1.25
1068	18,13(1)	76.	7.7	4.1	26	BD	51	BD	13	.0065	BD	.68
1069	18,13(2)	66.	16.4	5.4	2	43	57	74	105	.2553	BD	-
1071	18,14(2)	48.	16.1	4.4	19	BD	50	56	53	.0153	341	.6
1072	18,15	49.	18.8	11.7	37	12	47	-	192	.0075	BD	.44
1073	18,16	84.	9.0	5.3	BD	8	94	23	84	.4318	454	-
1074	18,17	74.	10.4	4.7	1	6	64	25	95	.1282	554	7.0
1076	18,19	56.	21.4	7.1	16	BD	41	BD	100	.0075	461	.9
1075	18,18	48.	22.9	7.36	12	18	30	BD	BD	.0400	455	-
1070	18,14(1)	64.	13.8	7.2	25	BD	118	62	103	.1885	1505	1.4

Fig.26(continued)

Rock Code	Grid Ref.	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba	CO2
1161	FN1	77.	12.4	7.2	10	49	183	70	129	.0054	799	.5
1162	FN2	68.	18.7	7.8	BD	66	76	4	206	.0211	1757	.5
1163	FN3	64.	18.6	7.7	BD	78	109	27	212	.0123	1693	–
1165	FN4	68.	13.1	12.6	36	65	97	35	112	.0228	1678	–
1166	FN5	63.	19.6	9.7	14	119	90	5	155	.0237	2629	.24
1167	FN6	69.	16.7	9.3	BD	32	295	99	188	.0011	1609	–
1168	FN7	64.	18.0	9.5	1	90	82	61	155	.0033	1544	.36
1170	FN8	68.	18.1	7.2	3	105	324	72	190	.0012	1773	–
1171	FN9	72.	16.3	9.9	15	69	118	27	162	.0194	2229	.43
1172	FN10	54.	16.3	6.8	BD	49	91	52	188	.0055	905	–
1173	FN11	60.	13.7	8.1	BD	47	100	18	129	.0081	1324	–
1174	FN12	68.	17.1	7.6	25	43	87	38	139	.0110	1399	–
1175	FN13	64.	20.5	7.6	56	51	BD	22	140	.0137	1603	–
1176	FN14	67.	13.3	6.0	61	10	140	82	107	.0342	1383	–
1177	FN15	98.	7.1	3.3	3	BD	51	1	56	.0119	95	–
1178	FN16	72.	17.9	2.6	26	9	35	BD	113	.0137	1176	2.97
1179	FN17	65.	18.0	8.3	11	25	69	112	110	.0218	1100	–
1180	FN18	56.	20.2	7.7	48	45	57	41	113	.0303	941	–
1181	FN19	68.	17.4	7.0	BD	26	84	BD	167	.0091	1455	.43
1182	FN20	62.	15.7	9.7	9	70	84	6	159	.0183	2759	–
1183	FN21	73.	16.0	6.8	53	BD	253	90	139	.0042	1004	.39
1184	FN22	58.	16.4	10.4	2	62	137	BD	59	.0184	1122	–
1185	FN23	62.	10.5	5.0	66	BD	40	61	148	.0458	687	–
1186	FN24	66.	18.0	8.7	30	9	73	BD	102	.0191	1557	–
1187	FN25	61.	17.1	5.0	1	BD	55	13	118	.0171	1419	–
1188	FN26	53.	17.3	7.9	54	25	80	39	147	.0092	1401	–
1189	FN27	69.	13.2	5.0	7	9	81	30	82	.0059	1317	–
1190	FN28	63.	20.1	6.6	17	22	272	85	78	.0014	1461	1.23
1191	FN29	101.	BD	1.57	BD	BD	BD	BD	130	.0040	BD	–
1192	FN30	61.	19.2	8.2	40	BD	283	105	71	.0138	1466	1.02
1193	FN31	63.	9.7	9.3	17	BD	84	30	86	.0197	634	–
1194	FN32	67.	21.7	4.9	8	9	39	38	61	.0064	1779	.67
1195	FN33	83.	13.0	3.7	5	3	33	BD	66	.0185	1201	–
1196	FN34	52.	14.0	8.8	87	40	64	64	755	.0273	200	1.91
1197	FN35	56.	16.9	10.4	23	85	98	54	566	.0334	BD	–
1198	FN36	65.	19.9	7.1	54	28	69	38	123	.0488	1175	1.14
1199.	FN37	68.	18.5	6.9	44	9	45	76	138	.0409	1645	–
1200	FN38	64.	16.6	9.1	27	1	58	BD	81	.0222	1424	–
1201	FN39	57.	28.7	3.6	24	9	23	49	61	.0148	2134	–
1203	FN41	60.	20.2	6.6	BD	13	53	15	155	.0130	1100	.08

ig.26(continued)

Rock Code	Grid Ref.	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba	CO2
1204	FN42	69.	18.9	5.5	5	7	45	BD	146	.0088	876	-
1205	FN43	69.	18.3	5.5	12	27	83	26	186	.0021	1393	-
1206	FN44	57.	13.6	7.5	56	54	77	9	327	.0160	107	-
1207	FN45	58.	27.5	4.3	BD	22	212	63	102	.0024	2032	-
1208	FN46	84.	10.7	3.9	BD	8	24	13	158	.0037	92	-
1209	FN47	63.	21.2	5.3	18	22	32	70	175	.0161	1598	-
1210	FN48	67.	17.4	8.2	29	11	73	24	87	.0308	1005	-
1211	FN49	66.	19.0	9.2	BD	67	74	3	147	.0244	1382	-
1212	FN50	63.	15.7	7.3	15	51	108	BD	153	.0097	1878	-
1213	FN51	68.	17.5	5.9	31	8	46	58	148	.0021	1072	-
1214	FN52A	67.	7.6	3.6	BD	BD	24	25	81	.0030	166	-
1215	FN52B	47.	13.9	4.5	5	30	83	39	122	.0037	562	-
1216	FN52C	52.	14.1	11.3	.2	42	94	2	53	.0063	1150	-
1217	FN53	50.	14.1	13.3	BD	182	68	10	243	.0190	980	-
1218	FN54	63.	19.3	8.2	35	15	62	9	149	.0090	1146	-
1219	FN55	48.	31.7	6.0	BD	72	38	4	242	.0319	1933	-
1220	FN56	74.	15.0	6.3	1	31	59	BD	130	.0166	1090	-
1221	FN57	26.	7.1	10.8	2	19	126	32	71	.0349	16	-
1222	FN58	65.	21.8	5.7	20	23	57	47	54	.0290	2099	-
1224	FN60	74.	12.0	7.2	56	35	118	33	58	.0256	352	-
1225	FN61	72.	19.7	5.7	3	20	44	46	113	.0061	798	-
1227	FN63	39.	11.9	13.1	5	36	120	24	212	.0059	1013	-
1228	FN64	45.	12.6	16.8	3	37	88	4	61	.0182	BD	-
1229	FN65	77.	8.1	5.6	20	12	29	41	118	.0083	444	-
1230	FN66	51.	18.1	6.8	BD	BD	23	15	180	.0053	847	-
1231	FN67	83.	11.8	6.5	BD	17	33	BD	93	.0081	611	-
1232	FN68	50.	17.2	7.9	5	86	134	37	79	.0072	1376	-
1233	FN69	60.	21.2	6.8	32	45	116	65	175	.0229	1330	-
1060	S001	c.100	2.5	1.0	5284	BD	132	42	BD	.0202	6	-
1066	S002	60.	19.4	8.9	BD	25	160	114	235	.0114	102	-
1081	S003	92.	21.1	4.8	889	54	162	141	32	.0196	4542	-
1120	S004	82.	7.6	4.2	8	4	58	79	42	.0686	317	-
1155	S005	93.	1.0	6.4	11962	28	1755	585	BD	.1801	47	-
1145	S008	83.	12.8	4.6	BD	5	41	BD	73	.0304	1465	-
1255	S014	61.	20.4	6.9	7	54	99	BD	233	.0057	1371	-
1149	FFS1	-	-	-	-	-	-	-	-	.0385	-	-
1148	FFS1(a)	61.	21.6	6.0	21	42	60	147	240	.0161	1392	-
1150	FFS3	60.	22.6	7.3	54	BD	80	78	190	.0220	1512	-
1152	FFS5	62.	22.7	8.4	31	BD	111	BD	171	.0360	1313	-
1153	FFS6	65.	22.0	7.5	42	74	109	23	172	.0092	1193	-

.26(continued)

ck Code	Grid Ref.	SiO_2	Al_2O_3	Fe_2O_3	Cu	Ni	Zn	Pb	Sr	Hg	Ba	CO_2
1249	SG7	82.	11.3	3.2	36	1	393	274	105	.0325	1022	-
1115	F/71/A	56.	11.9	9.6	50	23	86	27	186	.0084	72	-
1119	F/71/B	50.	12.1	11.3	39	34	85	34	87	.0061	53	-
1117	F/71/C	58.	20.1	8.5	35	36	71	15	228	.0082	1350	-
1106	FS9	52.	17.2	5.6	5	44	116	33	53	.0227	784	-
1111	FS12	35.	26.1	8.1	32	45	107	21	74	.0077	1308	-
1243	SG1	-	-	-	-	-	-	-	-	.3433	-	-
1244	SG2	-	-	-	-	-	-	-	-	.0414	-	-
1245	SG3	-	-	-	-	-	-	-	-	.0873	-	-
1246	SG4	-	-	-	-	-	-	-	-	.0857	-	-
1247	SG5(a)	-	-	-	-	-	-	-	-	1.3207	-	-
1247	SG5(b)	-	-	-	-	-	-	-	-	.1391	-	-
1256	SG5(b)(H)	-	-	-	-	-	-	-	-	.5205	-	-
1248	SG6	-	-	-	-	-	-	-	-	.7146	-	-
1250	SG8(a)	-	-	-	-	-	-	-	-	.0599	-	-
1250	SG8(b)	-	-	-	-	-	-	-	-	.024	-	-
1257	SFG	-	-	-	-	-	-	-	-	.3209	-	-

Fig.27 XRF Analyses of Rocks from the Southern Area.

Rock Code	MnO2	TiO2	CaO	K2O	Na2O	P2O5	Cr	Ce	La	S	Y	Rb	Th
1005	1.33	.99	.99	2.5	12.9	.11	90	116	53	15	22	118	13
1004	-	1.15	.76	3.8	-	.09	-	-	-	71	23	186	8
1003	1.96	.96	1.77	3.3	1.4	.56	78	99	46	26	29	141	15
1002	-	.36	1.16	.2	3.8	.04	-	-	-	18	15	11	11
1001	.31	.99	1.18	4.5	.8	.14	73	62	31	32	43	195	16
1007	-	1.04	.79	3.5	1.2	.07	-	-	-	22	26	169	14
1009	.2	-	-	-	1.4	-	1200	-	1	-	9	-	-
1008	-	.42	9.06	BD	-	.05	-	-	-	41	13	-	5
1010	.32	.42	4.25	BD	2.7	.04	8	-	3	31	11	-	.1
1015	-	.86	.62	5.2	.8	.03	-	-	-	328	11	252	15
1017	-	.85	6.76	.2	3.7	.14	-	-	-	74	14	2	5
1018	.26	.8	7.35	.3	3.0	.12	453	-	4	21	13	6	.3
1012	.38	.36	.98	1.0	1.7	.04	28	29	16	25	13	54	10
1014	-	.65	.71	3.2	.8	.10	-	-	-	353	23	165	14
1016	.2	.82	5.97	.1	2.7	.15	511	9	6	16	13	.4	2
1020	-	1.07	.65	4.0	.8	.07	-	-	-	242	25	193	15
1023	.19	.48	7.5	BD	1.3	.05	722	-	.5	31	11	.7	-
1022	-	1.11	.67	4.6	.7	.05	-	-	-	362	13	221	15
1021	.06	.52	.67	2.3	1.9	.05	51	17	6	217	11	122	12
1034	1.62	.83	1.23	3.0	1.5	.17	81	113	43	38	25	142	18
1035	-	1.06	.81	3.9	1.0	.09	-	-	-	49	22	183	14
1036	2.07	1.17	.82	3.4	1.6	.08	98	35	3	16	19	178	13
1037	1.16	1.0	4.14	2.5	1	.12	97	83	33	42	31	127	16
1123	-	1.11	.94	2.7	1.4	.13	-	-	-	104	22	98	9
1038	-	.84	.76	2.1	1.1	.09	-	-	-	31	26	96	11
1039	-	.88	.73	3.3	.8	.07	-	-	-	61	17	146	14
1121	.63	.97	1.12	4.1	1.4	.14	73	97	43	44	21	174	12
1033	.38	1.32	1.05	5.4	1.5	.23	110	104	43	134	53	235	20
1031	-	.61	.90	1.6	2.1	.06	-	-	-	70	18	71	7
1032	.71	1.07	.95	4.9	.6	.09	88	69	27	19	-	-	-
1046	-	.24	.73	.6	-	.04	-	-	-	162	8	27	6
1041	-	1.14	.82	4.1	-	.09	-	-	-	25	20	190	15
1040	-	1.02	1.10	3.4	1.0	.08	-	-	-	29	30	143	9
1052	-	.98	.80	3.7	-	.91	-	-	-	37	16	175	12
1057	-	.97	.90	3.2	1.7	.14	-	-	-	53	34	150	19
1058	-	.61	.74	3.9	1.3	.06	-	-	-	18	28	193	20
1059	-	-	-	-	-	-	-	-	-	-	19	150	10
1061	-	1.12	.90	3.0	-	.07	-	-	-	86	17	139	14
1086	-	1.17	.76	4.5	-	.08	-	-	-	63	20	210	11
1102	-	1.13	1.25	3.9	1.1	.09	-	-	-	50	18	165	15

27(continued)

Rock Code	MnO2	TiO2	CaO	K2O	Na2O	P2O5	Cr	Ce	La	S	Y	Rb	Th
1103	-	-	-	-	-	-	-	-	-	-	26	271	14
1063	-	.88	.86	5.1	-	.06	-	-	-	18	5	258	19
1085	-	-	-	-	-	-	-	-	-	-	30	223	17
1100	-	1.05	7.58	.5	-	.08	-	-	-	55	19	19	-
1084	-	1.00	.74	2.8	-	.06	-	-	-	86	21	125	14
1101	-	.59	.81	2.3	-	.11	-	-	-	1867	19	1115	10
1098	-	.64	7.82	BD	-	.06	-	-	-	36	12	BD	2
1096	-	1.25	.64	4.7	1.3	.03	-	-	-	672	17	275	14
1102	-	1.13	1.25	3.9	1.1	.09	-	-	-	50	18	165	15
1091	.24	.52	5.79	BD	3.0	.08	271	-	-	23	12	.6	4
1093	.09	.87	.76	1.9	2.8	.06	64	34	17	235	14	114	15
1094	-	1.21	.65	4.6	1.1	.07	-	-	-	763	16	260	19
1095	.05	1.19	.64	3.4	1.3	.05	121	2	9	442	18	212	10
1079	.05	1.21	.72	4.5	.9	.08	105	68	32	337	22	234	14
1069	-	1.08	.92	5.2	1.1	.09	-	-	-	21	18	252	13
1073	.05	.77	.72	1.6	2.3	.04	63	28	17	152	19	90	13
1074	-	.81	.85	1.9	2.3	.05	-	-	-	148	14	106	7
1070	.42	1.12	.70	4.0	1.4	.07	76	76	34	769	-	-	-

PART 2 DATA ANALYSIS

g. 28. Factor loadings [illegible] rocks of the Northern Area.

lement	Factor 1	2	3	4	5	6	7
SiO2	0.36	0.24	0.42	0.22	0.32	0.24	0.09
Al2O3	0.89	-0.12	-0.03	0.01	-0.01	0.02	0.06
Fe2O3	0.55	0.42	-0.23	-0.14	0.05	-0.19	-0.08
Cu	0.21	-0.06	-0.51	0.08	0.04	0.19	-0.28
Ni	0.49	0.51	0.22	0.16	-0.17	-0.02	-0.21
Zn	0.69	-0.07	-0.03	-0.18	0.23	-0.22	0.07
Pb	0.30	-0.00	-0.08	-0.53	0.04	0.34	-0.09
Sr	0.72	0.41	0.09	-0.29	-0.37	0.08	0.28
Hg	0.14	0.22	-0.58	0.34	-0.02	0.10	0.20
Ba	0.59	-0.46	0.15	0.15	-0.25	0.02	-0.04

Fig. 29. Field descriptions related to rocks with analyses above and below average Hg values.

Area	Below average	Comments	Above average
Clogau, N.	H.Bl.G.S; H.D.G.S; H.D.G.S; H.D.G.S.	Weathering seems to make no difference.	H.G.S; G.S; H.G.S; D.G.S;H.G.S;H.G.S; H.G.S;So.W.S; H.D.G.S;D.G.S;D.G.S; W.D.G.S;D.G.S.
Clogau, S.	L.G.W.S;H.B.S; So.L.G.S;So.G.S;G.S.	No difference	S.L.G.S;W.S;H.B.S; L.G.S.
Vigra, N.	H.Si.S.+F;D.G.S; W.D.G.S;S.G.S;G.S;H.G.S; H.Si.G.S.	Siliceous shales have less Hg	Be.S.+F;D.G.S;W.D.G.S; Be.S.+Si.F;D.G.S; Be.S.D.G.S;H.W.S; S.G.S;W.D.G.S; G.S;G.S;Be.S;S.+H.
Vigra, S.	Gr.S.+Qtz;G.S;G.S; L.G.S;D.G.S;	No difference	G.S;G.S;W.G.S;G.S.
Gamlan, N.	H.D.G.S;H.G.S; D.G.S;G.S;Gr.S.	Lower Hg in grits.	H.G.S;H.D.G.S;G.S.
Gamlan, S.	G.S;G.S;G.S;Gr.+Qtz; Gr;L.G.S;Gr;Gr;Be.S; Gr;Gr;D.G.S;G.S;Gr;G.r; M.G.S;Gr.	No difference	Gr;B.S;B.S;Gr.S;H.G.S; L.G.S;G.S;Gr;H.G.S; G.S;H.G.S;L.G.S; Gr;G.S;L.G.S;G.S;G.S; G.S;Gr;G.S;Gr.

KEY

Be. = Bedded.
Bl. = Blue.
B. = Black.
D.= Dark.
F. = Flag(s).
G. = Grey.
Gr. = Gritt(y)
H. = Hard.
L. = Light.
M. = Micaceous.
Qtz. = Quartz.
S. = Shale
Si. = Siliceous.
So.. = Soft
W. = Weathered.

g.30.Means and Standard Deviations.

	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba
VN	47.96	18.02	6.44	14	21	92	30	121	.0124	1264
	3.2	6.4	2.7	18	19	80	31	49	.0116	472
VS	52.32	15.87	652	13	15	85	39	81	.0123	1015
	2.5	4.8	2.1	15	19	53	44	80	.1669	1144
CN	55.13	17.18	7.63	25	34	91	36	132	.01832	1427
	2.4	2.0	1.7	20	27	58	36	39	.01039	476
CS	51.63	17.33	6.89	14	34	93	34	53	.02779	1412
	3.20	3.7	3.4	12	38	58	37	31	.05188	1783
GN	63.91	16.76	9.10	9	72	146	37	154	.01179	1727
	2.7	2.4	1.7	13	30	102	37	26	.01027	409
GS	49.29	14.67	7.13	22	43	104	42	101	.06663	877
	2.6	5.4	2.5	21	55	102	103	97	.1072	1165
IN	59.93	12.73	7.87	28	62	73	25	351	.01855	246
	2.8	3.4	3.8	36	67	34	27	263	.01066	365
IS	47.53	15.51	8.72	42	97	131	22	155	.01017	187
	2.4	5.3	2.6	35	84	135	43	101	.01829	313

VN = Vigra Flags of Northern Area
VS = Vigra Flags of Southern Area
CN = Clogau Shales of Northern Area
CS = Clogau Shales of Southern Area
GN = Gamlan Flags of Northern Area
GS = Gamlan Flags of Southern Area
IN = Igneous rocks of Northern Area
IS = Igneous rocks of Southern Area

Fig.31. Groupings in the Gamlan Flags of the Southern Area.

Group 1 - High Si02, low Al203, Low Fe203.

Grid Ref.	Si02	Al203	Fe203	Cu	Ni	Zn	Pb	Sr	Hg	Ba	
1,6	87.	6.7	3.1	11	BD	58	BD	83	.0295	8	*
5,3	85.	5.9	3.0	BD	BD	53	29	74	.0821	388	*
10,1	83.	10.3	4.2	BD	3	57	8	53	.0079	260	*
11,5	85.	6.6	3.4	8	BD	41	-	26	.0041	590	*
11,4	83.	6.2	5.2	BD	BD	30	-	BD	.0118	105	
11,6	79.	7.1	3.3	25	21	73	BD	BD	.0088	59	
18,13(1)	76.	7.7	4.1	26	BD	51	BD	13	.0065	BD	*

* - Grits

Group 2 - High Al203

Grid Ref.	Si02	Al203	Fe203	Cu	Ni	Zn	Pb	Sr	Hg	Ba
4,6	56.	18.7	6.5	7	BD	130	18	70	.0258	1441
5,2	55.	19.0	5.3	32	69	785	BD	244	.0070	329
6,5	60.	18.3	7.6	BD	24	65	BD	39	.0235	303
7,4	66.	19.6	8.0	38	62	158	74	44	.0334	57
5,5	67.	20.4	8.6	14	25	170	114	56	.0290	3187
8,2	57.	18.9	5.7	9	56	265	47	112	.1833	2112
10,8	63.	18.1	6.6	BD	62	96	76	189	.0127	2429
11,2	61.	18.7	8.6	16	14	96	BD	27	.0076	456
11,7	54.	19.2	7.0	25	50	54	BD	BD	.0320	522
11,3	38.	23.4	8.6	37	14	120	43	33	.0056	683

