A

T H E S I S

entitled

THE APPLICATION OF SOME DATA PROCESSING TECHNIQUES IN THE INTERPRETATION OF GEOCHEMICAL DATA

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JEFFREY KHALEELEE

Royal School of Mines
Imperial College

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A B S T R A C T

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The potential of a number of computerised procedures as interpretative aids were examined with data from multi-element regional geochemical surveys. The main problems are related to:

(i) manipulating large volumes of data for the preparation of geochemical maps in order to recognise the regional distribution;

(ii) distinguishing the regional variations for elements with very variable data to ascertain the correlation between the distribution and the bedrock geology;

(iii) establishing the geological and environmental controls and quantifying their influence at the individual sample sites.

The Calcomp 535 incremental plotter was shown to be ideal for the rapid production of geochemical maps displaying the individual sample data. However, the Stromberg-Carlson was also used to produce geochemical maps using symbols instead of numeric data, which allowed a more rapid interpretation of the data, though the maps could not be quickly produced.

The moving average technique was utilised as a method for distinguishing background trends in the regional data, and revealed more information than the geochemical maps compiled using either the Calcomp plotter or the Stromberg-Carlson recorder.

R-mode factor analysis of the regional data indicated all the previously recognised element associations and quantified their influence at the individual sample sites. A previously unrecognised association, Cr-Fe-Ga-Ti-V, was indicated. Detailed investigations on the drainage sediments, soils and rocks in N. E. Staffordshire confirmed the existence of this association, and indicated an enhancement of these elements in argillaceous rocks, whilst Fe,Ga and Ti were related to the bedrock clay content.

This study has indicated that computerised techniques for map production and areal analysis will facilitate the interpretation of regional geochemical data. However, R-mode factor analysis has provided results which were otherwise unobtainable or uninterpretable in the original data. It is concluded that these techniques may allow the compilation of simple geological maps from regional multi-element geochemical survey data.

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APPENDIX II

CHAPTER 1

INTRODUCTION AND PREVIOUS WORK IN APPLIED GEOCHEMISTRY.

1.1.0. INTRODUCTION

1.1.1. Aim of this study.

Regional geochemical surveys based on the multielement analysis of drainage sediments yield a large volume of data which must be displayed in the form of maps as a prelude to the interpretation of the data. This requirement poses a considerable problem in the manipulation of the data in order that the results may be plotted in map form. It is subsequently necessary to determine the manner in which the trace element concentrations vary over the area in order to correlate these patterns with the bedrock geology and other casual factors. The patterns for many elements are very complex due to the effects of lithological changes in the bedrock, variations in the surface environment, and to data variability caused by the random errors inherent in the sampling and analytical procedures. Apart from distinguishing the areal patterns displayed by single elements, it is also necessary to determine how the trace element associations vary over the area since these may give significant information concerning the bedrock geochemistry and lithology.

It is the purpose of this study to evaluate the extent to which computerised, statistical, mathematical and data processing procedures maybe utilised as interpretative aids for multielement regional geochemical data.

1.1.2. Procedure adopted in this investigation.

The approach adopted, has been to apply a number of computerised procedures to solve each of the three types of problems previously mentioned. The results from the different studies were then compared and the comparison was extended to the results of non-computerised procedures, where these had previously been employed.

A number of operational criteria have been developed as aids in the evaluation of the performance of the various techniques. The techniques should:-

(i) facilitate the rapid interpretation of the data;

(ii) reproduce and confirm those significant geochemical features already shown to exist; and to reveal hitherto unrecognised geochemical features, whose significance could be confirmed by detailed field and laboratory investigations.

The technique evaluation included an appraisal of the performance as related to these operational criteria.

The organisation of the material in this thesis includes an introduction to the applications of geochemistry in detailed prospecting and regional studies, descriptions of the areas from which the regional geochemical data was derived and then descriptions of the application of the techniques to each of the problems described in the preceeding section. The sections devoted to each technique include the description of the detailed investigation, and in the final chapter the procedures are evaluated and summarised, the conclusions made and future research suggested.

1.2.0. PREVIOUS WORK.

1.2.1. The origins of regional geochemical surveys.

The idea of independent geochemical mapping was first advanced by Fersman (1940). The concept was reiterated by Ginzburg (1957) principally for the purpose of mineral exploration, but also for examining the correlation of the geochemical patterns with topography, geology and bedrock paragenesis. The principal sampling media employed in the surveys, which he described, are soils taken from cores which frequently included the underlying bedrock.

The earliest geochemical surveys, described by Ginzburg (op. cit) were performed by two Chinese geologists Lu and Shi (1924) over a diorite intrustion, the bedrock samples were analysed for a number of elements, expressed as oxides, and the results were used for the interpretation of the paragenesis of the igneous intrusion.

The first applications of the technique for the purpose of prospecting were in the U.S.S.R. prior to the second world war and are described by Fersman (1939). Surveys in other parts of the world soon followed with that of Palmquist and Brundin in the U.K. (Brundin, 1939; summarised in Hawkes and Webb, 1962). This survey involved the sampling of vegetation rooted in soils over mineralised areas in Cornwall (Sn and W) and Wales (Pb and Zn). It was shown that higher concentrations existed in the vegetation near mineralised zones than over barren areas. The U.S. Geological Survey was the first to apply the technique of soil geochemical surveys in the U.S.A. (Hawkes and Lakin, 1949) and the technique was soon adopted by the larger North American mining companies.

The high cost of soil and vegetation surveys over large areas led in the 1950's to the establishment of drainage channel sediments as the optimum sampling medium. The basic assumption underlying the use of drainage sediments is that they are composed of both the mechanically dispersed products of bedrock weathering, which have been flushed into the drainage channels by surface run-off waters, and also of the soluble products, which are leached from the bedrock weathering products and exist at some stage as solutes in the soil or drainage waters. The drainage sediments are thus composite samples representing all bedrock types outcropping or sub-outcropping in the catchment area of a stream. Drainage sediments used for such a purpose are usually sampled from the tributary drainage since this restricts the size of the catchment

area and thus allows the data to be more easily interpreted. The advantages of this sampling medium is that it allows large areas to be geochemically surveyed at minimal cost because of the relatively low sample density. The disadvantage of this method is that the data can be rather more difficult to interpret than that derived from vegetation, soil, or bedrock samples, because:-

(i) the drainage sediment is a composite of various geochemical influences related to bedrock geology, the overburden, variations in the secondary environment and also to the effects of contamination by human agencies.

(ii) the bedrock undergoes a complex series of geochemical changes before it is transformed into drainage sediment and so the relationship between the bedrock and drainage sediment geochemistry maybe considerably modified.

An example of the use of drainage sediments for regional scale prospecting was that conducted in the temperate glaciated regions of New Brunswick and the Gaspé peninsula in Canada, by Hawkes et al (1956). The survey was initiated to locate possible areas of Cu, Pb, and Zn mineralisation. Orientation studies over known mineralised zones indicated the existence of anomalous trace element levels in the drainage sediments compared to those derived from barren areas. The main survey involved the collection of 15,000 drainage sediments from 4,900 sample sites over 27,000 square miles. The samples were analysed for the cold-extractable heavy metal

concentrations. The results revealed 43 geochemical anomalies. Detailed geochemical, geophysical and geological investigations on four of the most promising anomalies showed that these were related to significant mineralisation. The trace element distributions also revealed large scale variations apparently correlated with the disposition of the major lithological units. These results and those indicating the correlation between drainage sediment trace element concentrations and mineralised areas in Central Africa led Webb (1954, 1958b) to postulate the potential application of drainage sediment geochemical surveys on a regional scale to locate areas of increased mineral potential. It was also suggested that geochemical data might be useful as an adjunct to geologic mapping.

1.2.2. The evaluation of regional geochemical surveys in tropical savannah terrain.

Geochemical prospecting surveys based on soil, drainage water and drainage sediment analyses were first used in the tropical and sub-tropical savannah terrains of Central Africa in the mid 1950's (Tooms, 1955; Webb, 1958a; Webb and Tooms, 1959). These surveys indicated the suitability of these sampling media, when correctly employed, in locating areas of copper mineralisation in the bedrock.

The applicability of drainage sediments in characterising the bedrock geochemistry was further examined by the initiation of

an orientation survey over four areas in Zambia, preparatory to a detailed investigation in the Namwala Concession area, (Webb et al, 1964). These were carried out over single geological formations in the Copperbelt, the Feira carbonatite district, and in two unmineralised areas in the Zambezi valley and the Mpika areas respectively. It was shown that, relative to the other areas, the Copperbelt sediments over all the stratigraphic units, though only the Lower Roan Group are mineralised, were higher in Co and Cu, whilst the Feira carbonatite district drainage sediments exhibited enhanced background levels of Sr and V over all bedrock types. A further detailed orientation survey was carried out in the southern portion of the Namwala Concession area, Zambia, in the Nyawa district, centred around the Chinkozia norite body (Harden, 1962). The results showed that the drainage sediment distributions of Co, Cu and Ni could be correlated with the major lithologic units, whilst those obtained from the drainage waters were less satisfactory and were considerably affected by seasonal rainfall variations. This indicated the greater suitability of the drainage sediments, relative to the drainage waters, as the optimum sampling medium.

The main investigation over the 3,000 square miles of the Namwala Concession area involved the multielement (12) analysis of 4,000 drainage sediment samples at an approximate density of 1 sample per square mile. It was found that the major lithologic units were characterised by variations in the range and mean levels

for the elements Cr, Cu, Mn, Ni, Pb, V, Zn and to a lesser extent Co and Ti. Variations of the trace element levels were also observed within the major lithologic units. Areas of mineralisation were characterised by anomalously high levels of cold-extractable copper in the sediments. It was concluded that the drainage sediment data were dominantly controlled by the bedrock geochemistry and only to a subsidiary extent by the secondary environment.

1.2.3. The evaluation of regional surveys in tropical rain forest terrain.

Geochemical investigations based on soil and drainage sediment sampling were initiated in the tropical rain forest terrain of the Sula Mountains and Kangari Hills in central Sierra Leone in order to establish the secondary dispersion of arsenic, related to gold mineralisation, and molybdenum (Mather, 1959; Elliott, 1962). Areas of mineralised bedrock were shown to be characterised by anomalous levels of As and Mo in both the soils and in the drainage sediments. Mather concluded that the dispersion of arsenic is predominantly in solution in both soils and drainage sediments, whilst that of molybdenum is by both saline and mechanical dispersal mechanisms. Elliott, however, concluded that the dispersion of both arsenic and molybdenum is predominantly mechanical. The dispersion characteristics of these elements are considered to be affected by a number of factors, notably, the host rock lithology,

the type of mineralisation, the pedology and the areal ratio within the catchment of barren to mineralised bedrock. It was concluded as a result of these studies that drainage sediments might be used to indicate likely areas for As-Au and Mo mineralisation.

These results were the basis for initiating a more comprehensive multielement geochemical survey, using drainage sediments, over 1,000 square miles of a mineralised Pre Cambrian schist belt in central Sierra Leone (Viewing, 1963; James, 1965; Nichol et al, 1966). The elongate schist belt comprises metamorphosed geosynclinal sediments and igneous rocks set within the granite gneisses of the Basement Complex. Mineralisation within the schist belt includes sub-economic alluvial Au, as well as primary As-Au and Mo mineralisation. The geochemical survey indicated areas of anomalous As near the known As-Au mineralisation but in addition anomalous levels were located in other areas which were subsequently shown to be related to previously unknown As and As-Au mineralisation. A similar relationship between the drainage sediment Mo levels and the incidence of Mo mineralisation was also demonstrated. The ultrabasic rocks were characterised by high Cr and Ni levels; the metasediments were, compared to the basic and ultrabasic rocks, low in Co, Cr, Mn, Ni, Ti and V; and the granites were relatively low in all elements, except Pb. Apart from variations in trace element levels between the different lithologies, there were also significant variations within individual lithological types. It was concluded that the

dominant control of the drainage sediment geochemistry was the bedrock lithology, though partially modified by the variations in the pedology.

These conclusions were the basis for a similar survey over three other schist belts in the Basement Complex of eastern Sierra Leone which were known to have differing metallogenic associations (Garrett, 1966; Garrett and Nichol, 1967). The schist belts were characterised, as expected, by enhanced levels of Co, Cr, Cu, Mn, Ni, Ti, V and Zn compared to the granitic areas, which were higher in Pb. Variations in trace element patterns within the schist belts were for some elements correlated with variations in bedrock lithology or the presence of mineralisation. The most significant feature was that variations in the levels of Cr and Ni over basic and ultrabasic rocks between the individual schist belts indicated an increase in these levels to the south-east, where there are known occurrences of Cr mineralisation.

A further survey was carried out to establish whether the variations exhibited between the schist belts was also featured in the Basement Complex. This involved the collection of triplicate drainage sediment samples and in addition soil and bedrock samples, where these were obtainable near the drainage sediment sample sites. The mean drainage sample site density was 1 per 70 square miles. The drainage sediment results indicated that:-

(i) the elements Co, Cr, Cu, Mn, Ni, V and Zn displayed higher levels in the north-west and south-east with a low central trough. Those schist belts in the Basement Complex which have been investigated also display an increase towards the south-east in their relative Cr and Ni concentrations.

(ii) the areal trace element patterns were broadly comparable to those yielded by the soils and bedrock data.

These results were interpreted as confirming that:

(i) the Basement Complex was predominantly of metamorphic origin.

(ii) there are minor Cr, As-Au, and Mo metallogenic provinces in Sierra Leone.

It was concluded that provincial scale regional geochemical reconnaissance surveys based on drainage sediments might be used to delineate large scale areas of increased mineral potential as well as providing information of fundamental geological significance.

1.2.4. The evaluation of regional geochemical surveys in temperate regions.

Geochemical prospecting studies over potentially mineralised areas of the U.K. had indicated that primary and secondary dispersion

patterns related to Pb-Zn mineralisation were frequently observable in rocks, soils, drainage sediments and drainage waters (Webb, 1958b). Moreover, it was shown that the minus 80-mesh fractions of soils and drainage sediments were adequate sampling media in such studies. Geochemical studies in the Sn-mineralised areas of Cornwall had shown that in areas where mining or smelting activities had been carried out, the drainage sediments were frequently heavily contaminated by the ore metal (Hosking, 1959).

A regional geochemical survey over 10,000 square miles of Nova Scotia based on the Cu, Pb and Zn contents of the drainage sediments had shown that major and minor variations in bedrock geochemistry were reflected in that of the drainage sediments (Holman, 1962). A similar survey in the mineralised (As, Ag, Cu, Pb, Sb, and Zn) Bathurst-Jacquet district of New Brunswick involved the collection of 3,500 drainage sediments from all drainage channels (Boyle et al, 1966). The samples were analysed for 14 elements and maps were prepared to illustrate the areal dispersion patterns. The maps and follow-up work revealed a number of features, namely,

(i) most of the ore bodies were associated with higher concentrations of the ore elements in the sediments from the adjacent drainage channels.

(ii) the patterns displayed by the background levels of the trace elements correlated with the disposition of the major lithological types. This was especially noticeable between areas

underlain by Pennsylvanian sandstones and those underlain by Ordovician, Silurian and Devonian strata.

(iii) the trace element contents of the drainage sediments taken from over granitic bedrock areas displayed enhanced levels of Mo and W.

(iv) Drainage sediments with enhanced Mn contents generally displayed the same effect for all other trace elements. This was considered to have been caused by local precipitation of hydrous Mn oxides which would absorb the other elements.

The first multielement regional geochemical survey in Great Britain involved the collection of drainage sediments over 350 square miles of south Devon at a mean density of 1 sample per square mile (Webb, 1964). The survey was initiated to investigate the areal distribution of those elements, for which the samples were analysed, which might yield information of geological and agricultural significance. The results indicated the presence of a previously unrecognised Mo-rich facies in the Carboniferous bedrock of this area. The Mo-rich area correlated with that in which livestock were prone to Cu-deficiency. It was suggested that this might be caused by the high Mo content in the weathering products of the bedrock and by inference also in the overlying soils and in the herbage growing in these soils. The results of this study confirmed that regional geochemical surveys might yield significant information with respect to the incidence of livestock, crop and possible even human nutrition-

ally derived disorders. It was proposed that further investigations should be initiated in the British Isles in order to examine this potential use of regional geochemical data.

A further geochemical survey was undertaken in Co. Limerick, Eire, in which livestock were adversely affected by high concentrations of Mo and Se in the soils and herbage (Webb and Atkinson, 1965; Atkinson, 1967). The area is largely underlain by Carboniferous limestones overlain by a black marine shale sequence, the Clare shales, which underlie the Namurian sandstones and siltstones. The area was affected by the Weichsel glaciation and the drift though locally derived had been translocated from over the source bedrocks. The areal dispersion patterns for Mo revealed a correlation between the incidence of higher Mo levels and the suboutcropping Clare shales. Local modifications of this pattern were largely due to the glacial translocation of the drift, derived from these shales, over the younger Namurian bedrocks. The Mo contents of drainage sediments, soils and herbage were generally correlated and local modifications were ascribed to the operation of a number of environmental factors. Complementary drainage sediment studies in other areas, underlain by the approximate stratigraphical and lithological equivalents of the Clare shales, also exhibited the correlation between suboutcropping black shales and high Mo contents.

A similar drainage sediment survey over a granite area in Co. Wicklow, in which livestock were affected by Co-deficiency,

indicated that the drainage sediments derived from the granite had anomalously low Co-levels.

An investigation was made of the secondary dispersion of Cu, Hg, Pb and Zn around the Tynagh ore body in west central Eire (Donovan, 1965). The area is predominantly underlain by Carboniferous limestone and the orebody is considered to be formed by replacement of the limestone. The region has been subjected to glaciation but the till is locally derived. The results indicated well developed dispersion patterns of the ore metals in the glacial soils and tills associated with the boulder trains derived from the orebody. The anomalous dispersion trains in the associated drainage sediments were considered to be related to the soil-till material rather than to the source bedrock. The dominant dispersion mechanism was considered to be mechanical rather than hydromorphic. The latter mechanism being inhibited by the high pH induced by the high carbonate content of the soils and tills, which had been derived from the Carboniferous limestones.

These studies had shown that in temperate areas the drainage sediments reflect the bedrock geochemistry, except where this relationship is modified by the effects of glaciation, secondary environment and contamination caused by human activities, especially mineral exploitation. It was proposed that the results of the studies already conducted, warranted further investigation in order to examine the effectiveness of regional geochemical surveys, based

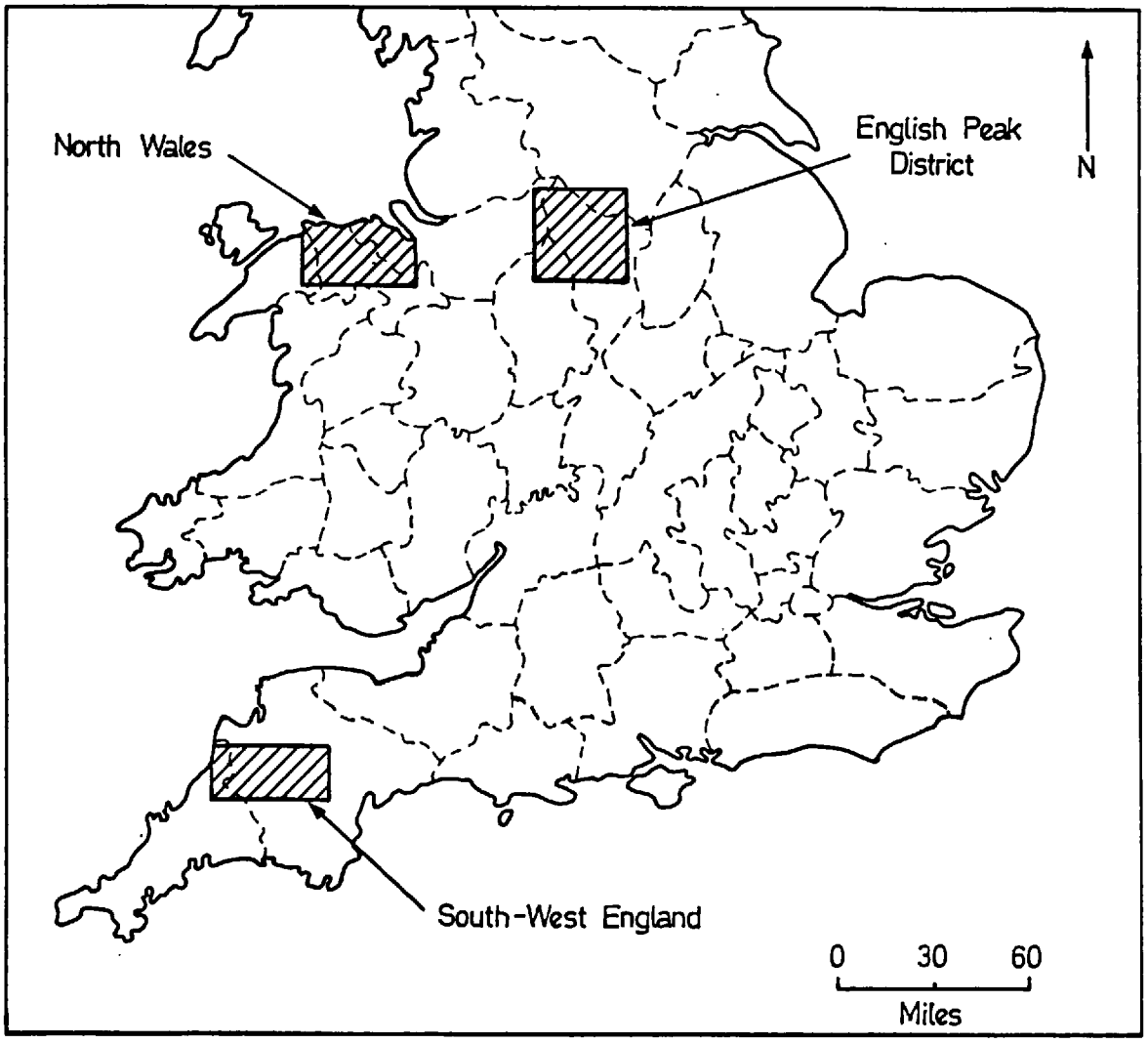
on drainage sediments, in revealing features related to mineralisation, bedrock geochemistry and the incidence of agricultural and human disorders in areas of complex geology. It was also proposed that the investigations should be conducted in areas wherein the effects of glaciation, secondary environmental variation and human contamination caused by mineral exploitation could be assessed so that procedural modifications might be devised in order to allow interpretation of the data.

Three areas were chosen as being suitable for the assessment of the potential value of multielement regional geochemical surveys based on drainage sediments (see figure 1). These were located in S.W. England, N. Wales and around the English Peak District (Nichol et al, 1967; Taylor et al, 1967; Fletcher, 1968; Horsnail, 1968; Taylor, 1968; Webb et al, 1968, a,b,c). The areas and the results of the reconnaissance survey and follow-up work performed prior to this investigation are described in detail in Chapter 2, and only a brief outline of the results and problems encountered within these areas is given at this stage.

A total of 2,700 samples were analysed for 16 elements and the reulting data were used in the compilation of geochemical maps for each element in each area. These maps were prepared by manual procedures but it seemed that the problem of manipulating such a large volume of data might be overcome by the application of computerised data processing techniques.

FIGURE 1. LOCATIONS OF THE REGIONAL SURVEY AREAS

(AFTER HORSNAIL, 1968)



Geochemical maps showing the trace element concentrations are difficult to interpret. Various procedures have been employed to increase the interpretability of the data. One of the most successful has been the graphical representation of the trace element compositions by symbols. These were either black and white or a whole range of different coloured circular symbols. Each symbol type represented a concentration range and by using 5 or 6 symbol classes, the main features of the areal distribution of the trace elements could be clearly defined. This was at first performed manually but again seemed to be an operation which could be successfully undertaken by computerised methods (Nichol et al, 1966).

Most of the elements, when the concentrations were displayed in symbolic form, showed fairly marked areal variations, though two notable exceptions were Ga (in all three areas) and Sn (N. Wales and the Peak District). However, there is a possibility that the symbolic display technique may not show subtle variations, which occur within a concentration range covered by one symbol type. It was apparent that other methods of areal pattern analysis should be employed to ascertain the amount of information being 'lost' by symbolic representation. There are computerised methods of areal analysis available, which can be used for this purpose and these have been examined in this investigation.

The symbolic geochemical maps indicated a number of features

and several of the more prominent of these were subjected to detailed investigations. The results and the problems posed by them are summarised below.

A number of trace element associations controlled by bedrock lithology were also elucidated, the most important of these were:-

(i) the elements As-Cu-Mo-V which were shown to be enriched in areas underlain by black marine shales in the Peak District and S.W. England.

(ii) the basic igneous rocks in S.W. England gave high levels of Cr-Ni-V (inter alia).

(iii) the granites in S.W. England were enhanced in Sn.

(iv) pyritic slates associated with volcanic rocks in N. Wales yielded high levels of Fe and Mo.

The problems encountered when interpreting the regional geochemical data have been principally related to the effects of contamination caused by mining and metallurgical activity and to regional variations in the secondary environment. These are discussed below:

(i) contamination caused by historical and recent mining or smelting operations have resulted in anomalously high levels

of the ore elements being present in the drainage sediments. This affects Sn (S.W. England) and also Pb, Zn and to a lesser extent Cu (all areas, but especially N. Wales and the Peak District). The effect of the contamination is to obscure the bedrock composition for the contaminant elements.

(ii) poorly drained soils tend to be both acid and chemically reducing. Such conditions facilitate the leaching from these soils of the mobile elements (As, Co, Cu, Fe, Mn, Ni and Zn) by percolating soil waters. The Eh-pH levels in the open drainage channels are considerably higher than those in the soil waters and when these flow into the drainage channels, hydrous oxides of Mn and Fe are precipitated. The remaining mobile elements are coprecipitated, to varying degrees, and this leads to anomalously high levels of these elements in the drainage channels of streams arising in waterlogged soil areas. Again the effect of this enhancement is to obscure the trace element concentration of the detrital material derived from the bedrock for these elements.

The problem posed by these masking effects is to determine how the bedrock geochemistry relates in the affected areas to those in other unaffected parts of the region.

These trace element associations are controlled by the geochemistry of the suboutcropping bedrock and also by non-geological

agencies for instance, secondary environmental variations and the effects of mining or smelting contamination. The establishment of these associations involved a considerable expenditure of time and money for their detailed evaluation and interpretation in the drainage sediments, soils and bedrocks. It is possible that computerised multivariate mathematical procedures, such as Factor Analysis, may be capable of indicating these associations from the regional trace element data derived from the drainage sediments. Thus speeding the interpretation of the data and lowering the costs. It is also possible that by employing some variant of these techniques it will be possible to reveal the bedrock contribution to the drainage sediment geochemistry in areas geochemically masked by non-geological effects.

CHAPTER 2

REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEYS IN ENGLAND AND WALES.

2.1.0. INTRODUCTION

Three areas in S.W. England, N.Wales and around the English Peak District were covered by regional surveys. Approximately 2700 drainage sediments were sampled in duplicate at an average density of 1 sample/sq.mile. The minus 80 mesh fraction was analysed spectrographically for 14 elements (Ag, Bi, Co, Cr, Cu, Fe (as Fe_2O_3), Ga, Mn, Mo, Ni, Pb, Sn, Ti, V) and colourimetrically for 2 elements (As and Zn). The analytical precision for the spectographic method established on a number of replicate (x 20) analyses varied between 24% and 80% at the 95% confidence level and is best for Cu and V and worst for Pb and Sn. The colourimetric method precision was not so established but is generally considered to be better than 50% (95% confidence level). The analytical data has been plotted onto maps for each area. The maps were interpreted and certain features of interest have been further examined. The results for each area are separately examined below.

2.2.0. S.W. ENGLAND

2.2.1. Location

The surveyed area covers 820 sq.miles mainly in north Devon

but also in north-east Cornwall; and is bounded by the National Grid lines 2100 (west), 2900 (east), 0764 (south), and 1102 (north). The principal towns are Bude, Crediton, Holsworthy, Launceston and Okehampton.

2.2.2. Geology

The area lies on the southern limb of an E - W trending syncline whose axis passes through Crediton, exposing Upper Palaeozoic sediments. Small isolated outcrops of Cretaceous and Tertiary sediments occur in the north and south-east. The granite bosses of Dartmoor and Bodmin Moor outcrop along the southern margin of the area. The stratigraphic succession is summarised in table I, and the geological map is shown in figure 2.

The Devonian sediments grade from the lower (Frasnian) slates and phyllites into the higher (Famennian) series of slates with silty and calcareous bands. The Dinantian rocks (Tournaisian and Visean) consist of siltstones, mudstones, shales, with spilitic and keratophyric tuffs, which are overlain by limestones, cherts and shales (locally very pyritic). The Namurian (shales with subordinate thin sandstones) is more argillaceous than the overlying Westphalian (shales with frequent massive sandstones). The Permian breccias, sandstones and marls contain carboniferous pebbles in the lower part (Cadbury beds) and untourmalinized lava pebbles in the overlying Bow beds. Detrital cassiterite, galena

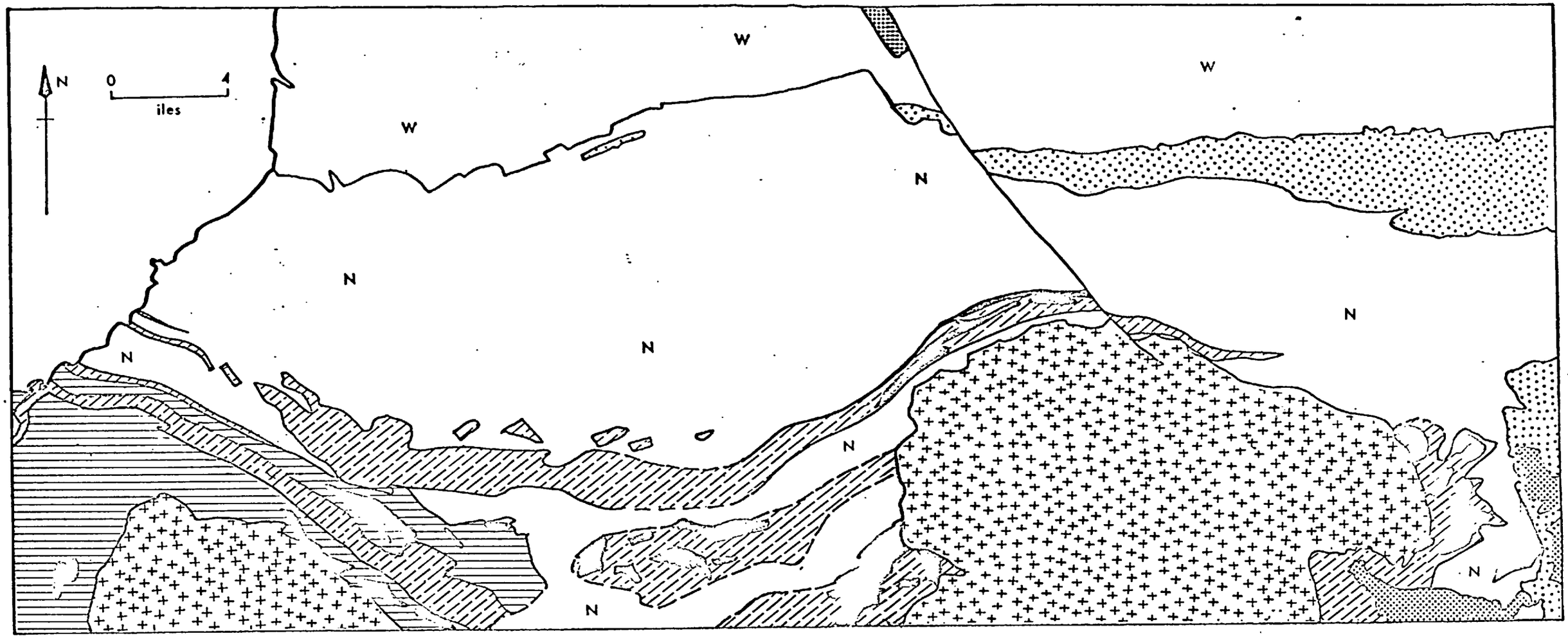


FIG. 2. GEOLOGY OF THE S.W. ENGLAND SURVEY AREA.
(based on information supplied by the
I.G.S., after Fletcher, op. cit.)

and sphalerite grains in the Permian suggests contemporaneous erosion of Carboniferous mineralised rocks with the deposition of Permian sediments.

Basic igneous sills, usually albite diabase, intrude the Devonian and Dinantian strata and are metamorphosed, where they lie in the metamorphic aureole of the granites. The granite intrusions comprise several types:-

(i) Porphyritic feldspathic (orthoclase) granite,

(ii) uniform fine grained granite,

(iii) aplitic and pegmatitic dykes, probably of later date and associated with the mineralisation.

The Dartmoor and Bodmin Moor granites are considered to be linked at depth from the results of gravity geophysical work (Bott et al, 1958).

The large fault truncating the Permian outlier west of Crediton is a dextral tear fault of presumed Tertiary age.

The area was not glaciated in Pleistocene times, the overburden is largely residual, except where periglacial conditions induced solifluction of the overburden to give the slump debris or 'Head' deposits.

Table 1. The stratigraphic succession of the S.W. England regional survey area. (modified after Dewey, 1948, and the I.G.S., 1967)

Era	System	Formation	Lithology
Quaternary	Post-pleistocene	Alluvium	Gravels, sands and fine earths.
		Peat	Peat deposits.
	Pleistocene	Head	Unconsolidated stony material.
	Eocene	Bagshot(?) beds	Rolled gravels with granitic sands.
Mesozoic	Tertiary		Clays, sands, gravel and chalk.
	Cretaceous	Upper Greensand	
	Permian		Breccias, sandstones and marls with thin basaltic flows.
		Dartmoor and Bodmin granites	Several granite types, porphyry biotite granite is the most common. Associated As, Cu, Pb, Sn, and Zn mineralisation.
Upper Palaeozoic	Carboniferous	Westphalian	Shales with sandstones
		Namurian	Shales with sandstones
		Dinantian	Shales, sandstones, cherts with limestone and volcanic rocks. Intruded by basic igneous rocks.

Table 1. (Continued)

Era	System	Formation	Lithology
Upper Palaeozoic	Devonian	Upper Devonian	Shales, slates, sandstones with limestones and volcanic rocks. Intruded by basic igneous rocks.

2.2.3. Mineralisation

The mineralisation can be classified into 3 types (after Dines, 1956, and Dearman, 1962).

(i) Fracture-filled, cassiterite-specularite bearing lodes, trending NE-SW, and usually found within the granites. The main concentrations occur in central Dartmoor (around Birch Tor), north-east Dartmoor and north Dartmoor (south of Okehampton).

(ii) Fracture-filled, metasomatic replacement lodes bearing As-Cu-Pb-Sn-Zn and barite, occurring mainly in the granite metamorphic aureole. The main centre lies in the Teign valley on the north-east margin of Dartmoor, where the lodes trend N-S; subsidiary centres occur in the Dinantian, south of Okehampton, where calcareous beds have been partially metasomatised.

(iii) Stratiform Mn-oxide deposits in the Dinantian cherts are considered associates of the episode of basic volcanicity.

2.2.4. Mining History

This area lies north of the main mineralised zone. The history is inferred and extrapolated from the more complete records of the main field.

Alluvial, placer Sn-deposits were worked on Dartmoor at least by the 12th century. Mining was restricted to these deposits with shallow trenching over the suboutcropping lodes. The main mining phase began late in the 15th century with shaft mining, reaching its acme (in the central Dartmoor field) by the late 18th century and its complete cessation by 1928.

13th century refining of the Sn-ores was by two-stage roasting. The roasting temperatures were boosted by the use of water-driven bellows and refining was carried out near streams and rivers. Smelter stacks were introduced relatively late and the Sn-fumes and slag will have contributed significantly towards soil and drainage sediment contamination.

The Pb-Zn-Ag mining was centred in the Teign valley, commencing possibly in the 14th century. Refining methods were similar to those for Sn and will have also contributed to contamination for these elements. After a hiatus, mining activity recommenced in the Teign valley in the 19th century to exploit the then commercially viable sphalerite ore, reaching its peak by the 1860s and its death by the turn of the century.

Cu and As production was from small deposits mainly on the northern margins of Dartmoor. Barite has been extensively exploited in the present century and large tonnages won.

Mining activity has virtually ceased in this area; known

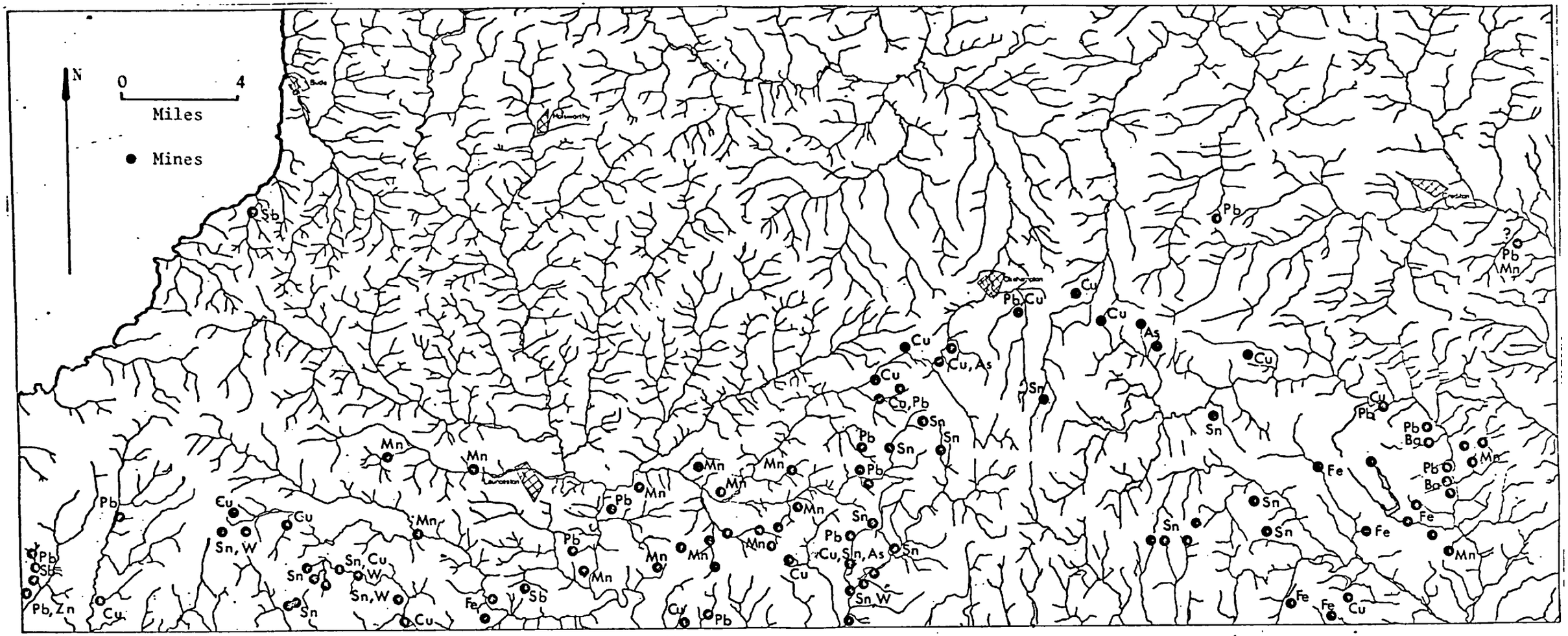


FIG. 3 MINING IN THE S.W. ENGLAND SURVEY AREA.
(based on Dines, op. cit., after Fletcher, op. cit.)

areas of mining are shown in figure 3.

2.2.5. Topography

The granites of Dartmoor and Bodmin moor form the highest ground, exceeding 800 ft east of the River Bovey and 1500 ft west of the river. The elevation decreases northwards rarely rising above 600 feet over the Carboniferous. Relief over the Namurian rocks is higher in the east than in the west, that over the Westphalian is generally high. (fig. 4)

2.2.6. Drainage

The major catchments drain either north (rivers Taw and Torridge) or south (rivers Exe, Tamar and Teign), only minor drainage channels flow to the west coast. The drainage density is fairly homogeneous and usually exceeds 3 miles/sq.mile (Horsnäll, 1968).

2.2.7. Climate

The lowest temperatures and highest rainfall (60-100 inches p.a.) are recorded over Dartmoor and Bodmin Moor, elsewhere the rainfall decreases from the west (40-50 inches p.a.) to the east (30-35 inches p.a.), see fig. 5.

2.2.8. Pedology

The soils are residual, except when developed over the 'Head' deposits. Soils developed over Carboniferous rocks have been mapped only in the Teign valley (Clayden, 1966) but similar types may be assumed over the remainder of the Carboniferous, with brown soils developed on the well-drained slopes and gley soils over flatter, less well-drained areas.

The Dartmoor soils may be classified into 4 categories (Clayden and Manley, 1964), all of which are naturally acid (pH≈4.5)

(i) Blanket bog and peaty gleys over the central high moorland.

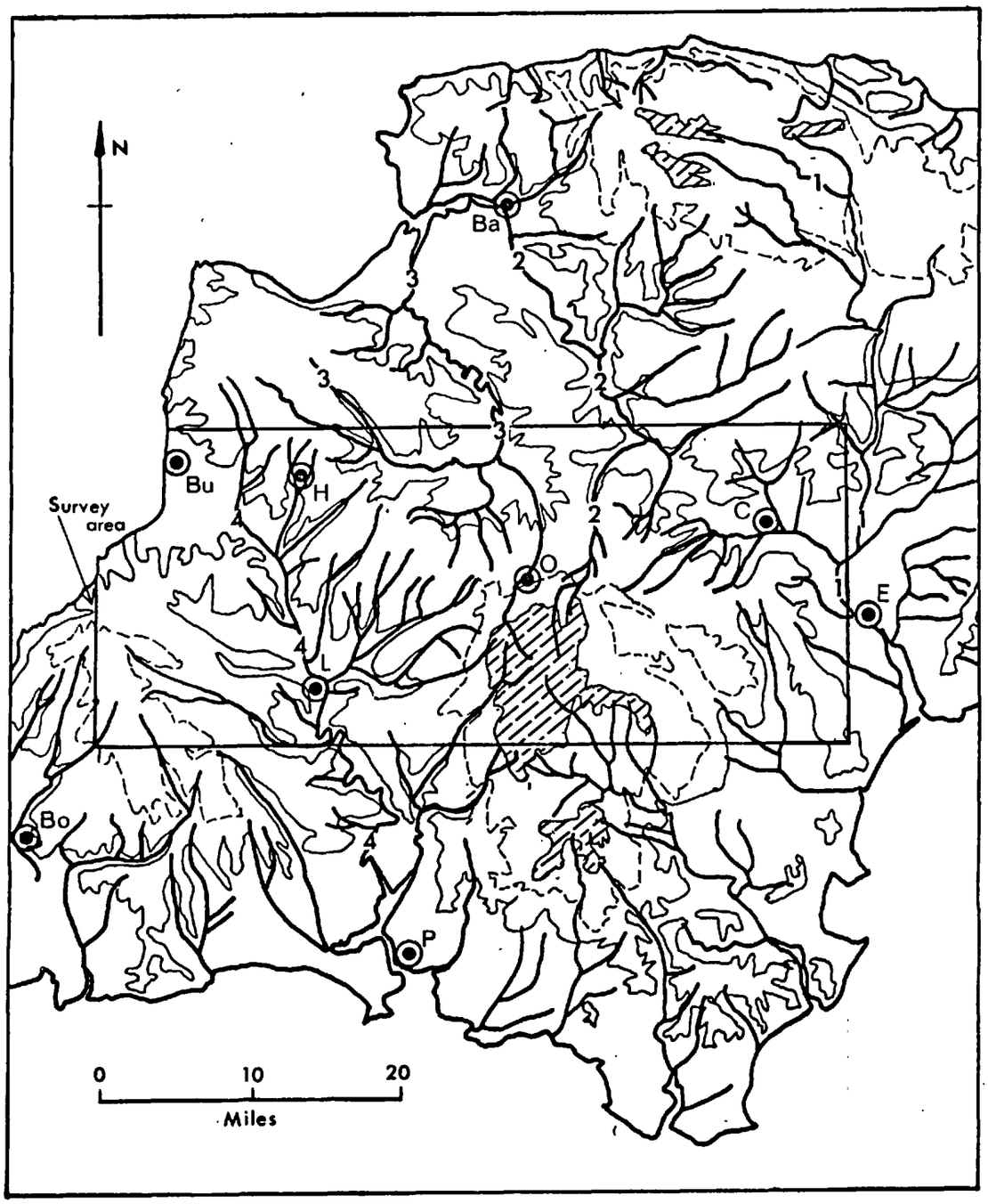
(ii) Peaty gleyed podzols around the central core.

(iii) Brown earths, succeeding the peaty soils on the lower ground in the north-east.

(iv) Valley bogs and peaty, ground water gley soils in the basins and valley floors.

2.2.9. Description of the regional geochemical reconnaissance data.

Geochemical maps have been prepared for As, Co, Cr, Cu, Fe (as Fe_2O_3), Mn, Mo, Ni, Pb, Sn, Ti, V and Zn (figs. 1-13, vol. 2.). The elements Ag, Bi and Ga have not been plotted because Ag and Bi



Key to rivers

1. R.Exe; 2. R.Taw; 3. R.Torridge; 4. R.Tamar; 5. R.Dart

Key to towns

Ba. Barnstable; Bo. Bodmin; Bu. Bude; C. Crediton; E. Exter; H. Holsworthy; L. Launceston; O. Okehampton; P. Plymouth

Fig. 4. Location and Topography of the Devon-Cornwall Survey Area (after Fletcher, op. cit.)

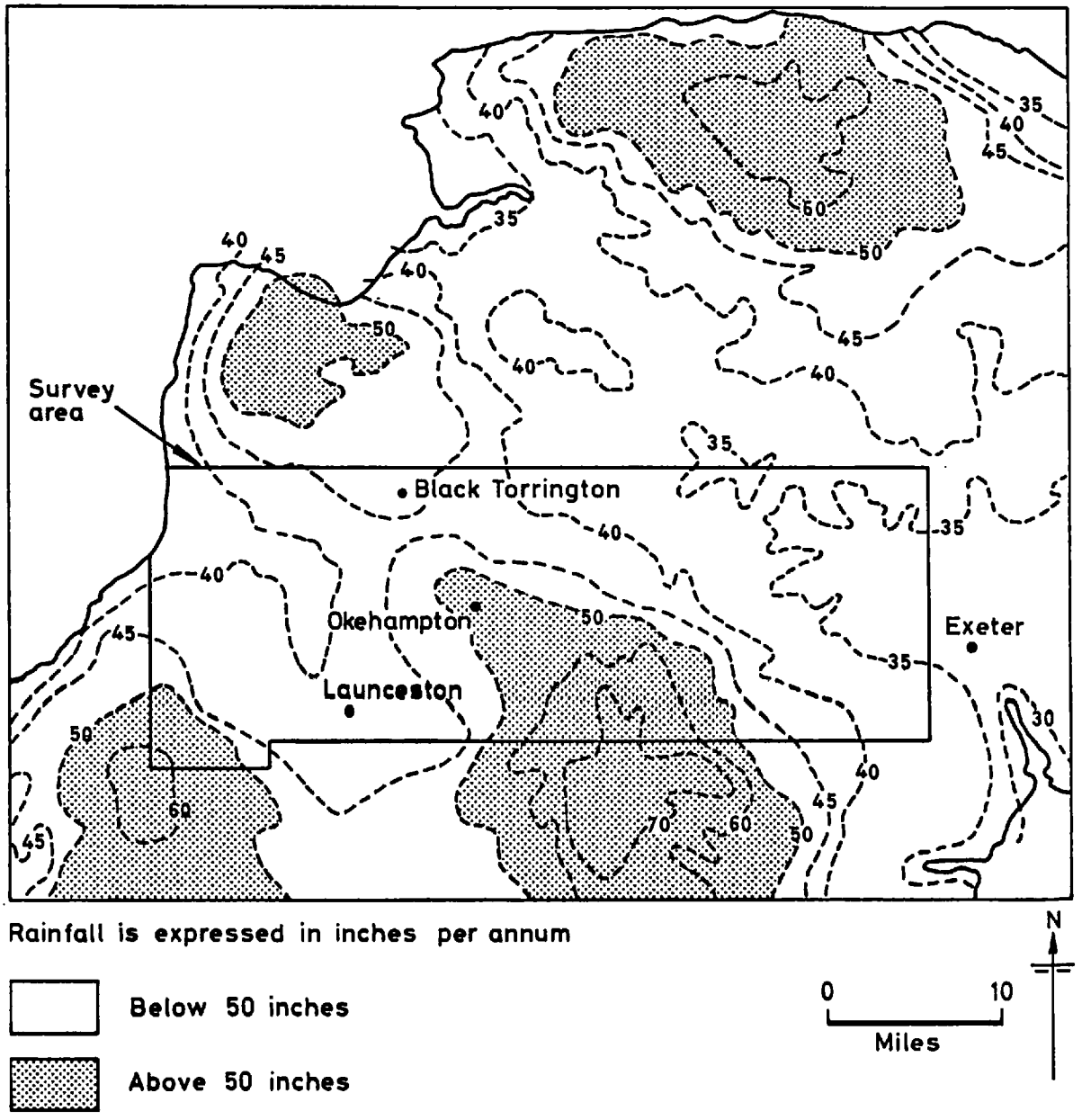


Figure 5. Rainfall of the South-West England survey area (After Horsnail op. cit.)

yield relatively few determinable concentrations, whilst Ga shows no distinctive patterns.

The grouping of values adopted for the trace element concentration are constant for all three areas and this obscures some meaningful variations most notably for Fe, Mo and Pb in this area. Each element's distribution pattern is briefly described and the main features are summarised at the end of this section.

Arsenic (Fig. 1. vol. 2.)

A broad, sinuous SSW-NNE belt of high values runs over the granites and their metamorphic aureole with values usually exceeding 15 ppm As, frequently over 30 ppm and with peaks at 1500 ppm. South of Launceston and on north-east Dartmoor the levels are lower. Elsewhere there are scattered highs, some are grouped along the Westphalian-Namurian and Permian-Namurian junctions. Values over the eastern Namurian are higher than in the west, but this may be a function of the WSW-ENE trend of the granite metamorphic aureole. Levels are slightly higher over the Namurian compared to the Westphalian.

Chromium (Fig. 2. vol. 2.)

Low levels (<30 ppm) occur over Dartmoor and high levels occur over the Devonian-Dinantian rocks, especially west of Dartmoor with levels between 150 and 300 ppm. Elsewhere there are scattered high values in the Teign valley, whilst the Namurian (predominantly

70-150 ppm) is higher than both the Westphalian (30-150 ppm) and the Permian (<70 ppm) except in the west where lower levels are found on the Namurian (30-150 ppm).

Cobalt (Fig. 3. vol. 2.)

Very low levels are found over north-east Dartmoor (usually <15ppm Co) and the Westphalian and Permian outcrops (majority <15). Elsewhere, levels are highest over the Dinantian-basal Namurian rocks with very high levels (>70 ppm) west of Launceston and east of Dartmoor.

Copper (Fig. 4. vol. 2.)

Levels are lowest over Dartmoor (usually ≤30 ppm, often <15 ppm) and the Westphalian (usually ≤30, and <15 in the east). A sinuous SSW-NNE belt of higher levels envelope the granite margins ranging from 30-150 ppm, with lower levels south of Launceston and east of Dartmoor. Concentrations from 15-70 ppm overlie the Namurian and Permian but are higher along the Namurian-Westphalian boundary (30-70 ppm).