Fig. 32 SiO2 distribution

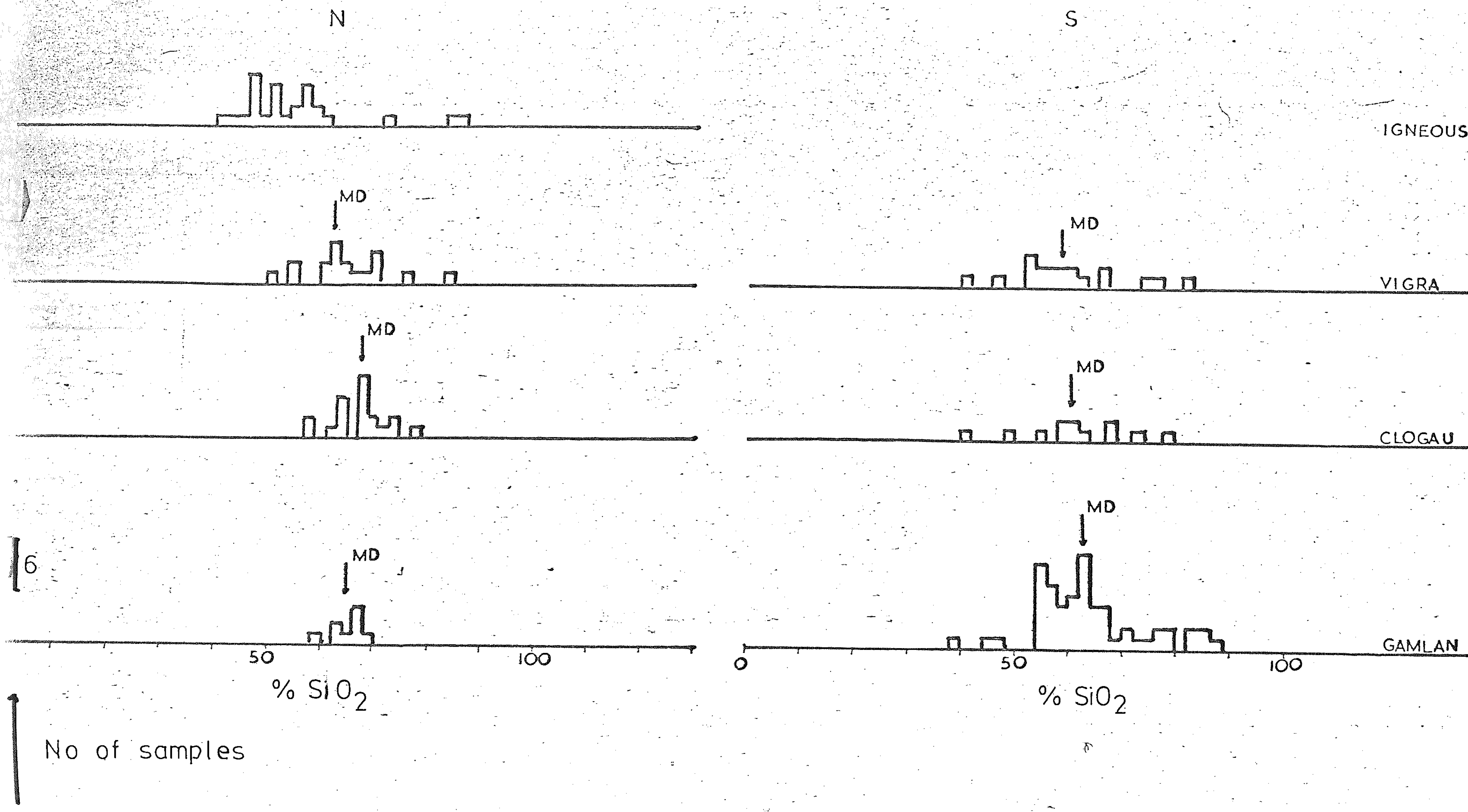


Fig. 33. Al203 distribution

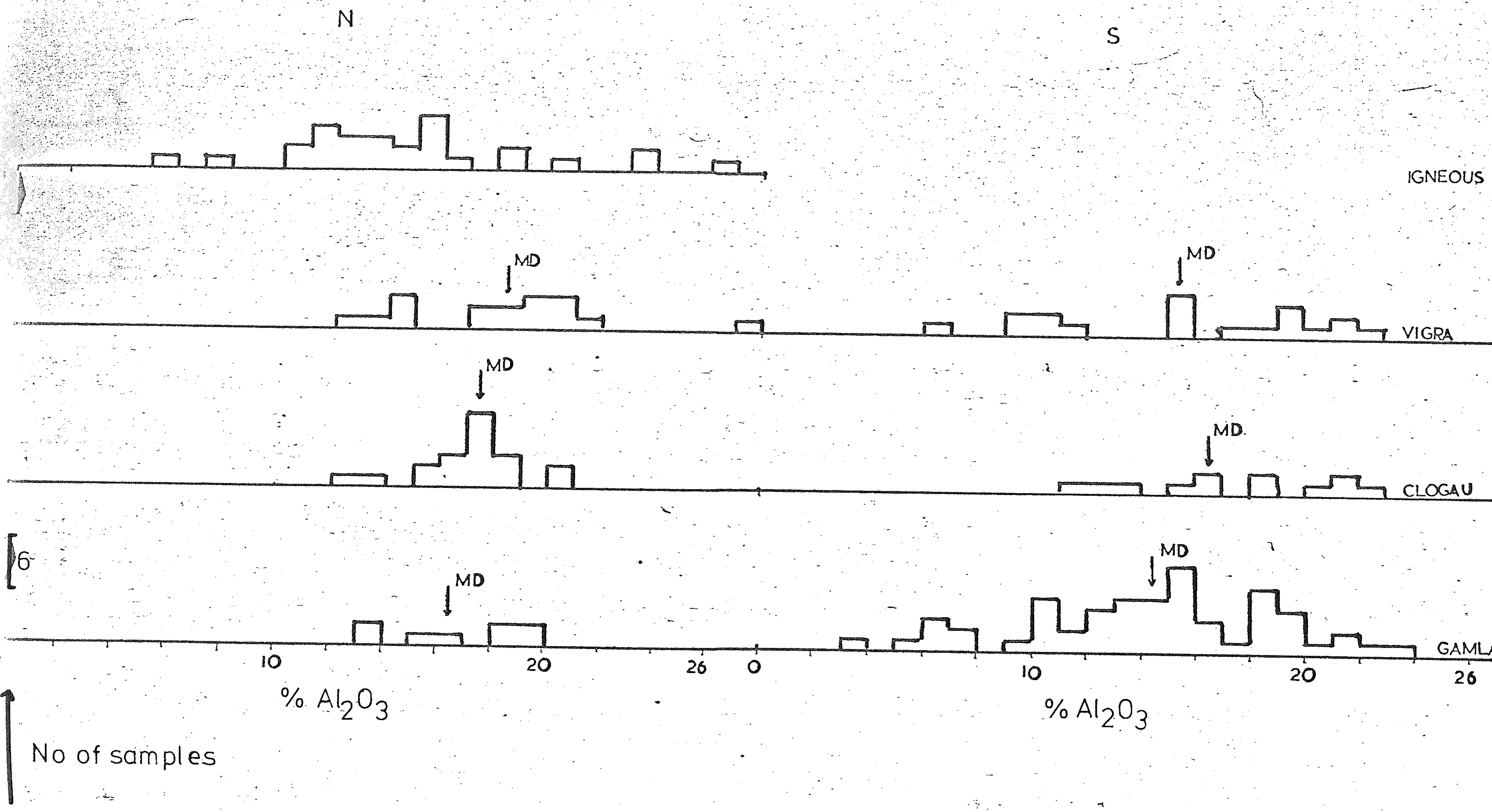


Fig 34. Fe203 distribution

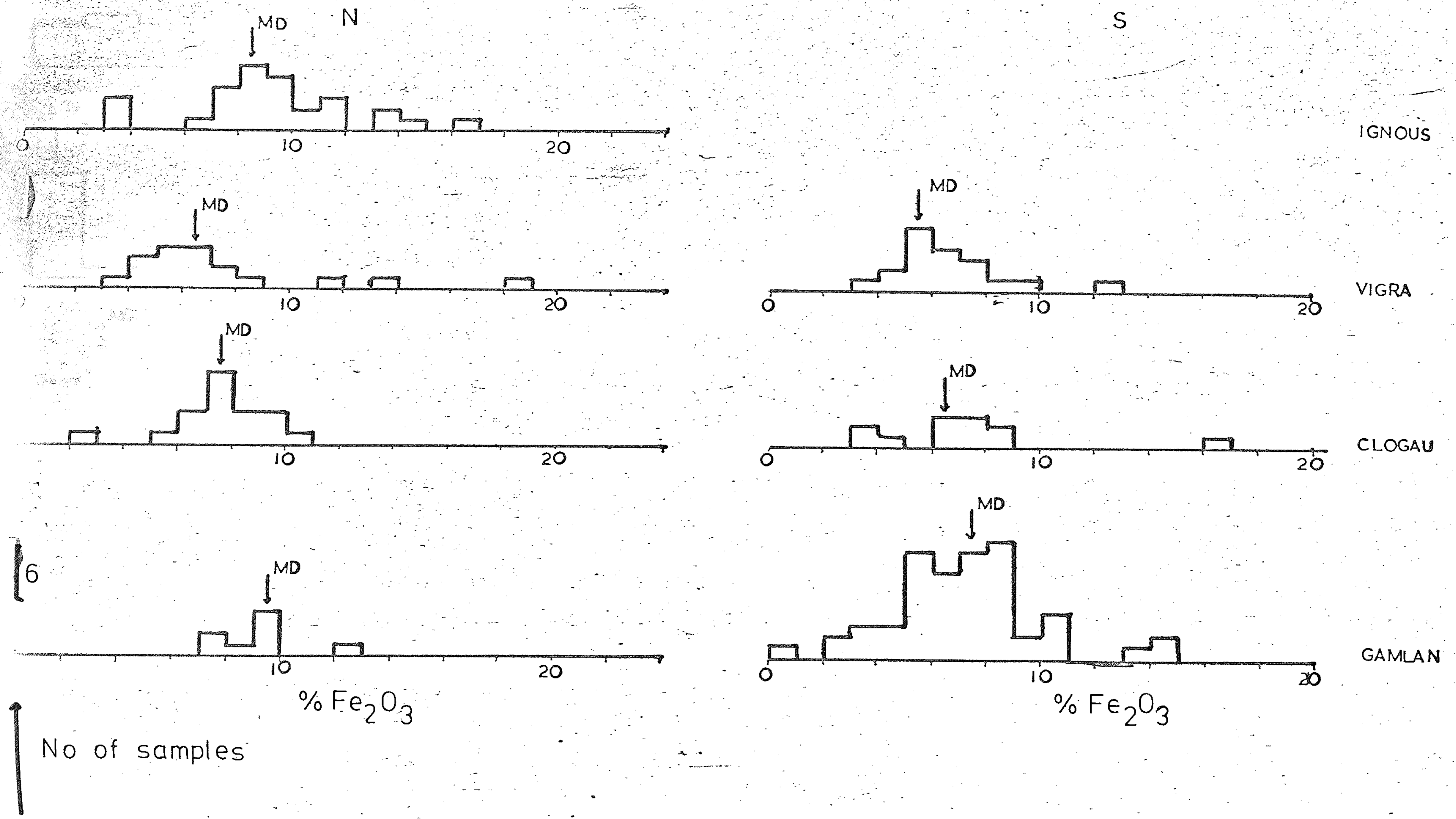


Fig. 35. Cu distribution

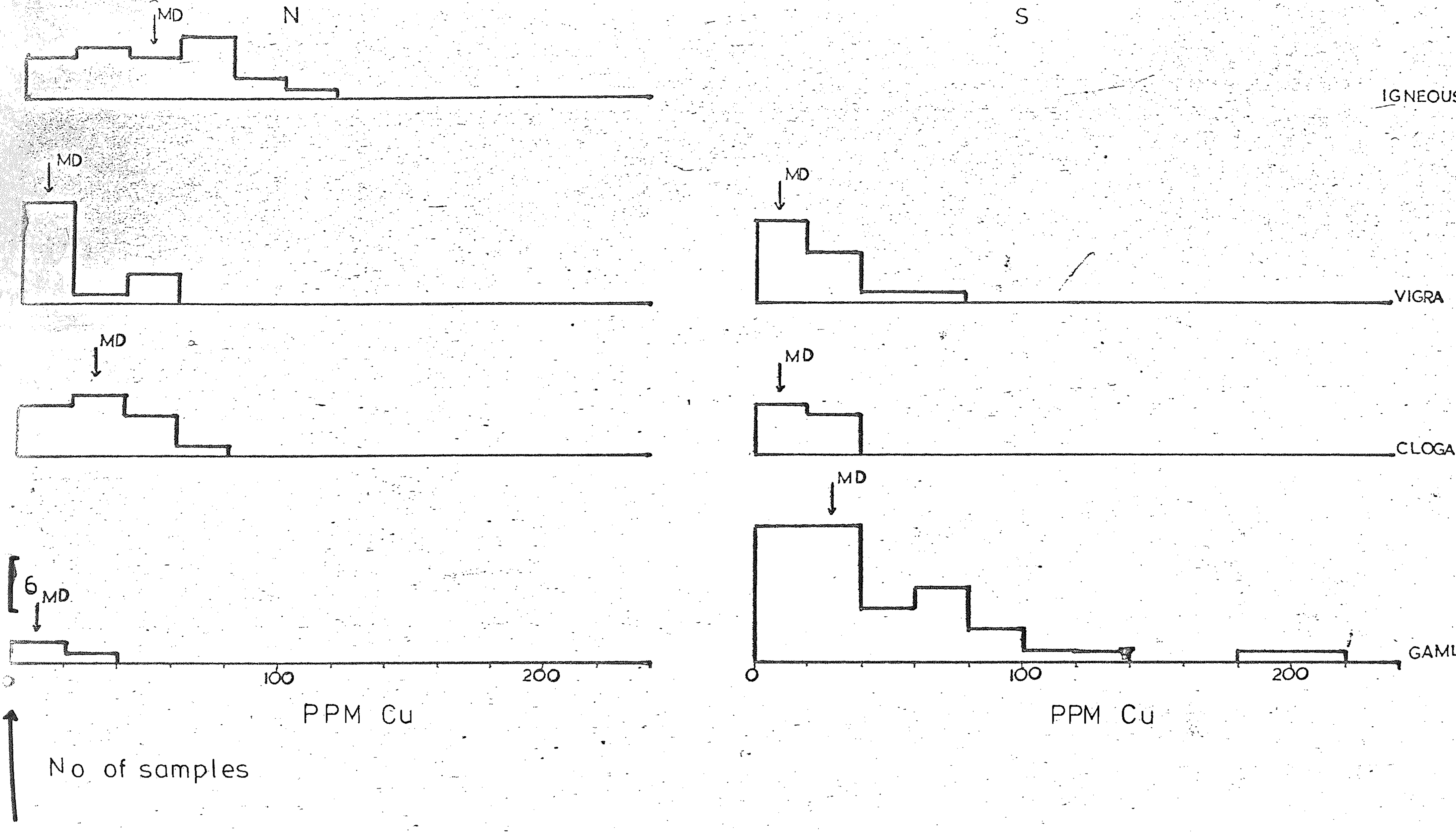


Fig. 36. Ni distribution

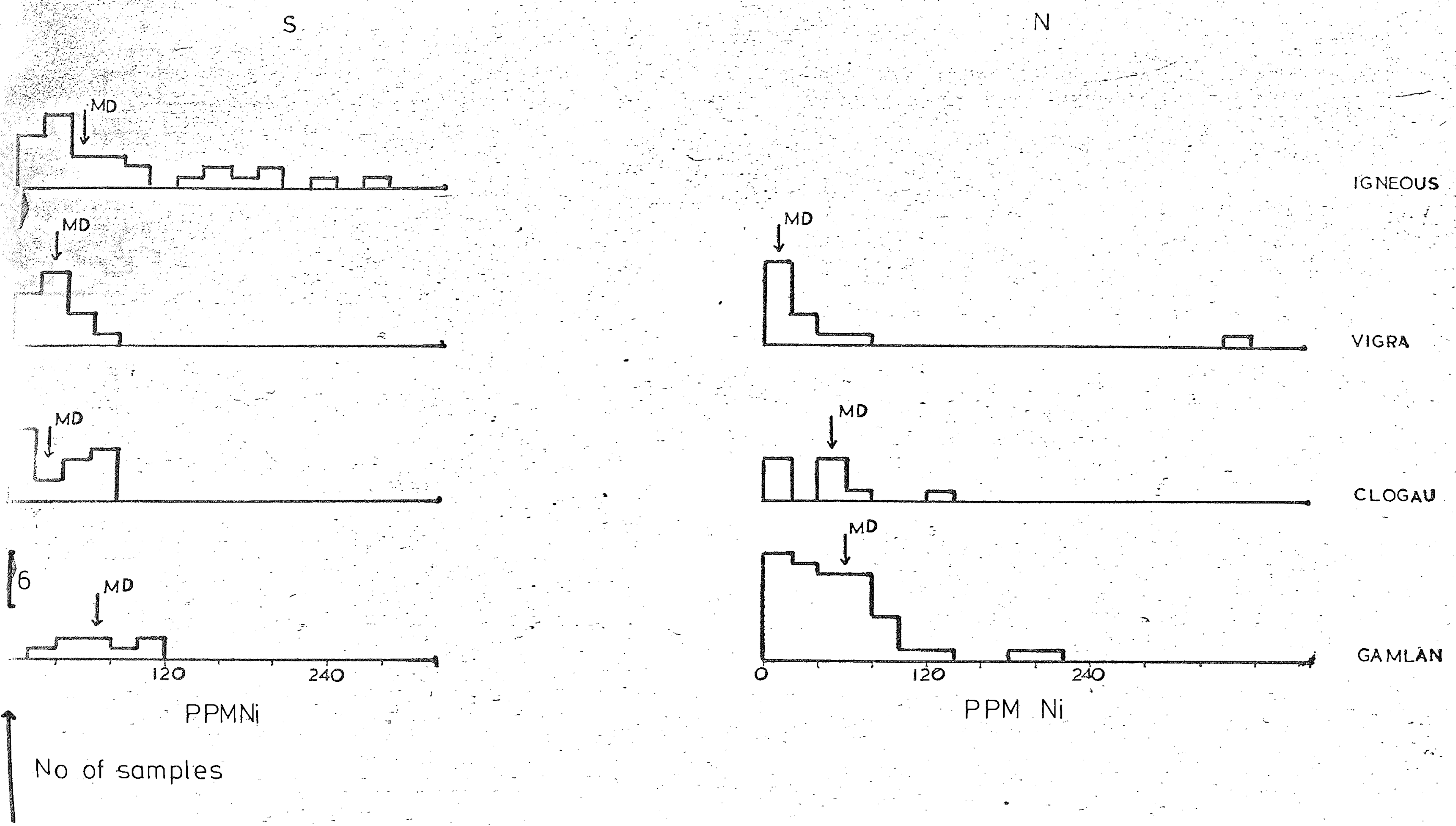


Fig. 37. Zn distribution

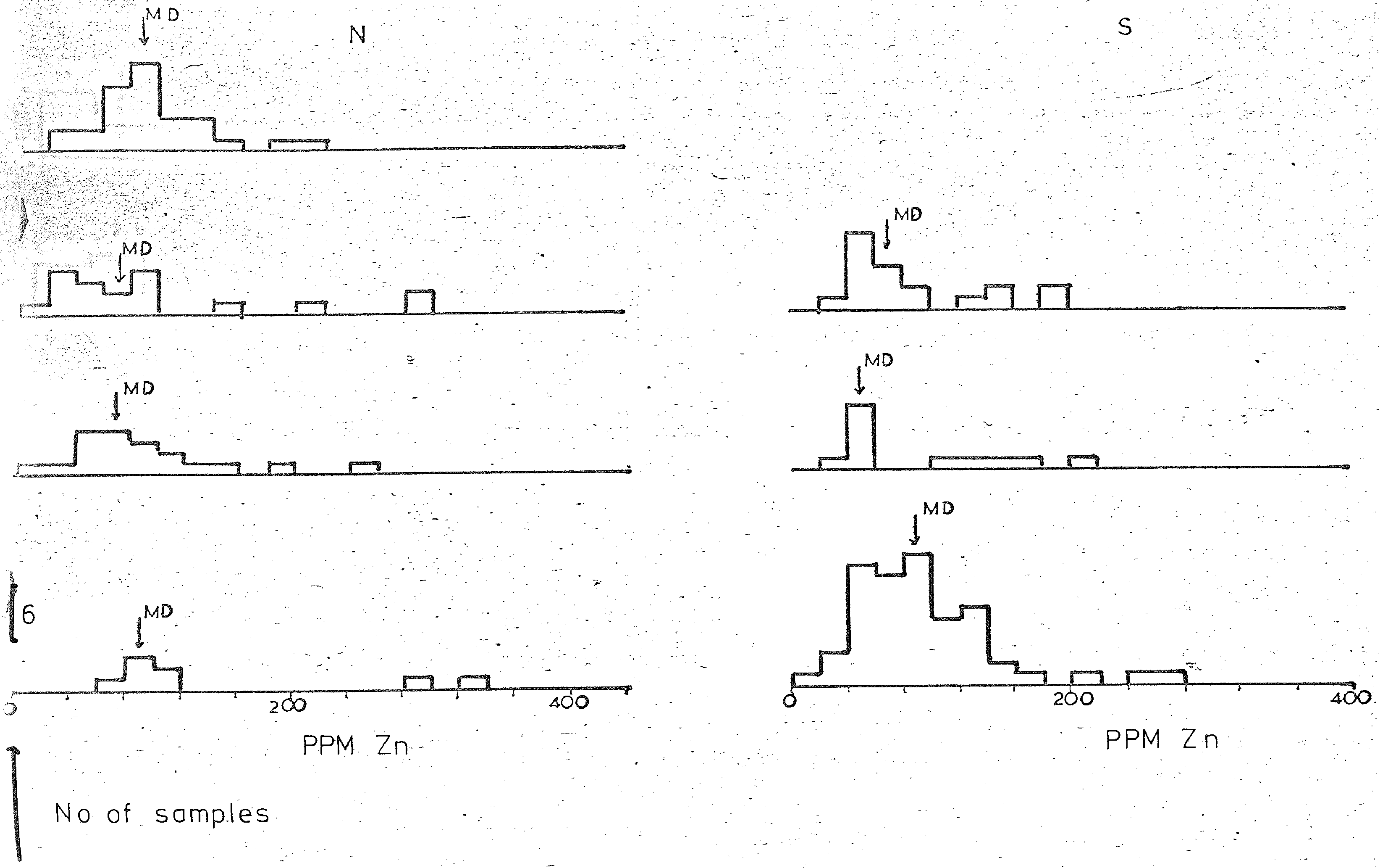


Fig. 38. Pb distribution

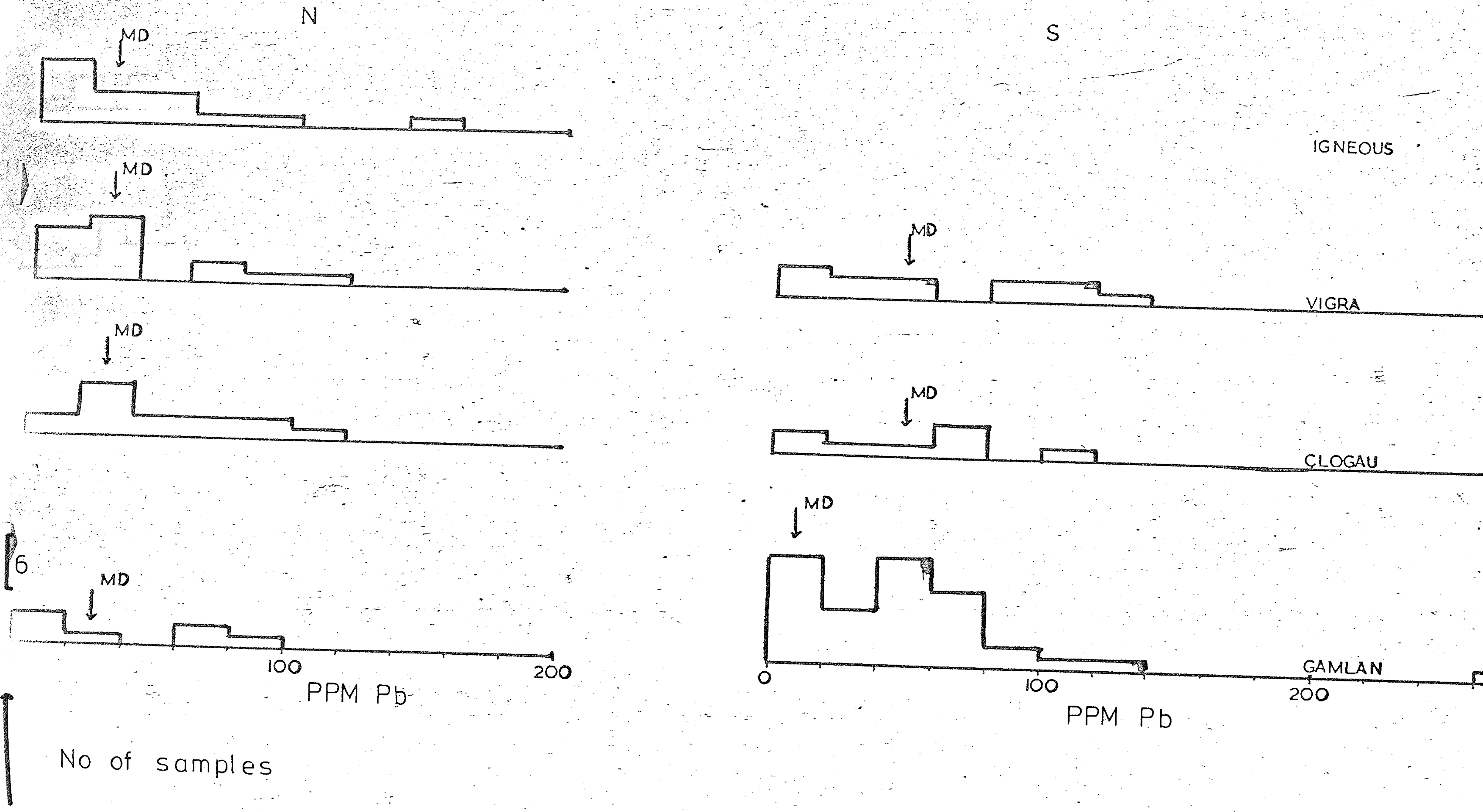


Fig. 39. Sr distribution

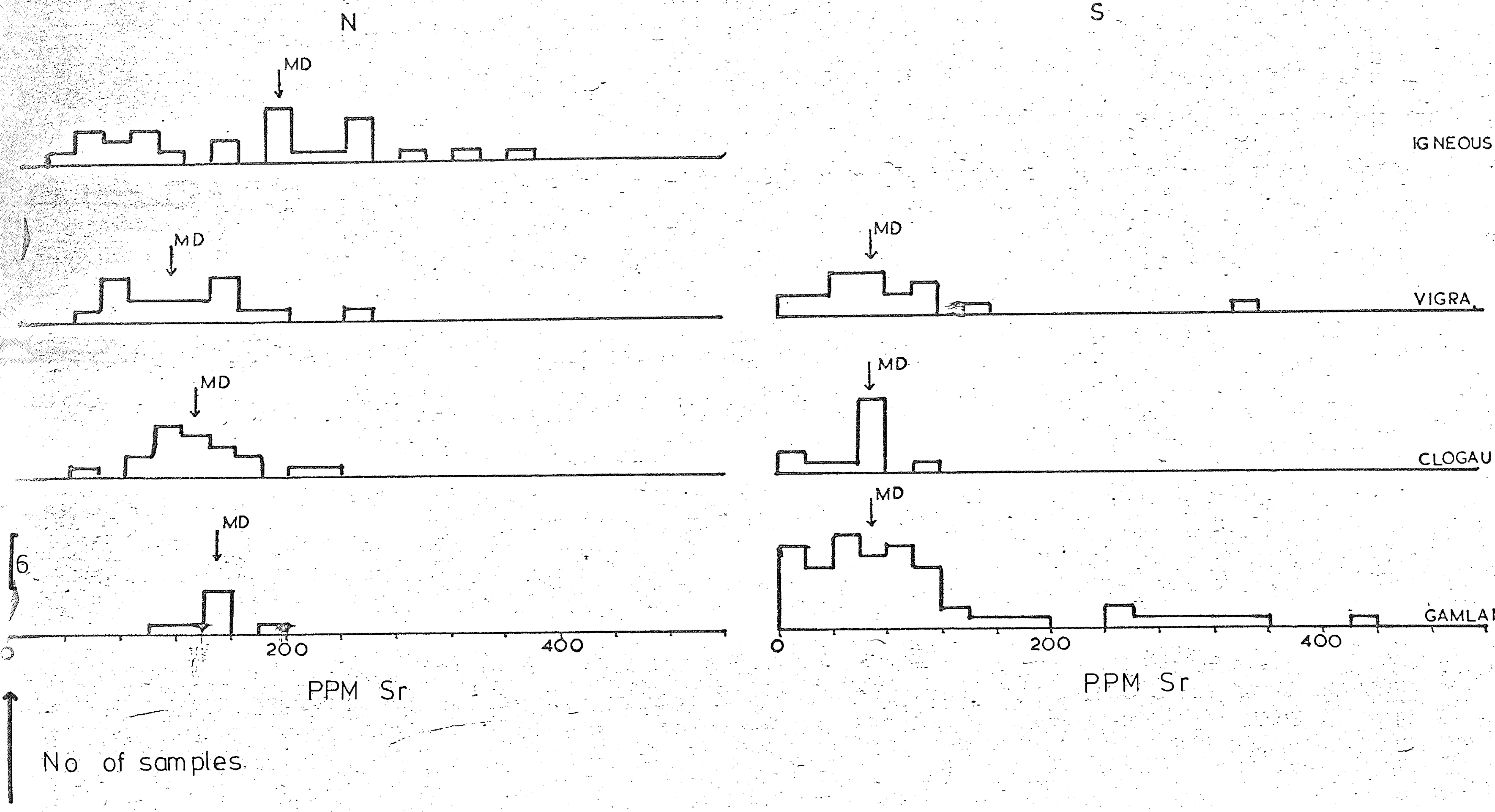


Fig. 40. Hg distribution

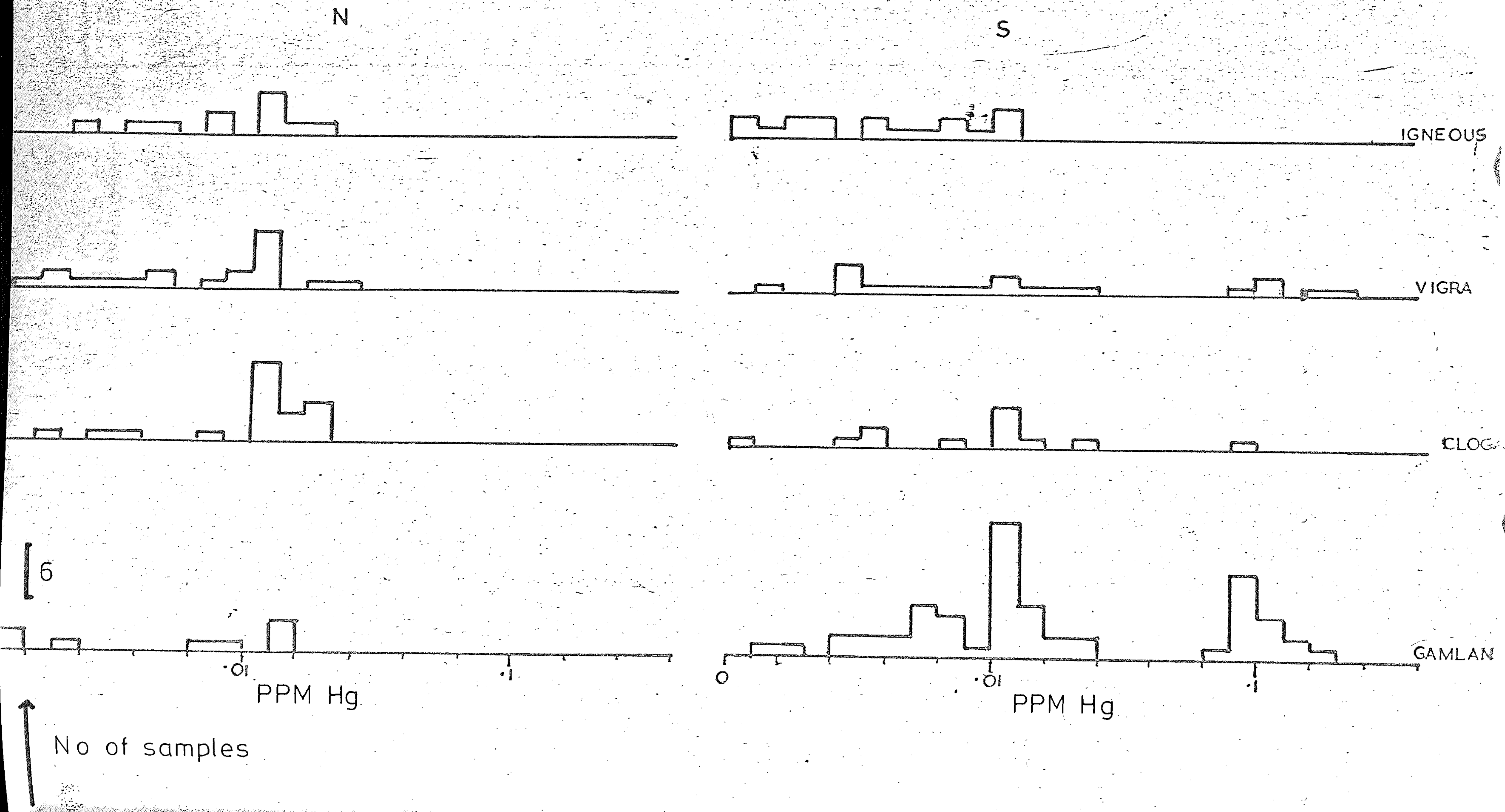


Fig. 41. Ba distribution

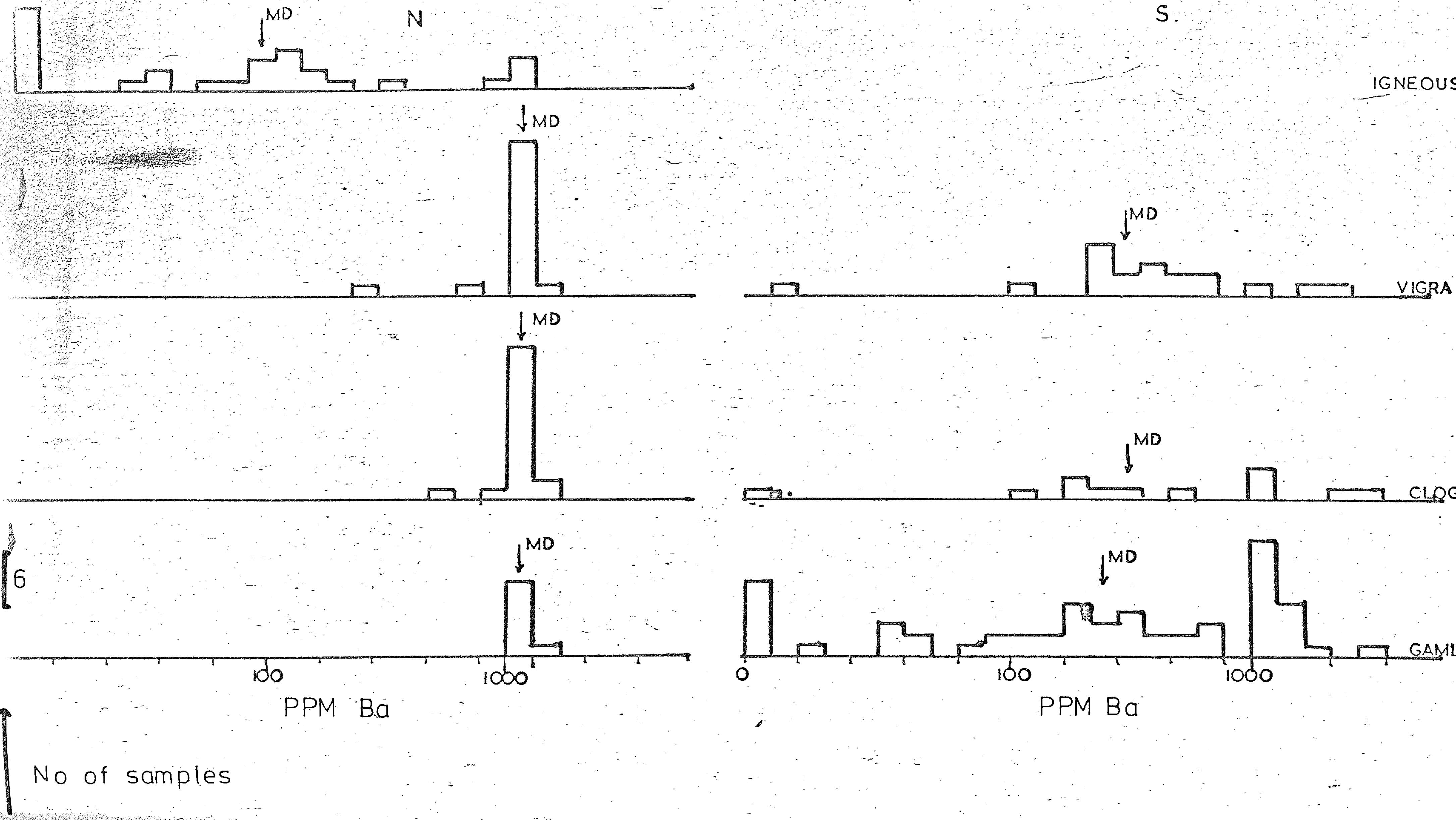


Fig.42. Comparison of frequency distributions between Northern and Southern Areas

Vigra Flags.

SiO_2	Distributions same. Higher values in Southern Area.
Al_2O_3	Wider distribution in Southern Area.
Fe_2O_3	Distributions same.. Higher values in Southern Area.
Cu	Distributions same
Ni	Distributions same. Higher values in Southern Area.
Zn	Distributions same. 2 higher values in Southern Area.
Pb	Distributions same.
Sr	Distributions same. Higher values in Northern Area.
Hg	Distributions same. Higher values in Southern Area.
Ba	Narrow distribution in Northern Area. Wider with higher values in Southern Area.

Clogau Shales.

SiO_2	Wider distribution in Southern Area.
Al_2O_3	" " " " "
Fe_2O_3	Distributions same. Higher values in Southern Area.
Cu	Distributions same.
Ni	Distributions same. Higher values in Southern Area.
Zn	Distributions same.
Pb	" "
Sr	Wider distribution and higher values in Northern Area.
Hg	Distributions same. Higher values in Southern Area.
Ba	Narrow distribution in Northern Area. Wider with higher values in Southern Area.

Gamlan Flags.

SiO_2	Wider distribution in Southern Area.
Al_2O_3	Distributions same. Higher values in Southern Area.
Fe_2O_3	Distributions same. Higher values in Southern Area.
Cu	" " " " " " "
Ni	Distributions same.
Zn	Distributions same. Higher values in Southern Area.
Pb	" " " " " " "
Sr	Single distribution in Southern Area. Two distributions in Northern Area.
Hg	Distributions same. Higher values in Southern Area.
Ba	Single narrow distribution in Northern Area. Wider distribution in Southern Area with higher values.

Fig.43. Median values and minimum enrichment values.

Area and	SiO2		Al2O3		Fe2O3		Cu		Ni		Zn		Pb		Sr		Hg		Ba	
Rock type	M	E	M	E	M	E	M	E	M	E	M	E	M	E	M	E	M	E	M	E
VM	61.	71.	18.5	22.5	6.5	12.5	10	70	30	70	70	230	30	110	110	190	.0095	.0350	1500	2500
VS	59.	77.	15.5	22.5	5.5	9.5	10	90	10	370	70	170	50	130	70	130	.0100	.4500	550	2500
CN	67.	75.	17.5	19.5	7.5	10.5	30	70	30	90	70	170	25	110	130	190	.0150	.0450	1500	3500
CS	61.	69.	16.5	22.5	6.5	9.5	10	50	50	130	50	190	50	130	70	130	.0150	.0550	550	2500
GM	65.	71.	16.5	20.5	9.5	13.5	10	50	70	130	90	130	30	110	150	210	.0085	.0350	1500	3500
GS	63.	85.	16.5	22.5	7.5	11.5	30	130	60	130	90	190	10	110	70	330	.0150	.3500	450	3500
I,E+S	49.	73.	13.5	21.5	8.5	14.5	50	110	50	210	90	170	30	110	190	350	-	-	95	1500

M = Median value

E = Minimum enrichment value

Fig.44.Comparison of Clogau Shales with average Black Shales.

Element	Vine (1970)	Green (1959)	Turekain(1961)	Present work (Clogau) North	Present work (Clogau) South
Al_2O_3	7.0	7.8	8.0	17.5	16.5
Fe_2O_3	2.0	4.3	4.72	7.5	6.5
Ba	300	800	580	500	550
Cu	70	38	45	30	10
Ni	50	21	68	30	50
Pb	20	20	20	25	50
Sr	200	299	300	130	70
Zn	300	80	95	70	50
$C_{TOT.}$*	3.53	2.27	-	0.5	1.5

* - Total carbon (sum of organic and inorganic carbon)

Fig.45. Enrichment values.

	Enrichment values										Area totals			Rock type totals		
	Si02	Al203	Fe203	Cu	Ni	Zn	Pb	Sr	Hg	Ba	E_{TOT}	E_{TR}	E_{TR-HG}	E_{TOT}	E_{TR}	E_{TR-HG}
VN	11.1	11.1	5.6	0	0	11.1	0	5.6	5.6	0	49.6	22.2	16.7	102.	64.2	53.4
VS	0	0	10.5	0	0	10.5	0	15.8	5.3	10.5	52.5	42.0	36.8			
CN	5.3	10.5	0	0	0	10.5	0	10.5	0	0	36.8	21	21	79.	45.9	37.6
CS	16.6	0	0	0	0	0	0	0	8.3	16.6	41.5	24.9	16.6			
GN	0	0	0	0	0	25.	0	0	0	0	25.	25.	25.	55.7	50.5	48.8
GS	0	1.7	3.4	0	8.5	3.4	5.1	5.1	1.7	1.7	30.6	25.5	23.8			
I	10.7	10.7	7.1!	0	7.1	10.7	3.6	10.7	0	0	60.6	32.1	32.1			

Fig 46. Mercury values from the Gwynfynydd mine and other areas.

Sample	Location and description	Mercury concentration in ppm
SG1	Sample of copper rich vein material	0.3433
SG2	Wall rock from right hand passage	0.0414
SG3	Wall rock 20yds. from SG1	0.0873
SG4	Igneous rock	0.0857
SG5(a)	Mineralised and altered shales	1.3207
SG5(b)	" " " "	0.5205
SG5(b)	" " " "	0.1391
SG6	Hard wall rock- probably igneous	0.7146
SG8(a)	Sample of quartz vein and country rock	0.0599
SG8(b)	" " " " " " "	0.0240
SFG	Sample of fault gouge from fault in southern area	0.3209

Fig.47.Igneous rocks- analytical groupings.

	Group 1	Group 2
Si02	44.-46.	54.-56.
Al203	11.-12.	15.-16.
Fe203	8.-9.	-
Cu	60-80	-
Ni	20-40	140-180
Zn	80-100	180-220
Pb	0-20	140-180
Sr	40-100	180-200
Ba	BD-10	100-200

Fig.48 Correlation matrix - transformed data. Factor loadings above 0.3 quoted.

	Si02		A1203		Fe203		Cu		Ni		Zn		Pb		Sr		Hg		Ba	
	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S
Si02	-	-	-	-	-	-	-	-	.36	-	-	-	-	-	-	-	-	-	-	-
A1203	-	-	-	-	.43	.36	-	-	.37	-	.63	-	-	-	-	-	-	-	.59	-
Fe203	-	-	.43	.36	-	-	-	-	.43	-	.42	.39	-	-	-	-	-	-	-	-
Cu	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.30	-	-	-
Ni	.36	-	.37	-	.43	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Zn	-	-	.63	-	.42	.39	-	-	-	-	-	-	-	-	-	-	-	-	.34	-
Pb	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	.32	-	.38	-	.31
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	.32	-	-	-	-	-	-
Hg	-	-	-	-	-	-	.30	-	-	-	-	-	-	.38	-	-	-	-	-	-
Ba	-	-	.59	-	-	-	-	-	-	-	.34	-	-	.31	-	-	-	-	-	-

Fig. 49 Sum of Squares reduction for all rock types from Northern and Southern Areas

Component No.	Accumulated value as % of total variance		% reduction due to each component	
	N.	S.	N.	S.
1	28.23	19.05	28.23	19.05
2	42.28	37.63	14.05	18.58
3	55.65	50.85	13.37	13.22
4	66.70	61.97	11.02	11.12
5	74.87	71.11	8.17	9.14
6	82.26	78.86	7.39	7.75
7	88.91	86.27	6.65	7.41
8	94.19	92.77	5.28	6.50
9	97.69	96.42	3.50	3.65
10	100.00	100.00	2.31	3.58

Fig.50 Principal Component Analysis - all rocks in North and South Areas.

	1		2		3		4		5		6		7		8		9		10	
	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S	N	S
Si02	-	-	.38	-	-	.48	.39	.56	.58	-	-	.30	.35	.42	-	.35	-	-.31	-	-
Al203.	.52	-	-	-	-	.34	-	-	-	-.58	-	-.32	-	-	-	-	-	-	-.81	.34
Fe203	.40	-.40	-	-.45	-.37	-	-	-	-	-	-.51	-	-	-	-	.41	.57	-	-	-.63
Cu	-	-	-.63	-	-	-	-	.57	-	.50	.35	-.33	-.37	-	.44	-.42	-	-	-	-
Ni	.35	-.40	.31	-	-	-	-	-	-	-	-	.57	-.57	-.60	-	-	-.50	-	-	-
Zn	.44	-	-	-.53	-	-	-	-.36	-	.36	-.47	-	-	-	.50	-	-.37	-	.34	.56
Pb	-	.50	-	-.36	-	-	-.72	-	.40	-	-	-	-	-	-.37	-	-	-.69	-	-
Sr	-	-	.39	-.47	-.46	-	-.38	-	-.46	-.31	.31	.36	-	-	.38	-.61	-	-	-	-
Hg	-	.36	-.43	-	-.47	-.44	.34	.40	-	-	-	-	.54	-.40	-	-	-	.43	-	-
Ba	.32	.30	-	-	.51	.57	-	-	-.45	-	.34	-.44	-	-	-	-	-	.36	.43	-

Fig.51 Factor Analysis - All sedimentary rock types in Northern and Southern Areas.

	1		2		3		4		5		6		7	
	N	S*	N	S	N	S	N	S	N	S	N	S	N	S
SiO_2	.36	-	.29	.11	.42	.38	.22	-	.32	.37	.24	.25	-	.26
Al_2O_3	.90	-	-	-.50	-	.38	-	.41	-	-	-	-	-	-
Fe_2O_3	.55	-	.42	-.73	-	-	-	-	-	-	-	-	-	-
Cu	-	-	-	-	-.51	-	-	-	-	.34	-	.25	-.28	-.30
Ni	.49	-	.51	-.40	-	-	-	-	-	.36	-	-.38	-.21	-
Zn	.69	.39	-	-.60	-	-	-	-.35	-	-	.22	-	-	-
Pb	.30	.81	-	-	-	-	-.51	-	-	-	.34	-	-	-
Sr	-	.36	.41	-	-	-	-	-	.36	-	-	-	.28	-
Mg	-	.44	.22	.16	-.58	-.36	.34	.48	-	-	-	-	.25	-
Ba	.59	.42	-.46	-	-	.60	-	-	-	-	-	-	-	-.24

Fig.52 Percent Sum of Squares reduction for each rock type in both areas

Component No.	GN	GS	CN	CS	VN	VS	IN	IS
1	34.57	23.31	22.31	29.37	46.89	28.11	57.47	31.39
2	29.34	16.64	17.12	27.91	17.28	21.66	17.77	18.19
3	15.27	14.87	15.34	14.04	11.77	15.27	13.50	12.85
4	10.94	10.69	12.78	10.73	8.18	11.53	8.86	12.38
5	5.58	8.37	12.40	7.09	6.52	10.06	2.40	9.60
6	3.08	6.92	7.62	4.18	5.09	5.22	-	5.66
7	1.22	6.60	6.55	3.96	3.13	4.12	-	3.86
8	-	6.21	2.99	1.63	0.88	2.47	-	2.96
9	-	3.35	2.43	0.97	0.15	1.34	-	2.47
10	-	2.98	0.45	0.12	0.02	0.22	-	0.84

53 Summary of factor scores for Gamlam Flags of both areas.

Gamlam North

	Factor 1	2	3	4	5	6
Si02		+		+	+	
Al203	−	−				
Fe203	+		+	+	−	
Cu	+	−	−			
Ni		−	+	+	+	
Zn	−	+	+			
Pb		+	+	+	−	
Sr	−					
Hg	+	−	−			
Ba		−	+		−	

Gamlam South

	Factor 1	2	3	4	5
Si02			+	+	+
Al203		+		+	
Fe203	−	+	−		
Cu		−	+	+	+
Ni		+		+	−
Zn	−	+			
Pb	−		+		
Sr	−	−		−	+
Hg	−		−		
Ba		+	+		

Fig. 54 Summary of factor scores for Clogau Shales of both areas

Clogau North			Factor		
	1	2	3	4	5
SiO_2	+		+	+	+
Al_2O_3	-	-			+
Fe_2O_3		-	-	+	-
Cu	+	+	-	-	
Ni	-	-		+	+
Zn			+	+	-
Pb	-	+	-		
Sr	-				
Hg	+	-	-	+	+
Ba	-	-		-	

Clogau South			Factor		
	1	2	3	4	5
SiO_2		+		+	+
Al_2O_3	-	-			-
Fe_2O_3	-	-	+		
Cu	+		+	+	-
Ni	-	-			+
Zn	-			-	
Pb	-	+		+	-
Sr	-	+		+	-
Hg	+	+	+	-	+
Ba	-	+		+	

Fig. 55. Summary of factor scores for Vigra Flags of both areas.

Vigra North	Factor				
	1	2	3	4	5
SiO_2	+			+	
Al_2O_3	+	+	+		
Fe_2O_3	+	−	+	−	
Cu		−			−
Ni	+	+	+		−
Zn	+				
Pb	+	−	+		+
Sr		+		−	+
Hg			−	−	−
Ba	+				

Vigra South	Factor				
	1	2	3	4	5
SiO_2			+	+	
Al_2O_3	+	+	−	+	
Fe_2O_3	−	+	+		
Cu	+	+		−	+
Ni		+			−
Zn	−				
Pb	−	−	+	+	
Sr		−	−		
Hg	−	−	+	+	
Ba		−	−	+	+

Fig. 56. Summary of factor scores for Igneous rocks of both areas.

Igneous North	Factor				
	1	2	3	4	5
SiO2			+		
Al2O3	-				
Fe2O3	-			+	
Cu		-			
Ni	-				
Zn	-	-			
Pb	-		-	-	
Sr	-				
Hg	-	-			
Ba			-	+	

Igneous South	Factor				
	1	2	3	4	5
SiO2	+		+		+
Al2O3		+			
Fe2O3	+			+	
Cu	+				
Ni	+	-			
Zn			+		
Pb		+		-	
Sr	+	+			
Hg				-	+
Ba		+	+	-	-

Fig. 57 Recurring factors for all rock types in Northern and Southern Areas.
Sedimentary Factors.

	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba
N1	+	+	+		+	+	+			+
VN1	+	+	+		+	+	+			+
VN2		+	−	−	+			+	−	
VN3		+	+		+		+		−	
VS2		+	+	+	+		−	+	−	−
CN4	+		+	−	+	+				−
CN5	+	+	−		+	−				
GS2		+	+		+	+		−		+
GS4	+		+		+		+			

Fig. 58 Recurring factors for all rock types in Northern and Southern Areas.
Major Mineralisation

	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba
S1						+	+	+	+	+
CS2	+	−	−		−		+	+	+	+
VS4	+	+		−			+		+	+
VS3	+	−	+				+	−	+	−

Fig. 59. Recurring factors for all rock types in Northern and Southern Areas.
Copper Mineralisation

	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba
S5	+			+	+				+	
CS5	+	−	+	+	−	−	−	+		
CN1	+	−		+	−		−	−	+	−
CS1		−	−	+	−	−	−	−	+	−
CS3			+	+					+	
VS5				+	−					+

Fig. 60. Recurring factors for all rock types in Northern and Southern Areas.
Mercury and Quartz

	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba
N4	+						−	−	+	
S2	+	−	−		−	−			+	
CS5	+	−		−	+		−	−	+	

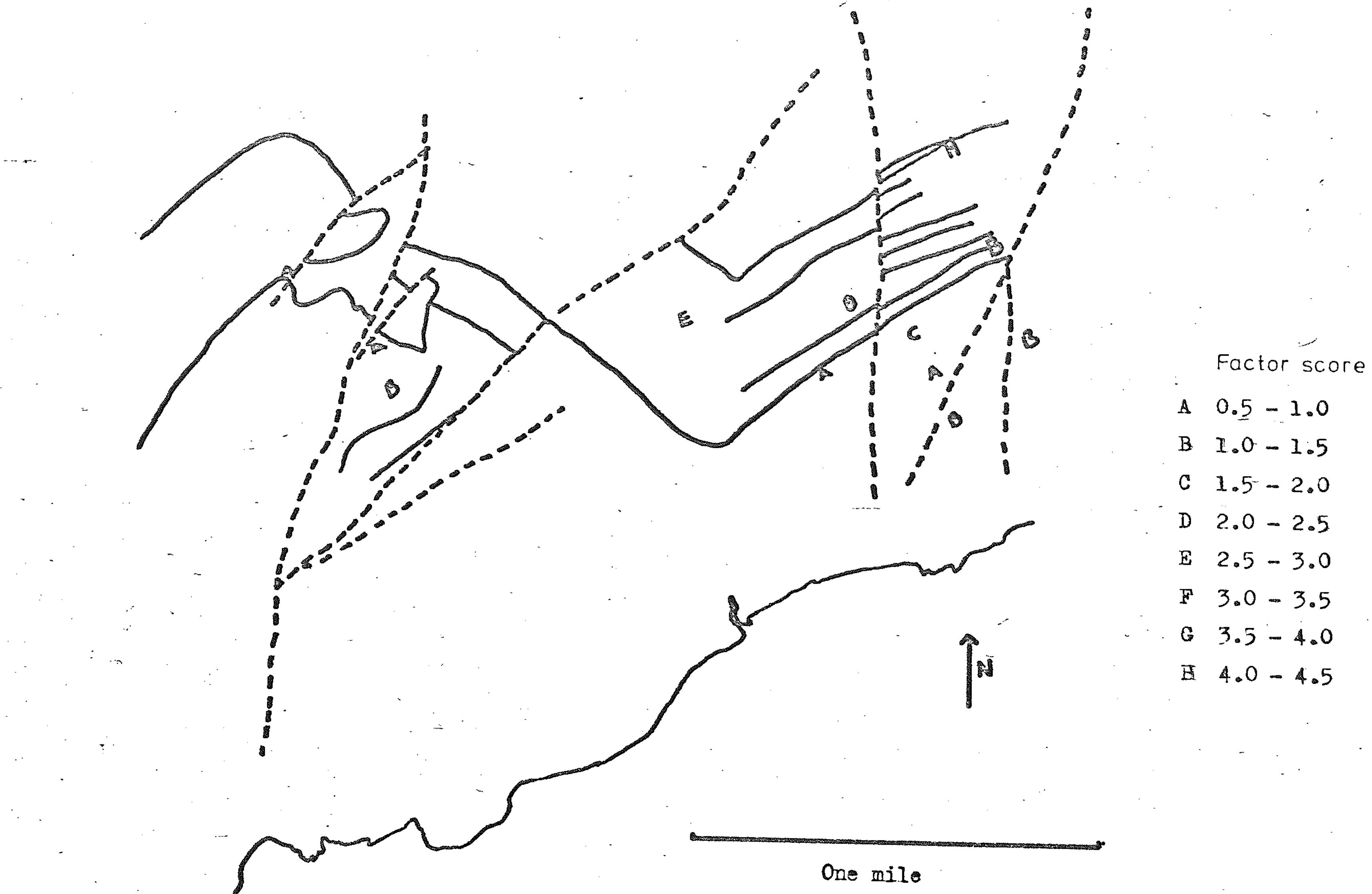


Fig. 61. Factor scores for major Pb mineralisation - individua rocks.

Outline map of Southern Area from Fig 6

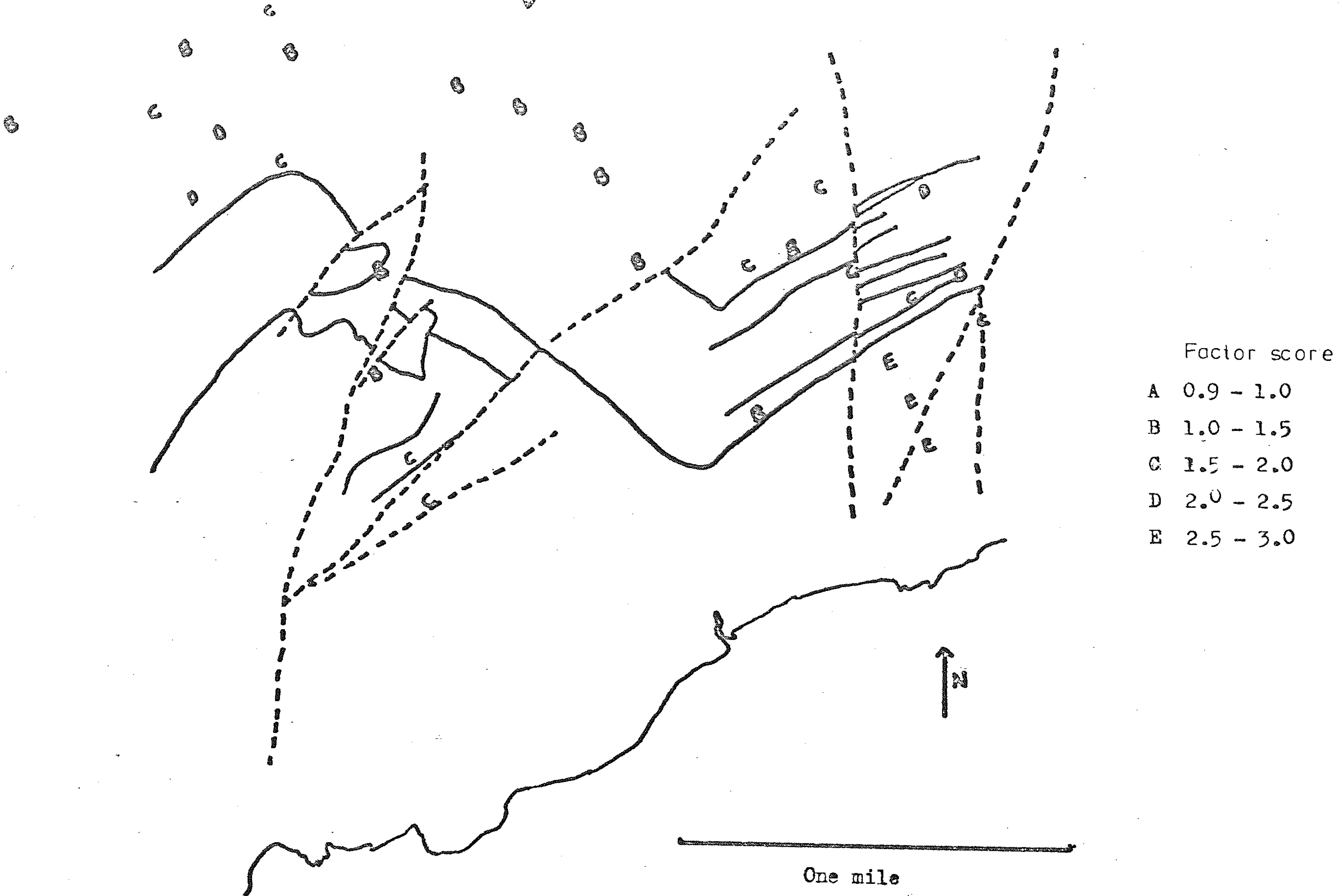


Fig. 62. Factor scores for major Pb mineralisation - all rocks

Outline map of Southern Area from Fig 6

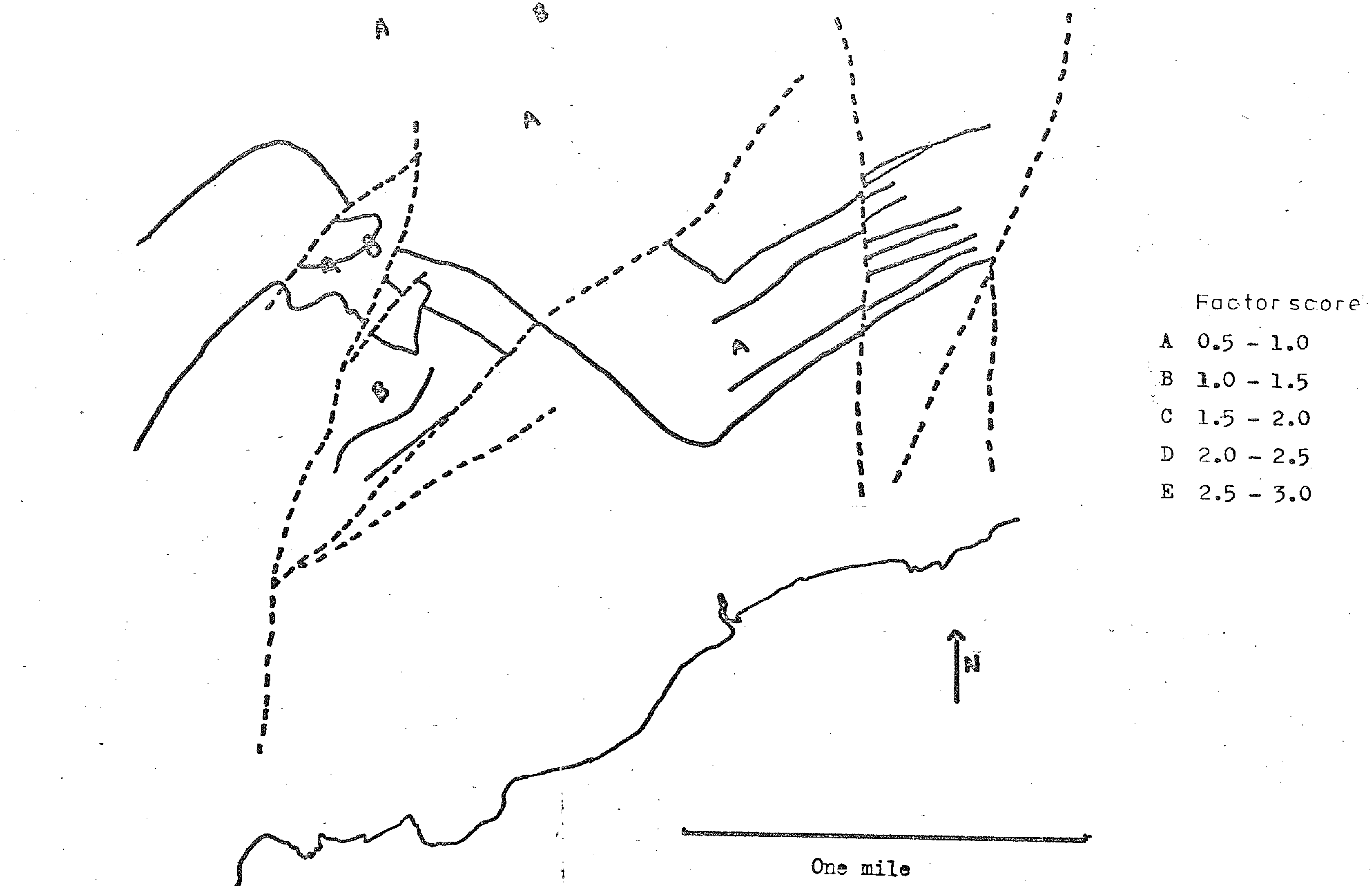


Fig. 63. Factor scores for Cu mineralisation - all rocks.

Outline map of Southern Area from Fig 6

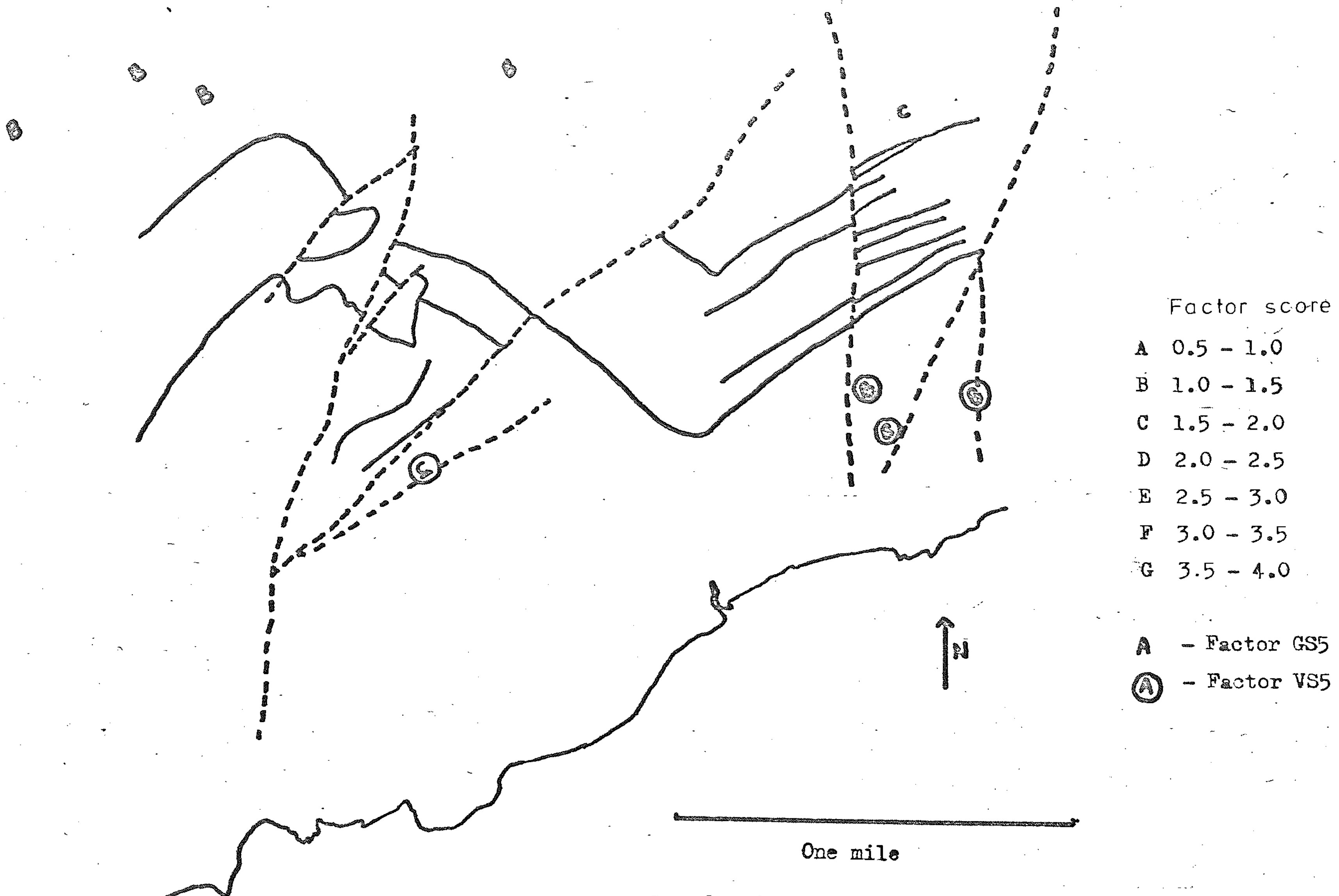


Fig.64. Factor scores for Cu mineralisation - individual rocks.

Outline map of Southern Area from Fig 6

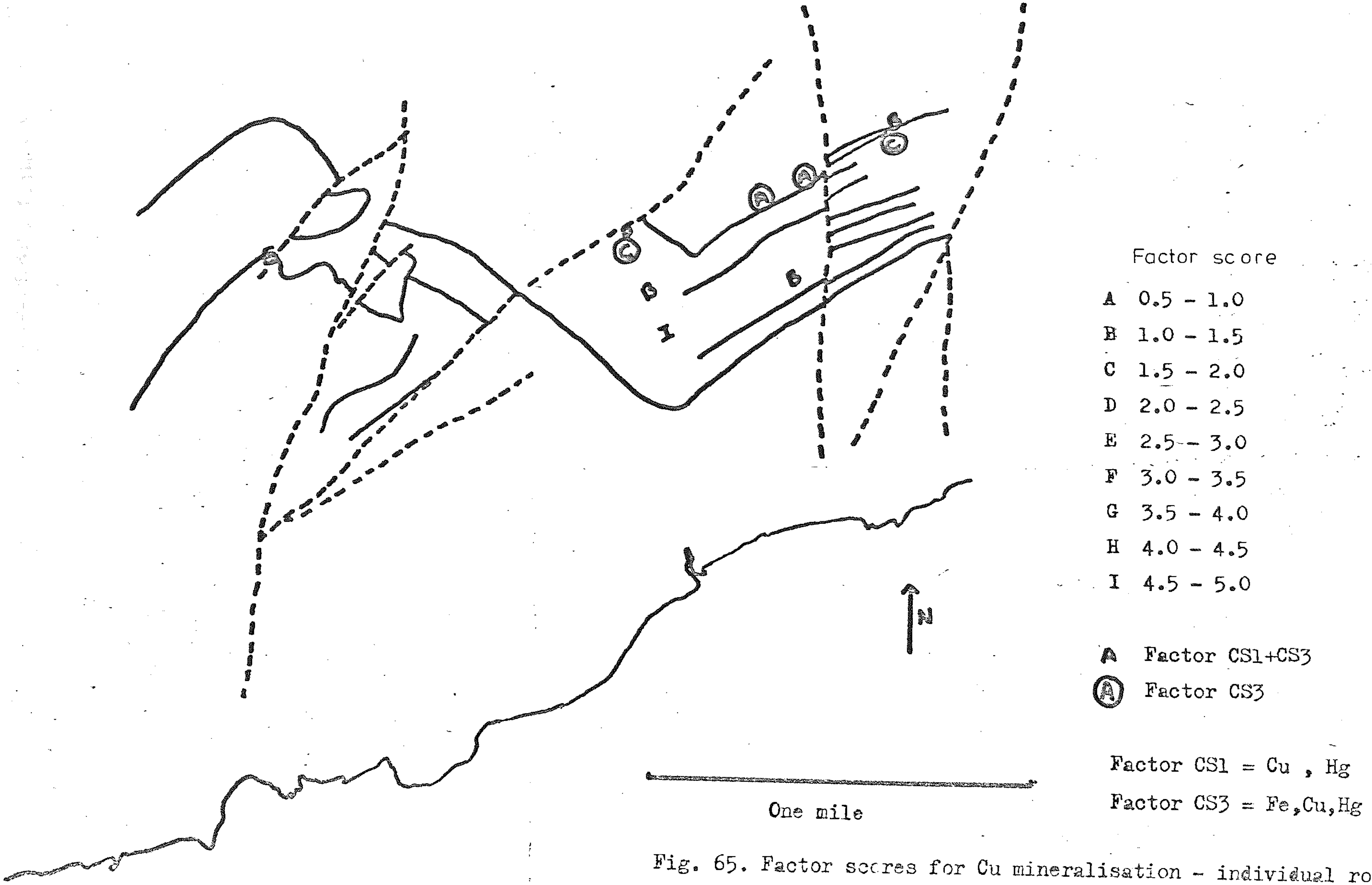


Fig. 65. Factor scores for Cu mineralisation - individual rocks.

Outline map of Southern Area from Fig 6

Fig.66. High Cu factor scores related to field description of sample.

Clogau Shales, South, factor 1

1127	Shaley
1082	Light grey shale
1088	Weathered shale
1101	Light grey shale
1071	Shale

Clogau Shales,South, factor 3

1087	Light grey shale
1084	Hard black shale
1083	Grey shale
1070	dark grey shale

Gamlan Flags,South, factor 5

1002	Gritty material
1015	Black shale
1016	Massive grit
1045	Intrusive
1041	Light grey shale
1052	Grey shale

Vigra Flags,South. factor 5

1140	Grey shale
1094	Grey shale
1095	grey Shale +,pyrite
1076	Shale

All rock types, Southern Area, factor 5

1129	Shale + vein quartz
1055	Greenish gritty material
1006	Shaley material containing vugs,looks baked
1139	Gritty material
1146	Jointed,hard grey shales.
1044	Hard gritty shale in outcrop next to quartz vein
1102	Igneous intrusion

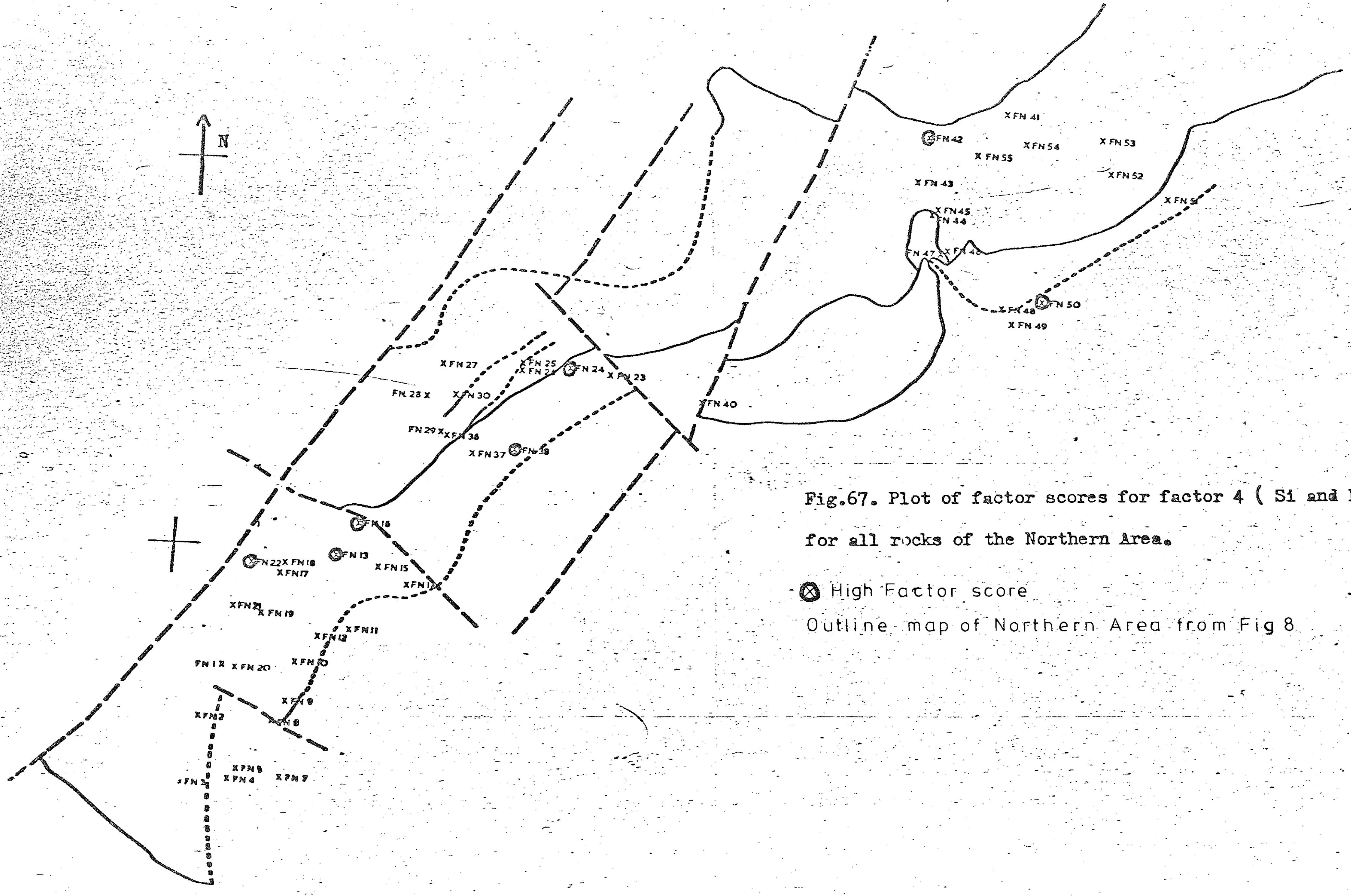


Fig.67. Plot of factor scores for factor 4 (Si and Hg
for all rocks of the Northern Area.

⊗ High Factor score

Outline map of Northern Area from Fig 8

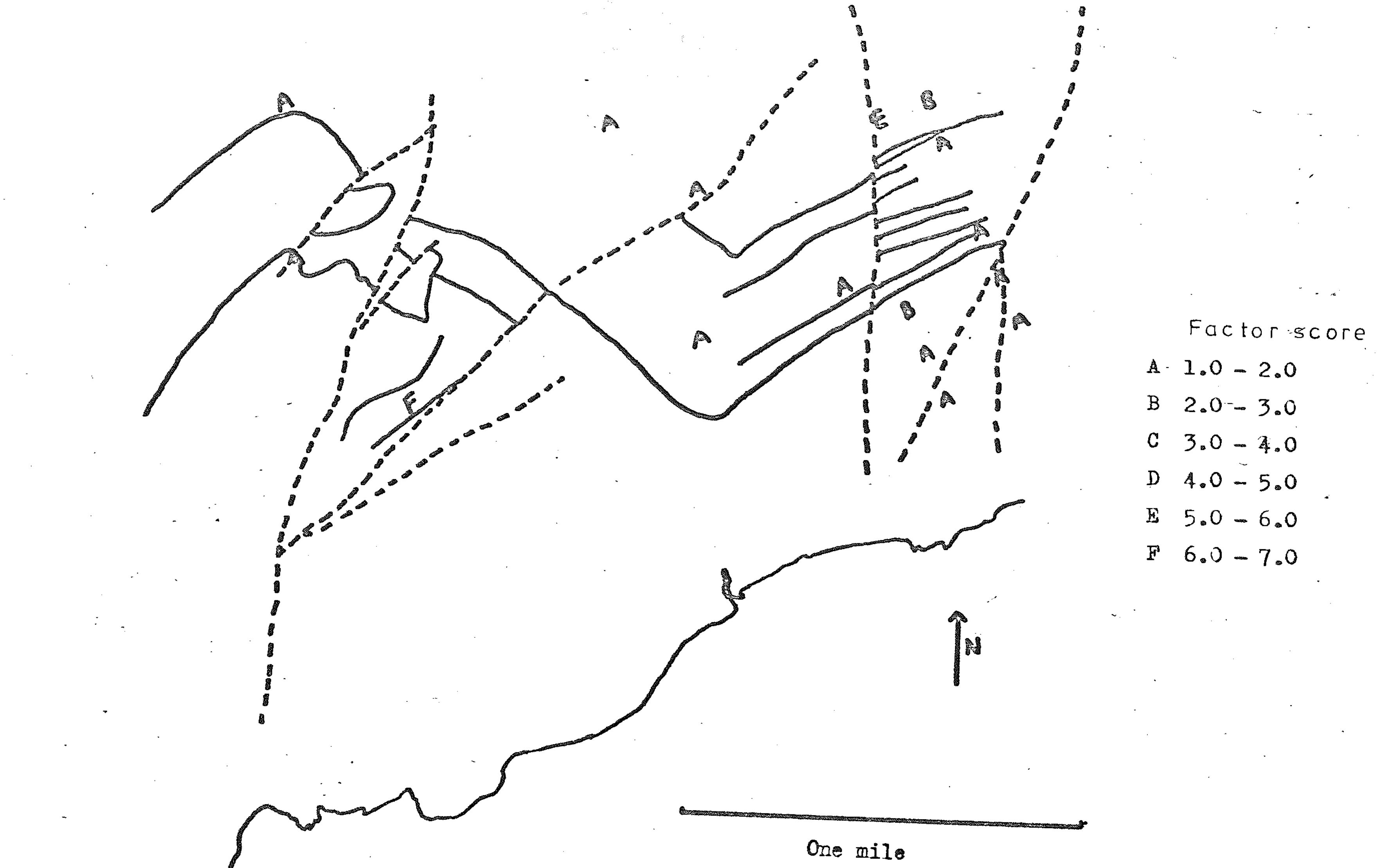


Fig. 68. Factor scores for Si and Hg factor – all rocks.

Outline map of Southern Area from Fig 6

Fig.69. Field descriptions of rocks plotted in Figs.67 and 68.

Factor 4 - Northern area association with field description.

1175	Hard grey shale
1178	Hard weathered grey shale
1184	Hard dark grey shale
1186	Dark grey shale
1195	Layered shale and siliceous flags.
1200	Dark grey shale
1204	Dark grey shale
1212	Hard igneous material
1220	Shale
1213	Shale

Factor 5 - Southern area association with field description.

1012	Grit with obvious quartz grains
1127	Shale
1021	Soft shale
1130	Igneous
1157	Quartz
1031	Medium corse grit
1046	Igneous - next to quartz vein
1053	Gritty shale
1058	Corse grit
1104	Hard black shale
1062	Greenish grit
1101	Light grey shale
1093	Grey shale
1094	Grey shale
1095	Grey shale and pyrite
1062	Layered grit
1068	Grit
1071	Shale
1073	Light grey shale
1074	Hard grey shale
1075	Grey shale

Fig.70. Recurring factors for all rock types in Northern and Southern Areas.

Quartz mineralisation

	SiO2	Al2O3	Fe2O3	Cu	Ni	Zn	Pb	Sr	Hg	Ba
N3	+			-					-	
S7	+			-						-
GN5	+		-		+		-			-
VN4	+		-					-	-	

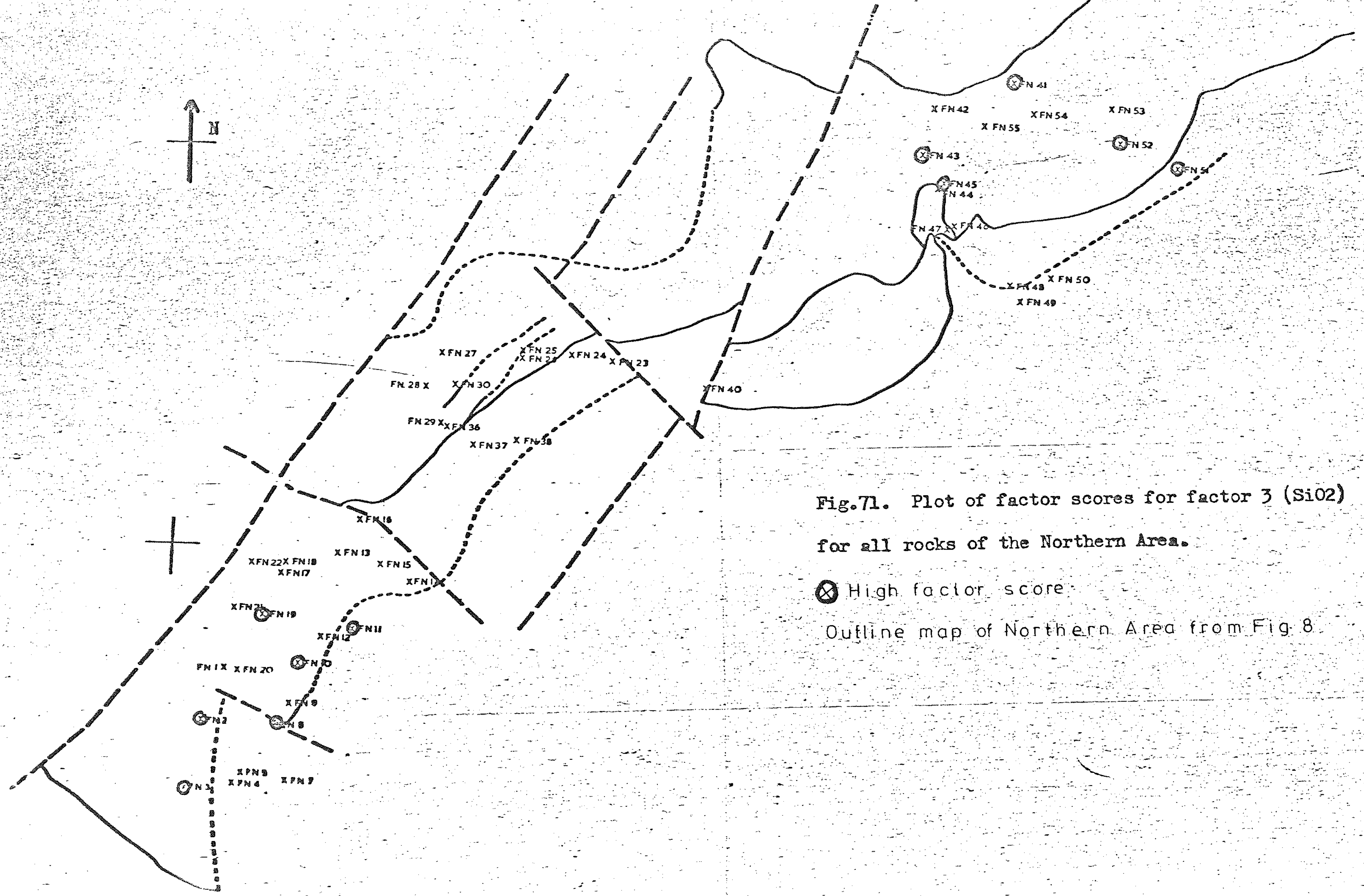


Fig.71. Plot of factor scores for factor 3 (SiO2) for all rocks of the Northern Area.

⊗ High factor score

Outline map of Northern Area from Fig 8

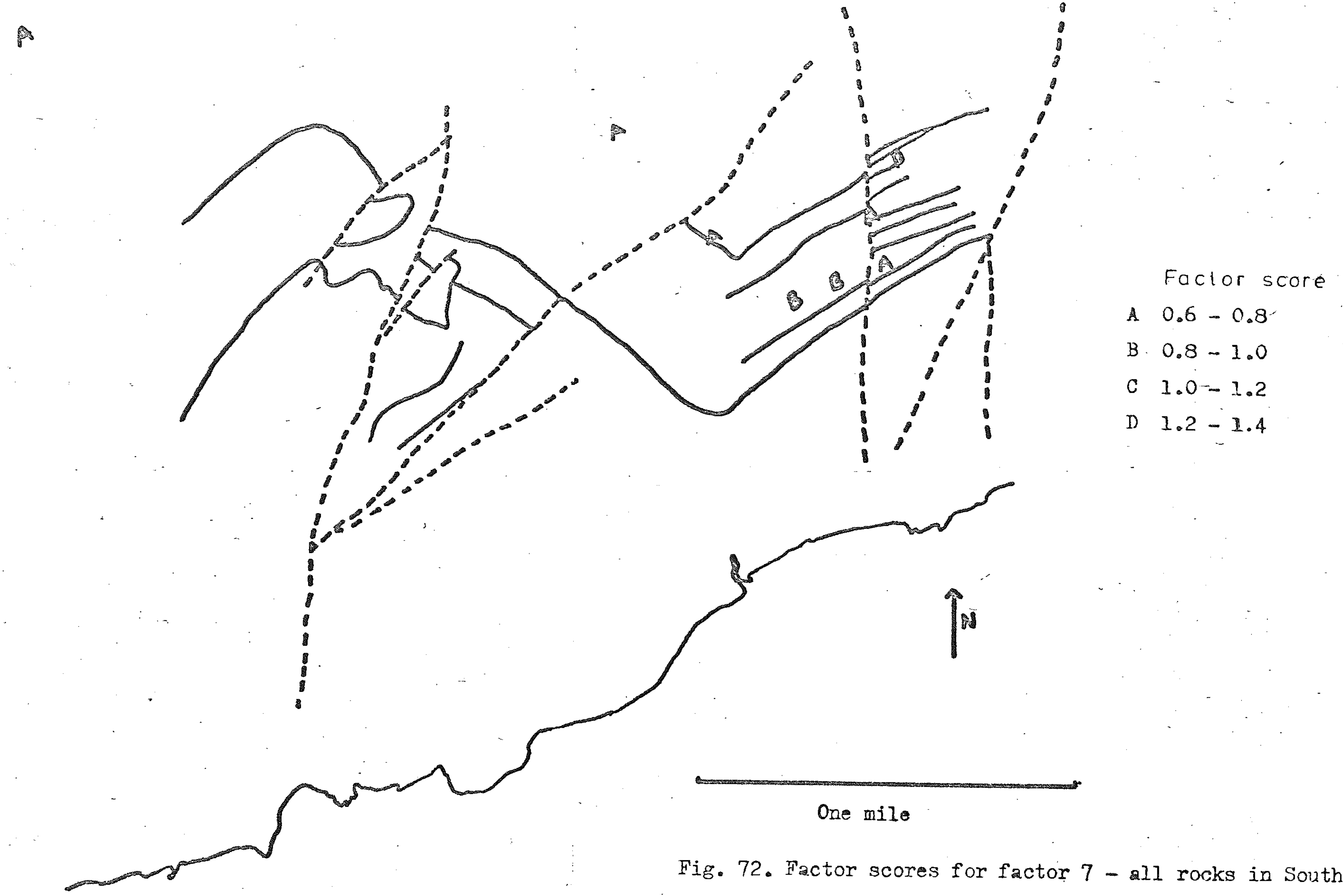


Fig. 72. Factor scores for factor 7 - all rocks in Southern Are
(see Fig.70)

Outline map of Southern Area from Fig 6

Fig. 73. Sum of squares reduction for A.A. and CO2 analysis - all rocks of Northern Area

Component No.	Accumulated value as % of total variance.	%reduction due to each component.
1	30.54	30.54
2	53.28	22.74
3	68.34	15.06
4	79.14	10.80
5	86.92	7.78
6	94.31	7.39
7	96.92	2.61
8	98.45	2.53
9	99.41	0.96
10	100.00	0.00

Fig. 74. Sum of squares reduction for A.A. and CO2 analysis - all rocks of Southern Area.

Component No.	Accumulated value as a % of total variance	% reduction due to each component.
1	22.3	22.3
2	39.6	17.3
3	54.3	14.7
4	63.5	9.2
5	71.9	8.4
6	78.8	6.9
7	84.9	6.1
8	90.6	5.7
9	95.0	4.4
10	98.5	3.5

Fig. 75 Summary of factor scores for all rocks in Northern Area, including CO_2

	Factor						
	1	2	3	4	5	6	7
SiO_2	+	+		+			
Al_2O_3	+		−				
Fe_2O_3	−	+					
Cu	−	−				+	
Ni	+	+				+	+
Zn	−						
Pb	−			+			
Sr		+		−		+	
Hg			−	−		+	
Ba			−				+
CO_2		−					+

Fig.76 Summary of factor scores for all rocks in Southern Area, including CO_2

	Factor						
	1	2	3	4	5	6	7
SiO_2			+	+			
Al_2O_3		−	+	+			
Fe_2O_3		−	−				
Cu			−	+			
Ni		−	−			+	
Zn	−	−					
Pb	−						
Sr	−						
Hg	−	+					
Ba	−		+				
CO_2	−				−		

Fig. 77. Distributions of MgO,CaO,K2O,Na2O,TiO2 and P2O5 for the Gamlan Flags of the Southern Area.

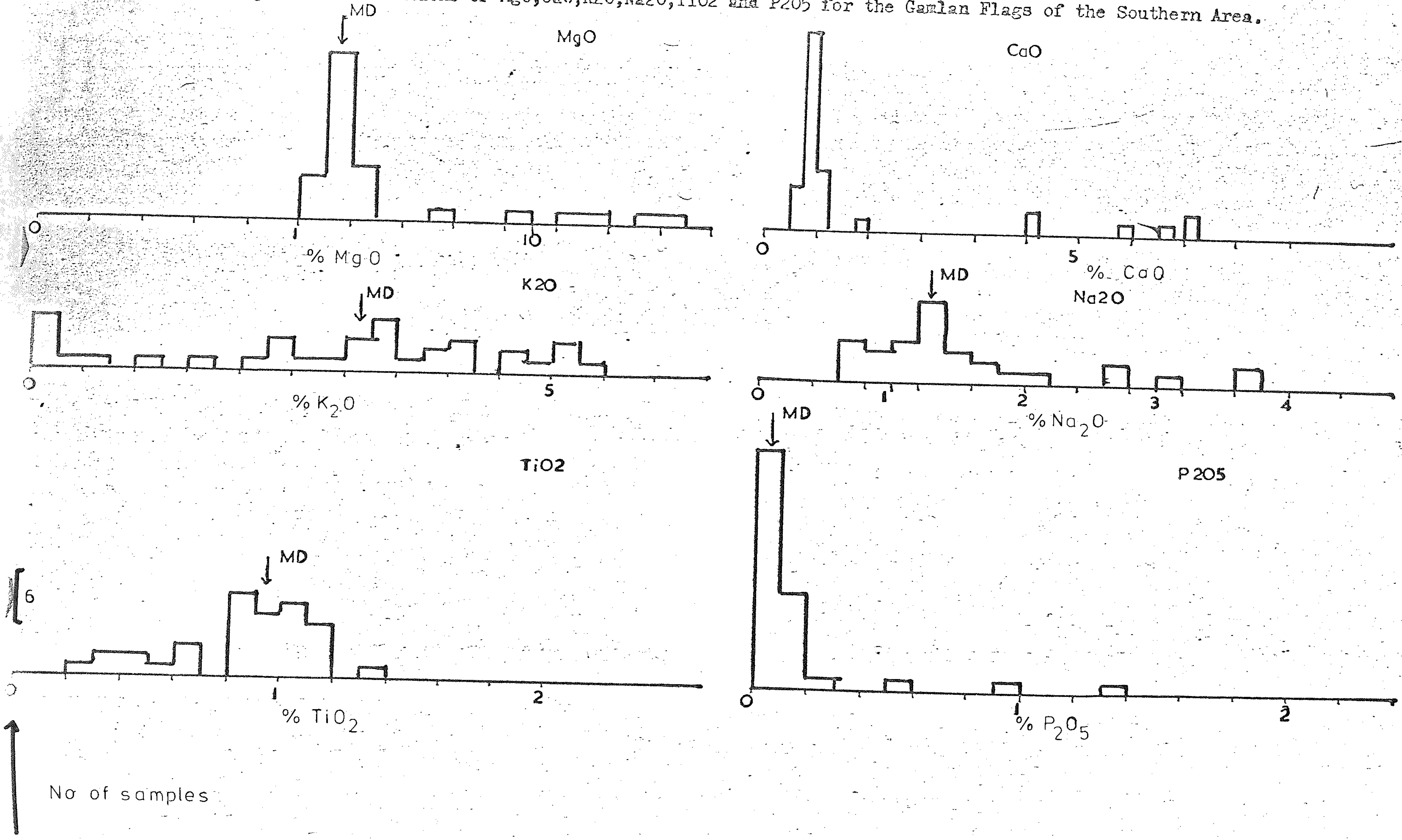


Fig. 78. Distributions of S,Rb,Y, and Th for the Gamlan Flags of the Southern Area.

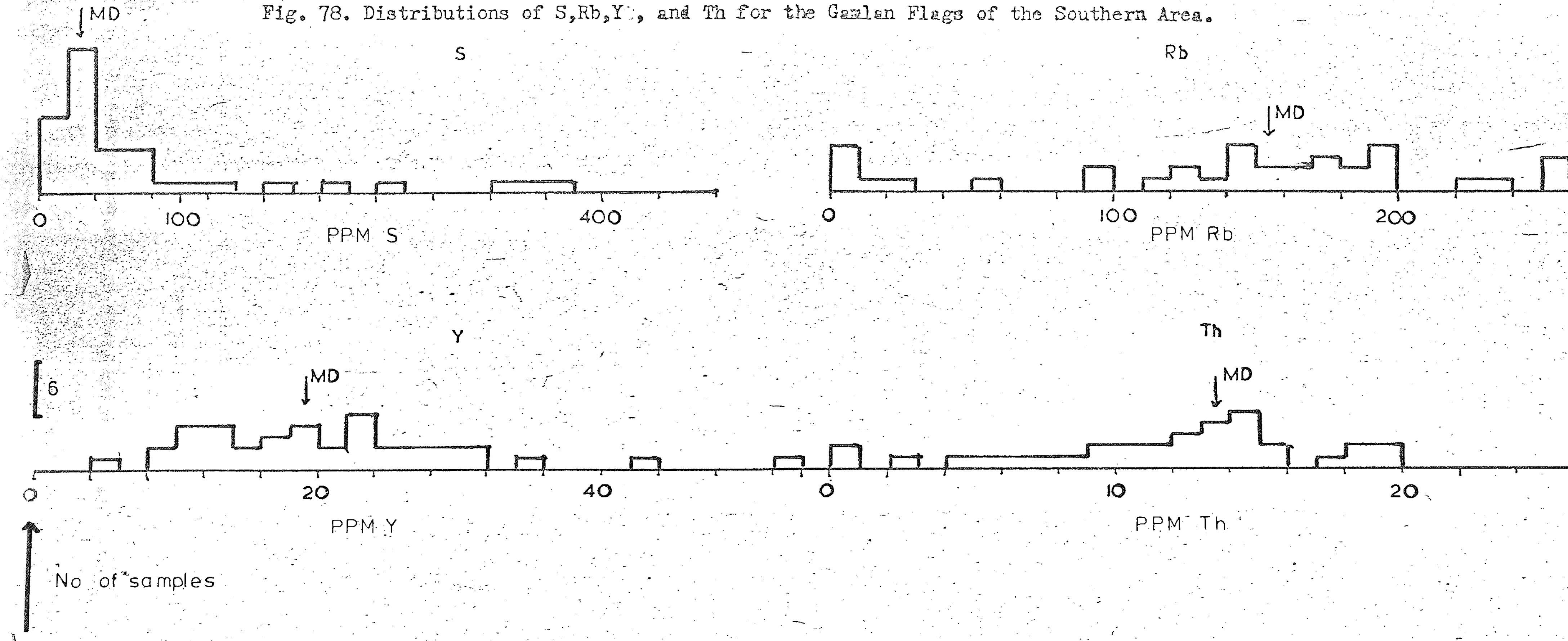


Fig. 79. Statistics - XRF analyses on Gamlan Flags of Southern Area.

Element	Mean	Standard deviation	Median	Minimum enrichment value
Na20	1.6	2.2	2.9	3.3
K20	2.9	1.7	3.12	5.37
CaO	1.8!	2.1!	0.87	6.12
MgO	-	-	2.5	13.5
Ti02	0.86	0.27	0.95	1.25
P205	0.15	0.18	0.05	0.35
S	82	100.6	30	270
Y	20	11	19	33
Rb	127	83	155	245
Th	11	6	13.5	20.5

Fig. 80. Enrichment values - Gamlan Flags of Southern Area: XRF analyses.

Element	No. of samples enriched	Total number of samples	% enriched
Na20	3	32	9.4
K20	0	36	0
CaO	3	36	8.3
MgO	1	31	3.2
Ti02	0	36	0
P205	3	36	8.3
S	3	37	8.1
Y	2	38	5.25
Rb	0	35	0
Th	0	36	0

Fig. 81. Percent sum of squares reduction for Gamlan Flags of the Southern Area. All XRF analyses.

Component No.	Percent sum of squares reduction
1	27.26
2	18.10
3	12.71
4	7.66
5	6.74
6	6.08
7	4.72
8	3.48
9	2.77
10	2.00
11	1.79
12	1.47

Fig. 82. Summary of factor scores (above 0.3) for XRF analyses of Gamlan Flags of the Southern Area.

	Factor						
	1	2	3	4	5	6	7
Si02	+						-
Al203	+	-	+	+			
Fe203				+		-	-
Mn02	-						
Ti02		-	+	+			
Ca0	-	+		+			
K20		-	+				
Na20	-			+		+	
P205					-		+
Cu				+	-		
Ni				+			
Zn				+			
Pb	-			+	+	+	
Sr				+			+
Ba					+		+
Hg	-				-		
Cr	-						
Ce	-	-					
La	-						
S	+						
Y		-	-				
Rb	+	-	-				
Th	+	-	-				

Fig. 83. Sum of squares contributions - Trend Surface Analysis.

Element	S.S. contribution.
Th	41.95
Sr	38.25
Rb	44.09
Y	38.68
Hg (N)	63.41
Hg (S)	38.98

Figs. 84 to 94 should be used in conjunction with the overlay in the rear pocket.

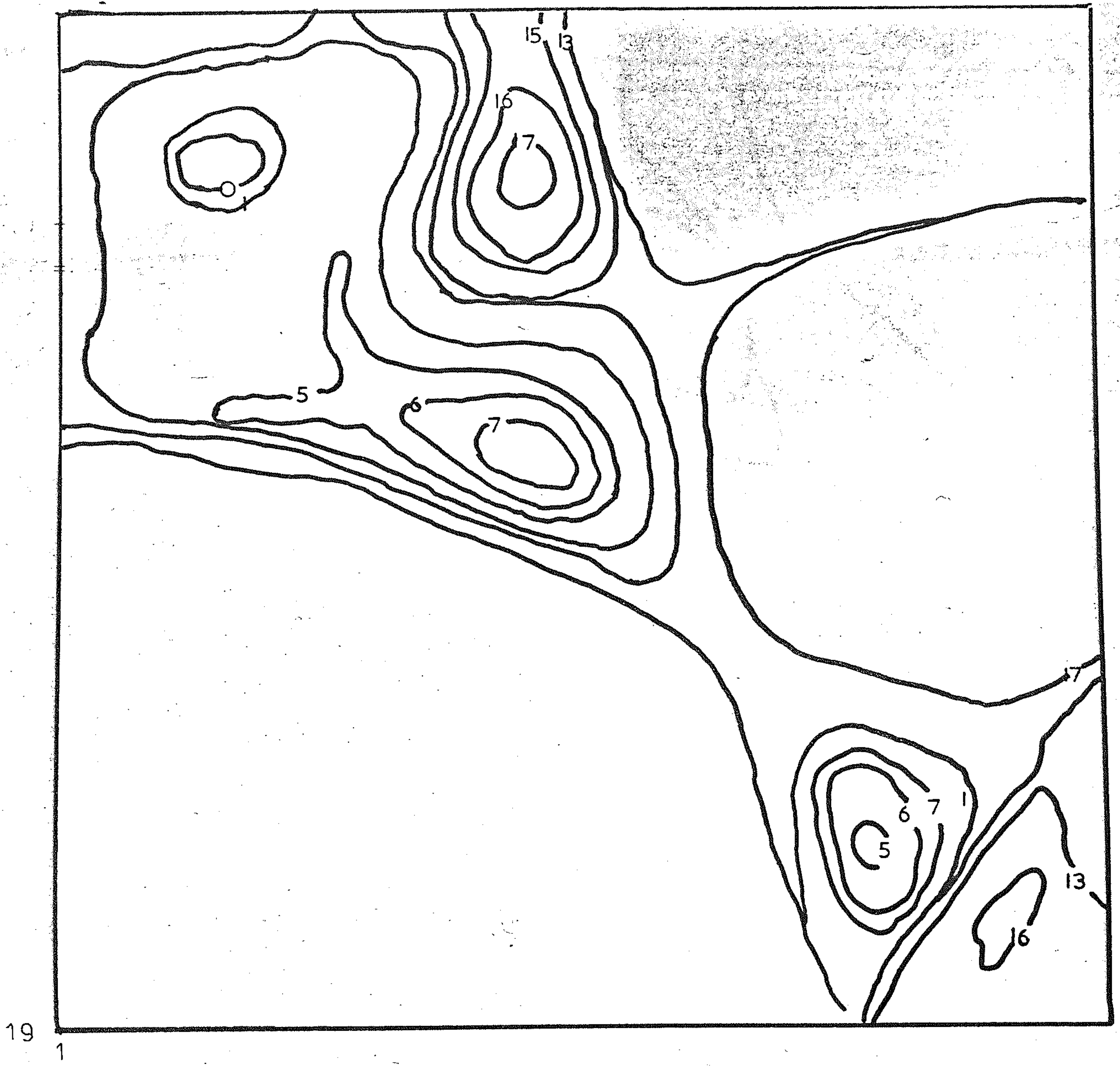


Fig. 84 Th Southern Area - Trend

U = 100

V = 40

Fig. 85 Th Souther

Residuals

U = 100

V = 40

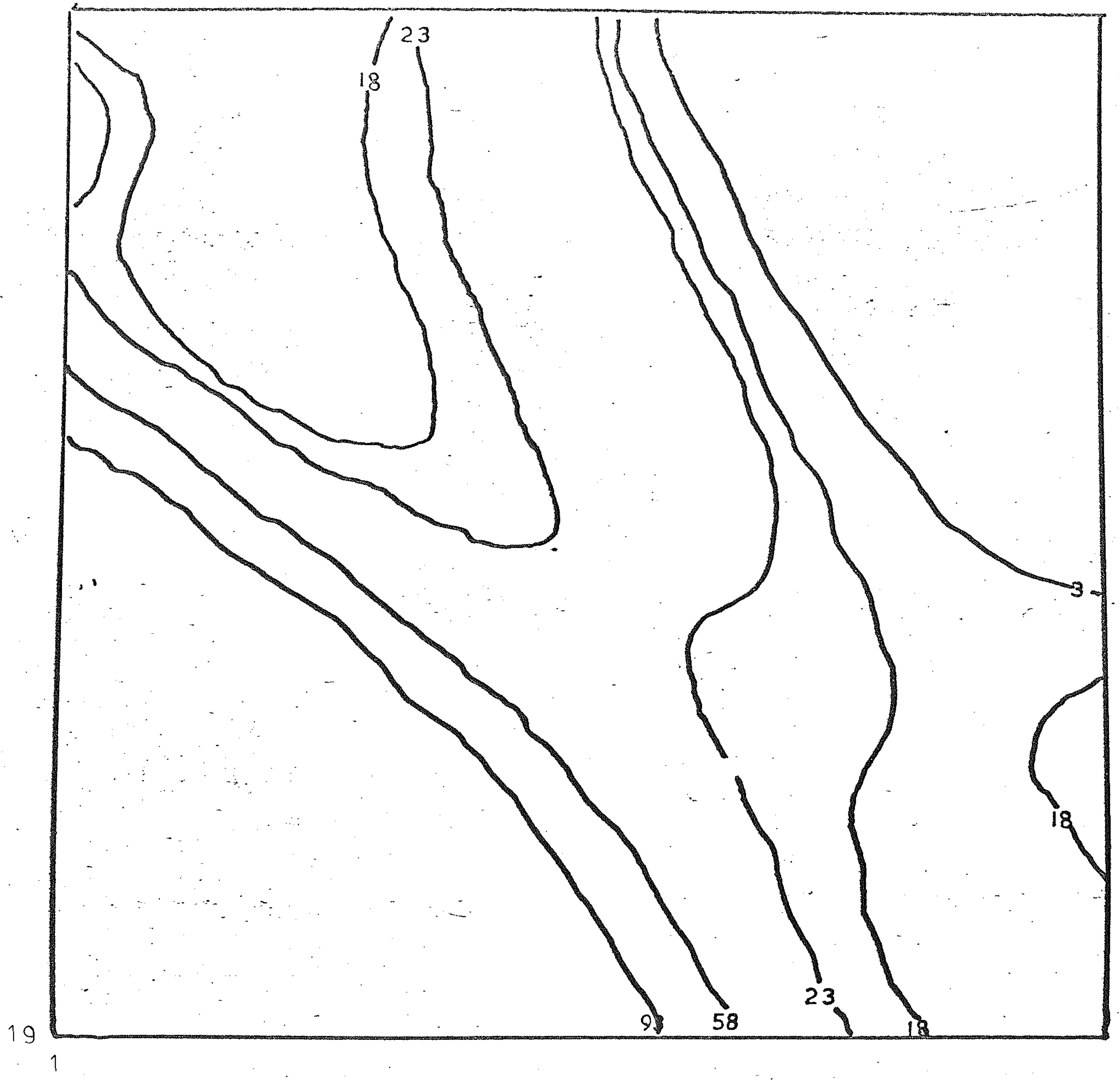


Fig. 86 Y Southern A

Trend

U = 120

V = 120

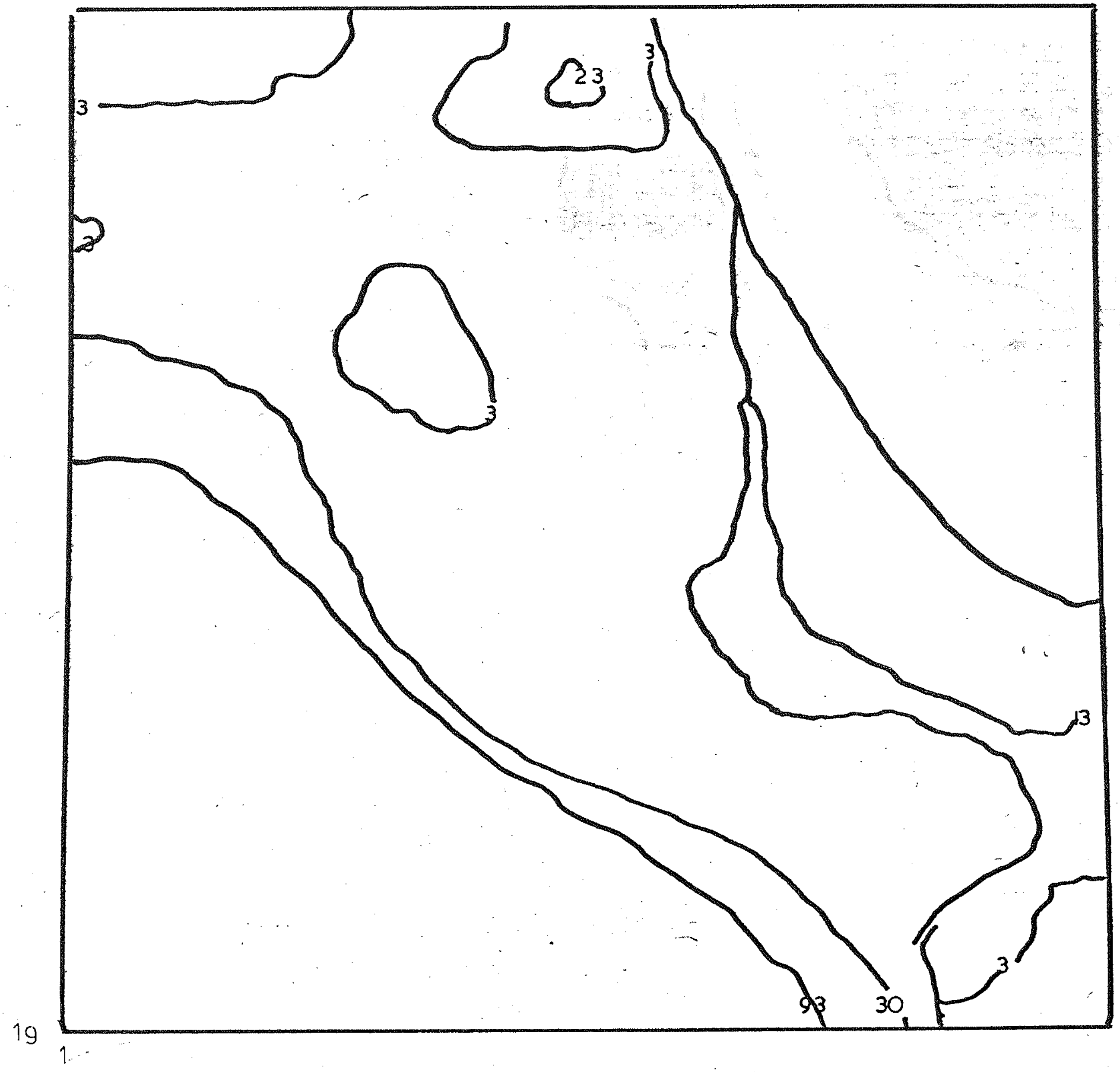


Fig. 87 Y Southern Area -
Residuals
U = 120
V = 120

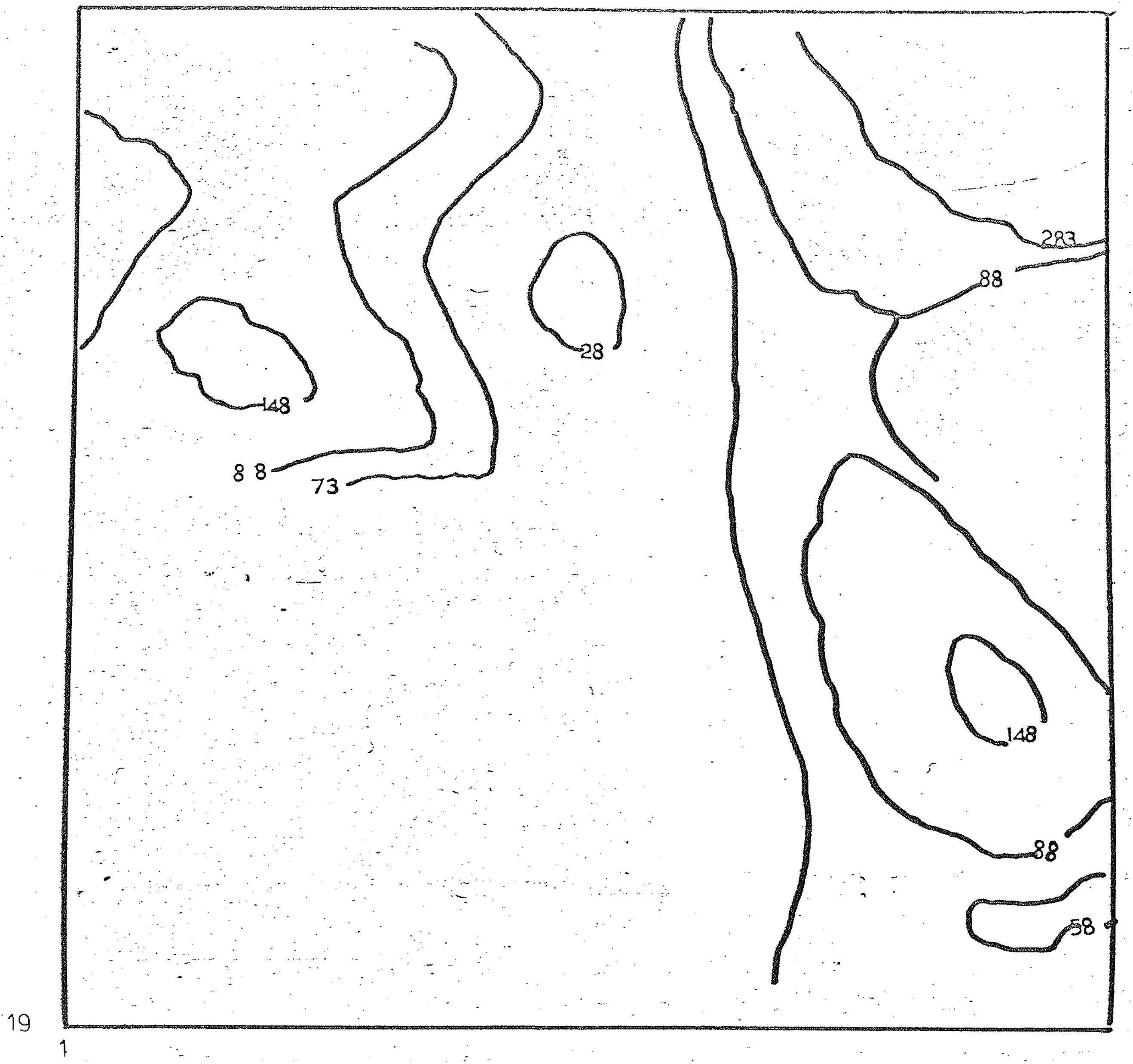


Fig. 83 Sr Southern Area
Trend
U = 45
V = 120

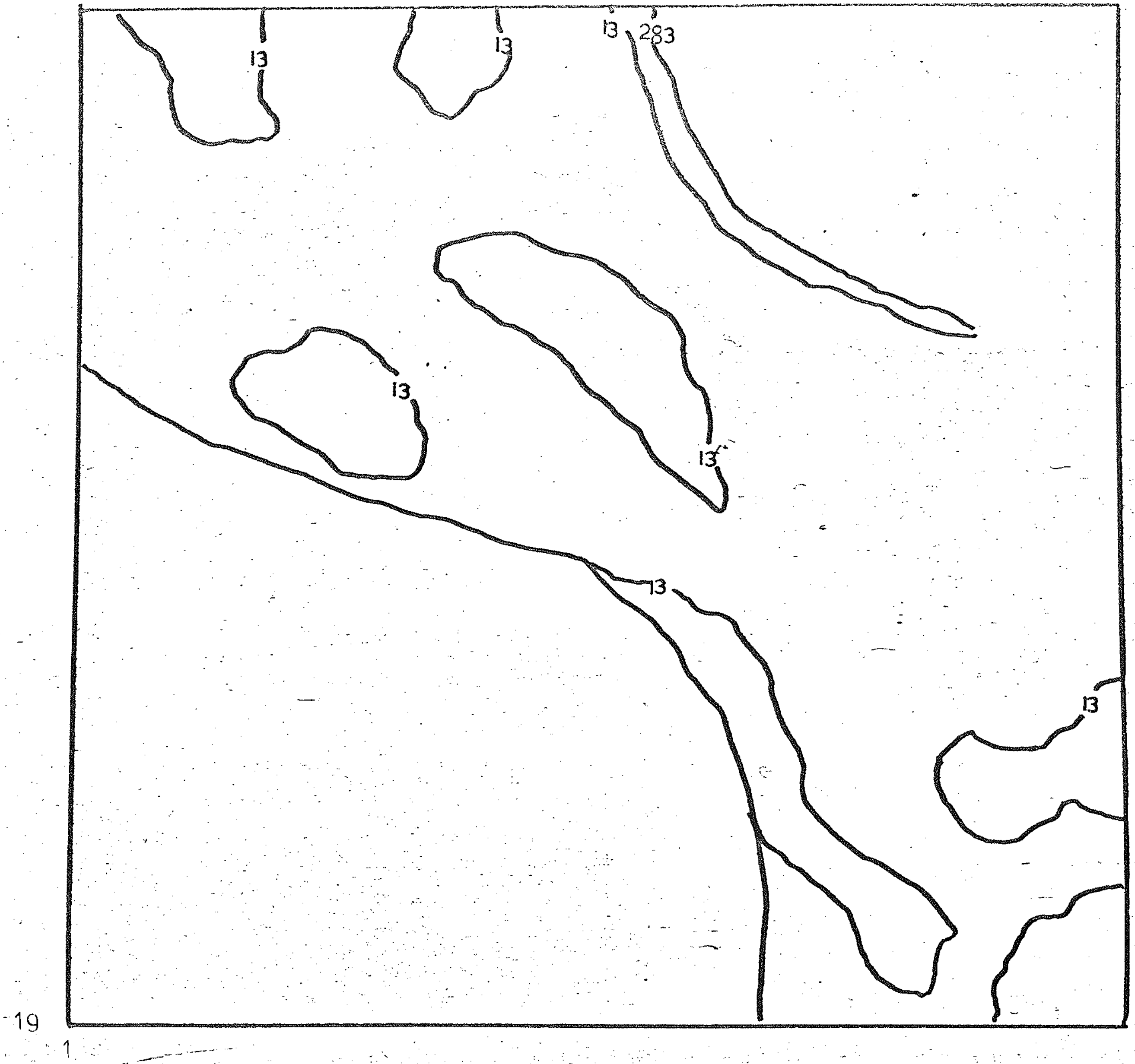


Fig. 89. Sr Southern A

Residuals

U = 45

V = 120

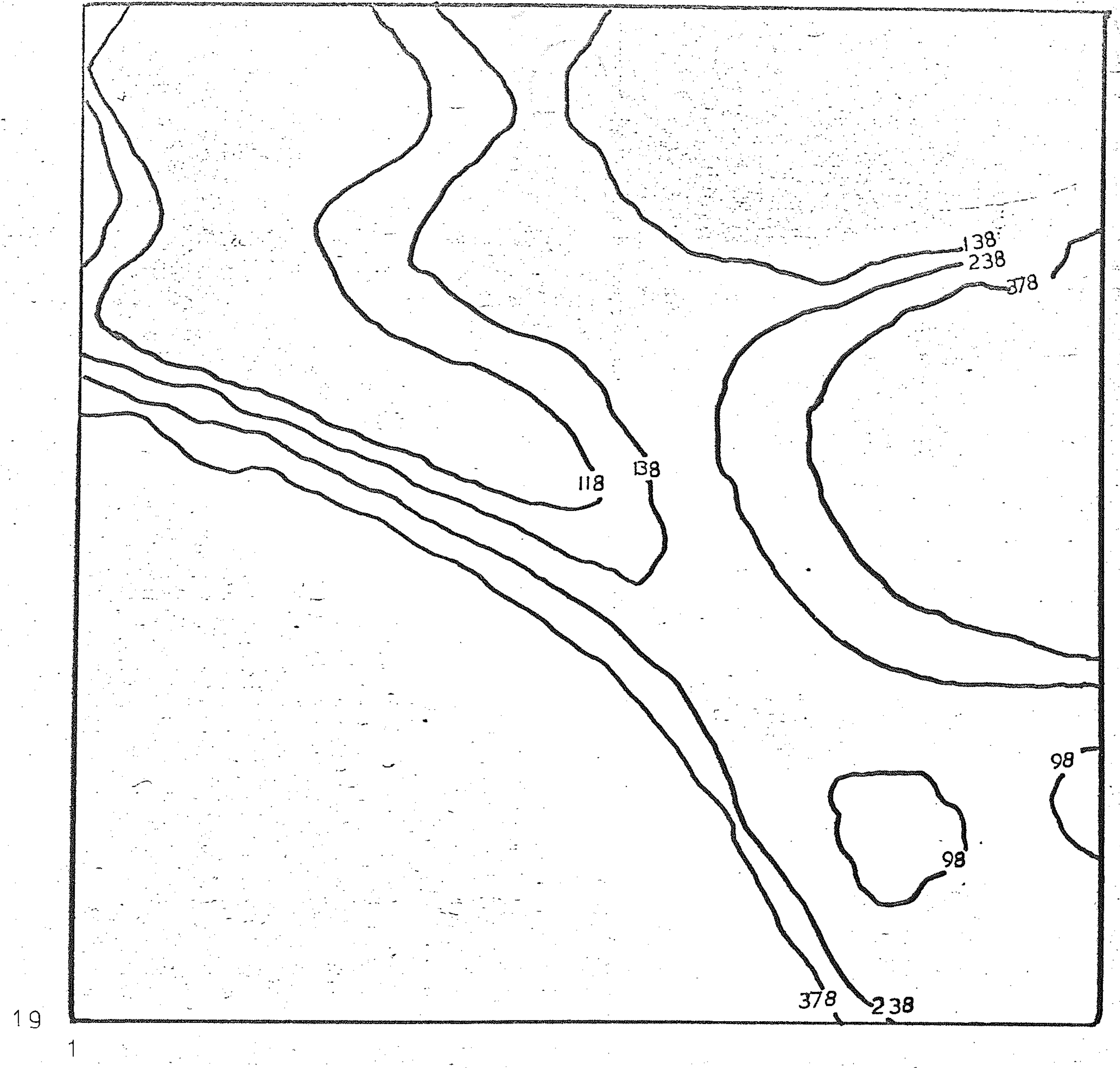


Fig. 90.Rb Southern Trend

U = 60
V = 90

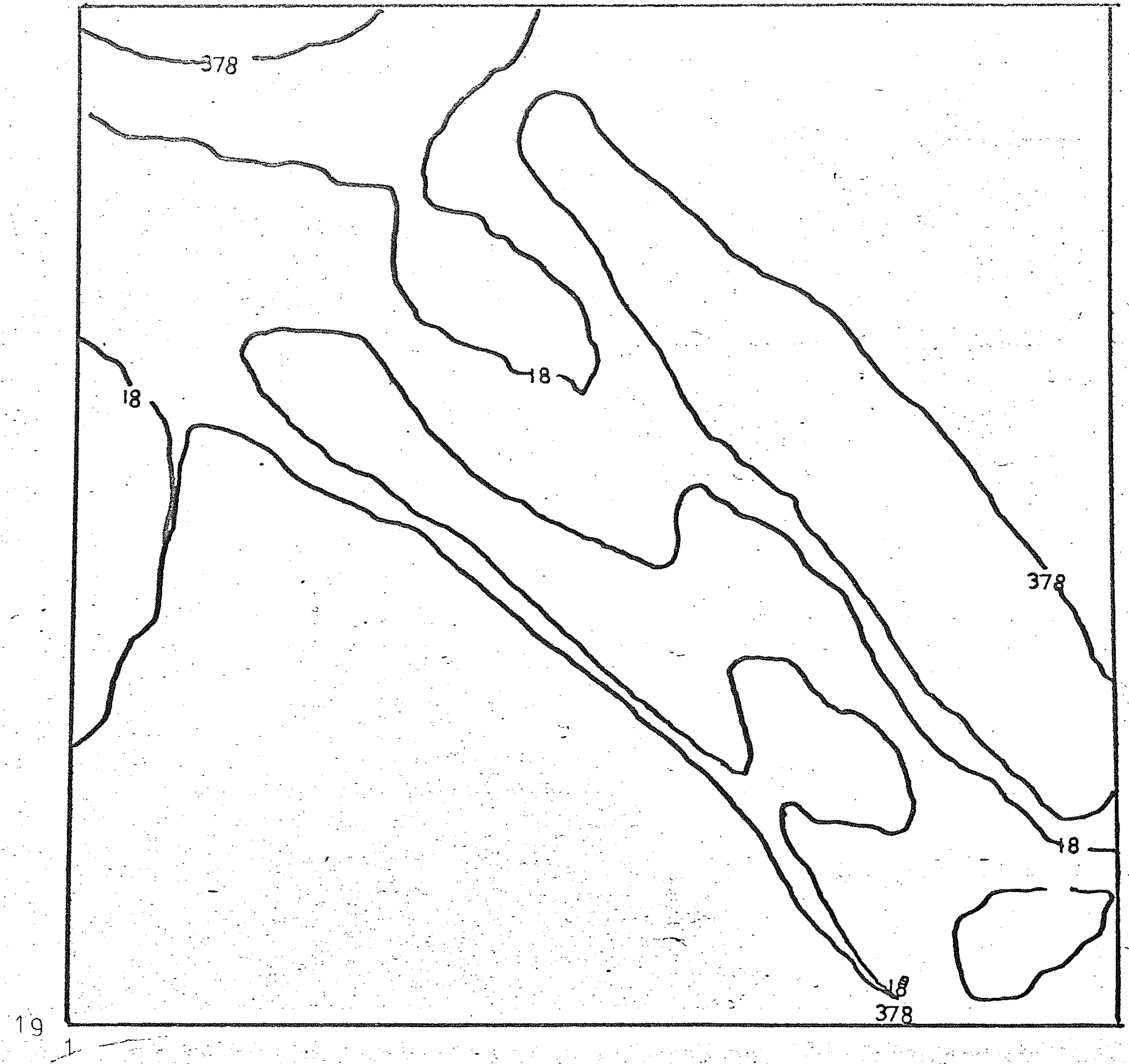


Fig. 91. Rb Southern A

Residuals

U = 60

V = 90

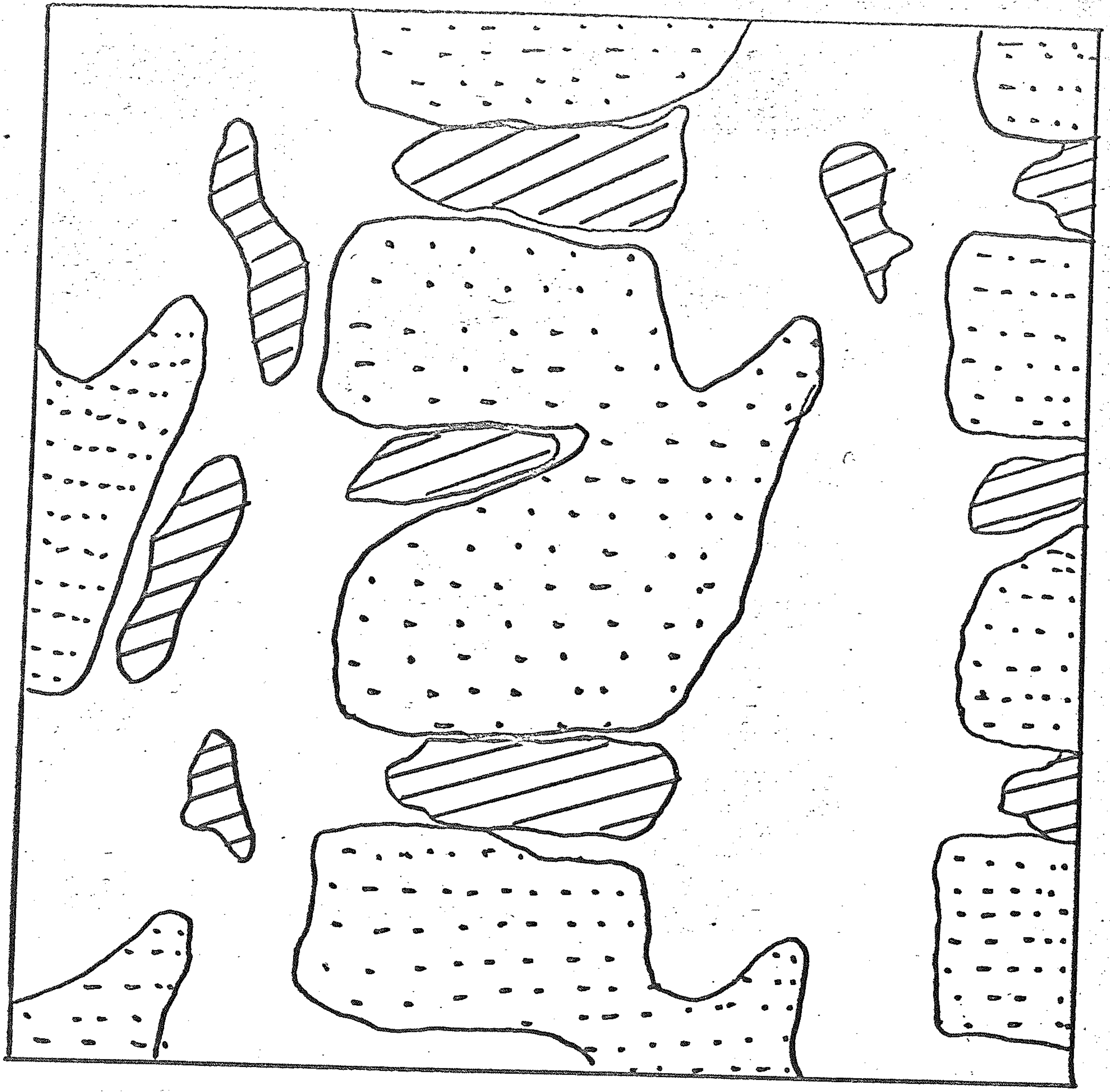


Fig. 92. Hg Northern Are
Trend

- High values
  (above 0.045)
- Low values
  (below 0.0)