Iron (Fig. 5. vol. 2.)

Lower levels occur over the Westphalian (usually 1.5-7.0%), Permian (usually 0.7-7.0%) and north-east Dartmoor (usually 0.7-7.0%). Elsewhere, levels fall between 3.0 to 7.0%, except in the high (>7.0%) belt enveloping the granites and also along the Namurian-Westphalian boundary, east of Holdsworthy.

Lead (Fig. 6. vol. 2.)

A concentration of high levels (>300 ppm, peaks ≃7000 ppm) occurs in the Teign valley. Elsewhere scattered higher concentrations overlie the Devonian-Dinantian-basal Namurian strata, north-west Dartmoor, and the Westphalian-Namurian junction, south of Bude and east of Holdsworthy.

Manganese (Fig. 7. vol. 2.)

Enveloping the granite aureole is a belt of higher levels (>700 ppm) and also along the Namurian-Westphalian contact, but the highest levels (>3000 ppm) occur over the Devonian-Dinantian-basal Namurian strata. The levels over Dartmoor are usually low (<700 ppm), except discontinuously along the northern margins. Lower levels overlie the Permian (majority <1500 ppm) and the western Namurian (majority <700 ppm) outcrops.

Molybdenum (Fig. 8. vol. 2.)

Lower concentrations (<3 ppm) predominate over most of the area. Higher levels (<2-15 ppm) overlie the Dinantian and basal Carboniferous strata, and also north-east Dartmoor.

Nickel (Fig. 9. vol. 2.)

Dartmoor bears low levels (usually <15 ppm) and to a lesser degree so do much of the Namurian, Westphalian, and Permian outcrops (15-70 ppm). The Namurian outcrop shows higher levels in the east (usually 30-70 ppm) than in the west. Higher levels (>150 ppm) are grouped

over the Devonian-Dinantian-basal Namurian beds, in the Teign valley and to the south of Crediton, and also along the Namurian-Westphalian junction, east of Holdsworthy.

Tin (Fig. 10. vol. 2.)

Overlying the granite and the metamorphic aureole levels exceed 30 ppm, with peaks at 700 ppm. Elsewhere there is a northerly decrease in levels, though the Permian bears marginally higher levels (<30 ppm) than the background.

Titanium (Fig. 11. vol. 2.)

The Devonian-Dinantian-basal Namurian strata underlie the highest levels (>7000 ppm). The Carboniferous bears concentrations between 1500 and 7000 ppm, levels are marginally higher over the eastern Namurian than in the west.

Vanadium (Fig. 12. vol. 2.)

Low concentrations occur over Dartmoor (usually <70, majority <30 ppm), the Westphalian-Permian (usually 30-150 ppm, majority <70 ppm) with similar levels over the Namurian, though these are lower over its western outcrop, compared to that in the east. The highest levels occur over the Devonian-Dinantian-basal Namurian strata.

Zinc (Fig. 13. vol. 2.)

Levels are generally higher over the granite aureole, and also in the Teign valley and south of Crediton with concentrations usually

ranging from 150 - 700 ppm, with peaks over 7000 ppm. Levels decrease northwards over the Namurian (70-300 ppm) and are lower still over the Westphalian-Permian strata (<40-150 ppm, with occasional peaks ≤300 ppm).

Other elements

The majority (16) of the 23 samples with detectable concentrations of silver were collected over the Dinantian between Launceston and Dartmoor, levels fall in the range 0.2 to 0.6 ppm. The highest concentration level (3.0 ppm) was recorded from the Teign valley. Limited numbers of sample analyses for Be, Sb and U showed higher levels over the granites compared to the sedimentary rocks. Samples with anomalous concentrations of Mo also exhibited enhanced concentrations of Se (1.9 ppm) compared to the background level (0.2 ppm).

An aureole of anomalous Hg concentrations around the E-W axis of the main mineralisation zone, through central Dartmoor, extends at least to the southern margins of the survey area.

Summary

There are similarities in the broad scale patterns exhibited by various trace elements, these are summarised below:

(i) Co, Cr, Cu, Mn, Ni, V and to a lesser extent As, Fe, Ti and Zn are lower over the Dartmoor granite

compared to the enclosing country rocks. The levels of Cr, Ni, and V are uniformly low over the granite whereas Mn, Co, Ni and Zn are higher in the west than the east and Ti shows the converse relationship.

(ii) Sn and to a lesser extent Pb are higher over the granites than over the country rocks.

(iii) As, Zn and to a lesser extent Co, Cu, Mn, Mo, Ni and Ti all exhibit higher levels in a sinuous belt along the northern margins of the granites except in the Launceston area which is low for As, Cu and Fe.

(iv) As, Co, Cr, Cu, Fe, V and to a lesser extent Mo, Ni, Ti and Zn are relatively lower over the Westphalian, especially over the eastern portion of the outcrop.

(v) Pb, Zn and Cu exhibit enhanced levels in the Teign valley.

(vi) Co, Cu, Fe, Mn, Ni and Ti are all higher south of Crediton.

(vii) As, Cu, Fe, Mn, Ni, Ti, V and to a lesser extent Pb, Sn and Zn show higher levels on the Namurian-Westphalian junction, east of Holdsworthy near Black Torrington.

2.2.10 Discussion and Conclusions

An 820 square mile area in Devon and Cornwall was sampled for drainage channel sediments at a density of 1 sample per square mile. A number of geochemical features have been indicated by stream sediment data and were confirmed by a limited number of bed-rock analyses.

The essential geochemical characteristics of the granites (higher Sn and Pb) and the country rock sediments (higher Co, Cr, Cu, Ni, Ti, V) were revealed by the drainage sediment data. The Dinantian sediments were shown to be enhanced in most elements, and it was possible to indicate which enhancements were caused by the diabase intrusions (mainly Cr, Ni, Ti). It was also possible to distinguish geochemical facies within the granite.

The main elements involved in the granite metasomatism were shown to be As and Sn and the metasomatic aureole was shown to be considerably broader than its thermal equivalent.

This information was only interpretable because of the dominant bedrock control of the stream sediment compositions.

Variations in the secondary environment may mask the bedrock controls for the more mobile elements (As, Co, Fe, Mn, Ni and Zn). The mobility of any element will be partially dependent on the resistance to weathering of the mineral phases in which it occurs.

The widespread contamination due to extinct mining and metallurgical activity masks the bedrock control of the ore-elements and makes the recognition of mineralisation anomalies a difficult task.

The regional data revealed a considerable quantity of geologically meaningful data. The following features had not previously been recognised:-

(i) the width of the metasomatic aureole;

(ii) the geochemical discontinuity across the Namurian-Westphalian boundary;

(iii) the marginally higher Sn-levels in the Permian;

(iv) the Mo-Se rich horizons in the Dinantian strata;

(v) the geochemical facies within the Dartmoor granite;

(vi) the ore-metal anomalies, which are unrelated to known sources of contamination.

One of the problems of interpreting this data lies in unravelling the geochemical features and controls represented in the drainage sediments. For example, drainage sediments derived from the Dinantian may represent in their trace element composition the following sources:

(a) disseminated pyrite;

(b) diabase intrusives;

(c) metasomatic alteration;

(d) mineralisation;

(e) dominant shale or chert lithology in the source bedrock.

Another example is posed by the drainage sediments from the Black Torrington or Dartmoor areas, whose trace element compositions are controlled in part by the bedrock geochemistry and in part by the secondary environment. It is one of the interpretative problems to assess which factors have operated upon, and to what extent they have influenced, the chemical composition of the drainage sediments.

A corollary of the previous statement is that the various geological controls will affect more than one element. Thus a number of elements will represent, in their areal dispersion patterns, the operation of one controlling factor. They will form a trace element association, examples would include:-

(i) As-Sn as the principal elements in the granite metasomatism;

(ii) As-Co-Fe-Mn-Ni-Zn as the most mobile elements in the secondary environment;

(iii) Cr-Ni-Ti as those elements which are most enhanced in the basic ingneous rocks.

The examination of multielement data leads to the recognition of a limited number of factors controlling the trace element composition in the drainage sediments. Conversely interpreting the data for each individual element in a multielement array yields very similar information about a small number of controlling factors, that is, the single element data is repetitious in respect of the information which it yields about the controlling factors.

It is possible that more information might be gleaned from the data if it were possible:-

(a) to identify the various controlling factors operating on the geochemical composition of any particular drainage sediment;

(b) to distinguish which elements were similarly affected by each controlling factor, that is, to identify the trace element associations relating to specific factors.

2.3.0. N. WALES

2.3.1. Location

The area surveyed covers 850 sq.miles in eastern Caernarvonshire, Denbighshire and Flintshire. Most of the area lies between the valleys of the rivers Conway (west) and Dee (east). The N.G.

boundary lines are 2680 (west) 3430 (east) 3400 (south) and 3850 (north).

2.3.2. Geology

The stratigraphic succession is given in Table 2 and the disposition of the major geological units is shown in figure 6.

Structurally, the area is the south-western segment of a lower Palaeozoic basin, exposing mainly Ordovician and Silurian strata. The basin is crossed by minor, WNW-ESE trending synclines and anticlines. The lower Palaeozoic strata are unconformably overlain in the east by Carboniferous (Dinantian) strata, which are themselves, unconformably overlain in the east by Permo-Triassic strata.

The Ordovician rocks are exposed in the western and south-western parts of the survey area; Cambrian rocks also outcrop in the south-western corner but were not included in the regional survey. The Silurian strata are exposed in the centre and west of the area, and also in the Clwydian Hills, east of the River Clwyd. Unconformable Carboniferous sediments form much of the northern coast, east of Llandudno and west of Abergele, as well as the western flank of the down-warped, down-faulted Vale of Clwyd. The main Carboniferous outcrop lies east of the Clwydian range with strata younging to the east and being unconformably overlain along the eastern margin of the survey area by the Permo-Triassic sediments, which

also form the floor of the Vale of Clwyd.

The Pleistocene fluvio-glacial deposits are most thickly deposited in the Vale of Clwyd and along the margins of the Dee estuary, whilst much of the Silurian and Permo-Triassic strata in the east is cloaked by varying thicknesses of Welsh and Northern derived drift. Recent alluvial deposits, for instance, wind blown sands and peat, occur at the mouth of the Clwyd valley and along the Dee estuary (see fig. 7).

The lower Palaeozoic basin and the WNW-ESE minor folding across it are of Caledonian age. The N-S tectonic flexures which formed the Vale of Clwyd and the Clwydian Range, are of Hercynian age. Both orogenies initiated transcurrent faulting of considerable displacement. The Hercynian phase caused the conjugate, normal fault system, which trends N-S and E-W.

Table 2. Stratigraphy in the North Wales survey area.

(After Smith and George, 1961; and pers.comm. I.G.S., 1969)

Geological formation			Lithology
Recent			Blown sands, peats and alluvium.
Pleistocene		Northern drift	Red silty clays, largely derived from the Trias,
		Welsh drift	Grey stony drift, largely derived from the local Palaeozoic formations.
		-	Fluvioglacial sands and gravels.
Permo-Trias		Bunter	Red sandstones and pebble beds.
Carboniferous	Silesian	Westphalian	Shales and sandstones with coal seams
		Namurian	Shales in the north (Holywell shales) and sandstones in the south (Cefyn-f-fedw sandstones).
	Dinantian	Carboniferous limestone	Predominantly limestone with basement beds of shales, sandstones and conglomerates.

Table 2 (continued)

Geological formation		Lithology
Silurian	Ludlovian	Shales, mudstones, siltstones and sandstones, some formations more arenaceous in the north and east, and more argillaceous in the south and west.
	Wenlockian	Calcareous mudstones underlain by thin alternating bands of laminated, silty mudstones and muddy siltstones. Striped silty mudstones with 4 major sandstone horizons from fine to conglomeratic in texture.
	Llandoverian	Mudstone.
Ordovician	Bala	Shales and mudstones with grits interbedded with volcanic ashes and lavas (rhyolites, andesites) intruded by dolerite dykes and granophyres.

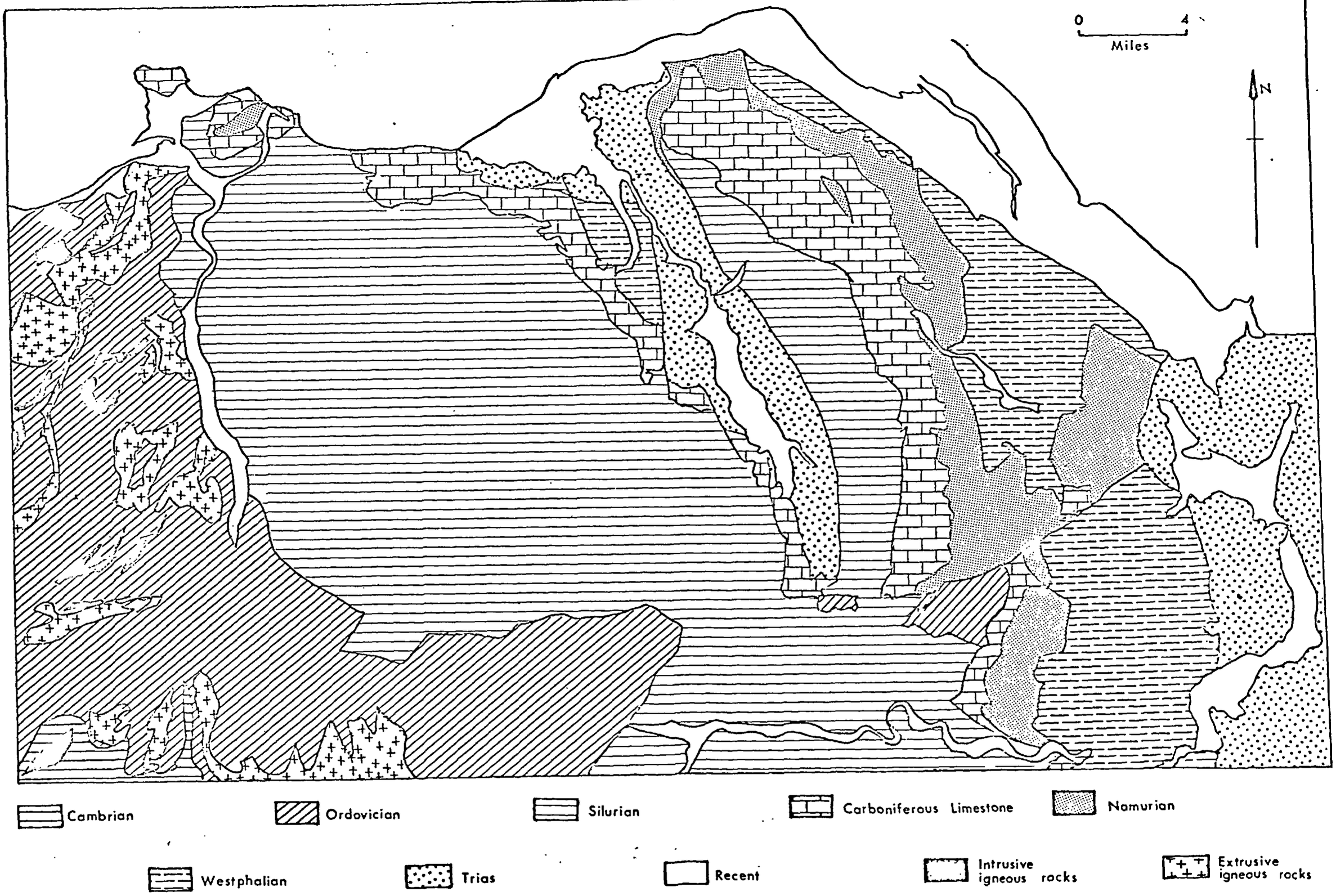


Fig. 6. GEOLOGY OF THE NORTH WALES SURVEY AREA - Based on I.G.S. maps
(after Fletcher, op. cit.)

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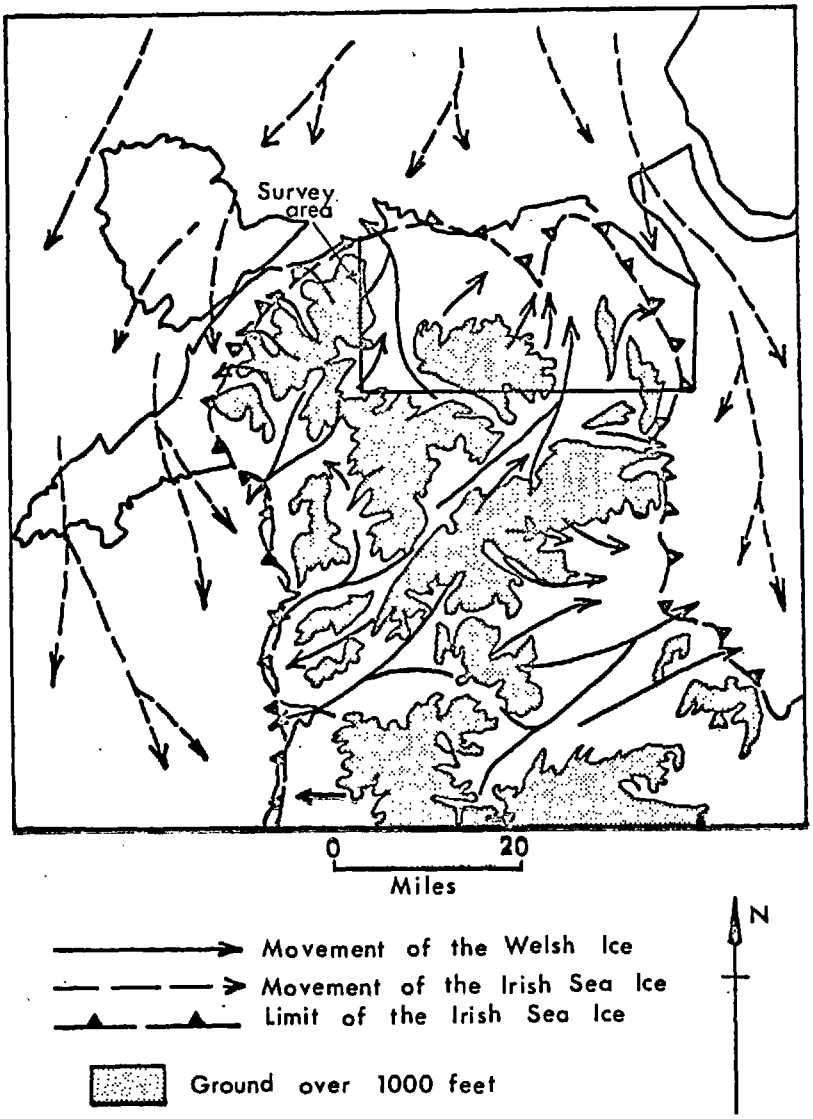


Fig. 7. The Extent of the Pleistocene Ice-Sheets in North Wales - based on Smith and George (1961), (after Fletcher, op. cit.)

2.3.3. Mineralisation

The mineralisation is located along Hercynian fault belts. Mineral deposits over the Ordovician are of two types:-

(i) Stratiform, syngenetic, pyrite deposits (Sherlock, 1918).

(ii) Fracture infilled N-S and E-W veins, bearing galena and sphalerite, usually within the Crafnant Volcanic series (Archer, 1959).

The Silurian mineralisation is also of two types:-

(i) Fracture infilled lodes bearing chalcopyrite with subsidiary sphalerite and galena in the sandstone-siltstone strata of the Llanfair-Talhaiarn district. (Archer, 1959).

(ii) Gold-bearing quartz veins in the Clwydian Hills.

The principal mineral deposits of this area occur within the Carboniferous (Dinantian) strata (Schnellman, 1939 and 1959). The main features are:-

(i) The N-S ore field extends from Halkyn (north) to Minera (south).

(ii) The steeply dipping, tabular lodes represent infilled open fractures.

(iii) The principal lode trend is E-W, with N-S cross-cut veins of only local importance.

(iv) The important ore minerals are galena, sphalerite with subsidiary chalcopyrite in a calcite gangue.

(v) The ore field and the individual veins exhibit regional zoning; sphalerite is the principal mineral in the north and south, whilst galena is more important in the central region.

There has been some relatively insignificant mineralisation in the sandstone overlying the limestone at Bwlchgwyn.

2.3.4. Mining History

Lead mining on the Carboniferous limestone may date from the Roman period. Mining was initially by surface trenching and later by shaft mining, until drainage problems caused the complete cessation of mining activity. Maximum production was reached in the latter half of the 19th century. The Minera mine closed in 1914, but Halkyn mine was intermittently worked until 1958. The total production of concentrates from this field has been estimated between 1.5 and 2.0 million tons of lead concentrates and 0.5 to 0.75 million tons of zinc concentrates (Taylor, 1968).

The Llanrwst field, worked in Roman times, also reached maximum production in the second half of the 19th century. Total

production of Pb-Zn concentrates did not exceed 5 per cent of the Halkyn-Minera field (Dewey and Smith, 1922). The largest single producer was at Trecastell, to the north of the main field, and the only deposit worked principally for pyrite was at Cae-Coch.

The Llanfair-Talhaiarn field was exploited for Pb and Cu ores between 1880 and 1905, production was relatively insignificant.

The result of these long continued mining and metallurgical activities has been to extensively contaminate the drainage channels and soils around the metalliferous areas. The position of the main fields is shown in figure 8.

2.3.5. Topography

The Snowdonian highlands extend into the west of the area and are terminated by the Conway valley. The Silurian forms the southern Denbigh Moors (1000-1400 feet), which descend north and east to the Denbigh Uplands (500-1000 feet) and finally down to the coastal plain of north Denbighshire. The glaciated tectonic depression of the Vale of Clwyd widens at its northern end to form an extensive coastal plain. The vale is bounded in the east by the Silurian inlier of the Clwydian Range, which rises steeply in the west and dips more gently to the east, beneath the unconformable Carboniferous and Permo-Triassic strata. The last named formation forms the low-lying Flintshire plain (see figure 9).

2.3.6. Drainage

The principal drainage systems are the catchments of the river Conway in the west and south-west, the river Clwyd in the centre, and the river Dee in the east and south (see figure 9). The average drainage density approximates to 3 miles per square mile, except in the Clwyd valley mouth, where an extensive network of drainage ditches has been developed.

Drainage sediments over the Silurian and Carboniferous strata are generally silty sands with shale and sandstone fragments. The faster streams, over the more intense relief of the Ordovician, yield little sediment of fine size fraction. The eastern, drift-covered area gives an adequate proportion of fine size stream sediments, the bedrock componenent being much diluted by residual and exotic drift.

2.3.7. Climate

The climate is maritime with high humidity and relatively equable seasonal temperatures, except over the high ground on the Snowdonian hills and the Denbigh moors.

The rainfall is lowest along the coast (25 inches p.a. in the Vale of Clwyd) rising over the high ground of the Denbigh moors (50 inches p.a.) to a maximum over the Snowdonian range (80 inches p.a.), see figure 10.

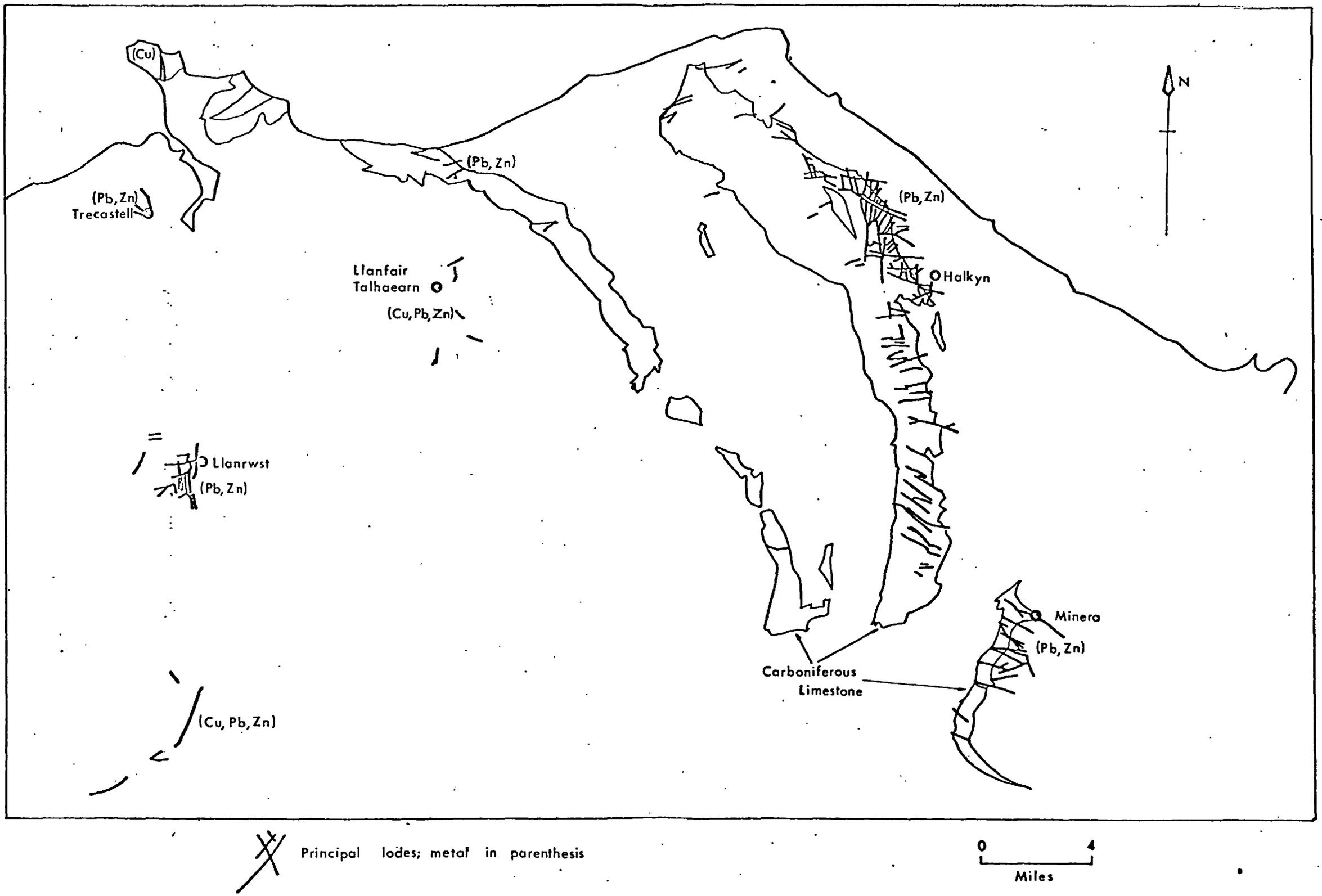
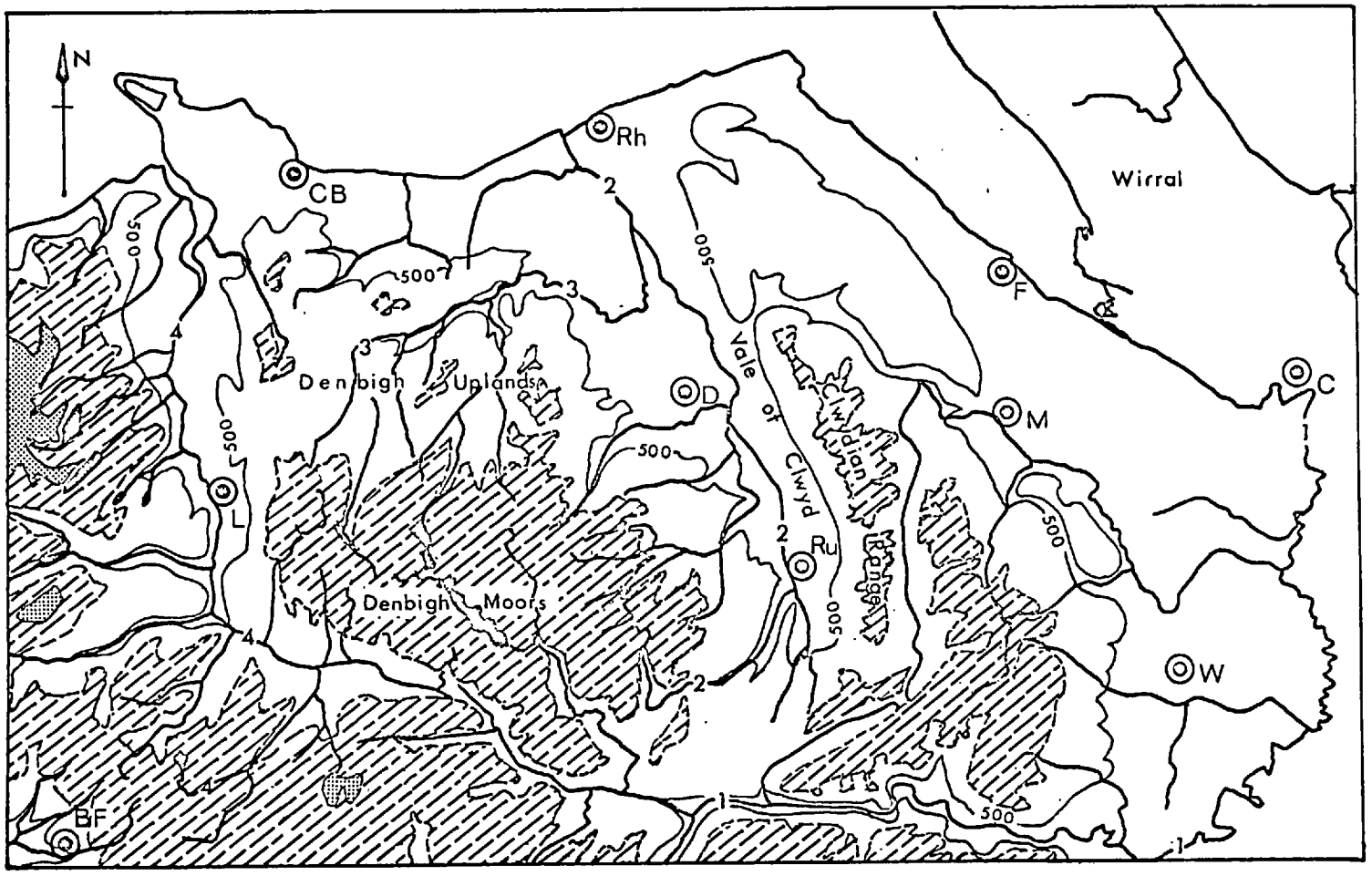


FIG. 8. MINERALIZATION IN THE NORTH WALES SURVEY AREA.
(based on I.G.S. maps, after Fletcher, op. cit.)



500 — 500 ft. contour

Towns

Ground above 1000ft.

Ground above 2000ft.

0 5 10

Miles

Key to rivers

1. R.Dee; 2. R.Clwyd; 3. R.Elwy; 4. R.Conway

Key to towns

B. BIaenau FFestiniog; C. Chester; CB. Colwyn Bay; D. Denbigh; F. Flint
L. Llanrwst; M.Mold; Rh. Rhyl; Ru. Ruthin; W. Wrexham

Fig. 9. Location and Topography of the North Wales Survey Area
(after Fletcher, op. cit.)

2.3.8. Pedology

The soils west of the Clwydian range have been described (Ball, 1960 and 1963). The Ordovician strata west of the Conway valley underlie podzolic and peaty gley soils. The Denbigh moors are covered by acid peaty gleys and podzolic soils, with hill peat deposits in the topographic depressions. Similar Silurian rocks in the Denbigh uplands bear freely-drained brown earths of low base status. The Denbighshire coastal plain and the Vale of Clwyd have a great variety of soils, principally of gley and imperfectly drained, brown earth type. The latter is typically developed over Northern Drift and alluvium deposits. The Carboniferous limestones are characteristically covered by freely drained, high base status, brown earths (see figure 11).

2.3.9. Description of the regional geochemical reconnaissance data

Geochemical maps have been prepared for As, Co, Cr, Cu, Fe (as Fe_2O_3) Mn, Mo, Ni, Pb, Sn, Ti, V and Zn (figures 14-26, vol.2.) Maps were not prepared for Ag, Bi and Ga. Ag and Bi were detectable in relatively few samples, and Ga revealed no apparently distinctive patterns. Some of the samples were analysed for Se.

The symbol concentration ranges were kept constant over all three reconnaissance areas and those used for Pb do not fully exhibit the distribution in this area. The areal dispersion pattern for

each element is briefly described and the main trends and associations are summarised at the end of the section.

Arsenic (figure 14, vol. 2)

Most concentration levels in the east are below the detection limit, but west of the Vale of Clwyd there are numerous concentrations over 7 ppm, especially over the Denbigh Moorlands and the western Ordovician outcrop. Peak levels of up to 300 ppm have been recorded in this last named area.

Chromium figure 15, vol. 2)

The most marked feature is the lower concentration level recorded over the Vale of Clwyd, and more generally over the drift covered eastern Silesian and Permo-Triassic outcrops. The Ordovician and Silurian strata bear relatively higher levels (majority, 70-150 ppm) compared with those (30-70 ppm) encountered over the other strata in the east and also in the Clwydian Hills, together with those from over the Ordovician rocks, south-west of Llanrwst.

Cobalt (figure 16, vol. 2)

Lower concentration levels characterise the Vale of Clwyd (usually ≤15 ppm) and the eastern half of the survey area, with marginally higher concentrations in the south-east (≤15-70 ppm). The Silurian west of the Clwyd river give values in the ≤5-30 ppm range over the Denbigh lowlands and uplands, but over the Denbigh Moors and the Snowdonian Ordovician, the majority of levels exceed 30 ppm and

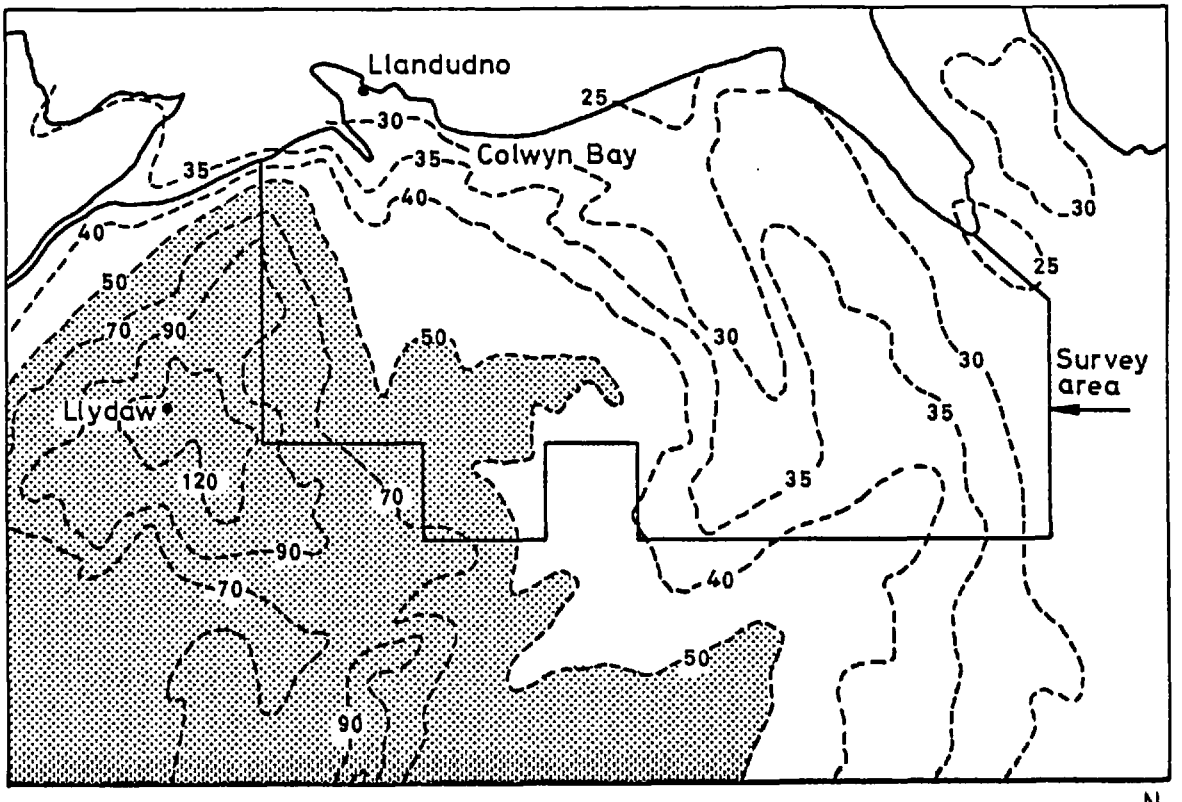


Figure 10. Rainfall of the North Wales survey area (After Horsnail op. cit.)

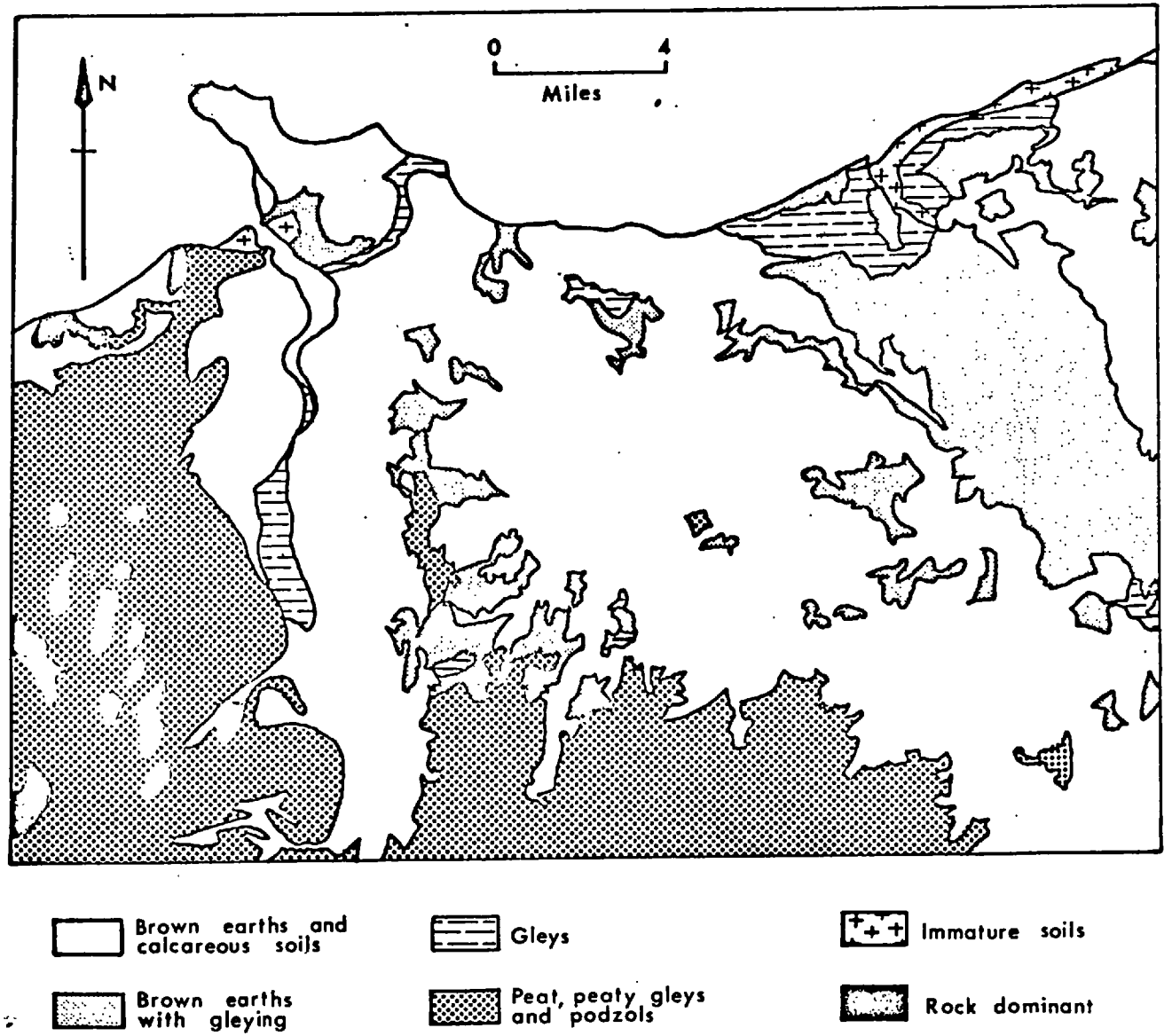


Fig. 11. Major Soil Groups of the Western Half of the North Wales Survey Area (modified from Ball,1960,1963, after Fletcher, op. cit.)

and frequently exceed 150 ppm.

Copper (figure 17, vol. 2)

The highest copper levels (>70ppm) cluster along the Ordovician-Silurian boundary in the west, over the Silurian south of Abergele (Llanfair-Talhaiarn area), and over the mouth of the Vale of Clwyd. The regional patterns exhibit a discontinuity at the base of the Dinantian. The Ordovician and Silurian concentration levels are higher (15-70 ppm) compared to those from over the post Silurian strata (< 2-30 ppm), though marginally higher levels are found over the Silesian (> 30 ppm), south of Connah's Quay.

Iron (figure 18, vol. 2)

A marked discontinuity in the concentration levels occurs at the western margin of the Vale of Clwyd. Concentrations over the Silurian are usually 1.5-7.0%, but over the Denbigh Moorlands and over the southern Ordovician outcrop the usual range is 3.0 - > 7.0%. The Vale of Clwyd shows a longitudinal discontinuity between the west (1.5-7.0%) and north, compared to the east (0.7-1.5%). The Clwydian Hills give lower concentration levels on westerly flowing streams (0.7-1.5%) compared to easterly flowing streams (1.5-3.0%). The Silesian outcrop exhibits concentrations from 0.7-3.0% with scattered peak values (<7.0%).

Lead (figure 19, vol. 2)

A belt of higher concentrations (> 150 ppm) follow the Dinantian and

and lower Silesian outcrop. Other highs occur over the Ordovician, south of Conway and south-west of Llanrwst, over the Silurian, south of Abergele (Llanfair-Talhaiarn), and finally in the mouth of the Vale of Clwyd. Apart from these anomalous levels the Ordovician is higher (30-150 ppm) than the Silurian (< 2-150), which is marginally lower in the north than elsewhere. The levels over the Westphalian and Permo-Triassic generally exceed 30 ppm whilst those in the Vale of Clwyd levels range from < 2-150, but are generally < 30 ppm.

Manganese (figure 20, vol. 2)

The lowest concentration levels occur in the Vale of Clwyd and over the Clwydian hills (< 10-300 ppm, usually). The levels over Carboniferous and Upper Silurian strata are higher (150-1500 ppm) with scattered peaks (>1500 ppm). The Ordovician and Denbigh Moors Silurian drainage sediments give very high levels (700 - >1500 ppm), the majority of concentrations exceed 1500 ppm.

Molybdenum (figure 21, vol. 2)

Concentrations are generally less than 3 ppm, with occasional higher values (≤15 ppm) over the post-Ordovician stratigraphic units. There are a cluster of high levels (>15 ppm) west of Llanrwst, over the Ordovician bedrock with peak levels exceeding 30 ppm.

Nickel (figure 22, vol. 2)

There is a pronounced discontinuity in concentration levels at the Silurian-Carboniferous junction, west of the Vale of Clwyd. The

Silurian sediments exhibit levels between 15->150 ppm (usually 30-70 ppm), and are marginally higher south of Denbigh (>70 ppm). The Carboniferous and Permo-Triassic outcrops have lower levels (<5-150 ppm; usually 15-30 ppm). The Ordovician is marginally lower (15-70 ppm) than the Silurian except in the south, and west of Llanrwst where higher levels (>70 ppm) occur.

Tin (figure 23, vol. 2)

The distribution pattern is ill-defined. The Ordovician has the highest levels (<5->70 ppm), whilst the post-Ordovician outcrop areas are generally lower (<7 ppm with scattered peaks >70 ppm). Triassic is marginally lower than the Silurian and Carboniferous. An area of higher values (>30 ppm) is situated over the Silurian and Carboniferous outcrops, west of Wrexham.

Titanium (figure 24, vol. 2)

The highest concentration levels (>3000 ppm; majority >7000) occur over the Ordovician. Lower levels are found over the Silurian (1500-7000 ppm) with scattered peaks (>7000 ppm). There is a sharp discontinuity in the concentration levels at the base of the Dinantian, west of the Clwyd valley, the younger sediments yield lower levels (700-3000 ppm) with scattered concentrations <700 ppm and>3000 ppm, the latter being relatively more common over the Permo-Triassic.

Vanadium (figure 25, vol. 2)

A pronounced change in the concentration levels occurs at the base

of the Dinantian, west of the river Clwyd. Over the Ordovician and Silurian the concentrations are higher (usually $\geq$70 ppm; majority >150 ppm) than over the post-Silurian strata ($\leq$ 5-70 ppm; scattered peaks $\geq$70, rarely $\geq$150), though south-south-west of Llanrwst on the Ordovician, the levels are relatively low. Higher levels ($\geq$70 ppm) are clustered in the northern Vale of Clwyd.

Zinc (figure 26, vol. 2)

The Ordovician, south of Conway and west of Llanrwst, bears clusters of higher concentration levels ($\geq$300 ppm, frequently $\geq$700 ppm). Similar levels occur along the Halkyn-Minera belt extending along the Rhyl-Prestatyn coast, another high area is in the Llanfair-Talhaiarn field, south of Abergele. The levels over the Silurian (70-300 ppm) are higher than over the post-Silurian sediments ($\leq$40-150 ppm), though scattered higher levels ($\geq$300 ppm) occur over both.

Other Elements

Ag usually shows levels below 0.2 ppm except in the old mining areas, where peak values $\leq$2 ppm have been recorded.

The Mo-rich drainage sediments from the Ordovician, west of Llanrwst gave Se levels $\leq$4 ppm compared to the background of 0.2 ppm.

Summary

Broadly similar distributions are displayed by a number of elements:-

(i) the geochemical discontinuity across the base of the Dinantian, west of the Clwyd valley, with higher

levels on the Ordovician and Silurian relative to the post-Silurian units for the elements Cr, Ti, V, and to a lesser extent Co, Cu, Fe, Mn, Ni and Zn.

(ii) As, Co, Fe, Mn and to a lesser extent Ni and Zn are enhanced over the poorly drained moorland areas on the Ordovician and Silurian outcrops in the south-west of the area.

(iii) Cu, Pb and Zn show their highest concentration levels over areas which have been the sites for the now extinct mining-metallurgical industry, namely:-

(a) the Halkyn-Minera field (Pb-Zn with subsidiary Cu)

(b) the Llanrwst field (Cu-Pb-Zn with subsidiary pyrite)

(c) the Llanfair-Talhaiarn field (Cu-Pb-Zn)

(iv) There are a number of small scale associations.

(a) Co, Fe, Ni, Ti, V and to a lesser extent Cr and Mn exhibit lower levels over the Silurian of the Clwydian Hills relative to the main outcrop in the west.

(b) Cr, Ni and V are relatively low on the Ordovician, south-west of Llanrwst.

(c) Cr and to a lesser extent Fe, Mn, Ni, Sn and Zn show enhanced concentrations at the Silurian-Dinantian junction, in the Llangollen area.

(d) Cu, Fe, Pb, Ti, V and Zn are relatively high south of Rhyl at the mouth of the Vale of Clwyd.

2.3.10 Discussion and Conclusions

The geochemical maps exhibit patterns related to bedrock geology including mineralisation, glacial drift, secondary environment and contamination. Further work has involved a limited number of soil and bedrock analyses. The results of this follow-up work have confirmed the following features:

(i) Higher levels of Cr, Ti, V and to a lesser extent Co, Cu, Mn, Ni and Zn occur over the lower Palaeozoic compared to later sediments The regional variations for those elements immobile in the secondary environment (Cr, Ti, V) are probably related to lithological variations in the suboutcropping bedrock.

(ii) The Denbigh Moors-Snowdonia area of the Ordovician and Silurian outcrops exhibit high levels of As, Co, Fe, Mn and to a lesser extent Ni and Zn. This has been shown to be due to the operation of secondary

environmental processes, whereby these elements were leached from acid, poorly drained soils and precipitated or coprecipitated in the drainage channels. Criteria have been developed to determine whether the Mn concentration is principally derived from detrital sources or from solution. The regional variation between lower and upper Palaeozoic strata for the elements Co, Mn, Ni and Zn is probably related to the change in secondary environment and climate (lower rainfall, higher temperature) from the climatically more extreme south-western highlands to the areas of lower relief in the east and north-east.

(iii) The extensive Pb-Zn and to a lesser extent Cu patterns are largely the result of mining and metallurgical contamination. Criteria have been developed to distinguish between anomalies caused by smelter contamination and those derived from mineralisation or mine dump contamination. However, anomalies recognised using these criteria have not yet been fully investigated in the field.

(iv) Smaller scale features include:-

(a) The depletion of Co, Fe, Ni, Ti, V and to a lesser extent Cr and Mn over the Clwydian Range

Silurian compared to the main outcrop. It is possible that the lower levels of Co, Fe, Mn and Ni are due to the difference in the secondary environmental conditions between the two areas.

(b) the enhancement of As, Cu, Pb, Mn, Mo, Sn and Zn over the Ordovician, west of Llanrwst, relative to those over the southern outcrop. The postulated controls here are:-

1. As-Mo levels are higher in the sub-outcropping basic volcanic rocks and black marine shales.
2. Cu-Pb-Zn levels are enhanced by mineralisation and mining-metallurgical contamination.
3. the higher concentrations of As-Mn-Zn may be due to differences in secondary environment between the two areas.

(c) the depletion of Cr, Ni and V over the Ordovician south-west of Llanrwst compared to the remainder of the outcrop. There are acid igneous intrusive and extrusive rocks (felsites) in the catchments of the streams yielding the low levels, and these igneous rocks probably have low concentrations of Cr, Ni and V.

(d) the enhanced levels of Cr and to a lesser extent Fe,

Mn, Ni, Sn and Zn at the Silurian-Dinantian junction in the Llangollen area. The enhancement of Fe, Mn, Ni and Zn indicates the operation of secondary environmental effects.

(e) the higher concentrations of Cu, Fe, Pb, Ti, V and Zn at the mouth of the Vale of Clwyd. The Cu-Pb-Zn association suggests smelter and mining contamination or mineralisation, probably the former.

(v) The effect of the drift cover over western portions of the survey area has been to mask the bedrock control. However, the drift has been shown to be geochemically very homogeneous irrespective of the source material. This indicates that the assigned drift provenances may perhaps be incorrect.

The unresolved problems in this area relate to the geochemical-geological control of the elements Cr, Ti and V. These show regional and local variations of pattern, presumably bedrock controlled, since they are relatively immobile elements, but the reasons have not yet been elucidated.

It has been demonstrated that the bedrock geochemistry will usually be the dominant control of the stream sediment composition. Areas in which intense secondary environmental processes are operative

will lead to the modification of the mobile element dispersion patterns so that the concentrations yielded by the drainage sediments will not represent the bedrock composition. Previous mining and metallurgical exploitation has produced extensive ore-element contamination within the drainage channels. Anomalous levels recorded for these elements will rarely relate to bedrock mineralisation and special evaluative procedures are necessary to determine the anomaly provenance. The effects of glacial drift are to mask the bedrock geochemical control of the drainage sediments by contributing material to the drainage channels, which reduces the proportion of bedrock derived weathering products in the drainage sediments.

2.4.0. THE ENGLISH PEAK DISTRICT

2.4.1. Location

The area lies principally in Derbyshire but includes adjoining portions of Staffordshire, Cheshire and Yorkshire. It covers 960 square miles bounded by N.G. lines 3400 (south), 3900 (north), 3900 (west), and 4400 (east). Only 760 sq. miles were sampled because of inadequate surface drainage in the larger urban areas and on the limestone plateau (see figure 14).

2.4.2. Geology

The stratigraphic succession is summarised in table 3, and

the disposition of the major units is shown in figure 12.

Structurally the area is centred on a N-S trending upper Palaeozoic dome. Carboniferous limestones are exposed at the dome core and are successively flanked by younger Carboniferous sediments of Namurian and Westphalian age. Minor N-S folds lie on the dome flanks, for instance, in the Mixon anticline. Permo-Triassic sedimentary rocks outcrop in the south and west where they lie unconformably over the Carboniferous strata.

The lower Carboniferous limestones outcrop in the centre of the area and in the subsidiary anticlines on the dome flanks. The limestones are massive and include chert bands, as well as extrusive and intrusive (basic) igneous rocks. The limestones are surrounded by marine shales interbedded with calcareous siltstones and non-feldspathic, often bioclastic sandstones of Viséan-Namurian age, henceforth called the Viséan-lower Namurian series (V-N series). These are flanked by rhythmically alternating argillaceous and arenaceous units and towards the upper part of the Namurian the deposits become deltaic. The Westphalian sedimentary rocks include non-marine shales, siltstones and fine sandstones with a few coal seams, and outcrop along the eastern margin and in limited exposures on the western margin of the survey area. The Permo-Triassic arenaceous deposits and marls mainly outcrop in the south and in small outliers west of the dome, for instance, west of Leek.

Extensive areas of Bunter Pebble beds occur along the base of the Permo-Triassic succession along the southern margin.

Glacial deposits, related to the Weichsel glacial period, mantle the lower ground up to the 1250 foot contour in the west (see figure 12). The drift, a reddish-brown, sandy clay, is believed to be derived from the Trias (Mackney and Burnham 1964). Sporadic deposits of older drifts occur on the higher ground beyond the Weichsel drift limits. Overburden on the limestone is considered to be partially derived from loess deposited under periglacial conditions (Cazalet, 1968; Piggot, 1962).

Table 3. Stratigraphic succession in the English Peak District survey area (after Edwards & Trotter, 1954)

Stratigraphic Formation			Lithology
Recent			Peat, alluvium, colluvium.
Pleistocene		New Drift (Weichsel)	Sandy drift, largely derived from Triassic strata.
		Older drift(s)	Solifluction earths; alluvial sands & gravels.
		Loess	Loess.
Permo-Triassic		Keuper	Red and green marls with beds of gypsum and rock salt and variable sandy beds at base.
		Bunter	Soft, fine-grained, red sandstones; occasionally pebbly; current bedded. Sands and breccias with limestone fragments & a calcareous matrix.
Carboniferous	Silesian	Westphalian	Shales and sanstones with coal seams.
		Namurian	Shales alternating with sandstones & grits, often feldspathic
			Marine shales with quartzites & calcareous siltstones.
		Viséan	Marine shales, argill. lsts., local calcareous ssts and massive bedded limestones.

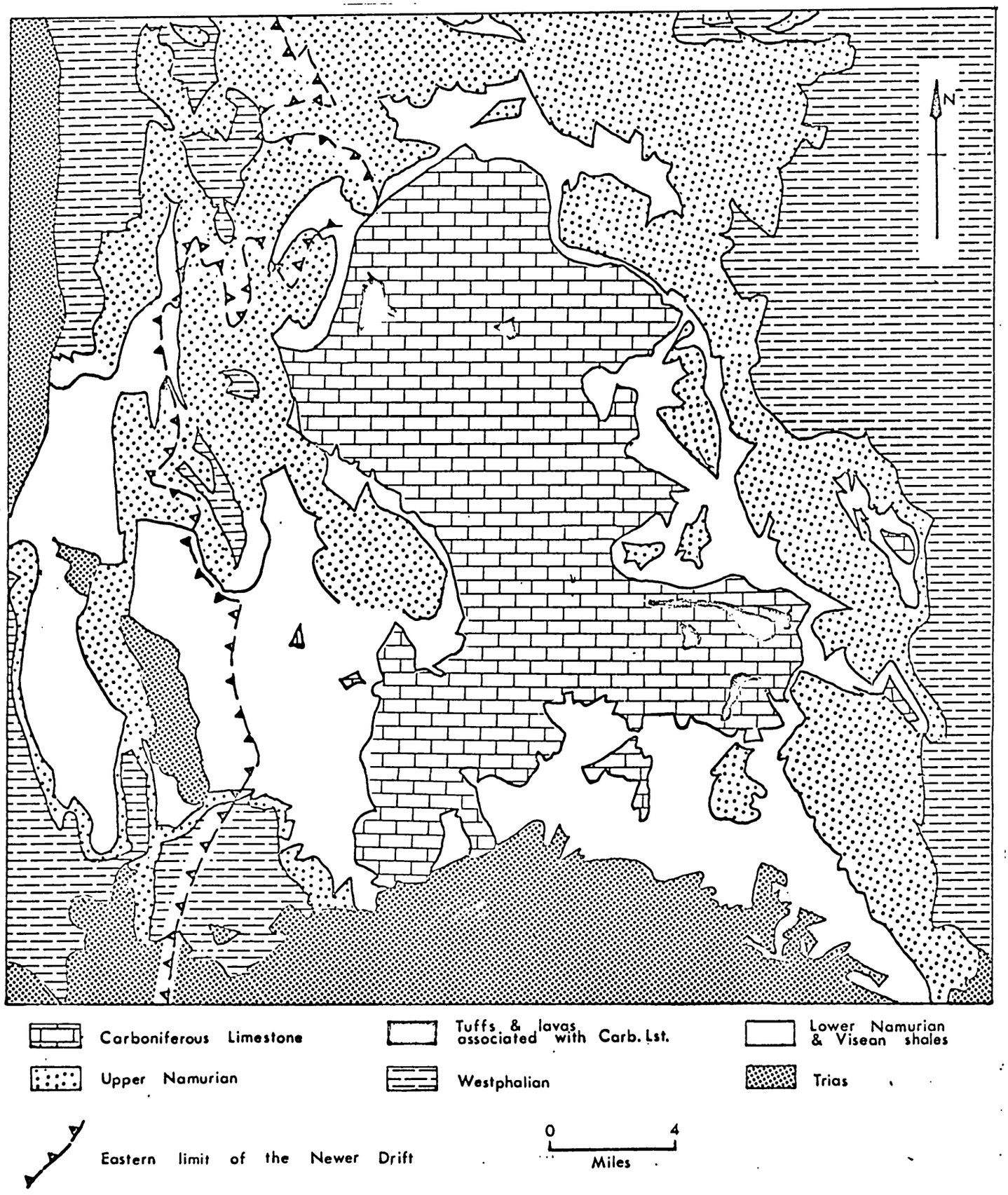


Fig. 12. GEOLOGY OF THE DERBYSHIRE-STAFFORDSHIRE SURVEY AREA - for sources see text. (after Fletcher, op. cit.).

2.4.3. Mineralisation

The type-mineralisation in this area consists of E-W trending, steeply dipping vein or replacement fracture systems. These occur predominantly on the eastern flank of the dome in a NW-SE trending zone. Two other minor centres occur west of the dome at Ecton Hill and in the Mixon anticline.

The minerals in the main field are principally galena with subsidiary sphalerite of local importance. Gangue minerals include barite, fluorite, calcite and occasionally subordinate quartz. The proportion of various gangue minerals shows a regional zoning indicating a centre of mineralisation to the east beneath the later sedimentary rocks (Schnellman & Wilson, 1947; Dunham, 1948). The mineralisation in the Ecton Hill-Mixon anticline is quite separate from the main field and produced small quantities of chalcopyrite ore. The main mineralisation is indicated in figure 13.

The ore shoots may extend for thousands of feet along the strike but seldom for vertical depths greater than 100 feet. The richest deposits are 'ponded' behind impervious, barren igneous horizons within the limestone, and also at the base of the overlying Viséan-Namurian (V-N) shale series.

2.4.4. Mining History

It is fairly certain that mining of Pb dates from the

Roman period and was also carried out in medieval times, this being the principal English Pb-producing district. Prior to 1550, smelting was performed in open hearths ("boles") constructed on west-facing hill slopes ("bole-hills") to utilise the prevailing winds for draught. The Namurian and Westphalian scarps east of the dome provided a wealth of bole-hills, only one certain locality is known west of the dome. The fumes from these smelters have yielded extensive soil contamination trains downwind. After 1550 smelting mills were introduced which utilised water power for the bellows and charcoal-wood-peat fuels. Their distribution was as wide as the bole-hills but they were situated on the banks of streams, which were contaminated by dump, slag and fume from the mills. Coal-fired cupola furnaces, introduced in the mid-eighteenth century, were situated north (Eyam-Baslow-Sheffield area) and south (Darley Dale-Wirksworth area) of the dome; the main site location controls were the proximity to:-

(i) water power, situated on the banks of larger tributaries ;

(ii) coal supplies from the Yorkshire and Nottinghamshire coalfields ;

(iii) the principal mining centres ;

(iv) the refined metal markets in Sheffield and Chesterfield.

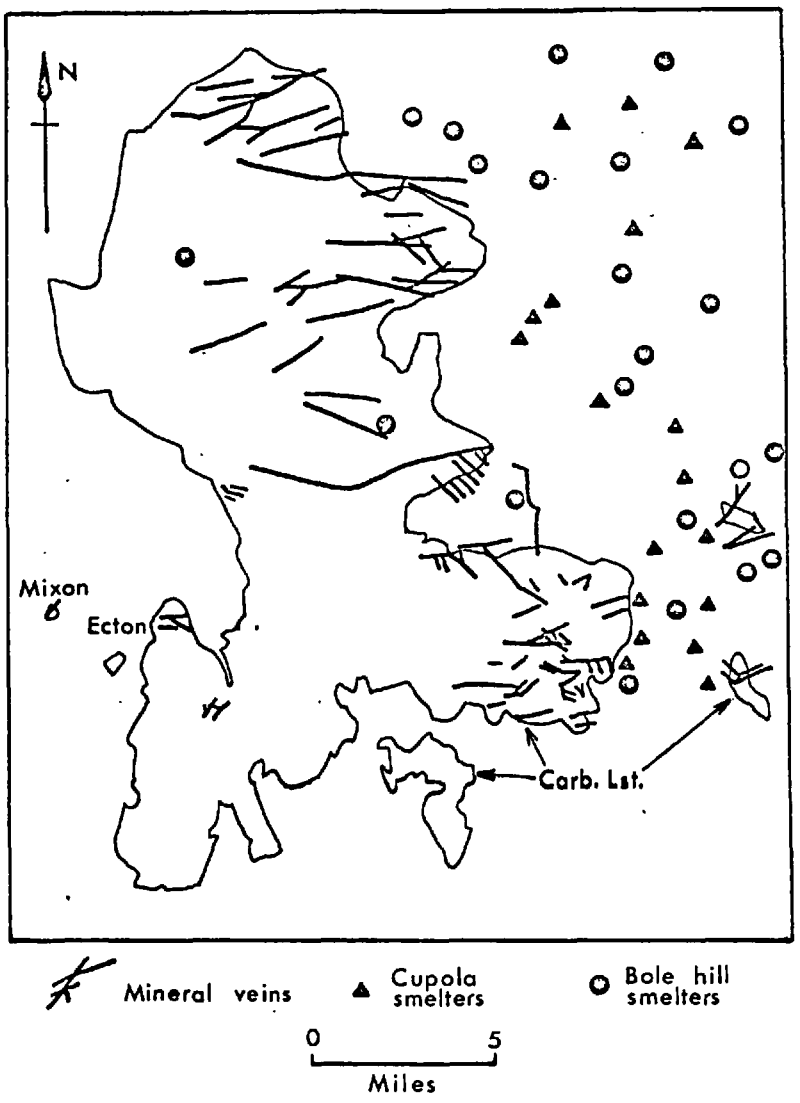


Fig. 13. **Mineralization and Smelting in the Derbyshire-Staffordshire Survey Area - for sources see text.**
(after Fletcher, op. cit.)

Peak production of Pb continued from late in the eighteenth century until the 1880s when many smaller mines closed down and larger mines expanded. The largest of these, Millclose - south-east of Alport, was exploited until 1940. Mining still continues in this area, principally for fluorspar with subsidiary barite and galena from the Glebe Mine, Eyam, on the north of the dome.

Copper ores were mainly smelted at Denby (Derbyshire), Whiston (Staffordshire), and during the production of brass at Cheadle (Staffordshire). The location of the main mining and smelter sites is indicated in Figure 13.

2.4.5. Topography

The limestone outcrop forms a central undulating plateau between 900-1000 feet high. This is bounded in the north and east by steeply incised valleys in the Viséan-Namurian argillaceous bedrock. These valleys separate the limestone plateau from the 1200-2000 feet scarps of the Namurian sandstones and grits, which gradually decrease in height towards the south. West of the limestone plateau are the north-east Staffordshire hills attaining maximum heights in excess of 1000 feet, which decline towards the Cheshire Plain. South of the dome, the higher Namurian hills (600-800 feet) merge southwards into the gentler Triassic relief of the Midland lowlands (Figure 14).

2.4.6. Drainage

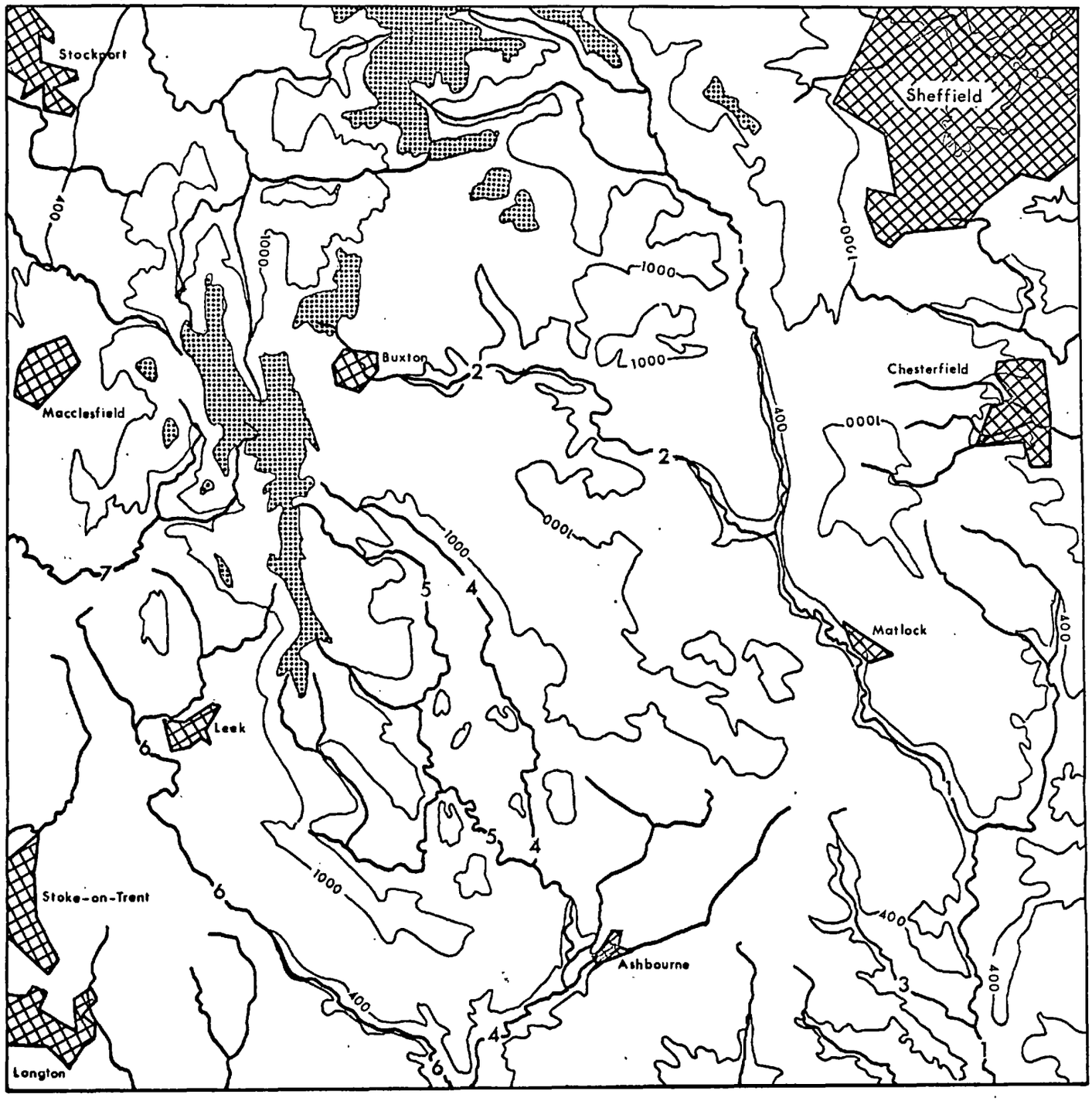
Surface drainage channels are rare over the limestone plateau, but elsewhere are well developed. Drainage channels are steeply incised over shale-sandstone interlayered strata but are not incised over suboutcropping shale bedrock. West of the dome, the stream channels are incised in the Newer Drift deposits except on the higher (>1250 feet) ground. South of the dome drainage channels are incised into the bedrock and its weathering products with the drift deposits stranded on the interfluves. Alluvium flanks the principal rivers but alongside tributaries is equally developed with colluvium. The main direction of drainage is to the south and east into the Trent basin (see figure 14).

2.4.7. Climate

The climate is north-west European and maritime, strongly modified by altitude. The mean annual rainfall is 30-40 inches, rising above 50 inches on the higher ground and falling below 35 inches over the lower relief in the south-eastern sector of the area. The 200 rain days per annum line runs NE-SW across the area, approximately corresponding to the 1250 foot contour (see figure 15).

2.4.8. Pedology

The soils north and east of Derby have been mapped



Key to rivers

1. R.Derwent; 2. R.Wye; 3. R.Ecclesbourne; 4. R.Dove; 5. R.Manifold; 6. R.Churnet 7. R.Dane

Fig. 14. Location and Topography of the Derbyshire-Staffordshire Survey Area. (after Fletcher, op. cit.)

(Bridges, 1962) as have those in Staffordshire, though in less detail (Mackney & Burnham, op.cit.) and around Hartington on the western margin of the limestone plateau (Cazalet, op.cit).

The limestone plateau develops acid, freely-drained brown earths with podsolised soils over the cherts and on the wetter uplands, whilst on the steeper, well-drained slopes are developed thin lime-rich rendzina soils. Gleyed soils are characteristic over the Namurian-Westphalian and over the western drift-covered areas. Peat deposits, peaty gleys and peaty gleyed podsols are found over the higher wetter uplands with blanket peat common at altitudes over 1300 feet, whilst the steeper slopes associated with these uplands bear acid brown earths. The sandstones-gritstones of the Carboniferous and Permo-Triassic underl well-drained sandy brown earths.

2.4.9. Description of the regional geochemical reconnaissance data

Geochemical maps have been compiled for As, Co, Cr, Cu, Fe (as Fe_2O_3), Mn, Mo, Ni, Pb, Sn, Ti, V and Zn (figures 27-39, vol. 2), but not for Ag, Ba, Bi, and Ga. Ag was detected in relatively few samples whilst Bi was detectable in none. The data for Ga showed no obvious distribution patterns and the Ba data was not available when the maps were compiled. A number of samples were also analysed for Se.

The individual element distributions are discussed in turn and the overall patterns are summarised at the end.

Arsenic (fig. 27, vol. 2)

A pronounced clustering of high values (>15 ppm) occurs over the Viséan-Namurian (V-N) shales flanking the limestone plateau. West of the limestone plateau, the V-N shales show a sharp geochemical discontinuity west of Leek, where the majority of the concentrations are less than 7 ppm. There is an extension of the high concentration levels north of the main Viséan-Namurian shale outcrop towards Buxton in streams draining the higher ground. Levels are low (≤ 5 ppm usually) over the remainder of the Namurian and the Permo-Triassic with scattered peaks. The Westphalian is marginally higher than the upper Namurian, more frequently exceeding 5 ppm.

Chromium (fig. 28, vol. 2)

The highest levels cluster over the V-N series (30-150 ppm, peaks ≥ 150 ppm) except to the west of Leek (majority < 70 ppm). Those outcrops west of the limestone outcrop are markedly higher than elsewhere. The upper Namurian levels are marginally lower (predominantly ≤ 70 ppm) than the Westphalian (majority 30-70 ppm, scattered peaks >70 ppm). The Permo-Triassic is very low (majority <30 ppm) except over the Keuper Marls where levels usually fall in the range 30-150 ppm.

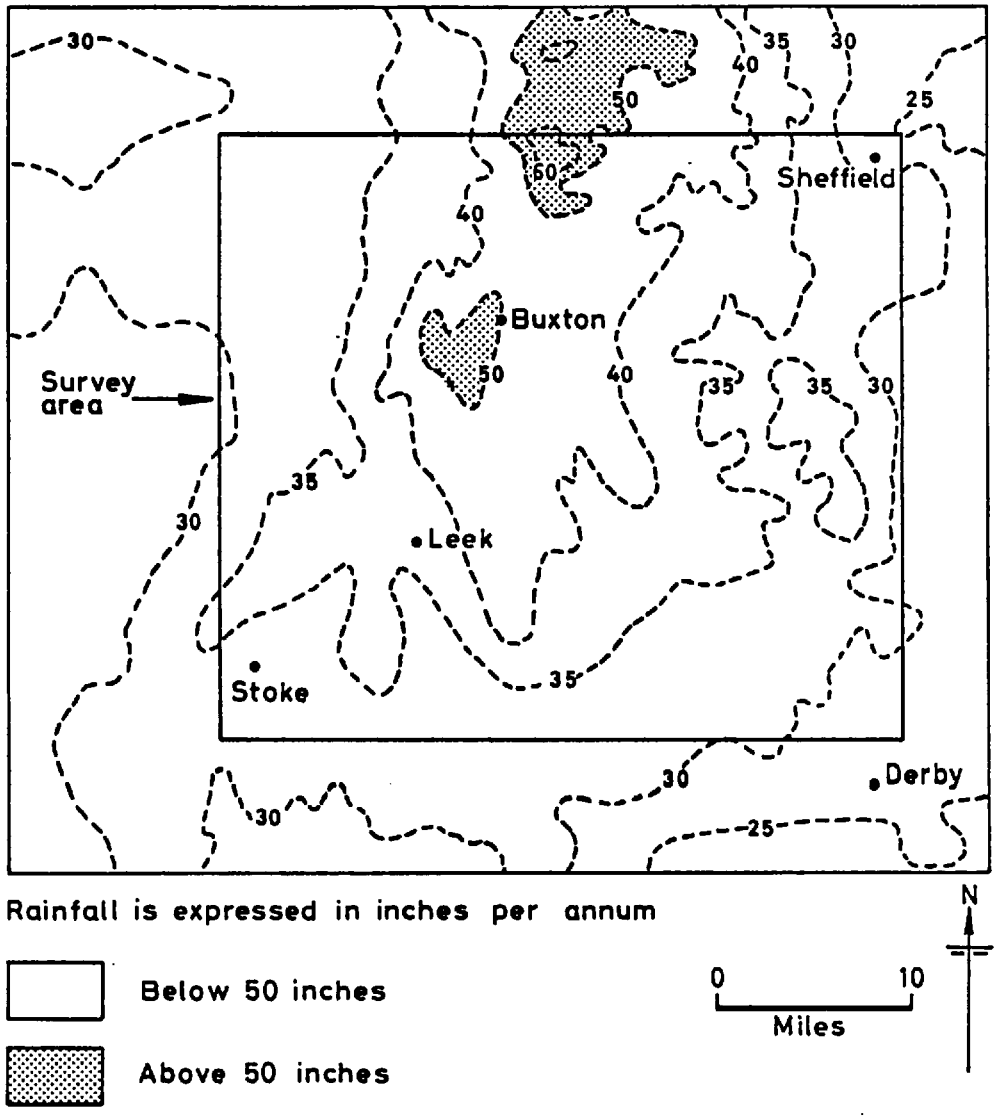


Figure 15. Rainfall of the English Peak District survey area (After Horsnail op. cit.)

Cobalt (fig. 29, vol. 2)

The Permo-Triassic is uniformly low (predominantly < 30 ppm; majority < 15 ppm) except near Carboniferous inliers. The V-N series west of the dome are marginally higher (usually 15-70 ppm) than elsewhere, except that portion west of Leek (< 30 ppm). The upper Namurian-Westphalian are comparable though slightly lower than the V-N series. Spasmodic highs (>70 ppm) in the north occur in streams draining the northern upper Carboniferous uplands.

Copper (fig. 30, vol. 2)

There is a strong clustering of high concentrations (> 30 ppm) over the V-N series, especially west of the dome, except for the low area west of Leek. The upper Namurian-Westphalian exhibit similar levels (predominantly 15-70 ppm) with scattered peaks (> 70 ppm). The Permo-Triassic shows marginally lower levels over the Bunter beds (15-30 ppm usually) compared to the Keuper beds (15-70 ppm). There is a cluster of high (30-70 ppm) concentrations in the streams draining the high ground over the Namurian-Westphalian outcrops, south of Buxton.

Ferric Oxide (fig. 31, vol. 2)

The V-N series bear higher concentrations (usually 0.7-3.0%) except west of Leek (< 1.5%) and on the eastern flank of the dome (< 1.5%) The upper Namurian has lower levels (< 1.5%, majority < 0.7%) than the Westphalian (majority 0.7-1.5%), which

exhibits higher levels (>1.5%) south of Sheffield. The concentrations on the Permo-Triassic are less than 0.7% except around the Namurian inliers. Streams draining the high ground south of Buxton yield higher levels (often 1.5% - >7.0%).

Lead (fig. 32, vol. 2)

A pronounced discrepancy occurs between the western low and eastern high levels. There are frequent peaks exceeding 700 ppm east of the dome over all geological formations. West of the dome are high levels around Ecton Hill and the Mixon anticline, but elsewhere the V-N seriss bear similar levels to the Westphalian (< 2-150 ppm) which are higher than those over the upper Namurian (majority < 30 ppm). The Permo-Triassic Bunter beds are higher (30-700 ppm) than the Keuper beds (< 2-150 ppm), again the western portion of the outcrop is lower than the east.

Manganese (fig. 33, vol. 2)

This shows a very 'noisy' pattern with very high values (> 1500 ppm) frequently found over the whole area. The southern Permo-Triassic outcrop exhibits lower levels (majority< 300 ppm), except in the east where higher levels (> 700 ppm) are found. Higher values are a spasmodic feature of those streams draining the high ground south of Buxton.

Molybdenum (fig. 34, vol.2)

A strongly developed clustering of higher levels (> 7 ppm,

peaks (70 ppm) can be associated with the V-N series with lower levels (usually <3 ppm) around and to the west of Leek. The concentration levels over the other formations are usually less than 3 ppm with scattered peaks (≤30 ppm).

Nickel (fig. 35, vol. 2)

The higher concentrations (> 70 ppm) cluster over the V-N series and are highest west of the dome (usually 30- >150 ppm), except to the west of Leek (predominantly 15-70 ppm). There are strong areal patterns within the V-N series especially west and south of the dome with the highest concentrations clustered together. The upper Namurian-Westphalian outcrops bear levels between 15-70 ppm with scattered peaks (> 150 ppm), more commonly occurring over the Westphalian. Levels are usually low over the Permo-Triassic outcrop (<30 ppm, predominantly).

Tin (fig. 36, vol. 2)

The patterns seem almost independent of the stratigraphic formations. Concentration levels are usually low (< 7 ppm) with scattered highs (> 15 ppm) more commonly found on the western and southern margins of the survey area and also in the north-western sector.

Titanium (fig. 37, vol. 2)

The pattern is unclear, but higher levels occur over the

V-N series (majority 1500-3000 ppm), except to the west of Leek, and to a lesser extent over the Westphalian and Keuper formations. The upper Namurian and Bunter formations give marginally lower concentrations (majority $<$1500 ppm).

Vanadium (fig. 38, vol. 2)

The V-N series, except to the west of Leek, and over the northern and eastern flanks of the dome bear high levels (majority $>$ 70 ppm). The remainder of the V-N series, the upper Namurian, and most of the Westphalian exhibit concentrations below 70 ppm, with rare peaks ($>$ 150 ppm). Locally clusters of higher (70-150 ppm) levels are found, for instance, north of Cheadle and between Sheffield and Chesterfield. The Permo-Triassic Bunter beds are lower (majority $<$ 30 ppm) than the Keuper beds (majority 30-70 ppm).

Zinc (fig. 39, vol. 2)

Concentration levels are higher (majority $>$150 ppm) over the V-N series, except to the west of Leek (majority $<$150 ppm). The upper Namurian exhibit levels between $<$40-300 ppm, but is lower in the west (majority 70-150 ppm) than in the east (majority $>$150 ppm). The Westphalian is associated with a very 'noisy' distribution ($<$40 - $>$700 ppm) and the Permo-Triassic shows much higher levels in the south-east (majority $>$150 ppm) than in the south-west (majority $<$150 ppm).

Other elements

Ba exhibits a pattern strongly coincident with that of Pb showing high values (1500-10,000 ppm) east of the dome, west of the dome near Ecton Hill (3000-10,000 ppm), and over the southern Permo-Triassic, especially south-west of Ashbourne ($>$10,000 ppm). Low levels ($>$1000 ppm) are common along the western margin.

Ag is normally undetectable, but detectable levels ($>$0.2 ppm) occur along the western margin (0.2-0.8 ppm) especially in the north-west over the drift covered Westphalian-Permo-Triassic outcrops. Localised moderately high concentrations are found over the V-N series around Ecton-Mixon, on the dome's west flank, in the south over the Permo-Triassic (south-west of Ashbourne), and east of the limestone dome, around Matlock.

Summary

A number of broad scale multielement patterns may be recognised. They are:-

(i) streams over the V-N series, especially west and south of the dome bear higher concentrations of As, Cr, Cu, Fe, Mo, Ni, V, Zn and to a lesser extent Co, Ti. The concentration enhancement is shown most markedly by Mo and As.

(ii) Pb, Ba and to a lesser extent Zn exhibit much higher levels east of the dome compared to the west,

concentrations are very variable.

(iii) the Permo-Triassic bears generally low levels of all trace elements except Pb, Sn, and Zn.

(iv) Small scale patterns are displayed for:-

(a) Ti, Fe and to a lesser extent Co, Cu, Ni are all enhanced south of Sheffield over the Westphalian;

(b) V and to a lesser extent As are concentrated over the Westphalian north of Cheadle;

(c) Zn and Cu are high around Cheadle;

(d) the Keuper beds apparently exhibit higher levels than the Bunter beds for the elements Cr, Cu, Ti and V; the reverse relationship is shown by Pb;

(e) the high ground south of Buxton is drained by streams yielding high levels of As, Cu, Fe and Mn.

2.4.10. Unaccountable geochemical patterns

A number of minor patterns cannot be totally accounted for in terms of the geology, secondary environment and history of the area. They are:-

(i) Cu, Fe, Mn, Ni, V, Ti enhanced over the Westphalian north of Cheadle possibly due to a facies variation or to the operation of secondary environmental effects or both.

(ii) Cu, Zn enhancement in the Cheadle area which may represent contamination from the brass foundries.

(iii) Ti and to a lesser extent Fe and other elements are enhanced on the Westphalian in the Sheffield-Chesterfield area, possibly reflecting facies change or contamination.

2.4.11. Discussion and Conclusions

The trace element distribution patterns exhibit a number of features correlatable with the bedrock geology, mineralisation or contamination, glacial drift and secondary environment. A limited number of bedrock and soil samples have been analysed, which have allowed the drainage sediment patterns to be further evaluated. The principal features are:-

(i) Broad scale patterns related to differences between major geological units:

(a) high As, Cu, Mo, V and Se over the marine shale-sandstone facies of Visean-lower Namurian age (the V-N series), particularly over the sub-outcropping black marine shales.

(b) notably low Co, Cu, Ni and V over the southern Permo-Triassic, which are probably caused by the lithology of these strata.

(c) high Mn and to a lesser extent Ti over the Westphalian, a feature which cannot be explained at present.

(d) Cr, Cu, Ni, V, Ti and to a lesser extent Co, Fe, Mn and Pb are enhanced in argillaceous bedrocks relative to arenaceous.

(ii) Contamination patterns related to mining-metallurgical industries have caused the masking of the bedrock (including mineralisation) control of the ore elements, notably, Pb, Ba and to a lesser extent Zn on the eastern flank of the dome. It is possible using the Pb : Zn ratio and also that of readily extractable Pb : total Pb in order to distinguish between contamination anomalies due to smelting and those related to other controls.

(iii) Glacial drift (Weichsel period) of variable thickness covers the western margin of the survey area, up to the 1250 foot contour. The geochemical features of the drainage sediments over the V-N series bedrocks, so strongly shown over drift-free areas, are completely masked. This is interpreted as indicating a massive dilution of the bedrock weathering products in the drainage channels by the exotic, barren overburden.

(iv) The influence of the secondary environmental effects in masking the bedrock controls can only be tentatively established in one area, over the high ground (>1400 ft.) south of Buxton. Elsewhere, it is considered to increase the variability of the mobile element concentrations, most notably for Mn.

The major unresolved problems in this area relate to:-

(a) The detailed evaluation of those criteria used to distinguish between mineralisation and contamination;

(b) the mineralogical control of those elements enriched in argillaceous rocks, that is, Cr, Cu, Ni, V, Ti and to a lesser extent Co, Fe, Mn and Pb.

It has again been demonstrated that the bedrock geochemical composition is the dominant geochemical control of drainage sediments except in areas covered by exotic drift, or where intense secondary environmental effects have been operative, or where extensive contamination patterns occur, especially those due to the operation of mining and metallurgical industries. It is not possible using the conventional approach to discriminate between the various contributions made by these various controls at any sample site except in a qualitative manner. Neither is it possible to establish the bedrock contribution in areas affected by intense contamination or secondary environmental effects and in those covered by exotic drift.

2.5.0. PROCEDURES UTILISED IN THIS RESEARCH

There are two types of problem in interpreting the regional multi-element data:-

(i) establishing the relation of the data to the known geological, pedological, topographical, climatic and historical information available for the area;

(ii) to simultaneously establish the areal variation of all the elements in order to appreciate the relative variation in trace element levels with respect to all the potential controls.

The second problem must be considered in greater detail. It is necessary, with multi-element data, to establish:-

(i) the controls acting upon the trace elements

(ii) the elements principally affected by each controlling factor

(iii) the relative importance of the various controls at each sample site.

It is apparent that to evaluate objectives (i) and (ii) requires more detailed information about geochemical processes, bedrock geochemistry and background information of an area than is usually available. Moreover, there is no established technique by which objective (iii) might be achieved. It is therefore necessary to adopt some other approach.

2.5.2. Procedures employed

It is possible using high speed digital computers and their off-line accessories to utilise certain procedures which may be useful as interpretative aids in regional geochemical studies. It is the purpose of this research to evaluate a number of these techniques.

The techniques employed are connected to those problems formulated in the previous section, and are described below:-

Interpreting areally distributed data involves two processes:-

(i) plotting the data in map form.

(ii) analysing the data in order to determine areal trends.

The first problem has been approached by using two techniques:-

(i) plotting raw data values using a CALCOMP graphical output plotter.

(ii) plotting the data in symbolic form using a Stromberg-Carlsan 4020 cathode ray plotter.

These techniques are described and evaluated in Chapter 3.

The problem of areal pattern analysis has been approached by considering two mathematical statistical techniques:

(i) fitting a two dimensional polynomial trend

surface to the data;

(ii) reducing the data variability so as to demonstrate the regional trends.

These techniques are briefly described and the method employed in this study is critically evaluated in Chapter 4.

The problem of simultaneously interpreting the multi-element data has been approached by applying those multivariate mathematical techniques known as Factor Analysis. The variant of these techniques chosen for this study, establishes trace element associations, based on the analysis of the multi-element correlation coefficients, and gives the relative strength of these associations at each sample site. The interpretative problem then resolves itself into establishing whether the associations revealed by the analysis are meaningful in geochemical terms, or whether they are mathematical abstractions. The technique is described in Chapter 5, and the applications and evaluation are described in Chapters 6 and 7.

CHAPTER 3

COMPUTERISED PROCEDURES I: AUTOMATED DATA PLOTTING

3.1.0. PROBLEMS ASSOCIATED WITH THE MANUAL PLOTTING OF GEOCHEMICAL DATA

Raw data derived from the regional geochemical surveys have hitherto been manually plotted onto maps. This required 5 persons (one caller and 4 plotters) for maximum efficiency. The maximum production rate approached 300 points per hour per plotter. The production of 13 trace element maps for 3 areas each of which bears approximately 900 sample sites can be accomplished in approximately 117 man-working-hours. If the cost of labour is set at £0.5 per hour then the costs will be £58.5 plus the materials used in plotting.

The advantages of the manual system lie in its flexibility. Analytical data can be plotted onto base maps showing sample locations as mapped during collection (accuracy). The analytical data can so be compiled that even closely adposed sample sites reveal their geochemical characteristics distinctly (clarity). The disadvantage of this system is the high probability of errors due to miscomprehension, fatigue and boredom

(imprecision) and the difficulty of interpreting a mass of areally distributed raw data (interpretability).

The interpretability can be radically improved by colouring the sample sites according to the element concentrations using about four or five concentration ranges. If a colouring production rate of 15 locations per minute is assumed, then the coloration will require an additional 39 man-working hours, which will cost an additional £19.5.

The problems associated with this method lie in the extravagant usage of labour which could be gainfully employed on less mechanical tasks and the possible imprecision of the results, which may be hard to correct. Moreover, the costings quoted above take no account of overhead costs, including a larger work force, which would be necessary for such work.

3.2.0. TECHNIQUES AND EQUIPMENT USED IN THIS STUDY

The data may be presented as raw numbers or subdivided into a number of concentration classes, each of which is represented by a symbol. The raw numbers have been plotted using a CALCOMP incremental digital plotter (model 563). The symbol plotting was accomplished using

a Stromberg-Carlsan 4020 computer recorder.

3.3.0. RAW DATA PLOTTING

This involves the writing of the sample data values of predetermined size at the appropriate locations on a map of predetermined scale.

3.3.1. Description of the CALCOMP model 563 plotter and its operational characteristics

The machine is small enough to fit on a desk top; the dimensions are 39.4 ins. wide, 14.8 ins. deep and 9.8 ins. high. The plotter consists basically of a motor driven horizontal roller which winds the paper onto the machine. A horizontal bridge is fitted parallel to and vertically over the roller along which the pen is moved. The pen may use a biro or liquid ink; various colours (black, red, blue and green) and line thickness are available. The chart paper is driven by marginal sprocket teeth on the drum which connect with appropriate holes on the paper.

The machine, which was designed for plotting one variable against another, may be connected directly to a computer (on-line) or it may be motivated by using magnetic tapes from the computer, which are used via a magnetic tape

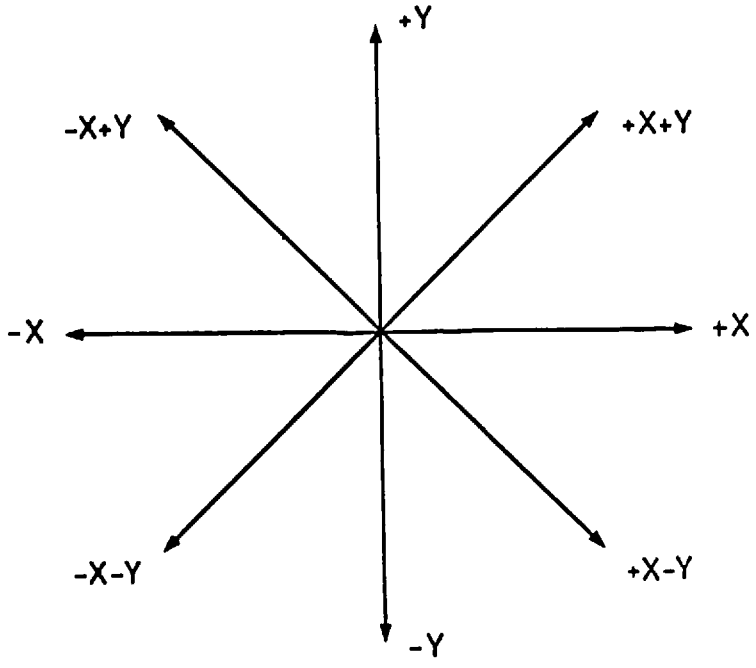
input deck (off-line).

The pen may be moved in 0.01 inch increments along any of 8 cartesian vectors in the plane of the chart paper. These are +x, -x, +x+y, +x-y, -x+y, -x-y, +y, -y (see fig. 16). Movement along the y-axis is achieved by that of the pen along the bridge, whilst x-axis movement is by the rotary action of the chart drum. The intermediate vectors are achieved by simultaneous movements of the pen and drum. Both the chart drum and the pen are capable of bidirectional movement. The maximum plotting speed is 200 steps or increments per second, which is equivalent to 2 inches per second. The maximum number of pen operations along the z-axis is 10 per second (5 up plus 5 down). The manufacturers claim an accuracy of $\pm$0.01 inch over the entire width and length of the chart paper. The rolls of chart paper, single sheets are also obtainable, are 31 inches wide and 120 feet long. The maximum permissible chart width is 29.50 inches.

3.3.2. Description of the computer programme

The manufacturers of the plotting machine (California Computer Products Inc.) have developed a number of computer programmes (soft-ware) which produce the machine language instructions for the operation of the plotter. Users of

FIGURE 16. POSSIBLE DIRECTIONS OF MOVEMENT FOR THE CALCOMP PEN RELATIVE TO THE CHART PAPER, EXPRESSED IN TERMS OF CARTESIAN VECTORS.



the plotting machine merely have to utilise the manufacturer-programmes as sub-routines in their own programmes, that used in this study is listed in Appendix 1. The salient operational features are described below.

The programme has a capacity of 2000 data values with their associated X and Y coordinates, which could be expanded without difficulty. A number of data transform options may be employed, they are:

(i) percentage range transformation $\frac{(X_i - X_{min}) \times 100}{X_{max} - X_{min}}$ where Xi is the data value of the ith sample, Xmin is the smallest value of all X_i values and Xmax is the largest.

(ii) reciprocal value transformation $\frac{1}{X_i}$ where Xi is the data value of the ith sample

(iii) standard value transformation $\frac{X_i - \bar{X}}{\sigma}$ where Xi is as before, $\bar{X}$ is the arithmetic mean of all the Xi values $\sum_{i=1}^{N} X_i/N$, where N is the number of data values and σ is the sample standard deviation

Real numbers may be plotted to any number of decimal places and the number will be rounded off. It is also possible

to add a constant increment to all the values if this is desired. Positive and negative values are plotted but only the latter with the appropriate sign.

The limitation upon data to be plotted lies not so much with the computer but with the length of the magnetic tape used for storing the data and the instructions for the plotter. The length of magnetic tape used for plotting a given number of data points is directly proportional to the distance the pen moves relative to the paper. It is therefore advisable to minimise the amount of movement of the pen relative to the paper. The main source for unnecessary pen motion is caused by the lack of areal ordering of the data, and a simple procedure for ordering the data has been incorporated into this programme. The data is sorted on the basis of the X coordinates from minimum (most westerly) to maximum (most easterly) prior to plotting. This saves plotting time and conserves space on the magnetic tape. It has also been suggested that a calculation for the minimum distance between all the sample sites would lead to even greater economies in both plotting time and magnetic tape conservation. (Howarth, pers.comm., 1969).

All the control parameters used within the programme have been externalised, so that the required parameter values are read in as data by the programme. This includes:

(i) the number of data decks to be processed;

(ii) the format of the data;

(iii) the position of the map origin with respect to the chart paper origin;

(iv) whether the transformation options for percentage range, reciprocals, or standardised values are to be taken;

(v) the length and scale of the axis;

(vi) the size and number of title characters and their position;

(vii) the size and number of decimal places required for the data values;

(viii) whether the option for incrementing all the data values is required.

3.3.3. Description of the CALCOMP output

The output has the X and Y axes drawn along the base and left hand margin respectively, along which, at one-inch intervals, are printed the relevant X and Y coordinates

to two decimal places. Titling information is placed above the upper margin of the map. The data values are so plotted that the lower-left-hand edge of the number corresponds to the sample site coordinates, and this should not be confused with the decimal point which is also plotted. A photographed example of a small CALCOMP map (real size) is presented below (fig. 17). The title characters are 0.25 in. high, whilst the numbers are 0.07 in. high.

3.3.4. Appraisal of the performance of the CALCOMP data plotting procedure

The time necessary to plot the data is directly proportional to the distance which the pen has to move relative to the chart paper. The relevant factors which affect the execution time of the data plotting include:-

(i) the size of the maps;

(ii) the number of data points;

(iii) the number of digits in the data values;

(iv) the degree of areal ordering of the data;

(v) the size of the data characters.

The time required for plotting a variable number of data points (100 to 900) with coordinates selected from a uniform random number distribution on a CALCOMP chart 25 inches square has been observed. The titling information

consists of 57 characters including blanks and punctuation, and each alphabetic character is 0.5 in. high. The data figures are 0.07 in. high. The plotting time data was plotted against the number of points. At each datum location 4 to 5 numerical characters were plotted. The data are presented in figure 18.

The cost of producing the maps will vary for different computer installations and time-pricing procedures. The computer time used for generating the magnetic tapes for all the CALCOMP maps previously described have been plotted against the number of data points (see figure 19). The cost for this project was merely that of the CALCOMP chart paper which costs £0.125 per foot. The cost of producing such maps would be much greater when hiring time on a commercial installation. If a pricing of £6 per minute (£360/hour) for computer time is assumed, the cost of the CALCOMP chart paper (the CALCOMP machine time being free) is relatively negligible. The cost of producing one map bearing 900 points, if this requires 5 minutes computer time, would be £30, and thus this procedure is quite inconceivable for any organisation other than in industry, which does not have free use of a computer installation.

The reliability of the machine varies according to usage

FIG. 17. AN EXAMPLE OF A SMALL CALCOMP MAP.

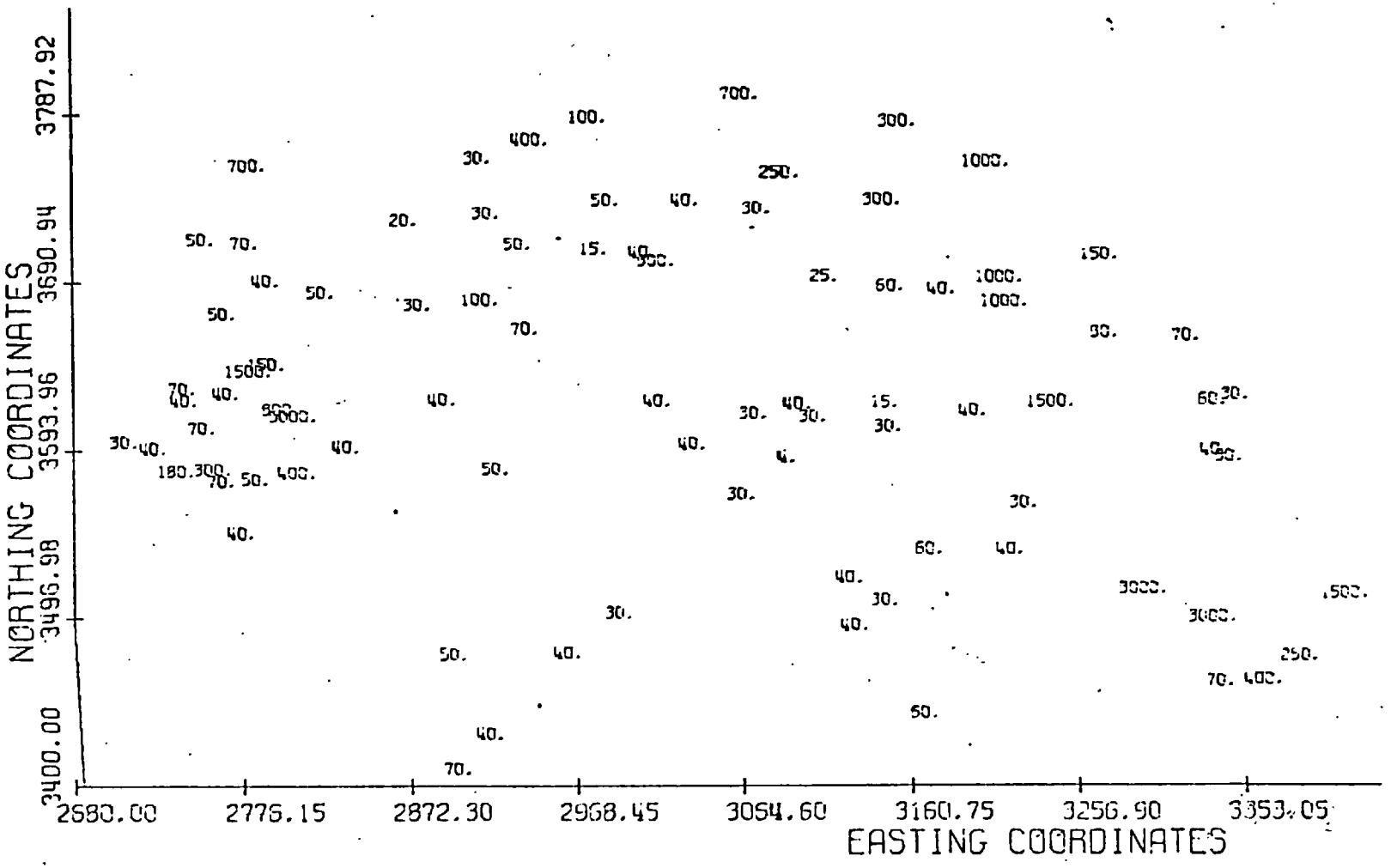
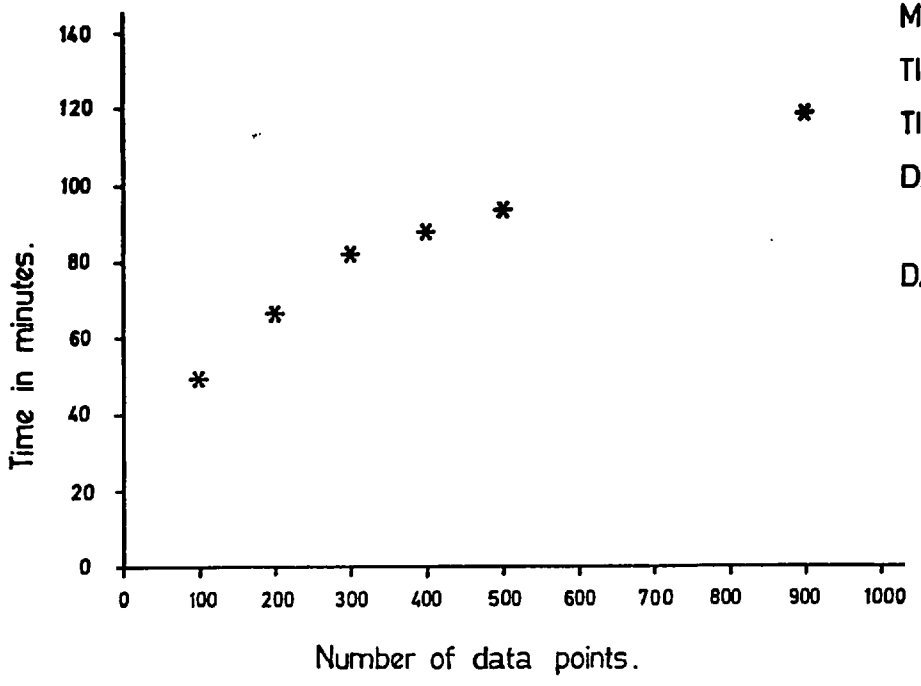


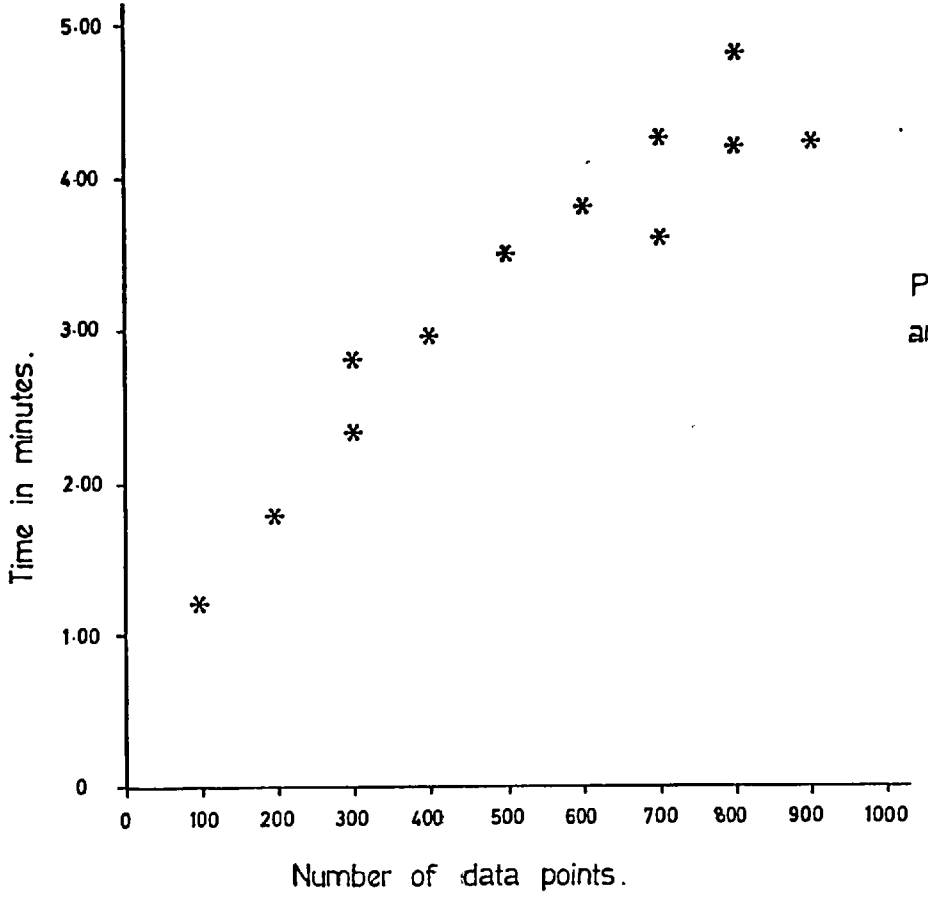
FIGURE 18. THE TIME REQUIRED BY THE CALCOMP INCREMENTAL PLOTTING MACHINE TO PREPARE MAPS OF A VARIABLE NUMBER OF NUMERICAL DATA.