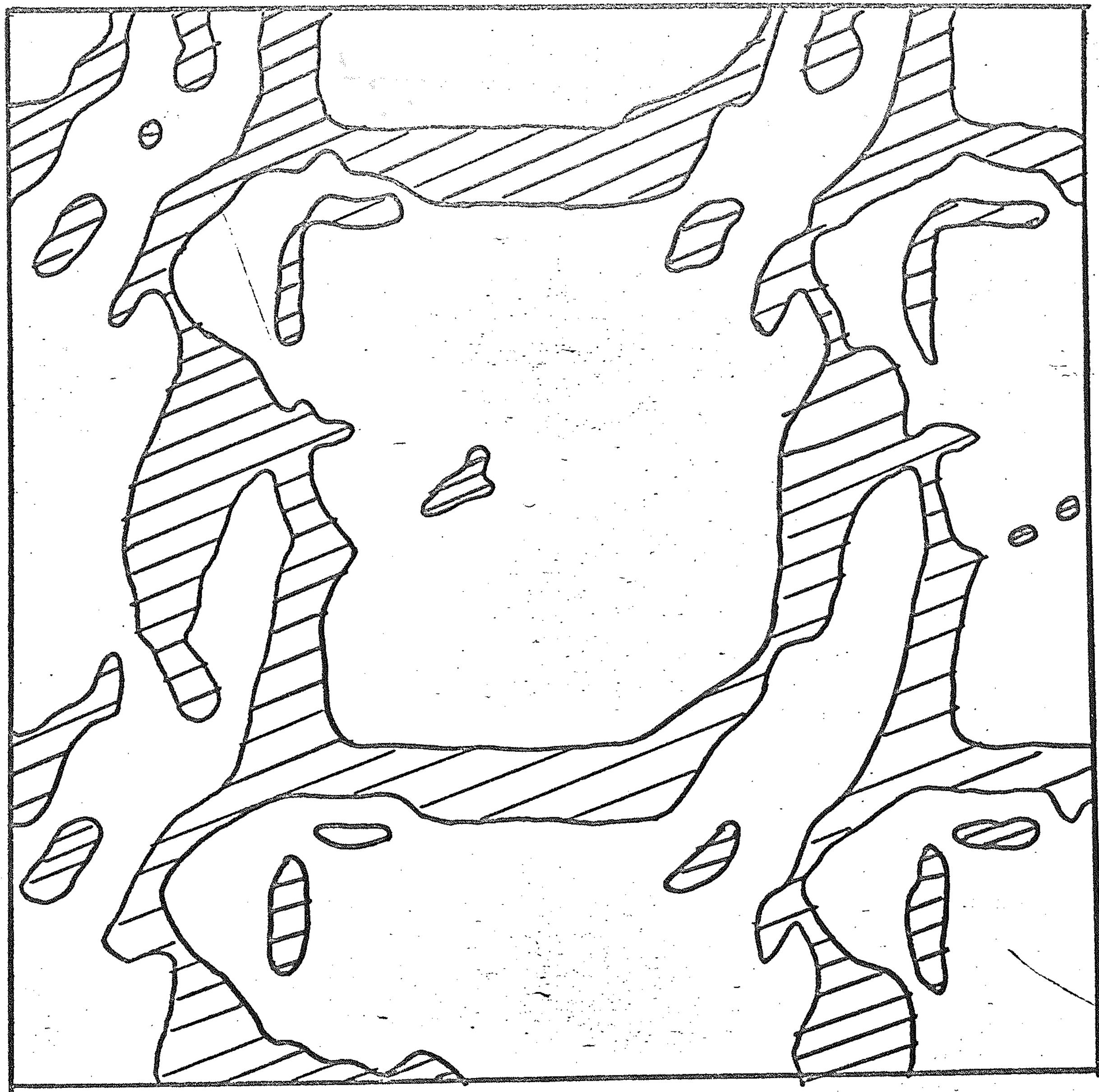


Fig. 93. Hg
Northern Area -
Residuals.

- High val

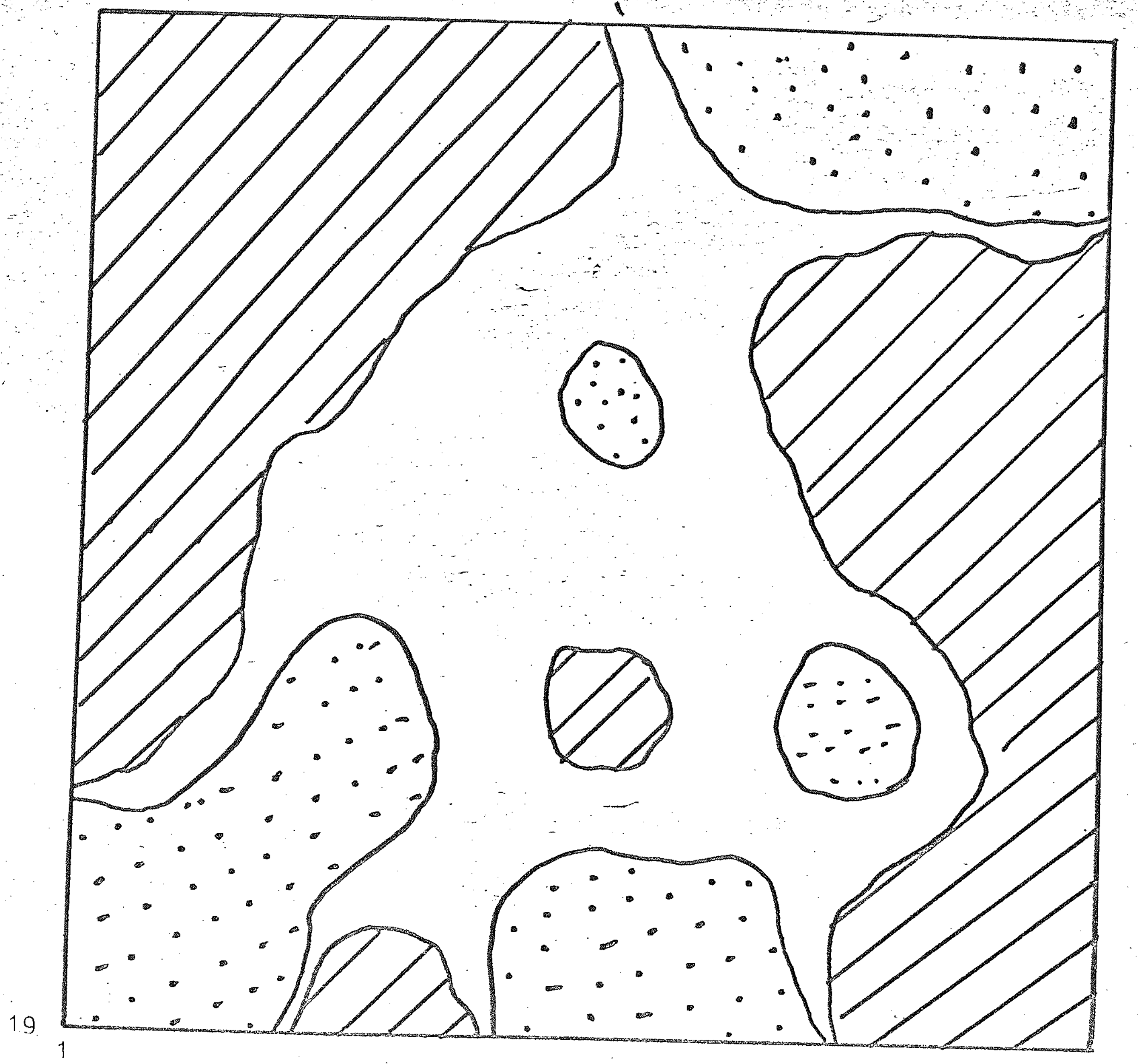


Fig. 94. Hg Southern Area Trend

- High values (above 0.072)
- Low values (below 0.0)

Fig. 95 Sr/Ba ratios.

Rock	Ba conc.	Sr conc.	Sr/Ba
GN	1500	150	0.100
GS	450-	70	0.15
CN	1500	125	0.083
CS	550	70	0.127
VN	1500	110	0.073
VS	550	65	0.118

CHAPTER 9.

DISCUSSION AND INTERPRETATION OF RESULTS.

9:1 PRELIMINARY EXAMINATION.

As a first step in the interpretation the analytical results were compared with the specimen field descriptions (Fig.29) to determine if there were any obvious groupings. This was done by checking the major and trace element concentrations for each rock type in each area against the field description. To assist this comparison the mean concentration of each element, in each rock type, in both the Northern and Southern Areas, was calculated (Fig.30). Only the Gamlan Rocks from the Southern Area showed any obvious groupings (Fig.31). Two groups were found:-

Group 1 - High SiO_2; Low Al_2O_3; Low Fe_2O_3;
These have low trace element concentrations compared with total averages (Fig.30), and all correspond with grit layers in the rock sequence. Thus these analyses can be taken to indicate the chemistry of these grit layers.

Group 2 - High Al_2O_3
These have high Zn and Ba concentrations compared with average values, and generally consist of shales and gritty shales. The fact that these shaley layers have high Ba and Zn will be used in later geochemical interpretations.

The remainder of the Gamlan Rocks in the Southern Area have a general chemical variation which cannot be readily interpreted.

A comparison was also made of Hg values with field description for each rock type. The Clogau Shales from both the Northern and Southern Areas are lithologically similar, and the intensity of weathering (visual field estimate) appears to have no correlation with their

Hg content. The weathered surface zones of these rocks probably have not lost Hg to any great extent. Results on the Vigra Rocks, from the Northern Area, indicate that the harder, siliceous shales contain less mercury than the other types. The same applied to the Gamlan Rocks from the Northern Area, where the more coarsely grained (gritty) members of the succession are associated with low Hg values. The Hg concentration in the rocks is thus inversely related to the hardness, or degree of silicification, of the host rocks.

9:2 GRAPHICAL ANALYSIS.

Frequency plots of elemental distributions were made for each of ten (10) elements for each rock type in both areas. A comparison was then made for the distributions in the rocks between the Northern and Southern Areas. (Figs.32 to 41), and this is summarised in Fig.42.

SiO_2 (Fig.32) has a more varied distribution in the Southern Area for all three rock types. This suggests that these rocks had a varied source of supply of sediment. Aluminium (Fig.33) has a similar distribution which suggests that the sediment supply for the Southern Area was either very varied, or that more than one supply source was present. Fe_2O_3 (Fig.34) has similar distributions in both areas but the high values vary with the rock type. This is interpreted to indicate that each different process of enrichment prevailed for each rock type.

Cu (Fig.35) has similar distributions in both the Northern and Southern Areas, except in the case of the Gamlan Rocks. The higher values were found in the South indicating that enrichment process occurred only in the Gamlan Rocks of the Southern Area.

Ni (Fig.36) shows the same distribution in both areas, although the higher values were found in the Southern Area. This indicates that some enrichment occurred there.

For Zn (Fig.37) the distributions are similar, but the Vigra and Gamlan Rocks have higher values in the Northern Area. This was taken to indicate that an enrichment of this metal occurred in this area.

Pb (Fig.38) has similar distributions in both areas, but it has fewer high values in the Gamlan Rocks of the Southern Area. In addition the higher values are present in the Northern Area compared with the Southern Area. This is taken to indicate that the Sr source of supply was close to or more intense in the Northern Area, or that more than one source of supply was present for that area.

The Hg distribution (Fig.40) consists of two basic parts; a lower bi-modal distribution, present in both the Northern and Southern Areas, which is the same for all rock types (including the igneous rocks); and a higher distribution present only in sedimentary rocks of the Southern Area. Because Hg behaves differently to the other elements it is discussed below in a separate section.

Ba (Fig.41) has a single narrow distribution in the Northern Area, with a higher median value than the wider distributions in the Southern Area. This indicates that the source of supply of Ba was closer to the Northern Area and that only one source of Ba was present. In the Southern Area the wider distribution with the lower median value may indicate that there was more than one source of supply. It may also indicate that this area was either further from the source or that the source was less intense than that for the Northern Area.

In general the above distributions can be taken to indicate that while various sources of supply were available to both areas, the Southern Area reflects the distribution of the Northern Area (in some instances on a reduced scale), but there are additional superimposed distributions. This initial analysis indicates that, in spite of the difference in sampling techniques used for the two areas, it is possible to distiguish high values or 'targets' in both areas. In addition it shows that the sampling frequency is sufficient to detect 'targets' of relatively immobile elements, such as Pb, assuming that high values are present as a result of local concentration processes.

9:3 COMPARISON WITH SHALE FROM THE OTHER AREAS.

To compare the rocks from this study with similar rock types studied by other authors the median value for each element was calculated (after Vine and Tourtelot, 1970). In the present work the median value was expressed as the centre of the class interval in which the 50th percentile occurred. (Figs.32 to 41 with summary Fig.42).

Because various workers (Gilby, 1968; Matley and Wilson, 1946) have stated that the most important rocks with regard to mineralisation in the area, are the Clogau Shales, described as 'black shales' they were compared with a number of average black shales (Fig.44).

Al_2O_3, Fe_2O_3, and Ba (the latter from the Northern Area only) all have higher values than reported for average shales. This is taken to indicate that more sediment was being supplied to the Clogau Shales than is normal for black shales. Copper tends to be lower than the average indicating that either less Cu was available,or that conditions for fixation of Cu did not exist. Another possibility is that Cu may have been released from the shales at a later date. Ni has a value within the range normal for black shales.

In the Northern Area, Pb has slightly higher values than average, but in the Southern Area it has appreciably higher values, indicating some form of enrichment.

Both Sr and Zn have values appreciably less than the average for black shales. Total carbon (see later discussion) has a lower median than the average. The above results make it clear that the Clogau Shales, commonly described as black shales, bear little chemical resemblance to black shales found in other parts of the world.

The Vigra Flags, and especially the Gamlan Flags, both contain black shale horizons, however no comparisons were made because the sampling was random and was not confined to any one facies in the formation. Although it is possible to separate out the black shales members by field descriptions it is likely that a bias would be introduced thus giving any results a very doubtful value.

9:4 ENRICHMENT.

To investigate the possible enrichment of some specimens with some elements, the enrichment index (after Vine and Tourtelot, 1970) was calculated for all rock types in both areas. The enrichment index was calculated by taking the minimum enrichment value to be the middle of the class interval above the class interval in which the 90th percentile falls. The enrichment index was computed for each rock type by adding the percentages of analyses for each element, in that rock type, which fall above the minimum enrichment value.

This procedure has the effect of defining which rock types show consistent extreme positive skewness to the element distributions. It is, in effect, a measure of 'the overall skewness' for one rock type. The average and median values and the minimum enrichment values for each rock type are listed in Fig.43. For each rock type percentage of samples above the minimum enrichment value is shown in Fig.45.

The first column, or Σ_{TOT}, represents the enrichment values for all of the elements. In each instance the Southern Area is found to be enriched, relative to the Northern one. The igneous rocks in both areas have a high degree of enrichment. The Vigra Flags show the highest degree of enrichment, followed by the Clogau Shales and finally the Gamlan Flags.

If trace metals only are used in the summation the Southern Area again shows a higher degree of enrichment than the Northern one. However, in the case of the

Clogau Shales and Gamlan Flags the difference between the two areas is much reduced. For the rock types the Vigra Flags show the greatest overall elemental enrichment, followed by the Gamlan Flags and then the Clogau Shales.

To examine the effect of metals introduced by sedimentary processes the sum of the enrichment of trace metals, minus the enrichment of mercury, was calculated (ΣTRACE-Hg). This shows reversals of order in the Clogau Shales and Gamlan Flags with the rocks of the Northern Area showing higher enrichments than those in the Southern one. The Vigra Flags again show a greater degree of enrichment in the Southern Area compared to that in the North.

To summarise, the rocks of the Southern Area have greater enrichment on a total element basis; however, if elements that are definitely associated with mineralisation are excluded (Si, Hg) then in the Southern Area the Vigra Flags have the highest enrichment values, and in the Northern Area the Clogau Shales and the Gamlan Flags have the highest enrichments.

It is concluded that the Clogau Shales and the Gamlan Flags behave in much the same way towards enrichment, either as a result of sedimentary or post depositional processes,or both. The Vigra Flags are enriched to a greater extent by both processes, especially in the Southern Area. In addition, the importance of the Clogau Shales as a centre of mineralisation (Gilby, 1968); Matley and Wilson, 1946) is brought into question. Whatever the answer it is clear that the trace element enrichment process is different in the Clogau Shales compared with the Vigra Flags.

9:5 MERCURY DISTRIBUTIONS.

The Hg distributions are basically bi-modal (Fig.40) in all areas with a third peak superimposed at high Hg values.

The two lower peaks for rocks of the Southern Area have no correlation with rock type. In the Northern Area the siliceous shales within the Vigra Flags, and the grits in the Gamlan Flags, contain less Hg than other members of the sequence.

The higher Hg values in the Gamlan Flags of the Southern Area (Fig.40) show no correlation with lithology. Both the shale and coarse grit members have high values. In the Vigra Flags high values occur only in the shale members; however there is an insufficient number of high values to allow a definite conclusion to be drawn. Similarly, in the Clogau Shales only one high value was detected. It should be noted that no high values were found in samples of igneous rocks from either area. The distributions of the low values in all rocks, including the igneous rocks, follows the same bi-modal pattern with peaks in identical places. This points strongly to the fact that the process by which Hg was introduced was similar for all rock types, irrespective of genesis or hardness. In addition, because the Hg distribution is similar in the igneous rocks the influx of Hg may have occurred some time after the igneous rocks had been emplaced.

Hg values for samples from the Gwynfynnydd Gold Mine are shown in Fig.46. Samples SG2, SG3, SG4, SG8(a) and SG8(b), all have normal Hg values, (i.e. within the bi-modal distribution). Sample SG1 is from a vein containing chalcopyrite. This has a high value as do samples SG5(a) and (b), which are altered shales. SG6 is from an igneous rock close to SG5 (Fig.20) and also has a high Hg value.

From this it is inferred that Hg is intimately associated with veining and is present in the vein materials. In addition high Hg values (including one at 1.3207 ppm - the highest recorded in the present work) are found in the desilicified country rocks around the veins. This may be the result of movement of Hg from the vein forming fluids into the porous country rocks. The high value in the adjacent igneous rock which has no apparent sign of alteration indicates that the Hg has moved independently of the 'toughness' of the rock. One sample, SFG, of soft fault gouge from a small fault, with less than 1cm between the fault surfaces in the Southern Area, had a high Hg value. No sign of either mineralisation in the fault plane or alteration of the surrounding country rocks could be seen. This is taken to indicate that Hg vapour was travelling along the fault plane and was retained by the fault gouge.

From the above information the following conclusions are drawn:-

a) The distribution of Hg is independent of the hardness of the rock. A suggestion is made that the factor controlling the deposition of Hg is related to the shale content of the country rock. A fine-grained shale retains more Hg than a more permeable grit.

b) Hg is closely associated with the major vein mineralisation in the Harlech Dome.

c) The lateral migration of Hg into the country rock from the major mineralisation phase is small, of the order of 20-30m.

d) Hg moved along all fractures, as well as those containing mineralisation.

e) Hg is not related to igneous intrusions except where they are close to centres of mineralisation, and then only to the same degree as the country rock.

f) The process of addition of Hg to all of the rocks is similar and produces the same peak (.01 - .03 ppm) in all rock types in both areas.

g) Two processes of Hg input are in operation, one to produce the low level distribution, and one to produce the higher values associated with mineralisation. These processes are discussed in Chapter 10.

In addition to the above conclusions further discussion of the chemistry is included in the section on statistics (9.7).

If the enrichment index for Hg alone is considered (Fig. 45) it can be shown that the Clogau Shales, in the Southern Area, have the highest degree of enrichment of all.

These conclusions, together with the fact that in terms of other elements, the Clogau Shales in the Southern Area have the lowest enrichment of other trace metals suggest that, assuming enrichment of Hg is due to the presence of mineralisation (b) above), Hg is a better indicator of mineralisation than any other element.

The Vigra Flags have about the same degree of Hg enrichment, in both areas, while the Gamlan Flags have virtually no enrichment.

9:6 IGNEOUS ROCKS.

Igneous rock types present in the Harlech Dome are a dolerite and a hornblende diorite (Gilby, 1968; Matley and Wilson, 1946). According to Gilby (1968) the latter rock type has sufficient quartz to allow it to be classified mineralogically as a dacite.

The distributions of SiO_2 and Al_2O_3 in the igneous rocks (Figs.32 and 33) are bi-modal. Examinations of individual analyses within this distribution distinguishes two groups of igneous rocks. These are shown in Fig.47. The rocks of Group 1 (Fig.47) are dolerites (Hatch and Wells, 1961). Rocks of Group 2 have a SiO_2 percentage lower than that quoted for a diorite - 68.72% (Hatch and Wells, 1961). It is possible that some SiO_2 may have been removed by 'post depositional changes' (Gilby, 1968). However it is more likely that the analyses represent the average composition for the acid member of the igneous suite in this area. Some of the specimens have higher SiO_2 values, but it was difficult to decide whether or not this is due to later silicification because some specimens contain growths of small secondary quartz crystals (Chapter 3).

It is likely that the classification used by Gilby (1968) and Matley and Wilson (1946) is misleading due to the difficulties of identification of mineral pseudomorphs in much altered rocks.

9:7 CORRELATION STATISTICS.

To compare the overall effect of mineralisation on the sedimentary rocks all chemical analyses from each area were submitted to correlation analysis. A comparison between the areas, with only co-efficients of correlation above 0.3 quoted, is shown in Fig.48; from this the following associations can be seen:-

> SiO_2 correlates with Ni in the Northern Area but is not correlated with any element in the Southern one.
>
> Al_2O_3 correlates with Fe_2O_3, Zn, and Ba in the Northern Area which may be a result of a detrital association (Chapter 7). In the Southern Area it correlates with Fe_2O_3 only, suggesting different processes occur in the two areas.
>
> Fe_2O_3 correlates in the Northern Area with Al_2O_3, Ni, and Zn, and with Al_2O_3 and Zn in the Southern one.
>
> Cu shows a correlation with Hg in the Northern Area.
>
> Ni correlates with SiO_2, Al_2O_3, and Fe_2O_3 in the Northern Area, but no correlation is present in the Southern Area.
>
> Zn correlates with Al_2O_3, Fe_2O_3, and Ba in the Northern Area, indicating a detrital association. In the Southern Area it correlates only with Fe_2O_3.
>
> Pb is correltated with Sr, Hg, and Ba in the Southern Area. This is thought to be the result of an association with mineralisation (Chapters 5 and 7).

Sr is associated with Pb in the Southern Area (see above).

Hg correlates with Cu in the Northern Area, and Pb in the Southern Area. This may represent two different occurrences of Hg.

Ba correlates with Al_2O_3 and Zn in the Northern Area, and Pb in the Southern Area. This indicates a detrital association in the North (Chapter 7) and an association with mineralisation in the South (Chapters 5 and 7).

It is concluded that the Northern and Southern Areas have a number of differences, especially in terms of elements related to mineralisation. Ba, Al_2O_3, and Hg have different associations in each area. In the Northern Area the association of Ba and Al_2O_3 is with detrital elements (Chapter 7), while in the South it is with elements related to mineralisation (Chapters 5 and 7).

Hg shows a fundamental difference in its associations, if Gilby's (1968) work is followed. In one area it is associated with an element (Cu) which was introduced by a high temperature type of mineralisation (Type 1). In the other areas it is associated with a lower temperature (Type 3) mineralisation (Pb) (Chapter 5).

9:8 COMPONENT AND FACTOR ANALYSIS.

Initially the analytical data was put through principal component analysis to determine the optimum number of components which would produce a significant reduction in the sum of squares variation. The data was then run through a factor analysis routine which ascribed all of the variance to the number of factors (from the component analysis) which produced a meaningful sum of squares reduction. All interpretation was done using factor analysis data because it produced a cleaner split of individual factor loadings (Appendix 7).

To abstract as much information as possible the data was sub-divided into individual rock types from the Northern and Southern Areas using field descriptions and geological maps (Matley and Wilson, 1946). The combined data for the sedimentary rocks for both the Northern and Southern Areas was run through the statistical programs. The data was then re-run through the programs, with each rock type for each area run as a separate group of data.

9:8:1 ALL ROCK TYPES COMBINED FOR NORTHERN AND SOUTHERN AREAS.

The sum of squares reduction for all the data from the sedimentary rocks of the Northern and Southern Areas are shown on Fig.49. The corresponding tables of principal components are shown, in abstract form, in Fig.50, only components with a value of above 0.3 are shown for the sake of clarity. This figure was arbitrarily chosen to show only high positive or negative associations. The first component in the Northern Area is relatively more important than the first component in the Southern Area (Fig.49) but beyond the second component each successive component has approximately the same effect. An arbitrary decision was made to include only the first 7 components in the varimax rotation (Appendix 7) because the last three components had relatively little effect. Factor analysis was therefore performed assuming that all of the variation was the result of only seven factors. The factor analysis is shown in Fig.51, only factor loadings above 0.3 being shown for clarity.

The factors are described below for the Northern and Southern Areas respectively:-

The Northern Area.

1st factor. SiO_2, Al_2O_3, Fe_2O_3, Ni, Zn, Pb, Ba.
This is a sedimentary factor from the associations of the major elements. The associations of Ni, Zn, Pb, and to a lesser extent Cu, indicates that some sedimentary enrichment has occurred in this area. This factor has a

strong influence indicating that the major cause of variation has a sedimentary origin.

2nd Factor. Fe_2O_3, Ni, Sr with lesser SiO_2 and Hg, negative (-ve) Ba.

The lack of association of Al_2O_3 and negative Ba, suggests that this is not a truly detrital factor (Chapter 7). The association of Sr and Hg is considered to be from a mixed carbonate/quartz vein-type mineralisation, possibly associated with some iron sulphide deposition. The association of Hg may, however, be due to this element being selectively concentrated by the factor, and therefore not associated with depositional processes. If this is the case then this factor could equally well be a detrital factor.

3rd Factor. SiO_2, -ve Cu, -ve Hg.

This factor probably represents the hard siliceous 'ringers', and shows up the silica-rich part of the succession. This is also suggested by the evidence described in Section 9:1.

4th Factor. SiO_2, Hg -ve Pb, -ve Sr.

This factor indicates a relationship between quartz and mercury, with no associated carbonates or other mineralisation.

5th Factor. SiO_2, Sr, Zn -ve Ba.

This shows a probable association of carbonate-quartz mineralisation, but without the presence of Ba. This lack of association of Ba with any mineralisation in this area ties in with the findings of Section 9:2 above, where Ba has a single narrow distribution.

6th Factor. SiO_2, Zn, Pb.

This factor probably represents Pb/Zn mineralisation in quartz veins, small quantities of which are found throughout the area.

7th Factor. Sr, Hg, -ve Cu, -ve Ni.

This association of Hg with Sr, and therefore probably with carbonate, without the presence of any metals, suggests that there is a further, non-mineralisation, mercury association.

In summary the major cause of element variation in the Northern Area appears to be sedimentary. Factors 1 and 3, and possibly Factor 2, are associated with the sediments indicating that mineralisation in this area is relatively minor (Fig.49). From the factor analysis the type of mineralisation found in this area is presumed to be a quartz/carbonate association with Zn, and a quartz association with Pb and Zn.

Hg has an association with sediments containing Fe and Ni, and with quartz and carbonates, rather than with base metal mineralisation. This leads to the idea that the distribution of Hg in the Northern Area is the result of non-mineralisation related processes. This is an important conclusion because most earlier authors have stated that the presence of Hg is indicative of mineralisation (Chapter 6). This apparent discrepancy can be resolved by taking either one of two differing view points;

(a) No mineralisation is present in this area, and the mercury was introduced independently, and distributed throughout the rock, the final concentration in the rock being related to the physical nature of the rock and its chemical composition.

(b) Mineralisation exists at depth, with the mercury permeating upwards and being distributed as above.

The Southern Area.

1st Factor. Zn, Pb, Sr, Hg, Ba.

This association is indicative of Pb/Zn mineralisation in carbonate gangue associated with Hg (Chapter 7). It is the major cause of elemental variation in the area (Fig.49). This is in agreement with the findings of Gilby (1968), who stated that the major mineralisation (Gilby's types 2 and 3) is a Pb/Zn association. The associations of Hg with this type of mineralisation, indicates that Hg was emplaced at a later stage during the mineralisation process (Chapters 5 and 7).

2nd Factor. SiO_2, Hg, -ve Al_2O_3, -ve Fe_2O_3, -ve Ni, -ve Zn.

This is the same association as Factor 4 in the Northern Area. It indicates that the same process occurred in both areas, but was more prominent in the South (sum of squares reduction of 18.59 cf 11.02 in the Northern Area, Fig.49).

3rd Factor. SiO_2, Al_2O_3, Ba, -ve Hg.

This factor is similar to Factor 1 in the Northern Area and represents the sedimentary geochemistry. The non-appearance of Pb and Zn in this area, as opposed to their appearance in Factor 1 in the Northern Area, is probably due to a "swamping" effect in which their predominant appearance in Factor 1 caused their association with Factor 3 to be much reduced.

4th Factor. Al_2O_3, Hg, -ve Zn.

This factor probably represents and association of Hg with vein wall rock alteration (Chapters 5 and 7 and Section 9:5 above) in which the Hg entered the porous, de-silicified and sericitised zone of the enclosing rocks.

5th Factor. SiO_2, Cu, Ni, -ve Al_2O_3, -ve Pb.

This factor may well represent the Type 1, high temperature mineralisation of Gilby (1968). The lack of association of Hg with this type of mineralisation suggests that Hg was only associated with the lower temperature, type 3, mineralisation (Chapter 7).

6th Factor. SiO_2, Cu, Zn, -ve Ni.

This probably represents the type 2 mineralisation of Gilby (1968), and again shows no association with Hg.

This again indicates that the Hg only occurred with, or is related to, the low temperature type 3 mineralisation (Chapters 5 and 7).

7th Factor. SiO_2, -ve Cu, -ve Ba.

This factor may represent the quartz, either in the 'ringers' as in Factor 3 in the Northern Area, or in quartz veins not associated with mineralisation.

In summary the major cause of variation (37.63%) in the Southern Area is mineralisation and related processes. The detrital factor only appears as factor 3 accounting for 13.22% of the variation. This compares with a detrital factor in the Northern Area which accounts for 28.23% of the variation (Fig.49). All the mineralisation types of Gilby (1968) are represented in the Southern Area.

Mercury is associated with the major, low temperature, late stage, type 3 mineralisation of Gilby (1968) but not with either of the higher temperature types. It is also associated with SiO_2, as in the Northern Area, but this factor has greater prominence in the Southern Area. Factor analysis of the combined sedimentary rock types of both the Northern and Southern Areas indicates a fundamental difference in the factors causing the most variation in element concentrations. In the Northern Area the predominant associations are sedimentary with a small contribution from mineralisation, while in the Southern Area the major contribution is from mineralisation-related factors. Hg is present in both areas but only shows strong associations with mineralisation in the Southern Area. In the Northern Area the association is with the sedimentary rocks. The interpretation is made here that the association of Hg in the Northern Area is purely the result of Hg being selectively absorbed by components of the rocks, with the source of mercury vapour originating in depth.

9:8:2 INDIVIDUAL ROCK TYPES FOR NORTHERN AND SOUTHERN AREAS.

The sum of squares reduction for the rock types treated separately from both the Northern and Southern Areas after component analysis is shown in Fig.52. Seven factors were used to describe all the variations but only 5 of these were used to describe the factors individually. This was because the last two factors gave little information and could not be interpreted with any degree of certainty. Significant factor scores were abstracted from the computer produced tables, and are shown in Figs.53 to 56). In general all factor scores above 0.3 are quoted.

1) Gamlan Flags - Northern Area (Fig.53).

Factor 1. Fe_2O_3, Cu, Hg, -ve Al_2O_3, -ve Zn, -ve Pb, -ve Sr, -ve Ba.

At first sight this factor appears to be related to the type 1 mineralisation of Gilby (1968), however the lack of association of SiO_2, negative Al_2O_3, and negative carbonate (Sr and Ba) associations indicate that it is more likely a detrital fraction associated with Fe and Cu rich layers, such as shales.

Factor 2. SiO_2, Zn, Pb, -ve Ai_2O_3, -ve Cu, -ve Ni, -ve Hg, -ve Ba.

This factor belongs to an association related to Pb/Zn vein mineralisation.

Factor 3. Ni, Zn, Pb, Ba, -ve Cu, -ve Hg.

The associations for this factor can either be detrital, or be with mineralisation. In the Northern Area, it is suggested, in Sections 9:1 and 9:8 (above), that Ba is only associated with detrital fraction and has only a single association in these rocks. Because this is the only factor involving a positive association of Ba in the Gamlan Rocks of the Northern Area, it is likely that this factor represents the detrital fraction.

Factor 4. SiO_2, Fe_2O_3, Ni, Pb.

This factor may either be a detrital or a mineralisation related factor.

Factor 5. SiO_2, Ni, -ve Fe_2O_3, -ve Pb, -ve Ba. This factor probably represents the very silica-rich members of the succession, comprising the hard, siliceous, layers present in the Gamlan Flags.

2) Gamlan Flags - Southern Area (Fig.53).

Factor 1. All the elements except SiO_2 show a negative association. SiO_2 shows an insignificant positive value. It is therefore assumed that this factor is related to a process or property of the rocks not described by the elements determined.

Factor 2. Al_2O_3, Fe_2O_3, Ni, Zn, Ba, -ve Sr. It is concluded that this association is a detrital factor, similar to Factor 3 for the Northern Area (Fig. 53).

Factor 3. SiO_2, Pb, Ba, -ve Fe_2O_3, -ve Cu, -ve Hg.

It is difficult to associate this factor with either sedimentary effects or post depositional alteration. The non-association of Hg suggests that it may be sedimentary (9:8:1), however it could also represent a mineralisation episode not associated with mercury enrichment.

Factor 4. SiO_2, Al_2O_3, Cu, Ni, -ve Sr.

This factor is a detrital factor because of the positive associations of SiO_2 and Al_2O_3.

Factor 5. SiO_2, Cu, Sr, -ve Ni.

This factor corresponds to the high temperature type 1 mineralisation of Gilby (1968) (Chapters 5 and 7).

The Gamlan Flags have a number of associations which are difficult to interpret. This is probably due to the variable nature of the rocks themselves (Chapter 2). Some clear sedimentary associations may be distinguished, and the overall impression is that sedimentary associations dominate the factor analysis. The lack of mineralisation related factors may result from either the limited mineralisation in the Gamlan, or the 'swamping' of mineralisation associations by the great sedimentary variations. Hg only shows a clear association with Factor 1 in the Northern Area. Because this factor appears on balance to be detrital, most of the Hg in the Northern Area is thus related to the detrital material represented by Factor 1. In the Southern area no such relationship of Hg was found. This raises the question as to the relationship of the high Hg values found in the Gamlan rock in this area (Fig.40). It is suggested that the Hg in the Gamlan Flags is associated by means of a physical rather than a direct chemical connection. This connection may be a surface absorption, with weak co-valent bond formation, rather than a definite chemical association with a particular element. This means that the Hg will be related to a particular component in the rock, e.g. clay minerals or carbon. This conclusion is important because it raises the question as to whether the associations of Hg, found in other rock types, are related to mineralisation, or are directly related to the composition of the host rock.

3) Clogau Shales - Northern Area (Fig.54).

Factor 1. SiO_2, Cu, Hg, -ve Al_2O_3, -ve Ni, -ve Pb, -ve Sr, -ve Ba.

This association indicates the Cu mineralisation (Type 1 mineralisation of Gilby, 1968) (Chapter 7).

Factor 2. Cu, Pb, -ve Al_2O_3, -ve Fe_2O_3, -ve Ni, -ve Hg, -ve Ba.

The association of Cu and Pb, without the influence of SiO_2 and Al_2O_3, is believed to be a detrital association, and may explain the higher enrichment index of the rocks in this area (Section 9:4).

Factor 3. SiO_2, Zn, -ve Fe_2O_3, -ve Cu, -ve Pb, -ve Hg.

The association of SiO_2 and Zn, with the negative association of Pb, may either indicate a type of mineralisation (without associated Hg) or it may be detrital. It is believed that it is associated with the mineralisation of the type shown by Factor 2 in the Gamlan Flags of the Northern Area.

Factor 4. SiO_2, Fe_2O_3, Ni, Zn, Hg, -ve Cu, -ve Ba.

This association is likely to be sedimentary despite the association with Hg. Hg, as stated above, can be associated with a particular detrital fraction.

Factor 5. SiO_2, Al_2O_3, Ni, Hg, -ve Fe_2O_3, -ve Zn.

This factor is also sedimentary in origin (association of SiO_2 and Al_2O_3) (Chapter 7).

4) Clogau Shales - Southern Area (Fig.54).

Factor 1. Cu, Hg, -ve Al_2O_3, -ve Fe_2O_3, -ve Ni, -ve Zn, -ve Pb, -ve Sr, -ve Ba.

This association is very like Factor 1 for these rocks in the Northern Area, but without the association of SiO_2. This factor must, from the above evidence and from Chapters 5 and 7, be ascribed to the copper mineralisation.

Factor 2. SiO_2, Pb, Sr, Hg, Ba, -ve Al_2O_3, -ve Fe_2O_3, -ve Ni.

This factor is clearly associated with the type 3 mineralisation (Chapters 3 and 7) of Gilbey (1968). It is in vein materials rather than in the country rock and has no positive Al_2O_3, which would be associated with wall rock alteration (sericitisation). This corresponds to field observations (Chapters 2, 5 and 7), in which very little wall rock alteration is present with the veins cutting the Clogau Shales.

Factor 3. Fe_2O_3, Cu, Hg.

This factor like Factor 1, appears to be associated with the high temperature type of copper mineralisation (Gilbey's 1968) Type 1, (Chapters 5 and 7).

Factor 4. SiO_2, Cu, Sr, Ba, -ve Hg.

This factor has associations which are related to carbonate type mineralisation. It may represent a period in which only carbonate/quartz veins were formed. The lack of an Hg association appears to indicate that this veining did not occur at the time of Hg input. The vein material was probably not a good host rock for later Hg.

Factor 5. SiO_2, Ni, Hg, -ve Al_2O_3, -ve Cu, -ve Pb, -ve Sr.

This association is similar to that of Hg with quartz, as described in Section 9:8:1 as representing a fracture type association with Hg entering fractures and permeating into the rocks.

For the Clogau Shales the first factor for each area appears to indicate that there is an association of Cu and Hg, which is in opposition to the evidence put forward in Section 9:8:1. This may be the result of a 'swamping' effect in which the association, being a relatively minor cause of variation when compared with the Gamlan Flags, which has a large variation caused by sedimentary factors, is obscured by the larger variation in other rock types. This means that Hg is associated with both Type 1 and Type 3 mineralisation (Gilby, 1968; Chapters 5 and 7). It is likely that the association would be present in the Clogau Shales because Hg is strongly associated with the Clogau Shales (four out of five factors in the Southern Area have a strong positive association with Hg).

For the second factors the difference between the two areas is clear. In the Northern Area this factor is detrital, while in the Southern Area it is associated with the major mineralisation of the area (Gilby's (1968) Type 3 (Section 9:8:1)). The other factors further indicate this difference of the remaining three factors; in the Southern Area, all are related to mineralisation, but in the Northern Area two are related to sedimentary processes.

Al_2O_3 shows few associations in the Clogau Shales probably because little wall rock alteration is present, and the only likely association is with sedimentary factors. Only in Factor 5, for the Northern Area, is there any sedimentary associations. This is of interest because no factor in the Southern Area shows any positive association of Al_2O_3. From this it is concluded that Al_2O_3 does not vary with any of the elements analysed. This is surprising because of the detrital nature of the Clogau Shales.

5) Vigra Flags - Northern Area (Fig.55).

Factor 1. SiO_2, Al_2O_3, Fe_2O_3, Ni, Zn, Pb, Ba.

This factor is ascribed to the detrital fraction of the sediments (Chapter 7).

Factor 2. Al_2O_3, Ni, Sr, -ve Fe_2O_3, -ve Cu, -ve Pb.
This factor is probably associated with the detrital fraction, but may represent a chemically different rock type within the succession.

Factor 3. Al_2O_3, Fe_2O_3, Ni, Pb, -ve Hg.

It is likely that this association is from the detrital fraction of the sediments (Chapter 7). The negative Hg indicates that this fraction is not a good host for Hg.

Factor 4. SiO_2, -ve Fe_2O_3, -ve Sr, -ve Hg.

This factor is associated with the quartz-rich part of the rocks. Whether this represents the quartz veins, or the hard 'ringers' is difficult to determine. The negative association of Hg does not distinguish quartz veins from 'ringers'.

Factor 5. Pb, Se, -ve Cu, -ve Ni, -ve Hg.

This factor probably represents carbonate veins with no Hg. It is impossible to state whether or not these veins are related to the low temperature type 3 mineralisation of Gilby (1968).

6) Vigra Flags - Southern Area (Fig.55).

Factor 1. Al_2O_3, Cu, -ve Fe_2O_3, -ve Zn, -ve Pb, -ve Hg.

The association of Cu with Al_2O_3 is indicative of wall rock alteration (Chapter 7). However, the lack of association with other elements related to mineralisation indicates a possible detrital association. It was not possible to assign this factor to either process.

Factor 2. Al_2O_3, Fe_2O_3, Cu, Ni, -ve Pb, -ve Sr, -ve Hg, -ve Ba.

From the association it is likely that this factor is associated with the detrital fraction in the rocks.

Factor 3. SiO_2, Fe_2O_3, Pb, Hg, -ve Al_2O_3, -ve Sr, -ve Ba.

This association belongs to the Type 3 mineralisation of Gilby (1968) (Chapter 7).

Factor 4. SiO_2, Al_2O_3, Pb, Hg, Ba, -ve Cu.

This factor is associated with mineralisation. The positive association of SiO_2 and Al_2O_3 means that the situation is not simple wall rock alteration. Al_2O_3 increases and SiO_2 decreases; However in veining the reverse is true. The association of Pb, Hg and Ba indicates that the factor is directly related to mineralisation. A possible explanation of the factor is that there is an intimate association of small scale veining and sericitisation producing the overall effect.

Factor 5. Cu, Ba, -ve Ni.

This association is probably related to the high temperature, Type 1, mineralisation of Gilby (1968) (Chapter 7).

The difference between the Northern and Southern Areas is shown by the above factors. The factors in the Northern Area are predominantly sedimentary, with some minor veining; however in the Southern Area they are predominantly related to mineralisation.

Hg has an association with the mineralisation in this rock type.

7) Igneous Rocks (Fig.56).

Very little information is obtained from statistical analysis of the data for the igneous rocks. In the Northern Area the only positive associations found are between Fe_2O_3 and Ba in Factor 4. This may represent an association resulting from carbonate mineralisation.

In the Southern Area Factor 2 shows an association of Al_2O_3, Pb, Sr and Ba with negative Ni. This is interpreted to represent an association of mineralisation with sericitisation. Factor 3 has an association of SiO_2, Zn, and Ba, also a mineralisation association. Factor 5 shows an association of SiO_2 and Hg, with negative Ba. This represents a fracture-type infilling mineralisation association.

The only associations of use in the igneous rocks are those associated with mineralisation. Hg is not associated with wall rock alteration and is present in a fracture-type setting. In view of the role played by the igneous rocks in opening fractures etc. to facilitate veining (Andrew, 1910; Matley and Wilson, 1946; Gilby, 1968), this would indicate that all the Hg was emplaced after the igneous rocks. Further the lack of any Hg values in the igneous rock studied (Section 9:2) means that the only mercury present belongs to the low level bi-modal distributions (Fig.40). This indicates that the igneous rocks have behaved in exactly the same way as the surrounding country rocks to the low level Hg. They have not accepted any high Hg values. This means that the igneous intrusions were not as important as the country rocks in the mineralisation process because there is no evidence of reaction (high Hg values) with the mineralising fluids.