PLOTTING PARAMETERS

MAP SIZE	25 ins. x 25 ins.
TITLE LENGTH	57 characters.
TITLE SIZE	0·50 ins. high.
DATA	4 or 5 numerical characters.
DATA SIZE	0·07 ins. high.

FIGURE 19. THE TIME REQUIRED BY AN I.B.M 7094 DIGITAL COMPUTER, USING A SOURCE PROGRAMME, TO PROCESS A VARIABLE NUMBER OF DATA IN ORDER TO GENERATE THE MACHINE INSTRUCTIONS FOR THE CALCOMP PLOTTING MACHINE.



Plotting parameters as for FIG. 18 and source program compilation time 0·47mins.

intensity since it appears not to be robust enough to endure continuous operation for long periods. However, it usually gives output which is correct. The most frequent fault is the failure of pen-operation commands to work. Thus occasionally lines are drawn connecting two points. The frequency of this fault is usually rather less than 0.1 per cent. It is not possible to store the data and plotting instructions on more than one magnetic tape because the machine frequently appears to be unable to plot the data of the second tape with reference to the previously established map origin. The frequency of this fault varies between 10 and 50 per cent.

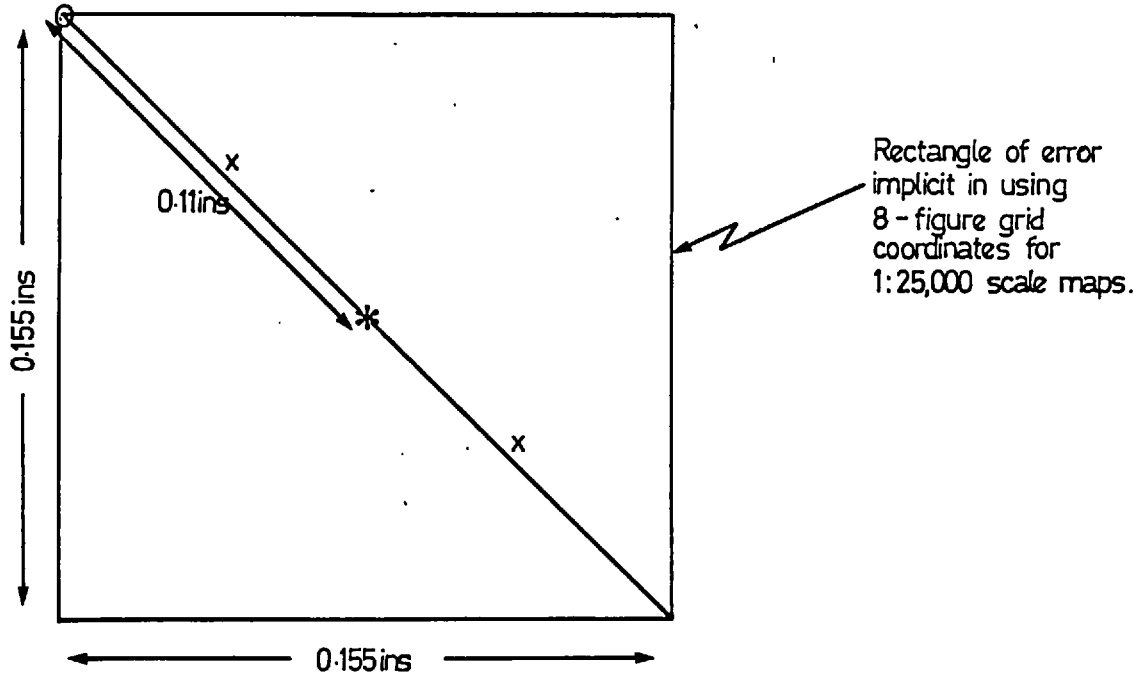
The accuracy of the machine is generally very good. There are sources of error caused by inadequacies which are inherent in the procedure adopted in this study. These errors occur in the scaling of the maps and the assignment of grid coordinates to data on the larger scale maps. The scaling of these maps is accomplished by giving the machine the X and Y coordinate increment between the map origin and one inch distance along the respective axes. The establishment of this quantity is subject to imprecision and the errors are cumulative away from the map origin and these may attain a magnitude of 0.1 inch, 25 inches away

from the origin. There is a larger source of errors in the allocation of 8 figure map coordinates to samples to be displayed on large-scale maps. An 8 figure grid coordinate for a map scale of 1 : 25,000 represents a square area of side length 0.155 inch. If the sample location is at the corner of this square and the machine plots the value at the square centre, then there is a maximum possible error of 0.11 in. (calculated by applying Pythagoras), see fig. 20. The second source of error may be overcome by using 10 figure grid coordinates for use with large scale maps.

The clarity of the output is primarily dependent on the character size employed for the data values. The smallest definable characters are 0.07 in. high, smaller characters are frequently ambiguous. The data values cannot be clearly perceived when overlapping of data values occurs, as over closely adposed sample sites. The clarity is also connected to the colour and thickness of the ink line employed. Red ink is the poorest and blue or black the best for ease of perception especially when the biro ink begins to run low. The optimum line thickness will depend on the character size employed.

The ease of interpretation of these maps is enhanced by

FIGURE 20. DIAGRAM ILLUSTRATING THE MAXIMUM ERROR CAUSED BY EMPLOYING AN 8-FIGURE GRID COORDINATE ON A MAP SCALE OF 1:25,000.



LEGEND

O Position of a sample location assigned a given 8-figure grid coordinate.

* Position of sample location as plotted by the CALCOMP plotter.

x The maximum possible error between real and plotted sample locations.

the scale flexibility, which allows data maps of a scale corresponding to those of the geology to be prepared. However, the interpretation of areally distributed numbers is difficult and modification of this technique is necessary. These include colouring the sample locations or using black and white symbols according to the trace element concentrations. Another approach is to contour the data. Automatic contouring programmes for irregularly spaced data are not yet freely available and manual contouring of the data over a geological base map has also been adopted as an interpretative procedure.

3.4.0. SYMBOLIC DATA PLOTTING

The data for each element over the three areas covered by the reconnaissance survey were subdivided into 5 classes according to the trace element concentrations. Each concentration class is represented by a coloured circular symbol. The symbol class intervals were chosen after inspection of the frequency distributions for each element in each of the three areas. These intervals are based on the spectrographic standard concentrations employed in the trace element analysis, which form a semi-logarithmic series with levels of 1, 2, 5, 10, 20, 50, etc. to 10,000 p.p.m. The symbol class intervals were chosen at the logarithmic

mid-points between these standard concentrations and the rounded-off symbol class intervals are 1.5, 3, 7, 15, 30, 70, 150, 300, 700, 1500, 3000, 7000, 15000 ppm.

The colour symbols were chosen to give a ranking from low concentrations to high and the colours used were yellow (lowest), green, blue and red (highest). The red class was subdivided into a small red symbol (lower) and a large red symbol (higher). The attempted relationship of the colour symbols to the frequency distribution are that the modal classes, those including the most numerous samples, are blue or green, so that anomalously low levels are yellow and anomalously high levels are red. However, because the symbol classes are constant for each element over the three reconnaissance areas, and some trace element frequency distributions are acutely positively shewed, this optimum relationship is frequently not obtained.

3.4.1. Description of the Stromberg-Carlsan 4020 computer recorder and its operational characteristics

This machine and its method of operation have been briefly described in the literature (Nichol et al, 1966), a slightly more detailed account is given here.

The computer recorder used for this work was that at

the A.W.R.E., Aldermaston. Basically the machine consists of an electron gun which fires a beam at a phosphorescent screen. En route to the screen the beam is focussed through one aperture of a ten-plate or matrix bearing 64 stamped-out characters or symbols in an 8 x 8 array. The focussing of the beam is achieved by 2 sets of "electrostatic selection plates" and is sufficiently precise so that only one character-aperture is used for each electron burst. The shaped electron beam is focussed onto a predesignated locus on the phosphorescent screen by a "focus coil" and a "deflection yoke". The focussed and shaped beam is accelerated by a "helical accelerator" in order to increase the brightness of the phosphor image. The symbol is finally displayed on the phosphorescent screen.

The screen represents over a million (1024 x 1024) possible locations, raster points. The matrix characters or symbols occupy 54 rasterpoints (9 (height) x 6 (width)). The image on the screen may be permanently recorded on 35 mm. film (with sprocket-holes) or 16 mm. film (without sprocket-holes) or on 8.0 in. square sensitised vellum paper exposed in a 9.5 in. camera.

The machine may be used on-line or off-line, the latter mode was employed for this work, and a magnetic tape was used

for storage of the plotting instructions.

3.4.2. Description of the computer programme

The programme was written by Dr. J.G.T. Jones of the A.W.R.E. at Aldermaston for use with UAIDE subroutines. The latter generate the appropriate machine language instructions necessary to motivate the computer recorder. The programme requires a large computer memory store, in excess of 32K, and for this reason was run on the computer installation at Aldermaston.

The programme subdivides the data for each element and in each area into 5 data classes on the basis of pre-specified intervals. Polygonal, pseudo-circular symbols are generated by adposing a large number of short vectors. The symbols are projected onto the phosphorescent screen at the appropriate location by employing a scaling factor to convert map grid coordinates into screen raster coordinates. This gives plots which conform to the selected scale, that is approximately 1 in. = 4 mi. The symbols of one concentration class are projected onto the screen and the images are recorded on 35 mm. film and also upon 8.0 inch square sensitised vellum paper. The procedure is repeated until all the data from the three areas has been processed.

3.4.3. Description of computer recorder output

The output from the Stromberg-Carlsan recorder consisted of rolls of 35 mm. film and of developed vellum prints. Each element in each area is represented by 6 plates, one title plate and six symbol plates, even when no sample was included within that symbol class, leaving the plate blank. The symbol plates bear the corners of the image (8.0 in.square) and usually a number of round symbols centred on the appropriate raster coordinates. The images are produced at approximately 1 in. = 4 mi. and thus only the south Pennine area can be produced on one plate; the S.W. England and N. Wales data had to be produced on two plates for each symbol class.

3.4.4. Preparation of the final maps

A considerable amount of preparatory work was necessary prior to producing the maps and this is described below.

The double plates which were produced for S.W. England and N. Wales were joined. The plate-image areas overlapped to a small extent and the margins of the plates were overlaid so that the marginal sample location symbols could be married. Those plates which had no marginal symbols could not be overlaid by the correct amount and so were joined at

the plate margins introducing an error in the E-W scale of the maps.

The programme employed for the symbol plotting did not draw the corners of the area on to the plates and so it was necessary to introduce these manually. The problem encountered here was that the vellum plates, which are wet developed and subsequently dried, are subject to shrinkage across the width of the paper. There is less shrinkage or a little stretching along the length of the paper due to the tension maintained by the rollers which wind the paper through the camera. There is thus a significant linear error along both axes but these are of different amounts and often of different sign. The map boundaries for the plates of these two areas had to be calculated. The method used was to measure the distance to the eastern margin of the most westerly and easterly symbols of the map. Then by using the same relationships on the original sample maps and employing a scaling factor it was possible to calculate and draw in the correct position of the eastern boundary on the symbol plates. A similar procedure was used to establish the northern boundary.

The symbol plates for the three areas exhibited insufficient contrast between the dark symbols and the white

vellum for the subsequent photographic reproduction. There were several reasons for this. The mode of symbol formation was by overlaying and adposing suitably orientated lines. Certain portions of the symbol are reactivated by the overlaying of these vectors and the reactivated parts are darker than the remainder. The zone of greater opacity covers a cruciform area at the centre of the 'circular' symbols. Another cause for the inadequate contrast was the uneven development of the vellum plates, because the developer fluid was not evenly distributed over the plates. To increase the contrast and to counteract these various effects, it was necessary to ink in many of the symbols by hand, and then to photocopy the plates to yield images suitable for the photographic work.

The scale of the plots approximated to 1 in. = 4 mi. The linear error involved in this approximation is cumulative away from the map origin in the south-west corner. The magnitude of the error was not significant for the smaller Derbyshire (8" x 8") maps but was significant for the larger maps of Denbighshire (7" x 11.7") and Devonshire (5.25" x 11.5"). To correct the scale error all the plates were photographed on to negatives at a slightly smaller scale, approximately 0.95 of the original. The negatives were

hand painted with liquid opaque to prevent defects in the photographic film later appearing on the maps. The painted negative images were then photographically transferred onto metal offset-litho plates, these are aluminium sheets coated with a photosensitive layer.

The maps were produced on 10 in. x 15 in. high quality printing paper by the technique of overprinting up to 9 images, each in a different colour, on the paper. The images included the frame with legend (black), drainage with main conurbations (grey), National Grid (blue), geology (pale sepia), and five sets of symbols (yellow, green, blue, small and large red). The non-symbol information was produced by a professional draughtsman and transferred photographically onto the off-set litho plates. The printing presented the problem of precise registration. This involved so adjusting the off-set litho plates that the small remanent scale errors were minimised, so that the coloured symbols were located as near as possible to the actual sample sites. It was necessary to check the registration against the original hand plotted sample location maps, which considerably reduced the productivity of the printing. Another lesser difficulty was maintaining constant ink colour tones, especially for those colours which

were mixed, for instance, grey (white and black), pale blue (white and blue), and pale sepia (white and sepia), for the total map production period.

The maps have already been presented in the discussion of the results of the regional reconnaissance survey.

3.4.5. Performance Appraisal

The production of the maps was a discontinuous process involving a variable number of persons and the overall timing cannot exactly be determined. The production time must take into account the following items against which are appended approximate maximum times in man-working hours (see table 4).

The costing of the maps must include the computing time, the SC-4020 plates, the photographic materials, off-set litho metal plates, off-set litho printing paper and then the labour. However, the overhead expenses involved in these procedures have not been costed and are therefore not included.

The computer data processing used 15 minutes at the rate of £360 per hour. The SC-4020 produced 236 plates at £0.1 each. The draughting of the base map information took 5 hours at £2 per hour. Photographic materials include

TABLE 4. Breakdown of the time necessary to produce the coloured symbol maps

	Man-working-hours
Preparation of the SC-4020 plates for photographic work	100
Draughting of the base map information, including geology, drainage, etc.	5
Photographic work including the preparation of the metal off-set litho plates	520
Off-set litho printing	1400
Total	2025

the 414 sheets of photocopying paper at £3.10. per 100 sheets; the 14 in. x 18 in. photographic film, 207 sheets at £24 per 50 sheets; and lastly there is the cost of 207 metal off-set litho plates at £9 per 500 plates. The off-set litho printing costs include the paper and of minor importance the printing ink. There were 500 maps of each element from each of the three areas, up to 50 sheets per element per area must be allowed for registration and trial runs. Thus a minimum of 21,500 sheets were required at £2.175 per ream. The labour costs, excluding those of the draughtsman have been assessed at £0.5 per hour, this is a quite arbitrary costing and, if the work was carried out externally by specialist firms, would be considerably higher.

The costing information is summarised in table 5.

The accuracy of the final maps is fairly good except that the symbols are very large with regard to the map scale and in areas where the drainage channels are close together it is not obvious which stream supplied the sample. The registration of the symbols relative to the drainage channels is not always exact and a compromise registration solution often had to be adopted.

TABLE 5. Breakdown of the production costs of the coloured symbol maps

Computer time	£90.00
SC-4020 prints	23.40
Photographic materials	
Photocopying paper	14.00
14" x 18" photographic film	99.50
Off-set litho metal plates	37.00
Off-set litho paper	93.50
Sundries to include	
Off-set litho ink	10.00
Liquid opaque, washing fluid for offset litho. Paint brushes, adhesives, plate processing solution	20.00
Labour:- Draughtsman	10.00
Other	1010.00
Total	£1407.40

The reliability of the method is mainly dependent on the robustness of the machinery and on the conscientiousness of the photographic and printing staff in minimising the various sources of error and in optimising the registration. The technique is complex and for best results requires someone with experience to oversee the whole operation.

The clarity of the maps is very good with respect to the trace element and drainage distribution, but in areas of complex geology, especially where the sample density is high, it is sometimes difficult to see the geological boundaries.

The interpretability of the maps is good for establishing the regional variations and for establishing geological control of these trends. It is not good for distinguishing subtler, though perhaps significant variations occurring within a range of values represented by one colour symbol. There is also the difficulty of establishing the relationship between topography and trace element levels, for instance, in the high moorland areas of N. Wales.

Most of the problems with these maps relate to the

symbol size adopted; these could without loss of clarity be reduced to half scale. It is also advisable to restrict the choice of symbol classes to one area alone and to have more classes within that area. This will ensure that the detailed trace element information for each area is shown to best effect. There seems little that can be done about the scaling errors introduced by this method and these are a function of the rigidity of the integer ratio relationship required between the map grid coordinates and the SC-4020 raster coordinates.

3.5.0. DISCUSSION

3.5.1. Comparison of the manual and automatic plotting procedures

Time and cost are inter-related features and will be considered simultaneously. If computer time has to be hired then the manual method is the cheapest method and whilst slower than the CALCOMP maps, especially for a large number of points, can be produced much faster than the SC-4020-Offset -litho maps. If the computer time and plotting machine time is freely available as it often is within large commercial or research organisations with their own computer installations, then the CALCOMP maps become both the quickest and cheapest, whilst the off-set litho

maps still remain the slowest, though for 500 copies of each element in each area the overall cost is lower than £3 per complete set, which is comparable to the cost of producing one set of CALCOMP maps.

The qualities of accuracy and reliability are demonstrated in various ways by the different techniques. Manual plotting is best for the accurate placing of the data at the sample location but the reliability with which this is done will be variable and sometimes poor. The machine methods can operate only within the accuracy levels of the method but are more reliable since they are not subject to fatigue though they are to failure. Machine failure faults are usually more easily perceived than those due to human mistakes.

The clarity and interpretability of the data are poorest for the CALCOMP and manual maps compared to the off-set litho maps. However, the first two are more flexible in that they may be used in conjunction with a whole number of base maps of, for instance, geology, topography, pedology, climatic in order to effect an interpretation. The symbol maps on the other hand give a means of making a very fast appreciation of the areal variation and its correlation with respect to the bedrock geology.

3.5.2. Conclusions

It is apparent that the method of map production chosen must be decided on the basis of the proposed map usage, available computer facilities, available labour and financial considerations. The main features are enumerated below:-

(i) Machine data plotting is feasible when the data plotting requirement does not justify permanent staff appointments, and may even then be economically attractive because it allows a reduction in the salary payroll.

(ii) If machine plotting techniques are used CALCOMP maps are the quickest to produce, but they are harder to interpret, though more flexible than the symbol maps. The costs vary according to whether or not the computer and machine plotting time is free. CALCOMP maps are the cheapest of all types with free computer time and are the most expensive if computer time has to be hired.

(iii) The symbol maps give the clearest relationship between regional geochemistry and geology but are not as flexible as the manual and CALCOMP types, in that the last two may be used in conjunction with a whole range of relevant base maps

including those of the pedology, geology, topography, climate, drainage status and land usage in the survey area.

CHAPTER 4

COMPUTERISED PROCEDURES II: SURFACE TREND ANALYSIS

4.1.0. INTERPRETATIVE PROBLEMS ASSOCIATED WITH REGIONAL GEOCHEMICAL DATA

It is frequently difficult to distinguish subtle trends in the regional distribution of trace element data, because of data variability related to changing bedrock geochemistry, secondary environment and the effects of random errors. Computerised procedures may distinguish the regional trends, and two techniques were considered for the U.K. regional data.

4.2.0. TREND SURFACE ANALYTICAL TECHNIQUES

There are two basic procedures for trend surface analysis; one involves fitting mathematical surfaces of various forms to the data, for instance, polynomial trend surface analysis, and the alternative method is to reduce the data variability by using smoothing techniques, for instance, the moving average technique.

The basic difference between these procedures is that mathematical surfaces of varying complexity are fitted to the whole data set whilst the smoothing procedure involves fitting planes over relatively small portions of the survey area and building a mosaic of these into a complex surface.

4.3.0. POLYNOMIAL TREND SURFACE ANALYSIS

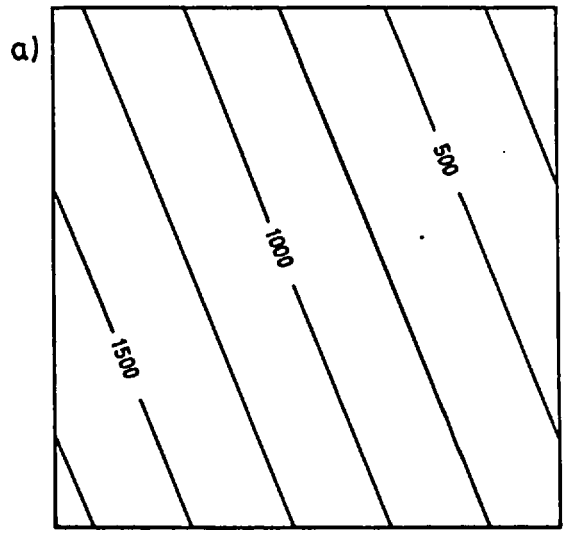
4.3.1. THEORETICAL BASIS OF THE TECHNIQUE

The mathematical basis of the technique has been described in various texts, for instance, Krumbein and Graybill (1966). The present account has been restricted to the conceptual framework of the technique.

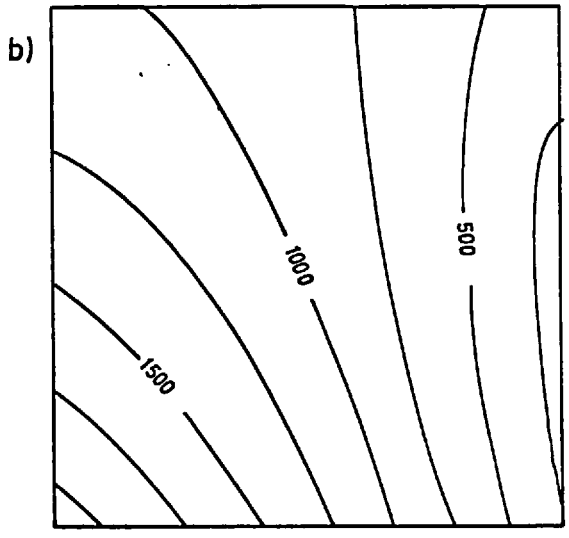
The fundamental assumption of polynomial fitting techniques is that the sample trace element concentrations are a function of their location, and this distribution may be approximated by polynomial equations representing various types of surface, for instance, planes (first degree (1°) surface), troughs or swells (second degree (2°) surface) and more complex types (third degree (3°) and higher (n^{o}) surfaces), examples are shown in figure 21 a, b, and c. The polynomial surface is usually fitted employing the least squares criterion.

The chosen polynomial equation is used to generate a value at each sample location (trend value) and the deviations of the sample values from the trend values (residual values) may also be mapped. The residual values may well be geologically meaningful (Grant, 1957), but the basic assumption of the technique is that these are randomly distributed about the polynomial surface, and form a gaussian distribution. The polynomial surface has been

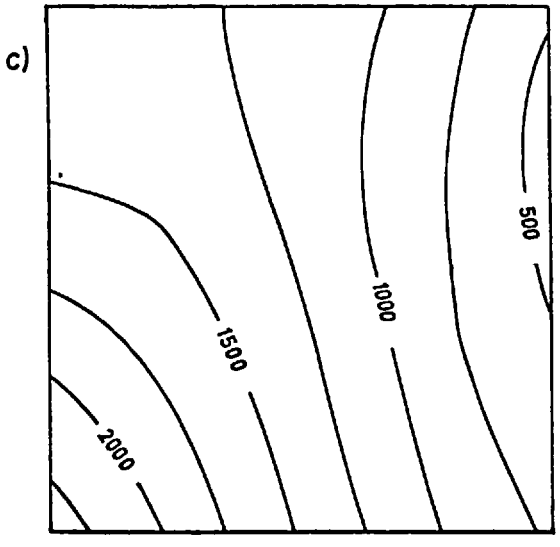
FIGURE 21. DIAGRAMMATIC REPRESENTATION OF FIRST, SECOND AND THIRD DEGREE POLYNOMIAL TREND SURFACES (FROM HARBAUGH & MERRIAM, 1968).



First degree surface.



Second degree surface.



Third degree surface.

shown to be a regression surface about which it is possible to compute confidence limits (Krumbein, 1963). Another assumption is that higher order polynomial surfaces more closely approximate the real distribution. Computer programmes are available, for processing up to 500 data (O'Leary et al, 1966) for surfaces up to 8° (McIntyre, 1963).

4.3.2. Review of the applications of polynomial trend surface analysis

The geological applications of this technique have been widespread. A more complete account may be obtained from Krumbein and Graybill (op. cit.) and Harbaugh and Merriam (1968), but a selection of the geological fields of study are summarised below:-

(i) geophysical data obtained for mineral exploration (Grant, 1957);

(ii) sedimentary petrological data (Krumbein, 1957);

(iii) igneous petrological data (Whitten, 1959);

(iv) soil geochemical data obtained during mineral exploration surveys (Connor and Miesch, 1964);

(v) drainage sediment, soil and bedrock geochemical data collected during regional geochemical studies (Garrett, 1966).

4.3.3. Restrictions on the general applicability of polynomial trend surface analysis

The large number of applications of the technique have

allowed the operational characteristics to be evaluated and these are summarised below:

(i) the technique is most applicable for data homogeneously distributed over an area and where the data levels change in a continuous manner;

(ii) the optimum number of data which may be meaningfully processed has been tentatively set between 20 and 300 (Agterberg, 1964);

(iii) pronounced inhomogeneities in the sample distribution may induce the generation of polynomial trend surfaces bearing little relation to the geological trend, because this procedure extrapolates the trend over unsampled areas (Nordeng, 1965);

(iv) biased and geologically unfeasible surfaces may be fitted even to homogeneously distributed data which include clusters of high and low values. This effect is particularly pronounced on the higher order ($>3^{o}$) surfaces (Krumbein and Graybill, 1966);

(v) the residual values should form a gaussian distribution, if the surfaces are to be used as regression surfaces (Krumbein and Graybill, op. cit.), but it has been suggested that this property is not essential for numerous data (Agterberg, 1964);

(vi) it has also been suggested that data exhibiting a

log-normal distribution should be log-transformed prior to polynomial trend surface analysis (Garrett, 1968);

(vii) the validity of employing this form of analysis to data representing more than one population has also been questioned (Garrett, 1968);

(viii) the closer representation of higher polynomial surfaces, relative to lower surfaces, has been challenged by Krige (1966) from the results of studies made for mine valuation purposes in the South African goldfields.

4.3.4. Discussion and Conclusions

The U.K. regional survey geochemical data exhibits the following characteristics:

(i) the background variability is high, necessitating the use of surface trend analytical techniques;

(ii) the samples are inhomogeneously distributed, with clustering at stream intersections and no samples representing inaccessible areas or those without adequate surface drainage;

(iii) the regional variations of the trace element distributions frequently exhibit discontinuities with clustering of high and low values;

(iv) the trace element data exhibit frequency distributions between significantly positively and negatively skewed, and usually represent more than one population;

(v) the data populations include between 600 and 900 values.

The majority of these characteristics ((ii) to (v)) invalidate the use of polynomial trend surface analysis and consequently this technique was rejected in favour of the moving average procedure.

4.4.0. MOVING AVERAGE ANALYSIS

4.4.1. Theoretical basis of the technique

The technique has been described by Krige and Ueckerman (1962), the variant employed in this study has been fully described by Khaleelee (1966). A brief summary of the theoretical and mathematical concepts are included in this section.

The regional survey area is subdivided into rectangles of pre-determined size and shape, which overlap by a prescribed amount. The data within each rectangle is used to compute the mean ($\overline{M}$); variance (σ^2_M); standard diviation (σ_M); ratio of search area variance (σ^2_M) to the total data variance (σ^2_T), which is termed the variance ratio (V_R); and the deviation of the search

area mean ($\bar{M}$) from the total data mean ($\bar{X}_T$) expressed in total data set standard deviations (σ_T), which have been termed Z-values (Z_V). The mathematical definitions are given below:

(i) the moving average ($\bar{M}$),

$$\bar{M} = \frac{\sum_{i=1}^{n} X_i}{n} \qquad \text{eq. 4 - I}$$

where X_i is the trace element concentration for sample i, and n is the number of samples in the search area.

(ii) the moving variance (σ^2_M),

$$\sigma^2_M \quad \frac{\sum_{i=1}^{n} X_i^2 - n.\bar{M}^2}{n - 1} \qquad \text{eq. 4 - II}$$

(iii) the moving standard deviation (σ_M),

$$\sigma_M = \sqrt{\sigma^2_M} \qquad \text{eq. 4 - III}$$

(iv) the variance ratio (V_R),

$$V_R = \frac{\sigma^2_M}{\sigma^2_T} \qquad \text{eq. 4 - IV}$$

(v) the Z-values (Z_v),

$$Z_v = \frac{\bar{X}_T - \bar{M}}{\sigma_T} \qquad \text{eq. 4 - V}$$

The values for each parameter may be plotted as maps. The

location of the values within each search area are calculated by computing the mean values of the easting ($\bar{E}$) and northing ($\bar{N}$) co-ordinates. The defining equations are:-

(i) $$\bar{E} = \frac{\sum_{i=1}^{n} E_i}{n} \qquad \text{eq. 4 - VI}$$

(ii) $$\bar{N} = \frac{\sum_{i=1}^{n} N_i}{n} \qquad \text{eq. 4 - VII}$$

where E_i and N_i are the easting and northing co-ordinate locations of sample i, and

n is the number of samples falling within each search area.

If the parameters are to be used for a probabilistic interpretation, it is necessary to normalise the data frequency distribution prior to the analysis.

The fundamental assumptions of the technique are:-

(i) the search area data represents a single gaussian population;

(ii) the search area data may be represented by a horizontal plane through the moving average ($\bar{M}$);

(iii) the individual data represent their immediate vicinity.

(iv) the moving averages are normally distributed about the total data set mean.

There is no guarantee that the search area samples represent a single population, however, in a relatively small area, this premise is more plausible than when it is extended to data from the whole survey area.

The representation of the search area data by a horizontal plane will not be an excessive simplification if the trend within the search area is small. If the search area does not include a large number of samples or too large an area then this constraint should be met. If a large number of data are included within the search areas then the degree of 'smoothing' will be excessive and regional contrasts may be depressed. Therefore, the size of the search area relative to the sample density is critically important.

An attempt has been made to use objective criteria for the selection of optimum search area sizes, using the variance reduction from the moving averages to the total data set (Garrett, 1966). However, there is no criteria available for establishing the optimum variance reduction.

One possible criterion could be that the variance reduction should be equal to that proportion of the total data variance ascribable to sampling and analytical errors. The assumption is that:

$$\sigma_T^2 = \sigma_M^2 + \sigma_E^2 \qquad \text{eq. 4 - VIII}$$

where σ^2_T, σ^2_M, σ^2_E, refer to the variance of the total data set, the moving averages and the analytical and sampling errors respectively. Another assumption is that the variance ascribable to the regional trend (σ^2_{TREND}) is given by the relationship:

$$\sigma^2_{TREND} = \sigma^2_T - \sigma^2_E \qquad \text{eq. 4 - IX}$$

so that if

$$\sigma^2_M = \sigma^2_T - \sigma^2_E \qquad \text{eq. 4 - X}$$

then

$$\sigma^2_M = \sigma^2_{TREND} \qquad \text{eq. 4 - XI}$$

These relationships indicate that if the variance reduction caused by moving average analysis is equal to the error variance then it may be assumed that the smoothing has removed the random error component and represents only the trend component of the data variability.

The premise that the drainage sediment data represent the geochemistry of the area adjacent to the sample site is basically invalid. The sediments represent the weathering products of the catchment area upstream from the sample site, which is thus located at the boundary of the area which it represents. If the survey region is large so that the ratio of the sampled catchment area to the total survey area is small, as they are in the U.K. regional survey areas,

then the approximation involved in the original assumption is also correspondingly small.

Moving average analysis enhances the autocorrelations within the regional data, and as a result, the mean value of the moving averages ($\bar{X}_M$) does not equal the total data mean ($\bar{X}_T$) (Garrett, pers. comm. 1969), that is:

$$\bar{X}_M \neq \bar{X}_T \qquad \text{eq. 4 - XII}$$

Therefore, the Z-values do not form a gaussian distribution about the mean of the total data set and consequently cannot be used as a probabilistic parameter. Nevertheless, this parameter is useful for indicating very subtle trends, as for data with a small concentration range, because the standard deviation for such data will also be small and hence subtle concentration variations will be heightened in the Z-value variations.

Another feature of the technique is that when the search area straddles geochemical discontinuities, the moving variance, standard deviation and variance ratio values will be enhanced, relative to geochemically homogeneous areas. Therefore, these parameters will characterise zones of high geochemical relief, as for instance, on the junction between geochemically distinct bedrock units.

4.4.2. Review of the geological applications of the moving average technique.

An early use of this technique with geological data was in

the field of sedimentary petrology (Potter, 1955; Schlee, 1957; Pelletier, 1958). The theoretical basis was expanded and the modified technique was employed for the analysis of gold assay data, for mine valuation purposes, in the South African goldfields (Krige and Ueckerman, 1963). A slightly modified and computerised version of the same procedure has been used to analyse the areal distribution of tin assay data from Malaysia (Leigh and Thomas pers. comm., 1966). The technique has been used for soil geochemical data in N. America (Connor and Miesch, 1964). Regional geochemical data of drainage sediments in Sierra Leone have also been processed with moving average analysis (Garrett, 1966).

4.4.3. Computation of the two-dimensional moving average parameters

The computer programme used in this study is modified from that written by Dixon and Khaleelee (Khaleelee, 1966). The modifications include the facility of plotting the parameters as maps using the Calcomp incremental plotter. The plotting procedure is similar to that described in Chapter 3, and a complete programme listing is given in Appendix II.

The programme capacity is for up to 1800 sample data, each sample is characterised by the coordinates and the data for one element. The computations yield those parameters previously described (section 4.4.1.) and in addition the data population mean, variance and standard deviation.. The data may be processed

both untransformed or log-transformed (base 10), depending upon the data frequency distribution.

The compilation time of the source programme is 0.73 minutes on an IBM 7094 computer, and computation times are dependant on the number of data and the number of parameter maps which are required. The time requirement for Calcomp chart preparation has already been considered (chapter 3) and the same considerations are applicable here.

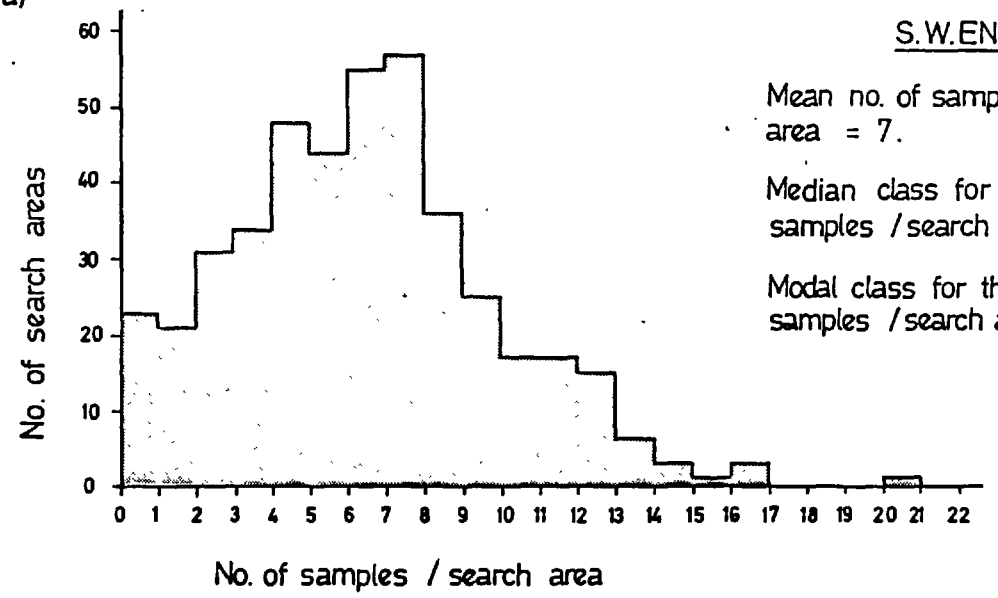
A series of moving average analyses of the molybdenum data from the Peak District, using different search area sizes and degrees of overlap, indicated that for this sample density (1 sample/ sq.mi.) a search area of 4 km^2 was the optimum in reducing random variability without excessively smoothing the data. A search area overlap of 50 per cent was found to be adequate, larger overlaps produce more numerous parameters and these could not all be included on a single Calcomp magnetic tape. The same search area size and overlap have been used for all the U.K. geochemical data, since the sampling density is nearly constant and because the available time prevented the separate evaluation of an optimum procedure for each element in the three survey areas. The criterion developed in section 4.4.1. for objectively selecting the optimum search area size have not been employed, since there was no data available to allow the estimation of the sampling plus analytical error variance.

The regional survey data has been log-transformed for those elements with positively skewed distributions. The mean sample density per search area in the three survey areas varies between 4 and 10, and the frequency distributions are illustrated in figures 22 a, b, c. The high proportion (approximately 25 per cent) of search areas including less than 4 samples are probably derived from the margins of sampled area. The relatively higher proportion of 'under-filled' search areas in the Peak District is caused by the central unsampled zone over the Carboniferous limestones, which increases the marginal periphery of the sampled area. The moving average parameters from the 'underfilled' search areas are probabilistically invalid but still retain their validity as the best available parameters for the search area.

Calcomp maps have been produced for the moving averages, Z-values, and variance ratios. The remaining two parameters have not been utilised, since preliminary work indicated that the variance ratio yields the same information. The parameter maps have been manually contoured over geological underlays, and so the interpretations are completely subjective. The contour intervals for the moving averages correspond to the spectrographic standards (or to their logarithmic mid-points), whilst the intervals for the other two parameters were selected to heighten the correlation between the parameter distribution and the bedrock geology.

FIGURE 22. FREQUENCY DISTRIBUTION OF THE NUMBER OF DRAINAGE SEDIMENT SAMPLES IN EACH SEARCH AREA FOR THE MOVING AVERAGE ANALYSIS OF THE THREE U.K REGIONAL SURVEY AREAS.

a)



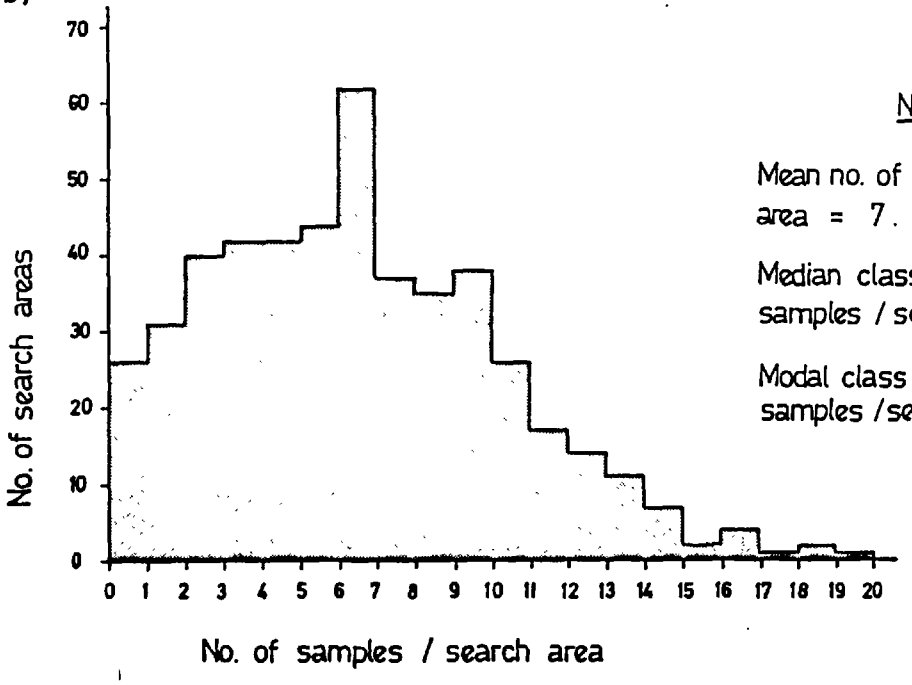
S.W.ENGLAND

Mean no. of samples / search area = 7.

Median class for the no. of samples / search area = 7.

Modal class for the no. of samples / search area = 8.

b)



N. WALES

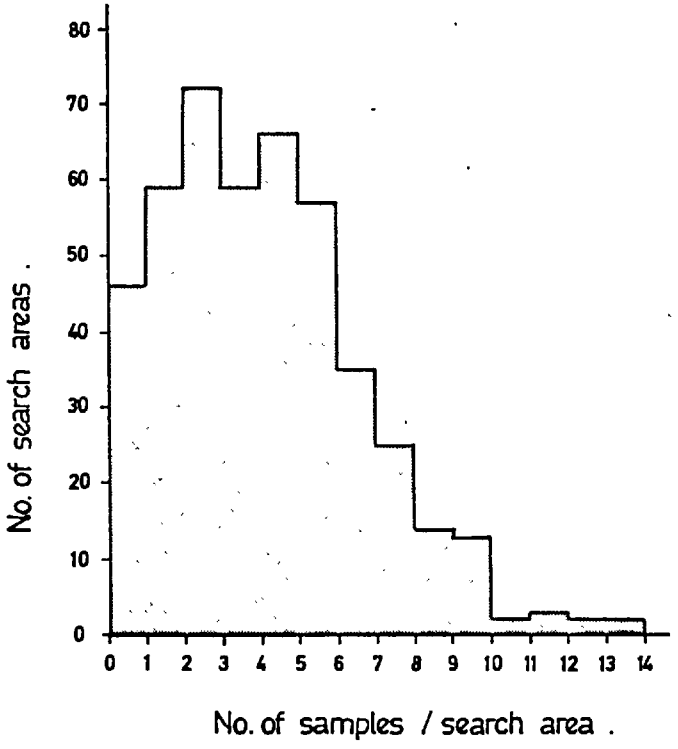
Mean no. of samples / search area = 7.

Median class for the no. of samples / search area = 7.

Modal class for the no. of samples / search area = 7.

FIGURE 22. CONTINUED

c)



PEAK DISTRICT

Mean no. of samples / search area = 9.

Median class for the no. of samples / search area = 4 .

Modal class for the no. of samples / search area = 3.

4.5.0. RESULTS OF THE MOVING AVERAGE ANALYSIS

The regional survey data has been analysed and the parameter maps have been compared to the colour symbol maps with respect to the quantity of information which they indicate. The results are briefly described for each region in the following sections.

4.5.1. Moving average analysis of the regional reconnaissance data: S.W. England

The analysis included the data for As, Cr, Co, Cu, Fe, Ga, Ge, Pb, Mn, Mo, Ni, Sn, Ti, V and Zn and the maps are presented in volume 2 (figures 40-83 inclusive). The elements Ag and Bi have been excluded because few of the samples had detectable concentrations.

ARSENIC

Moving average (fig. 40, vol. 2)

A broad aureole of enhanced levels (>15 ppm) envelop the granites and extend over the lower Namurian. Four N-S zones (>7 ppm, peaks >15 ppm) run from the aureole onto the Westphalian. The highest levels (>300 ppm) occur over the granites, but western Dartmoor shows higher levels (>70 ppm) than in the east (<30 ppm). The Namurian levels are higher in the east (>7 ppm) than in the west (usually <7 ppm), whilst the Westphalian levels are generally low (<7 ppm).

Z-values (fig. 41, vol. 2)

This distribution emphasises lower levels over the eastern and western boundaries of the Westphalian, and higher values along the northern continuations of the Sticklepath fault and the Teign valley.

Variance ration (fig. 42, vol. 2)

High variance zones (>1, peaks >2) occur over the granites and their country rocks.

The moving average parameters confirm the symbol map distribution but also indicate the N-S zones of enhancement crossing the Carboniferous outcrop.

CHROMIUM

Moving average (fig. 43, vol. 2)

Peak concentrations (>110 ppm) occur over the Devonian-Dinantian outcrops with lower levels over the Namurian (70-110 ppm) especially in the west (<70 ppm). There are low levels (<70 ppm) over the Westphalian and Permian, except over the Sticklepath fault, a narrow zone to the east and also along the coastal boundary (all >70 ppm). There are low levels over the Bodmin (<70 ppm) and Dartmoor (<30 ppm) granites, and the latter has lower levels in the west (<15 ppm) than in the east (15-30 ppm).

Z-values (fig. 44, vol. 2)

This confirms the moving average distribution with no additional significant features.

Variance ratio (fig. 45, vol. 2)

The main high variance zones (>1) trend NNW-SSE across the Devonian-Dinantian strata, north of Bodmin, and also envelop the eastern Dartmoor granite contact.

The moving average parameters emphasise the higher levels over the Westphalian, but otherwise confirm the symbol map distribution.

COBALT

Moving average (fig. 46, vol. 2)

Higher levels (>30 ppm) occur over the country rocks bounding the granites and over the eastern Namurian, but not that in the west (<30 ppm). The Westphalian levels are higher in the west (usually >15 ppm, peaks >30 ppm) than in the east (<15 ppm usually). Lower levels (<7 ppm) occur over the eastern Dartmoor granite compared to the west (<15 ppm).

Z-values (fig. 47, vol. 2)

Two N-S zones of marginally enhanced values (>0) cross the western Namurian outcrop (c.f. arsenic), and also occur over

the northern extensions of the Teign valley and the Sticklepath fault.

Variance ratio (fig. 48, vol. 2)

High variance zones (>1) occur over the granite margins and over the upper Namurian outcrop.

The moving average parameters clarify the distribution over the Carboniferous, compared to the symbol maps. The Z-values indicate the enhanced N-S zones including those north of the Teign valley and along the Sticklepath fault.

COPPER

Moving average (fig. 49, vol. 2)

Discrete zones of higher concentrations (>50 ppm) occur over the Dinantian outcrop, and a broad E-W zone of enhanced levels (>30 ppm) envelops the granite contact and the lower Namurian, which also extends over the Namurian and Westphalian, west of the Sticklepath fault. The Westphalian and Permian bear intermediate levels (>15 ppm) with scattered lower zones (<15 ppm). The Bodmin granite bears marginally higher values (<30 ppm) than the Dartmoor granite (usually <15 ppm, except in the north-west, 15-30 ppm).

Z-values (fig. 50, vol. 2)

Higher zones ($>+1$) are emphasised over the Dinantian and the northern Bodmin granite outcrops.

Variance ratio (fig. 51, vol.2)

A complex distribution with high variance (>0.5, peaks >4.0) enveloping the Dartmoor granite periphery and trending NNE-SSW from the Bodmin granite onto the Westphalian outcrop.

The moving average parameters confirm the symbol distribution but emphasise the higher values along the northern Bodmin granite margin.

IRON (expressed as Fe_2O_3)

Moving average (fig. 52, vol. 2)

The granites bear low concentrations ($<3.0\%$), except over north-western Dartmoor ($>3.0\%$, peaks $>15.0\%$). High concentrations ($>7.0\%$) occur north and north-east of the granites over the Carboniferous strata. The Namurian is generally high (often $>7.0\%$, usually 3.0-7.0%) except in the west ($<3.0\%$), whilst the Westphalian is usually low ($<3.0\%$), except north-west of Okehampton ($>7.0\%$) and along the Namurian-Westphalian junction, west of the Sticklepath fault ($>3.0\%$).

Z-values (fig. 53, vol. 2)

This complex distribution confirms the moving average patterns but indicates a more extensive enhanced zone north of Bodmin moor and reveals marginally enhanced zones (>0) along the Sticklepath fault and zones to the west.

Variance ratio (fig. 54, vol. 2)

Another complex distribution with high variance zones along the granite contacts and adjacent to the Westphalian-Namurian junction. Scattered zones of high variance are scattered over the Namurian particularly in the west, but also over the Sticklepath fault.

The moving average parameters distinguish the enhanced zones over the Sticklepath fault and the central Namurian outcrop but otherwise confirm the symbol distribution.

GALLIUM

Moving average (fig. 55. vol. 2)

High concentrations (>30 ppm) occur over the Bodmin and northern margins of the Dartmoor granite. Intermediate concentrations (23-30 ppm) envelop the metamorphic aureole and trend NE-SW across the central Namurian outcrop. The Westphalian and western Namurian outcrops have lower levels (with large areas <15 ppm).