9:8:3 SUMMARY OF THE FACTOR ANALYSIS FOR INDIVIDUAL ROCK TYPES.

Each factor for each area was tabulated and recurrent factors extracted. Four groups of factors were found, and these are shown in Figs.57, 58, 59 and 60.

1) Sedimentary Factors (Fig.57).

The association of SiO_2, Al_2O_3, Fe_2O_3 and Ba determines the sedimentary nature of the factor (Chapter 7). Ni is present in all the sedimentary factors indicating its presence is limited to sedimentation. This is in agreement with the findings of Vine (1966). It is worth noting that Vine (1966) reports that Ni is not concentrated in fresh water. Ni is only enriched in the Gamlan Rocks of the Southern Area (Section 9:4, and Figs.36 and 45). It is inferred that a somewhat restricted circulation may have occurred during deposition of the Clogau Shales and the Vigra Flags leading to decreased salinity. In addition Ni does not have an association with any of the major factor groupings. After Ni, Al_2O_3 and Fe_2O_3 are the most common sedimentary factors; followed by SiO_2 (Fig.57). Zn and Pb have associations with this group, but Ba has fewer associations and Cu and Sr have little association. The lack of association of Cu with the major sedimentary factor group indicates that either Cu was absent at the time of sedimentation or that this element is associated with another factor group. Because no enrichment of Cu is found (Section 9:4) it is postulated that either Cu was not available at the time of deposition, or that conditions were not suitable for the entrainment of Cu in the sediment. It was suggested, by Vine (1966), that Cu correlates strongly with carbon. As carbon is abundant in the shaley parts of the succession (Chapter 2) it is suggested that conditions there were favourable for the deposition of Cu. Because of this it is inferred that Cu was not readily available during sedimentation.

Hg has no association with the sedimentary factors. This indicates that it is not of sedimentary origin.

2) Major Mineralisation Factors (Fig.58).

These factors show associations of Pb and Hg with Ba and

SiO_2, and to a lesser extent, Sr. They indicate a low temperature mineralisation with quartz and carbonates representing the Type 3 mineralisation of Gilby (1968) (Chapters 5 and 7). To determine the distribution of the major mineralisations the individual factor scores (above 0.5) for the relevant factors (Fig.58) were plotted on the sampling grid for the Southern Area (Fig. 61). When compared with a plot of factor 1 for all rocks of the Southern Area (Fig.51), the extent of the mineralisation was seen to be limited to the Southern Area of the grid around two main centres; those of St. David's Hill and Y-Vigra. This difference is explained by the fact that the Gamlan Rocks, when treated individually do not have any factors related to mineralisation of this type. This suggests that the Gamlan Rocks, showing high factor scores in Fig.62, reflect a very weak association which is 'swamped' by the other factors in these rocks when taken in isolation (Fig.61). The association of this factor with two definite areas is in keeping with Gilby's (1968) work, in which he stated that this type of mineralisation is confined to certain definite areas, associated with major fractures.

The strong association of Pb and Hg in this factor indicates that the presence of Hg can be used as an indicator for this type of mineralisation thus reinforcing the ideas put forward in Section 9:5. From this factor it also can be shown that the major Pb mineralisation (Type 3) is present only in the Southern Area of the Harlech Dome.

3) Copper (Cu) Mineralisation (Fig.60).

This mineralisation is indicated by an association of SiO_2, Cu and Ni in factors for the rocks of the Southern Area taken as a whole (Fig.51). It corresponds to the high temperature type of Gilby (1968). It is noticeable that the combined factor analysis for all of the rock types for the Southern Area does not show an association of Hg. However, where individual rock types are analysed for both Northern and Southern Areas separately, an association with Hg is found (Fig.59). To resolve this difficulty in the Southern Area, the individual factor scores (above 0.5) for the combined rock types, the individual rock type showing an association with Hg, and the individual rock types not showing an association with Hg were plotted on the sampling grid (Figs. 63, 64 and 65). From these plots is seen that the Cu mineralisation, shown by factor analysis of the combined rock types for the Southern Area, falls in a different area to the plots of the Cu and Hg factors for the individual rock types. This thus indicates an essential difference between the factors.

A study of the positions of the high factor scores, for the Cu/Hg association (Fig.65),indicates that they occur around the area of the St. David's Mine. The associations of SiO_2, Cu, and Sr plot in a different position away from the areas of mineralisation (Fig.64). Neither of these correspond to the combined plot (Fig.63). As a further aid the field descriptions of the rocks, with high factor scores in each of the relevant factors were examined (Fig.66). From this it was seen that the factor for the combined rocks (55 in Fig.66) includes a high proportion of rocks that have been affected by mineralisation. Individual rock factors do not show any relation to obviously mineralised specimens.

It is concluded that two episodes of mineralisation involving Cu are present. The first is indicated by factors SV5 in Fig.59 (plotted in Fig.64). Hg is not related, and these factors approximate in distribution to the combined rock factor (Fig.63). This is probably related to a small scale mineralisation which is present over the whole area of the Harlech Dome. The second episode is indicated by factors NC1, SC1, and SC3 (Fig.59), and plotted in Fig. 65. These factors are grouped around the two main areas of mineralisation; St. David's Hill and Y-Vigra, and are probably related to the major vein mineralisation in the area (Andrew, 1910; Matley and Wilson, 1946; Gilby, 1968).

4) Hg and SiO_2 Factor.

This factor is present in both the Northern and Southern Areas when all rock types are considered together. In addition it is present in the Clogau Shales of the Southern Area (Fig.60), as shown by plotting samples with high factor scores (above 0.5) on the sampling grid (Figs. 67 and 68). The distribution of points in the Northern Area follows the line of major faulting. In the Southern Area no such correlation is obvious, possibly because of the complexity of the faulting.

If the field descriptions of the rocks, plotted in Figs. 67 and 68, are compared (Fig.69) no difference can be seen between those from either the Northern or the Southern Areas. In both areas shales, grits and igneous rocks are included in this factor. This shows that it is the result of a post-depositional process. In addition, obviously mineralised samples eg sample 01230 from exposures near to that from which a sample having a high factor score in factor 5 was taken, have a negative score in this factor. This indicates that the factor is not related to mineralisation. It is suggested that this factor indicates a relationship between SiO_2 and Hg, and the fracture zones.

The SiO_2 is present in the form of quartz in a late stage deposit associated with tensional fracturing.

5) SiO_2 Factor.

A number of factors show only SiO_2 as being important (Fig.70). Scores for these factors, in both the Northern and Southern Areas, are plotted as the sample grids (Figs. 71 and 72). The orientation of the points, especially those in the Northern Area, is linear and is interpreted as being associated with faulting. Since few samples have any obvious quartz veins it is suggested that enrichment of the whole rock with SiO_2 has occurred. This is consistent with evidence from thin sections examination where existing quartzes in the sediment are seen to have grown. Also quartz grains are found which have grown in some of the ignecus rocks (Chapters 2 and 3). This factor differs from the previous one, involving SiO_2 and Hg, in that the SiO_2 and Hg factor is more widespread and is not as regular. This suggests a different mechanism for the process causing the factors. Because the SiO_2 factor is more regular, and appears to be related to fractures, it is likely that the process producing this factor operated over a limited range around major fractures. It is believed that low temperature solutions containing quartz passed along fractures and moved from there into the country rocks. Since the solubility of quartz increases rapidly above ambient temperature (Helgeson and Garrels, 1968) this factor may be the result of a very late stage process. This is believed to have been the last process to occur in the area.

9:8:4 FACTOR ANALYSIS INCLUDING CO_2.

CO_2 was determined only on a small number of randomly selected rock samples (Chapter 7). Because of this the initial factor analysis was done without the inclusion of CO_2. Samples with CO_2 analyses were run separately. These samples were statistically analysed in the same way as all others, with an initial analysis for all the rocks of each area, followed by analyses for individual rock types in each area.

The analysis for individual rock types did not reveal any useful information because of the small number of samples involved (55). The results were not used because of the danger of introducing spurious results.

The sums of squares reduction for both the Northern and Southern Areas are shown in Figs.73 and 74. Seven factors were included in the analysis and all factors with loadings above 0.2 are listed in Figs.75 and 76. The rocks of the Northern Area have associations of CO_2 with Ni and Ba in Factor 7, which accounts for very little of the variation. This association is a carbonate association, the Ni indicating that it is probably a detrital carbonate (Section 9:8:3). No associations are shown by data from the Southern Area. It is concluded that either CO_2 shows a lack of association with any of the elements determined, or that the analysis does not represent the underlying factors. Comparison with factors previously determined for all of the rocks from each area (Fig.51) indicates that the two sets of analyses produce different results. This is to be expected in an area of such variation where a large number of samples must be analysed to give a true picture. This is clearly not true in the case of the CO_2 analysis. In addition the analysis does not distinguish between organic carbon and carbonate carbon but produces an analytical result which is a sum of the two. In factor analysis this will not show up in a factor associated with either pure organic carbon, or pure carbonate, until all of the variation due to factors which contain a proportion of each have been removed, i.e. at the higher factor numbers. This type of CO_2 analysis thus cannot be included in factor analysis.

9:9:1 GRAPHICAL AND STATISTICAL ANALYSIS OF THE GAMLAN FLAGS OF THE SOUTHERN AREA.

The Gamlan Flags have a great deal of variation (Section 9:8). Because of this XRF analysis for a number of elements was carried out on 34 randomly selected samples of these rocks (Chapter 7). The results were plotted on frequency diagrams (Figs.77 and 78), and means and standard deviations are given in Fig.29.

The oxides MgO, CaO, Na_2O, P_2O_5 and the element S, show a marked positive skewness (Figs.77 and 78), which is reflected in the enrichment values shown in Fig.80. All other elements have a normal distribution (Fig.79) except for Th which has a negative skewness. The elements and oxides which show the greater enrichment, i.e. Na_2O, CaO, P_2O_5, and S, are related to the carbonate mineralisation suite of elements. Comparing this with the enrichment values for the other elements determined (Fig.45), Ni, Pb, and Sr show high enrichments further confining the relation to mineralisation (Chapter 7). The analyses were then run through a component analysis program to produce sums of squares reductions (Fig.82). Factor analysis was then performed assigning all of the variation to seven factors. Factor loadings above 0.25 are shown in Fig.82.

Factor 1. SiO_2, Al_2O_3, S, Rb, Th, -ve MnO_2, -ve CaO, -ve Na_2O, -ve Pb, -ve Hg, -ve Cr, -ve Ce, -ve La.

It is likely that this association represents one of the detrital fractions of the Gamlan Rocks because Th, in the present context, is a detrital element (Vine and Tourtelot, 1970). The association of S is interesting in this context as the sulphide minerals occur in the shale layers (Chapter 2). This is interpreted to mean that this factor is associated with shale horizons in the Gamlan Rocks. The negative associations therefore indicate which elements are not associated with these shales.

Factor 2. CaO, -ve Al_2O_3, -ve TiO_2, -ve K_2O, -ve Ce, -ve Y , -ve Rb, -ve Th.

This factor probably represents a pure calcite association because no other elements are positively associated.

Factor 3. Al_2O_3, TiO_2, K_2O, -ve Y , -ve Rb, -ve Th.

This factor is associated with the detrital fraction, because of the TiO_2 and K_2O (Vine, 1966). The negative association of Y , Rb and Th, indicates that, rather than being deposited as a precipitate, the deposit is more likely to have formed from a particular material, because these three elements are associated with detrital deposition (Vine, 1966).

Factor 4. Al_2O_3, Fe_2O_3, TiO_2, CaO, Na_2O, Cu, Ni, Pb, Sr.

This factor appears at first sight to be related to the mineralisation; however the lack of association of S suggests that it is a sedimentary factor. The association of Al_2O_3 and Fe_2O_3 indicates an association with the clay fraction of the sediments. It is concluded that there is some enrichment of the sediment with the metals Cu, Ni, Zn, and Pb.

Factor 5. Pb, Ba, -ve P_2O_5, -ve Cu, -ve Hg.

Pb mineralisation associated with some Ba has produced this factor. The lack of association with CaO indicates that calcite was not part of the mineralisation.

Factor 6. Na_2O, Pb, -ve Fe_2O_3.

No clear cause can be related to this factor.

Factor 7. P_2O_5, Sr, Ba, -ve Fe_2O_3.

A carbonate association, other than that associated with calcite, is ascribed to this factor.

In general much of the variation is believed to be the result of sedimentary factors. For trace metals the lack of association of S and CaO is of interest. That of S may be the result of a 'swamping' effect by other factors. Such an effect would completely mask the relatively minor variation of the metals with S by the large sums of squares reductions produced by other factors. The non-association of CaO with the metals, and its lone appearance in Factor 2, indicates that two separate occurrences of carbonates are present. The first is with Ba and Sr, representing the carbonates in mineralisation. The second is with CaO in calcite included in the sediments as a precipitate (Factor 2). A slight association of CaO with Ba, Sr, and metals would be masked by the high association it has in Factor 2.

The overall result of this part of the study is similar to that described in Section 9:8, in that it is difficult to obtain clear individual factors because of the large amount of variations in the Gamlan rocks. This emphasises the point that where a geochemical survey is to be carried out in areas of varied geology, the analysis of a few carefully selected elements produces more useful information than a complete analysis in which a large number of elements are involved.

9:9:2 TREND ANALYSIS.

Because of the rapid lithological variation in the Gamlan Flags, little information can be obtained from detailed analysis. An attempt to smooth out the variation, and produce an overall view of the sedimentary conditions, was done by putting selected elements from the Southern Area through the program FOURFIT. This produced a third degree surface, and a residual map. The elements Sr, Rb, Yt, and Th were selected so that as little association as possible with mineralisation was likely.

Initial wavelengths were set to lie within the grid boundaries, and the program was set to search for the best fit on the third degree trend (Appendix 8). The sum of squares contribution produced by each trend is shown in Fig.83. The output maps were contoured by hand to produce the trend and residual maps (Figs.84 to 91).

The trend maps have two types of trend. The first type, including Th, consists of a series of Th highs arranged along the area investigated. The second type, including Rb, Sr and Y , consists of a basin elongated NNW-SSE.

Trend 1 consists of a series of highs in the Gamlan Flags, and in the Clogau and Vigra Shales. The best fit produced with reference to the residual map (Fig.85) is in the area of the Gamlan Flags. The sum of squares contribution of 41.95% indicates that this is a real trend (Chapter 6).

The trend therefore indicates that a local concentration of Th is present in certain areas. Geochemically Th generally has sedimentary associations. It is precipitated from solution only at low pH values because of the very high ionic potential of its 4+ ion. From the concept of the basins of deposition in the area (Fig.22) (Price, 1963), it is believed that the high Th values pick out areas in the basin which had a low pH. This is further supported by the correlation coefficient of Th on CaO being - .508, and that, in the factor analysis, Th is not associated with CaO and has a negative association with it in Factor 2. The highs in Fig.84 thus indicate small areas of relatively high pH which were likely to have been associated with reducing conditions. In the area around St. David's Hill a definite elongated low in the Th trend is associated with a major fault (Fig.84, sampling grid ref.16, 17). Examination of the residual map (Fig.85), indicates that the residuals are low in this area, and therefore the effect is real. From this it would seem that Th is an indicator of major faultings in this area.

Trend 2 is elongated with the same pattern for each element (Figs.86-91). The sums of squares contributions (Fig.83) indicate that the trends are significant, and comparison with the residuals indicates that the major features of the trends are real (Chapter 6). Geochemically in this area Rb, Sr and Y are all associated with the clay fraction of sediments (Vine, 1966; Vine and Tourtelot, 1970) (Chapter 7 and 9:8). It is noticeable that these trends cut across the geological boundaries between the Gamlan Flags, the Clogau Shales, and the Vigra Flags. The fact that this is a real effect, and not caused by a lineation in the data extending a trend beyond its limits, is proved by the residual maps. It is further supported by the Th map (Fig.84), which indicates that a change in pattern (around the fault zone, sampling grid ref. 16, 17) even at the end of an established trend line, will produce a change in the computed pattern. This was interpreted to show that the same processes continued throughout the depositional history of all the rock types involved. Because these elements are associated with the clay fraction (Fig.82), it is likely that they are absorbed from the water by the minerals. It is suggested that the source of the shales must have been much the same throughout the times of deposition for the Gamlan Flags, the Clogau Shales, and the Vigra Flags.

9:10 TREND ANALYSIS OF MERCURY (Hg) DATA.

The distribution of Hg was investigated by submitting the data for both the Northern and Southern Areas to trend analysis. All rock types in each area were included in the analysis and a third degree trend extracted. The sums of squares reductions are shown in Fig.83.

9:10:1 NORTHERN AREA.

The trend and residual maps were hand contoured (Figs.92 and 93). Because of the low concentrations involved only high and low values are shown to avoid confusion. More detailed contouring produces a confused series of contour lines.

The sum of squares reduction for the trend in this area is 63.41%, which indicates that the trend reflects, to a high degree, the inherent variation.

Generally the distribution of mercury is independent of the rock type because the trend lines cross geological boundaries. The high values of the distribution (Fig.92) appear to be associated with areas of numerous igneous intrusion (e.g. at Grid refs. 72, 14; and 50, 20).

It is inferred that the output of Hg was by a process which was not dependent on rock type. It is suggested that the centres of igneous intrusion are related to high values in the bi-modal distribution (Fig.40). Because the igneous rocks are not enriched in Hg (Section 9:5), it is suggested that the intrusions acted purely as lines of weakness along which the Hg moved prior to permeating the country rock. It also spread from these major features along other lines of weakness.

9:10:2 SOUTHERN AREA.

The trend map was hand contoured to show high and low values (Fig.94). No residual map was produced because the number of samples involved caused difficulties by requiring too much core storage in the computer. The sum of squares contribution of the trend, 38.98%, (Fig. 83) indicates that the trend is significant.

Examination of the trend map (Fig.94) allowed the interpretation that the Hg is not associated with any one rock type because the major trend lines cross geological boundaries. However there is some suggestion that the Vigra rocks are associated with low Hg values.

The high Hg values are closely associated with the areas of mineralisation around St. David's Hill and Y-Vigra. A further two areas of high values are found, one around Grid reference 10, 14, near to old mine workings; the other is a broad area of high values in the North West (NW) corner of the area. Only a few old workings and veins are present in this latter area, thus the high cannot be explained by tailings from the existing workings. It is believed that a belt of mineralisation is present in this area, and that it is probably associated with lodes in the Vigra Flags, which are present to the West of the area studied (Fig.3). This, in association with the conclusions of Section 9:5 and 9:8, indicates that Hg is a good indicator for mineralisation.

CHAPTER 10.

SUMMARY OF CONCLUSIONS.

10:1 INTRODUCTION.

Two separate causes of elemental variation in bedrock, using a relatively small number of samples were distinguished. Analysis of a small number of carefully selected elements is believed to be more useful, in distinguishing a number of causes of elemental variation, than a full analysis for all major elements and a large number of trace elements. The use of a number of interlinked techniques, provides more useful information than one or two techniques used in isolation.

Factor analysis (Chapter 9, Section 8) divided the causes of elemental variation into two major groups; one from sedimentary effects; and one from mineralisation. Relatively non-mineralised (in the commercial sense), and mineralised areas were distinguished using the ore metals Cu, Zn, Pb as indicator elements, and Hg as a pathfinder element.

Each of the causes of variation, and the distribution of Hg and its use in the determination of the sequence of events leading to the mineralisation, is discussed in the following sections.

10:2 SEDIMENTARY ROCKS.

The sediments were deposited in an elongated basin with an approximately N-S axis (Price, 1963). To the N.E. shelf conditions occurred, and the influx of clay and precipitate material was probably from an associated land mass. The supply of this type of sediment in the Southern Area continued throughout the time of deposition of the Gamlan Flags. This basin was cut off from the open sea, was probably less saline than sea water, and in it black shales were deposited. Within the main basin of deposition strongly reducing conditions were developed in local basins in which the waters had a low pH.

Around the margins of the main depositional basin masses of quartz-rich rocks must have effectively eroded to supply the coarse sediments. The siliceous layers in the sedimentary sequence are thought to have formed as a result of turbidity current deposition (Price, 1963). The thinner layers probably had a local source; however the source of the thicker layers was an area of land to the N.E. (Price, 1963).

The concept of shale deposition whose source was the same throughout Gamlan, Clogau and Vigra times is inferred from the trend analysis. This is in direct opposition to the views of Price (1963), who stated that the axial flow of sediment finished at the end of Gamlan time, and that marginal flow then became all-important. The suggestion that the depositional basin was cut off from the open sea in Gamlan, Clogau and Vigra times is supported by the fact that Ni shows enrichment and relatively low values, while being strongly associated with a detrital factor. The lack of enrichment of Cu, which would be expected under the prevailing reducing conditions, may be due to Cu being in short supply at that time. An alternative is that Cu was subsequently leached out (see Section 5 below). The above suggestion is in agreement with the work of Price (1963), who suggested that the basin was cut off in Clogau times, and that of Mohr (1959) who suggested that it was cut off in Manganese Shale times.

The existence of smaller basins within the larger one, having a low pH and reducing conditions, is suggested by the distribution of Th (Chapter 9, Section 9:2), and its negative association with Ca (Chapter 9, Section 9:1; and Price, 1963; Adams and Weaver, 1958).

The presence of a land mass to the N.E. of the Harlech Dome, as suggested by Matley and Wilson (1946), Price, 1963), and Gilby (1968), is further indicated by the Sr/Ba ratios for each rock type in both areas. Mohr (1959) stated that low Sr/Ba ratios are indicative of shallow water deposition because Ba is absorbed in hydrolysates more strongly than Sr, and is therefore largely removed in near-shore sediments (Price, 1963). For each rock type the Sr/Ba ratio is smaller in the Northern Area (Fig.95), indicating an approach to shelf conditions.

The presence of local sources of sediment is indicated by the occurrence of original, fresh orthoclase feldspar grains in the more "gritty" rocks of the Southern Area (Chapter 2). It is suggested that the parent rock was of grandioritic composition on the basis of the proportions of feldspar types found in the sediments.

10:3 MINERALISATION.

Broad aspects of two different types of mineralisation were distinguished from complex trace element variations in the different types of country rock. A Cu mineralisation was found in both the Northern and Southern Areas, and a Pb/Zn mineralisation was found only in the Southern Area. The Cu mineralisation is associated with SiO_2 in both areas. The Pb/Zn mineralisation is associated with Ba and Sr, and in some instances also with SiO_2. Wall rock alteration, indicated by a positive factor loading of Al_2O_3, and a negative factor loading of SiO_2, was found in the Southern mineralised area in the Gamlan and Vigra Flags. No association of wall rock alteration with the Clogau Shales was found.

Plots of individual factor scores on the sampling grid for the mineralisation related factors show up areas of mineralisation. These agree with previously published maps of lodes and workings (Andrew, 1910; Gilby, 1968). All the above information is in agreement with the interpretation made by previous authors (Andrew, 1910; Matley and Wilson, 1946; Gilby, 1968) from detailed work on the veins. The exception is the presence of Cu mineralisation in the Northern Area which indicates that the Cu mineralisation is more widespread than was previously apparent.

Sampling on the pattern used in the present work provides sufficient information to characterise base metal concentrations.

10:4 MERCURY (Hg) DISTRIBUTION.

The distribution of Hg has two major features; a low level, bi-modal distribution, common to both Northern and Southern Areas; and a series of higher, anomalous values found only in the Southern Area.

The lower level, bi-modal distribution was found to have a concentration ranging between 0.001 and 0.2ppm. This is low compared to concentrations found in similar sediments, e.g. a concentration of 1.0ppm Hg was found in recent marine clays (White, 1967), and a value between 0.1 and 0.3 ppm is common in shales (White, 1967). To explain this low Hg concentration in the rocks studied, and the fact that the distribution is similar both in sedimentary and igneous rocks, it is necessary to examine the factors which influence the concentration and subsequent movement of Hg in Shales, Flags and Igneous rocks.

In modern sediments and waters the natural Hg is commonly supplied from volcanic activity and hot springs (James, 1962; Jonasson and Boyle, 1972; White, 1974). Experimental work (Krauskopf, 1956) has shown that organic material concentrates Hg. Horn (1970) and Jenne (1970) reported that Hg forms stable complexes with organic compounds, and Cameron and Jonasson (1972) found significant correlation between Hg, S, and organic carbon in Archean and Aphebian shales. Krauskopf (1956) found that Hg was absorbed by microcrystalline Fe and Mn oxides. Lockwood and Chen (1973) indicated that Mn oxides may be important scavengers of Hg in fresh or brackish water. Jenne (1970) suggested that the absorptive efficiency of microcrystalline solids is increased if they are coated with clay minerals. Consideration of the above information allows the conclusion that conditions, favourable for the removal from sea water, and concentration in the sediments of Hg probably occurred in rocks of the area studied. It is therefore likely that when the sediments were deposited they contained a significant concentration of Hg.

During diagenesis a decrease in Hg concentration commonly occurs (Mc.Neal and Rose, 1974; Ozerova and Aydin'yan, 1966); however it is unlikely that this would have reduced the concentrations to the levels found. This also does not explain the distribution of this element being common to both the sedimentary and the igneous rocks (Fig.40). Rocks of the Harlech Dome area have been subjected to regional, chlorite grade metamorphism (Matley and Wilson, 1946), and this may have reduced the Hg concentration. Moiseyev (1971) suggested that Hg may be mobilised from sediments by a magmatic heat source, and presumably metamorphism would have a similar effect. Marowsky and Wedepohl (1971) noted a decrease in Hg content of rocks with increasing grade of metamorphism; However Jovanovic and Reed (1968),and Ozerova and Aydin'yan (1966), found that Hg was not lost during metamorphism. Cameron and Jonasson (1972) suggested that the apparent stability of Hg in metasediments is due to the formation of very stable organo-Hg complexes. From the above it appears likely that a redistribution of the Hg did not occur during the regional metamorphism. A redistribution of Hg however has taken place and the association with rock types is the result of their ability to 'bind' Hg. This has been noted by other workers (Garrett, 1974; Goldschmidt, 1954; and White, 1967), particularly for SiO_2 and Hg. A suggestion as to the most likely method of movement is made in the section on mineralisation.

The high Hg concentrations (0.1 - 0.4 ppm, Fig.40), were found exclusively in the Southern Area. These are related to both the Cu and the Pb/Zn mineralisations (Chapter 9). The relationship with Cu, Pb and Zn indicates that Hg was transported in hot water solutions (Chapter 7), and allows the conclusion that Hg is a pathfinder element for Cu and Pb/Zn mineralisation in the

Harlech Dome. In addition a high concentration of Hg was found in a fault gouge in which there was no apparent evidence for fluid flow or mineralisation. In this instance it is believed that Hg was transported in the vapour phase along the fault plane. It was suggested by James (1966) that Hg is concentrated in epithermal mineral deposits, and that as the temperature of deposition increased, so the concentration of Hg in the deposit decreased. In the present work it was not possible to distinguish between the two types of mineralisation by using Hg concentrations, because the relationships were shown by factor loadings, and not by direct analysis of mineral deposits.

10:5 ORIGIN OF THE MINERALISATION.

In recent years the role of meteoric and formation waters, in the formation of mineral deposits, has become recognised (O'Neil et al, 1973; Degens and Ross, 1969; Craig, 1966; Clayton et al, 1968; White, 1967 and 1974). It is believed that such waters carry metals in solution, usually in complex form. These waters may carry the metals exclusively, or mixed with up to 5% of magmatic water (O'Neil and Silberman, 1974). The source of the metals in base metal deposits may result from either hot magmatic rocks, or leaching of sedimentary rocks with which the hot waters are in contact (White, 1974). The Salton Sea, and Red Sea brines provide convincing evidence for the latter process (White, 1974).

It is suggested that the mineralisation is of the type associated with hot springs and that deposition occurred close to the surface (Gilby, 1968). The effect of a high level of heat flow in such deposits was to cause circulation of formation or meteoric water through the rocks. This water probably redistributed the Hg and removed some in solution. This effect may also explain the apparent lack of Cu in the area (Chapter 9) as a result of leaching by these hot waters. The movement of solutions through the rocks to form the veins resulted in Hg being deposited only where the environment was favourable. This is the favoured explanation for association found.

The sequence of events relating the geological history and the mineralisation is presented below, and is summarised in Fig.96.

1) Heat flow increased during compression of the area (Chapter 4) and produced basement mobilisation (Figs.14 and 15) and the start of structural doming.

2) Basic dykes were emplaced along tensional fractures produced by the uplift.

3) Regional metamorphism of chlorite grade occurred.

4) Compressional forces decreased allowing the dome to begin to rise rapidly. This rise caused the deep-seated fractures produced by the compression to open (Matley and Wilson, 1946; Gilby, 1968).

5) Hot solutions containing Cu, of either or both formation and magmatic water moved up along major faults, and Cu and Hg were precipitated on contact with Shales (due to a favourable temperature and reducing conditions in the shales (Helgeson and Garrels, 1968)). In addition meteoric water may have been mixed with the solutions thus facilitating the precipitation (Helgeson, 1964; White, 1974).

6) These solutions heated the sediments at higher levels, and this resulted in the circulation of the formation and meteoric waters in them. Hg was redistributed in the sediments, and may have leached some metals into the solutions, thus adding to the mineralisation. This effect slowly spread Eastwards, from a centre on the Western side of the dome, as a result of progressive heating. The spread of the solutions meant that a progressive decrease in temperature occurred towards the East, and resulted in the Cu being precipitated there lower in the sequence. The more stable complexes (Au, Pb, Zn) were carried further to the East (O'Neil and Silberman, 1974). This spread is shown by

Fig. 96. Structural and mineralisation history of the Harlech Dome.

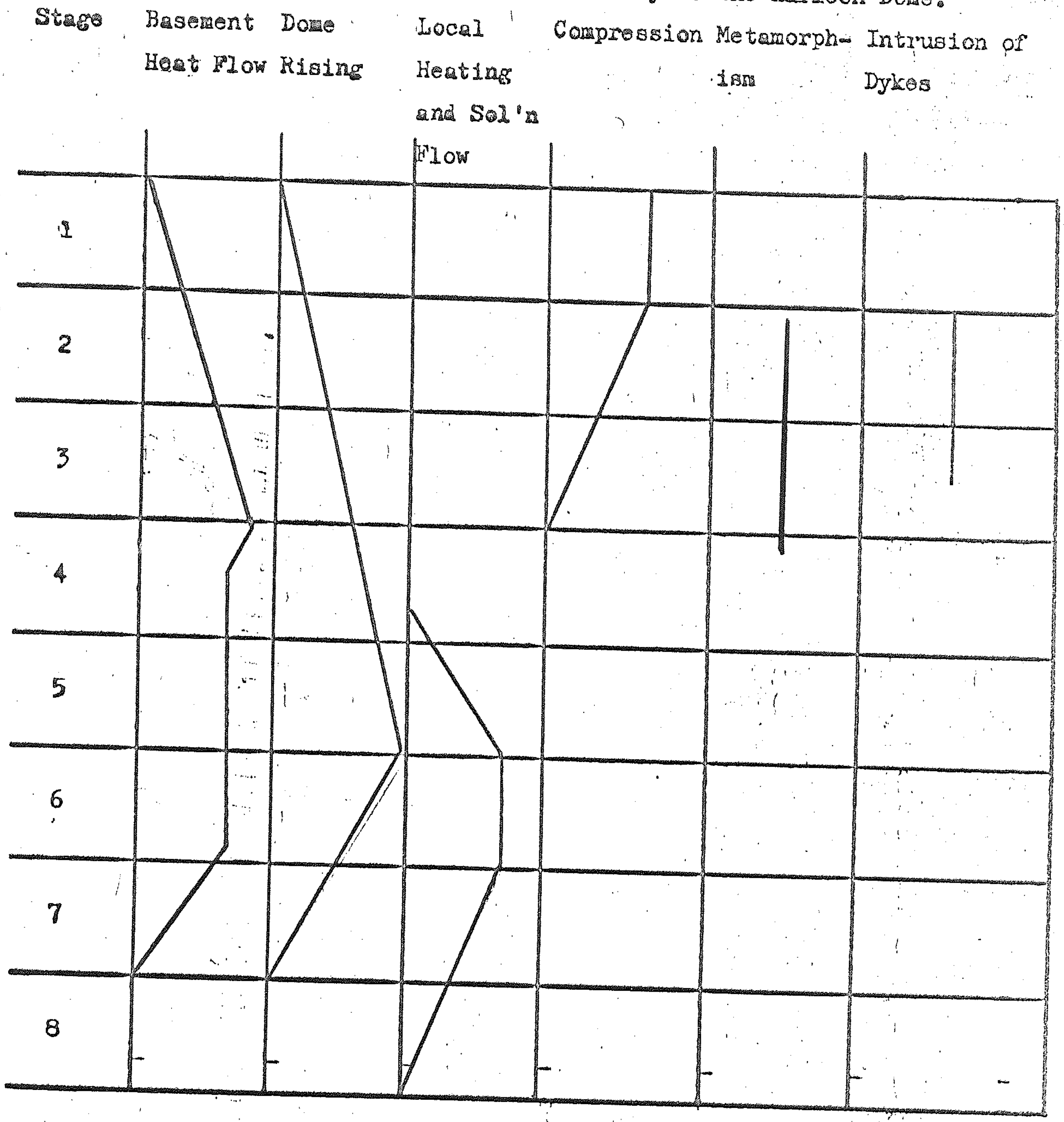


Diagram is a composite taken from the work of Matley and Wilson (1946), Powell (1955), Price (1963), Gilby (1968) and the present work. Sloping lines indicate a build up (from the left) of the episode.

Gilby (1968) in his study of mineralisation. Spread of the mineralisation Northwards is shown by the distribution of Cu (Chapter 9); however only small quantities of Ph/Zn mineralisation are indicated. It is postulated that this area was distant from the heat source and was reached only by the initial stages of the mineralisation. After the initial stage the mineralisation declined because more fissures reduced the pressure available to transport the solutions over long distances.

7) The heat flow diminished and circulation of hot water slowed. Deposition of the minerals occurred at greater depths, and only low temperature deposits of SiO_2 were able to permeate the uppermost rocks (present erosion level). The heat flow reduction corresponded with, and may have caused, the end of uplift in the area.

8) During the final stages of cooling Hg, in the vapour phase, rose from lower level deposits along fractures and fissures into rocks of the upper levels.

The suggestion made by O'Neil et al (1973) that:-

"Exploration to deeper levels in existing epithermal deposits might prove useful", is relevant in the light of the interpretation of the origin of the mineralisation made in this study.

10:6 DISCUSSION.

The interpretation from the present work of both the sedimentary and mineralisation related processes are in agreement with those of previous workers (Gilby, 1968; Price, 1963; Mohr, 1959). The present approach, which uses a simple sampling program and relatively few samples, allows detailed information to be obtained, on both sedimentary and mineralisation related processes. It is suggested that, rather than analysing a large number of samples for a large number of elements, it is more useful to obtain fewer analyses, and to extract all the latent information contained in the data. A minimum number of analyses however must be obtained in order to produce statistically viable results. Close attention must be paid to detail, in both sampling and analytical procedures, to exclude the possibility of introduction of systematic errors.

Clear indications of mineralisation are produced in the Southern Area despite the lack of anomalous values in the data. The Hg results prove its value as an indicator of mineralisation, and show that it can yield valuable information about the origin of base metal deposits. Hg analyses are valuable to reduce the area investigated to one small enough for sampling on a 200-400m grid which may delineate exploration targets.

10:7 FURTHER WORK.

The methods used in this work should be repeated in an area of known mineralisation, without using a control area, to discover if it will outline the mineral deposits.

A further study of rocks from the lower horizons in the Harlech Dome should be made to check the theory of the origin of the mineralisation. If the lower horizons are deficient in trace metals related to mineralisation, and these deficiencies cannot be related to the depositional environment or diagenetic changes, then the proposed theory is strengthened. Determinations outlining low concentrations of Au, Ag, Cu, Pb and Hg, over a wide area of the Dome, would show up effects of leaching processes, provided that account is taken of the sedimentary factors.

APPENDIX I.

ATOMIC ABSORPTION SPECTROPHOTOMETRY (A.A.S.) ANALYSIS.

A1:1 INTRODUCTION.

Three major problems are encountered in the analysis of geological materials by this method. These are:-

1) Dissolution of silicate materials
2) Removal of interference effects.
3) The detection and measurement of trace quantities of an element in a complex matrix.

Most of the early dissolution techniques were based on the addition of 5ml of hydrofluoric acid and 1ml of perchloric acid to 0.5g of powdered rock in a platinum or teflon crucible. The mixture was then gently fumed to dryness and the mixture was then taken up in concentrated hydrochloric acid. Variations of this method include a second dissolution and either fuming off with hydrofluoric acid or a mixture of hydrofluoric and sulphuric acid to remove silica as the volatile SiF_4 (Reilley 1961). Some of the published methods include neutralisation with ammonium hydroxide to protect the stainless steel burner parts of some atomic absorption instruments (Belt, 1964).

A similar technique, used when refractory compounds are involved, is to fume the rock powder with a sodium carbonate flux. This technique gives excellent results for refractory compounds, but losses of volatile trace elements occur. Thus it is not widely applicable for the analysis of geological materials in which elements such as Zn and Pb are present.

After dissolution various extraction techniques are used to isolate specific elements. The commonest method used is the A.P.D.C. - M.I.B.K. (amino pyrrolidine dithiocarbamate-methyl isobutyl ketone) method. In this method the pH of the solution is adjusted to a specific value, according to the element being extracted, and a 1% solution of A.P.D.C. added; followed by a measured volume of M.I.B.K. after shaking and separation, the A.P.D.C. - element complex is taken up into the organic (M.I.B.K.) layer. Standard solutions are treated in the same way (Bernas,1968).

Solvent extractions, combined with ion exchange, has also been used to concentrate elements.

All the above methods rely on either the removal of interfering elements, e.g. fuming off of SiF_4, or removal of the element to be determined from the matrix.

In the present work these techniques were found to be unacceptable for the following reasons:-

a) At the evaporation and fuming off step, great care is required to prevent sample losses due to spattering etc. This requires close attention to each stage in the preparation.

b) Because of the large number of analyses required, the time taken using such methods is too long.

c) In the present work silicon was to be determined, and as it was considered preferable to carry out all the determinations on a single solution a new method was required. All other methods require a separate dissolution for silicon.

For the above reasons, although a trained analyst can obtain excellent results for a relatively small number of samples, a different method was derived in order to facilitate analysis of large numbers of samples. The method developed overcame these disadvantages in that it was rapid, simple and precise

A1:2 RAPID DISSOLUTION TECHNIQUE FOR SILICATES.

To overcome some of the difficulties encountered in the analysis of silicate materials by A.A.S. Bernas(1968) developed a new method in which silicates were dissolved under pressure. Hydrofluoric acid was used in the dissolution, and the fluoride ions remaining in solution neutralised with boric acid. This technique was designed to allow direct determination of the element concentrations without further treatment.

The method developed is outlined below:-

a) About 50mg of rock powder was accurately weighed into a P.T.F.E. lined pressure vessel of 50ml capacity. 0.5ml of aqua regia was added to 'wet' the powder, and to dissolve carbonates. 3.0ml of 48% hydrofluoric acid was then added, swirled, and the pressure vessel sealed.

b) The pressure vessel was then heated for 30-40 minutes at 110°C in an oven, and then allowed to cool.

c) After cooling the pressure vessel was unsealed, and the solution transferred to a 50ml polythene beaker where 2.8g of boric acid was added. The solution was stirred to dissolve the boric acid.

d) The resulting clear solution was transferred to a 100ml graduated glass flask, and made up to the mark with distilled water.

e) This solution was transferred to a polythene storage bottle within 2 hours of preparation (see below).

f) Standards were prepared using pure metals dissolved in acid. Working standards were prepared containing 3ml of 48% hydrofluoric acid and 2.8g boric acid per 100ml of solution.

g) Unknown solutions for analysis were aspirated directly into the Atomic Absorption Spectrophotometer, and the absorbance values obtained compared with those of the above working standards.

The results of analyses of U.S.G.S. standard rocks G1 and W1, carried out using this method, showed good agreement with accepted values (Fig.A1).

The method has some definite advantages over previous methods in that:-

a) The decomposition under pressure in a closed container precluded the possibility of any loss of volatile elements, or loss of material by spattering.

b) All elements, including silicon, were determined directly on the same solution(assuming that their concentrations were within the analytical range of the instrument).

c) Neutralisation of the fluoride ions by boric acid had the practical advantage of permitting the use of glass volumetric apparatus in the dilution stages.

d) The neutralisation also produced a constant matrix effect which tended to blanket out matrix effects caused by other elements.

A1:3 THEORY OF THE METHOD.

The neutralisation of fluoride ions by boric acid is a two stage exothermic reaction producing fluoroboric acid

$$H_3BO_3 + 3HF \rightleftharpoons HBF_3OH + 2H_2O$$

$$HBF_3OH + HF \rightleftharpoons HBF_4 + H_2O$$

Fluoroboric acid (HBF_4) hydrolyses in a stepwise manner to hydroxy fluoroborate ions: BF_3OH^-, $BF_2(OH)_2^-$, $BF(OH)_3^-$ and H_3BO_3 with hydrofluoric acid as a co-product (Kirk-Othmer, 1966; Sharp, 1954).

The equilibrium conditions for this hydrolysis reaction have been extensively studied (Ryss, 1956); however Bernas(1968) investigated the conditions that would be

Fig. A1. Analytical Results for Standard Rocks W1 and G2.

Element	W1				G2			
	A	B	C	D	A	B	C	D
SiO_2^*	52.64	48.10	52.65	52.55	69.20	65.01	69.10	-
$Fe_2O_3^*$	11.17	10.94	11.20	10.75	2.67	2.58	2.70	-
$Al_2O_3^*$	14.85	15.50	15.87	14.81	15.42	15.95	15.60	-
TiO_2^*	1.07	1.13	1.08	1.03	0.48	0.50	0.46	-
CaO^*	10.96	11.13!	10.83	10.50	1.95	2.73	1.83	-
MgO^*	6.62	6.98	6.59	6.52	0.75	0.71	0.75	-
Na_2O^*	2.07	2.04	2.11	2.11	4.05	4.08	4.00	-
K_2O^*	0.64	0.64	0.60	0.64	4.46	4.47	4.45	-
V^+	120	-	209	240	26	-	100	-
	320	-	-	-	60	-	-	-
Cu^+	80	120	-	-	2	-	16	-
	150	-	-	-	17	-	-	-
Ni^+	55	63	-	-	2	-	20	-
	88	-	-	-	14	-	-	-
Pb^+	5	50	-	-	15	-	50	-
	10	-	-	-	43	-	-	-
Sr^+	180	205	-	-	235	-	473	-
	300	-	-	-	650	-	-	-
Zn^+	20	80	-	-	42	-	73	-
	95	-	-	-	138	-	-	-

KEY

A = U.S.G.S. accepted

B = Buckley & Cranston, 1971.

C = Langmyhr & Paus, 1968.

D = Bernas, 1967.

* = Oxide Percent.

\+ = ppm.

necessary to arrest,or inhibit, for a sufficiently long time, the hydrolytic decomposition process to an analytically acceptable limit in the presence of the ionic constituents of a silicate rock. Bernas (1968) showed that in the presence of an excess of boric acid, the hydrolytic decomposition of fluoroboric acid was supressed for at least two hours. In this time contamination of the solution by silicon from the glass apparatus was found to be insignificant.

Al:4 ADAPTATIONS OF THE METHOD.

The basic method of Bernas(1968) was used by Langmyhr and Paus (1968) to provide a comprehensive technique for the decomposition and analysis of silicates. Four variations of this method were employed, two of which assumed that silica was not being determined, and involved a "fuming off" stage with hydrofluoric acid. The remaining two methods involved a"Bernas type" technique, one of which was further adapted for use in this study.

The technique involved heating the sample with hydrofluoric acid to a temperature, below the boiling point of hydrofluoric acid (112.0°C, for an azeotropic mixture of hydrogen fluoride and water containing 38.26% HF), in a 60ml capacity, screw topped, polypropylene bottle. Subsequently a saturated solution of boric acid was added, and the bottle re-heated to dissolve any precipitated fluorides. The resultant clear solution was analysed using standards made up in a solution containing approximately the same concentrations of matrix elements as the unknown solution. Results obtained using this technique for U.S.G.S. standard rocks G2 and Wl agreed well with the published values (Fig.Al).

The basic method was further developed by Buckley and Oranston (1971) who were able to determine 18 elements in a single decomposition using a P.T.F.E. lined bomb. The unknown solutions were compared with standards in which all 18 elements had been added to a single solution, in such quantities that the final concentration was above that of the upper limit expected in the unknown. Each working standard prepared contained similar concentrations of hydrofluoric acid, boric acid and aqua regia (used to 'wet' the sample) as the rock (unknown) solution under investigation.

Analyses of U.S.G.S. standard rocks G2 and W1, using this method, agreed well with published values (Fig.A1).

Each of the above modifications differ both in detail and in elements determined. For the present work it was necessary to examine each method, and to select the best combination with reference to the rock types under investigation.

A1:5 SELECTION OF ANALYTICAL METHOD.

The rock types involved, and the number of samples to be analysed, were considered when selecting the method of decomposition and analysis.

The rock types were black to grey carbonaceous shales, quartz-rich grits, vein quartz and basic igneous intrusions. The major element concentrations in these rocks varied between 40% and 99% SiO_2, 0.0 and 25% Al_2O_3 and 0.0 and 30% Fe_2O_3. Analyses for the major element oxides, as well as for the elements Cu, Ni, Zn, Pb, Sr, Ba and Hg, were required.

Any method considered had to provide a rapid analysis for as many elements as possible in a single solution. Also the dilution steps involved in the method had to bring the element concentration in the final solution within the optimum working range of the instrument (Perkin-Elmer, 1968). Optimum working ranges and limits of detection for the elements are shown in Fig.A2.

The determination of mercury was carried out using a flameless technique, and a separate solution (Appendix 2)

Fig. A2. Optimum working ranges and detection limits - Atomic Absorption Analysis

Element	Wavelength (A)	Detection Limit (ppm)	Sensitivity (ppm)	Optimum Working Range (ppm)
Al	3093	0.1	1.3	10 - 150
Ba	5536	0.005	0.36	5 - 100
Cu	3247	0.005	0.15	2 - 20
Fe	2483	0.01	0.15	1 - 10
Hg	2537	——— COLD VAPOUR TECHNIQUE ———		
Ni	2320	0.01	0.15	2 - 25
Pb	2833	0.03	0.7	4 - 40
Si	2516	0.1	1.5	20 - 200
Sr	4607	0.01	0.2	2 - 20
Zn	2138	0.002	0.025	0.2 - 3.0

A1:6 DEVELOPMENT OF THE RAPID DISSOLUTION METHOD.

The Bernas(1968) method, as adapted by Langmyhr and Paus (1968), was chosen for trial purposes (see above). A literature survey revealed that numerous combinations of conditions had been used, some of which were contradictory. This meant that experimental verification of the chosen method was necessary (Fig.A3).

An important basic premise of each of the methods, described in the literature (Fig.A3), was the neutralisation of the hydrofluoric acid remaining in solution after dissolution of the SiO_2. This was carried out either with boric acid, or with aluminium (III) chloride hexahydrate. This was done to provide a "constant matrix effect", and to allow the solution to be handled in standard glassware. However because aluminium (III) chloride was required in large quantities (Fig.A3), and was difficult to obtain in a pure state, the boric acid method was adapted for the present works.

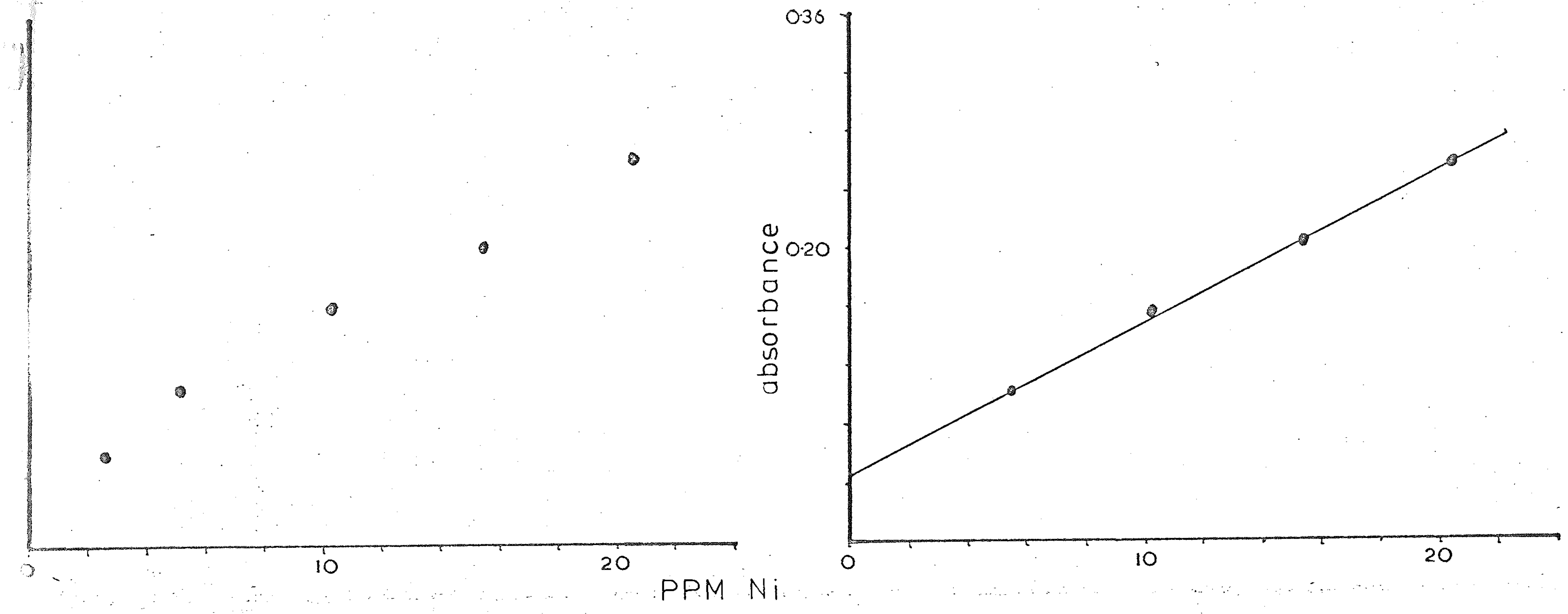
A1:6:1 EFFECT OF BORIC ACID.