Z-values (fig. 56, vol. 2)

The Dartmoor granite has higher levels ($>+1$) than the enclosing country rocks, but otherwise the distribution is similar to the moving average.

Variance ratio (fig. 57, vol. 2)

Scattered areas of higher variance occur along the Westphalian-Namurian junction and along the Dinantian outcrop.

The regional geochemical relief for Ga was insufficient to compile a symbol map and the regional distribution had been previously unrecognised.

GERMANIUM

A constant concentration (400 ppm) of this element was added to the drainage sediment samples subjected to spectrographic analysis, as an internal standard. Analytical matrix effects caused by the drainage sediment mineralogy might be related to the subouteropping bedrock lithology and should thus display a regional variation. Moving average analysis of the Ge concentrations should then detect regional analytical bias.

Moving average (fig. 58, vol. 2)

There is a regional distribution, with lower concentrations (<350 ppm) over the southern portion and higher concentrations

(> 350 ppm) over the northern half of the survey area. Peak levels (> 400 ppm) occur over the Westphalian whilst low levels occur over the Dartmoor granite and Dinantian outcrops.

Z-values (fig. 59, vol. 2)

This distribution confirms the higher levels over the Westphalian relative to those from the south of the survey area.

Variance ratio

This parameter revealed no significant information and thus has been excluded.

LEAD

Moving average (fig. 60, vol. 2)

The granites, particularly north-eastern and north-western Dartmoor, bear higher concentrations (> 70 ppm, peaks > 150 ppm), but marginally enhanced levels (> 30 ppm) occur over the Dinantian and eastern Namurian outcrops, and trend NNW-SSE along the Sticklepath fault and also to the west.

Z-values (fig. 61, vol. 2)

Discrete haloes of enhanced levels (> 0) occur around the granites, but otherwise the distribution confirms that of the moving average.

Variance ratio (fig. 62, vol. 2)

High variance zones occur over the Dartmoor granite margins,

the Westphalian and western Namurian outcrops.

Moving average analysis has clarified the background Pb distribution and has indicated the slight enhancement over the Sticklepath fault, but does not as clearly display the high levels in the Teign valley compared to the symbol map.

MANGANESE

Moving average (fig. 63, vol. 2)

High concentrations (>1500 ppm) occur over the Dinantian, lower Namurian and central Westphalian outcrops, extending over north-western Dartmoor and also to the north of the moor. The western Namurian bears low levels (<700 ppm) compared to the east (large areas >1500 ppm).

Z-values (fig. 64, vol. 2)

Lower levels (<0) over the Permian and marginally enhanced values (>0) along the Sticklepath fault, are emphasised otherwise the distribution confirms that of the moving average.

Variance ratio (fig. 65, vol. 2)

High variance zones (>1, peaks >2) follow the Bodmin granite contact, the Dinantian and northern Dartmoor granite outcrops, and are scattered adjacent to the Permian-Westphalian junction west of the Sticklepath fault.

The moving average parameters indicate a marginal enhancement along the Sticklepath fault but otherwise confirm the symbol distribution.

MOLYBDENUM

Moving average (fig. 66, vol. 2)

Marginally enhanced levels ($\geq$ 2.5 ppm) occur over the Dinantian and basal Namurian strata and over north-western Dartmoor, elsewhere, levels are at or below the detection limit (2 ppm).

Z-values (fig. 67, vol. 2)

The Namurian, except in the west, has marginally enhanced concentrations relative to the Westphalian, otherwise the distribution is similar to the moving average.

Variance ratio (fig. 68, vol.2)

High variance zones (>1, peaks >2) occur over the Dinantian-basal Namurian strata, north-western Dartmoor, and adjacent to the Permian-Namurian junction.

The moving average parameters confirm the symbol distribution but indicate a general enhancement over the Namurian, relative to the Westphalian.

Moving average (fig. 69, vol. 2)

High concentrations ($>$ 70 ppm) occur over the Dinantian, west of Dartmoor, and over the eastern Namurian, which is generally higher ($>$50 ppm) than in the west ($<$50 ppm, with areas $<$ 30 ppm). The Westphalian bears intermediate levels (30-50 ppm) except in the west ($<$ 30 ppm), whilst the granites have low values ($<$30 ppm) especially Dartmoor ($<$15 ppm), which has an impoverished marginal facies ($<$ 7 ppm).

Z-values (fig. 70, vol. 2)

This parameter confirms the moving average distribution but emphasises lower levels over the eastern and western Westphalian relative to the central portion, adjacent to the Sticklepath fault ($>$0).

Variance ratio (fig. 71, vol. 2)

High variance zones ($>$0.5) follow the Dinantian outcrop and the northern granite contacts, extending over the Dartmoor granite, with other zones over the eastern and western Namurian outcrops.

The parameters distinguish a marginal enhancement over the Sticklepath fault and an impoverishment over the Dartmoor granite margins.

TIN

Moving average (fig. 72, vol. 2)

The highest concentrations ($>$ 300 ppm) occur over the granite contacts, but western Dartmoor bears relatively low levels ($<$ 150 ppm) compared to the north-western portion ($>$ 700 ppm). A broad aureole of enhanced levels ($>$ 7 ppm) extends over the Namurian which also occur along the Namurian-Westphalian junction, the Permian and eastern Namurian outcrops.

Z-values (fig. 73, vol. 2)

A marginal enhancement is indicated over the Sticklepath fault and over a more westerly zone, levels over the Westphalian are more variable than was indicated by the moving average, but otherwise, the distributions are similar.

Variance ratio (fig. 74, vol. 2)

High variance zones ($>$ 0.5) follow the Dartmoor granite contact, the Dinantian outcrop north of Bodmin moor, and are scattered over the central Namurian outcrop.

The moving average parameters confirm the symbol distribution but also indicate enhanced N-S zones over the Sticklepath fault and also further to the west.

TITANIUM

Moving average (fig. 75, vol. 2)

High concentrations (>7000 ppm) occur over the Dinantian strata north and east of Bodmin moor, whilst the granites are usually low (<3000 ppm), with higher levels over western Dartmoor (1500-3000 ppm) than in the east (<1500 ppm). The Namurian bears intermediate levels (3000-7000 ppm) except over the central and western portions (<3000 ppm), with marginal enhancements (>3000 ppm) over the Sticklepath fault and a more western zone. The Westphalian concentrations are low (≤ 3000 ppm) except in the west and over the Sticklepath fault.

Z-values (fig. 76, vol. 2)

This parameter merely confirms the moving average distribution.

Variance ratio (fig. 77, vol. 2)

This complex distribution indicates high variance zones along the Devonian-Dinantian outcrops, north and east of Bodmin, over the Dartmoor granite contact, along the Permian outlier, and scattered over the western Namurian.

The parameters clarify the distribution over the Namurian-Westphalian and indicate enhancements over the Sticklepath fault and a more westerly zone.

VANADIUM

Moving average (fig. 78, vol. 2)

High concentrations (>115 ppm) occur over the Dinantian, north and east of Dartmoor, the eastern, west-central and extreme western Namurian outcrops. The Westphalian and Permian bear low levels (< 70 ppm) except over the Sticklepath fault and also to the west (> 70 ppm). The granites are usually very low (<30 ppm), except near the contacts (30-70 ppm).

Z-values (fig. 79, vol. 2)

This parameter accentuates the relatively lower levels over the granite, Westphalian, and extreme eastern Namurian outcrops relative to the remainder of the survey area.

Variance ratio (fig. 80, vol. 2)

High variance zones (>1) follow the Dartmoor granite contact, trend NW-SE across the western Devonian-Carboniferous outcrops and are scattered over the western Namurian.

These parameters indicate the N-S enhanced zones over the Sticklepath fault and to the west, and clarify the distribution over the Namurian.

ZINC

Moving average (fig. 81, vol. 2)

Low concentrations (usually < 110 ppm) occur over the

Permian, Westphalian and granite outcrops, but are higher (>150 ppm, peaks >300 ppm) over the Dinantian and basal Namurian. The Namurian concentrations in the east are higher (>150 ppm) than in the centre (110-150 ppm) and west (<110 ppm) and this distribution is similar over the Westphalian with higher levels in the east (>110 ppm) than in the west, (>70 ppm).

Z-values (fig. 82, vol. 2)

This parameter confirms the moving average distribution but emphasises the higher levels ($>+1$) over the Dinantian north of Bodmin moor and east pf Dartmoor, and the general enhancement over the Devonian-Dinantian-lower Namurian relative to the younger strata.

Variance ratio (fig. 83, vol. 2)

High variance zones (>0.5) occur over the granite contacts, along the Permian outlier, and scattered over the western Namurian and Westphalian.

These parameters have merely confirmed the symbol map distribution.

Discussion

It is possible to summarise those features revealed or emphasised by the moving average analysis. They are:

(i) slightly enhanced levels of As, Cr, Co, Fe, Mn, Mo, Ni, Pb, Sn, Ti, V and Zn along the Sticklepath

fault and also along a NE-SW zone further to the west.

(ii) regional distributions of Ga and Ge, which appear, in the former case, to correlate with the disposition of the major geological units.

(iii) zones of enhanced variance around the granites for As, Cr, Co, Cu, Fe, Pb, Mn, Ni, Sn, Ti, and V.

(iv) zones of enhanced variance along the Dinantian outcrop for Cr, Ga, Mn, Mo, Ni and Ti.

The slight enhancement along the Sticklepath Tertiary tear fault may be spatially related to the dextral translocation, which displaced the trace element enriched Dinantian strata to the north, on the western side of the fault. This mechanism may account for the enhancement over the southern portion of the fault but fails to explain the enhancement over the northern extension in the Westphalian bedrock. The enhancement of As, Co, Fe, Mn, Mo, Ni and Zn, all mobile in the secondary environment, suggests that the enhancement may be partially controlled by the drainage status of the soils. However, the enhancement of Cr, Sn, Ti and V, all immobile in the secondary environment in this area (Horsnail, 1968), suggests a lithological, albeit subtle, control. The same considerations apply to the zone of enhancement west of the Sticklepath fault.

The enhancement of Ga over the granite intrusions is in accordance with the previously recognised high abundance of this element in granitic rocks (Goldschmidt, 1954).

The Ge distribution is in opposition to those displayed by most elements, and indicates relatively high analytical bias in the north (over upper Namurian-Westphalian-Permian strata) and low bias in the south (over lower Namurian-Dinantian-Devonian-Granite outcrops). The total bias approximates 25 per cent of the mean Ge concentration. If all analyses had been adjusted to 400 ppm Ge, it is certain that the multi-element regional contrasts would be enhanced by approximately 25 per cent.

The high variance zones along the granite-country rock contacts and also over the Dinantian outcrop indicate geochemical discontinuities across these features. The high variance over the Dinantian is caused by the high geochemical contrast between the Dinantian sediments and the intruded basic rocks.

4.5.2. Moving average analysis of the regional reconnaissance data: N. Wales

The analysis included data for Ag, As, Cr, Co, Cu, Ga, Ge, Fe, Mn, Mo, Ni, Pb, Sn, Ti, V and Zn and the maps are presented in volume 2 (figures 84-127 inclusive). The element Bi has been excluded because few samples had detectable concentrations. The element Ge has been included for the reasons detailed in the previous section (4.5.1.).

ARSENIC

Moving average (fig. 84, vol. 2)

Concentration levels are usually uniformly low (< 7 ppm) except west of Llanrwst (> 7 ppm) and in the south-west of the survey area, especially over the Denbigh moorlands (15-30 ppm, peaks > 30 ppm).

Z-values (fig. 85, vol. 2)

This parameter distribution yields additional information to that of the moving average. Marginally enhanced concentrations (> 0) are indicated over the Ordovician-Silurian junction and form a sinuous zone connecting the northern Vale of Clwyd and the Denbigh moorlands, smaller zones occur west of Minera and east of Prestatyn and Wrexham.

Variance ratio (fig. 86, vol. 2)

High variance zones (>1) envelop the margins of the areas with high As concentrations.

The moving average parameters, particularly the Z-values, confirm the symbol map distribution.

CHROMIUM

Moving average (fig. 87, vol. 2)

Higher concentrations (>70 ppm) generally occur over the lower Palaeozoic outcrop, especially around Conway (>150 ppm)

and south-west of Minera, but do not include the Ordovician south-west of Llanrwst or the Clwydian Hills Silurian (30-70 ppm, < 30 ppm in the north). The upper Palaeozoic outcrops east of the Clwyd valley bear enhanced concentrations (> 70 ppm) west of Mold and along the Dee estuary with peak levels (> 300 ppm), south of Chester, but elsewhere concentration levels are lower (30-70 ppm).

Z-values (fig. 88, vol. 2)

These confirm the moving average distribution but also indicate low zones (< -1) east of Prestatyn, on the western flank of the Clwydian Hills, north of Wrexham, south and north of Mold and in an E-W zone through Mold. The values in the Clwyd valley mouth are higher (> 0) than those in the vale particularly over the Silesian outcrop (< -1). A N-S zone of higher values follows the Dinantian outcrop, near the southern boundary of the survey area.

Variance ratio (fig. 89, vol. 2)

High variance zones (> 1) are scattered adjacent to the Ordovician-Silurian junction, along the Clwyd valley and the Silesian outcrop, including the Silesian-Permian boundary.

The moving average parameters, notably the Z-values, have merely confirmed the symbol distribution.

Moving average (fig. 90, vol. 2)

High concentrations (> 30 ppm, peaks > 70 ppm) occur over the Denbigh moors, eastern Snowdonia, and the Ordovician west of Wrexham. Moderate enhancements (> 15 ppm) occur west of the Clwyd valley and in a NNE-SSW zone over the Silesian south of Connah's Quay. Elsewhere, levels vary between 7 and 15 ppm, except north of Wrexham and north-east of Denbigh (< 7 ppm).

Z-values (fig. 91, vol. 2)

A complex pattern indicating higher values (> 0) over the lower Palaeozoic outcrop, west of the Clwyd valley, with high level zones (> +1, peaks > +3) trending E-W south of Llanrwst onto the Denbigh moors and then swinging south from the moors. Low levels (< -1) occur in a sinuous zone between Ruthin and Flint and over the Permo-Triassic in the northern Clwyd valley and the main eastern outcrop.

Variance ratio (fig. 92, vol. 2)

High variance zones (> 0.5) occur over the Silesian, around the Denbigh moors, over the northern Clwydian hills, and around Penmaenmawr.

The moving average parameters confirm the distribution indicated by the symbol map.

Moving average (fig. 93, vol. 2)

The highest concentrations ($\geq$ 70 ppm) occur over the Llandudno peninsula and the Ordovician, west of Llanrwst, with moderate enhancement (30-70 ppm) over the whole lower Palaeozoic outcrop, except the Denbigh moors and Clwydian hills, over the Halkyn-Minera mineralised zone and the northern Clwyd valley, over a N-S zone south of Connah's Quay and scattered over the Permo-Triassic in the Clwyd valley and also in the east, notably around Chester and east of Wrexham. Elsewhere, levels are intermediate (15-30 ppm) except south of Wrexham and around Flint ($\leq$ 15 ppm).

Z-values (fig. 94, vol. 2)

A more complex distribution confirming that of the moving averages, but also indicating low zones ($\leq$ -1) along the Carboniferous-Permian boundary, and over the Clwydian range.

Variance ratio (fig. 95, vol. 2)

High variance zones ($\geq$ 1) trend WNW-ESE across the western lower Palaeozoic outcrop, over the eastern Silesian and the Carboniferous-Permian boundary, over the northern Clwydian hills, also east of Rhyl and along the centre of the Clwyd valley.

The moving average parameters confirm the symbol distribution but with less clarity.

GALLIUM

Moving average (fig. 96, vol. 2)

Higher levels ($>$ 15 ppm) occur over much of the lower Palaeozoic and Dinantian outcrops, west of the Clwyd valley, and over the southern and eastern Clwydian hills, with greater enhancements over the central Silurian and western and southern Ordovician outcrops. Elsewhere, intermediate levels (7-15 ppm) predominate except over the western and northern Clwydian Range and over the Central Silesian outcrop ($<$ 7 ppm).

Z-values (fig. 97, vol. 2)

This distribution confirms that of the moving averages but yields less detail west of the Clwyd valley.

Variance ratio (fig. 98, vol. 2)

Zones of high variance trend N-S along the Clwyd valley, over the Dinantian-Silesian outcrops east of the vale, and are scattered over the Silurian and Permo-Triassic.

The concentration range for this element was insufficient for symbolic representation. The moving average analysis has indicated a previously unrecognised distribution which is similar to those of Cr, Fe, Ti and V.

GERMANIUM

Moving average (fig. 99, vol. 2)

A complex pattern indicating higher levels (> 450 ppm) in the east than in the west (< 450), and also indicating generally high analytical bias (levels usually>400 ppm).

Z-values (fig. 100, vol. 2)

This confirms the higher levels in the east compared to the west.

Variance ratio

This distribution exhibited no significant features and has been excluded.

The regional distribution indicates a relative analytical bias of approximately 10 per cent against the regional trend of all elements except Ag, Pb, Sn and Zn.

IRON

Moving average (fig. 101, vol 2)

Higher concentrations (> 3%) occur over the lower Palaeozoic outcrops, west of the Vale of Clyd, and over the Silesian and Permo-Triassic in the Chester area, but the highest levels (> 7%) occur over the southern and western Ordovician outcrops and the Denbigh Moors. Intermediate levels (1.5-3.0%) occur over the Dinantian, parts of the Silesian, the western Clwyd valley and northern Clwydian hills, whilst elsewhere levels are lower (<1.5%).

Z-values (fig. 102, vol. 2)

This confirms the moving average distribution but emphasises higher levels (> +1) over the Denbigh moors, southern Ordovician, and that west of Llanrwst.

Variance ratio (fig. 103, vol. 2)

High variance zones (> 0.5) occur over the Denbigh moors, the western Ordovician, the Clwydian hills, the central Silesian outcrop and along the Clwyd valley.

The moving average parameters confirm the symbol distribution but with less clarity.

LEAD

Moving average (fig. 104, vol 2)

High concentrations (> 300 ppm) occur over the mineralised

zones, the Llantseilo mountain area south-west of Minera, along the Ordovician-Silurian boundary south of Conway, whilst peak values (>700 ppm) are restricted around Halkyn, Minera, west of Llanrwrst, between Rhyl and Prestatyn. The Carboniferous outcrops west of the Clwyd valley and the Llanfair-Talhaiarn area are associated with intermediate levels (>70 ppm). The western lower Palaeozoic and Clwyd valley Permo-Triassic are marginally lower (30-70 ppm) than the eastern Permo-Traissic outcrop (30-150 ppm).

Z-values (fig. 105, vol. 2)

This displays less detail than the moving average distribution, but confirms the higher levels (>+1, peaks > +2) associated with the mineralised areas with marginal enhancements (>0) over the eastern Permo :-Triassic and on the Abergele-Chester coastline.

Variance ratio (fig. 106, vol. 2)

High variance zones (>1) occur over the Halkyn-Minera axis, Llanrwst, Llanfair-Talhaiarn, south of Conway, and along an arcuate axis between Denbigh and Prestatyn, around Connah's Quay, and east of Wrexham.

The moving average parameters confirm the symbol distribution but emphasise the descrete areas of enhanced levels around Halkyn and Minera, contrary to the continuous zone suggested by the symbol map.

MANGANESE

Moving average (fig. 107, vol. 2)

The highest concentrations (>700 ppm, peaks 3000 ppm) occur over the western Ordovician and the Denbigh Moors. The main Silurian, Silesian, Permo-Triassic and the western Clwyd valley flank Dinantian are generally enhanced (> 300 ppm, scattered areas > 700 ppm) relative to the Clwyd valley, the Clwydian Hills and other Dinantian outcrops.

Z-values (fig. 108, vol. 2)

These confirm the moving average distribution except that low levels (< -1) are indicated along the eastern Clwyd valley and western Clwydian Range, around Colwyn Bay and to a lesser extent (<0) over the north-eastern and south-eastern Silurian and northern Silesian outcrops.

Variance ratio (fig. 109, vol. 2)

High variance zones (>0.5) cover the western Ordovician, Denbigh Moors, southern Dinantian, Silesian, and Permo-Triassic outcrops and are scattered over the northern Silurian, Silesian and Vale of Clwyd outcrops.

The moving average parameters confirm the symbol distribution but clarify the variation over the Silesian outcrops.

MOLYBDENUM

Moving average (fig. 110, vol 2)

High concentrations (> 3 ppm) occur west of Llanrwst, Colwyn

Bay and Wrexham, and north-west of Holywell, elsewhere concentrations are at or below the detection limit (2 ppm).

Z-values (fig. 111, vol, 2)

Enhanced zones (> 0) occur over the Ordovician-Silurian boundary, the Denbigh moors, the Halkyn-Minera axis, the northern Clwyd valley, the Llandudno peninsula and scattered over the main Silurian outcrop.

Variance ratio (fig 112, vol 2)

High variance zones (>0.5) follow the Ordovican-Silurian junction (peaks >8) and occur around Holywell (peaks >4) and the central Silesian.

The moving average parameters, notably the Z-values, indicated marginal enhancements over the Ordovician-Silurian boundary and Silesian outcrop, which were not evident from the symbol distribution.

NICKEL

Moving average (fig. 113, vol 2)

The highest concentrations (>50 ppm, peaks> 70 ppm) occur around the Denbigh moors, the north-western Ordovician-Silurian outcrops, and along the Dinantian-Silesian boundary WSW of Wrexham. Lower levels (<30 ppm) occur over the northern Clwyd valley, the central Clwydian hills, the central and eastern Silesian and south-

ern Permo-Triassic outcrops.

Z-values (fig. 114, vol. 2)

These confirm the moving average distribution but also indicate high levels ($> +1$) west of Llanrwst, and low levels (< -1) along the eastern Clwyd valley, the Permo-Triassic outcrop and its junction with the Carboniferous and scattered areas over the Carboniferous west of Flint.

Variance ratio (fig. 115, vol. 2)

A complex distribution with high variance zones (> 0.5) associated with the Denbigh moors, the Clwydian hills and the central Silesian outcrop, scattered zones also occur over the Ordovician and Permo-Triassic outcrops.

The moving average parameters confirm the symbol distribution but clarify the variations over the Silesian outcrop.

SILVER

Moving average (fig. 116, vol. 2)

Higher concentrations (> 0.3 ppm) occur adjacent to the Silurian-Ordovician boundary, around the Denbigh moors, in the Clwyd valley, around Rhyl, along the Silesian outcrop, and over the Permo-Triassic south of Chester.

Z-Values (fig. 117, vol.2)

This distribution indicates additional enhanced (> 0) zones

along the north Denbigh coast and scattered over the southern Ordovician outcrop.

Variance ratio (fig, 118. vol, 2)

High variance zones cover much of the Ordovician, Silesian and northern Permo-Triassic outcrops and also occur adjacent to the Denbighshire and Flintshire coasts.

The concentration range for silver was insufficient for symbolic representation but the moving average analysis has indicated a regional distribution with similarities to those of Cu, Mo, Pb, and Zn.

TIN

Moving average (fig. 119, vol. 2)

Higher concentrations ($>$ 7 ppm) occur over the Ordovician and basal Silurian, Silurian-Dinantian boundary west of Ruthin, the Silurian and Carboniferous south-west of Wrexham, and Silesian outcrops both into the east and in the Clywd valley.

Z-values (fig. 120, vol. 2)

This distribution indicates additional enhancements along the north Denbigh coast and the central Clwyd valley, and over the Permo-Triassic adjacent to Chester.

Variance ratio (fig. 121, vol. 2)

High variance zones occur over the Ordovician-Silurian and

Silurian-Dinantian boundaries, the Silesian outcrop including the boundary with the Permo-Triassic.

The moving average parameters indicate a subtle regional distribution which is not evident from the symbol map.

TITANIUM

Moving average (fig. 122, vol 2)

Higher concentrations (3000-7000ppm) occur over much of the western lower Palaeozoic and Dinantian outcrops, the south-eastern Clwydian hills, and more rarely over the northern Silesian and Permo-Triassic. The western Clwyd valley bears higher levels (> 1500 ppm) than the eastern zone (< 1500) extending over the Clwydian range. The values over the main Dinantian outcrop (1500 -3000 ppm) are higher than those over much of the central and southern Silesian (<1500 ppm), but are similar to those over the eastern Permo-Triassic (1500 - 3000 ppm).

Z-values (fig. 123, vol.2)

These confirm the moving average distribution but indicate additional enhanced zones over the north-western Ordovician and Silurian outcrops and over the central Silurian.

Variance ratio (fig. 124. vol 2)

High variance zones (>0.5) are largely restricted to the Vale of Clwyd, the Silesian and northern Permo-Triassic outcrops, two

isolated E-W trending zones occur over the western lower Palaeozoic outcrop.

The moving average parameters confirm the symbol distribution but clarify the variations over the Silesian outcrop.

VANADIUM

Moving average (fig.125, vol.2)

Higher concentrations (>150 ppm) occur over the Ordovician and central Silurian outcrops west of the Clwyd valley, and moderately enhanced levels (70-150 ppm) are located over the extreme northern Silesian outcrop and less commonly over the Clwydian hills. Elsewhere, intermediate levels (30-70 ppm) occur except over the northern and central Silesian (<30 ppm).

Z-values (fig.126, vol.2)

This indicates a geochemical discontinuity between the western (>-1, peaks >0) and eastern (<-1) Clwyd valley flanks, and distinguishes marginally enhanced zones (>-1) trending NNW-SSE from Connah's Quay and also over the Permo-Trias around Chester.

Variance ratio (fig.127, vol.2)

High variance zones (>0.5) occur over the Ordovician-Silurian boundary and more extensively along the Clwyd valley, the southern Dinantian-Silesian junction, the eastern Clwydian hills and scattered over the Silesian and Permo-Triassic outcrops.

The moving average parameters confirm the symbol distribution but clarify the variations over the Silesian and Permo-Triassic outcrops.

ZINC

Moving average (fig.128, vol. 2)

Enhanced concentrations (>300 ppm) occur over the Ordovician-Silurian boundary, around Minera, and over an arcuate zone from Mold to Abergele with peak levels (>1500 ppm) along the Halkyn-Minera and Rhyl-Prestatyn axes and to the west of Llanrwst. Low concentrations (< 150 ppm) occur over the northern Clwydian hills, the northern Denbigh Dinantian outcrops, and in linear zones south of Flint and along the Silesian-Permian boundary, extending over the southern Permo-Triassic.

Z-values (fig. 129, vol. 2)

This parameter distinguishes areas of enhanced concentrations (> 0) over the eastern Denbigh moors, and of depressed values (<-1) along the eastern Clwyd valley flank.

Variance ratio (fig. 130, vol. 2)

High variance zones (> 0.5) occur adjacent to and over the Ordovician-Silurian boundary, around Rhyl, along the Silesian outcrop, scattered over the Clwyd valley and over the Silurian and Permo-Triassic outcrops.

These parameters confirm the symbol distribution but clarify the background variations notably over the Silurian and Silesian outcrops.

Discussion

Features which have been recognised as a result of moving average analysis are summarised and discussed below.

The distribution of Ga is similar to those of Cr,Fe,Ti and V with higher levels over the western lower Palaeozoic outcrops and a discontinuity at the base of the Carboniferous, with depressed concentrations over the upper Palaeozoic outcrops. Research has indicated that these elements are immobile in the secondary environment (Horsnail, 1968) and consequently these regional distributions must be due to changing drainage sediment, and by inference bedrock mineralogy.

The subtle enhancement of Ag and Mo is distinguished along the Ordovician-Silurian boundary, the Halkyn-Minera axis, and over the Denbigh moors. The enhanced Mo concentrations over the Ordovician west of Llanrwst have been associated with pyritic black shales associated with volcanic rocks (Horsnail 1968). These may extend further north, possibly being attenuated or less pyritic, which would explain the subtlety of the geochemical feature. The higher Ag levels may be associated with Pb-Zn mineralisation and mining in the Llanrwst field, or with the Mo-rich pyritic shales. The en-

hanced levels over the Silesian may be associated with mining or contamination from the Halkyn-Minera ore field. Another possible cause is the presence of previously unrecognised Mo-rich black marine shale facies in the Namurian strata, similar to those located both in the Peak District and S.W.England (Fletcher,1968). The enhancement of these elements over the Denbigh moors may reflect secondary environmental effects causing enrichment in the drainage channels by the mechanism postulated by Horsnail (1968).

The Ge distribution reflects analytical bias operating against the regional trends of Cr,Fe,Ga,Ti and V (inter alia). If the trace element concentrations were corrected for a Ge concentration of 400 ppm,then the regional patterns of these elements would be enhanced by approximately 10 per cent.

The regional distribution of Sn, which is obscured by data variability in the symbol map, is clarified by the moving average analysis, though the geological significance of these variations is not obvious.

The moving average parameters have clarified the distribution of Fe,Ni,Ti,V and Zn over areas of high data variability.

The variance ratio levels are generally highest along geochemical discontinuities which in this area coincide with:-

(i) geological boundaries as between the Silurian and Dinantian for Cr,Fe,Ga,Ti and V,

(ii) the margins of areas with poorly drained, leached overburden,

as on the Denbigh moors for As,Co,Fe,Mn,Ni and Zn

(iii) areas of intense mineralisation and contamination, as along the Halkyn-Minera axis for Pb and Zn.

4.5.3. Moving average analysis of the regional reconnaissance data: English Peak District.

The analysis included data for As,Co,Cr,Cu,Fe,Ga,Ge,Pb,Mn, Mo,Ni,Sn,Ti,V and Zn. The elements, Ag and Bi, were excluded because few samples had detectable concentrations, and Ge has been included for the reasons given in section 4.5.1. The results are described below and the maps are presented in volume 2 (figures 131-174).

ARSENIC

Moving average (fig. 131, vol. 2)

The highest concentrations (>15 ppm, peaks >30 ppm) occur mainly over the Viséan-Namurian (V-N) shale series which underlie extensive enhanced areas (> 7 ppm) west and south of the limestone plateau, the former zone extends north over the moorlands towards Buxton and southwards between Longton and Cheadle. Similar levels (> 7 ppm) are scattered over the Westphalian and Permian.

Z-values (fig. 132, vol. 2)

This parameter yields greater detail than the moving average indicating marginally enhanced (> -0.5) zones over much of

the western dome flank, the eastern Westphalian and the northern Namurian.

Variance ratio (fig. 133, vol. 2)

High variance zones (>1, peaks > 2) occur over the V-N outcrops and the Westphalian around Cheadle.

The moving average parameters confirm the symbol distribution, but the Z-values clarify the distribution over the Namurian and younger strata.

CHROMIUM

Moving average (fig.134,vol.2)

Higher concentrations (50-70 ppm) occur over the Visean-Namurian (V-N) and Westphalian outcrops, with peak values (> 70 ppm) more common over the V-N bedrock. Intermediate levels (30-50 ppm) overlie the Namurian sandstone and Permo- Triassic outcrops, but the latter includes scattered areas with low concentrations (< 30 ppm).

Z-values (fig. 135, vol.2)

This parameter confirms the moving average distribution but also indicates the greatest enhancement (> +0.5, peaks > +1.0) over the stratigraphically younger parts of the V-N series, which are offset from the highest As levels over the basal part of the succession. The lowest levels (< -1.0) are scattered over the Permo-

Triassic and the northern Namurian and Westphalian outcrops.

Variance ratio (fig. 136, Vol.2)

High variance zones are associated with the V-N series, Westphalian and Permo-Triassic outcrops usually scattered along the outcrop boundaries.

The moving average parameters clarify the distribution over the post V-N strata compared to the symbol map.

COBALT

Moving average (fig.137 vol. 2)

Higher concentrations (>30 ppm, peaks > 70 ppm) occur over the Visean-Namurian (V-N) and Westphalian outcrops which are both generally enhanced(often >20 ppm). The lowest concentrations (>15 ppm) principally occur over the Namurian and Permo-Triassic outcrops.

Z-values (fig. 138, vol. 2)

This parameter confirms the higher levels over the V-N and Westphalian outcrops relative to the other formations, particularly over the southern Permo-Triassic outcrop.

Variance ratio (fig. 139, vol. 2)

High variance zones (>0.5) occur discontinuously over the margins of the V-N and Westphalian outcrops but are scattered over all units.

The moving average parameters confirm the symbol distribution but clarify the variation over the Namurian outcrops.

COPPER

Moving average (fig. 140, vol. 2)

The highest concentrations (> 50 ppm, peaks > 70 ppm) occur over the Viséan-Namurian (V-N) and less commonly over the Westphalian but both units are generally enhanced (> 40 ppm). The Namurian, especially in the north-eastern quadrant, and the southern Permo-Triassic usually underlie low concentrations (< 30 ppm).

Z-values (fig. 141, vol. 2)

These confirm the moving average distribution but indicate very high levels (> +1) over the V-N and Westphalian outcrops east of the limestone plateau and also to the west (V-N) and southwest (Westphalian). Very low concentrations (< -1) are indicated over the eastern Namurian and southern Permo-Triassic outcrops.

Variance ratio (fig. 142, vol. 2)

High variance zones (> 0.5) are associated with the V-N series and those Westphalian outcrops with enhanced Cu concentrations.

The moving average parameters confirm the symbol distribution but clarify the variations over the Namurian.

GALLIUM

Moving average (fig. 143, vol.2)

The highest concentrations (15-30 ppm) occur over the Visean-Namurian and Westphalian outcrops but also overlap onto the other units. The lowest concentrations (< 7 ppm) are scattered over the V-N outcrops but are more common over the Permo-Triassic.

Z-values (fig. 144, vol. 2)

This distribution confirms that of the moving average but indicates lower concentrations (< 0, with areas <-1) over the western V-N and Westphalian outcrops and also over the Permo-Triassic and the margins of the Carboniferous limestone outcrop.

Variance ratio (fig. 145, vol. 2)

High variance zones (> 0.5) follow the Namurian-Westphalian boundary in the east, and occur over the V-N series and its boundaries with the Namurian and Permo-Triassic. West of the dome, high variance zones tend to overlie the junction between argillaceous and arenaceous units.

The concentration range of this element has precluded symbolic representation and prevented the recognition of the regional distribution of this element.

GERMANIUM

Moving average (fig. 146, vol. 2)

This distribution is very complex and inconsistent but levels appear to be more frequently lower (< 350 ppm) over the

Westphalian and higher (>450 ppm) over the Visean-Namurian (V-N) outcrops, though these enhanced levels do occur over the Permo-Triassic and north-eastern Westphalian outcrops.

Z-values (fig. 147, vol. 2)

Higher concentrations (>+0.5) occur over the boundaries between the argillaceous (V-N, Westphalian) and arenaceous (Namurian, Permo-Triassic) units west of the dome, whilst lower levels (< -0.5) occur over the southern Permo-Traissic, along the eastern V-N and Namurian boundaries and also scattered over the eastern and north-western Westphalian. The distribution indicates marginally higher levels on the western relative to the eastern dome flank, and marginally lower levels over the Westphalian and southern Permo-Traissic outcrops relative to other units.

Variance ratio

This parameter indicated no significant features and has thus been excluded.

These parameters indicate an analytical bias of approximately 25 per cent whose main effect is the relative reduction of trace element concentrations over the Westphalian and southern Permo-Triassic outcrops, and more subtly the relative enhancement of trace element concentrations on the western relative to the eastern dome flank.

IRON

Moving average (fig. 148, vol.2)

Higher concentrations (>3.0%) occur over the Visean-Namurian and Westphalian outcrops with lower concentrations over the Namurian (< 1.5%-3.0%) and Permo-Traissic (< 1.5%) outcrops.

Z-values (fig. 149, vol. 2)

This distribution confirms that of the moving averages but indicates relatively lower levels over the V-N and Westphalian outcrops in the east of the survey area.

Variance ratio (fig. 150, vol. 2)

High variance zones (>0.5) generally follow the boundaries between the more argillaceous (V-N, Westphalian) and arenaceous (Namurian, Permo-Trais) units.

These parameters clarify the distribution over the Namurian and Westphalian and indicate a geochemical discontinuity between the argillaceous and arenaceous units which was not obvious from the symbol distribution.

LEAD

Moving average (fig. 151, vol. 2)

The highest concentrations (>300 ppm, peaks> 700ppm) occur around the northern, eastern and south-eastern margins of the limestone plateau and are associated with a broad zone of enhanced con-

centrations (>150 ppm), which overlap onto the eastern Westphalian and southern Permo-Triassic outcrops. The background levels tend to be higher (> 30 ppm) over the Permo-Traissic and the Visean-Namurian (V-N), notably over the Mixon anticline (> 70 ppm) than over the Namurian outcrops (< 30 ppm). The Westphalian exhibits variable concentrations perhaps marginally lower west of the dome (15-70 ppm) than to the east (< 70 ppm).

Z-values (fig. 152, vol. 2)

This distribution indicates lower concentrations (<-0.5) over the V-N series west, relative to those east (> -0.5), of Leek. The lower Namurian levels (<-0.5) and higher Westphalian levels (> -0.5) are also emphasised.

Variance ratio (fig. 153, vol. 2)

High variance zones occur north and east of the limestone plateau and to a lesser extent north of Buxton and around Mixon on the western dome flank.

These parameters confirm the symbol distribution, but clarify it west of the limestone plateau.

MANGANESE

Moving average (fig. 154, vol. 2)

The highest concentrations (> 700 ppm, peaks> 1500 ppm) occur more commonly over the Visean-Namurian (V-N) and Westphalian units,

whilst lower levels (<300 ppm, with extensive areas <150 ppm) occur over the Permo-Triassic with marginally higher, though variable, values over the Namurian.

Z-values (fig.155, vol. 2)

This distribution confirms that of the moving averages with higher levels over the V-N and Westphalian (>0, peaks $>+1$) relative to the Namurian (<0, occasionally <-1) and Permo-Triassic (<0, commonly <-1) outcrops.

Variance ratio (fig. 156, vol. 2)

This complex distribution indicates high variance zones over the V-N series and along the Namurian-Westphalian and the southern Carboniferous-Permo-Triassic boundaries.

The moving average parameters confirm the symbol distribution but clarify the variation over the Namurian and Westphalian units.

MOLYBDENUM

Moving average (fig. 157, vol. 2)

The highest concentrations (>3 ppm, peaks >15 ppm) occur over the Viséan-Namurian (V-N) series, notably the basal parts of the succession, and are scattered over the Namurian and Westphalian units, whilst elsewhere levels are at or below the detection limit (2 ppm).

Z-values (fig. 158, vol.2)

These confirm the moving average distribution with the greatest enhancement (> +1) over the basal V-N outcrops.

Variance ratio (fig. 159, vol. 2)

High variance zones (> 0.5) occur over the eastern and western dome flanks particularly over the Westphalian and the margins of the V-N series outcrop.

These parameters merely confirm the distribution indicated by the symbol map.

NICKEL

Moving average (fig. 160, vol. 2)

The highest concentrations (> 70 ppm, peaks >100 ppm) occur over the basal Visean-Namurian (V-N) series west and south of the limestone plateau, and scattered over the Westphalian, but both these units generally underlie enhanced levels (> 40 ppm) which frequently overlap onto the Namurian. Lower concentrations usually occur over the Namurian (< 40 ppm) and Permo-Triassic (< 30 ppm) outcrops.

Z-values (fig. 161, vol. 2)

This distribution also indicates high levels over the V-N (> 0), especially over the basal portion (> +1), and more variably over the Westphalian (-1 to +1); intermediate levels occur over the Namurian (<0, scattered areas < -1) and north-western Permo-Triassic

(≤ 0) with low values over the southern Permo-Triassic (< -1).

Variance ratio (fig. 162, vol. 2)

High variance zones occur on the eastern and western dome flanks over the V-N outcrop and along the Namurian-Westphalian boundary.

The moving average parameters confirm the symbol distribution but clarify the variations over the Namurian and Westphalian outcrops.

TIN

Moving average (fig. 163, vol. 2)

Enhanced concentrations (> 6 ppm, peaks > 15 ppm) occur scattered over all units but less frequently over the Visean- Namurian outcrop, usually levels are at or below the detection limit (5 ppm).

Z-values (fig. 164, vol. 2)

This parameter indicates enhancement (> 0, peaks $> +1$) associated with the mineralised anticlines at Crich and Ashover and more extensively over the Permo-Triassic south of Cheadle.

Variance ratios (fig. 165, vol. 2)

High variance zones are associated with all areas displaying enhanced Sn concentrations, and occur over the Permo-Triassic south of Cheadle, the eastern Namurian outcrop and in a NW-SE trending zone

in the north-western quadrant of the survey area.

The Z-value parameter has indicated regional patterns not clearly discernible from the symbol map.

TITANIUM

Moving average (fig. 166, vol. 2)

The highest concentrations (>1500 ppm) occur over the Visean Namurian (V-N) and Westphalian (peak values 3000 ppm) outcrops but frequently overlap onto the Namurian on the eastern and western dome flanks. Lower levels (< 1500 ppm) largely cover the other units and the western portion of the survey area.

Z-values (fig. 167, vol. 2)

This parameter confirms the moving average distribution but indicates the lowest values (≤-1) over the discontinuous basal (Bunter) beds of the southern Permo-Triassic and over the arenaceous units outcropping adjacent to the western boundary of the survey area. The highest levels are indicated over the upper portions of the V-N series (> +0.5) and scattered over the Westphalian (>+1).

Variance ratio (fig. 168, vol.2)

The high variance zones are often associated with the boundaries between the more argillaceous (V-N, Westphalian) and arenaceous (Namurian, Permo-Triassic) units, but the distribution is quite complex.

The moving average parameters confirm the symbol distribution but emphasise the enhanced levels over the upper, relative to the basal, V-N series outcrop.

VANADIUM

Moving average (fig. 169, vol. 2)

The highest concentrations ($>$ 70 ppm, peaks $>$ 90 ppm) occur over the basal Visean-Namurian (V-N) series but are scattered over the V-N and Westphalian outcrops. Both these units and the upper Permo-Triassic underlie enhanced cencentration levels ($<$ 50 ppm), whilst lower levels ($<$ 50 ppm) commonly occur in the west of the survey area and over much of the Namurian and basal Permo-Triassic outcrops.

Z-values (fig. 170, vol. 2)

This parameter merely confirms the moving average distribution without indicating additonal significant features.

Variance ratio (fig. 171, vol. 2)

The high variance zones ($>$0.4) occur over the boundaries between the predominantly argillaceous (V-N, Westphalian) and arenaceous (Namurian, Permo-Triassic) outcrops.

The moving average parameters confirm the symbol distribution but clarify the variations over the Namurian and Westphalian outcrops.

ZINC

Moving average. (fig. 172, vol. 2)

The higher concentrations are associated with extensive contamination mainly on the northern, eastern and south-eastern flanks of the limestone plateau, with scattered peak levels (>700 ppm) notably at Matlock and west of the Crich anticline, but also associated with limestone outcrops exposed in the cores of anticlines west and south of the dome. The background levels are higher (>160 ppm) over much of the Visean-Namurian (V-N) and Westphalian outcrops, notably over the basal V-N succession (>300 ppm). An extensive area of enhanced values (>160, peaks >300 ppm) occurs over the south-eastern Permo-Triassic outcrop, but elsewhere this unit and the Namurian generally exhibit low concentrations (< 160 ppm).

Z-values (fig. 173, vol. 2)

These confirm the moving average distribution but indicate two areas of depressed concentrations (< -1) over the southern and north-western Permo-Triassic.

Variance ratio (fig. 174, vol.2)

High variance zones blanket the eastern flanks of the dome and cover much of the Westphalian on the western flank, in addition to the V-N outcrop, east of Leek.

The moving average parameters merely confirm the symbol distribution without adding any significant features.

Discussion

The moving average analysis has indicated the following features.-

(i) the Ga distribution exhibits subtle correlations with higher concentrations over the Viséan-Namurian and Westphalian outcrops, intermediate levels over the Namurian, and lower levels over the Permo-Triassic.

(ii) the Ge distribution indicates a weak geological correlation with marginally lower, though variable, concentrations over the Westphalian, and also a slight regional trend with relatively depressed levels on the eastern, compared to the western, side of the dome.

(iii) Mo,Ni,V, and Zn are enhanced over the basal Viséan-Namurian (V-N) succession, whilst Cr and Ti are enhanced over the upper part of the V-N series.

(iv) Ti and V are relatively enhanced over the Keuper (Permo-Triassic) outcrop relative to the levels over the more arenaceous basal (Bunter) beds.

4.5.4. General Discussion

The moving average and Z-value distributions display all the regional trends recognised from the symbol maps of all three survey areas. The analysis has indicated regional distributions for Ga, which in N. Wales and the Peak District were generally similar

to those of Cr,Fe,Ti and V, whilst in S.W. England it was similar to those of As and Sn.

The moving average analysis has been used to investigate possible analytical bias ... induced by lithologically controlled matrix effects. The regional variations in the spectrographically determined concentration levels of the internal standard element, Ge, have been examined. These have been shown to exhibit regional trends in all three survey areas, though these were less pronounced in the Peak District.

The results have indicated that in N. Wales and S.W. England the analytical bias has reduced the regional contrast between high and low concentrations for most of the elements, in the Peak District, the Westphalian concentration levels have been depressed as a result of analytical bias. It is recommended that all spectrographic results, even for the semi-quantitative methods employed in applied geochemistry, should be corrected for variations in the concentration level of the internal standard element. Such a procedure will facilitate the interpretation for those elements, which exhibit subtle regional trends over a small concentration range, for instance, Ga.

The moving average analysis has elucidated subtle trends of two types:-

(i) those obscured by the class intervals employed in the colour symbol maps, for example:-

(a) the very slightly enhanced levels (2-3 ppm) of Mo which occur along the Halkyn-Minera mineralised belt in N. Wales.

(b) the distribution of Ga, in all three survey areas, which after a preliminary examination had been adjudged to show no significant distribution features.

(ii) those trends which are obscured by variable data levels and are revealed by the exaggeration of the auto-correlation in the regional data which is induced by moving average analysis, as employed in this study. Examples of this effect are:-

(a) the apparently higher levels of Cr,Co,Cu,Fe,Mn,Ni,Pb,Sn, Ti, and V over and adjacent to the Sticklepath fault zone in S.W.England

(b) the distribution of Ag,Mn,Mo,Ni,Pb,Ti,V and Zn over the Silesian outcrop and the regional distribution of Sn in the N. Wales survey area.

(c) the distribution patterns over the Namurian sandstone series outcrops for the elements As,Co, Cu, Fe,Pb, Mn, Ni and V, and also the regional distribution of Sn in the Peak District survey area.

The geological relevance of the additional features revealed by the moving average analysis are related to:-

(i) the geochemical significance of these subtle variations, which decrease when sampling and analytical errors are high; and

(ii) to the geological meaningfulness of the geochemical variations.

The individual features have been described and so it will suffice to repeat that that the trends described for Ga in all three areas and the additional variations shown by Mo and Ag in N.Wales appear to correlate with the regional variations of other elements. Thus, they are probably controlled by the same causal agencies as for those elements. The significance of the zones of higher variance caused by very variable data levels must depend on the cause of the data variability, be the cause geological (including mineralisation), secondary environmental, or contamination.

The usefulness of the various parameters computed in the moving average analysis may be assessed by the additional information which they yield. The moving average and Z-value maps exhibit essentially the same information. However, by virtue of the different units they represent and thus on the different contour intervals employed may give complementary information. An example of this is afforded by the distribution of the moving average and Z-values for As in S.W.England, where the Z-values give additional detailed information, notably the lower concentrations at the eastern and western extremities of the Westphalian outcrop. The variance ratio data indicated areas of high data variability, whether the regional distribution of this parameter yielded much useful information is questionable. The high data variability inherent in

the semi-quantitative analysis of drainage sediment samples, the low areal density of these samples, the complex provenance of the sediments and their physical displacement from the material from which they were derived must reduce the usefulness of this parameter. It may be noted that zones of high variability are quite evident from a scrutiny of the colour symbol and, to a lesser extent, the moving average maps.

The moving average and colour symbol maps both represent attempts to ascertain areal trends in the data by smoothing out the excessive variability. The symbol maps represent data smoothed according to the spread of the trace element concentration frequency distributions, which have been subdivided into a maximum of 5 concentration classes. The moving average analysis smoothes data according to the values of the adjoining sample sites which weight the local moving average. This effect maximises the auto-correlation within the data and thus accentuates trends in the distribution. The associated parameters are only probabilistically meaningful if the data follows a unimodal, gaussian or lognormal frequency distribution. This situation is not frequently attained but does not invalidate the qualitative use of these parameters.

The computations involved in the moving average analysis can inflict certain liabilities upon the data. The main disadvantage is that the individual sample sites are lost, because the moving average parameters are located at the centroid of the samples which

they represent. A consequence of this procedure is that when the locations of the individual sample sites are required this method of analysis has, in the past, not been suitable. It is theoretically possible to modify the computer programme so that it will compute the deviations of the individual samples from the regional trend. The programme listed in Appendix II includes this facility. However, the modifications were introduced too late for the regional reconnaissance data to be analysed using the modified programme.

The results from the moving average parameters and colour symbol maps are briefly compared below:-

(i) the moving average parameters and the colour symbol maps yield essentially the same regional trends, but those of the former are often more detailed.

(ii) the main direct expense in both methods relates to the computation time, which is greater for the moving average maps. However, this is probably more than balanced by the greater number of personnel and higher overhead costs required to prepare the colour symbol maps.

(iii) when there is a requirement for contour maps displaying the regional, background trends, then the moving average analysis is the preferred technique. However, if the individual sample site concentrations are required then the symbol maps are preferable, though they may be superceded by the latest

modifications of the moving average technique, previously described.

4.6.0. SUMMARY AND CONCLUSIONS

The properties of the regional reconnaissance survey data related to:-

(i) inhomogeneous areal distributions.

(ii) discontinuities in the trace element concentration gradients.

(iii) complex distribution patterns.

(iv) large numbers of data values to be processed.

have rendered the polynomial trend surface technique inapplicable as the technique for areal analysis of the data used in this study.

The moving average technique was used for the areal analysis. The results compared favourably with those yielded by the colour symbol maps. They were, if anything, rather more detailed especially with subtle variations or for data displaying a small concentration range.

This examination has indicated that the moving average is the most meaningful parameter, but that the Z-value and variance ratio parameters may provide complementary information.

The direct costs of moving average analysis are comparable to those of producing the colour symbol maps but the indirect costs, including overhead expenditure, are considerably smaller. Moreover, the results of the moving average analysis are much more

quickly available.

It may be stated in conclusion that when there is a requirement for the areal analysis of numerous and complex data, in order to produce detailed contour maps displaying the regional trends in the background concentrations of trace elements, then the moving average techniques may be gainfully employed.

CHAPTER 5

COMPUTERISED PROCEDURES III: FACTOR ANALYSIS

5.1.0. PROBLEMS ASSOCIATED WITH INTERPRETING MULTI-ELEMENT REGIONAL GEOCHEMICAL DATA

5.1.1. Assessing the provenance of drainage sediment samples

Drainage sediment samples are derived to varying degrees from the weathering products of all bedrock types outcropping or suboutcropping in the catchment area. The sediment geochemistry may also display the effects of secondary environmental variation, contamination due to human activities and the presence of exotic overburden, that is, overburden not derived from the bedrock over which it lies. The sediments therefore frequently have a complex provenance. It is impossible from an examination of the individual drainage sediment geochemical data to assess quantitatively or with any degree of accuracy the contributions of the various agencies controlling the trace element compositions.