To determine both the effect of boric acid on the analytical results, and the optimum sample dilution, a series of standards, containing nickel and copper, were made up. In addition hydrofluoric acid was present in the same concentrations in each standard. The standards were made up in boric acid solution of varying concentrations to produce a series of solutions with known concentrations of metals and boric acid. Blank solutions, containing hydrofluoric acid and boric acid, were also prepared. Both standards and blanks were determined, on a Perkin-Elmer 303 Atomic Absorption Spectrophotometer, using standard instrument settings (Perkin-Elmer, 1968), and mean absorbances of a duplicate determination was plotted (Fig.A4 a, b, c and d; Fig.A5 a, b, c, and d).

Fig. A3. Comparison of dissolution methods.

Sample Weight (g)	Wetting Agent & Vol.	HF Vol. used (ml)	Container	Dissolution Time & Temp.	Neutralisation	Author(s)
0.1	-	1 - 2	Pt lined bomb	- 425	25 ml of 65g $AlCl_36H_2O$ in 250 ml.	May & Rowe, 1959
0.2	5 ml H_2O 1 ml HNO_3	5	P.T.F.E. lined bomb	30min. 110	-	Langmyhr & Paus, 1969b.
0.2	1 ml H_2O	5	P.T.F.E. lined bomb	15 min 95	-	Langmyhr & Paus, 1969c..
1.0	H_2O to moisten	43 of 50% HF	Plastic Beaker	Until Decom--posed 95	20 ml sat'd boric acid sol.	Langmyhr & Paus, 1969a.
0.5	-	11.5	-	- 110	-	Langmyhr & Kringstad, 1966.
0.2	2 ml HCl 2 ml HNO_3	2.5	P.T.F.E. lined bomb	10 min 110	25 ml sat'd boric acid sol.	Langmyhr & Paus, 1970.
0.2	5 - 6 drops H_2O	10 + 10 ml conc. $HClO_3$	Plastic beaker	- 95	400 ml of 25% $AlCl_36H_2O$ sol.	Langmyhr & Sveen, 1965.
0.1	1 ml Aqua Regia	6	P.T.F.E. lined bomb (after Bernas 1968)	30 - 60 min. 100	5.6 g boric acid	Buckley & Cranston, 1971.
0.05	0.5 ml Aqua Regia	3	P.T.F.E. bomb	30 - 40 min. 110	2.8 g boric acid	Bernas, 1968.

Fig. A4. Plots of absorbance against element concentrations for various boric acid concentrations. - Ni.


Ni(a) 25 ml

Ni(b) 50 ml

Fig. A5. Plots of absorbance against element concentration for various boric acid concentrations. - Cu

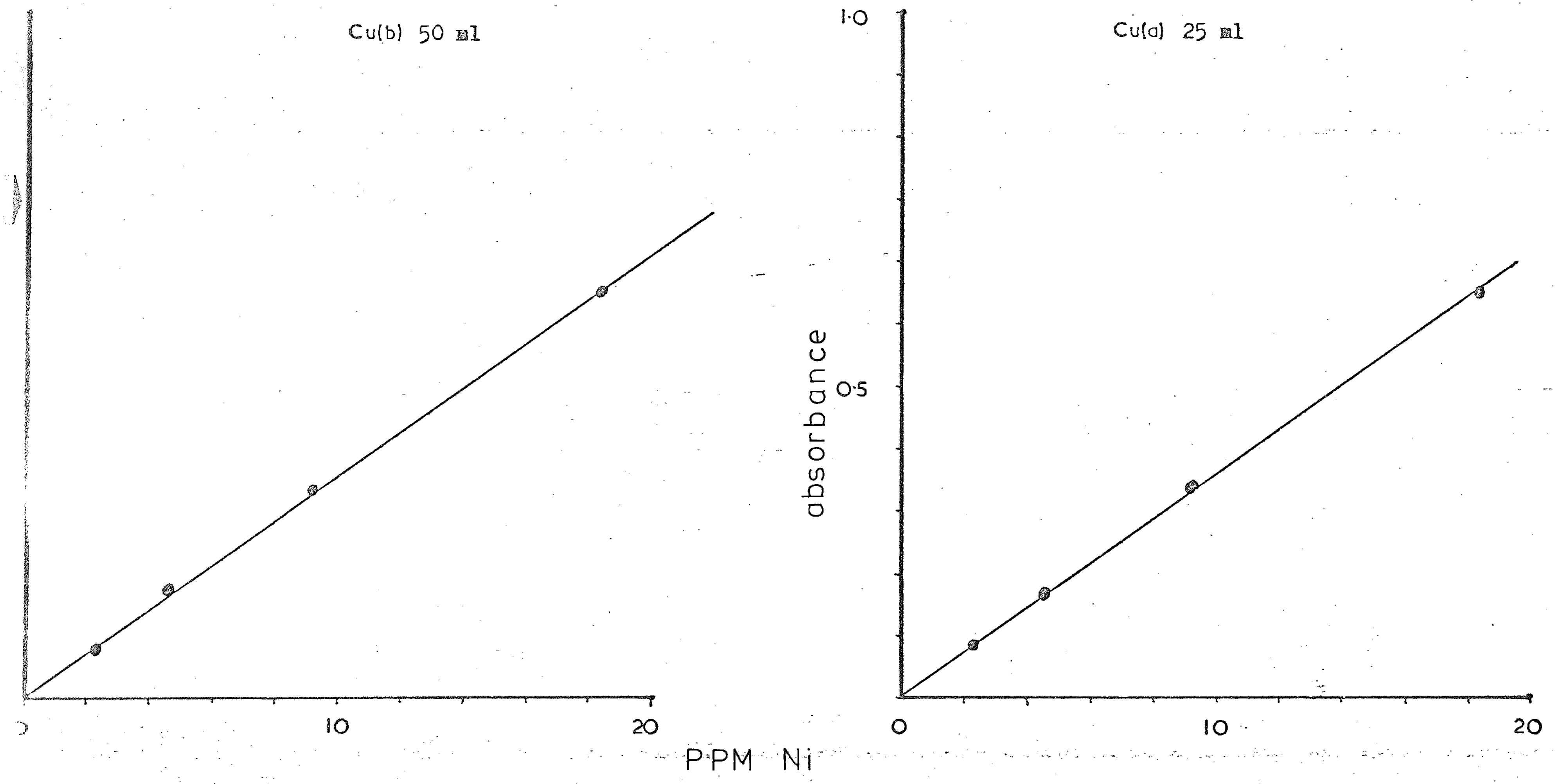
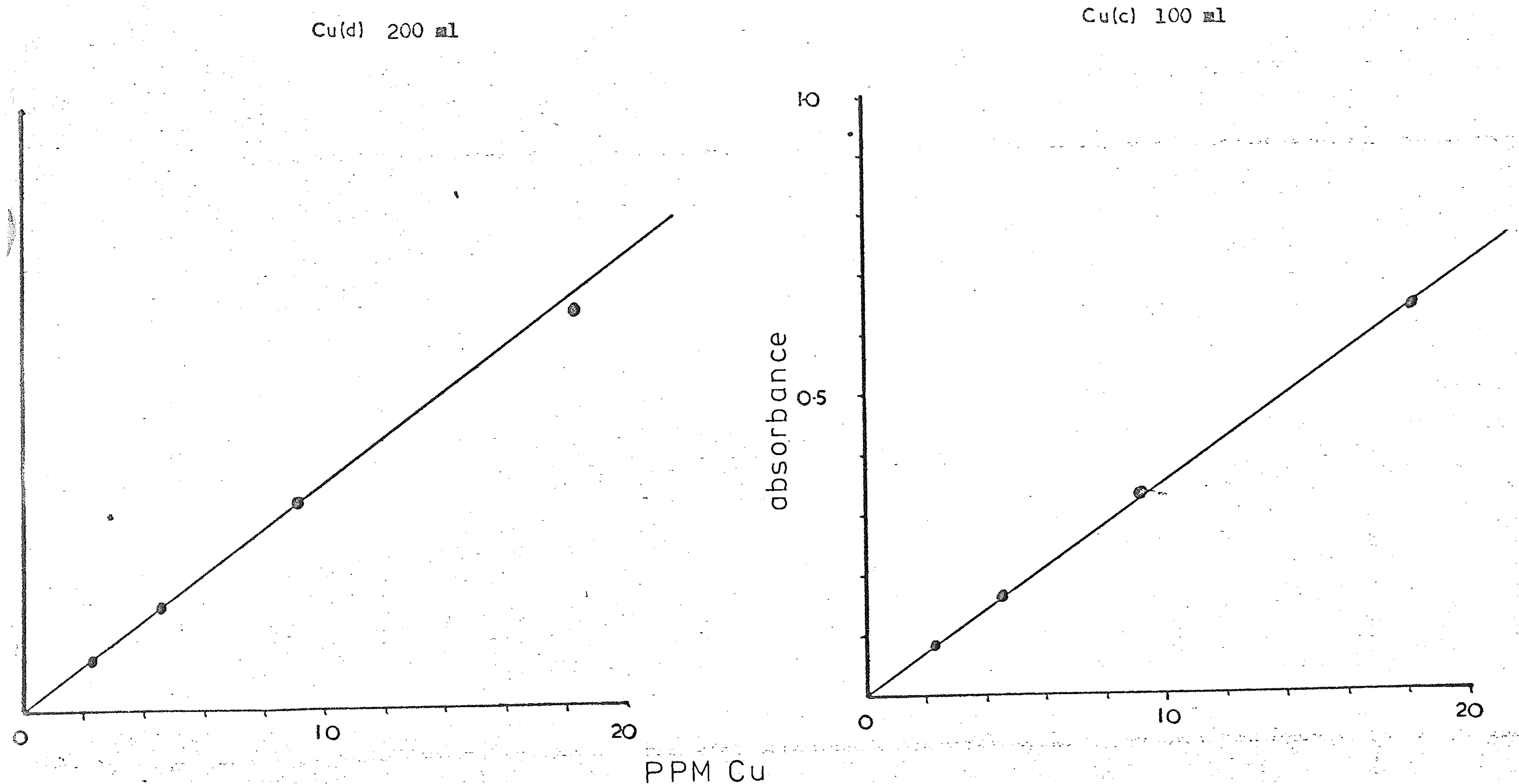


Fig. A5. (cont'd).



Cu(d) 200 ml

Cu(c) 100 ml

Nickel and copper were selected for this test because copper absorbs above 2500° Å, and is less effected by matrix effects than nickel, which absorbs at wavelengths less than 2500 Å (Fig.A2).

Generally the results for copper were linear, although a slightly greater coefficient of variation was found at higher matrix concentrations (Fig.A4 a). Results for nickel were generally not linear, and showed considerable variation. The variation was particularly apparent on the 25ml dilution curve (Fig.A5 a). For 50ml and greater dilutions the results were linear above 6 g ml^{-1}; below this the line tended to curve to zero concentration.

These results plus the difficulties experienced in transferring materials to make up solutions of 25ml, and on dissolving boric acid, meant that it was essential to dilute to at least 50ml.

A1:6:2 EFFECT OF SILICA.

The effect of silica (SiO_2) on the determination of low concentrations of trace elements can be significant. To evaluate this effect a series of solutions were made up, each containing gold, copper, iron and nickel, with varying concentrations of SiO_2.

Absorbance values were determined for each element in turn, using standard conditions (Perkin-Elmer, 1968), and were plotted against element concentrations (Fig.A6 a, b, c and d). For all elements, except iron, the points lay on straight lines. These graphs showed that the absorbance readings for each element increased with increasing SiO_2 concentration. This was similar for all element concentrations. This phenomenon was almost certainly the result of a "salt effect" in which the concentrated solution was dried in the flame to produce solid particles which physically obstructed the light path and produced an apparent absorption.

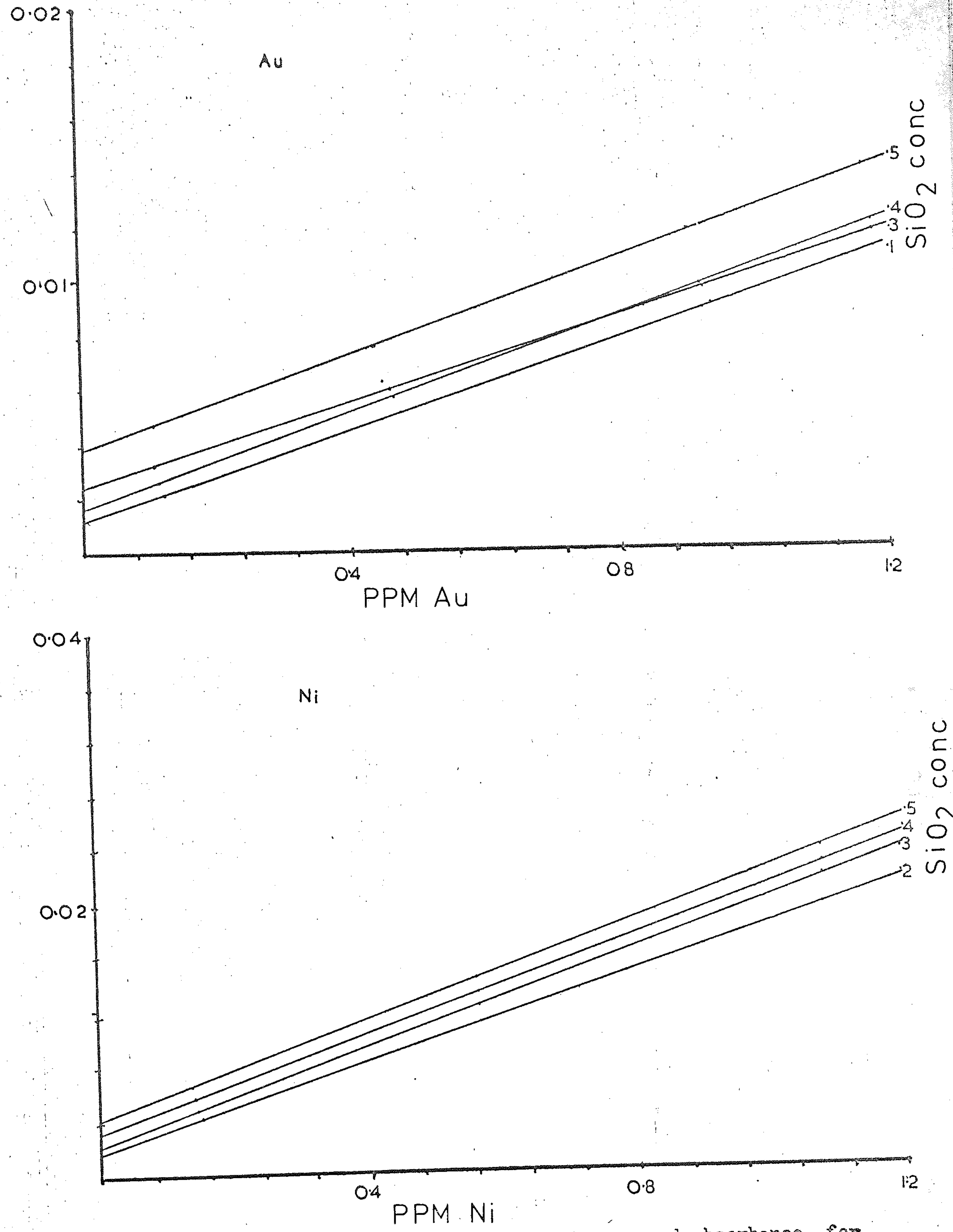


Fig. A6. Plot of actual concentration against measured absorbance, for Au,Ni,Fe and Zn, in solutions of varying SiO$_2$ concentrations.

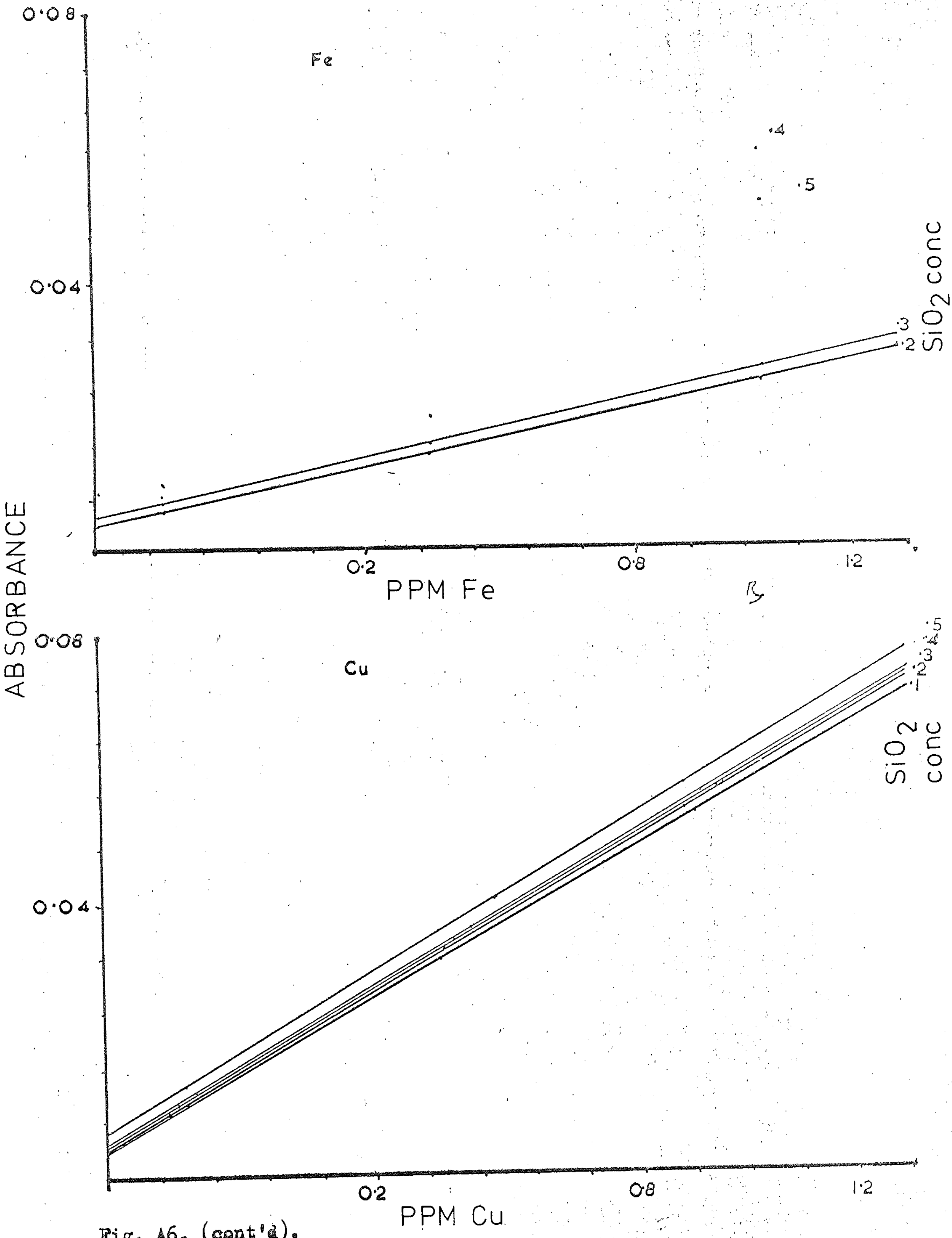

0·08
Fe
·4
·5
0·04
3
·2
SiO2 conc
ABSORBANCE
0·2
0·8
1·2
PPM Fe
0·08
Cu
5
4
3
2
1
SiO2 conc
0·04
0·2
0·8
1·2
PPM Cu

Fig. A6. (cont'd).

The effect of SiO_2 on the measured concentrations was greater for wavelengths below 2500 Å (Fig.A2), and the differences between curves was less for lower SiO_2 concentrations.

The above results, together with those for boric acid, determined the quantity of rock powder to be used. 0.2g of rock in a maximum of 50ml of final solution was selected since this meant that the maximum SiO_2 concentration (in the case of pure quartz) fell on the lowest (0.2g) curve (Fig.A6 a, b, c and d). Average SiO_2 contents (40-70%) fell below the line. If the variation of SiO_2 content in the samples to be analysed (i.e. from 40% to 100% SiO_2) was superimposed on the 0.2g line of the graphs (Fig.A6 a, b, c and d) an estimate of the likely errors in the determinations could be made (Fig.A7). These errors, although small, were significant because, for an 0.2g rock sample, and a 50ml final sample volume, they were effectively multiplied 250 times. To minimise this error the solution used to dilute the standards was made up to contain the equivalent of 70% SiO_2 in a 0.2g sample of rock. This reduced the maximum errors by 50% (Fig.A7).

A1:6:3 DECOMPOSITION VESSELS USED.

The containers recommended for dissolution vary from author to author (Fig.A3), and a number of 'bombs' of different design are commercially available (May and Rowe, 1965; Langmyhr and Paus, 1968; Bernas, 1968).

In the present work screw topped linear polypropylene bottles were used for general analyses, and a 'teflon' lined bomb was used for the dissolution of more resistant rocks (Bernas, 1968). In practice the 'bombs' were found to be necessary only for shales with a high clay content, and igneous rocks containing rutile, this was necessary because both clay minerals and rutile are

Fig. A7. Error in Atomic Absorption results produced by SiO_2 concentration.

Element	Absorption wavelength (A).	Maximum error* (ppm)	Error assuming 70% SiO_2 in matrix solution. (ppm).
Cu	3247	0.024	0.012
Au	2428	0.084	0.042
Ni	2320	0.104	0.520

* Maximum error is taken as the difference between concentration values for the 0.2 and 0.3 g SiO_2 lines taken at the 1.0 ppm intercept.(Fig. A6)

Fig. A8. Matrix solution composition, per litre.

HF (48%)	60ml
Aqua Regia	10ml
Boric acid solution (saturated)	500ml
SiO_2	1.2g
$FeCl_3$	0.806 g
Sodium citrate	12.79 g
Aluminium ammonium sulphate	0.505 g.

Fig. A9. Standard compositions and concentrations of stock solutions.

Solution	Standard used	Solvent	Concentration (ppm)
Al	S/P $Al_2(SO_4)_3(NH_4)_2SO_4.24H_2O$	D.D. H_2O	1000
Ba	S/P $BaCO_3$	Dil. HCl	1000
Cu	S/P CuO	Dil. HNO_3	1000
Fe	S/P Fe sponge	Dil HCl	1000
Hg	S/P $HgCl_2$	Dil HCl	1000
Ni	S/P Ni sponge	Dil. Aqua Regia	1000
Pb	S/P $Pb(NO_3)_2$	D.D. H_2O	1000
Si	S/P SiO_2	48 % HF	4000*
Zn	S/P ZnO	50 % HCl	1000

S/P = SPECPURE (Johnson Matthey)

D.D. = Double distilled.

* = Merck 'Titrisol' also used.

resistant to dissolution by the 'bottle' technique.

A1:6:4 HEATING METHOD.

a) Bombs.

These were heated in a fan assisted drying oven, with thermostatic control, and an excess temperature cut-out. To ensure that overheating did not occur the oven was stabilised at the set temperature (120°C) for at least one hour before the bombs were inserted.

b) Polypropylene bottles.

These were treated with care because, if heated to 120°C, the plastic softened and the bottles leaked. In addition the HF-water azeotrope used boils at 112°C creating a pressure and causing leakage. Because a temperature of approximately 100°C was required a fan assisted oven, rather than a water bath was used. To overcome softening problems the bottles were pre-heated in the oven for three minutes, removed, and the tops re-tightened. A weighing check showed that this technique prevented loss of contents.

Two other problems; cracking and poor sealing due to uneven rims, were overcome by visual inspection of each bottle, and rejection of doubtful ones. This was done before each bottle was used, and bottles were used for a maximum of four times each.

A1:6:5 WETTING AGENTS.

Before adding hydrofluoric acid (HF) to the rock powder it was necessary to add a wetting agent (Bernas, 1968; Langmyhr and Paus, 1968) to ensure complete attack. The variety of wetting agents used are given in Table A3.

Langmyhr and Paus (1968) investigated the role of mineral acids in the decomposition of rocks and concluded that acids, other then hydrofluoric, do not help in the reaction. Moistening with water, however, did produce a small increase in the rate of reaction. For sulphides, and rocks containing sulphide minerals, the addition of a mineral acid assisted the decomposition. Many of the rocks investigated in the present work contained sulphides, and because of this 1ml of aqua regia was added to each rock powder.

Al:6:6 HYDROFLUORIC ACID.

A high concentration of fluoride ions can cause precipitation of less soluble fluorides. Because of this the minimum possible quantity of hydrofluoric acid was used. An estimate of the quantity of acid required was made from the equation for the reaction of SiO_2 and HF:-

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

(neglecting higher fluorides)

Assuming that most of the HF will be used in the dissolution of the SiO_2, a 0.5g sample of SiO_2 requires 1.5ml of 48% hydrofluoric acid to dissolve it completely. Allowing for other reactions, and taking into account handling difficulties for small volumes of liquid, 5.0ml of 48% hydrofluoric acid was used.

Al:6:7 DIGESTION PERIOD.

The time needed for digestion was found to vary according to the major element composition of the rock. A rock containing 99% quartz dissolved under the above conditions in 10-15 minutes; however a rock containing a high proportion of clay minerals commonly took over one hour. For the majority of rocks, encountered in present work, dissolution was completed in 30 minutes. If after this time the solution still contained gritty particles the bottles were heated for a further 20-30 minutes. Cloudiness in the solution was assumed to be the result of fluoride precipitates in suspension (see later).

A1:6:8 NEUTRALISATION.

After cooling, the excess fluoride ions were neutralised with boric acid to provide a 'constant matrix effect' (Bernas,1968), and to allow the solutions to be handled in glass apparatus. Boric acid was found to be the most convenient complexing agent, and was used in all analyses. Recommended quantities for the addition vary (Fig.A3). Bernas(1968) recommended the addition of 2.8g of solid boric acid. In the present work difficulty was experienced in dissolving this quantity; consequently 25ml of a saturated solution of boric acid, as recommended by Langmyhr and Paus (1969), was used.

Replicate analyses on the rocks from the study area, and on a wide range of international standard rocks, showed considerable variation. Silica-rich rocks gave good results; basic and ultra-basic rocks gave low results; and standard shales gave variable results.

Examination of the sample solutions, from rock types which gave variable results, revealed that small quantities of a white precipitate remained in the bottles after dissolution. This precipitate was analysed by X-ray fluorescence, and the results showed that the major components of the precipitate were calcium and aluminium, with small quantities of silicon and potassium. The ratio of X-ray counts for calcium to aluminium remained constant for different rock compositions. This indicated that the quantity of calcium and aluminium precipitated was dependent on some external factor. Solubility data for these elements indicated that calcium and aluminium fluorides were very sparingly soluble. This was taken to indicate that calcium and aluminium fluorides were precipitated when the solutions became saturated.

To redissolve the precipitate it was necessary to remove the excess fluoride ions from the solution by the addition of an excess of boric acid. In practice this was done by adding 50ml of a saturated solution of boric acid to the rock solution, and heating it for a further 30 minutes. After this treatment a clear solution was produced in all instances, and analysis of the international standards gave results close to the accepted values (see later).

A1:6:9 PROBLEMS WITH CARBONACEOUS ROCKS.

Many of the rocks studied, particularly the Clogau Shales, contained up to 3% by weight of carbon. This carbon remained behind, on dissolution of the rock, as a fine-grained deposit in the bottom of the polypropylene bottle. Attempts to remove the carbon, by means of chemical oxidation, were unsuccessful. Removal of the carbon by heating in a stream of oxygen was not possible because losses of volatile elements, e.g. Pb, Zn, Cd occurred.

Carbon in shales is commonly thought to absorb elements, such as gold and zinc, onto the surface of the particles. X-ray fluorescence analysis on standard black shales showed no systematic difference between X-ray fluorescence analysis of the whole rock, and atomic absorption analysis of the whole rock, with the carbon removed by centrifuging. These results showed that the carbon had not absorbed a significant quantity of trace elements; consequently all dissolved rock samples were centrifuged to remove any carbon deposits.

A1:7 DECOMPOSITION METHOD ADOPTED.

The following scheme for decomposition of the rocks was used for all A.A.S. analysis.

1) About 0.2g of the 250 mesh rock powder was accurately weighed into a screw topped, wide mouthed, polypropylene bottle.

2) 1 ml of aqua regia was added, and the bottle swirled to ensure wetting of the rock powder.

3) 5 ml of 48% hydrofluoric acid was added, the bottle swirled, and the top tightly screwed on.

4) The bottles were placed in an oven, set at 95°C, for 3 minutes until the polypropylene had softened slightly. They were then removed and the tops tightened. The bottles were replaced in the oven, and heated for 30 minutes, or until all of the rock powder visible as small gritty particles had dissolved. At this point precipitated fluorides were visible as a cloudy white precipitate.

5) The bottles were removed from the oven and, after cooling for 5 minutes, 50ml of a saturated solution of boric acid was added. The bottles were then sealed and heated in the oven for a further 30 minutes.

6) The bottles were removed, cooled, and the contents centrifuged in polythene tubes to remove carbon. The solution, together with washings, was transferred to a 100 ml, Grade A, graduated flask, and made up to the mark with double distilled water. The solution was then transferred to a 250 ml polypropylene bottle for storage.

A1:8 ATOMIC ABSORPTION ANALYSIS.

In all of the present work a Perkin-Elmer, model 303, double beam, atomic absorption spectrophotometer (A.A.S), equipped with chart recorder read out, was used.

In A.A.S. analysis a number of interferences occur which produce a non-linear calibration curve of concentration against absorbance. Two types of interference were particularly relevant to the present work and needed to be overcome.

The first was ionisation interference, in which the population of neutral atoms of a particular element in the flame (the absorbing atoms) was influenced by the concentration of other more easily ionised elements. In addition ionisation of a particular element occurred, which reduced the population of neutral atoms of that element to such an extent that poor sensitivity was produced. This interference was overcome by adding an excess of an easily ionised element which completely ionised in the flame. This effectively removed all available electrons, and supressed the ionisation of other, less readily ionised, elements. In the present work sodium ions, in the form of sodium citrate, were added to both standard and unknown rock solutions.

The second type of interference can be broadly termed matrix interference. This has the effect of increasing the absorption of a particular element due to salts in the solution drying out in the flame to form solid particles. These particles then physically obstructed the light beam and produce an apparent absorption effect. This was overcome either by diluting the solution to reduce the concentration of the matrix; or by providing standards with similar matrix composition. In trace element analysis dilution was not always possible and the method used was to prepare standards with a similar matrix composition. This approach was also used by Bernas(1968), and Buckley and Cranston (1971). In the present work it was found that the matrix interferences were only of importance in the determination of the trace elements. This corroborated the work of Buckley and Cranston (1971). Elements requiring a standard with a similar matrix composition were Cu, Ni, Zn, Pb and Sr. Ba only required an ionisation supressor, and Si, Al and Fe, were determined directly against a concentrated aqueous standard without any dilution.

The matrix solution was made to contain all of the reagents added during the rock dissolution, together with the amount of silica that would be present in the average rock (see Section Al:6:2 above). In addition sodium, in the form of sodium citrate, was added to act as an ionisation supressor. The composition of the matrix solution is given in Fig.A8.

Standard metal solutions were prepared from 'specpure' (Johnson-Matley) compounds, dissolved in A.R. acid, to produce an element concentration of approximately 1000 ppm. For silicon a solution with a concentration of 4000 ppm was prepared to take into account the high concentration of silicon in the rock solutions. The standard compositions and concentrations are given in Fig.A9).

Composite secondary standards containing Cu, Ni, Zn, and Sr, each with a concentration of approxiamtely 100 ppm., were prepared, together with single element standards for Ba and Pb, of similar concentrations. The 1000 ppm standards were prepared yearly; while the 100 ppm standards were prepared monthly in order to combat absorption onto the container walls (see below).

A1:9 CHANGES IN SOLUTION COMPOSITION WITH TIME.

Standards, with concentrations less than 100 ppm, tended to change with time. This effect, which was a decrease in concentration of the metal in solution, was found to be the result of a 'plating out' onto the walls of containers, and onto any particulate matter present.

To examine this effect a series of standards, containing copper and nickel, were made up. They were determined twice, once immediately, and again after 6 days. The results of these experiments are shown in Fig.A10 a, b, c and d. They show that a loss of approximately 4 ppm occurred over a period of 6 days, after storage in the polythene containers. This meant that dilute standards (less than 100 ppm) had to be made up daily, and that rock solutions were determined within one day of being made up.

The working standards were prepared from the 100 ppm aqueous standards, using a Hook and Tucker auto diluter Mark II, with the matrix solution as the diluent. Frequent checks were made on the instrument, by weighing dispensed quantities of distilled water, to ensure that the settings did not change. (Fig.A11).

Fig. A10 Decrease in Standard Concentration with time (b determined 6 days after a).

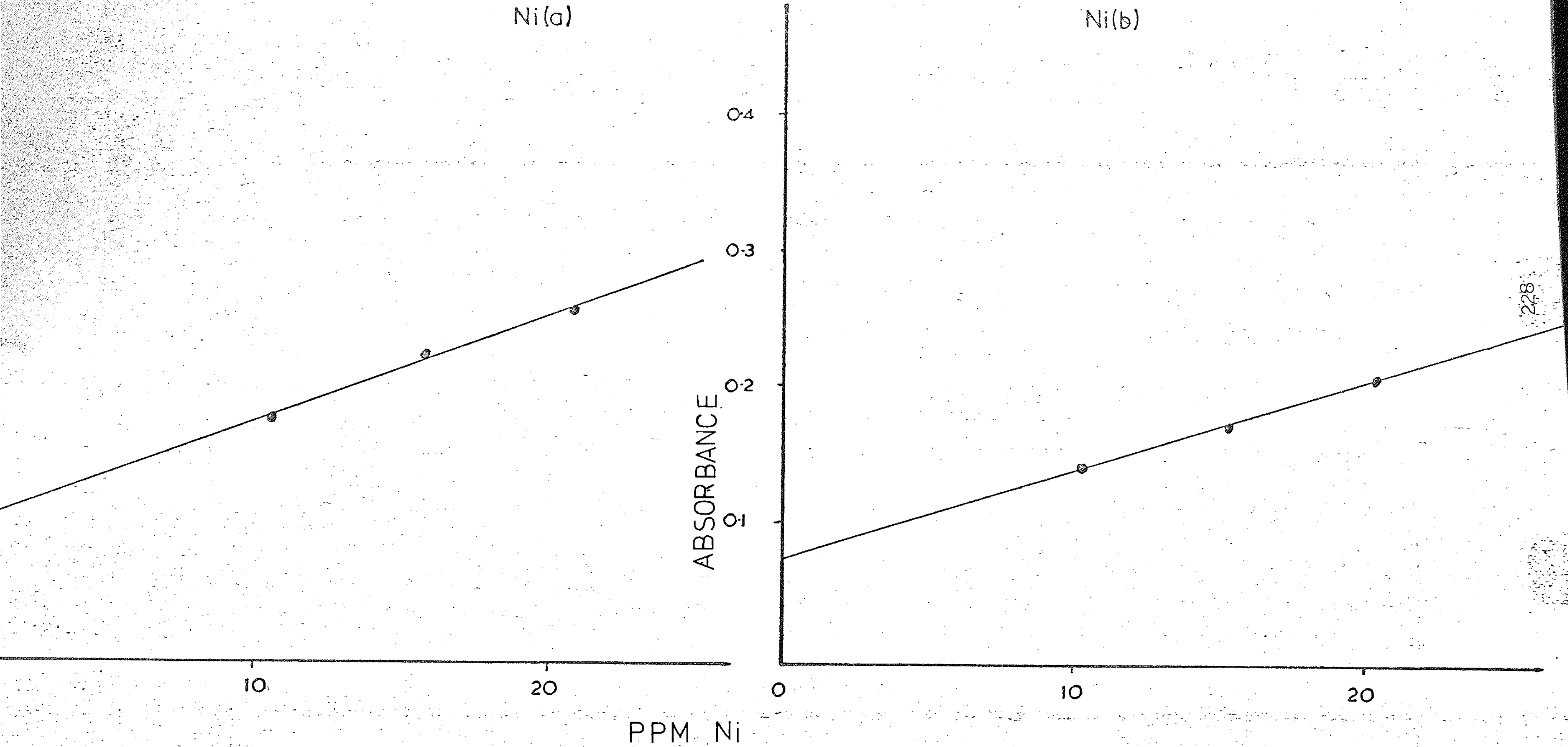
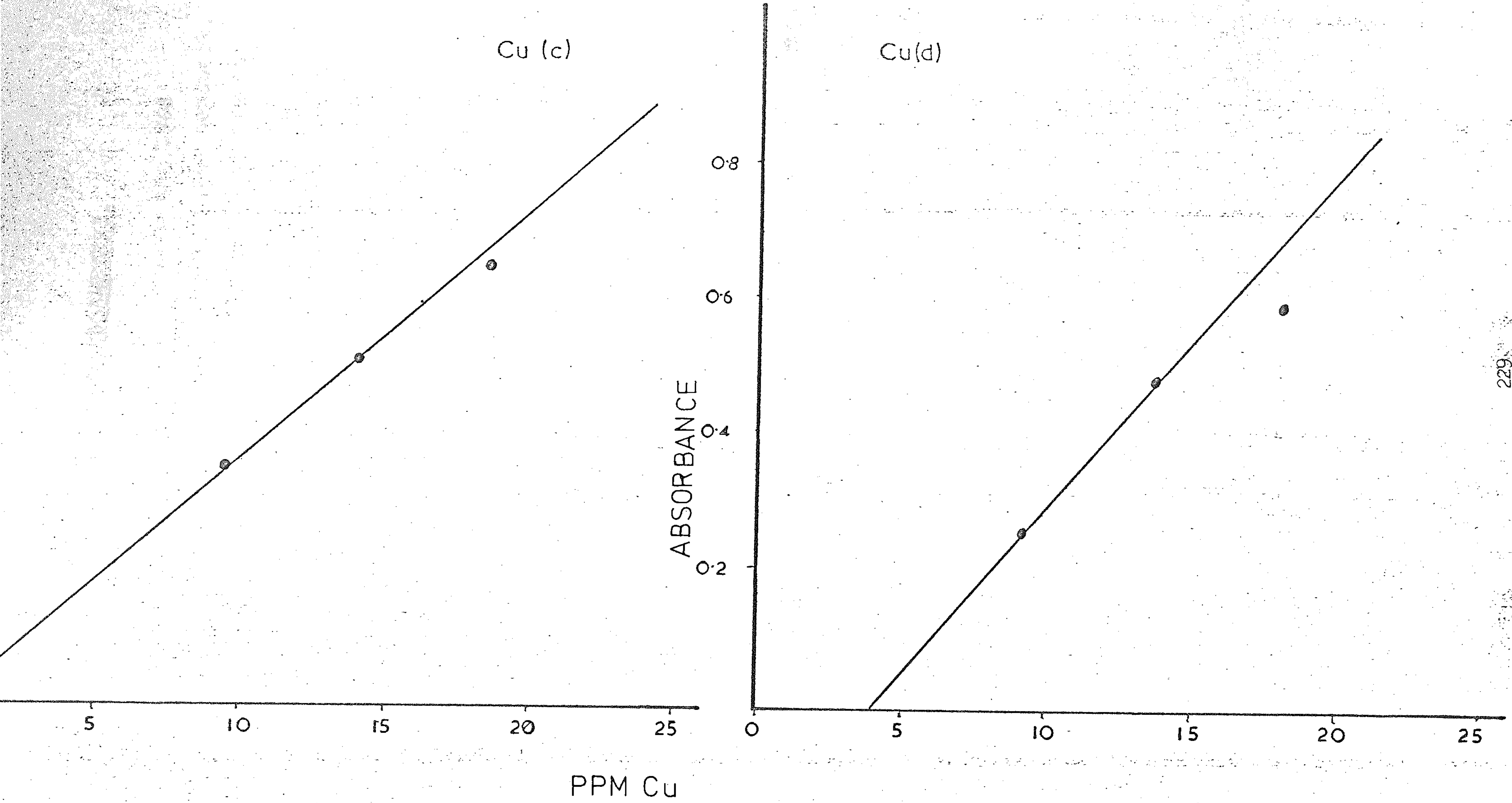


Fig. A10 (cont'd)



A1:10 INSTRUMENTAL OPERATING PARAMETERS.

Instrument settings used were taken from the 1968 edition of the Perkin Elmer Atomic Absorption Handbook. The method of analysis varied from element to element and is summarised in Fig.A12.

Standards were made up to bracket the sample concentrations as closely as possible. At least three standard concentrations were used for each analysis. Standards were run before and after each set of unknowns, with no more than nine unknowns being run between the sets of standards. Where blank solutions were used to correct for matrix absorption, they were run between each standard and each unknown.

Unknown solutions which produced absorbances above the highest standard were re-determined using more concentrated standards so long as they were within the optimum working range of the instrument (Fig.A2). For concentrations outside this range the instrumental conditions were changed, and the sensitivity decreased. All the major elements were determined in this way using concentrated standards, because it was found to give more reproducible results than dilution of the sample solution.

A1:11 ACCURACY AND REPRODUCIBILITY OF THE METHOD.

To determine accuracy and reproducability of the method, standard rocks, similar in composition to the rocks in the present work, were analysed a number of times over the period of the analytical work. The results of these analyses are summarised in Fig.A13. The results indicated that, for rocks of this type, i.e. shales and basic intrusives, the method gave results which agree well with accepted values and, more important, were precise.

Fig. A11. Change in dilution factors with time.

Instrument setting	Dilution factors			
1	50.17	50.44	49.20	51.02
2	67.87	68.79	80.71	70.78
3	95.90	97.35	99.37	98.65
4	178.41	158.91	175.10	164.96

Fig. A12. Atomic Absorption analysis conditions.

Element	Flame	Analytical conditions
Cu	Air/ acetylene	Multielement standard in matrix solution with blank matrix solution run between each standard and unknown
Ni	Air/ acetylene	
Zn	Air/ acetylene	
Pb	Air/ acetylene	Single element standard in matrix solution. Blank matrix solution run between each standard and unknown.
Sr	N_2O/ acetylene	Sodium citrate added to unknown. Run against composite standard in matrix solution. Blank matrix solution run between each standard and unknown.
Ba	N_2O/ acetylene	
Fe	Air/ acetylene	Burner rotated through 90°. Unknowns run against concentrated aqueous standards.
Al	N_2O/ acetylene	Burner rotated through 90° . Unknowns run against concentrated aqueous standards.
Si	N_2O/ acetylene	

Fig. A13. Analysis results for standard rocks.

	Si02		Al203		Fe203		Cu		Sr		Zn		Ba	
Standard	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
QMCI3	50.56	49.65	12.87	13.07	16.17	16.25	170	140	141	-	112	71	500	-
QMCI3	50.72	49.65	13.15	13.07	16.37	16.25	167	210	181	-	127	109	571	-
QMCI3	49.46	49.65	13.17	13.07	16.55	16.25	166	-	183	-	117	-	638	-
QMCI3	-	49.65	-	13.07	16.45	16.25	167	-	181	-	121	-	589	-
BMSA4	-	46.50	14.52	15.2	10.32	10.00	209	190	117	290	255	120	-	-
BMSA4	-	46.50	13.40	15.20	10.25	10.00	-	190	73	190	127	120	-	-
CGMA4	-	-	20.96	19.00	8.02	8.30	79	25	93	120	123	120	-	-
CGMA4	-	-	21.86	19.00	7.98	8.30	70	25	105	120	163	120	-	-

X = present work.　　　Y = Recommended value

QMCI3 = Queen Mary College Standard Dolerite, Ardnamurchan.

BMSA4 = University of Southampton Black Marine Shale, Samlesbury, Lancs.

CGMA4 = University of Southampton Cannock Grey Mudstone, Cannock, Staffs.

APPENDIX 2

Mercury Analysis.

A2:3. Introduction.

The background level of Hg in most crustal rocks varies between 0.001 and 0.1 ppm. The analytical techniques used must therefore be capable of accurate and precise determinations over this range.

Four techniques have been used for Hg determinations in rocks. The Russion workers, pioneers in the field of Hg geochemistry, used an adaption of emission spectrography, however little information is available on methodology or measurement ranges.

In the U.S A. and in the U.K. workers such as Vaughn (1964 and 1967), and Sears (1971) used a cold vapour technique. This involved heating the rocks, and condensing the Hg vapour in a gold trap. The Hg was driven out of the trap by heating and passed into an ultra violet (U.V.) measuring cell.

Other workers, Jovanovic and Reed (1968), have used neutron activation analysis to determine very low levels of Hg with high accuracy,

The fourth technique, an adaption of which was used in the present work, is one used by Omang and Paus (1971) in which Hg is leached from the rocks, using acid, and then released from solution by reduction with stannous chloride and air. The Hg vapour is then measured using a conventional A.A.S. equipped with a glass cell in the light path.

A2:2. Analytical Techniques Used.

Analysis for such low levels of Hg requires that contamination from outside sources must be kept to a minimum. All reagents used must therefore, either be obtained 'mercury free', or purified before use.

All containers and glassware used must have all traces of Hg removed from them. In addition care must be taken in storage of samples to prevent Hg loss (Kougievskii, 1970).

The instrument used was a Perkin Elmer, model 303, Atomic Absorption Spectrophometer, equipped with a model 56 chart recorder, and a Perkin Elmer flameless mercury kit. The experimental layout is shown in Fig. A14.

About 1g of rock powder (250 mesh) was accurately weighed into a 60 ml capacity, screw topped, polypropylene bottle, and 50 ml of aqua regia added. The bottle was swirled and the cap screwed on tightly. The bottles were then heated in an oven for one hour at 60°C, then removed and allowed to cool.

The contents of the bottle, including undissolved rock powder, were quantitatively transferred to the bubbler bottle (Fig.A14). The chart recorder was started, together with the air pump. At this stage the bubbler was in distilled water, and the absorption tube (B) bypassed (Fig. A14). 10 ml of stannous chloride solution was then added to the acid solution in the bubbler bottle, which was immediately swirled, and the bubbler inserted. After a peak was observed, which slowly fell off due to Hg loss from the system, the air flow was allowed to pass through the absorption tube (B), packed with activated carbon, until the recorder trace fell to the base line.

Standards were run before each batch of analyses. These were prepared by adding known quantities of a standard Hg solution to 50 ml of the acid leach solution. In addition reagent blanks were

Fig. A14. Apparatus layout - cold vapour Hg determination.

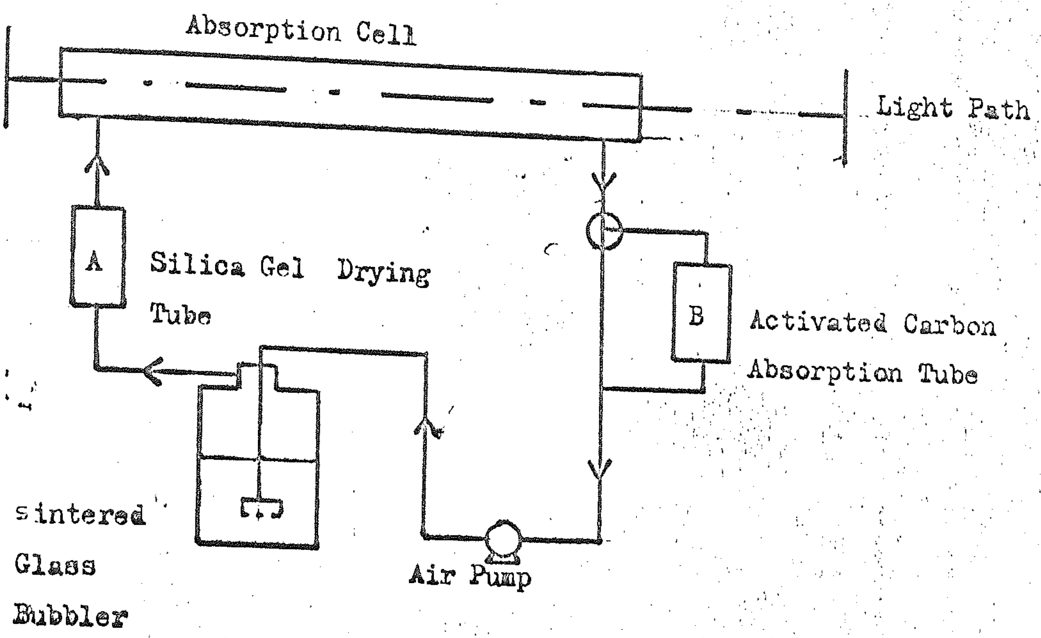


Fig. A15. Analytical precision for Hg determination.

Sample Number	Determination		
	1	2	3
G.R. 2,3	.3380	.2752	.3101
G.R. 12,5	.0276	.0279	.0275
G.R. 18,13(2)	.2552	.2138	.1253

run at the beginning and end of each batch of samples analysed. (Generally 20 samples were determined at one time).

All glassware was cleaned after each determination by washing in concentrated nitric acid, rinsing with water, washing with 'teepol' detergent, washing in hot water and finally rinsing in fresh double distilled water.

The reagents were made up and purified as follows :-

The acid leaching solution consisted of a mixture containing 4 moles of sulphuric acid (AR), and 0.5 moles of nitric acid (AR), per litre. It was purified by adding 5 g of stannous chloride to each batch of prepared solution, and bubbling air through the solution for one hour.

The stannous chloride solution was prepared as a saturated solution of AR stannous chloride in water, and was purified by having air bubbled through it for one hour.

When each new batch of reagents was prepared they were checked to ensure that they gave a low blank value. In addition a reagent blank was determined before each group of samples was leached, because it was found that contamination occurred if the reagents were stored for more than one week.

A check was also carried out on the quantity of Hg present in the air in the laboratory, before each batch of samples was determined.

A2 : 3. Discussion of Technique Used.

This relies on the Hg being removed from the powdered rocks by the acid leaching solution. Because the rock has a finite grain size, Hg contained within the mineral grains will not be leached out.

However, in the present work it is believed that most of the Hg was likely to have been present around grain boundaries. This is based on the belief that Hg was introduced after solidification of the rocks. To check this idea some rock samples were completely dissolved, and analysed for Hg, using the technique developed by Omang and Paus (1971). At the low levels of Hg involved, typically of the order of 0.1 to 0.001 ppm, no significant systematic difference was detected between the two methods.

Both of the above methods rely on a heating step thus it is important to determine if any Hg loss occurred at that stage, and if replicate samples of the same rock would give identical results. To do this standards were prepared in the leaching solution. A number of these were heated in an oven for one hour at 60°C. These were analysed, and compared with standards which had not been heated, but which were identical in every other way. No significant difference was detected between the two sets of standards.

Precision was checked by analysing a number of rocks repeatedly over a period of weeks. These were determined along with batches of samples, and were not treated in any special way. The results obtained (Fig. A15) show that precision is sufficiently high, even at the low levels involved, to allow meaningful conclusions to be drawn from the analytical results.

APPENDIX 3

A3:1 CARBON ANALYSIS.

The method used for carbon analysis is an adaptation of previously published methods (Goulden, 1960).

The apparatus used consisted of a furnace operating at temperatures between 1100° and 1200°C in which the sample, contained in an alumina boat, was heated in a stream of purified oxygen. Carbon dioxide formed by the oxidation of carbon was absorbed in a weighed U tube packed with soda asbestos (Fig.A16).

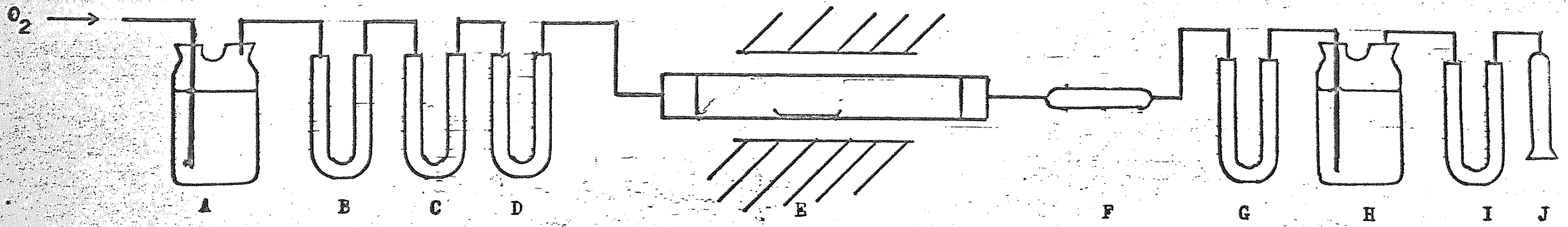
The furnace was allowed to stabilise, and the oxygen was passed at 200-300ml min $^{-1}$ for one hour. Between 1 and 2g of powdered rock (250 mesh) was weighed into a pre-ignited alumina combustion boat. The soda asbestos tube was removed, stoppered, and wiped with a clean, lint-free cloth. It was then placed on a balance pan and weighed after 5 minutes. The U-tube was re-connected to the apparatus, and the alumina boat slowly inserted into the hot zone of the furnace, over a period of 10 minutes. After 30 minutes the soda asbestos tube was removed, stoppered, wiped, and weighed. The gain in weight was calculated as CO_2 loss from the sample. Blanks were also run to determine background values.

Calibration of the apparatus was carried out by running a series of artificial standards, made by mixing known quantities of carbon and calcium carbonate with crushed quartz. These were determined repeatedly to check the precision of the method. Results of these checks are shown in Fig.A17.

A3:3 DISCUSSION OF THE METHOD.

This method determines carbon, from carbonate, and carbonaceous material. This gave a measure of the total carbon in the sample. Because of the number of samples involved a separate determination of carbonate carbon was not attempted, and thus the results must be interpreted in terms of total carbon. From Fig.A17 it can be seen that precision is satisfactory, although the results are

Fig. A16. Diagram of Carbon train.



KEY

A - Concentrated sulphuric acid.

B - Soda lime.

C - Calcium chloride.

D - Magnesium perchlorate.

E - Furnace; temperature set at 1100 - 1200°C. Contains alumina boat with sample.

F - Granulated manganese dioxide backed by a layer of anhydrous magnesium perchlorate.

G - Magnesium perchlorate

H - Chromium trioxide solution.

I - Soda asbestos.

J - Soda asbestos.

Fig. A17. Accuracy and precision for CO_2 analysis.

Standard $CaCO_3$ containing 44% CO_2

Determination	Result (% CO_2)
1	40.08
2	38.20
3	39.00

Standard of carbon in SiO_2 containing 3.6% carbon.

Determination	Result (% carbon)
1	3.1
2	2.9
3	3.2

consistently low. Because the data analysis used comparative methods, and the precision was the same for both high and low carbon values (Fig.A17), the method was considered to be satisfactory.

APPENDIX 4.

A4:1 DIAMOND DRILLING.

Samples of bedrock, from the drift covered valley bottom in the Southern Area (North of Bontddu - around SH 659 203) were produced by diamond drilling using a Craelius Minuteman portable drill.

Before drilling, a hand auger and a hammer seismograph were used to determine the depth and nature of the cover. This was found to consist of between 1 and 4m of stiff blue clay overlying the Gamlan Flags and Grits (Fig.A18). Four holes were augered through the cover and core samples of the bedrock taken.

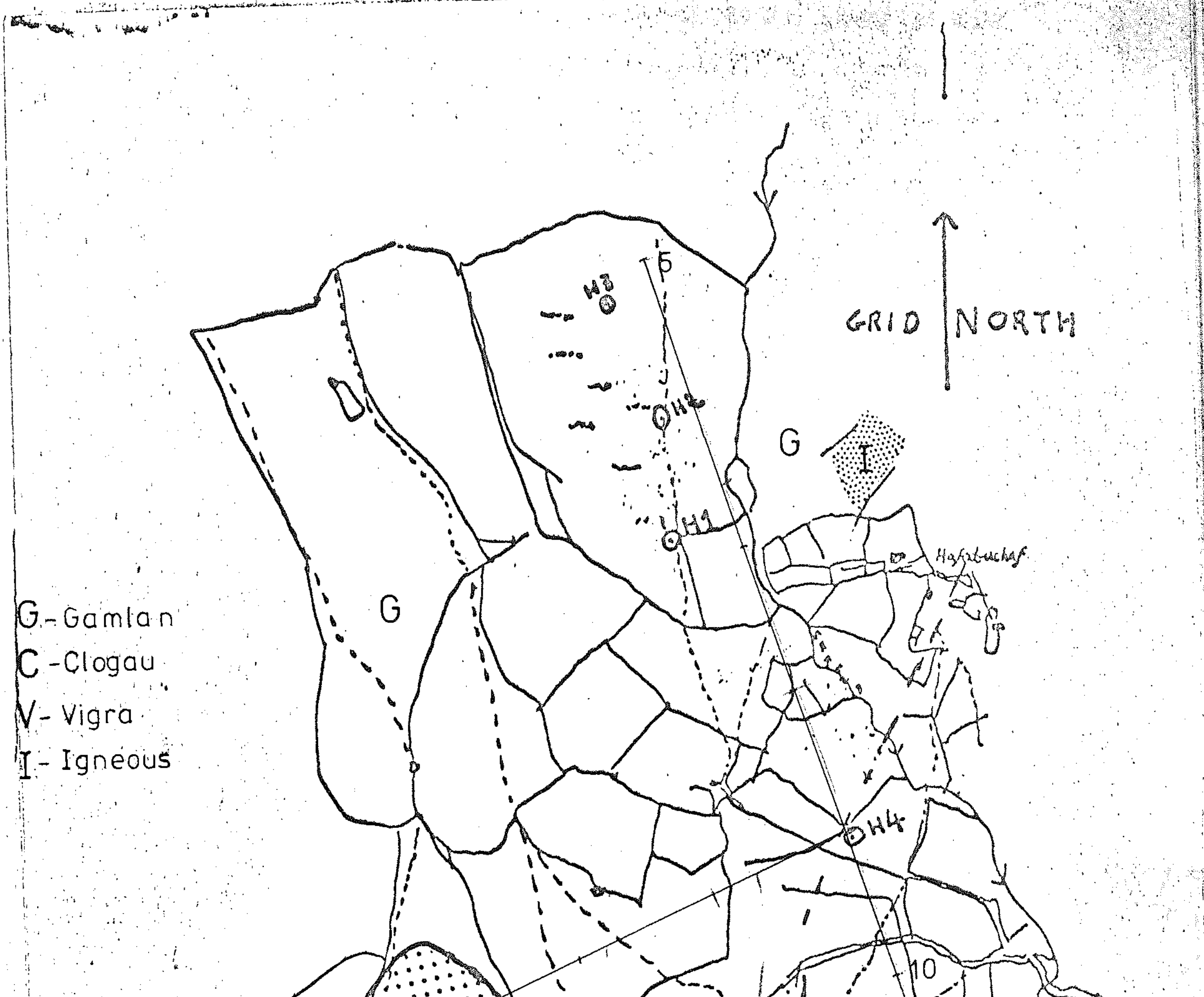
Core recovery varied between 20% and 50% because the rocks encountered were alternating shales and sandstones. The samples probably contained less shale than was present in the sequence as this was broken in the core barrel and lost. Samples for analysis were hand picked from the cores.

The locations of the core samples are shown in Fig.A18.

A4:2 DRILL RECORDS.

Hole 1	Cover 1.8m. Cored for 1.8m. Core broken due to alternating shales and flags in rock. Core consisted of siliceous layers up to 3cm thick, alternating with fragments of grey shale. Core recovery was 48%, most of this being from the siliceous layers.
Hole 2	Cover 2m. Cored for 0.8m. Core consisted of broken pieces of siliceous rock, with a small number of black shale fragments. Core recovery 25%.
Hole 3	Cover 3.0m. Cored for 2.8m. Core very broken. Most of the core consisted of rounded pieces of grit interspersed with fragments of light grey shale. Some pieces of hard shale, up to 3cm in length, were also recovered. Core recovery 21%.

Fig. A18. Drilling location map.



Scale - Six inches to one mile.

Hole 4 Cover 3.4m. Cored for 1m. 0.4m of core obtained. Core consisted of hard grey shale for first 0.2m, followed by 0.2m of broken fragments of siliceous rock mixed with shale fragments.

Core recovery 40%.

APPENDIX 5.

ATOMIC ABSORPTION ANALYSIS DATA HANDLING.

A5:1 INTRODUCTION.

To calculate element concentrations, from percent absorption readings (output as peak heights on a chart recorder trace), it was necessary to plot a graph of standard concentrations against a $\log_{10}$ function of absorption (the relationship follows Beer's Law). To simplify the calculation it was assumed that this relationship was linear. This is true, assuming that the concentrations lie within the optimum working range of the instrument (Appendix 1). The absorptions produced for the unknown were then compared with this graph, and concentrations determined directly. This assumed that absorptions, for both standards and unknowns, fall on the same straight line. This assumption is valid only if the following conditions are met:-

1) Blank or background absorbance value, has been removed,
2) The unknown concentrations lie between standard values.
3) Matrix and interference effects are the same for both standard and unknown.

To speed up the above calculations a program was written for a programmable calculator, and this was used to calculate element concentrations for all analytical results.

5:2 PROGRAM DESCRIPTION.

The equipment used was a Hewlett Packard HP 9800 calculator, equipped with a 500 step program memory, and 100 data registers. In addition a cassette memory unit was used, together with a mathematics block, and cassette memory unit control block.

The program consists of six files stored on the cassette memory tape. The first of these files, file 0, was loaded manually into the calculator memory, and this acted as a control program to call in the correct order, each of the other five files, making up the main body of the program.

Operation of the program was as follows:-
After loading file 0 the scale expansion used on the A.A. instrument (Appendix 1) was entered. The first of the five program files was then loaded automatically. Data from the chart records was entered, starting and finishin with a background or blank reading. The order of input was blank standard or unknown, blank. Standards were entered lowest value first. After the standards were entered up to nine unknowns were entered, followed by the same standards in the reverse order (highest first). Up to seven standards were run, which completely bracketed the absorption values for the unknowns. When all the data had been entered a negative number was entered, and the calculator proceeded to the next part of the program in which the number of data points, the number of standards, and the number of unknowns were entered. After this the concentrations of the standards were entered, the lowest concentration (in $\mu g\ ml^{-1}$) being entered first.

As each absorption value was entered the absorbance was calculated according to the relation:-

$$\text{Absorbance} = (1- (\log_{10} (100-\%\ \text{absorption}))$$

and the absorbance stored. The average blank value was calculated from the blank absorbances on each side of a standard or unknown, and subtracted from that standard, or unknown. The standard absorbances, before and after the unknown absorbances, were then averaged and stored. Calculations of the unknown concentrations was done by finding standard absorbance values, above and below the unknown absorbances, and assuming a straight line relationship between the two (see Section A5:1). The dilution factor was read in, followed by the weights of the rock powders that had been dissolved to produce the unknown solutions. The program then multiplied the concentration by the dilution factor, and divided by the weight of the rock powder dissolved to produce a value for concentration of the element in the rock sample. This value was printed out.

The program then stored the sample weights for use in subsequent calculations and reloaded file 0 ready for the next set of analytical data.

A complete program listing, and set of operating instructions, is on file in the Department of Geological Sciences, University of Aston, in Birmingham.

APPENDIX 6

DATA HANDLING PROGRAMS

A6:1 Introduction.

Two data handling programs, SORT and ABST were written in FORTRAN 4 to speed up and simplify data handling. These programs also acted as link programs for the main data analysis programs.

A6:2 Storage of Data - Program SORT.

This program accepted data from punched cards, punched tape, or magnetic disc and stored it in standard format as a master file on either punched tape or cards (see Chapter 6). The input to the program was as follows :-

```
      READ (IN, 10) AN, PN, V, U
10    FORMAT (410)
      READ (IN, 20) CODE, CONC, CON
20    FORMAT (10, F0.0,10)
```

Data, in the form of a series of element analyses, was input to the computer, and stored on magnetic disc, under a file name input with the data. The relevant system control card is :-

```
INPUT USER NO., FILENAME
```

A typical set of input data is shown in Fig.A19. This stored data is then run through program SORT using the following cards :-

Card 1

```
UAFORTRAN *TRI S03,OWNPD, TIME 200, DA1 !(*DA,KWOR20, BUCK1), *TPO OTE1,
EXIT, LI-
```

Card 2

```
NES 9000, *TRO S16, LOAD SORT
```

Card 3

Blank card

Card 4

****

Fig. A19. Input Data to Program SORT.

```
INPUT SGP0614,S03
1165  0000  33  42          - Sample description
14  67.87  1
13  13.05  1
26  12.52  1
80  0.03  1
82  35.00  1
30  97.00  1                  Element  analysis
28  65.00  1
29  36.00  1
38  112.00  1
56  1678.00  0
1173  0000  39  34
26  8.09  1
14  59.93  1
13  13.69  1
30  100.00  1
82  18.00  1
29  0.00  1
38  129.00  1
56  1324.00  1
28  47.00  1
80  0.008  0
    -                  |
    -                  |  - Repeat data
    -                  |
    -                  |
1046  7412  11  4
39  8.00  1
38  17.00  1
37  27.00  1
90  6.00  1
82  10.00  9
****   -   -   -   -  End of data
```

In card 1 *TRI referred to the previously stored data file; *TRO to the new data that was being input; and *TPO to the new, updated data file being produced. Card 2 was a program control card. The above illustration means that a set of data was already stored on a file and was to be updated. If this card contained a digit in Column 1 the program created a new data file, and did not search through existing ones (see below).

In operation the stored data file was read directly onto a direct access storage disc (*DA in card 1). The first card of the input data was then read in (Fig. A19), and the rock analysis number compared with each analysis number already on the stored data file. If this number was not present on the stored data file, the rock analysis was added to the end of the new data file. If, however, the analysis number was already present on the stored data file, the input analysis was read in and stored at the end of the element analyses previously stored on the new data file. This process was repeated until all of the input data had been processed. Data is stored on the storage file in the same format that it is input.

A program listing is shown in Fig. A 20.

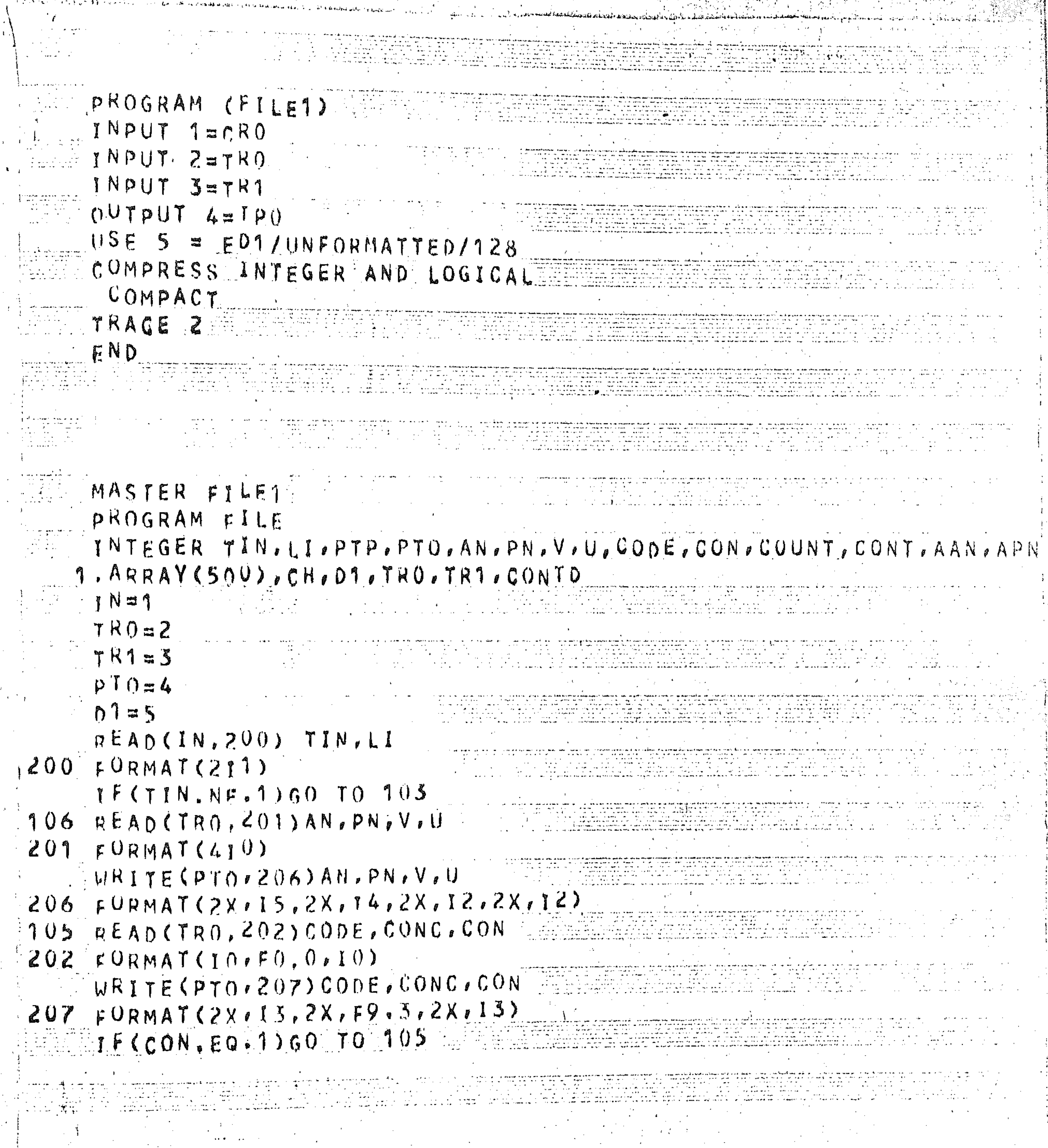
A6: 3 Retrieval of Data - Program ABST.

This program reads in the stored data file, and abstracts information from it. This information was then stored on magnetic disc in a form suitable for input either to the statistical analysis program or the trend analysis program.

Option 1 - Output for Program FOURFIT (trend analysis)

Program Fourfit required the input of a series of single element analyses together with an identification code and grid reference. To provide this program ABST read in a list of rock analysis numbers,

Fig. A20. Listing of program SORT.



```
      PROGRAM (FILE1)
      INPUT 1=CR0
      INPUT 2=TR0
      INPUT 3=TR1
      OUTPUT 4=TP0
      USE 5 = ED1/UNFORMATTED/128
      COMPRESS INTEGER AND LOGICAL
       COMPACT
      TRACE 2
      END
```

```
      MASTER FILE1
      PROGRAM FILE
      INTEGER TIN,LI,PTP,PTO,AN,PN,V,U,CODE,CON,COUNT,CONT,AAN,APN
     1.ARRAY(500),CH,D1,TR0,TR1,CONTD
      IN=1
      TR0=2
      TR1=3
      PT0=4
      D1=5
      READ(IN,200) TIN,LI
  200 FORMAT(2I1)
      IF(TIN.NE.1)GO TO 103
  106 READ(TR0,201)AN,PN,V,U
  201 FORMAT(4I0)
      WRITE(PT0,206)AN,PN,V,U
  206 FORMAT(2X,I5,2X,I4,2X,I2,2X,I2)
  105 READ(TR0,202)CODE,CONC,CON
  202 FORMAT(I0,F0.0,I0)
      WRITE(PT0,207)CODE,CONC,CON
  207 FORMAT(2X,I3,2X,F9.3,2X,I3)
      IF(CON.EQ.1)GO TO 105
```

Fig. A20. (cont'd)

```
      IF(CON.EQ.0)GO TO 106
      GO TO 131
      COUNT=0
  103 READ(TR0,201)AN,PN,V,U
      COUNT=COUNT+1
      WRITE(D1)AN,PN,V,U
  107 READ(TR0,202)CODE,CONC,CON
      WRITE(D1)AN,PN,V,U
      IF(CON.EQ.1)GO TO 107
      IF(CON.EQ.0)GO TO 103
      REWIND D1
      CH=0
      CONT=0
  115 READ(TR1,201)AN,PN,V,U
  110 READ(D1)AAN,APN,AV,AU
      IF(AN.EQ.AAN)GO TO 108
  109 READ(D1)CODE,CONC,CON
      IF(CON.EQ.1)GO TO 109
      IF(CON.EQ.0)GO TO 110
      WRITE(PTO,206)AN,PN,V,U
  114 READ(TR1,202)CODE,CONC,CON
      IF(CON.EQ.1)GO TO 111
      IF(CON.EQ.0)GO TO 112
      CON=0
      WRITE(PTO,207)CODE,CONC,CON
      GO TO 113
  111 WRITE(PTO,207)CODE,CONC,CON
      GO TO 114
  112 WRITE(PTO,207)CODE,CONC,CON
      REWIND D1
      GO TO 115
  108 CONT=CONT+1
      ARRAY(CONT)=AN
  124 WRITE(PTO,206)AN,PN,V,U
  119 READ(TR1,207)CODE,CONC,CON
      IF(CON.EQ.1)GO TO 116
      IF(CON.EQ.0)GO TO 117
      CH=1
      CON=1
      WRITE(PTO,207)CODE,CONC,CON
      GO TO 118
  116 WRITE(PTO,207)CODE,CONC,CON
      GO TO 119
  117 CON=1
      WRITE(PTO,207)CODE,CONC,CON
  118 READ(D1)CODE,CONC,CON
      IF(CON.EQ.1)GO TO 120
      IF(CON.EQ.0)GO TO 121
      IF(CH.NE.1)GO TO 122
      IF(COUNT-CONT)127,127,125
  120 WRITE(PTO,207)CODE,CONC,CON
      GO TO 118
  127 WRITE(PTO,207)CODE,CONC,CON
      GO TO 131
  122 CON=0.
      WRITE(PTO,207)CODE,CONC,CON
      REWIND D1
      GO TO 115
  121 IF(CH.NE.1)GO TO 123
      IF(COUNY-CONT)128,128,125
  128 CON=9
      WRITE(PTO,207)CODE,CONC,CON
```

Fig. A20. (cont'd)

```
      GO TO 131
  123 WRITE(PTO,207)CODE,CONC,CON
      GO TO 115
  125 CON=0
      WRITE(PTO,207)CODE,CONC,CON
  113 CONTD=CONT
      REWIND D1
  129 READ(D1)AN,PN,V,U
      DO 126 I=1,CONT
  126 IF(AN.EQ.ARRAY(I)) GO TO 140
      CONTD=CONTD+1
      WRITE(PTO,206)AN,PN,V,U
  130 READ(D1) CODE,CONC,CON
      IF(CON.EQ.1) GO TO 144
      IF(CON.EQ.0) GO TO 145
  144 WRITE(PTO,207) CODE,CONC,CON
      GO TO 130
  145 IF(COUNT-CONTD)146,146,147
  147 WRITE(PTO,207) CODE,CONC,CON
      GO TO 129
  146 CON=9
      WRITE(PTO,207) CODE,CONC,CON
      GO TO 131
  140 READ(D1) CODE,CONC,CON
      IF(CON.EQ.1) GO TO 140
      IF(CON.EQ.0) GO TO 129
  131 CONTINUE
      STOP
      END
```

from cards, which were to be output. The next card contained the atomic number of the element whose concentrations were to be output. The next card contained a FORTRAN 4 statement of the output format for the data.

The stored data file was then read, one analysis at a time, and the analysis numbers checked against the stored input data. When an analysis number that was required in the output data was found, the elements stored under this number, on the stored data file, were checked to ensure that the one required in the output was present. If this was found, the analysis number, grid reference and element concentrations were then stored in the output file. If the correct element concentration was not found a warning was printed out. (Fig. A 21).

Option 2 - Output for I.C.L. Statspackage.

The input to this program consists of a table of element concentrations with rock identification numbers (analysis numbers). The input to program Abst consisted of a series of cards, containing the analysis numbers required in the output, followed by a series of cards giving the atomic numbers of the elements whose concentrations were to be output.

After this information had been read in, the stored data file was read in, one analysis number at a time. This was checked against the required output information, and, if found to be present, the element concentrations and the analysis number were written in the output file. Because the statistical analysis program can accept differing numbers of variables, these have to be written in a set format, six to line, with continuation cards if necessary. The output from program Abst was arranged so that it was compatible with this format. If either an analysis number, or an element, was not present in the stored data file, a warning was printed out. An example of

Fig. A21. Output data from program ABST to program ITFIT.

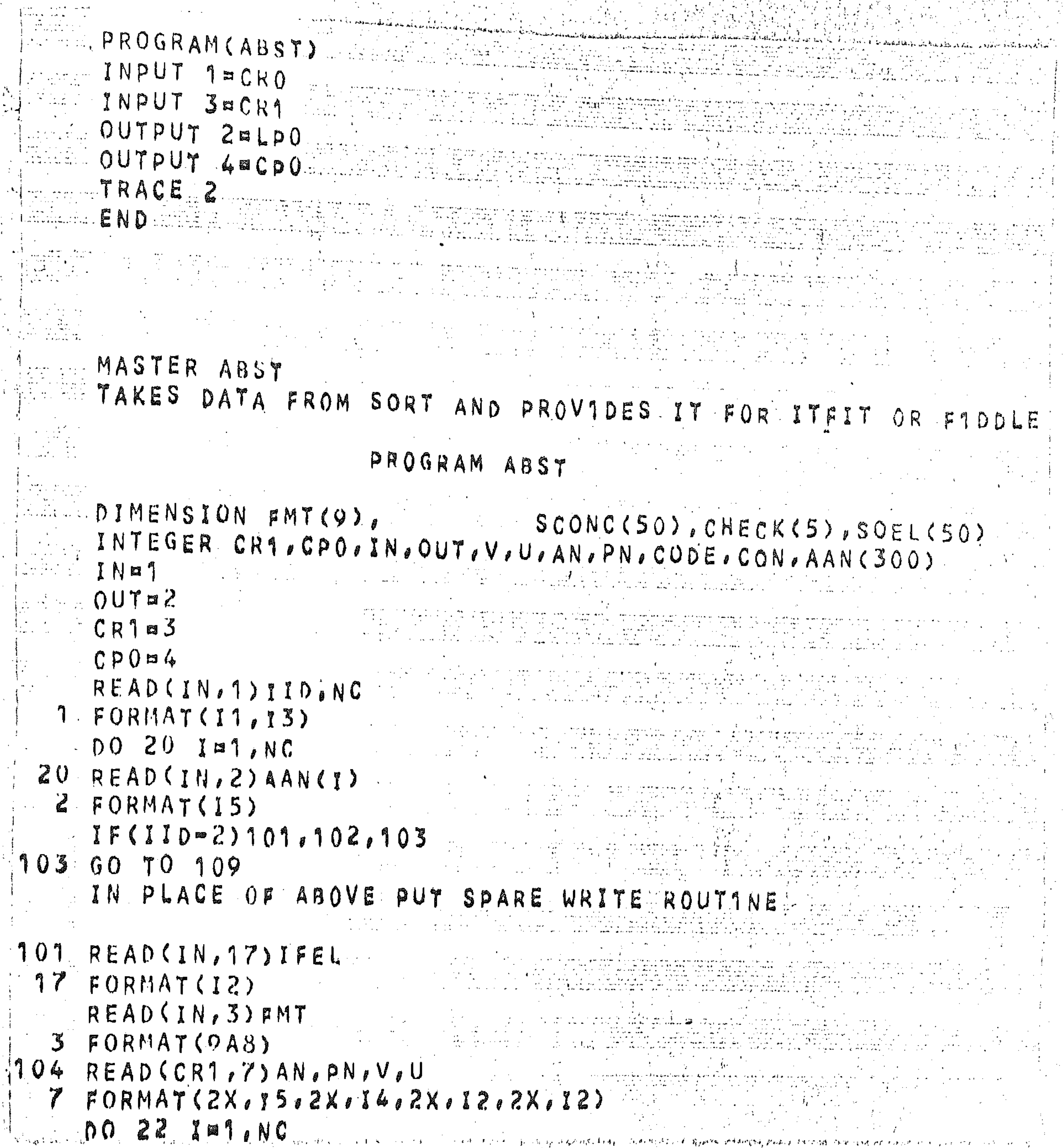
```
1069     13.00   18.00   18.00
1039      9.00    7.00   17.41
1020      9.00    5.00   24.79
1017      7.00    4.00   14.71
1015      6.00    4.00   11.00
1007      2.00    2.00   26.00
1005      4.00    7.00   22.00
1022      7.00    6.00   13.00
1102     16.00   13.00   18.00
1040     10.00   11.00   30.00
1096     19.00   15.00   17.00
1057     10.00   12.00   34.00
1058     11.00   12.00   28.00
1038      8.00    7.00   26.00
```

the output is given in Fig. A 22. A complete listing of program Abst is given in Fig. A 23.

Fig. A22. Output data from program ABST for input to STATSPACKAGE.

```
2001   1.47   10.41   0.72   8.19   3.02   5485.00   8.25
,   0.31   3.68   109.00   82.36   53.58   157.00
2002   0.57   56.35   0.66   0.76   0.00   1532.00  5.22
,   0.02   5.30   66.31   94.82   196.00   47.94
2003   1.10   66.68   0.00   8.10   0.00   10289.00   6.00
,   0.16   4.65   57.46   90.69   225.00   65.81
2004   0.36   12.05   0.75   0.00   0.00   18362.00   3.78
,   0.00   7.71   70.94   91.56   54.42   81.63
2006   0.13   31.80   0.00   14.78   0.00   3229.00   7.69
,   0.55   0.68   151.00   80.31   110.00   44.76
```

Fig. A23. Listing of program ABST.



```
      PROGRAM(ABST)
      INPUT 1=CR0
      INPUT 3=CR1
      OUTPUT 2=LP0
      OUTPUT 4=CP0
      TRACE 2
      END



      MASTER ABST
      TAKES DATA FROM SORT AND PROVIDES IT FOR ITFIT OR FIDDLE

                          PROGRAM ABST

      DIMENSION FMT(9),            SCONC(50),CHECK(5),SOEL(50)
      INTEGER CR1,CP0,IN,OUT,V,U,AN,PN,CODE,CON,AAN(300)
      IN=1
      OUT=2
      CR1=3
      CP0=4
      READ(IN,1)IID,NC
    1 FORMAT(I1,I3)
      DO 20 I=1,NC
   20 READ(IN,2)AAN(I)
    2 FORMAT(I5)
      IF(IID-2)101,102,103
  103 GO TO 109
      IN PLACE OF ABOVE PUT SPARE WRITE ROUTINE

  101 READ(IN,17)IFEL
   17 FORMAT(I2)
      READ(IN,3)FMT
    3 FORMAT(9A8)
  104 READ(CR1,7)AN,PN,V,U
    7 FORMAT(2X,I5,2X,I4,2X,I2,2X,I2)
      DO 22 I=1,NC
```

Fig. A23. (cont'd)

```
 22 IF(AAN(I).EQ.AN)GO TO 105
    GO TO 110
204 WRITE(OUT,12)IFEL,AN
 12 FORMAT(1X,10HNO ELEMENT,I2,15HFOUND IN SAMPLE,I5)
    GO TO 104
110 READ(CR1,13)CODE,CONC,CON
 13 FORMAT(2X,I3,2X,F7.3,2X,I3)
    IF(CON.EQ.1)GO TO 110
    IF(CON.EQ.0)GO TO 104
    GO TO 109
105 READ(CR1,13)CODE,CONC,CON
    IF(CODE.EQ.IFEL)GO TO 106
    IF(CON.EQ.1)GO TO 105
    IF(CON.EQ.0)GO TO 204
    GO TO 109
106 UU=U
    VV=V
    WRITE(CPO,FMT)AN,UU,VV,CONC
  9 FORMAT(1X,I5,2X,F6.0,2X,F6.0,2X,F6.2)
107 IF(CON.EQ.1)GO TO 108
    IF(CON.EQ.0)GO TO 104
    GO TO 109
108 READ(CR1,13)CODE,CONC,CON
    GO TO 107
102 READ(IN,4)NE
  4 FORMAT(I3)
    DO 21 I=1,NE
 21 READ(IN,5)SOEL(I)
  5 FORMAT(I5)
    READ(IN,3)FMT
113 READ(CR1,7)AN,PN,V,U
    IOUT=0
    DO 23 I=1,NC
 23 IF(AAN(I).EQ.AN)GO TO 111
    WRITE(OUT,14)AN
 14 FORMAT(10HNO SAMPLE ,I5,5HFOUND)
112 READ(CR1,13)CODE,CONC,CON
    IF(CON.EQ.1)GO TO 112
    IF(CON.EQ.0)GO TO 113
    GO TO 109
111 DO 24 J=1,100
    SCONC(I)=0
 24 CHECK(I)=0
119 READ(CR1,13)CODE,CONC,CON
    DO 25 J=1,NE
 25 IF(SOEL(I).EQ.CODE)GO TO 114
    IF(CON.EQ.1)GO TO 119
    IF(CON.EQ.0)GO TO 117
118 IOUT=1
    GO TO 117
114 SCONC(J)=CONC
    CHECK(J)=1
116 IF(CON.EQ.1)GO TO 115
    IF(CON.EQ.0)GO TO 117
115 READ(CR1,13)CODE,CONC,CON
```

Fig. A23. (cont'd)

```
      GO TO 116
117   DO 26 J=1,NE
26    IF(CHECK(J).EQ.0) GO TO 120
121   IF(NE.GT.7)GO TO 122
      WRITE(CPO,27)AN,(SCONC(I),I=1,NE)
27    FORMAT(1X,I5,7(2X,F6.2))
      GO TO 123
122   WRITE(CPO,27)AN,(SCONC(I),I=1,NE)
      WRITE(CPO,28)(SCONC(I),I=1,NE)
28    FORMAT(2X,1H,,7(2X,F6.2))
      GO TO 123
120   WRITE(OUT,12)SOEL(J),AN
      GO TO 121
123   IF(IOUT.EQ.1)GO TO 109
      GO TO 113
109   CONTINUE
      STOP
      END
```

APPENDIX 7

Statistical Analysis.

A7: 1 Introduction

Statistical analysis was performed using the I.C.L. STATSPACKAGE, which is able to compute a whole series of statistical functions according to input information. Detailed operating instructions are given in the I.C.L. STATSPACKAGE manual.

A 7 : 2 Theory of Component and Factor Analysis.

Both component and factor analysis were developed at the beginning of this century by psychologists who wished to divide a complex set of variables into a number of distinct patterns or factors. The technique has been used in geology in the past two decades, with the advent of automatic methods of analysis (emission spectrography and X-ray fluorescent spectrometry), and computers to handle the data.

The first use of this technique in geochemistry was by Imbrie and Purdy (1962), Imbrie and Van Andle (1964), and McCammon (1966). Since then it has been used on an increasing variety of problems, from the genesis of ore minerals in the Witwatersrand gold deposit Saager and Esselaar,(1969) to the interpretation of patterns of regional geochemical data (Nichol, 1973). An introduction to, and description of, the technique was given by Krumbein and Graybill (1965), Morrison (1967) and Anderson (1971).

Statistical methods may be divided into two groups; those dealing with single variables, and those dealing with a number of different varaibles, at the same time. In geochemical studies a number of variables are present, and multivariate statistics are necessary to handle the data satisfactorily. The ultimate aim of this type of statistical analysis is to determine the number of different causes of the variations in element concentrations. A whole range of different causes may be interacting, e.g.sedimentary depositional environment, metamorphism, hydrothermal activity, weathering, leaching, sampling, analysis, and the statistical analysis should be capable of resolving the effects of each of these.

The types of analysis used in the present work were principal component analysis and R-mode factor analysis.

Principal Component Analysis.

To perform this analysis it is assumed that the observations were drawn from a population with a multi-variate distribution. The observations were written in the form of a table of element concentrations in different samples; or a matrix, X :-

$$X = \begin{array}{ccc} X_{11} & \text{--------- --} & X_{1p} \\ \text{-----} & \text{-----} & \text{-----} \\ \text{-----} & \text{-----} & \text{-----} \\ X_{N1} & \text{----------- -} & X_{Np} \end{array}$$

For geological data, which may be in a number of different units with a wide variation, the analysis is carried out on a simplified or standard matrix. In this work it was carried out on a correlation matrix of standard scores. To form this matrix the variables were standardised to unit variance, i.e. all the units were made the same by changing them to units of variance.

$$\frac{Z_{ij} = X_{ij} - \bar{X}_j}{S_j} \quad \text{where } \bar{X}_j = \text{column means}$$

$$S_j = \text{column standard deviation}$$

From this a correlation matrix was calculated. Because the interpretation is simplified if the relationship between the variables is approximately linear, the original data matrix was transformed before operations to a linear form. The majority of elements are probably log normally distributed (Ahrens, 1954), thus the $\log_{10}$ of each concentration may produce a better correlation

Extraction of the principal components involved a series of matrix operations which had the following physical analogue. The correlation matrix had each variable set on an axis in N-dimensional space. The observations were then plotted with respect to these axes. The resulting distributions can be imagined as being elongated in certain directions.

The principal axis was then rotated through space, until the sum of the squares of the deviations of the observations from this axis was at a minimum. This is the same as putting the axis along the centre of the greatest elongation of the distribution. The direction cosines (relative to the original axes) of the first principal axis are the elements of the first characteristic vector. This gave the first component which accounted for the maximum amount of variance. New axes were then taken, at 90° to the principal axis, and rotated above the principal axis until the sum of the squares of the deviations of the observations from this new axis was a minimum. This then gave the second component. This process theoretically can be continued until the number of components are equal to the number of variables. However, because higher order components explain very little of the variance only the first five components are commonly determined, and of these, only the first three are generally of use.

In this type of analysis each component is uncorrelated with all of the others, i.e. the axes are orthogonal by definition. The reasons for the variation in trace element concentrations may be correlated to some extent and this leads to poor resolution of components. Because of this it was necessary to apply factor analysis to the data.

Factor Analysis.

Three types of factor analysis are available. These are R-mode, Q-mode and P-mode types. The R-mode analysis is the only one relevant to the present work. Q-mode analysis is used to classify multi-variate observations, and P-mode analysis contains a time dimension, not as yet used by geologists.

R-mode analysis is used to identify the number of independent variables in a set of observations. It has been used extensively by geologists, both in sediment studies (Imbrie and Purdy, 1962), and in exploration geochemistry (Dahlberg, 1969; Armour-Brown and Nichol, 1970).

In this analysis a correlation matrix was operated on to extract the factors. The operation was the same as for principal component analysis except for two important differences. The first is that the principal axes were not defined so as to be at 90°, i.e. the factors may be correlated. The second is that when all the axes had been positioned in space they were again rotated rigidly, to minimise the sum of the squared deviations. In factor analysis all the variation is assumed to be accounted for by a set number of factors, i.e. the factors are normalised.

Factor analysis produces factors which have the following properties :

1) The factors may be correlated.

2) The factors are normalised.

3) The final rotation (Promax method, Hendrickson and White, 1964) is equivalent to finding the best fit values for the common factor and specific variates after removal of the random, or the experimental variation.

More detailed discussions of factor analysis are given in works by Harmon (1967), Roozeboom (1966), Rummell (1966), Fruchter (1954), Van de Geer (1971), and Nie et al (1970). Geological applications of factor analysis are to be found in Harbaugh and Merriam (1968), Krumbein and Graybill (1965), and Miller and Kahn (1962).

In the present work the principal component analysis was first performed to give an indication of the number of relevant components causing the variation. Factor analysis was carried out with the variation normalised to the number of factors inferred from the component analysis.

A7 : 3 Program Operation.

A detailed description of the programs, and the control cards necessary to run it, is given in the I.C.L. STATSPACKAGE manual. In the present work the control cards and data were assembled in the correct order on magnetic disc (Chapter 6), and then run through the program. Output was directly to the line printer. A complete file ready for input to the statistical analysis program is shown in Fig. A 22.

APPENDIX 8

Trend Surface Analysis.

A8:1. Introduction.

Trend surface analysis of map data is widely used in the study of areal variations in both geologic and geographic variables (Timperley et al, 1972; Krumbein and Graybill, 1965).

In general Double Fourier maps are better for distinguishing small scale local variations from broad scale trends, than conventional polynomial trend analysis. Recent developments in the technique now allow irregularly spaced data as opposed to regularly gridded data to be analysed (James,1966).

Fourier analysis is described in detail by Harbaugh and Preston (1965) and Bhattacharrya (1965).

The program used in the present work is an adaptation of James's (1966) program FOURFIT.

A8:2. Theory.

The Double Fourier serries may be defined in several ways, but in this work the definition produced by James (1966a) was used.

$$F(U,V) = {}^{KC}_{i=0}\ {}^{LC}_{j=0}\ CC_{ij} \cos(2\ iU/M)\cos(2\ jV/N)$$

$$+ {}^{KC}_{i=0}\ {}^{LS}_{j=1}\ CS_{ij} \cos(2\ iU/M)\sin(2\ jV/N)$$

$$+ {}^{KS}_{i=1}\ {}^{LC}_{j=0}\ SCij \sin(2\ iU/M)\cos(2\ jV/N)$$

$$+ {}^{KS}_{i=1}\ {}^{KS}_{j=1}\ SSij \sin(2\ iU/M)\sin(2\ jV/N)$$

Where U= the N-S co-ordinate axis increasing to the S and with the origin at the N map edge.

V= the E-W axis increasing to the E and with the the origin at the W map edge.

$X_{(U,V)}$= mapped variable.

M= maximum U value plus one

N= maximum V value plus one

KC= maximum cosine harmonic in U direction

LC= maximum cosine harmonic in V direction

KS= maximum sine harmonic in U direction

LS= maximum sine harmonic in V direction

If M is even, $KC=M/2; KS=(M-2)/2$

If N is even, $LC=N/2; LS=(N-2)/2$

If M is odd, $KC=KS=(M-1)/2$

If N, is odd, $LC=LS=(N-1)/2$

CC_{ij}, CS_{ij}, SC_{ij}, SS_{ij} are the coefficients of the series The coefficients of the above were derived by using the least squares method. (Krumbein and Graybill, 1965). The number of coefficients calculated (equivalent to terms in a polynomial equation) is greater in the case of Double Fourier analysis due to the fact that the S matrix (a matrix of unconnected sums of squares and cross products of the above Fourier terms) does not progressively increase in size as it does in the case of polynomials.

It can be shown that

$$CC_{ij}=(w/(MN) \substack{M-1\\U=0} \substack{N-1\\V=0} X_{(U,V)} \cos(2\ iU/M)\ \cos(2\ jV/N)$$

$$CS_{ij}=(w/(MN) \substack{M-1\\U=0} \substack{N-1\\V=0} X_{(U,V)} \cos(2\ iU/M)\ \sin(2\ jV/N)$$

$$SC_{ij}=(w/(MN) \substack{M-1\\U=0} \substack{N-1\\V=0} X(U,V) \sin(2\ iU/M)\ \cos(2\ jV/N)$$

$$SS_{ij}=(w/MN) \substack{M-1\\U=0} \substack{N-1\\V=0} X_{(U,V)} \sin\ (2\ iU/M)\ \sin(2\ jV/N)$$

Where

$w=1$ if $i=0$ (or KC, when M is even) and $j=0$ (or C when N is even)

$w=2$ if $i=0$ (or KC, when M is even) or $j=0$ (or LC when N is even)

$w=4$ if i is not zero (or KC when M is even and j is not zero (or LC when N is even).

If computations are carried out for all combinations of (ij), then the number of coefficients obtained will be equal to the number of data points, and the resulting surface will completely fit the data ie. 100% of the variability will be accounted for.

The wavelengths used in the calculation define the period of repetition of the surface, and mean that extrapolation outside the data area is not possible except in the case of regular surfaces. In addition the wavelength chosen will affect the degree of fit of the chosen surface.

In the present work the surface chosen for the trend was the equivalent of a 3rd degree polynomial. Initial work indicated that the sum of squares deviation, between the calculated surface and the actual surface, varied considerably according to the fundamental wavelength chosen. To enable a better fit to be obtained the program was re-written to form part of a search routine in which a search was carried out to find the best fit fundamental wavelength for the third degree surface.

Program description.

The program read in four control cards with the title, followed by two further control cards. The first control card determined the search parameters, and the second card determined the initial wavelengths, and indicated the number of terms to be used. After these the input format of the data was read in, followed by a card which defined the area to be output in the form of a map. A series of cards, containing coded information on individual terms used in the equation was then read in.

The operation of the program was controlled by master segment FOUR which, in addition to reading in the above parameters, called

SUBROUTINE FIT. This subroutine calculated a trend surface using given wavelengths, and produced a sum of squares deviation between calculated and actual values. The sum of squares value was then stored, and one of the wavelengths (either U or V) was changed by an amount read in on the first control card. Subroutine FIT was called again, and a new sum of squares deviation calculated. This was then compared to the previous value. The process was then repeated, changing each wavelength in turn,until the sum of squares differences between sucessive wavelengths was less than a predetermined value, read in on card 1. In addition, as convergence was approached, the wavelength increment (or decrement) was repeatedly halved to obtain the best fit.

When convergence had been obtained a total fit surface was calculated, using the determined wavelengths. The trend surface was then subtracted from the total surface to produce a set of residuals.Each of these surfaces was then printed out in the form of a contour map. This map could be expanded to any scale by using the options on control card 3. Scaling up was achieved by printing out the final map in sections if necessary.

The search routine used in this work was adapted from that developed by Smith (1975), who also discussed its merits relative to other types of search routine.