5.1.2. Information redundancy

It is clear from the reconnaissance survey and the follow-up work previously described that certain elements, displaying broadly similar patterns can be related to the same control. Thus in the English Peak District, As and Mo display similar dispersion patterns and have been shown to be enhanced, together

with Cu and V, in drainage sediments derived from areas underlain by black marine shales (Fletcher, op. cit.). The data for these elements are giving the same information about this one geological control. The repetition of information yielded by these individual elements is termed information redundancy. It would be most advantageous, were it possible, to display all that geochemical information relating to the occurrence of black marine shales on a single map. Similar problems are posed by other established trace element associations in each of the three areas, that is, the problem of information redundancy is general for the data being analysed.

5.1.3. The dimensionality of the data

The assessment of the intercorrelations between all the trace elements for each area involves either the simultaneous appraisal of maps for all the trace elements or the comparison of all possible pairs of trace element maps. This would be a tedious procedure and could only result in a qualitative evaluation of the intercorrelations. The human mind cannot easily evaluate the interrelationships between a large number of variables, the dimensions of the data are too great. This is termed the problem of dimensionality.

5.2.0. AIM OF THE STUDY

It was considered that, by applying the appropriate

computerised multivariate analytical techniques, it might be possible to overcome the problems posed in the preceding section. If the techniques were to achieve this end completely, then they must:

(i) treat the data for all the elements simultaneously.

(ii) reduce the information redundancy so that the inherent features of the multi-element data are brought out.

(iii) indicate the proportions of the different geochemical features present in the individual drainage sediment sample trace element data, that is, to unravel the provenance of the data.

5.3.0. TECHNIQUES EMPLOYED IN THIS STUDY

The techniques chosen as appropriate for use with the multi-element regional geochemical data are known collectively as Factor Analysis. This name is applied to a series of procedures which are used to analyse multivariate numerical data and which re-express the data in terms of mathematically derived variables or factors, which may be geochemically meaningful.

5.3.1. Historical development of Factor Analysis

The statistical basis of the technique was published by Karl Pearson (1901) in presenting the method of principal axes'. This theoretical basis was utilized by Charles Spearman, when,

beginning in 1904 and continuing for forty years, he applied and developed the technique. The principal use of these procedures was the analysis of data collected in psychometric studies. The result of his work and that by others, notably Burt, Garnett, Holzinger, Pearson and Thomson over a period of years was the development of a variety of related procedures known collectively as Factor Analysis.

The techniques were principally applied during this early period for the analysis of data derived from a battery of psychological tests. The results were interpreted as indicating the existence of a common factor related to intelligence and several specific factors related to aptitudes. It was realised by the 1930's, in the work of Garnett and others, that the technique could be applied to locating a number of group factors rather than one general and several specific ones. Thurstone (1931) initiated the application of matrix algebraic techniques in order to overcome the computational problems involved in this form of analysis. The computational procedures for determining the most statistically meaningful principal axes were developed by Hotelling during the 1930's.

Major developments, in more recent times, have been centred around optimising the computational procedures and rationalising the theoretical framework. Another development has been the utilisation of electronic digital computers for performing the

computations. This has increased the rapidity of the analysis as well as allowing an increase in the number of variables and subjects which may be simultaneously processed. The techniques have been extensively applied in the psychological sciences and their general usefulness and applicability has been demonstrated.

The procedural variants included within Factor Analysis are termed modes and each is specified by a particular letter. Thus, in the earth sciences, the two variants most used at the present time are the Q-mode and R-mode techniques. Both of these procedures begin with a matrix which quantifies the similarity either between each pair of subjects or samples (Q-mode) or between each pair of variables (R-mode). Q-mode analysis classifies all the subjects or samples in terms of mathematically derived end-members, whilst R-mode analysis classifies all the variables in terms of new mathematically derived variables.

5.3.2. Computer programmes employed in this study

Computer programmes for the performance of R- and Q-mode analysis on geological data have been written by Manson and Imbrie (1964) and Garrett (1967). The former programme performs a Q-mode analysis which incorporates an optional modification by Imbrie. Thus, instead of classifying the samples in terms of theoretical end-members, they may be classified in terms of those real samples whose composition most closely approximates to those of

the theoretical end-members.

The data used in the study described in this chapter has been processed using both the Manson and Imbrie (R- and Q-modes) and the Garrett (R-mode) programmes.

5.3.3. Previous usage of Factor Analysis in geology

The techniques of factor analysis have only really been applied to geological data in the past decade.

One of the earliest applications of the Q-mode technique was by Imbrie and Purdy (1962) in using this procedure to objectively classify sediments from the Great Bahama Bank into facies types on the basis of the sediment particle compositions.

Krumbein and Imbrie (1963) utilised the same technique to classify 31 boreholes from south-eastern Colorado and western Kansas. The data used, related to the thickness (in feet) of 4 lithological types. The factor solution classified the boreholes in terms of three end-members in which one lithological type was most strongly developed.

Imbrie and Van Andel (1964) employed Q-mode analysis to classify the heavy mineral composition of sediment samples taken from the Gulfs of California and Orinoco. The results of the classification were used to deduce the provenance of the individual

samples and to assess the current distributions within these gulfs. R-mode analysis was also employed to distinguish heavy mineral associations which could be related to specific sources of the basin sediments.

Both Q-mode and R-mode techniques were used to screen data related to the faunal content and major element geochemistry of one lithological unit of the Permian Americus limestone in Kansas and Oklahoma (Harbaugh and Demirmen, 1964). The R-mode analysis indicated associations of faunal types with major elements, and the Q-mode analysis classified the samples into associated groups. The results were used to establish facies boundaries in the limestone unit.

Another application of both Q-mode and R-mode procedures was upon purely geochemical data derived from drainage sediment samples from the north Nimini Hills area in Sierra Leone (Garrett, 1966; Nichol et al, 1967 and 1969). The Q-mode analysis was used to classify the sediments in relation to a number of end-members (3 and 4), one of which was related to an area of metamorphosed ultrabasic rocks and two of which were related to geochemically distinct granitic facies. The sample population was split into two equal nested subsets of 50 samples each. The results of Q-mode upon the subsets was equivalent to that on the total set. The R-mode analysis was used to indicate 3 associations, but in the absence of any sample scores on the individual samples it was

difficult to interpret some of these.

R-mode analysis has been used to classify 10 variables related to the lithological composition and fragment shapes and sizes in 39 sedimentary rock samples (Griffiths, 1961). Three of the factor associations were considered to be related to:-

(i) mean current velocity;

(ii) variability of current velocity;

(iii) variation in the lithic fragments in the material.

A further study on measured properties of detrital sediments was used to provide associated variables (Griffiths, 1966). The results were used to provide a petrogenetic interpretation. Similar procedures were applied to data from several sandstone formations. It was suggested that one factor analytic procedure might be to employ Q-mode analysis to establish sample population subsets; and then to apply R-mode analysis to the separate subsets in order to define the lithological and sedimentological characteristics within each subset.

Reyment (1964) has used R-mode analysis to classify morphological characteristics of Foraminifera into associated groups. The same technique has been applied to geochemical data related to the composition of scapolites (Middleton, 1964). The results were used as evidence for the existence of three trace element

associations:

(i) Ge, Ga, Li;

(ii) B, Rb;

(iii) Mn, Pb.

The geochemical significance of the associations was not established.

The R-mode technique has been used to classify petrographic features of the Upper Cambrian Reagan sandstone formation of central and north-western Kansas, in order to identify associated variables (McElroy and Kaesler, 1965).

Heavy mineral assemblages of sediments have been analysed by R-mode procedures. The results defined mineral associations which could be ascribed to specific bedrock types (Briggs, 1965).

A facies study of the Leavenworth limestone formation was made by R-mode analysis of mineralogical and chemical data derived from these rocks (Toomey, 1966). The results were used to compile facies maps of this formation.

An application of R-mode analysis as an interpretative aid for major and minor elemental compositions of tektites has been made (Miesch et al, 1966). The major component concentrations were expressed as percentages and in order to overcome induced correlations due to closure effects (Chayes, 1960, 1962), the major element concentrations were re-expressed as ratios of the SiO_2 concentrations in each sample. The R-mode analysis was

performed on the ratio data and it was considered by the authors that the technique provided theoretical variables which could be easily interpreted.

Multi-element regional geochemical data related to drainage sediments from the Nimini Hills schist belt, Sierra Leone, was subjected to R-mode analysis (Garrett and Nichol, 1969). The results included scores for each sample on all the factors, and these factor scores were used to compile maps of the factor distributions. The optimum factor model resolved 12 elements into 9 factors. The trace metal associations and their related areal patterns were employed in the interpretation of the geological meaning of each factor. The authors considered 7 of the factors to be related to bedrock lithology (5) or secondary environment (2), whilst the two remaining factors were tentatively correlated with the presence of hitherto unrecognised bedrock mineralisation. The technique of R-mode analysis was concluded to be of value in screening multi-element geochemical data and providing more easily interpretable variables.

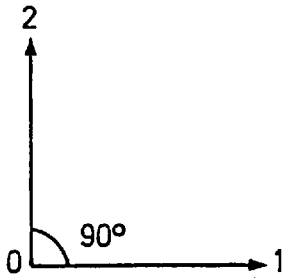
5.3.4. Theoretical basis to Q-mode and R-mode factor analysis

Both these procedures utilise a matrix of similarity co-efficients as the starting point for the analysis. The Q-mode technique analyses the similarity between the samples whilst the R-mode analyses that between the variables.

It is possible to represent the correlation between samples or between variables geometrically (Fruchter, 1954). Thus if two samples or variables are represented two dimensionally by vectors (see figures 23a, b, c, d) then the correlation between the two vectors is given by:

FIGURE 23. VECTORIAL REPRESENTATION OF CORRELATION COEFFICIENTS (after FRUCHTER, 1954).

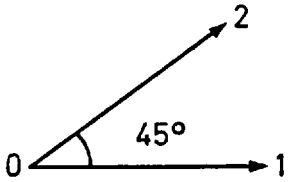
a)



r = 0·00

No correlation between variables 1 and 2.

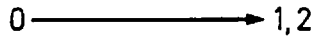
b)



r = 0·707

A degree of positive correlation between variables 1 and 2.

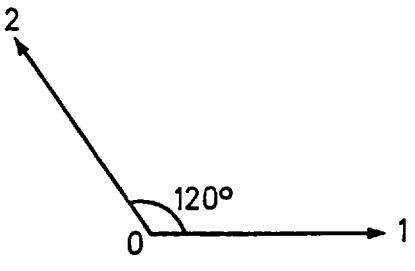
c)



r = 1·00

Perfect correlation between variables 1 and 2.

d)



r = −0·50

A degree of negative correlation between variables 1 and 2.

$$r_{12} = V_1 V_2 \cos {}^{O}_{12} \qquad 5\text{-I}$$

where r_{12} is the correlation between the two variables

V_1, V_2 are the lengths of the vectors representing the numerical values of variables 1 and 2 respectively,

and ${}^{O}_{12}$ represents the angle between the two vectors.

If the vectors are of unit length such that:

$$V_1 = V_2 = 1.00 \qquad 5\text{-II}$$

then equation 5-I simplifies to

$$r_{12} = \cos {}^{O}_{12} \qquad 5\text{-III}$$

The relationship described in eg. 5-II can only be utilised if the data for all the samples (R-mode analysis) or all the variables (Q-mode analysis) cover the same numerical range. If there is a large discrepancy in the numerical ranges of the concentration levels of the variables, then the correlations between them, using equation 5-I, will reflect the correlation between the variables with the higher concentration levels, whilst those with the lower numerical values will exert a negligible effect. It is thus advisable, to transform all the data to the same numerical scale. The transformations employed on the data used in this study have been of two types:-

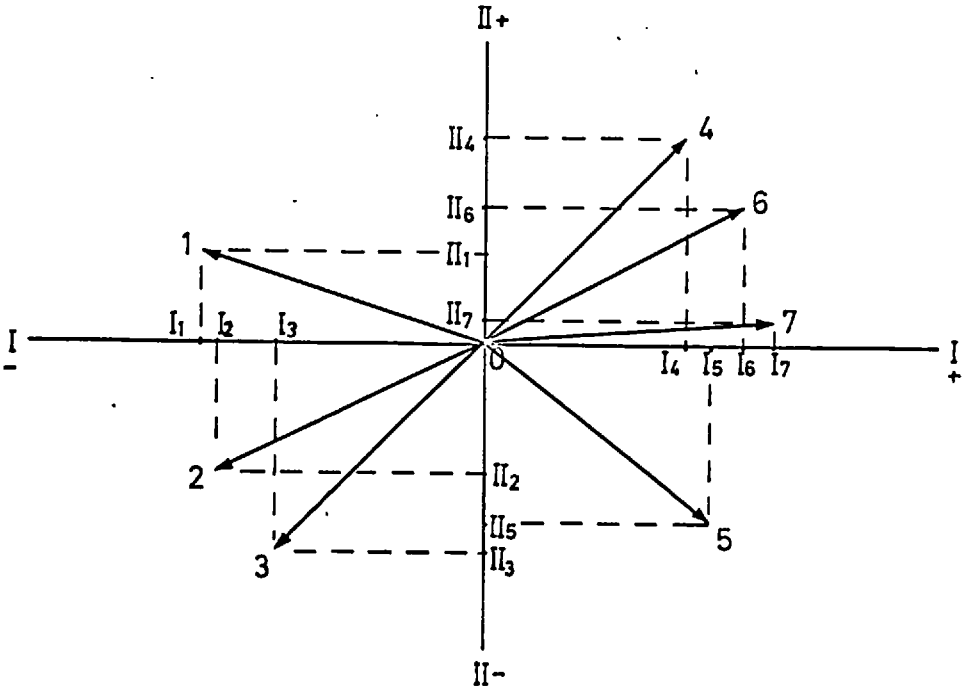
(i) prior to R-mode analysis, the data has been standardised in terms of standard deviation units about the arithmetic mean, using the equation for standard value transformations given in section 3.3.2.

(ii) before Q-mode analysis, the data levels have been re-expressed as a percentage of the total numerical range encountered for each variable in the sample population, using the percentage range transformation given in section 3.3.2.

When 3 variables (or samples) are represented vectorially then the vectors will be plotted in three dimensional space, whilst n variables (or samples) will be plotted vectorially in n-dimensional space. It is apparent that those variables (or samples) which are correlated will be represented by vectors which are separated by acute angles (less than 90°) whilst those which are uncorrelated or negatively correlated will be separated by obtuse angles (equal to or greater than 90°).

It is the function of that form of factor analysis known as principal components analysis to construct axes in the multi-dimensional space (hyperspace), so that the axes coincide with the clusters of vectors, representing correlated variables. This may be represented graphically for a number of vectors projected onto two dimensions (see figure 24). The vectors (1, 2, ...7) are shown in relation to two principal axes (I and II). The projections of the vectors on the principal axes are termed vector loadings, and the scale is so chosen that the vector loadings may vary between +1.00 and -1.00. The first principal axis (I) is so constructed that the variance of all the vector

FIGURE 24. VECTORIAL REPRESENTATION OF PRINCIPAL COMPONENTS ANALYSIS



LEGEND

$\frac{I}{II}$ Principal component axes.

1-7 Variables represented as Vectors.

I_1-I_7 Projections of Vectors 1-7 on axis I (Vector loadings).

II_1-II_7 Projections of Vectors 1-7 on axis II.

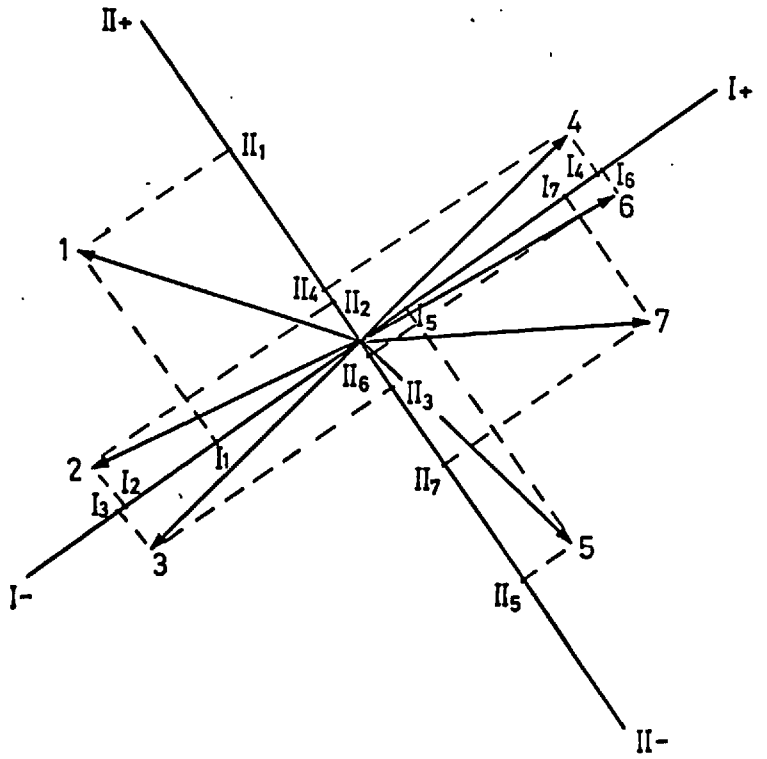
loadings (I_1, I_2, ...I_7) upon it are a maximum. The second principal axis (II) is perpendicular to the first, the perpendicular relationship between them is described as orthogonal, and the axis is so constructed that the variance of the residual vector loadings (II_1, II_2, ...II_7) upon it are also a maximum. For n-dimensional space there may be n principal axes all mutually perpendicular (orthogonal), if the variance of the vector loadings upon the i th axis is designated σ_i^2 , then the relationship between the vector loading variance upon all the axes may be represented as

$$\sigma_I^2 > \sigma_{II}^2 > \sigma_{III}^2 > \ldots > \sigma_i^2 > \ldots > \sigma_n^2 \qquad 5\text{-IV}$$

Thus the first axis accounts for the maximum variance and the following axes account for successively less of the variance. If the same number of axes are used as there were variables (or samples) then this is described as a principal components solution, if fewer axes are used, the solution is termed a principal axis solution.

The principal axes are seldom used as the final solution for geological data. A further stage involves the rotation of the axial complex so that the orthogonal (perpendicular) relationships are preserved, but the total variance of all the vector loadings on the axes is maximized. The relationship is shown graphically in figure 25. The new vector loadings are termed the rotated axis (or factor) solution, where each axis is known as a factor. Again the variance of the vector or factor loadings (I_2, I_2, ...I_7) on factor I is greater than that on factor II, that

FIGURE 25. VECTORIAL REPRESENTATION OF THE ROTATED FACTOR SOLUTION



LEGEND

I, II Rotated factor axes.

1,2...7 Vectors representing variables.

I_{1-7} Vector loadings on factor I for variables 1-7.

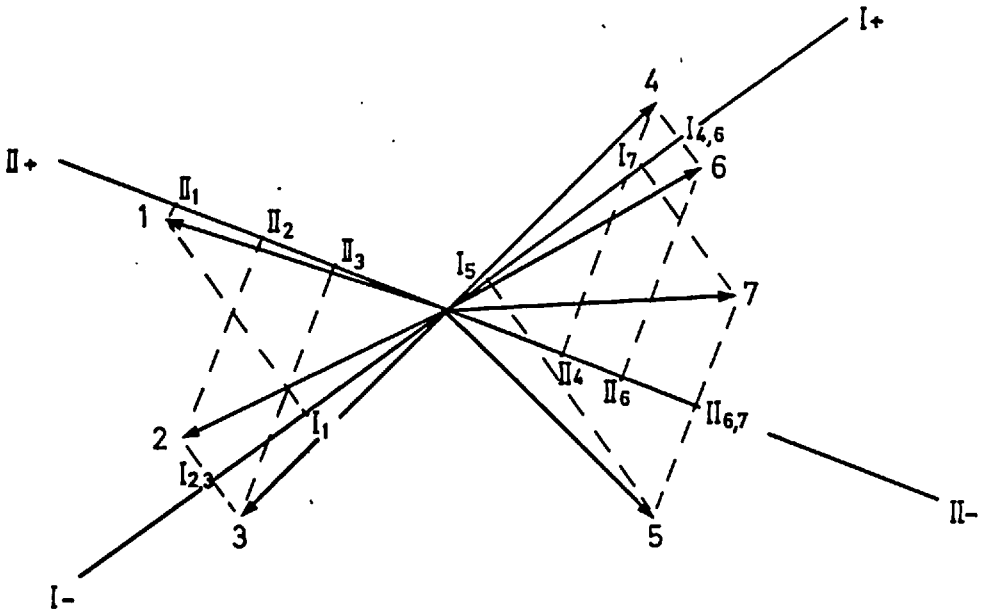
II_{1-7} Vector loadings on factor II for variables 1-7.

is, for an n factor model the relationship in equation 5-IV is preserved.

The rotated factor (or axis) solution is sometimes used as it stands, but for some applications of factor analysis a further manipulation of the axes is undertaken. This involves the separate rotation of each axis in turn in order to maximise the variance of the vector loadings upon it, but the constraint of orthogonality is no longer maintained. The axes are no longer mutually perpendicular, and thus, are not statistically independent. The solution is termed the oblique factor (or axis) solution and the obliquity of the axes introduces a correlation between the axes and the factor (or vector) loadings upon them. The relationship is shown graphically in figure 26, where it may be seen that the two axes (I and II) are no longer perpendicular. The factor (or vector) loadings on the oblique factors constitutes the oblique factor solution. Once again for an 'n' factor model the relationship between the variances of the vector loadings described in equation 5-IV is maintained.

The Manson and Imbrie Q-mode oblique solution is slightly different from the solution displayed in figure 26, for instead of using the maximum factor (or vector) loading variance as the sole criterion for the oblique axes direction, Imbrie causes the oblique axis to lie in the same line as the nearest sample vector.

FIGURE 26. VECTORIAL REPRESENTATION OF THE OBLIQUE FACTOR SOLUTION



LEGEND

I, II	Oblique factor axes.
1,2,..7	Vectors representing the variables.
I_1 -I_7	Vector (or factor) loadings on factor I.
II -II	Vector (or factor) loadings on factor II.

Thus, in figure 26, factor II would be made coincident with vector 1.

The basic assumptions of factor analysis are that the variable or sample vectors are grouped into vector clusters. Moreover it is also assumed that the degree of correlation between the vectors is proportional to the projection of the vector on to the factor axis, which is known as the factor (or vector) loading. The sum of the squared factor (or vector) loadings for each variable or sample will for the ideal factor solution equal 1.00. This sum is termed the communality, and will only equal 1.00 when all the correlations of that variable (or sample) have been completely described by the factor loadings. The communality can vary between 1.00 and 0.00, the latter value implies that none of the correlations of the individual vector have been accounted for by the factors since all the factor or vector loadings are equal to zero. Thus the value of the communality gives some measure of the degree to which the factors account for the total correlations of each variable (or sample).

The variance of the factor loadings for each factor axis is termed the eigenvalue associated with that factor. It is inherent to the factor solution that the first axis accounts for the maximum variance and thus has the largest eigenvalue. The remaining factor axes account for successively less of the factor loading variance and are consequently associated with

successively smaller eigenvalues. The sum of the eigenvalues for the principal components solution, in which the number of factor axes equals the number of the variable or sample vectors, is equal to the sum of the communalities. An example will illustrate this: for 16 variables an ideal solution, for instance, the principal components solution, will yield communalities of 1.00 on each vector, and thus the sum of the eigenvalues associated with all 16 factors will also equal 16.00. If less factors are extracted than are used in the principal components solution, that is, if a principal axis solution is chosen, then the sum of the eigenvalues may be less than that for the ideal factor model. An example might be that for 16 variable (or sample) vectors only 8 factors are extracted, the sum of whose associated eigenvalues is 12. It follows that the proportion of the factor model eigenvalue sum to the ideal eigenvalue sum represents some measure of the data variance being accounted for by the factor model. If the previous example is used to illustrate this point; the sum of the eigenvalues on the 8 factor model is 12, compared to the maximum attainable sum of 16; the 8 factor model can thus be described as accounting for 75 per cent of the total data variance. Thus the efficiency of any factor model may be quantitatively assessed by the percentage of total variance which it accounts for. There is no objective manner for selecting the optimum number of factors to be extracted. Two generalised

criteria described in the literature are to select only those factors whose eigenvalues:

(i) exceed 1.00 (Harman, 1967); or

(ii) form a relatively gradual descending series without large breaks

It is apparent that the number of factors extracted may be a subjective choice. A small number of extracted factors yields a simple solution in terms of the decrease in the number of variables which must be interpreted. However, the percentage of the total variance accounted for by such a simple model might result in a significantly large proportion of the available information being unused. Moreover, the composition of the individual factors in such a model might be very complex, thus rendering the interpretation of each factor more difficult. The selection of a model with a large number of factors poses a converse set of problems. Thus a large part of the total variance is explained by the factor model and the individual factors are more easily interpreted, but the reduction in the number of variables to be interpreted relative to the initial data is smaller.

It has been previously stated that both R-mode and Q-mode factor analysis are made on a matrix of similarity coefficients, which quantitatively define the similarity of each variable (or sample) to all other variables (or samples). The two most commonly used similarity measures in geological studies are the product moment correlation coefficient (Pearson, 1904) and the cos θ coefficient

(Imbrie and Purdy, 1962). The product moment coefficient (r) between variables is defined as:-

$$r_{xy} = \frac{\sum_{i=1}^{N} Z_{ix} \cdot Z_{iy} - N. \bar{Z}_x. \bar{Z}_y}{N. \sigma_x . \sigma_y} \qquad 5\text{-V}$$

where r_{xy} is the correlation coefficient between variables X and Y;

Z_{ix} is the standardised value on variable X for sample i;

Z_{iy} is the standardised value on variable Y for sample i;

$\bar{Z}_x$ is the mean standardised value of variable X;

$\bar{Z}_y$ is the mean standardised value of variable Y;

- σ_x is the standard deviation of the standardised values (Z_{ix}) about $\bar{Z}_x$;

σ_y is the standard deviation of the standardised values (Z_{iy}) about $\bar{Z}_y$;

N is the number of samples.

The value of r may vary between -1.00 and +1.00, that is,

$$-1.0 \leq r \leq +1.0$$

The product moment correlation coefficient between samples employs the same formula except that :-

r_{xy} is the correlation between samples X and Y,

so that X and Y refer to samples instead of variables,

i refers to the ith variable,

and N is the number of variables.

If the frequency distributions of the variable (or sample) values,

X and Y, are gaussian, then

$$\bar{Z}_x = \bar{Z}_y = 0 \qquad \text{5-VII}$$

and equation 5-V simplifies to

$$xy = \frac{\sum_{i=1}^{n} Z_{ix} \cdot Z_{iy}}{N \cdot \sigma_x \cdot \sigma_y} \qquad \text{5-VIII}$$

The relationship in the foregoing equation is only applicable when the frequency distributions of X and Y are gaussian (or normal). It is frequently necessary to transform the data prior to calculating the coefficient, in order to obtain gaussian distributions. The product moment correlation coefficient evaluates the extent to which the values of X and Y covary in a linear fashion. Extreme values of r_{xy} are shown below and their meaning is described:

(i) $r_{xy} = +1.00$ indicates perfect linear correlation between X and Y with all points falling on a straight line.

(ii) $r_{xy} = -1.00$ is evidence for perfect negative correlation between X and Y, again all points fall on a straight line.

(iii) $r_{xy} = 0.00$ indicates no correlation at all between X and Y,

with the points being randomly scattered in the covariance plot. These relationships are exhibited graphically in figure 27. The cos θ similarity coefficient is defined (after Manson and Imbrie, op cit) as :-

$$\cos \theta_{xy} = \frac{\sum X_i \cdot Y_i}{\sqrt{\sum X_i^2 \cdot \sum Y_i^2}} \qquad 5\text{-}\underline{\underline{IX}}$$

where Cos θ_{xy} is the measure of the similarity between variables (or samples) X and Y.

X_i is the value of X for the ith sample (or variable).

Y_i is the value of Y for the ith sample (or variable).

The value of cos θ may vary between - 1.00 and +1.00, that is

$$-1.00 \leqslant \cos \theta \leqslant +1.00 \qquad 5\text{-}\underline{X}$$

If the variables (or samples) X and Y are represented vectorially (see figure 28) then the angle subtended between vector X and Y is θ. If the two vectors are perfectly aligned (figure 28a) then $\theta = 0^{\circ}$, cos θ = +1.00 and perfect positive correlation exists between the vectors,

when $\theta = 90^{\circ}$, $\cos \theta = 0.00$ and there is no correlation between the vectors (figure 28b). Finally, if the vectors subtend an angle between them of 180° (figure 28c) then $\cos \theta = 1.00$ and the vectors demonstrate perfect negative correlation.

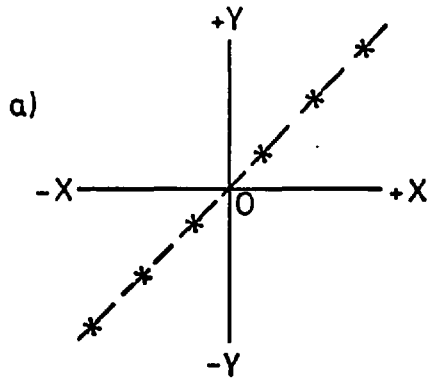
The $\cos \theta$ similarity coefficient is recommended for use on data which covers the same numerical range, since variations in the numerical value scale of X and Y can bear an irrelevant effect on the value of $\cos \theta$.
It is frequently necessary to transform the data, two recommended procedures are :

(i) percentage range transformation, where

$$T_i = \frac{X_i - X_{Min}}{X_{Max} - X_{Min}} \times 100 \qquad 5\text{-XI}$$

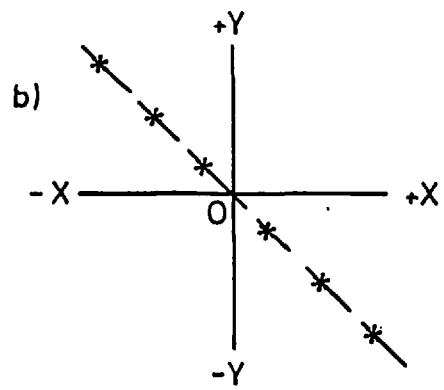
where T_i is the transformed variate value for sample (or variable) i.

FIGURE 27. ILLUSTRATING THE RELATIONSHIP BETWEEN LINEAR CORRELATION AND VALUES FOR THE PRODUCT MOVEMENT CORRELATION COEFFICIENT (r).



r = +1·00

Perfect positive correlation between X and Y.



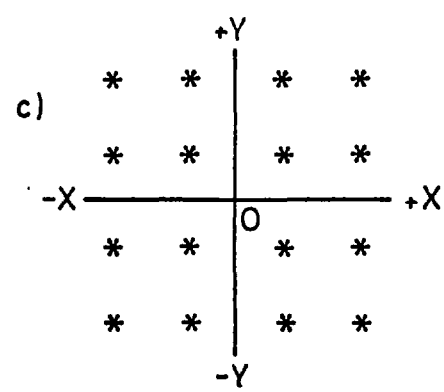
r = -1·00

Perfect negative correlation between X and Y.

LEGEND

* Datum points plotted graphically for two variables X against Y.

– – Linear trend for X values against Y values.



r = 0·00

No correlation between X and Y.

FIGURE 28. THE GRAPHICAL REPRESENTATION OF SIMILARITY MEASURES BASED ON THE ANGULAR RELATIONSHIPS BETWEEN VECTORS.

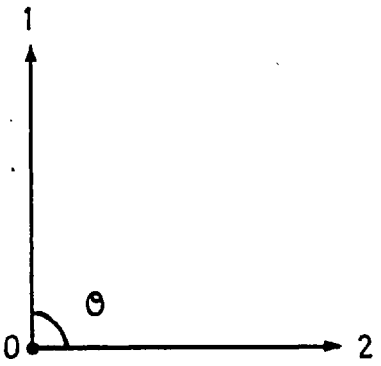
a)



$\Theta = 0°$

Cos. Θ = +1·00 (perfect positive correlation)

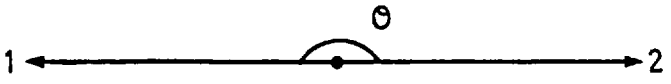
b)



$\Theta = 90°$

Cos. Θ = 0·00 (no correlation at all)

c)



$\Theta = 180°$

Cos. Θ = -1·00 (perfect negative correlation)

X_i is the untransformed numerical value for variate X on sample i.

X_{min} and X_{max} are the minimum and maximum numerical values within the sample population of X values.

(ii) standardisation

$$Z_{xi} = \frac{X_i - \bar{X}}{\sigma_x} \qquad \text{5-XII}$$

where Z_{xi} is the transformed variate (X) value for sample (or variable) i.

X_i is the untransformed variate value for sample (or variable) i.

$\bar{X}$ is the mean value of all X_i values

and σ_x is the standard deviation of X_i values about the mean $\bar{X}$.

If the standardised value is substituted into equation 5-IX then

$$\cos\theta_{xy} = \frac{\sum Z_{xi} \cdot Z_{yi}}{\sum Z_{xi}^2 \cdot \sum Z_{yi}^2} \qquad \text{5-XIII}$$

since $$\sigma_x^2 = \frac{\sum Z_{xi}^2}{N} \qquad \text{5-XIV}$$

and $$\sigma_y^2 = \frac{\sum Z_{yi}^2}{N} \qquad \text{5-XV}$$

then equation 5-IX may be rewritten to give:-

$$\cos\theta_{xy} = \frac{\sum Z_{xi} \cdot Z_{yi}}{N \cdot \sigma_x^2 \cdot \sigma_y^2} \qquad \text{5-XVI}$$

or $$\cos\theta_{xy} = \frac{\sum Z_{xi} \cdot Z_{yi}}{N \cdot \sigma_x \cdot \sigma_y} \qquad \text{5-XVII}$$

This is identical to equation 5-VIII and so the relationship between r_{xy} and $\cos \theta_{xy}$ becomes

$$r_{xy} = \cos \theta_{xy} = \frac{\sum Z_{xi} \cdot Z_{yi}}{N. \sigma_x . \sigma_y} \qquad 5\text{-XVIII}$$

This relationship is only true if standardised values for X and Y are used in the computations and if the X and Y frequency distribution are gaussian so that $\bar{Z}_x = \bar{Z}_y = 0$. Thus it follows that providing these constraints are valid then the factor analysis of a matrix of product moment or cos θ correlation coefficients will be identical. However, for geochemical data the gaussian distribution constraint is rarely upheld even after the data has been subjected to the standard normalising transformations.

The matrix of correlation coefficients is always square and symmetrical. The values in the principal diagonal represent the correlation of the variables (or subjects) with themselves. It is normal in studies based on these correlations to insert values of 1.00 in the principal diagonal positions, thus indicating that the variables (or subjects) are perfectly correlated with themselves. However, the values used in the principal diagonal are critically important for factor analysis, and the optimum procedure is the subject of some controversy (Harman, op.cit.). It is generally agreed that the ideal value to be inserted should be the communality of the variable (or subject), which the factor model will yield. However, since this cannot be ascertained until after the

factor analysis and since the analysis cannot be performed until values are placed in these positions, it is necessary to use some other value measure. The controversy relates to whether unities (1.00) should be placed in these positions or whether the highest correlation coefficient exhibited by the variate (or subject) under consideration should be inserted. If a principal components solution is adopted then all the communalities will be 1.00 and unities can be used. However, if a principal axis solution is chosen then the communalities will not equal unity, and the fewer factors extracted, the less valid will be the use of unities in the diagonal. The procedure adopted in this study has been to insert unities in the principal diagonal because the first stage in the analysis was always to obtain a principal components solution.

The factor analysis can be used to give unrotated and rotated orthogonal solutions and also a non-orthogonal oblique solution. The orthogonal factor (or vector) loadings for any variable (or subject) on any factor are stochastically independent, or uncorrelated, with factor loadings of that same element on other factors. The vector loadings for elements on the oblique factors are not stochastically independent but are correlated to varying degrees with loadings on the other factors. There is again a certain amount of controversy as to whether the rotated orthogonal or oblique non-orthogonal factors are preferable. The main advantage of orthogonal solutions is that because they are

uncorrelated, the results may be utilised for further multivariate statistical analysis, when this property is of critical importance. The main advantage of oblique factors is that by not forcing the data onto orthogonal axes, but by allowing the factor axes to be aligned along those of the vector clusters, they may provide models which more nearly approach reality in the natural environment. The procedure adopted in this study has been to compare the rotated and oblique solutions, in order to choose the solution which appeared to be more geologically meaningful.

The Manson and Imbrie Q-mode programme (op.cit.) produces unrotated, rotated and oblique factor solutions for any number of factors up to 100, for a maximum of 100 samples. The results give the vector leadings of each sample on each factor. The vector loadings may vary between -1.00 and 1.00 but the highest loadings are always positive. The orthogonal solutions are mathematically derived and though only a few samples exhibit very high loadings ($\geqslant$0.900) on them, the factors are difficult to interpret. The oblique solution selects factors which coincide with certain samples of extreme geochemical compositions. The remaining samples are then classified against these 'end-members', so that the vector loadings represent the degree of similarity of the samples to the end-member.

The Manson and Imbrie R-mode programme will process an unlimited number of samples with data for up to 100 variables.

The vector loadings for unrotated, rotated and oblique solutions are given for factor models with up to 100 factor axes. The factor (or vector) loadings represent the importance of any particular element on a factor. The oblique solution selects a single element as the end-member. The remaining factor loadings in an oblique factor represents the similarity or, in geochemical parlance, the coherence between the other elements and the end-member.

The oblique factor solutions of the Garrett R-mode programme (op.cit.) are different from those of Manson and Imbrie. The orthogonal factors are identical except that the order may be changed. The factor loadings including those which are high may be negative or positive, ranging between -1.000 and +1.000. Moreover, whilst the orthogonal solutions are similar to those of Manson and Imbrie, the same is not true for the oblique solutions, where one element is not selected as an end-member. The effect of the oblique solutions is to heighten the contrast between the high and low factor loadings, compared with the rotated solution. It is also possible to control the intensity of this contrast by selecting solutions of varying obliquity. The procedure adopted in this study was to employ the solutions of minimum obliquity. Another feature of this programme is that after producing the rotated and oblique solutions it is possible to generate sample scores on each of the factors. These factor scores (Rscores,

after Garrett, op.cit.) represent the degree to which the factor is represented in each sample. The computational mechanism by which the factor score (R) is derived is shown below:

$$R_{ij} = \sum_{k=1}^{N} V_{kj} Z_{ki} \qquad 5\text{-XIX}$$

Where R_{ij} is the factor score of sample i on factor j;

V_{kj} is the vector loading of element k on factor j;

Z_{ki} is the standardised concentration of element k on sample i;

and N is the number of elements included in the R-mode analysis. An important property of the factor score population is that it has zero mean ($\overline{X} = 0$) and unit variance ($\sigma^2 = 1.00$), that is, the factor scores are standardised values. When the factor score populations are gaussian then these factor scores may be assumed to be probabilistically meaningful. Another noteworthy feature is that if the sum of the vector loadings is negative, then the factor scores indicating a high component of that factor will also be negative. Such a factor is henceforth referred to as a negative factor. The converse relationship holds for positive factors.

5.4.0. COMPARISON OF R-MODE AND Q-MODE PROCEDURES ON GEOCHEMICAL DATA

An orientation study was initiated to establish which of the two factor analytical procedures was the most relevant for

interpreting the regional geochemical data.

5.4.1. Evaluation procedure

The factor solutions for both modes have been used for the evaluation. The Q-mode programme (Manson and Imbrie, 1964) computes sample scores on each factor and these values may be plotted onto maps in order to illustrate the areal dispersion patterns. The R-mode programme (Manson and Imbrie, op.cit.) does not compute sample scores and consequently only the factor solutions from the two modes are comparable.

The alternative R-mode programme (Garrett, 1967) has also been employed because it employs a different oblique solution procedure to the Manson - Imbrie programme. The oblique solution from the Garrett programme has been compared to the rotated and oblique solutions from the Manson - Imbrie R-mode programme.

The data used for the evaluation forms part of the N. Wales regional reconnaissance survey data. This area was chosen in preference to the other two because:

(i) the main geological units are large, the boundaries between them are well defined and, consequently, the majority of sampled catchments lie wholly within a single geological unit.

(ii) the main geochemical features for this regional

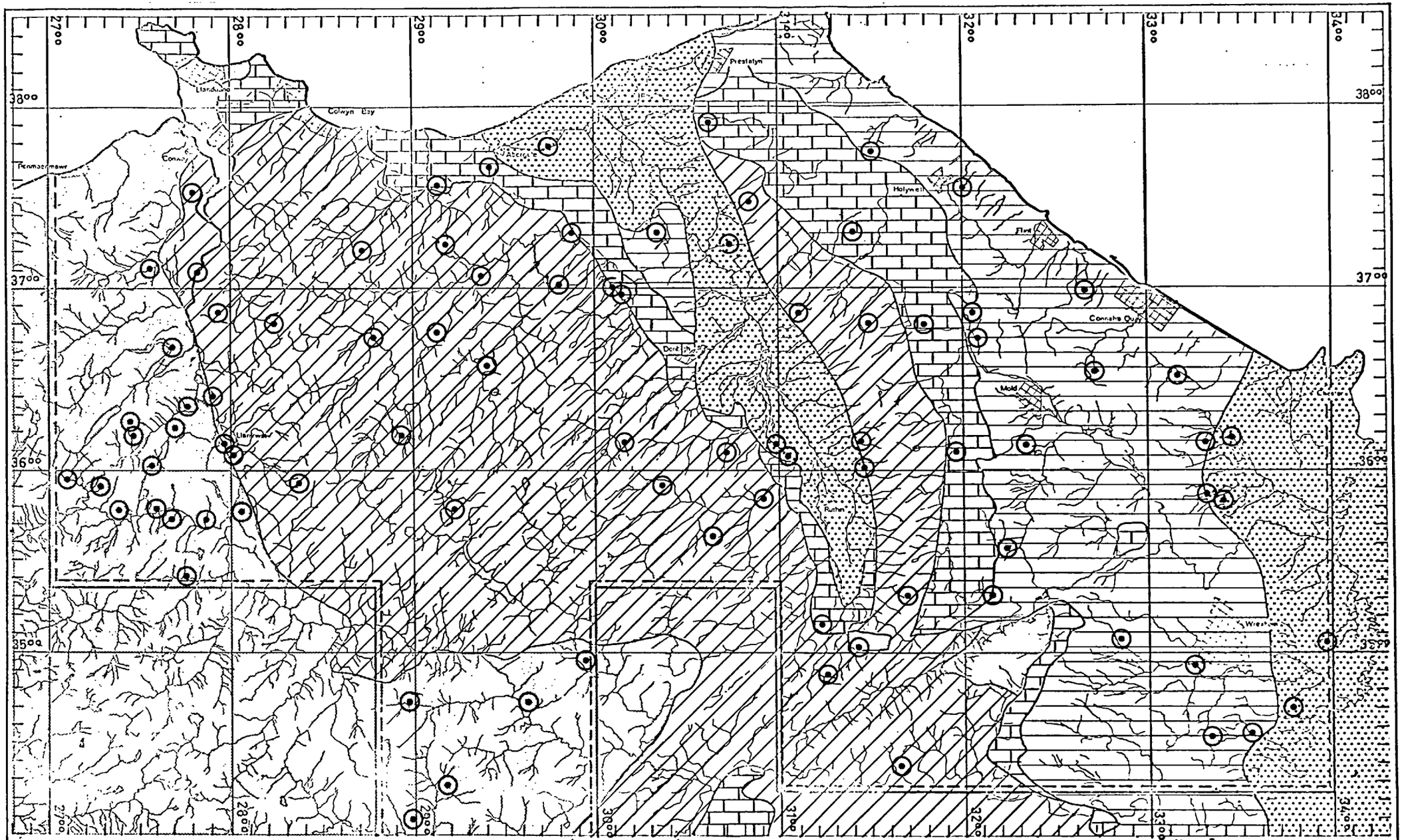
data have been largely established and evaluated.

The evaluation has involved the R- and Q-mode analysis of three subsets drawn from the N. Wales data. It was necessary to use subsets because the Q-mode programme only processes up to 100 sample data simultaneously, and consequently it would have been impossible to process the total data set. Three subsets were analysed because this number was considered to be the minimum required for a rigorous evaluation of the stability of the R- and Q-mode solutions.

The subsets were constituted in such a manner as to avoid the introduction of any new major source of bias. The regional survey area was subdivided into nine equal sized sub-areas. A maximum of 10 drainage sediment samples were selected from each sub-area. The sub-area sampling was so contrived that each major geological unit represented within the sub-area was sampled. The number of samples representing each geological unit represented within each sub-area approximates to the numerical proportion of the total sub-area samples over each unit. This numerical bias was preserved in the subsets to facilitate extrapolation of the results to the whole population. The subsets were comprised of 86, 87, and 86 samples respectively.

The areal distributions of the three subsets are displayed in figures 29, 30, and 31. The geochemical composition of the

FIGURE 29 THE DISTRIBUTION OF DRAINAGE SEDIMENT SAMPLES OF SUBSET 1 IN THE N.WALES REGIONAL SURVEY AREA



REGIONAL GEOCHEMICAL RECONNAISSANCE
STREAM SEDIMENT SURVEY

DENBIGHSHIRE

Sampled area

Project 65
May 1967
Applied Geochemistry Research Group
Imperial College, London, S.W.7.

N

0 1 2 3 4
miles

GEOLOGICAL KEY

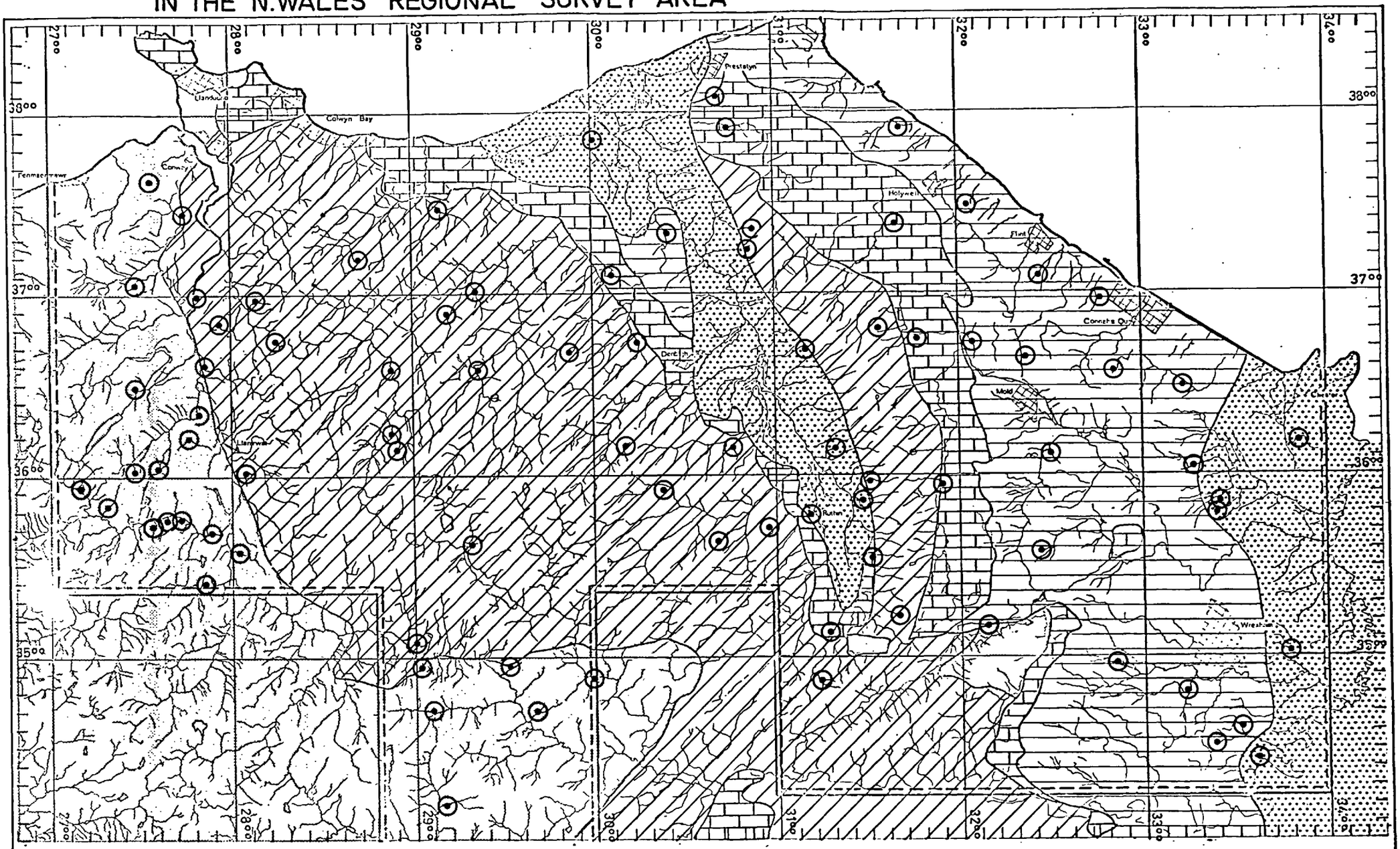
- PERMO-TRIASSIC (Red sandstones with subordinate shales)
- SILESIAN (Shales, sandstones, seat-clay and coal)
- DINANTIAN (Limestones with subordinate shales and cherts)
- SILURIAN (Soapy mudstones with subordinate sandstones)
- ORDOVICIAN (Slates and acid volcanics with subordinate dolerites)

SUBSET 1

⊙ SAMPLE LOCATIONS

Regional Geochemical Survey for N.E.R.C.
(Institute of Geological Sciences)

FIGURE 30 THE DISTRIBUTION OF DRAINAGE SEDIMENT SAMPLES OF SUBSET 2 IN THE N.WALES REGIONAL SURVEY AREA



REGIONAL GEOCHEMICAL RECONNAISSANCE
STREAM SEDIMENT SURVEY

DENBIGHSHIRE

Sampled area

Project 65
May 1967
Applied Geochemistry Research Group
Imperial College, London, S.W.7.

N

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miles

GEOLOGICAL KEY

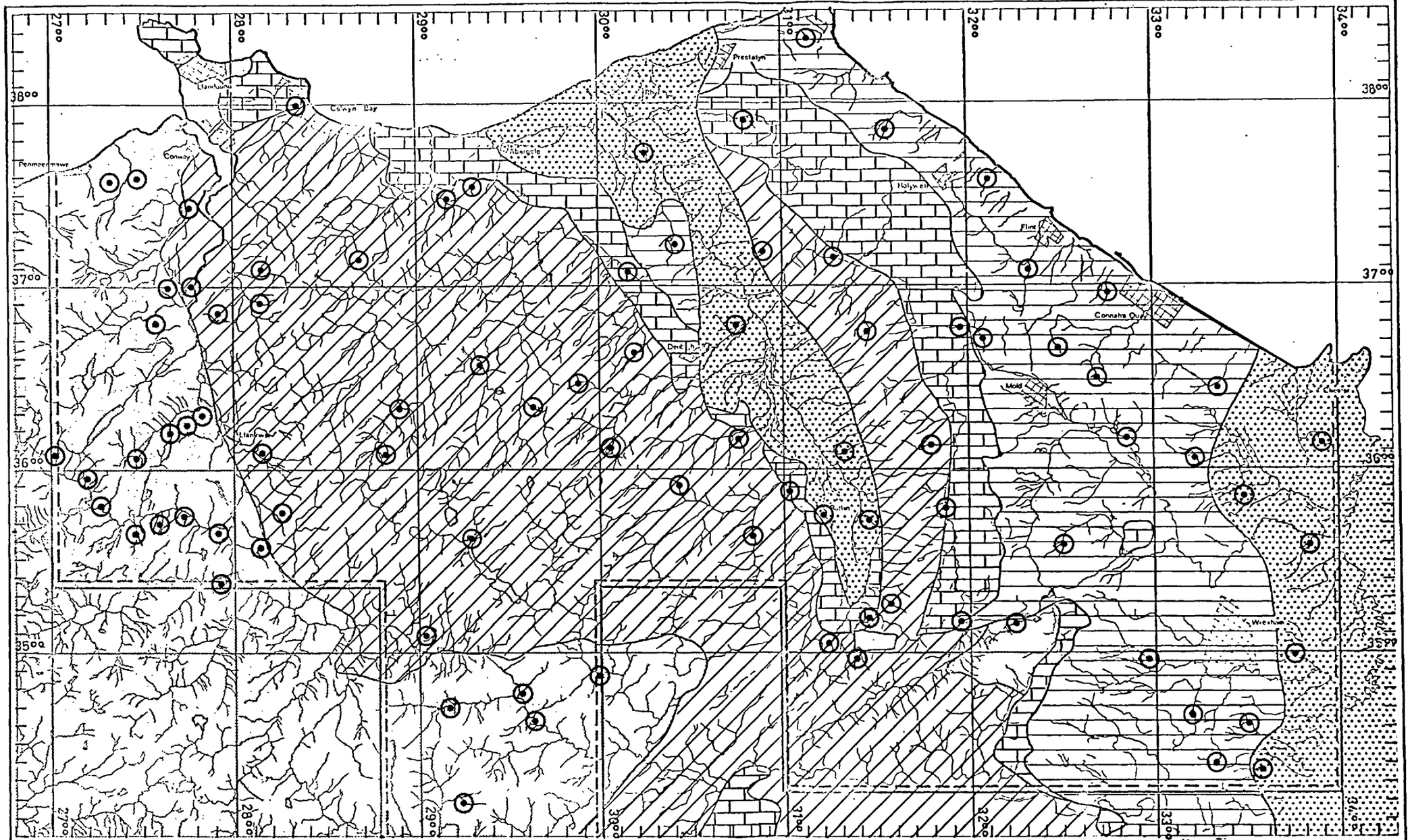
- PERMO-TRIASSIC (Red sandstones with subordinate shales)
- SILESIAN (Shales, sandstones, seat-clay and coal)
- DINANTIAN (Limestones with subordinate shales and cherts)
- SILURIAN (Soopy mudstones with subordinate sandstones)
- ORDOVICIAN (Slates and acid volcanics with subordinate dolerites)

SUBSET 2

⊙ SAMPLE LOCATIONS

Regional Geochemical Survey for N.E.R.C.
(Institute of Geological Sciences)

FIGURE 31 THE DISTRIBUTION OF DRAINAGE SEDIMENT SAMPLES OF SUBSET 3 IN THE N. WALES REGIONAL SURVEY AREA



REGIONAL GEOCHEMICAL RECONNAISSANCE
STREAM SEDIMENT SURVEY

DENBIGHSHIRE

Sampled area

Project 65
May 1967
Applied Geochemistry Research Group
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0 1 2 3 4
miles

GEOLOGICAL KEY

- PERMO-TRIASSIC (Red sandstones with subordinate shales)
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SUBSET 3

⊙ SAMPLE LOCATIONS

Regional Geochemical Survey for N.E.R.C.
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subsets was checked by establishing for each, the geometric means of all trace elements to be included in the analysis, (see table 6). It may be seen that the agreement is good for the elements Ag, As, Co, Cr, Cu, Ga, Fe, Mn, Mo, Ni, Sn, Ti, and V but is less good for Pb and Zn. Subset II shows somewhat lower levels for Pb and Zn compared to the other two subsets. It was considered that apart from these two elements, the agreement was sufficiently good to use these unmodified subsets for the evaluation of factor analysis.

Continued.

Table 6: Geometric mean trace element concentration levels in the three subsets from the N. Wales regional survey data.

Element	Subset I	Subset II	Subset III
Ag	<0.2*	<0.2	<0.2
As	6	5	5
Co	20	20	20
Cr	64	61	67
Cu	33	33	34
Fe	2.78 %	2.74 %	2.90 %
Ga	17	17	18
Mn	581	571	580
Mo	<2	<2	<2
Ni	37	36	40
Pb	90	68	81
Sn	6	5	7
Ti	2899	2857	2929
V	78	73	82
Zn	249	187	239
No. of Samples	86	87	86

* Concentrations in ppm unless otherwise specified.

5.4.2. Criteria for evaluating R- and Q-mode factor analysis

The comparison between factor solutions of these two modes would depend on the extent to which they could indicate within each subset those trace element associations known to exist within the N. Wales regional survey area. These associations are summarised below:-

(i) As-Co-(Cu)-Mn-Zn-(Fe): controlled by variations in the secondary environment (elements within parentheses are weaker members of the association).

(ii) (Ag-Cu)-Pb-Zn: caused by contamination related to mining and metallurgical operations as well as to mineralisation.

(iii) (Fe)-Mo: found in areas underlain by pyrite-rich Ordovician volcanic rocks.

(iv) (Cr-Ga-Fe-Ti-V): this has not been recognised as an established association, but the elements all exhibit similar regional dispersion patterns.

The ability of the factor modes to identify these associations will demonstrate the applicability of these techniques for the interpretation of multi-element regional data. The extent to which the solutions agree for the different subsets is an expression of the stability of these associations. It is clear that if results from the subset data are to be extrapolated to the total data set, then it is vital that the results for the

individual subsets should exhibit good agreement. A corollary of this is that, only if results from the data subsets can be extrapolated to the total data set, can results from the total set be confidently extrapolated to the whole regional survey area.

5.4.3. Results of the R-mode factor analysis

Introduction

The orthogonal and oblique solutions from R-mode analysis of the untransformed subset data have been obtained for the 2, 3, 4, 5 and 10 factor models using the Manson and Imbrie programme (op. cit.). The oblique factor models from the R-mode analysis have also been obtained using the Garrett programme (op. cit.) with untransformed and log-transformed subset data. The rotated solutions from the Garrett programme have not been presented since they are nearly identical to those from the Manson - Imbrie programme, only the order of the factors is different.

The R-mode factor solutions have been summarised and tabulated in order to demonstrate the significantly associated elements represented by each factor. The associations have been constituted by including only those elements with factor (or vector loadings) in excess of $\pm$0.200. Moreover, elements with loadings between /0.200/ and /0.299/ have been included only as

tentative members of each factor association, and this status has been indicated in the tables.

The individual factor solutions have been evaluated in terms of the stability of the factor associations in the three subsets. The geochemical validity of the factor associations are discussed at the end of the section.

Principal axis solutions (unrotated orthogonal factors)

The unrotated factor associations have been summarised in tables 7 and 8.

The 10 factor model displays associations which generally decrease in size from the first to the last factor. All factors, except number 1, include both positive and negative associations. The majority of the elements in factor 1 are common to all three subsets. The elements Ag, Pb, and Zn are present in the positive component of the factor 2 association. The lower factors (3 to 10) sometimes exhibit a measure of agreement between at most two elements, in the positive association whilst the negative components indicate considerably less agreement.

The lower factor models (2, 3, 4, and 5) include associations which are essentially the same as their equivalents in the 10 factor model. An example will clarify this last statement, the associations in the 5 factor model are almost identical to factor associations

Table 7. The trace element associations indicated by the R-mode factor analysis in the 10 factor model for unrotated, orthogonal axes.

Factor	Subset 1	Subset 2	Subset 3
1	Fe,Ga,Co,V,Cu,Ti,As, Ni,Mo,Mn,Cr,Sn, (Zn,Ag). ∅	Fe,V,Ga,Ti,Ni,Co, Cr,Mn,As,Mo,Cu.	Ti,V,Ga,Fe,Cu,Ni, As,Co,Sn,Mo,Mn,(Cr).
2	Zn,Ag,Pb,Mo,As, (Sn) +ve.* Ti,Cr,V,(Ni,Ga)-ve.	Pb,Zn,Ag,Mo,Mn, As,(Cu) +ve. Cr,(Ga,V,Ni) -ve.	Zn=Pb,Ag,Cu +ve. Mn,(Co) -ve.
3	Mn,Sn +ve. Ag(Cr,Ni,V,Pb,Zn) -ve.	Mn,As,Co +ve Cu,Ni,Cr,Zn,Pb, (Mn) -ve.	Mn,Co,(Pb,Zn) +ve. Ni,Ga,(V,Fe) -ve.
4	Mo,As,(Zn) +ve. Pb,Ag=Ni,(Mn) -ve ≠	Mo,Fe,(As) +ve. Cr,(Zn,Pb,Co,Mn, Ga) -ve.	Mo,Fe,(Cu) +ve. V,Ga,(Cr,Sn,Ti) -ve.
5	Ni,(Mo,Cr) +ve. (Ti) -ve.	Sn +ve. (Ag,Cr) -ve.	Cr,Ni +ve. Sn,(V) -ve.
6	Co,Cr +ve. (Ti=Sn,V,Zn) -ve.	Cu,(Co,Ni)+ve. Ag,Sn,(V,Ga)-ve.	Ag,(Ga) +ve. Sn,(Cr) -ve.
7	Co,Ni +ve. Cr -ve.	Ag,Cu +ve. (Cu,Pb,Zn)-ve.	Ag,Cr +ve. Ni,(Zn) -ve.
8	Cr +ve. Mo,(Fe,Ti) -ve.	Ni +ve. Cu,As -ve.	Ni,Sn,(Ag) +ve. (Ti) -ve.
9	(Ag) +ve. Cu(Ti) -ve.	Cr +ve. (Ga,Cu) -ve.	Cu,(As) +ve. (Pb,Fe) -ve.
10	(Ti) +ve. (V,Sn) -ve.	(As) +ve. (Sn) -ve.	As,(Mo) +ve. Cu -ve.

LEGEND

* +ve, -ve; refers to the sign on the vector (or factor) loadings $\geq$/0.200/.

≠ Ag=Ni; the vector (or factor) loadings on Ag and Ni are equal.

∅ (Zn,Ag); the vector loadings for Zn and Ag lie in the range /0.200/ to /0.299/.

Table 8. The trace element associations indicated by the R-mode factor analysis in the 5, 4, 3, and 2 factor models for unrotated orthogonal axes.

Factor		Subset 1	Subset 2	Subset 3
5 FACTOR MODEL	1	Fe,Ga,Co,V,Cu,Ti,As, Ni,Mo,Mn,Cr,Sn, (Zn,Ag). ∅	Fe,V,Ga,Ti,Ni,Co,Cr, Mn,As,Mo,Cu.	Ti,V,Ga,Fe,Cu,Ni,As, Co,Sn,Mo,Mn,(Cr).
	2	Zn,Ag,Pb,Mn,As, Cu,(Sn) +ve* Ti,Cr,V,(Ga), -ve.	Pb,Zn,Ag,Mo,Mn, As,(Cu) +ve. Cr,(Ga,V,Ni) -ve.	Pb=Zn,Ag,Cu +ve. Mn,(Co) -ve.
	3	Mn,Sn +ve. Ag,(Cr,Ni,V,Pb, Sn) -ve.	Mn,As,Co +ve. Cu=Ni,Cr,Zn,Pb, (Mo) -ve.	Mn,Co,As,(Pb, Zn) +ve. Ni,Ga,(V,Fe) -ve.
	4	Mo,As +ve. Pb,Ag=Ni,(Mn) -ve.	Mo,Fe,(As) +ve. Cr,(Zn,Pb,Co,Mn, Ga) -ve.	Mo,Fe,(Cu) +ve. V,Ga,(Cr,Sn,Ti) -ve.
	5	Ni,(Mo,Cr) +ve. (Ti) -ve.	Sn +ve. (Ag,Cr) -ve.	Cr,Ni +ve. Sn,(V) -ve.
4 FACTOR MODEL	1	Fe,Ga,Co,V,Cu,Ti,As, Ni,Mo,Mn,Cr,Sn, (Zn,Ag)	Fe,V,Ga,Ti,Ni,Co,Cr, Mn,As,Mo,Cu.	Ti,V,Ga,Fe,Cu,Ni,As, Co,Sn,Mo,Mn,(Cr).
	2	Zn,Ag,Pb,Mo,As,Cu, (Sn), +ve. Ti,Cr,V,(Ni,Ga) -ve.	Pb,Zn,Ag,Mo,Mn, As,(Cu) +ve. Cr,(Ga,V,Ni) -ve.	Pb=Zn,Ag,Cu +ve. Mn, (Co) -ve.
	3	Mn,Sn, +ve. Ag,(Cr,Ni,V, Pb,Zn) -ve.	Mn,As,Co +ve. Cu=Ni,Cr,Zn, Pb,(Mo) -ve.	Mn,Co,As,(Pb, Zn) +ve. Ni,Ga,(V,Fe) -ve.
	4	As,(Zn) +ve. Pb,Ag=Ni,Mn -ve.	Mo,Fe,(As) +ve. Cr,(Zr.,Pb,Co, Mn,Ga) -ve.	Mo,Fe,(Cu) +ve. V,Ga,(Cr,Sn,Ti) -ve.
3 FACTOR MODEL	1	Fe,Ga,Co,V,Cu,Ti, As,Ni,Mo,Mn,Cr,Sn, (Zn,Ag).	Fe,V,Ga,Ti,Ni,Co, Cr,Mn,As,Mo,Cu.	Ti,V,Ga,Fe,Cu, Ni,As,Co,Sn,Mo, Mn,(Cr).
	2	Zn,Ag,Pb,Mo,As,Cu, (Sn), +ve. Ti,Cr,V,(Ni,Ga) -ve.	Pb,Zn,Ag,Mo,Mn, As,(Cu) +ve. Cr,(Ga,V,Ni) -ve.	Pb=Zn,Ag,Cu +ve. Mn,(Co) -ve.
	3	Mn,Sn +ve. Ag,(Cr,Ni,V, Pb,Zn) -ve.	Mn,As,Co +ve. Cu=Ni,Cr,Zn,Pb, (Mo) -ve.	Mn,Co,As,(Pb,Zn) +ve. Ni,Ga,(V,Fe) -ve.

Table 8 (continued).

Factor		Subset 1	Subset 2	Subset 3
2 FACTOR MODEL	1	Fe,Ga,Co,V,Cu,Ti,As, Ni,Mo, Mn, Cr,Sn (Zn,Ag).*	Fe,V,Ga,Ti,Ni,Co,Cr, Mn,As,Mo,Cu.	Ti,V,Ga,Fe,Cu,Ni, As,Co,Sn,Mo,Mn,(Cr).
	2	Zn,Ag,Pb,Mo,As ∅ Cu,(Sn) +ve. Ti,Cr,V,(Ni,Ga)-ve.	Pb,Zn,Ag,Mo,Mn, As,(Cu) +ve. Cr,(Ga,V,Ni) -ve.	Pb=Zn,Ag,Cu +ve. Mn,(Co) -ve.

LEGEND

* (Zn,Ag); parentheses indicate that the vector loadings for Zn and Ag are on the range /0.200/ and /0.299/.

∅ +ve, -ve; these indicate the sign on the vector (or factor) loadings $\geq$ /0.200/.

1 to 5 in the 10 factor model. The same feature is apparent with models with less than 5 factors though minor changes are apparent.

The common associations indicated by the 5 and 10 factor solutions are:-

(i) Fe-Ga-Ti-V; which resembles the tentative association of elements showing similar regional patterns in N.Wales. Moreover, this association always appears as the first association and is thus, mathematically, the most important.

(ii) Pb-Zn; this constitutes the mineralisation-metallurgical contamination association and appears as the second most important association.

(iii) As-Co-Mn; which does not appear in subset 1, resembles an incipient form of the mobile element association affected by variations in the secondary environment.

(iv) Mo-Fe; this association, which in subset 1 is featured as Mo-As, might represent the geochemical association controlled by the suboutcropping of pyritic volcanic rocks in the Ordovician strata.

Rotated orthogonal factor solution

The rotated factor associations have been summarised in tables 9 and 10.

The 10 rotated factors solution exhibits a number of

generally significant features. The number of elements included in the factor associations is generally reduced compared to the unrotated factor associations, and no factors include both positive and negative associations. Similar associations do not necessarily occur in the equivalent factors, for instance, factors 4 (Pb-Ag-Zn-(Cu)) and 6(Co-Fe-As-(Mn-Ga)) in subset 1 are very similar to factors 2 and 3 respectively in subsets 2 and 3. The agreement between four of the factor associations in the three subsets is quite good, these are:-

(i) factor 1 in all three subsets for the elements Fe, Ga, Ni, V, and Ti.

(ii) factor 4 (subset 1) and factor 2 (subsets 2 and 3) for the elements Ag, Pb and Zn.

(iii) factor 6 (subset 1) and factor 3 (subsets 2 and 3) for the elements As, Co, Fe and Mn.

(iv) factor 5 (subset 1) and factor 4 (subsets 2 and 3) for the elements Fe and Mo.

The remaining factor associations exhibit little agreement between the three subsets.

The 5 rotated factor model, unlike the unrotated model does not display such a close similarity to the factor associations of the 10 factor model. Moreover, the last factor also includes both positive and negative associations. The agreement between 4 of the factor associations, factors 1 to 4 in all three subsets

Table 9. The trace element associations indicated by the R-mode factor analysis in the 10 factor model for rotated, orthogonal axes

Factor	Subset 1	Subset 2	Subset 3
1	V,Ga,Ti,Fe,Co,Ni, Cr,(Cu)*	Ga,V,Ti,Fe,Cr,Ni,(Co).	V,Ga,Ti,Fe,Ni, (Sn,Cu).
2	Zn,As,Cu,Mo,Ag, (Ga).	Zn,Pb,(Ag).	Pb,Zn,Cu,Ag.
3	Sn,Mn,(As,Fe).	Mn,Co,As,Fe.	Mn,Co,As,(Ti).
4	Pb,Ag,Zn,(Cu).	Mo,Fe,As,(Ni, V).	Mo,Fe,Cu,(Ti).
5	Ni,(Ga).	Sn.	Cr.
6	Co,Fe,As,(Mn, Ga).	Cu,(Ni).	Sn.
7	Cr	Ag.	Ag,(Pb).
8	Mo,Fe,Cu,Ag, (Zn,As).	Ni,(Ga).	Ni,Ga,(Fe).
9	Cu,(Zn,Sn)	Cr,Ti,(Ni)	Cu,(Zn)
10	Ti,(Mn)	As	As

LEGEND

* ( ); parentheses indicate that the vector (or factor) loadings on the enclosed element(s) are between /0.200/ and /0.299/.

Table 10. The trace element associations indicated by the R-mode factor analysis in the 5,4,3 and 2 factor models for rotated, orthogonal axes.

Factor		Subset 1	Subset 2	Subset 3
5 Factor Model	1	V,Ga,Ti,Fe,Co,Cr, Ni,As,(Cu).*	Cr,Ga,Ti,V,Ni,Fe, Cu,Co.	V,Ga,Ti,Sn,Ni, Fe,Cu.
	2	Mo,Zn,Cu,As,Ag,Fe, (Ga).	Pb,Zn,Ag,Cu, (Mo).	Zn,Pb,Ag,Cu.
	3	Mn,Sn,As,(Co, Fe).	Mn,Co,As,Fe, (V,Ti,Ga).	Mn,Co,As,(Ti).
	4	Pb,Ag,(Zn,Cu).	Mo,Fe,Cu,Ni, As,V.	Mo,Fe,Cu,Ni, (Ti).
	5	Ni,Cr,(Fe,Cu, V) +ve∅ (As). -ve	Sn,(Ni) +ve. (Ag) -ve.	Cr,Ni,(Ga).
4 Factor Model	1	V,Ga,Ti,Fe,Ni, Cr,Co,Cu.	Ga,V,Cr,Ti,Ni, Fe,Cu,(Co, Mo).	V,Ga,Ti,Ni,Sn, Cr,Fe,Cu.
	2	Zn,Mo,As,Cu,Ag, Fe,(Ga).	Zn,Pb,Ag,Cu, (Mo).	Zn,Pb,Ag,Cu.
	3	Mn,Sn,As,Co, Fe.	Mn,Co,As,Fe, (V,Ti,Ga).	Mn,Co,As,(Ti).
	4	Pb,Ag,Zn,Cu,Ni.	Mo,Fe,As, (V,Ti,Ga).	Mo,Fe,Cu,Ni, (Ti).
3 Factor Model	1	V,Ga,Fe,Ti,Cr,Co, Ni,Cu,(Mo,As). +ve. (Pb). -ve.	V,Ga,Ni,Ti,Cr, Fe,Cu,Mo,(Co).	Ga,Ti,V,Fe,Ni, Cu,Mo,Sn, (Cr,As).
	2	Zn,Ag,Mo,Cu,As, Pb,(Fe).	Pb,Zn,Mo,Ag,Cu.	Zn,Pb,Ag,Cu.
	3	Mn,Sn,As,Fe, Co,(Cu,Mo).	Mn,As,Co,Fe, (V,Ti,Ga).	Mn,Co,As,(Ti).
2 Factor Model	1	V,Ga,Fe,Ti,Co,Cr,Ni, Mn,Cu,(As,Sn). +ve. Pb -ve.	V,Ga,Fe,Ti,Cr,Co, As,Mn,Cu,Mo.	Ti,V,Ga,Fe,Ni,As, Cu,Co,Mn,Sn, Mo,(Cr).
	2	Zn,As,Cu,Ag,Mo,Pb,Sn, Fe,Mn,(Co).	Pb,Zn,Mo,Ag,Mn, As,Cu,(Fe,Co) +ve. (Cr) -ve.	Zn,Pb,Ag,Cu +ve. (Mn,Co) -ve.

LEGEND

* ( ); parentheses indicate factor (or vector) loadings between /0.200/ and /0.299/.

∅+ve,-ve; indicate signs of two opposed trace element associations included within the same factor.

is quite good, though the factor order differs in subset 1. The last factor includes Ni in all three subsets but otherwise they exhibit little agreement.

The lower factor models (2, 3 and 4) include associations which are similar in all three subsets but the order of elements within the factors and of the factors themselves, particularly for subset 1, tends to be different.

The agreement between the rotated factor associations and those previously recognised is better than for the principal axis solution. Examples of this closer agreement can be observed in the four factor model for subset III, where Cr is included (as well as Ni and Sn) with the Fe-Ga-Ti-V association; the association Mo-Fe appears in the 5 factor model, subset I, but is still associated with As (as well as Ag, Cu and Zn). The mobile element association As-Co-Fe-Mn-Ni-Zn is more completely constituted in the 4 rotated factor model of subsets I and II than it was in the unrotated solutions.

The main trace element associations are again clearly represented in the 10 factor models, but at least four factors in each subset represent essentially single elements.

It may be concluded that the effect of rotating the orthogonal axes has been to improve the interpretability of the factors

and their agreement with the known trace element associations.

Oblique, non-orthogonal factor solutions 1: Manson and Imbrie programme

The oblique factor associations derived from the Manson and Imbrie programme have been summarised in tables 11 and 12.

The 10 factor model includes a large proportion (between 4 and 5) of the factors with both positive and negative associations. The number of elements in the factor associations are not reduced but are redistributed into opposing associations (positive and negative). The similarity between the factor associations is in general not as good as that observed in the rotated factor solution. There are similarities between the following factor associations:-

(i) factor 1 (subsets 1, 2 and 3) for the elements Ga and V.

(ii) factor 6 (subset 1) and factor 3 (subsets 2 and 3) for Co, Fe and Mn.

(iii) factor 8 (subset 1) and factor 4 (subsets 2 and 3) for Fe and Mo.

A number of other factors have single elements in common but since they do not have common trace element associations, they have not been discussed. An association of Pb and Zn appears in factor 2 of subsets 2 and 3, but this does not appear in subset 1, where it is split between factors 2 and 4.

The 5 factor model exhibits a higher degree of agreement

Table 11. The trace element associations indicated by the R-mode factor analysis in the 10 factor model for oblique, non-orthogonal axes

Factor	Subset 1		Subset 2		Subset 3	
1	V,Ga, Ag, (Fe) Mn.	+ve.* -ve.	Ga,V,Ti,Fe.		V,Ti,Ga,Fe.	
2	As,Zn,Ga,Ag,(Mn). ϕ		Zn,Pb.		Pb,Zn.	
3	Sn,Mn (Zn)	+ve. -ve.	Mn,Co,Ti,Pb, Fe.		Co,Mn,Fe,(Ti).	
4	Pb,Ag.		Mo,Ti,Fe, V,Pb (Co)	 +ve. -ve.	Mo,Fe, (Zn)	+ve. -ve.
5	Ni,(Ga)		Sn.		Cr.	
6	Co,Fe,(Mn) Zn,Ag.	+ve. -ve.	Cu.		Sn.	
7	Cr.		Ag (Ti)	+ve. -ve.	Ag (Ti)	+ve. -ve.
8	Mo,Fe,Ag,Mn (Ga)	+ve. -ve.	Ni,Co Ti,(V)	+ve. -ve.	Ni,Ga (Ti,Mn)	+ve. -ve.
9	Cu,Zn Mn,Ag,Fe	+ve. -ve.	Cr,Ti		Cu,Zn.	
10	Ti,Mn,Fe.		As Sn,Pb	+ve. -ve.	As,(Zn) Fe	+ve. -ve.

LEGEND

* +ve,-ve; indicate signs of two opposed trace element associations included within the same factor.

ϕ ( ); parentheses indicate factor (or vector) loadings between /0.200/ and /0.299/.

Table 12. The trace element associations indicated by the R-mode factor analysis in the 5,4,3 and 2 factor models for oblique, non-orthogonal axes

Factor		Subset 1	Subset 2	Subset 3
5 Factor Model	1	V,Ti,Ga,Co,Fe,As, Cr,(Cu).Ø	Cr,Ga,Ti,V,Ni, Fe,Cu,(Co).	V,Ga,Ti,Sn,Ni,Cu, Fe.
	2	Mo,Zn,Cu,As,Ag, * (Fe,Ga) +ve. Ti -ve.	Zn,Pb,Ag,Cu, +ve. (As,V,Fe) -ve.	Zn,Pb,Ag,Cu,(As)
	3	Mn,Sn,Co,Fe, As.	Mn,Co,As,Fe, Ti,V,Ga.	Mn,Co,As.
	4	Pb,Ag,(Zn,Cu).	Mo,Fe,Ni,Cu, V,(Ti,Ga).	Mo,Fe,Cu,Ni.
	5	Ni,Cr +ve. As,Zn -ve.	Sn,Ni,(Cu) +ve. Ag -ve.	Cr,Ni,(Fe) +ve. (Sn,Ag) -ve.
4 Factor Model	1	V,Ga,Fe,Ti,Ni,Cr, Co,Cu,(Mo,As)	Cr,Ga,Ti,V,Ni, Cu,Fe,(Co)	Ga,V,Ti,Ni,Sn, Cr,Fe,Cu.
	2	Zn,Mo,As,Cu,Ag (Fe,Ga) +ve. (Ni) -ve.	Zn,Pb,Ag,Cu +ve. (As,V,Fe) -ve.	Zn,Pb,Ag,Cu(As,Sn).
	3	Mn,Sn,As,Co, Fe,(Cu).	Mn,Co,As,Fe Ti,V,Ga.	Mn,Co,As.
	4	Pb,Ag,Ni, +ve (As) -ve.	Mo,Fe,Ni,Cu V,As,(Ti,Ga).	Mo,Fe,Cu,Ni.
3 Factor Model	1	V,Ga,Fe,Ti,Cr,Ni, Co,Mn,Cu,Mo,(As).	V,Ni,Ga,Ti,Cr, Fe,Cu,Mo,(Co).	Ga,Ti,V,Fe,Cu, Ni,Mo,Sn,(Cr).
	2	Zn,Ag,Mo,Cu,As, Pb,Fe.	Pb,Zn,Mo,Cu,Ag (Fe,Ni).	Zn,Pb,Cu,Ag,As, (Mo).
	3	Mn,Sn,As,Co, Fe,(Cu).	Mn,As,Co,(Fe) +ve. Ni,Cr,(Cu) -ve.	Mn,Co,As.
2 Factor Model	1	Fe,Ga,V,Co,Ti,Ni, Cr,Cu,Mn,As,Mo,Sn. +ve. (Pb) -ve.	V,Fe,Ga,Ti,Ni,Co, Cr,Mn,As,Cu,Mo.	Ti,V,Ga,Fe,Ni,Co, As,Mn,Cu,Sn,Mo,Cr.
	2	Zn,Ag,Pb,Mo,As, Cu,Sn +ve. Cr,V,Ti,Ni,Ga -ve.	Pb,Zn,Mo,Ag,Mn, As,Cu,Fe,Co +ve. (Cr) -ve.	Zn,Pb,Cu,Ag,(Mo) (Mn,Co).

LEGEND

* +ve,-ve; indicate signs of two opposed trace element associations included within the same factor.

Ø ( ); parentheses indicate fadtor (or vector) loadings between /0.200/ and /0.299/.

between the first 4 factor associations than is shown by the equivalent factors in the 10 factor model. The association of Ag, Cu, Pb and Zn is constituted in factor 4 (subset 1) and 2 (subsets 2 and 3). However, the order of the factors differs between subset 1 and the other subsets, and so does the order of the elements within the associations. There is a still higher proportion of factors with both positive and negative associations than was observed in the rotated factor models. The same features, which have been discussed above, are shown by the 2, 3, and 4 factor models, except that the factor associations become more complex, than those of the rotated factors (including a larger number of elements) without showing better agreement with the known element associations. It is possible that this last feature is a function of the oblique solution procedure employed by Manson and Imbrie (op.cit) in the computer programme used for this analysis.

The degree to which the same trace element associations occur in all three subsets is variable. Subsets 2 and 3 generally show good agreement, for instance, in the 10 oblique factor model, the associations of factors 1-4 and 7 are very similar. The reason for the poor agreement of subset 1 with the other two is probably caused by the large effect that a small number of geochemically distinct samples will have on the correlation coefficients of a small sample population.

One example will suffice to illustrate the effect of population inhomogeneity upon the trace element correlations. The majority of samples in subset 1 bear concentrations of Sn too small to be detected by the analytical methods employed in this study. The detectable Sn concentrations appear to be distributed in a random manner (but see chapter 4). However, Sn is very consistently associated with Mn and the other mobile elements in the factor associations of subset 1, a feature not shown by the other subsets. Moreover, Sn is generally considered to be highly immobile in the secondary environment. The trace element concentration data indicated that two samples of the subset contained anomalous Sn-levels (150 ppm). Both of these samples also bear anomalous Mn (15,000 ppm) and other mobile element concentrations. It is considered that these samples have been largely responsible for inducing the apparent correlation between Sn and the mobile elements. It is evident that similar types of bias will be less easily introduced when the sample population is large.

Oblique non-orthogonal factor solutions 2: Garrett programme. Untransformed Data

The oblique factor solutions derived from the Garrett programme are summarised in tables 13 and 14. The 10 factor model consists of factors with significantly fewer elements than were observed in previous factor models. A high proportion of the factors (between 2 and 4) are unielemental, that is, including one element with a factor loading exceeding /0.200/. There is only one

Table 13. The trace element associations indicated by the R-mode factor analysis (Garrett programme), upon untransformed data, in the 10 factor model for oblique, non-orthogonal axes

Factor	Subset 1	Subset 2	u ·
1	V, Ti, Ga, Fe.	Ga,V,Ti,Fe (Cr) *	V,Ga,Ti(Fe).
2	Zn,As,Cu,Ga,(Mo)	Zn,Pb.	Pb,Zn.
3	Sn,Mn.	Mn,Co,As(Fe).	Co,Mn,As
4	Pb,Ag.	Mo,Fe (As,Ni)	Mo, Fe.
5	Cr.	Sn.	Cr.
6	Co,As,Fe, +ve.ø Zn -ve.	Cu.	Sn.
7	Ni.	Ag.	Ni, Ga.
8	Mo, Fe.	Ni +ve (Ti) -ve	Ag.
9	Cu, (Zn).	Cr (Ti).	Cu (Zn)
10	Ti (Mn)	As	As

LEGEND

* ( ); parentheses indicate a factor (or vector) loading between /0.200/ and /0.299/.

ø +ve, -ve; these indicate the signs of two opposed trace element associations included within the same factor.

Table 14. The trace element associations indicated by the R-mode factor analysis (Garrett programme), upon untransformed data, in the 5,4,3 and 2 factor models for oblique, non-orthogonal axes.

Factor		Subset 1	Subset 2	Subset 3
5 Factor Model	1	V,Ti,Ga,Fe,Co Cr,(As).*	Cr,Ga,Ti,V,Ni Fe,Cu,Co.	V,Ti,Ga,Sn,(Ni)
	2	Mo,Zn,Cu,As,Ag ø (Fe) + (Ti) -	Zn,Pb,Ag,Cu.	Zn,Pb,Ag,Cu.
	3	Mn,Sn,(Co,As, Fe)	Mn,Co,As, Fe, + (Ni) -	Mn,Co,As.
	4	Pb,Ag.	Mo,Fe,Ni Cu,As,V	Mo,Fe,Cu(Ni)
	5	Ni,Cr + As -	Sn,(Ni) + Ag	Cr,Ni - (Sn) +
4 Factor Model	1	V,Ga,Ti,Ni Fe,Cr,Co(Cu) - (Zn) +	Cr,Ga,Ti,V,Ni Fe,Cu,(Co)	V,Ga,Ti,Ni,Sn, Cr.
	2	Zn,Mo,As,Cu,Ag (Fe,Ga)	Zn,Pb,Ag,Cu.	Zn,Pb,Ag,Cu.
	3	Mn,Sn(Co,As, Fe).	Mn,Co,As, Fe,(Ti,V).	Mn,Co,As.
	4	Pb,Ag,(Ni).	Mo,Fe,As, (Cu,Ni) - Cr +	Mo,Fe,Cu(Ni)
3 Factor Model	1	V,Ga,Ti,Fe Cr,Ni,Co,Cu.	Ni,V,Ga,Cr,Ti Fe,Cu,Mo.	Ga,V,Ti,Fe Ni,Cu,Mo,Sn(Cr).
	2	Zn,Ag,Mo,Cu, Pb,As.	Pb,Zn,Mo,Ag, Cu.	Zn,Pb,Ag,Cu(As).
	3	Mn,Sn,As(Co, Fe) - (Cr) +	Mn,As,Co, Fe(V).	Mn,Co,As.

Factor		Subset 1	Subset 2	Subset 3
3 Factor Model	1	V,Ga,Fe,Ti, Co,Cr,Ni,Mn,Cu (As) - Pb,(Zn,Ag) +	V,Fe,Ga,Ti Ni,Cr,Co,As, Mn,Cu,Mo.	Ti,V,Ga,Fe,Ni As,Co,Cu,Mn,Sn, Mo(Cr).
	2	Zn,Ag,As,Mo,Cu Pb,Sn,Fe, (Mn,Co) + (Cr) -	Pb,Zn,Mo,Ag, Mn,As,Cu(Fe, Co).	Zn,Pb,Ag,Cu(Mn,Co).

LEGEND

* ( ) ; parentheses indicate a factor (or vector) loading between /0.200/ and /0.299/.

ϕ +, -; these indicate the signs of two opposed trace element associations included within the same factor.

factor (factor 8, subset 2) which includes both positive and negative components.

The 10 oblique factor solution (table 13) from the Garrett programme using untransformed data produces factors approximating to the known associations listed in section 5.5.2. However, most of the factor associations are incomplete, most notably in subsets 1 and 3, for the associations:-

(i) As-Co-Cu-Fe-Mn-Zn; only As and Co appear in all three subsets.

(ii) Ag-Cu-Pb-Zn; this is split into a number of separate factors of which Pb-Zn, Cu-Zn, and the unielemental Ag associations are most common.

(iii) Cr-Fe-Ga-Ti-V; Cr is absent.

The 5 factor model includes a higher proportion (between 1 and 2 factors) of factors with both positive and negative associations, and the agreement between the principal associations of factors 1 to 4 in the different subsets is better than in the 10 factor model. Similar features are shown by the lower factor models (2,3 and 4), and the elements in the factor associations increase in these lower models.

Oblique, non-orthogonal factor solutions 3: Garrett programme

Log-transformed data

The oblique factor solutions derived by the analysis of

log-transformed data are summarised in tables 15 and 16.

The 10 factor model includes only one factor with both positive and negative associations. There is a high proportion of unielemental factors (between 3 and 4). Three of the factor associations are similar, namely:

(i) factor 1 (subsets 1, 2 and 3) for Cr, Fe, Ga, Ni, Ti and V.

(ii) factor 2 (subsets 1, 2 and 3) for Pb and Zn.

(iii) factor 5 (subset 1) and 3 (subsets 2 and 3) for Co, Fe and Mn.

The 5 and lower factor model exhibits a considerable increase in the number of elements in each association, and still includes at least one factor with both positive and negative components. The 5 factor model indicates the following associations:-

(1) Ag-Cu-Pb-Zn; with other variably associated elements.

(2) As-Fe-Mo; which is split in subsets 1 and 2 between the secondary environment association and another factor

(3) Cr-Fe-Ga-Ti-V; which with other variably associated elements, notably Co, Cu and Ni, always constitute factor 1.

(4) As-Co-Cu-Fe-Mn-Zn; this is represented by the factor association, As-Co-Fe-Mn.

Table 15. The trace element associations indicated by the R-mode Factor analysis (Garrett paogramme), upon log-transformed data, in the 10 factor model for oblique, non-orthogonal axes.

Factors	Subset 1	Subset 2	Subset 3
1	Ti,V,Ga,Fe,Cu, Co(Cr,Ni). *	Ti,Ga,Cr,V, Fe,Ni(Co)	Ti,V,Ga,Fe,Cu (Ni,Cr).
2	Pb,Zn,Cu.	Pb,Zn.	Pb,Zn,Cu.
3	As,Co,(Fe).	Mn,Fe,Co,	Mn,Co,Fe +ve ϕ (Cu) -ve.
4	Sn	Sn	Mo(Fe,Cu).
5	Mn,Co(Fe).	Ag	Ag
6	Mo	Mo(As) +ve. (Co) -ve.	Sn.
7	Cr.	Cu.	Cr.
8	Ni,Co.	Ni,Co.	Ni(Fe).
9	Ag	As,Co.	As
10	Zn +ve. (Cu,Co) -ve.	Cr +ve. (Zn) -ve.	Cu(Co)

LEGEND

* ( ); parentheses indicate a factor (or vector) loading between /0.200/ and /0.299/.

ϕ +ve,-ve; these indicate the signs of two opposed trace element associations included within the same factor.

Table 16. The trace element associations indicated by the R-mode factor analysis (Garrett programme), upon log-transformed data, in the 5, 4, 3 and 2 factor models for oblique, non-orthogonal axes.

Factor		Subset 1	Subset 2	Subset 3
5 Factor Model	1	V,Cr,Ga,Ni,Ti, Fe,Co,Cu.	Cr,V,Ga,Ti,Ni, Fe,Cu,Co.	Ga,V,Ni,Ti,Cr, Fe,Cu,Co,Sn +ve. (Pb) -ve.
	2	Pb,Ag,Zn,Mo, Cu(Ni). *	Pb,Zn,Cu(Ni, Ag).	Zn,Pb,Cu,Sn, (Ag,Cr).
	3	As,Mo,Fe (Ag ∅ Co,Mn) +ve. Ni(Pb) -ve.	Mn,As,Co,Fe, (Mo).	Mo,As,Co,Sn, Fe (Ti).
	4	Sn,Cu.	Sn.	Mo,Cu(Fe ,As) +ve. Cr -ve.
	5	Mo,Ag,Co(Fe)	Ag,Mo,(Zn,As) +ve. (Ni) -ve.	Ag,(V)
4 Factor Model	1	Ni,V,Ti,Ga,Cr Fe,Co,Cu,Mn.	Cr,V,Ga,Ti,Ni Fe,Cu,Co.	Ga,V,Ni,Cr,Ti Fe,Cu,Co,Sn.
	2	Pb,Ag,Zn,Mo,Cu Ni.	Pb,Zn,Ag,Cu, Mo.	Pb,Zn,Ag,Cu(Sn).
	3	As,Mn,Fe,Co Mo(Cu) -ve. (Ni) +ve.	As,Mn,Co,Fe Mo.	Mn,As,Co,Sn Fe,(Ti)
	4	Sn,Cu -ve (Ag) +ve	Sn(Ni) +ve. (Ag) -ve.	Mo,Cu,(Fe,As) +ve. (Cr) -ve.

Factor		Subset 1	Subset 2	Subset 3
3 Factor Model	1	V,Ni,Ti,Ga,Cr, Fe,Co,Cu Mn.	Cr,V,Ga,Ni,Ti Fe,Cu,Co (Sn,Zn).	Ga,V,Ni,Cr,Ti Fe,Cu,Co,Sn.
	2	Pb,Zn,Ag,Cu,Mo (Sn,Ni).	Pb,Zn,Ag,Cu Mo.	Pb,Zn,Ag,Cu, (Sn).
	3	As,Mn,Mo,Sn Fe,Co(Ga,Sn)-ve (Ni) +ve.	As,Mn,Co,Fe Mo(Ti,V)	As,Mn,Co,Mo, Fe,Sn(Ti,Zn).
2 Factor Model	1	V,Fe,Ga,Ti Co,Cr,Mn,Cu,As.	V,Ga,Ti,Fe Cr,Co,Ni,Mn, Cu,As,Sn(Zn).	Fe,Ti,Ga,V,Co,Ni Cr,Cu,Mn,Sn,As (Mo,Zn).
	2	Zn,Pb,Mo,Ag,Cu Sn,As,Mn(Fe)+ve (Cr) -ve	Pb,Zn,Ag,Mo,Cu As,Mn	Pb,Zn,Ag,Cu,Mo (As,Sn).

LEGEND

* ( ) ; parentheses indicate a factor (or vector) loading between /0.200/ and /0.299/.

ø +ve,-ve; these indicate the signs of two opposed trace element associations included within the same factor.

Factor models with less than 5 factors (tables 5 and 16), show an increasingly poor representation of the known associations due to the inadequate number of factors. The effect of this is to destroy the less pronounced associations and to redistribute the constituent elements over the remaining factors, and this effect is displayed by all the factor solutions. This tendency towards a progressive destruction of the known associations is the lowest factor factors (2-4) has meant that they cannot be considered as effective representations of the geochemical data and consequently, they are not considered further.

The 5 oblique factor model from the log-transformed data, using the Garrett programme, has been seen to be superior for indicating the known associations in all three subsets to the oblique solutions from untransformed data, irrespective of the computer programme employed. Moreover, the oblique solution from the log-transformed is marginally superior to the 5 rotated factor model from the Manson-Imbrie programme, most notably, in the constitution of the mobile trace element association (namely As-Co-Cu-Fe-Mn-Zn).

Geochemical validity of the factor associations

The factor analysis has confirmed the existence of those trace element associations which had been revealed by previous investigations. These and the factor models in which they are most completely represented are discussed below.

The associations located as the most important in the subsets by all factor models has been the previously unrecognised association, Cr-Ga-Fe-Ti-V, though this has not been fully constituted in all three subsets by any but the oblique solution from log-transformed data (Garrett programme).

The contamination association related to mining activity ((Ag-Cu)-Pb-Zn) has been variously constituted within all the factor solutions, though less completely in the oblique solutions from the untransformed data, irrespective of the computer programme employed.

The secondary environment association (As-Co-(Cu-Fe)-Mn-Zn+) is never fully constituted, though it appears in truncated form in all factor solutions. The association is most fully expressed in the rotated orthogonal solutions and in the lower models (5 factors and below) of the Garrett oblique factor solution from the log-transformed data.

The trace element association enriched within the pyritic black shales in the Ordovician strata (Fe-Mo) is less completely constituted than those which have already been described. The association is most fully represented in the orthogonal rotated solution, together with a variable number of different elements in the three subsets.

Discussion

It seems apparent from this study that both the order of

variables in the factors and the relative order of factors in any model are not of prime importance. The associations which have been stable in all three subsets have sometimes shown considerably variation in the ordering of the trace elements, for instance, in the factor 1 association in table 15. The order of the factors is also of little apparent geochemical significance. An example to illustrate this may be seen in table 9, where the factor 8 (subset 1) association is apparently one of the least important factors mathematically, and yet its geochemical significance has been established beyond doubt.

This study has indicated that a log-transformation may radically improve the meaningfulness of the oblique factor models derived from the analysis of geochemical data. There seems little practical advantage in using oblique rather than rotated factor solutions, though the former are considered preferable in that they may more closely represent the correlations between the trace element associations within the regional geochemical data.

5.5.4. Results of the Q-mode factor analysis

The Q-mode factor analysis solutions from the orthogonal, unrotated and rotated axes are virtually uninterpretable since they relate to theoretical, mathematically derived mixtures of samples. It is nearly impossible to define the geochemical characteristics of this mixture. The oblique solutions relate to individual samples

(end-members) of extreme chemical composition, whose geochemical characteristics may be evaluated. The solutions for 4 models, those with 5, 4, 3 and 2 end-members have been examined.

The geochemical features of the end-members have been determined by expressing their individual trace element concentrations as percentages of the total range encountered within the subset from which they were derived. This procedure has been adopted because an identical transformation was applied to the subset data prior to the Q-mode analysis. The percentage data are summarised in tables, 17, 18, 19 and 20. The information from these figures has been simplified in table 21 in order to highlight the geochemical characteristics. The elements which are relatively high (exceeding 50 per cent) within each end-member sample are listed. When few elements in an end-member exceed 50 per cent then those elements, with the relatively highest concentrations are listed and if the percentage range value is less than 50 per cent the element is enclosed in parentheses.

It is necessary to establish the extent to which the Q-mode analysis can identify the known trace element associations listed and described in section 5.5.2., which briefly summarised are:-

(i) As-Co-(Cu)-Mn-Zn-Fe

(ii) (Ag-Cu)-Pb-Zn.

(iii) (Fe)-Mo.

(iv) Sn.

(v) (Cr-Fe-Ga-Ti-V).

The procedure adopted has been to examine the geochemical composition of the end-members, relative to that of the subset from which they were selected. If the technique is capable of characterising the association then it would be expected that each of the associations would be represented in one end-member, and this would be manifested by the relatively high concentrations of the relevant trace elements in each of the end-members. The similarity between the known associations and those characterised by the Q-mode end-members is recognisable but the factor associations are usually considerably modified, for instance, in the 5 factor model, factors 3 (subset 1), 5 (subset 2) and 4 (subset 3) all represent mineralisation. The end-member representation varies for each subset. This is related to the invariant geochemical composition of the real samples chosen as end members; each of which reflects the complex provenance and the interaction of multiple controls operating upon them. It is apparent that the correspondence between the known trace element associations and those indicated by Q-mode analysis is likely to be poor for drainage sediment data.

Another feature of the Q-mode solutions is the poor agreement between the subsets. This is probably related to the fact that Q-mode analysis selects end-members of extreme composition. These may yield either very high concentrations for certain elements or

Table 17. The percentage range concentrations of the elements in the Q-mode factor analysis end-members for the 5 factor model in the three subsets.

	Subset I					Subset II					Subset III				
Element	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Ag	16	0	‡100	0	0	0	0	0	0	18	0	48	0	0	0
As	1	0	0	0	‡78	0	0	‡94	0	9	‡76	0	0	0	15
Co	8	3	12	5	32	16	2	‡100	2	6	15	1	3	5	2
Cr	41*	‡100	19	7	19	16	0	9	5	9	11	0	*11	7	11
Cu	11	8	*25	*18	18	11	*11	16	3	*47	12	7	4	*20	12
Fe	14	6	10	4	33	*27	1	*40	1	7	20	0	3	2	13
Ga	38*	13	17	6	‡58	‡100	0	32	0	19	‡57	8	9	15	‡57
Mn	1	2	3	1	‡100	4	0	‡100	0	2	*46	0	4	1	10
Mo	0	0	0	0	0	0	0	0	0	5	0	0	0	0	0
Ni	24*	13	*35	*24	13	19	*11	11	0	11	14	7	*21	*21	14
Pb	1	0	‡100	4	0	0	1	1	0	*29	0	4	1	*40	1
Sn	0	0	12	0	‡100	0	0	3	0	5	5	0	0	12	8
Ti	52‡	5	13	5	‡ 52	*29	0	‡52	* 9	16	‡69	0	3	11	*48
V	73‡	8	8	3	35	*46	3	*35	* 8	14	‡74	6	*17	6	17
Zn	0	0	*25	1	0	2	3	1	0	‡100	0	0	1	*47	1

‡ Indicate those percentage range concentrations over 50%.

* Indicate those percentage range concentrations which are relatively high but fall below 50%.

Table 18. The percentage range concentrations of the elements in the Q-mode factor analysis end-members for the 4 factor model in the three subsets

Element	Subset I				Subset II				Subset III			
	1	2	3	4	1	2	3	4	1	2	3	4
Ag	0	0	**74	0	0	0	0	0	0	*48	0	0
As	0	0	**55	0	0	0	**94	0	**76	0	0	0
Co	18	5	25	3	2	2	**100	2	15	1	3	5
Cr	26	7	11	**100	*12	*5	9	0	11	0	*11	7
Cu	18	*18	**52	8	0	3	16	*11	11	7	4	*20
Fe	28	4	*36	6	5	1	*40	1	20	0	3	2
Ga	**58	6	*33	*13	*32	0	32	0	*57	9	9	15
Mn	2	1	20	2	4	0	**100	0	*47	1	4	2
Mo	0	0	10	0	0	0	0	0	5	0	0	0
Ni	*35	*24	*35	*13	14	0	11	*11	14	7	*21	*21
Pb	0	4	**63	0	1	0	1	1	0	4	1	*40
Sn	3	0	1	0	0	0	3	0	5	0	0	12
Ti	*37	5	13	5	*16	*9	*48	0	**69	0	3	11
V	**73	3	8	8	8	*8	*35	3	**74	6	*17	6
Zn	0	1	*35	0	0	0	1	3	0	0	1	*47

** Indicate those percentage range concentrations over 50 per cent

* Indicate those percentage range concentrations which are relatively high but fall below 50 per cent.

Table 19. The percentage range concentrations of the elements Q-mode factor analysis end-members for the 3 factor model in the three subsets.

Element	Subset I			Subset II			Subset III		
	1	2	3	1	2	3	1	2	3
Ag	0	5	**74	0	0	0	0	*48	0
As	0	0	**55	0	0	**61	**76	0	*33
Co	5	1	25	2	2	23	15	1	3
Cr	*48	*11	11	*23	0	12	11	0	11
Cu	8	*11	**52	*16	*11	11	12	7	4
Fe	19	0	*36	7	1	*30	20	0	3
Ga	**58	0	*33	*19	0	**73	**57	9	9
Mn	1	0	20	1	0	*47	*46	0	4
Mo	0	0	10	0	0	3	5	0	0
Ni	*35	*13	*35	11	*11	19	14	7	*21
Pb	0	0	**62	1	1	0	0	4	1
Sn	0	0	1	0	0	25	5	0	0
Ti	**68	5	13	**61	0	1	**69	0	3
V	**73	0	8	*46	3	**73	**74	6	*17
Zn	0	0	*35	2	3	3	0	0	1

** Indicate those percentage range concentrations over 50 per cent.

* Indicate those percentage range concentrations which are relatively high but fall below 50 per cent.

Table 20. The percentage range concentrations of the elements in the Q-mode factor analysis end-members for the 2 factor model in the three subsets.