The program was tested using a set of data contained in James (1966b) The data was taken from a contour map (Fig.A24), and handcontoured by a volunteer who had not seen the original map (Fig.A25, Fig.A26). This contoured data was then run through the program with the search routine and arbitary initial wavelengths. The trend surface calculated

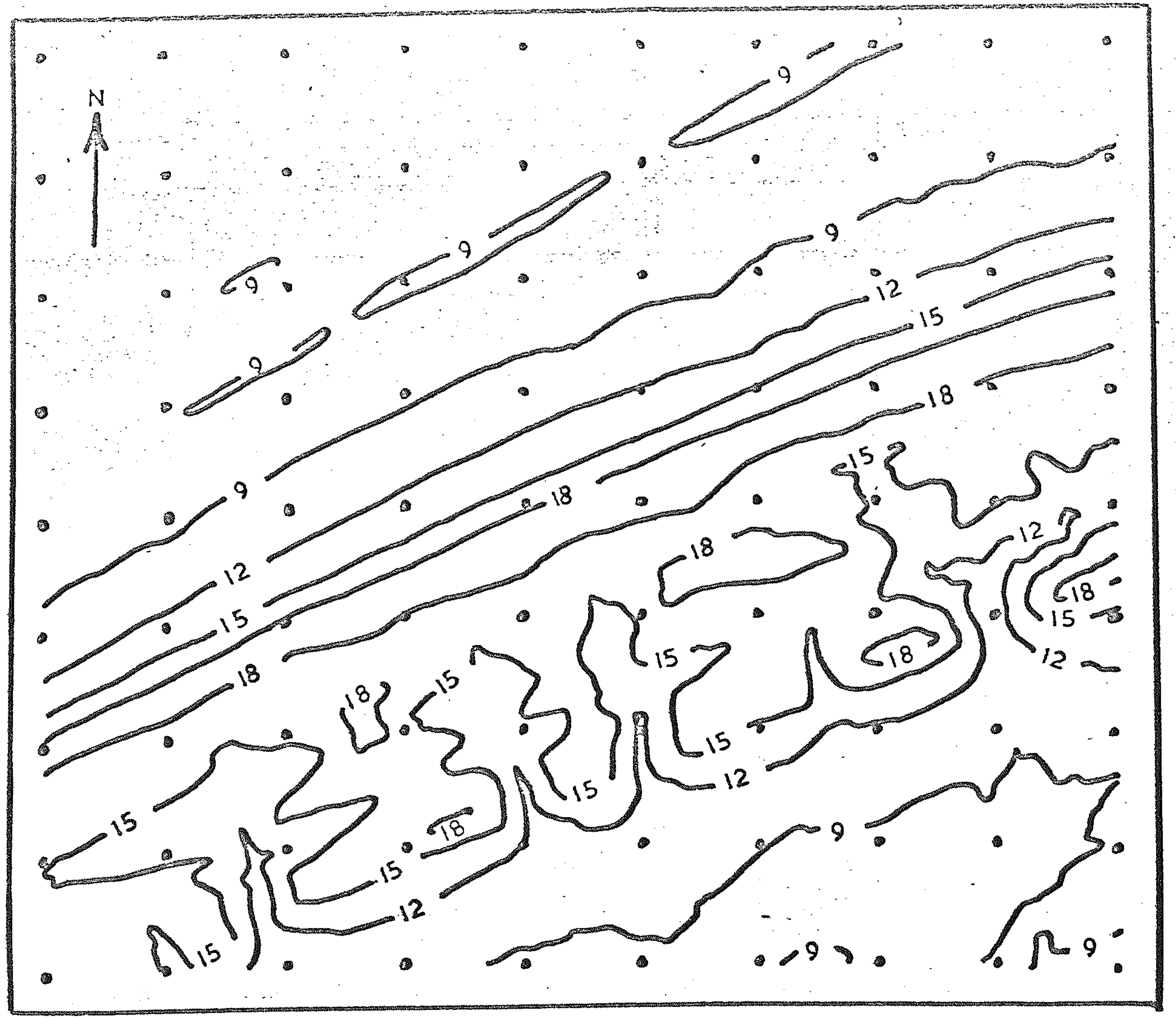


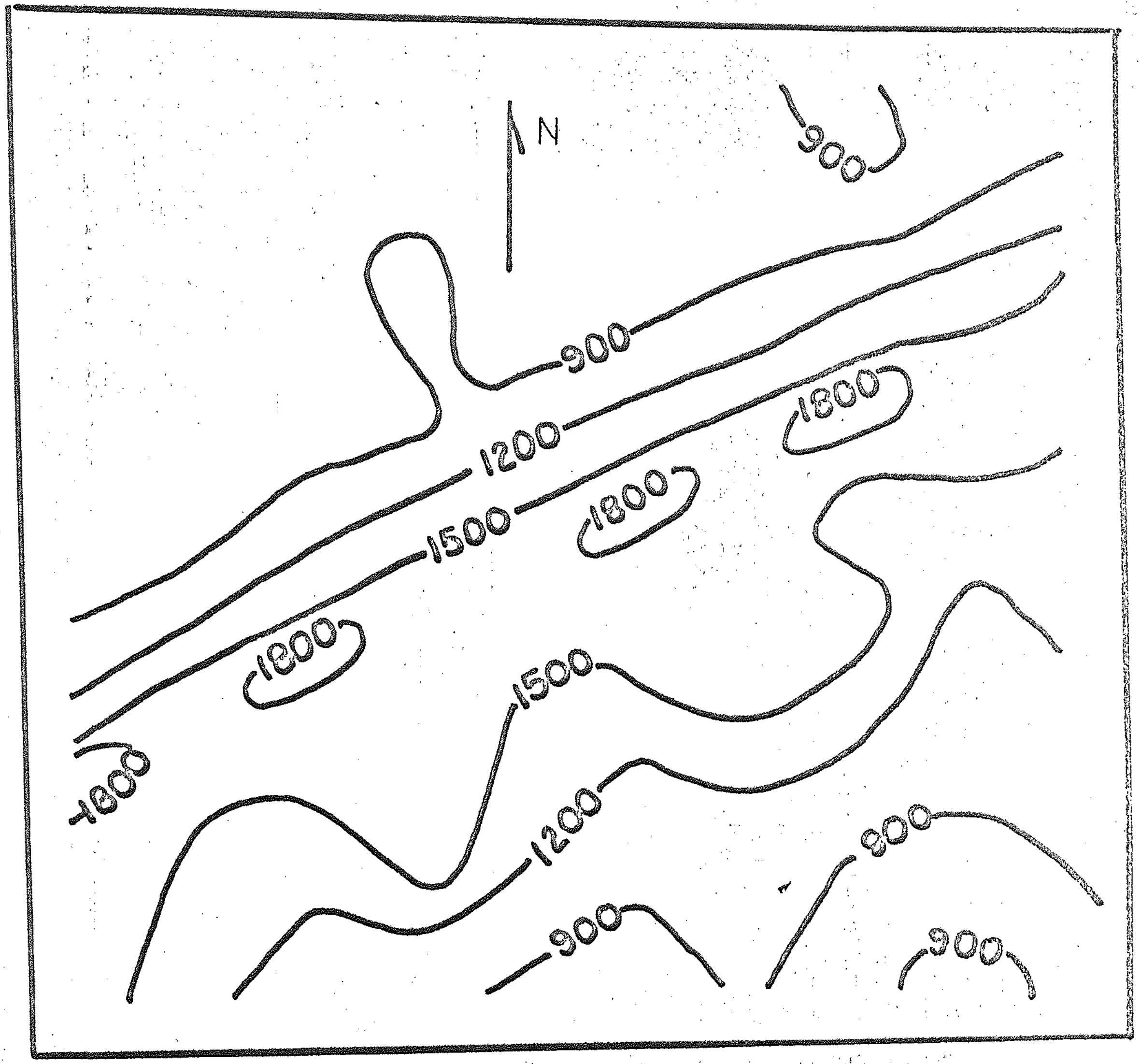
Fig. A24. Original test contour map for Fourfit

Diagram is a topographic map with varied relief to test the performance of the trend surface program under different conditions. Points (•) show places were spot heights have been read off to produce Fig A25.

Fig. A25. Data grid for test of Fourier analysis program (taken from Fig. A24)

680	650	720	820	760	680	720	1000	690	750
670	650	760	880	750	680	730	770	880	970
690	760	750	950	730	800	980	1110	1340	1680
700	850	770	880	1050	1220	1570	2010	1740	1670
740	860	1080	1320	1730	1930	1670	1400	1490	1380
1030	1310	1820	1790	1770	1640	1690	1640	1060	1400
1860	1720	1610	1620	1410	1200	1460	1170	980	960
1650	1400	1300	1720	1180	1030	910	860	850	950
1660	1390	980	1040	870	870	910	760	940	770

Fig. A26. Hand contoured test map.



This map should be compared with the original in Fig A24.

was a third degree surface which used coefficients in blocks 0, 1, and 2 (James, 1966). The resulting trend surface maps, the complete fit surface, and the residuals are shown in Fig.A27, Fig.A28, and Fig.A29, and compared to the maps of the third degree fit, and the full fit, in James (1966b).

From these results the trend, Fig.A27, produced by program FOURFIT was seen to compare well with the hand contoured map, Fig.A26; however the major features were shifted slightly Southwards. The full fit (Fig. A28) was seen to correspond well with the hand contoured map. From the residuals it is clear that the worst fit was in the area where rapid alternations of height occurred ie. along the central ridges. To solve the problem of poor fit in places like this a restriction was put on the wavelength search so that only short wavelengths, capable of producing a surface that would fit short term variates, were included. However this meant that long term trends were suppressed. In the present work, it is the long term trends that are important. The plot of the search surface is shown in Fig.A30. This indicates that the best fit surface was a long low valley with a flat bottom. The search routine assumed that there was only one minimum to the surface, which was not completely true. However, as long as initial wavelengths were chosen which were a fraction of the area covered by the data, a true best fit was produced.

For the present work the trend analysis had to be able to separate large scale trends from rapid local variations caused, either by analytical error, or by local concentrations of trace elements. To do this the third degree fit was found to be sufficient, as higher degrees of fit started to reflect local variations, and lower degrees of fit did not reflect long term trends with any degree of accuracy.

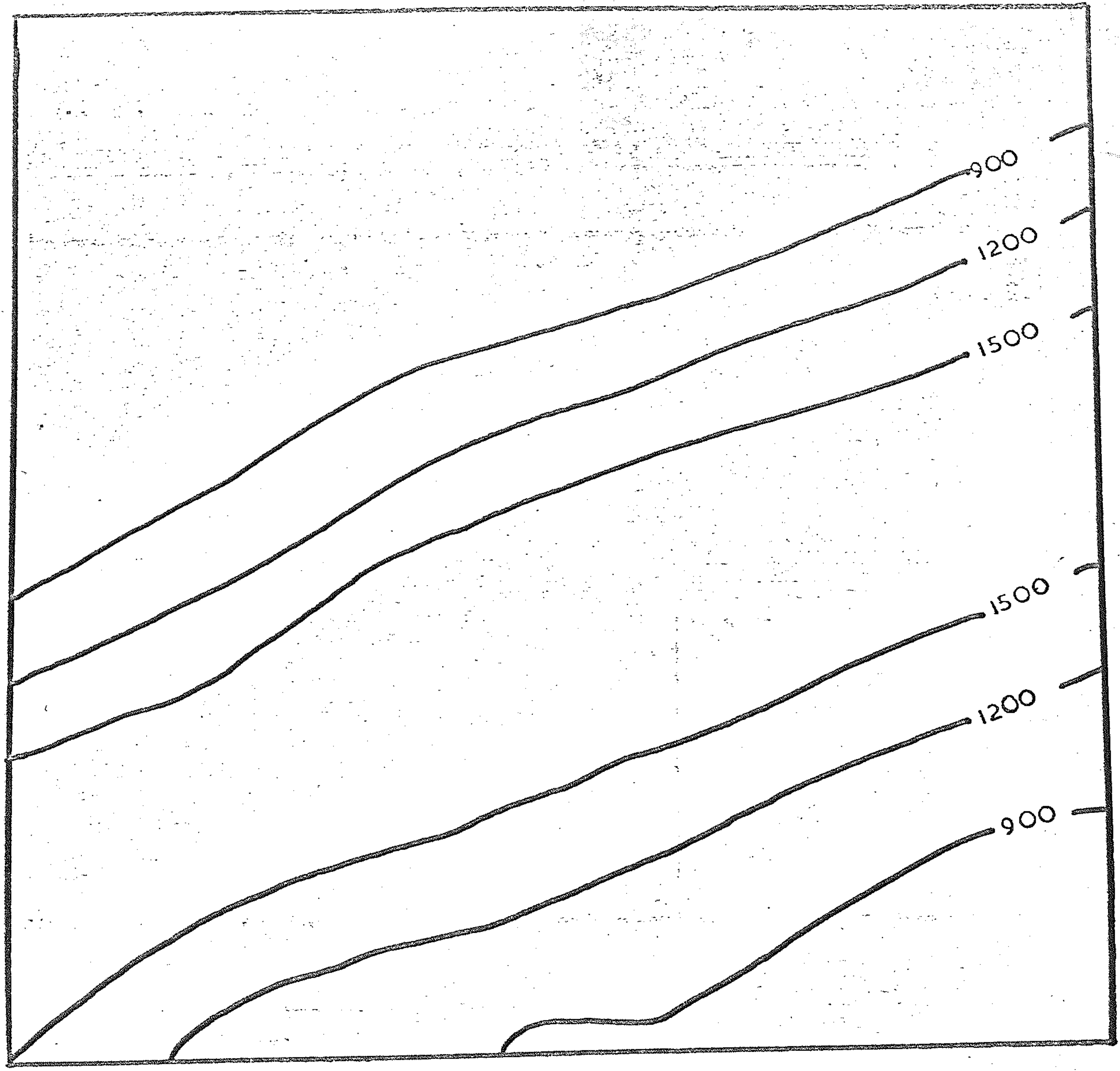


Fig. A27. Fourfit test data - Trend Surface

Map should be compared with original im Fig A24 and hand drawn map in Fig A26..

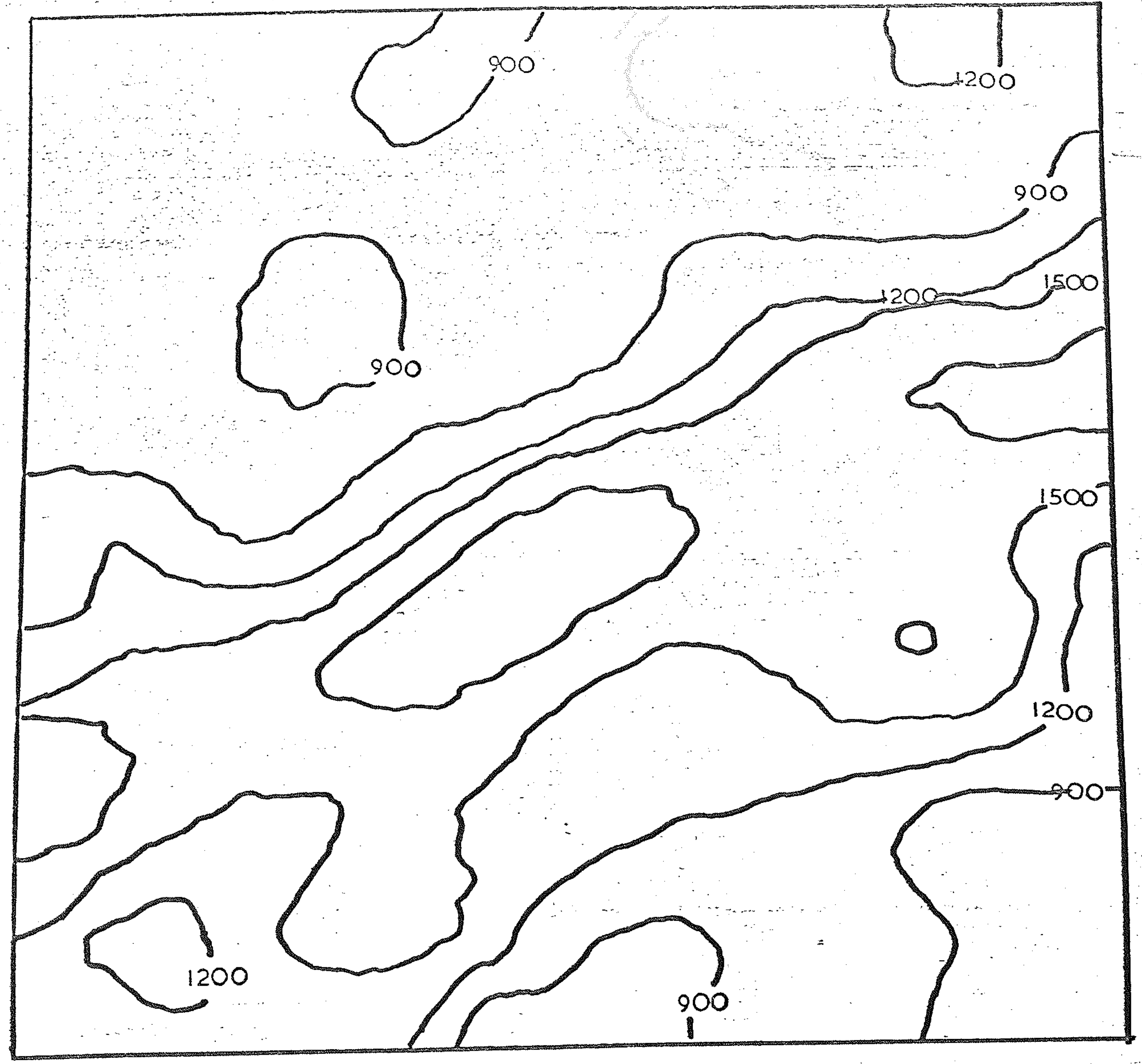


Fig. A28. Fourfit test data - Total Surface.

Map should be compared with original in Fig A24 and hand drawn map in Fig A26

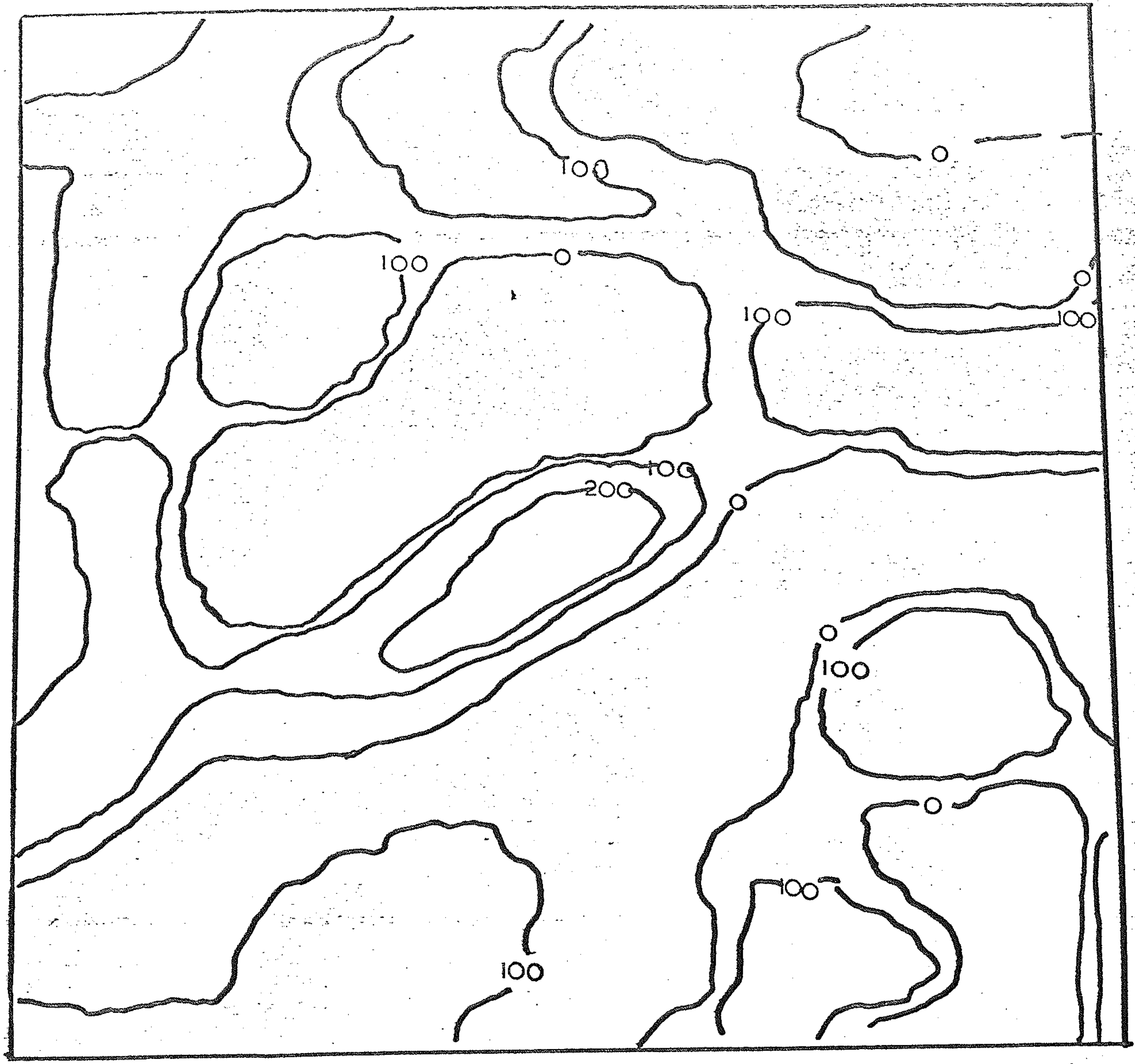


Fig. A29 Fourfit test data - Residuals. Compare with Fig A27

Fig. A30. Search surface for test data on program ITFIT.

Plot of sum of squares contributions against wavelengths.

U wavelength

V wavelength	1	3	5	7	9	11	13	15	17	19	21	23	25
3													
5													
7					70								
9													
11													
13					84	89							
15													
17													
19						89		88					
21													
23					35	89		88					
25													
27					85	89		88					
29													
31					85	89		88					
33													
35													
37						89							
39													
41													

Fig. A31 E(sum of squares reduction) for random data.with no trend.
(after James,1966)

Harmonic order of surface	E(SS reduction)
1	6.61 %
2	19.83 %
3	39.67 %
4	66.12 %
5	100.00 %

It has been pointed out, with regard to polynomial trend analysis, that some trend surfaces, on which some work has been based, show a poorer fit than that obtainable with random data. To test the lowest acceptable level of significance James (1966b) calculated the percent sum of squares accounted for,produced by the Fourier trend program, when data which had no trend and was normally distibuted, was run through the program. Fig.A31 shows the data. A value of 88.88% sum of squares accounted for was produced by the test data for the third harmonic surface. This indicates that the surfaces produced were significant (cf. Fig.A31). In all instances in the present work the significance of the surface was carefully examined before conclusions were drawn.

A complete listing of the program is given in Fig.A32.

Fig. A32. Listing of program FOURFIT.

```
      LIBRARY(ED,SUBGROUPONE)
      PROGRAM(ITFIT)
      INPUT 1=CR0
       INPUT 3=CR0
      OUTPUT 2=LP0
      COMPRESS INTEGER AND LOGICAL
      EXTENDED DATA
      TRACE 0
      END



      MASTER FOUR
      PROGRAM FOURFIT
********************
      A DOUBLE FOURIER SURFACE FITTING PROGRAM FOR
      IRREGULARLY SPACED DATA

       NOD1=FRACTION OF ORIGINAL 'V' WAVELENGTH IN WHICH TO SEARCH
       NOD2=FRACTION OF ORIGINAL 'U' WAVELENGTH IN WHICH TO SEARCH
       NL= NO. OF SEARCH STEPS REQUIRED
       CHSSQ=RATIO OF SUM OF SQUARES VARATION ON WHICH TO END SEARCH
       VINC=NUMBER OF MAPS IN THE 'V'DIRECTION
       UINC=NUMBER OF MAPS IN THE 'U'DIRECTION
       IF IP NOT EQUAL 2 THEN PRINT OUT REDUCED
       IF KOUNT EQUAL TO 1 NO SEARCH REQUIRED
********************
      INTEGER CR1
      REAL NOD1,NOD2
      INTEGER VINC,UINC,OUT
      DIMENSION TITL(36),FMT(9),IDEN(200),II(100),JJ(100),D(200),
     1G(100),IDT(100),SC(100),C(100),COMP(200),RES(200),U(200),V(200)
       DIMENSION FF(100),FRF(100)
      COMMON/BB/ VV(70),UU(42),CH(20),BASE,CONTOUR(19),BLANK,
     1S(90,90),P,UW,VW,UL,UH,VL,VH,U0,V0,CVAL(42,70)
      COMMON/CC/VINC,UINC,IP,VB,VN,UB,UN

      READ CONTROLS AND DATA

      IN=1
      OUT=2
      CR1=3
    1 READ(IN,100) TITL
    3 WRITE(OUT,100)TITL
  100 FORMAT(9A8)
      READ(IN,1003)KOUNT,NOD1,NOD2,NL,IP,CHSSQ,VINC,UINC
 1003 FORMAT(I1,1X,2F5.3,2(1X,I2),F10.7,2(2X,I2))
      ITOP=0
      READ(IN,101) UW,VW,OPA,OPB,OPC,OPD,M,N,U0,V0
  101 FORMAT(2F6.0,4F1.0,2I3,2F6.0)
      WRITE(OUT,200)UW,VW,OPA,OPB,OPC,M,N,U0,V0
  200 FORMAT(///5X,11HMASTER CARD,5X,12HU WAVELENGTH,3X,F8.2,10X,
     112HV WAVELENGTH,3X,F8.2,//10X,15HCOMPUTED VALUES,3X,F1.0,5X,
     28HCOSY MAP,3X,F1.0,5X,12HCOMPLETE FIT,3X,F1.0,//10X,17HNO COEFF
     3TREND,2X,I5,5X,11HNO DATA PTS,3X,I6,5X,9HWAVE ORIG,2X,2F6.2)
EPARATOR OMITTED AT ABOUT COLUMN 12, LINE 0052 , COMMA ASSUMED
```

```
      READ(IN,100)FMT
      IF(OPB.NE.1) GO TO 5
    4 READ(IN,102) UL,UH,VL,VH,BASE,CINT
      WRITE(OUT,4100)UL,UH,VL,VH,BASE,CINT
 4100 FORMAT(////10X,8HMAP CARD,5X,4HUMIN,2X,F6.2,5X,4HUMAX,2X,F6.2
     15X,4HVMIN,2X,F6.2,5X,4HVMAX,2X,F6.2,//20X,4HBASE,2X,F8.2,10X,
     216HCONTOUR INTERVAL,2X,F6.2)
      DO 135 K=1,19
  135 CONTOUR(K)=BASE+(CINT*K)
    5 READ(IN,103)(II(I),JJ(I),IDT(I),I=1,M)
  103 FORMAT(26(3I1))
      DO 6 K=1,N
      READ(CR1,FMT) IDEN(K),U(K),V(K),D(K)
    6 CONTINUE
  102 FORMAT(4F6.0,2F6.2)
  203 FORMAT(2X,4(I4,2X,F5.2,2X,F5.2,2X,F10.4,2X))
      MP=0
      JM=0
      LL=0
      MM=0
      KK=0
      ASSQ=0.0
      PSSQ=0.1
      IF(KOUNT.EQ.1) GO TO 4056
      C2=VW/NOD2
      C1=UW/NOD1
      CALL FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2                            ASSQ,OPA,OPB,OPC,OPD,M,
     3N,         CINT,IN,OUT)
      JM=JM+1
      PSSQ=ASSQ
      A=ASSQ
      ASSQ=0.0
      WRITE(OUT,4052)UW,VW,PSSQ
      GO TO 4053
 4070 CONTINUE
 4054 PSSQ=ASSQ
 4055 IF(UW.EQ.0)GO TO 4056
      IF(JM.GT.NL) GO TO 4056
      ASSQ=0.0
      KK=0
 4053 CONTINUE
      VW=VW+C2
      CALL FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2                            ASSQ,OPA,OPB,OPC,OPD,M,
     3N,         CINT,IN,OUT)
      JM=JM+1
      B=ASSQ
      CZ=(A-B)/A
      IF((ABS(CZ)).GT.CHSSQ) GO TO 5002
      VW=VW-C2
      GO TO 4060
 5002 A=B
      IF(JM.GT.NL) GO TO 4056
      IF(PSSQ-ASSQ)4057,4058,4058
 4059 KK=0
 4057 KK=KK+1
      ASSQ=0.0
      VW=VW-C2
      IF(VW-C2)4061,4061,4062
 4061 VW=VW*0.5
      JK=2
      GO TO 4063
 4062 VW=VW-C2
      JK=1
 4063 CALL FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2                            ASSQ,OPA,OPB,OPC,OPD,M,
     3N,         CINT,IN,OUT)
      JM=JM+1
      IF(JM.GT.NL) GO TO 4056
      B=ASSQ
      CZ=(A-B)/A
      IF((ABS(CZ)).GT.CHSSQ) GO TO 5001
      A=B
      IF(PSSQ-ASSQ)4064,4058,4058
 4058 PSSQ=ASSQ
      ASSQ=0.0
      GO TO 4065
 5001 MP=1
```

```
4064  IF(MK-2)4066,4067,4067
4067  VW=VW*2.0
      GO TO 4068
4066  VW=VW+C2
4068  IF(MP.EQ.1) GO TO 4060
      ASSQ=0.0
      KK=KK+1
4065  CONTINUE
      UW=UW+C1
      CALL FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2                               ASSQ,OPA,OPB,OPC,OPD,M,
     3N,         CINT,IN,OUT)
      JM=JM+1
      IF(JM.GT.NL) GO TO 4056
      B=ASSQ
      CZ=(A-B)/A
      IF((ABS(CZ)).GT.CHSSQ) GO TO 5003
      UW=UW-C1
      GO TO 4060
5003  A=B
      IF(PSSQ-ASSQ)4069,4070,4070
4069  KK=KK+1
      ASSQ=0.0
      UW=UW-C1
      IF(UW-C1)4071,4071,4072
4071  UW=UW*0.5
      MM=2
      GO TO 4073
4072  UW=UW-C1
      MM=1
4073  CALL FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2                               ASSQ,OPA,OPB,OPC,OPD,M,
     3N,         CINT,IN,OUT)
      JM=JM+1
      B=ASSQ
      IF(JM.GT.NL) GO TO 4056
      CZ=(A-B)/A
      IF((ABS(CZ)).GT.CHSSQ) GO TO 5004
      A=B
      IF(PSSQ-ASSQ)4074,4070,4070
5004  MP=1
4074  IF(MM-2)4075,4076,4056
4076  UW=UW*2.0
      GO TO 4077
4075  UW=UW+C1
4077  IF(MP.EQ.1) GO TO 4060
      KK=KK+1
      IF(KK-3) 4055,4055,4078
4078  C2=C2*MOD2
      C1=C1*MOD1
      LL=LL+1
      IF(LL-10)4055,4055,4056
4060  CONTINUE
4056  WRITE(OUT,4079)UW,VW,PSSQ,JM
      IP=2
      CALL FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2                               ASSQ,OPA,OPB,OPC,OPD,M,
     3N,         CINT,IN,OUT)
4052  FORMAT(2X,19HINITIAL WAVELENGTHS,4X,2HU=,F4.1,2X,2HV=
     1F4.1,4X,22HINITIAL SUM OF SQUARES,E12.6)
4079  FORMAT(////4X,17HFINAL WAVELENGTHS,4X,2HU=,F4.1,2X,
     12HV=,F4.1,6X,20HFINAL SUM OF SQUARES,E12.6,2X,
     212HNO. OF LOOPS,I2)

      MAPPING OPTION FOR COMPUTED SURFACE

      IF(OPB.NE.1.0) GO TO 69
   51 IF(ITOP.EQ.1) GO TO 70
      DO 6010 IK=1,100
6010  FF(IK)=C(IK)
      IFF=0
      VM=VH
      VB=VL
      UM=UH
      UB=UL
      UD=(UM-UB)/UINC
      VD=(VM-VB)/VINC
      DO 1234 JZ=1,UINC
      UN=UB+UD
      DO 2345 JX=1,VINC
```

```
      DO 6012 IK=1,100
      WRITE(OUT,9000) FF(IK)
 9000 FORMAT(2X,F12.6)
 6012 C(IK)=FF(IK)
      VN=VB+VD
   52 DO 53 I=1,42
      UU(I)=((P*(UB-UO))/UW)+(P*(I-1)*(UN-UB))/(41.0*UW)
      DO 53 J=1,70
   53 CVAL(I,J)=0.0
      DO 54 J=1,70
   54 VV(J)=((P*(VB-VO))/VW)+(P*(J-1)*(VN-VB))/(69.0*VW)
      DO 63 K=1,42
      DO 63 L=1,70
      DO 55 I=1,M
      UII=II(I)*UU(K)
      VII=JJ(I)*VV(L)
      IF(IDT(I).EQ.1) GO TO 58
   56 IF(IDT(I).EQ.2) GO TO 59
   57 IF(IDT(I).EQ.3) GO TO 60
   61 CVAL(K,L)=CVAL(K,L)+C(I)*   SIN(UII)*   SIN(VII)
      GO TO 62
   58 CVAL(K,L)=CVAL(K,L)+C(I)*   COS(UII)*   COS(VII)
      GO TO 62
   59 CVAL(K,L)=CVAL(K,L)+C(I)*   COS(UII)*   SIN(VII)
      GO TO 62
   60 CVAL(K,L)=CVAL(K,L)+C(I)*   SIN(UII)*   COS(VII)
   62 CONTINUE
   55 CONTINUE
   63 CONTINUE
      CALL COZYMAP(1)
      WRITE(OUT,4005)
 4005 FORMAT(1H1,20X,15HSYMBOL MEANINGS,//10X,6HSYMBOL,5X,7HMAX VAL,//)
      DO 4000 K=1,19
      WRITE(OUT,4001)CH(K),CONTOUR(K)
 4001 FORMAT(13X,1A1,6X,F10.4)
 4000 CONTINUE
      GO TO 84
   70 DO 71 K=1,42
      UU(K)=((P*(UB-UO))/UW)+(P*(K-1)*(UN-UB))/(41.0*UW)
      DO 71 L=1,70
      S(K,L)=0.0
      VV(L)=((P*(VB-VO))/VW)+(P*(L-1)*(VN-VB))A(69.0*VW)
      DO 72 I=1,M
      UII=II(I)*UU(K)
      VII=JJ(I)*VV(L)
      IF(IDT(I).EQ.1) GO TO 73
   74 IF(IDT(I).EQ.2) GO TO 78
   79 IF(IDT(I).EQ.3) GO TO 80
   81 S(K,L)=S(K,L)+C(I)*   SIN(UII)*   SIN(VII)
      GO TO 82
   73 S(K,L)=S(K,L)+C(I)*   COS(UII)*   COS(VII)
      GO TO 82
   78 S(K,L)=S(K,L)+C(I)*   COS(UII)*   SIN(VII)
      GO TO 82
   80 S(K,L)=S(K,L)+C(I)*   SIN(UII)*   COS(VII)
   82 CONTINUE
   72 CONTINUE
   71 CONTINUE
      CALL COZYMAP(2)
      DO 83 I=1,42
      DO 83 J=1,70
   83 S(I,J)=S(I,J)-CVAL(I,J)
      CALL COZYMAP(3)
      GO TO 76
   69 CONTINUE
   84 IF(OPG.NE.1.0) GO TO 99
      IF(IFF.EQ.0) GO TO 6100
      WRITE(OUT,9001)
 9001 FORMAT(2X,8HIFF.EQ.0)
   75 DO 6016 IK=1,100
      WRITE(OUT,9000) FBF(IK)
 6016 C(IK)=FBF(IK)
      M=N
      ITOP=1
      GO TO 70
   99 CONTINUE
   76 CONTINUE
      VB=VN
 2345 CONTINUE
      VB=VL
      UB=UN
 1234 CONTINUE
 6100 READ(IN,103)(II(K),JJ(K),IDT(K),K=1,N)
```

```
      WRITE(OUT,9002)
 9002 FORMAT(2X,8HIFF.EQ.1)
      M=N
      ITOP=1
      CALL FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2
     3N,       CINT,IN,OUT)            ASSQ,OPA,OPB,OPC,OPD,M,
      DO 6014 IK=1,100
 6014 FDF(IK)=G(IK)
      IFF=1
      GO TO 70
      STOP
      END

LENGTH  1544, NAME  FOUR         - WARNINGS

      SUBROUTINE FIT(TITL,FMT,IDEN,II,JJ,D,G,IDT,SC,C,COMP,
     1RES,U,V,
     2                        ASSQ,OPA,OPB,OPC,OPD,M,N,           CINT,
     3IN,OUT)
      REAL NOD1,NOD2
      INTEGER VINC,UINC,OUT
      DIMENSION TITL(36),FMT(9),IDEN(200),II(100),JJ(100),D(200),
     1G(100),IDT(100),SC(100),C(100),COMP(200),RES(200),U(200),V(200
      COMMON/BB/ VV(70),UU(42),CH(20),BASE,CONTOUR(19),BLANK,
     1S(90,90),P,UW,VW,UL,UH,VL,VH,UO,VO,CVAL(42,70)
      COMMON/CC/VINC,UINC,IP,VB,VN,UB,UN
      IN=1
      OUT=2
      ASSQ=0.0
C
C     COMPUTE S,BETA,HAT,AND G MATRICES
C
      P=2.0*3.1415926
   76 DO 10 I=1,M
      G(I)=0.0
      DO 10 J=1,M
   10 S(I,J)=0.0
      DO 11 K=1,N
      UA=P
      UA=(P*(U(K)-UO))/UW
      VA=(P*(V(K)-VO))/VW
      DO 12 I=1,M
      UII=II(I)*UA
      V(I=JJ(I)*VA
      IF(IDT(I).EQ.1 ) GO TO 16
   13 IF(IDT(I).EQ.2) GO TO 17
   14 IF(IDT(I).EQ.3) GO TO 18
   15 SC(I)=    SIN(UII)*   SIN(VII)
      GO TO 19
   16 SC(I)=    COS(UII)*   COS(VII)
      GO TO 19
   17 SC(I)=    COS(UII)*   SIN(VII)
      GO TO 19
   18 SC(I)=    SIN(UII)*   COS(VII)
   19 G(I)=G(I)+SC(I)*D(K)
   12 CONTINUE
      DO 20 I=1,M
      DO 20 J=1,M
   20 S(I,J)=S(I,J)+SC(I)*SC(J)
   11 CONTINUE
C
C     SOLVE FOR COEFFICIENTS
C
      K=0
   21 CONTINUE
      K=K+1
      IF(K.EQ.M) GO TO 25
   22 DO 23 I=K,M
      IF(    ABS(S(I,K)).LE.0.0001)GO TO 3000
      XY=S(I,K)
      G(I)=G(I)/XY
      DO 95 J=K,M
   95 S(I,J)=S(I,J)/XY
 3000 CONTINUE
   23 CONTINUE
      L=K+1
      DO 24 I=L,M
      IF(S(I,K).NE.1.0) GO TO 3002
 3001 CONTINUE
```

```
      G(I)=G(I)-G(K)
      DO 24 J=K,M
      S(I,J)=S(I,J)-S(K,J)
 3002 CONTINUE
   24 CONTINUE
      GO TO 21
   25 C(M)=G(M)/S(M,M)
      L=M-1
      DO 30 I=1,L
   30 C(I)=G(I)
      I=M
   26 CONTINUE
      I=I-1
      K=I+1
      IF(K.EQ.1) GO TO 29
   27 DO 28 J=K,M
   28 C(I)=C(I)-S(I,J)*C(J)
      GO TO 26
   29 CONTINUE
      IF(IP.NE.2) GO TO 180
      WRITE(OUT,1001)
 1001 FORMAT(1H1//20X,12HCOEFFICIENTS,//10X,4HUSUB,4X,4HVSUB,4X,4HTYPE,
     14X,12HCOEFFICIENTS,//)
      DO 180 K=1,M
      WRITE(OUT,1000)II(K),JJ(K),IDT(K),C(K)
  180 CONTINUE
 1000 FORMAT(10X,3(I4,4X),F12.6)

      COMPUTED VALUES AND RESIDUALS

      IF(OPA.NE.1) GO TO 50
      IF(IP.NE.2) GO TO 5600
   31 WRITE(OUT,110)
  110 FORMAT(1H1,30X,29HCOMPUTED VALUES AND RESIDUALS,//)
 5600 CONTINUE
      SS=0.0
      TSS=0.0
      TS=0.0
      DO 32 K=1,N
      COMP(K)=0.0
      RES(K)=0.0
      UA=(P*(U(K)-U0))/UW
      VA=(P*(V(K)-V0))/VW
      DO 33 I=1,M
      UII=II(I)*UA
      VII=JJ(I)*VA
      IF(IDT(I) .EQ.1) GO TO 37
   34 IF(IDT(I) .EQ.2) GO TO 38
   35 IF(IDT(I) .EQ.3) GO TO 39
   36 COMP(K)=COMP(K)+C(I)*   SIN(UII)*   SIN(VII)
      GO TO 40
   37 COMP(K)=COMP(K)+C(I)*   COS(UII)*   COS(VII)
      GO TO 40
   38 COMP(K)=COMP(K)+C(I)*   COS(UII)*   SIN(VII)
      GO TO 40
   39 COMP(K)=COMP(K)+C(I)*   SIN(UII)*   COS(VII)
   40 CONTINUE
   33 CONTINUE
      RES(K)=D(K)-COMP(K)
      IF(IP.NE.2) GO TO 5601
      WRITE(OUT,111)IDEN(K),U(K),V(K),D(K),COMP(K),RES(K)
  111 FORMAT(10X,I4,5X,2(F6.2,4X),3(F10.4,5X))
 5601 CONTINUE
      SS=RES(K)*RES(K)+SS
      TS=TS+D(K)
   32 TSS=TSS+D(K)*D(K)
      TS=TS/N
      AS=TS*TS*N
      VAR=(TSS-AS)/(N-1)
      ST=VAR**0.5
      ZS=100.0*(1.0-(SS/(TSS-AS)))
      F=((N-M)*(TSS-AS-SS))/((M-1)*SS)
      IDS=M-1
      IDR=N-M
      WRITE(OUT,112)
  112 FORMAT(///10X,9HDATA MEAN,8X,12HST DEVIATION,7X,8HVARIANCE,7X,
     115HPCT SS CONTRIBN,8X,7HF RATIO,2X,6HDF NUM,2X,8HDF DENOM)
      WRITE(OUT,113)TS,ST,VAR,ZS,F,IDS,IDR
  113 FORMAT(/10X,5(F12.4,5X)2(I3,5X))
EPARATOR OMITTED AT ABOUT COLUMN 29, LINE 0457 , COMMA ASSUMED

   50 CONTINUE
      DO 4051,K=1,N
```

```
4051  ASSQ=ASSQ+RES(K)*RES(K)
      WRITE(OUT,4090)ASSQ
4090  FORMAT(2X,15HSUM OF SQUARES=,E12.6)
      WRITE(OUT,5010) UW,VW
5010  FORMAT(2X,F8.2,4X,F8.2)
      RETURN
      END

ENGTH    936, NAME  FIT              = WARNINGS

      SUBROUTINE COZYMAP(IOP)
      INTEGER VINC,UINC,OUT
      REAL MOD1,MOD2
      DIMENSION PR(140)
      COMMON/BB/ VV(70),UU(42),CH(20),BASE,CONTOUR(19),BLANK,
     1S(90,99),P,UW,VW,UL,UH,VL,VH,UO,VO,CVAL(42,70)
      COMMON/CC/VINC,UINC,IP,VB,VN,UB,UN
      IN=1
      OUT=2
      IF(IOP.NE.1) GO TO 2
    1 WRITE(OUT,100)
  100 FORMAT(1H1,//,20X,13HTREND SURFACE)
      GO TO 5
    2 IF(IOP.NE.2) GO TO 4
    3 WRITE(OUT,101)
  101 FORMAT(1H1,//20X,26HTOTAL SURFACE, FOURIER FIT)
      GO TO 5
    4 WRITE(OUT,102)
  102 FORMAT(1H1,//,20X,28HRESIDUALS FROM FOURIER TREND)
    5 CONTINUE
      WRITE(OUT,150)
  150 FORMAT(/12X,1HU,30X,1HV)
      DO 6 J=1,70
    6 VV(J)=VB+((J-1)*(VN-VB))/69.0
      DO 7 I=1,42
    7 UU(I)=UB+((I-1)*(UN-UB))/41.0
      WRITE(OUT,111) VV(1),(VV(J),J=10,70,10)
  111 FORMAT(//21X,F6.2,7(F6.2,4X),/24X,1H*,8X,1H*,6(9X,1H*))
      WRITE(OUT,112)
  112 FORMAT(23X,72(1H-))
      IF(IOP.NE.1) GO TO 51
   50 DO 52 I=1,42
      DO 52 J=1,70
   52 S(I,J)=CVAL(I,J)
   51 CONTINUE
      DO 10 I=1,42
      DO 9 J=1,70
      PR(J)=BLANK
      IF(CVAL(I,J).LT.BASE) GO TO 14
      DO 11 K=1,19
      IF(S(I,J).LE.CONTOUR(K)) GO TO 13
   11 CONTINUE
      K=20
   13 PR(J)=CH(K)
   14 CONTINUE
    9 CONTINUE
      IF(I.EQ.1.OR.MOD(I,6).EQ.0)GO TO 15
      WRITE(OUT,113)(PR(J),J=1,70)
  113 FORMAT(23X,1HI,70A1,1HI)
      GO TO 10
   15 WRITE(OUT,114)UU(I),(PR(J),J=1,70)
  114 FORMAT(16X,F6.2,2H*I,70A1,1HI)
   10 CONTINUE
      WRITE(OUT,112)
      RETURN
      END

NGTH    286, NAME  COZYMAP

      BLOCK DATA
      DIMENSION CH(20)
      COMMON/BB/ VV(70),UU(42),CH      ,BASE,CONTOUR(19),BLANK,
     1S(25,25),P,UW,VW,UL,UH,VL,VH,UO,VO,CVAL(42,70)
      DATA CH   /1H1,1H8,1H/,1H5,1H.,1H3,1H*,1H2,1H+,1H6,1H,,1H9,1H-,1H
     1,1H=,1H4,1H(,1H7,1H),1HS/
      DATA BLANK/1H /
      END
```

APPENDIX 9.

CRUSHING AND GRINDING OF ROCK SAMPLES.

A9:1 INTRODUCTION.

Comparative techniques were used in data analysis; thus the method of grinding was very important. because at this stage there was the greatest risk of contamination. Removal of all risks of contamination is clearly very difficult. The method used, while reducing contamination to a minimum, ensures that any contamination produced was the same for each sample.

Contamination from the crushing and grinding surfaces depends largely on the hardness of the material being reduced. Rocks undergoing direct comparison of trace elements should therefore be of similar hardness to minimise errors. In the present work this was not always the case and great care was taken at all stages in the interpretation of the results. The results were subjected to factor analysis and because of this the situation was eased somewhat because the hardness of the rock depends almost entirely on the quartz content. Therefore any factor involving a relationship between SiO_2, Fe and Ni was closely investigated to determine whether the Fe and Ni came from the rocks or were due to metallic contamination from the jaw crusher.

Cross contamination from dust and equipment was kept as low as possible by carrying out the crushing and grinding in a clean room with an efficient dust extraction system.

A9:2 CRUSHING.

The samples were split, using a hydraulic splitter, with hardened steel jaws, into 2cm fragments. A few fragments were retained as a reference, and the rest were run through a jaw crusher, with hardened steel jaws, mounted in a dust extraction cabinet. In addition a dust extraction hood was mounted next to the jaws to prevent fine material escaping. The hood was mounted in such a way that fines were not selectively removed from the crushed sample. A single pass was sufficient to reduce all the rocks to an average size of 0.5cm.

The crushed rock was collected in a fibre glass tray, from which it was poured directly into labelled polythene sample bags.

After each rock sample had been passed through the jaw crusher, some 200g of washed quartzite pebbles were run through to remove any remaining sample fragments. The quartzite used was from a single batch from a single source. The one batch was used for all rock samples, and each 200g was passed only once. The jaw crusher was carefully cleaned using a stiff wire brush and compressed air jet with the dust extraction equipment running before the next sample was passed.

A9:3 GRINDING.

A 500g sample was taken on a random basis from the material collected from the jaw crusher. This was ground, in 200g lots, in a 'Tema' swing mill equipped with a 100ml tungsten carbide grinding barrel. During the 30 seconds grinding time selected, the mean grain size of the rocks was reduced to 60-200 mesh, depending on its hardness. This sample was further split, using a stainless steel sample splitter. A 200g sample was taken which was further ground for 2½ minutes in the 'Tema' mill. This reduced the average grain size to below 200 mesh. These samples were all stored in labelled polythene bags.

The handling and sample splitting was carried out in the open laboratory without dust extraction, to ensure that no selective removal of fine material occurred.

The 'Tema' mill barrel was cleaned between each sample by grinding 100g of the crushed quartzite for 40 seconds. After this the barrel and grinding rings were washed in warm tap water; dried with paper; and allowed to dry fully in air.

The sample splitter was cleaned using a compressed air jet in a dust extraction cabinet.

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