Element	Subset I		Subset II		Subset III	
	1	2	1	2	1	2
Ag	0	5	0	0	0	*48
As	*33	0	0	0	0	0
Co	*39	1	2	2	8	1
Cr	*48	*11	*12	0	7	0
Cu	18	*11	0	*11	12	17
Fe	*45	0	5	1	8	0
Ga	**79	0	*32	0	*36	9
Mn	10	0	4	0	4	0
Mo	0	0	0	0	0	0
Ni	24	*13	4	*11	14	7
Pb	1	0	1	1	0	4
Sn	12	0	0	0	1	0
Ti	**84	5	*19	4	*38	0
V	**73	0	8	3	*38	6
Zn	0	0	0	3	1	0

** Indicate those percentage range concentrations over 50 per cent.

* Indicate those percentage range concentrations which are relatively highest but fall below 50 per cent.

Table 21. The relatively most enhanced elements in the Q-mode factor analysis end-members in the three subsets for the 5,4,3 and 2 factor models.

Factor Model		Subset I	Subset II	Subset III
5 Factor Model	1	V,Ti,(Cr,Ga,Ni)*	Ga,(V,Ti,Fe)	As,V,Ti,Ga,(Mn)
	2	Cr	(Ni,Cu)	(Ag)
	3	Pb,Ag,(Ni,Cu,Zn)	Mn,Co,As,Ti,(Fe,V)	(Ni,V,Cr)
	4	(Ni,Cu)	(Ti,V)	(Zn,Pb,Ni,Cu)
	5	Mn,Sn,As,Ga,Ti	Zn,(Cu,Pb)	Ga,(Ti)
4 Factor Model	1	V,Ga,(Ti,Ni)	(Ga,Ti,Cr)	As,V,Ti,Ga,(Mn)
	2	(Ni,Cu)	(Ti,V,Cr)	(Ag)
	3	Ag,Pb,As,Cu,(Fe,Ni Zn,Ga)	Co,Mn,As,(Ti,Fe,V)	(Ni,V,Cr)
	4	Cr,(Ga,Ni)	(Ni,Cu)	(Zn,Pb,Ni,Cu)
3 Factor Model	1	V,Ti,Ga,(Cr,Ni)	Ti,(V,Cr,Ga,Cu)	As,V,Ti,Ga,(Mn)
	2	Ni,Cr,Cu	(Cu,Ni)	(Ag)
	3	Ag,Pb,As,Cu,(Fe, Ni,Zn,Ga)	V,Ga,As,(Mn,Fe)	(As,Ni,V)
2 Factor Model	1	Ti,Ga,V,(Cr,Fe,Co, As)	(Ga,Ti,Cr)	(V,Ti,Ga)
	2	(Ni,Cr,Cu)	(Cu,Ni)	(Ag)

LEGEND

* ( ); parentheses represent elements with percentage range concentrations below 50 per cent.

generally very low concentrations for all elements. To cite an example, in the 5 factor model, factor end-members 4 (Subset 1), 2 and 4 (subset 2), and 2, 3, 4 (subset 3) all bear low concentrations in their respective subsets.

The results of Q-mode analysis can only be interpreted for the oblique solution when real samples are chosen as end-members. The geochemical characteristics of the end-members do not show clear and unequivocal agreement with the known element associations. The agreement in end-member geochemical characteristics between the subsets is poor. It may be concluded that Q-mode analysis is not an appropriate technique for analysis of drainage sediment geochemical data when it is desired to elucidate the trace element associations within the data.

5.5.0. SUMMARY AND CONCLUSIONS

5.5.1. Summary

It has been shown that:

(i) the R-mode factor associations

  (a) more closely represent the known trace element associations than those indicated by Q-mode analysis; and

  (b) are present in each of the three subsets whilst the geochemical characteristics of the factors selected by Q-mode analysis are less stable and

are apparently more influenced by the composition of the sample population.

(ii) the effect of applying a log-transformation to the trace element data prior to the R-mode analysis may effect a considerable improvement in the similarity between the factor associations and those which have been demonstrated by other methods.

(iii) there may be little practical advantage in employing either orthogonal rotated or non-orthogonal oblique factors in preference to one-another when using the Garrett programme, since they both yield comparable results.

Conclusions

The following conclusions were derived from the results of this study. They are:-

(i) R-mode factor analysis is the more appropriate technique for the processing of the multi-element regional reconnaissance data.

(ii) it is necessary to analyse data which has been log-transformed prior to the factor analysis, as well as untransformed data, in order to subjectively assess which data mode is the more suitable.

(iii) the Garrett R-mode factor analysis programme (RSCORE)

selects factors, which are closely related to known trace element associations, and this programme is therefore suitable for the analysis of the regional survey data.

(iv) it is advisable to examine all possible factor models in order to select that which most adequately represents the known trace element associations in the data, for instance, if 15 variables are being processed, all models from 2 factors to 15 factors should be examined.

The conclusions developed in this chapter have been utilised in the analysis of the regional, reconnaissance survey lata. The results of which are described in Chapter 6.

CHAPTER 6

THE APPLICATION OF R-MODE FACTOR ANALYSIS TO THE REGIONAL GEOCHEMICAL DATA.

6.1.0. The problem to be investigated.

Multielement geochemical data yields information pertinent to the geochemistry of the bedrock including mineralisation, to variations in secondary environment, and to contamination effects due to human activities. The recognition of these features and the evaluation of their relative effects involves costly and time consuming procedures for the detailed investigation of all areas of interest. It is possible that the causative controls operating upon the data may be recognised and evaluated less expensively and more quickly by applying mathematical techniques designed to analyse multivariate data.

6.2.0. Aim of the investigation.

The purpose of this study is to determine whether the multivariate analytical technique of R-mode factor analysis will confirm the known trace element associations previously recognised within the three surveyed areas. It is also hoped that additional, previously unrecognised, associations may also be revealed by the analysis.

6.3.0. Procedure adopted for the analysis of the regional data.

A set procedure was adopted for the analysis of the regional

data in each of the three surveyed areas:-

(i) The data was processed both with and without a logarithmic transformation(to base 10) in order to allow a subjective choice of the more suitable data mode. The criterion being the agreement between the trace element associations shown by the factor analysis and those already known to exist within the data.

(ii) The oblique solutions were used in preference to the rotated solutions. The latter assumes that no correlations exist between the trace element associations. It was felt that this is probably an unjustified simplification and that the correlations between the oblique factors more closely reflected the true relationships between the trace element associations.

(iii) The programme used for the analysis was RSCORE (Garrett, 1967), because it includes the facility for computing the individual sample scores on each factor association. The factor scores have been plotted onto maps and the variations in the areal dispersion patterns have been interpreted in terms of the bedrock geology, secondary environment and human contamination effects.

(iv) The RSCORE programme allows the additional facility of varying the intensity of the oblique solutions. This is achieved by setting two input parameters, KMIN and KMAX, to values greater than 1. The KMIN value decides the mini-

mum obliquity and the KMAX value the maximum obliquity of the solutions. The programme may be used to calculate a number of oblique solutions ranging in intensity from KMIN to KMAX. It was found that in a series of trials in each survey area that for KMAX=2, the solutions exhibited heightened contrasts between the highly associated and the negligibly associated elements in a factor. However, more highly oblique solutions tended to suppress the minor elements in the factor associations. A subjective compromise was made by using the solution of minimum obliquity, that is, where KMIN=KMAX=2.

(v) For each area 15 elements were included in the analysis, except for S.W. England where Ag, which seldom has values over the detection limit, was excluded. All factor solutions between 15 (or 14) and 2 factors were examined before a subjective choice was made of the optimum model. The criteria employed for choosing the optimum solution were:-

(a) all the known major associations should be present.

(b) the model chosen should be the simplest fulfilling criterion (a).

(c) the model should neither exhibit excessive agglomeration nor excessive fragmentation of the known associations.

(vi) The selected factor model was used in order to generate the sample factor scores (Rscores), which were automatically

punched on computer output cards.

(vii) The areal patterns displayed by the Rscores were analysed using the moving average programme (see Section4.4.0), and the results were plotted as maps using the Calcomp automatic plotter.

(viii) The regional distribution patterns exhibited by the Rscores were used, together with the a priori information available for the various trace element associations, in order to interpret the results.

6.4.0. RESULTS OF THE FACTOR ANALYSIS OF THE REGIONAL DATA,I: S.W. ENGLAND.

6.4.1. Associations indicated by R-mode Factor Analysis.

The trace element associations indicated by the reconnaissance survey have been described in Chapter 2(Section 2.2.9). The regional data was subjected to R-mode analysis both with and without a prior log-transformation. The factor associations for all models between 14 and 2 factors have been summarised in tables 22 and 23.

The first problem was to decide whether the log-transformed or natural numbers gave the best factor solution. The procedure employed was to decide which data mode gave factor associations closest to those already identified in the data.

The main associations in the raw data are represented in the factor solutions of both natural and log-transformed data values.

Table 22

The Trace element associations indicated by R-mode analysis of the untransformed trace element data from S. W. England, for all models between 2 and 14 factors.

Factors	1	2	3	4	5	6	7
Factor Models							
14	Ni	Pb,Zn	Sn	Mo	Cu	Ga	As
13	Ni	Pb,Zn	Sn	Mo	Cu	Ga	As
12	Co,Ni	Pb,Zn	Sn	Mo	Cu	Mn	As
11	Ti,V(Ni)*	Pb,Zn	Sn [V] ≠	Mo	Cu	Mn(Ni)	As
10	Cr,V,Ti Ni	Pb,Zn	Sn	Mo	Cu	Mn,Ni	As
9	Cr,Ti,V Ni	Pb,Zn	Sn	Mo	Cu	Mn,Co, Ni	As
8	Cr,Ti,V, Ni	Pb,Zn(Co)	Sn [(V)]	Mo,Fe (Co)	Cu	Mn,Co,Ni Fe	As(Mn,Mo)
7	Cr,Ti,V Ni(Ga)	Pb,Zn,Co (As,Ni)	Sn,Ga	Mo,Fe Co,(V)	Cu	Mn,Co,Ni (Fe ,Sn) [Ga]	As,Mo
6	Ti,Cr,V Ni,Ga (Fe) [(Sn)]	Pb,Zn,As	Sn,Ga(As)	Mo,Fe As(Co)	Cu	Mn,Co,Ni Fe (Zn,Sn) [Ga]	
5	Ti,Cr,V Ni,Fe (Ga,Co) [As]	Pb,Zn,Co, Mn,Ni,As	Ga,Sn,As	Mo,Fe Co(As, Mn)	Cu		
4	Ti,Cr,V Ni,Fe (Ga,Co) [(As)]	Pb,Zn,Co Mn,As,Ni	Ga,Sn,As	Mo,Fe Cu,Co,As (Mn)			
3	V,Ti,Cr Ni,Fe Co,Mo,Ni (Ga,Cu)	Pb,Zn,Co As,Mn,Ni Fe (Mo)	Ga,Sn,As				
2	Pb,Zn,Co As,Mn,Ni Fe ,Mo	V,Cr,Ti Ni,Fe Co,Mn,Mo [Sn]					

8	9	10	11	12	13	14
Mn	Fe	Ti	Cr	V	Co	(Zn) [(Pb)]
Mn	Fe	Ti	Cr	V	Co	
Ga	Fe	Ti	Cr(Ni)	V		
Ga	Co,Fe	Co,Ni,V	Cr(V,Ni)			
Ga(V)	Co,Fe	Ti,Fe				
Ga(V)Fe,Co	Co,Fe (Ni)					
Ga						

LEGEND

*( ); parentheses indicate factor loading between /0.200/and 0.299/ for the enclosed elements.

≠[ ]; square brackets indicate that the enclosed elements bear a significant factor loading >/0.300/, of opposite sign to those of the dominant association in that factor.

Table 23.
The Trace element associations indicated by R-mode analysis of the log-transformed trace element from S. W. England for all models between 2 and 14 factors.

FACTOR 1 Factor Model		2	3	4	5	6	7	8	9	10	11	12	13	14
14	Cr,V,Ni	Pb	Mn	Mo	As	Ga	Cu	Sn	Zn	Fe	Co	Ti	V	Ni
13	Cr,V,Ni (Ti) *	Pb	Mn	Mo	As	Ga	Cu	Sn	Zn	Fe	Co,Ni	Ti	V	
12	Cr,V,Ni (Ti)	Pb	Mn	Mo	As	Ga	Cu	Sn	Zn	Fe	Co,Ni	Ti		
11	Cr,V,Ni Ti	Pb	Mn	Mo	As	Ga	Cu	Sn	Zn	Ti,Fe	Co,Fe, Ni			
10	Ti,Cr,V Ni(Fe)	Pb	Mn(Ni)	Mo	As	Ga	Cu	Sn [V,Cr]	Zn	Co,Fe (Ni)				
9	Ti,Cr,V Ni(Fe)	Pb(Zn)	Mn,Co, Fe ,Ni	Mo(Fe)	As	Ga(Sn)	Cu(Mn)	Sn	Zn					
8	Ti,Cr,V Ni,Zn, (Fe)	Pb,Zn	Mn,Co Fe,Ni,	Mo,(Fe)	As	Ga(Fe Sn)	Cu(Mn)	Sn(Ti,Mn)						
7	Ti,Cr,V Ni,Zn (Fe)	Pb,Zn Sn,(Cu)	Co,Mn, Fe, Ni,(Zn)	Mo(Fe)	As,Sn	Ga,Sn, (Fe)	Cu(V, Cr)							
6	Cr,V,Ti Ni,Cu, Zn(Fe) Sn ≠	Ga,Sn (Ti, Fe)	Co,Mn Fe, Ni,(Zn)	Mo,Cu, (Fe)	As,Sn (Cu)	Pb,Zn, Cu(Sn)								
5	Cr,V,Ti Ni,Fe,Cu Zn,Co,Mn [Sn]	Ga,Sn (Ti) Co,Ni	Pb,Zn,Mn Fe ,Sn Co	Mo,Fe, Cu,Co,Zn	As,Sn, (Mn,Cu)									
4	Cr,V,Ti Ni,Fe,Cu Zn,Co,Mn (Ga) [Sn]	Pb,As, Sn,Zn Mn,Ga, Cu	Ga,Sn [Mn,Co,Ni]	Mo,Fe Cu,(Co)										
3	V,Cr,Ti Ni,Cu, Fe ,Zn Ga(Co) [Sn]	Ga,Sn, As,Pb Cu(Zn)	Mn,Co,Mo Fe Zn Pb,Ni,Cu As											
2	Ni,V,Cr Co,Zn,Ti Mn,Cu Mo,(Pb) [Sn]	Sn,Pb As,Ga Cu,Zn (Mo)												

LEGEND

*(); parentheses indicate a factor loading between /0.200/ and /0.299/ for the enclosed elements.

≠[ ]; square brackets indicate that the enclosed elements bear a significant factor loading, ⩾/0.300/, of opposite sign to those of the dominant association in that factor.

An association, possibly related to the basic igneous rocks outcropping in this area, (Cr, Ni, Ti with Co, Fe, Mn, V) appears as the principal factor in solutions from both data modes. The log-transformed association includes Cu and Zn in the lower models, for instance, all associations below 7 factors; whereas the untransformed models include Ga, which is more typically enhanced in the granitic rocks.

The granite rock association (Ga and Sn) is also present in the solutions from both data modes. It is variously associated, albeit weakly, with As, Cu, Fe , Ga, Pb, Ti and Zn, and it is also antipathetically related to Co, Mn and Ni in the lower models (below 8 factors) of the log-transformed data. The same factor association is represented in the untransformed data and is associated fairly constantly with As. The untransformed data mode thus seems to give a better representation of this association since As is quite a feasible associate of Ga and Sn whereas those of the log-transformed data solutions are less geochemically feasible.

The secondary environment association (As, Co, Fe , Mn, Ni) is present in the higher models (above 5 factors) for both data modes but is also associated, though weakly, with Zn (log-transformed data) and Sn and Zn (untransformed data). Sn is generally considered to be a rather immobile element in the secondary environment, whilst Zn is mobile. The log-transformed association is therefore more feasible than that from the untransformed data.

The metasomatic aureole association (As, Cu, Pb, Sn and Zn) is poorly represented in the untransformed data models whereas the logarithmic data displays this association as two sub-groups in the 6 and 7 factor models. The constitution of these sub-groups is Pb-Zn-Sn-Cu and As-Sn-Cu which display some degree of overlap in that the elements Sn and Cu appear in both associations. Their separate constitution may or may not be geologically valid.

The Dinantian sedimentary rocks which are characterised by high Mo concentrations, are represented by factors in both data modes. The log-transformed associations above the 5 factor model include Cu and Fe , whilst lower models variously include Co, Zn and other mobile elements. The untransformed data association include As, Co, Cu, Fe , Mn and V. The superior association is perhaps that from the log-transformed data since this is less complex, however, insufficient information is available for these Mo-rich horizons to accurately select the better association.

These are the main associations recognised both from the initial interpretation of the data and also from the results of factor analysis. There is little to choose between the different data modes. This is possibly because there is little reduction in the number of significantly skewed trace element(from 13 to 11) frequency distributions, when the log-transformation is applied.

It is considered that, on balance, the log-transformed data has given the closest approximation to those trace element associations already known, especially with regard to that forming the geochemical

aureole around the granite. The log-transformed data solutions were therefore used, in order to select the optimum factor model.

The known element associations are all represented to varying degrees in all models above that of 5 factors, since in the lower models there is an increasing agglomeration of the known trace element associations. However above factor 6, the known trace element associations begin to break up, for instance, the presence of the essentially unielemental factors 4 (Mo) and 7 (Cu) in the 7 factor model. The 6 factor model was therefore chosen as the optimum solution and this model has been used to compute the factor scores (Rscores) for the individual samples.

6.4.2. Moving average analysis of the factor score data derived from the regional reconnaissance survey data in S.W. England.

Introduction.

The regional variations of the factor scores were analysed with the moving average technique. The only parameter utilised was the moving average. The moving average analysis of the regional survey trace element data indicated that the variance ratio maps did not reveal much significant additional information, and so this parameter has not been used. The factor scores are standardised values, as mentioned in section 5.3.4., and consequently the moving average values for the factor scores will be identical to the Z-values, and thus it was unnecessary to produce the mapped Z-values. The analysis has only been used on those factors which might yield confirmatory or

additional information to that already gained from the previous application of other computerised procedures, Thus unielemental factors have not been included and in some cases neither have polyelemental factor associations, but the reasons for their exclusion are detailed in the text, at the relevant place.

Description of the results.

The moving average patterns for the factor scores in the S.W. England survey area are described below:-

(i) Factor 1; Cr-V-Ti-Ni-Cu-Zn, negative factor; (fig.175,vol.2).
Sn, positive factor.

The highest concentration levels for this association (-2.0) occur over the Devonian and Dinantian outcrops, which are associated with basic igneous rocks. The lowest concentrations (+2.0) are found over the Dartmoor and Bodmin granites, and there is a noticeable increase in these levels (+2.0 but +1.0) towards the northern margins of the granite intrusion, and also over the central portion of the Dartmoor granite outcrop.

The Carboniferous and Permian generally bear intermediate concentrations but the Namurian outcrop is usually marginally higher (0.0) than the Westphalian and Permian (0.0), except in the centre and west of the survey area where the levels are more comparable.

The concentrations of this association are most enhanced over those country rocks which are associated with basic igneous activity. Thus, this factor probably relates to the geochemistry of these basic

rocks, which are greatly enhanced in Cr-Ni-V-Ti, relative to granites, and, to a lesser extent, also to most sedimentary rocks (Goldschmidt, 1954). However, the variation of this association over the Carboniferous outcrop, especially in relation to the contrast between the higher values over the more argillaceous Namurian compared to the more arenaceous Westphalian, would indicate that this association might also be related to the argillaceous content of these sedimentary rocks. An interesting feature, pertinent to this last hypothesis, is that the lower concentrations of this association over the western outcrop of the Namurian can be correlated with the observations of some other workers (L.Moore, pers.comm.,1969). These have noted that the lithology of the bedrock forming the western part of the Namurian outcrop is more similar to that of the Bude formation (Westphalian usually) than it is to the Crackington formation (Namurian usually).

(ii) Factor 2; Ga-Sn-(Ti-Fe), positive factor. (fig.176,vol.2)

The highest concentrations of this association ($> +1.0$) occur over the granite outcrops of Bodmin Moor and Dartmoor. An aureole of higher concentration levels (> 0.0), between 2 to 4 miles wide, covers the country rocks adjacent to the granite contact. The levels over the Namurian outcrop are intermediate (< 0.0, but > -1.0), except in the extreme west where they are low (< -1.0). The Westphalian and Permian generally exhibit low concentrations (usually < -1.0). This distribution is in accordance with the results of pure geochemical researches, which indi-

cate higher levels of Ga in both granites and clay-rich (hydrolysate) sedimentary rocks, and also the enhancement of Sn in many granites (Goldschmidt, op. cit.).

(iii) Factor 3; Co-Mn-Fe-Ni-(Zn), positive factor. (fig.177,vol.2).

The lowest concentrations of this association occur over the granites, with one exceptional area over north-west Dartmoor, which has very high values ($>+1.0$). Other areas of high concentrations are scattered over the Dinantian outcrops and over the Namurian-Westphalian, north-west of Okehampton and also to the east of Bude. An extensive zone of high values ($>+1.0$) occurs over the Namurian along the eastern boundary of the survey area, whilst over much of the Carboniferous outcrop there is a complex variation of concentrations in the range -1.0 to + 1.0. There are generally higher values over the western Namurian than in the east, and this trend is reversed over the Westphalian.

This association is composed of elements which are affected by changes in the Eh-pH regime of the overburden. The result is that these more mobile elements are leached from poorly drained, acid soils and are precipitated and coprecipated in the higher Eh-pH environment of the open drainage channels (Horsnail, 1968). An additional feature relating to the enhancement of this association over the Dinantian, is the presence in this strata of low sub-economic manganese ore bodies, which have possibly contributed to the enhanced concentrations of these elements (Dines, 1956).

(iv) Factor 4; Mo-Cu-(Fe), positive factor. (fig.178, Vol.2)

The higher concentrations (>0.0) occur over the Dinantian and Namurian (except in the extreme west) strata, with the greatest enhancement ($>+1.0$) over the basal Namurian and Dinantian outcrops. There are other, small areas with high contrations ($>+1.0$) scattered over the central Namurian. The granites tend to have lower values (<0.0 but >-1.0) except adjacent to the igneous contact where very low scores are recorded (<-1.0). The Westphalian has generally low values (<0.0, with large areas <-1.0), whilst the Permian is marginally higher (<0.0, with scattered areas >0.0).

The trace element association Mo-Cu has already been identified in this area and is related to the presence of molybdeniferous black marine shale horizons in the Dinantian and basal Namurian succession (Fletcher, 1968).

(v) Factor 5; As-Sn-(Cu), positive factor. (fig.179, vol. 2)

The highest concentrations for this association occur over the northern margin of the Dartmoor and Bodmin moor granites and the enhanced levels ($>+1.00$) extend over the Dinantian and Devonian (north of the Bodmin granite). There is an extensive aureole around the granites of marginally enhanced values (>0.0), which is between 2 and 5 miles wide. Outside this aureole, there are additional higher zones over the Permian inlier, south of Crediton and also over the northern continuation of the Sticklepath fault, at the Namurian-Westphalian junction. Otherwise the concentration levels outside the aureole are

low (< 0.0), with an extensive area with very low concentrations (< -1.0) over the Namurian outcrop, north of Launceston, and an additional smaller zone occurs over the Westphalian. Another anomalously low zone (< 0.0), relative to the surrounding levels, occurs over the north-eastern outcrop of the Dartmoor granite.

The sedimentary country rocks fringing the granites include known and exploited deposits of As, Cu and Sn, north of the Dartmoor granite, and also of Cu and Sn, north of the Bodmin granite(Dines, 1956). The marginally higher levels over the Permian inlier are possibly related to the higher Sn concentrations which have previously been noted over this outcrop. However, the higher zone over the Stickle-path fault may be related either to secondary environmental agencies since both As and, to a lesser extent, Cu are mobile elements or they may be related to minor mineralisation along the fault zone.

(vi) Factor 6; Pb-Zn-Cu-(Sn), positive factor. (fig.180, vol.2)

The zone of highest concentrations ($> +2.0$) occurs in the Teign valley, whilst other areas of lesser enhancement ($> +1.0$) are scattered over the margins of both the Bodmin and Dartmoor granites. An aureole, up to 5 miles wide, of marginally enhanced concentrations (> 0.0) encircles each of the granites. An extension of the enhanced values ($> +1.0$) occurs north of the Bodmin granite over the Dinantian strata. The concentrations over the remainder of the survey area are rather low (< 0.0) and there are scattered small zones of very low values (< -1.0) over the Carboniferous outcrop.

The Teign valley has been the site of a considerable amount of Pb, Zn and to a lesser extent Cu mining and these metals have also been mined from the country rock bounding the granite margins. The anomalous levels of this association are probably related to contamination from the mining and beneficiation of these ores as well as to the mineralisation itself.

Discussion

The constitution of the factors and the distribution of the factor scores have shown that the factor associations are related to the bedrock geochemistry (factors 1,2 and 4), mineralisation and contamination (factors 5 and 6) and secondary environmental variations (factor 3) in this area. The usefulness of the mineralisation factors for distinguishing between areas with different suites of metallic ores has not been evaluated, and neither have the marginal enhancements of these factors along the Sticklepath fault (factor 6) or to the north of Launceston (factor 5).

It is considered that the analysis has succeeded in distinguishing the known trace element associations and in demonstrating their regional distribution.

6.5.0. RESULTS OF THE FACTOR ANALYSIS OF THE REGIONAL DATA, II: N.WALES.

6.5.1. Associations indicated by R-mode factor analysis

The trace element associations indicated by the reconnaissance survey and follow-up work have been summarised in Chapter 2 (section 2.3.10).

A total of 15 elements were processed, the analysis was conducted with both log-transformed and untransformed data. The effect of the log-transformation was to increase the number of significantly skewed frequency distributions from 13 to 14. All solutions between the 2 and 15 factor models, for both data modes are displayed in tables 24 and 25.

The lower Palaeozoic association (Cr,Fe , Ga,Ti, V and also Co,Cu, Mn, Ni, Zn) is represented in all factor solutions of both data modes. The association is most completely represented in the log-transformed data. All but the lowest models in the untransformed data (less than 4 factors) omit the elements Co, Cr, Cu, Mn,Ni, and Zn, or, constitute some of them into a separate association of Cr-Ni-Cu. Most of the log-transformed data solutions include Co ,Cr, Cu and Ni.

The secondary environmental association of mobile elements (As Co, Fe ,Mn, and also Ni, Zn) are also represented in most solutions for both data modes. However, Ni is only tentatively represented in some of the untransformed solutions, namely, the 5 and 6 factor models.

Table 24 296
The trace element associations indicated by R-mode analysis of the untransformed trace element data from N. Wales; for all models between 2 and 15 factors.

Factor	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Factor Model															
15	V,Ga,Ti Fe	Pb	Mn	Cr	Mo	Sn	Ag	Cu	Zn	Co	As	Ni	Ti	Fe	≠ Ga [V]
14	V,Ga,Ti Fe	Pb	Mn	Cr	Mo	Sn	Ag	Cu	Zn	Co	As	Ni	Ti	Fe	
13	V,Ga,Ti Fe	Pb	Mn(Fe) *	Cr,Ni	Mo,Fe	Sn	Ag	Cu	Zn	Co	As	Ni(Fe)	Ti		
12	Ti,V,Ga Fe	Pb	Mn(Fe)	Cr,Ni	Mo,Fe	Sn	Ag	Cu	Zn	Co	As	Ni(Fe) [Ti]			
11	Ga,V,Ti Fe	Pb	Mn,Fe	Cr,Ni	Mo,Fe	Sn	Ag	Cu	Zn	Co(Ni)	As				
10	Ga,Vi,Ti Fe	Pb	As,Mn	Cr,Ni	Mo,Fe	Sn	Ag	Cu	Zn,As	Co,Mn,Ni Fe					
9	Ga,V,Ti Fe	Pb,(Zn) [(As)]	Mn,Co,As Fe	Cr,Ni	Mo,Fe	Sn	Ag	Cu(As)	Zn,As						
8	Ga,V,Ti Fe	Pb,Zn	Mn,Co,As Fe	Cr,Ni,Cu	Mo,Fe	Sn	Ag	Cu,As,Zn							
7	Ga,V,Ti Fe	Zn,Pb (Cu)	Mn,Co,As Fe	Cr,Ni,Cu	Mo,Fe As,Cu	Sn	Ag								
6	Ga,V,Ti Fe (Ni)	Ag,Pb,Zn	Mn,Co,As Fe	Cr,Ni,Cu	Mo,As,Zn Cu,Fe [(Ag)]	Sn									
5	Ga,V,Ti Fe (Ni)	Pb,Ag,Zn	Mn,Co,As Fe (Ni)	Cr,Ni,Cu	Mn,Sn,Cu As,Zn Fe [(Ag)]										
4	Ga,V,Ti Fe (Mo)	Zn,Pb,Ag Mo,Cu(As)	Mn,Co,As Fe (Sn)	Cr,Ni,Cu											
3	V,Ga,Ti Ni,Cr Fe	Zn,Pb,Cu Ag(As,Sn)	Mn,Co,As Fe,Mo (Sn) [(Cr)]												
2	V,Ga,Ti Fe Ni,Cr (Co,Cu, Mn)	As,Zn,Pb Mo,Mn,Co Cu,Fe Ag													

LEGEND

* ( ); parentheses indicate a factor loading between /0.200/and/0.299/ for the enclosed elements.

≠ [ ]; square brackets indicate that the enclosed elements bear a significant factor loading, ≥/0.300/, of opposite sign to those of the dominant association in that factor.

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Table 25

The trace element associations indicated by R-Mode analysis of the log-transformed trace element data from N.Wales, for all models between 2 - 15 factors.

Factors	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Factor Models															
15	Ga,Ti,V Fe(Cr)	Pb	Mn	Sn	Mo	Ag	Zn	Ni	Cu	Cr	As	Co	Ti	V	Fe
14	Ga,Ti,V Fe(Cr,Ni, Co)	Pb	Mn(Fe)	Sn	Mo	Ag	Zn	Ni	Cu	Cr	As	Co	Ti	V	
13	Ga,V,Ti Fe(Cr,Ni Co)	Ag	Mn(Fe)	Sn	Mo	Zn	Pb	Ni	Cu	Cr	As	Co	Ti		
12	Ti,Ga,V Fe(Cr, Ni,Co)	Ag	Mn(Fe)	Sn	Mo	Zn	Pb	Ni	Cu	Cr	As	Co			
11	Ti,Ga,V Fe(Cr, Ni,Co)	Ag	Mn,Co Fe	Sn	Mo	Zn	Pb	Ni,Co	Cu	Cr	As				
10	Ti,Ga,V Fe,Cr (Co,Cu)	Mn,Co, Pb(Fe. As)	As	Sn	Mo	Ag	Zn(Pb)	Ni,Co (Cu)	Cu,Pb	Cr					
9	Ti,Ga,V Fe,Cr Cu	Pb,Cu(Mn)	Mn,As, Co,Fe	Sn	Mo(As)	Ag	Zn	Ni,Co Cu(Cr)	Cr[Cu (As)]						
8	Ti,Ga,V Fe,Cr Cu(Ni,Co)	Pb,Cu	Mn,As,Co Fe	Sn	Mo(As)	Ag	Zn(Pb)	Ni,Cr (Co)							
7	V,Ga,Ti Cr,Fe Ni,Cu,Co [Pb]	Zn,Pb(Cu)	Mn,As,Co Fe	Sn	Mo(As)	Ag	Pb,Cu(Cr Co) [As]								
6	V,Ga,Ti Cr,Fe Ni,Cu,Co	Zn,Pb,Cu	Mn,As,Co Fe	Sn,Cu	Mo,As	Ag									
5	Va,Ga,Ti Cr,Fe Ni,Cu,Co [Pb]	Pb,Zn, Cu	Mn,As,Co Fe	Sn,Cu Ag	Mo,As										
4	V,Ga,Ti Cr,Fe Ni,Cu,Co [Pb]	Ag,Zn Pb,Cu (Mo)	As,Mn, Co,Fe Mo	Sn,Cu Mo,Pb Ag]											
3	V,Ga,Ti Cr,Fe Ni,Cu,Co	Pb,Zn Cu,Ag Mo,Sn	As,Mn,Co Mo,Fe (Sn)												
2	V,Ga Fe, Ti,Cr=Ni Co,Mn,Cu As(Sn) [Pb]	Pb,Zn Mo,Cu As,Ag Sn,Mn(Co)													

LEGEND

* (); parentheses indicate a factor loading between /0.200/ and /0.299/ for the enclosed elements.

≠[ ]; square brackets indicate that the enclosed elements bear a significant factor loading, ≥/0.300/, of opposite sign to those of the dominant association in that factor.

Whilst Zn is never included in the solutions. The untransformed data is considered marginally superior in representing this association.

The association due to mineralisation and contamination (Pb, Zn and also Cu) is again represented in most solutions for both data modes. However, it is more completely described in the log-transformed data solutions since it is excluded from all untransformed models above that of 4 factors, except possibly in the 7 factor model.

The volcanic rock-black marine shales association (Fe, Mo) is represented in both data mode solutions, though it is combined with Cu, Fe and Zn in solutions of the untransformed data.

The associated low levels of Cr, Ni and V south-west of Llanrwst may be represented by the Cr-Ni-Cu association, which appears in the 4 to 5 factor models of the untransformed data.

The choice between the two data modes is difficult. The log-transformed data bears a more complete expression of the lower Palaeozoic and mineralisation associations, as well as yielding a simpler expression of the volcanic-black shales association. The untransformed data yields a marginally more complete mobile element association, and, in addition, indicates a new association, Cr-Ni-Cu, which is possibly related to sub-outcropping basic igneous rocks, which are present in the area underlain by Ordovician strata.

A compromise solution was adopted by obtaining the factor scores

for factor models from both the untransformed and log-transformed data.

The untransformed data solution selected for computing the factor scores was the 6 factor model. Higher factor models exhibit fragmentation of the associations, for instance, the unielemental factor 7 (Ag) in the 7 factor model, despite the coincidence between the moving average patterns for Ag, Pb and Zn. Lower models display agglomeration of the associations, for instance, factor 5 in the 5 factor model combines Sn with the volcanic rock-black marine shales association, which reflects the similarities between the moving average patterns of As,Mo, and Sn, but which in this area does not appear to be a geochemically viable association.

The choice of the 'best' solution for the log-transformed data was more difficult but the 6 factor model was also chosen. Lower models exhibit a certain amount of association agglomeration, for instance, the last association of the 5 factor model combines Sn and Cu with an antipathetic Ag to form an a sociation which was subjectively considered to be non-significant. Higher factor models display fragmentation of the associations and reconstitution of the existing associations, for instance, the last association of the 7 factor model combines Pb, Cu, Cr, Co with the antipathetic As, which was also considered to be geochemically non-significant.

6.5.2. Moving average analysis of the R-mode factor scores derived from the regional reconnaissance survey data from N.Wales.

Introduction

The factor scores from the 6-factor models derived from both the untransformed and log-transformed trace element data have been utilised for the examination of the regional distribution of the factor scores. A number of factors of apparently negiligible importance have been excluded, namely, from the untransformed data, factor 6 (Sn) and from the log-transformed data, factors 4 (Sn,Cu) and 6 (Ag). The sixth factor in both cases is unielemental and does not display any more information than is apparent from the moving average analysis of respective trace element data. Factor 4 (Sn,Cu) has been excluded because the association is not considered to be significant, either in terms of the bedrock geology or the mineralisation encountered in this area. The procedure has been to employ only the moving average parameter for those reasons given in section 6.4.3, and the results are described for the untransformed data factors first, and subsequently for the log-transformed data factors.

Moving average analysis of the Rscores derived from the untransformed data.

(i) Factor 1; Ga-V-Ti-Fe-(Ni), positive factor,(fig.184, vol. 2)

The highest concentrations of this association (> +1.0) are located along the Ordovician-Silurian junction, west and north of Llanrwst, over the southern portion of the main Ordovician outcrop and over the central-southern area of the main Silurian outcrop. The main outcrop of the lower Palaeozoic strata have marginally en-

hanced concentrations (>0.0) with extensive areas bearing higher levels ($>+0.7$). However, the Silurian outcropping in the Clwydian Hills is generally low (<0.0, with extensive areas <-1.0), a feature shared by much of the survey area to the east of the Vale of Clwyd. There appears to be a change in values across the Silurian-Dinantian junction, west and south-south-east of the Clwyd valley, and the zero contour runs sub-parallel to this stratigraphic boundary. The Silesian outcrop concentrations are generally very low (<-1.0), except adjacent to the more enhanced Dinantian strata (<0.0, but >-1.0). The Permo-Triassic also generally exhibits low values (<0.0), especially over extensive areas both in the Vale of Clwyd and over the main eastern outcrop where scores below -1.0 occur.

The high concentrations of this association occur over areas which are underlain by sedimentary plus igneous (acid and basic) rocks and also those underlain by completely sedimentary bedrocks, whilst the low concentrations appear over totally sedimentary outcrops, more notably of upper Palaeozoic age. The elements Fe and Ni are the only members of the factor association which are significantly mobile in the secondary environments encountered in this area, the remaining elements are relatively immobile (Horsnail,1968). Therefore, it is apparent that since the principal elements of the association are immobile, and since the levels vary over areas completely underlain by sedimentary bedrock, this association may be related to the mineralogy of these rocks. The discontinuity in

factor score values over the stratigraphic units outcropping east and west of the Vale of Clwyd would indicate that the drainage sediment mineralogy and geochemistry over these bedrocks are different. If this feature is not entirely caused by glacial drift then it must be controlled by the bedrock mineralogy.

(ii) Factor 2; Ag-Pb-Zn, positive factor. (fig.179, vol. 2)

The zones of enhanced values (> 0.0) extend over the Halkyn-Minera mineralised belt (peak values > +2.0), the Llanrwst and Llanfair-Talhaiarn fields. There are in addition small areas of similarly enhanced concentrations notably around Conway on the north Denbigh coast; over the Silurian west of Ruthin and also to the east of Llanrwst; covering a small part of the eastern Permo-Triassic; and over a more extensive area across the northern Clwydian Hills and Vale of Clwyd.

The regional distribution of these factors scores are related principally to the widespread and intense contamination patterns which principally affect Pb and Zn. The distribution of this factor association also indicates the location of the main fields of mineralisation.

(iii) Factor 3; Mn-Co-As-Fe-(Ni), positive factor. (fig.180, vol.2)

There are enhanced concentrations of this asscciation (> 0.0) over the western and south-western portions of the survey area, underlain by bedrock of Ordovician and Silurian age. The highest values (> +1.0, peaks > +2.0) occur over extensive areas on the Denbigh Moors

and the eastern foot-hills of Snowdonia. The association concentration levels decline to the north (< 0.0) and to the east, whilst values over much of the Vale of Clwyd, Clwydian Range, and the north Denbighshire plain are even lower (< -0.3). Marginally higher values occur over the Silesian and Permo-Triassic, east and south-east of a line through Connah's Quay and the southern end of the Clwyd Valley, usually ranging between 0.0 and -0.3.

This factor association includes those elements which have been shown in this area to be most effected by variations in the secondary environment (Horsnail, 1968). The mechanism has been described in connection with a similar factor association distinguished within the S.W. England survey data. The contours for these factor scores to the west of the Clwyd valley show some correspondence with the regional rainfall destribution (fig. 10).

(iv) Factor 4; Cr-Ni-Cu, positive factor. (figure 181, vol.2)

A broad swathe of intermediate values (> 0.0, peak levels $> +1.0$) cross the main lower Palaeozoic outcrop in a NW-SE direction, connecting the area of enhanced concentrations ($> +1.0$, peaks $> +4.0$) around Conway to the southern boundary of the survey area, due south of Mold. Marginally lower levels occur both to the west, but particularly to the east of this high zone. Very low scores (< 0.5) occur in zones along the Silesian outcrop, south of Flint and west of Prestatyn and also along the Westphalian-Permo-Triassic junction. However, higher concentrations (> 0.0) occur over most of the Permo-

Triassic, with very high levels (>+2.0) south of Chester, and also over the Silesian, south of Connah's Quay.

The principal element in the factor association, Cr, is considered to be relatively immobile in the secondary environment of this area (Horsnail, op.cit.), but the remaining two, Ni and Cu are more mobile. Thus the pattern of higher scores over the Denbigh moorlands may be related to enhanced concentrations of these mobile elements due to the operation of secondary environmental processes. However, the very strong variations displayed in the north and eastern parts of the survey area suggest the operation of other factors of which the most likely is the variation in drainage sediment mineralogy, possibly related to the bedrock lithology.

(v) Factor 5; Mo-As-Zn-Cu-Fe, positive factor. (fig.182,vol.2)

Zones of enhanced concentrations of this association (> 0.0) occur along the now extinct mining areas of Halkyn-Minera, Llanrwst, and Llanfair-Talhaiarn, but the peak values (>+2.0) occur over the Ordovician strata, west of Llanrwst. Other areas of enhanced levels (> 0.0) occur over the Ordovician-Silurian junction, on the eastern Snowdonian foothills and the Denbigh Moors and also, in the north, around Rhyl.

The elements in this association are considered to represent three separate controls, namely:

(i) contamination related to mining and mineral beneficiation operations (Zn, Cu);

(ii) variations in the secondary environment, which affect the mobile elements (As,Fe, Zn and to a lesser extent Cu and Mo);

(iii) sub-outcropping pyritic black marine slates of Ordovician age which are notably enriched in Mo and Fe.

The mineralisation contamination control is responsible for the higher levels over the old mining areas. The secondary environmental effect leads to the enhancement over the Denbigh moorlands and eastern Snowdonian hills. The sub-outcropping pyritic slates are the source of the very high scores west of Llanrwst. It is considered that since this factor represents several controls, it is of little value as an aid to unravelling the complex provenance of the trace element data.

Moving average analysis of the Rscores derived from the log-transformed data.

(i) Factor 1; V-Ga-Ti-Cr-Ni-Cu-Co, positive factor.
(fig.183 vol. 2)

The main feature of the regional distribution is the higher trace element association concentrations occurring over the lower Palaeozoic ($\geq$ 0.0, with large areas $\geq$ +0.7), compared to those over the upper Palaeozoic outcrops ($\leq$ 0.0, with large areas $\leq$ -1.0). The Clwydian Range Silurian outcrop is anomalous in that the values over it, resemble those of the upper Palaeozoic and not those over the main Silurian outcrop.

The higher concentrations (>+0.7) over the Ordovician outcrop occur in the north and also in the south-east, in the latter area there is an extensive zone with values in excess of +1.0. Elsewhere, levels are moderately high (> 0.0) except for a small area south-west of Llanrwst (<0.0).

The Silurian outcrop area is moderately enhanced (> 0.0), with a wide band of higher values (> +0.7, peaks> +1.0) trending NW-SE. The Clwydian Hills outcrop gives generally low values (< 0.0), except in the extreme southern portion (> 0.0), whilst in the north very low concentrations are encountered (< -1.0).

The Dinantian outcrops bear values between +0.7 and -1.0 but there are scattered areas with concentrations outside this range. The values over the Silesian are usually low (< 0.0),and a large proportion of the area bears very low values (< -1.0).

The Clwyd valley Permo-Triassic outcrop exhibits a marked contrast across its width with higher concentrations in the west (< 0.0) than in the east (< -1.0). The main outcrop in the Dee Valley shows variable values, which are higher around and to the south of Chester (>0.0), but elsewhere are lower (<0.0), with very low values north-east of Wrexham (< -1.0).

The principal elements in this association (V,Ga,Ti,Cr) are considered to be immobile in the secondary environments encountered in this area (Horsnail, 1968), whilst the subsidiary elements (Ni,Cu,

Co) are more mobile. It is therefore considered that variations in these factor scores are related to changes in the drainage sediment mineralogy, and also by inference, the bedrock lithology. The enhanced levels over the north-western Ordovician outcrop may be related to the occurrence of basic igneous rocks, certainly the lower levels south-west of Llanrwst occur in an area with acid igneous rocks, which would be expected to have low concentration levels in the elements of this association.

(ii) Factor 2; Zn-Pb-Cu, positive factor. (fig. 184, vol. 2)

The highest concentrations of this association (>+2.0) occur over an extensive zone along the Hylkyn-Minera belt and also on a smaller scale around Llanrwst, whilst much lower levels (> 0.0) occur over the Llanfair-Talhaiarn district. Other areas with enhanced values occur along the northern coast, between Rhyl and Prestatyn (> +2.0) and around Conway; over the Permo-Triassic higher levels are found east of Wrexham (> +2.0) and south of Chester (> +1.0). A further area of enhancement occurs over the extreme south eastern outcrop of the western Silurian.

The background patterns indicate moderately higher concentration zones (> 0.0) along the Ordovician-Silurian junction; across the centre of the main Silurian outcrop; over much of the Carboniferous outcrop, east of the Clwyd valley; and over the main outcrop of the Permo-Triassic. There are zones of lower values on the western flanks

of the Clwydian Range (<-1.0), over the Carboniferous south of Connah's Quay (<0.0) and also south of Mold (<0.0) and along the Carboniferous-Permo-Triassic junction.

The main features of this distribution are without doubt associated with contamination related to the exploitation of lead, zinc and copper in the survey area.

(iii) Factor 3; Mn-As-Co-Fe, positive factor. (fig. 185, vol. 2)

Enhanced concentration levels (>+1.0) form a NW-SE trending zone over the western Ordovician and Silurian outcrops and include much of the Denbigh Moors and the eastern Snowdonian foothills. Elsewhere, levels are low (<0.0), except over large areas of the Silesian and Permo-Triassic, where the concentrations are marginally higher (>0.0). Areas of very low concentrations (<-1.0) occur over the Vale of Clwyd, the Clwydian Range and over the Dinantian, west of Mold.

The main features of the distribution of these trace element association concentrations are related to the operation of secondary environmental effects, which lead to the enhancement of mobile elements in the open drainage channels in areas of acid, poorly drained soils.

(iv) Factor 5; Mo-As, positive factor. (fig. 186, vol.2)

Higher concentrations of this association occur in a zone which is associated with the Ordovician-Silurian junction (>0.0) in the west, but which swings out to the east over the Denbigh moors and then south again over the Ordovician. The highest values occur west of Llanrwst

(>+2.0, with peaks >+5.0) and along the southern Ordovician-Silurian junction (>+1.0). Elsewhere, moderately higher values (>0.0) occur south of Rhyl, flanking the Clwyd valley, south of Connah's Quay and a zone of very high concentrations occurs south of Holywell. The remainder of the area generally exhibits low relief with values falling in the range 0.0 to -1.0.

The high concentrations west of Llanrwst are related to the outcropping of pyritic slates but elsewhere the higher levels are usually related to enhanced As concentrations, which in this area are caused mainly by the operation of secondary environmental effects.

Discussion

It is clear that both the untransformed and the log-transformed data modes provide factor associations related to the same controls. However, the constitution of the factor associations does vary between the solutions derived from the different data modes.

The regional distribution for similarly constituted factors from the two modes are closely comparable. However, where the factor associations differ appreciably, for instance, between the two factor 5 associations, with the untransformed data giving Mo-As and the log-transformed data yielding Mo-As-Zn-Cu-Fe, then the regional patterns are not so closely comparable.

Another feature indicated by this study is that whilst the constitution of a factor association might suggest the main control,

this may not be a complete interpretation. An example to illustrate this point,is given by Factor 4 from the untransformed data, constituting an association (Cr-Ni-Cu), which was initially assigned to a basic igneous bedrock control. However, the regional distribution patterns have indicated that the intensity of this association also varies greatly over sedimentary bedrock formations. Therefore, the initial interpretation was incomplete, consequently it is necessary to examine the distribution of a factor, prior to interpreting its significance.

Conclusions

The R-mode factor analysis of the regional survey data has indicated the known trace element associations and in addition, has indicated the association Ga-Ti-V, which may also include Cu, Co, Cr, Fe and Ni. The regional distribution of the factor scores from those factors representing known trace element concentrations reflected the distribution of their established controls. The distribution pattern for the previously unrecognised association suggested that this was possibly related both to the presence of sub-outcropping basic igneous rocks, but also to changes in the mineralogy of sedimentary bedrock formations.

6.6.0. RESULTS OF THE FACTOR ANALYSIS OF THE REGIONAL DATA; III: THE ENGLISH PEAK DISTRICT.

6.6.1. Associations indicated by R-mode Factor Analysis

The trace element associations discovered from the reconnaissance survey and subsequent follow-up work have been summarised in Chapter 2, section 2.4.11.

The complete set of oblique solutions for all models between 15 and 2 factors were examined both for the untransformed and log-transformed data. The results have been summarised and tabulated (see tables 26 and 27).

The choice between the untransformed and log-transformed solutions was made on the basis of the number of known trace element associations revealed from each data mode.

The untransformed data solutions include the known associations due to:-

(i) mineral contamination (Pb-Zn) in all models between 4 and 10 factors.

(ii) black marine shales (As-Cu-Mo-V) in all models between 4 and 8 factors.

The untransformed data also indicates two other associations which were identified in the N. Wales data, namely:

(i) the mobile element association (Co-Mn-Ni with Fe and Cu)

(ii) The association, correlated in N. Wales with the lower Palaeozoic bedrock, (Cr-Fe-Ga-Ti-V, etal).

The elements Ag,Cr, and Sn are in higher models (above 6 factors) formed into unielemental factors but in lower models they are combined either

Table 26

The trace element associations indicated by R-mode factor analysis of untransformed trace element data from the regionsal reconnaissance survey in the English Peak District, for all models between 2 and 15 factors.

Factors	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Factor Models															
15	Ti	Pb	Co,Mn,Ni	Mo	Sn	Cr	Ag	Cu	Fe	As	Zn	Ga	Ni	V	Mn[Co]
14	Ti	Pb	Mn,Co,Ni	Mo(V)	Sn	Cr	Ag	Cu	Fe(Ni)	As	Zn	Ga	Ni(Co)	V(Ni)[(Co)]	
13	Mo,V(Ni)	Pb	Mn,Co,Ni	Ti(V)	Sn	Cr	Ag	Cu	Fe(Ni)	As	Zn	Ga,V	Ni[Mn]		
12	Mo,V(Ni)	Pb	Co,Mn,Ni	Ti(V)	Sn	Cr	Ag	Cu(Ni, Co)	Fe(Ni)	As	Zn	Ga,V			
11	Ti,Ga,V	Pb	Co,Mn,Ni	Mo,V,Ni (As)	Sn	Cr	Ag	Cu(Ni, Co)	Fe(Ni)	As[(Ga)]	Zn				
10	Ti,Ga,V	Pb,Zn	Co,Mn,Ni	Mo,V(Ni As)	Sn	Cr	Ag	Cu(Ni, Zn Co)	Fe(Ni)	As[(Ga)]					
9	Ga,Ti,V Fe (As)	Pb,Zn	Mn,Co,Ni Fe	Mo,As," Ni, (Cu)	Sn	Cr	Ag	Cu(Co, Zn)	Fe,As						
8	Ga,Ti,V Fe	Pb,Zn	Mn,Co,Ni Fe(Cu)	As,Mo,V Fe,Cu,Ni	Sn	Cr	Ag	Cu[Fe]							
7	Ga,Ti,V Fe	Pb,Zn	Co,Mn,Ni Fe(Cu)	Mo,As,V Cu,Ni,Fe	Sn	Cr	Ag								
6	Ga,Ti,V Fe,Ag)	Pb,Zn	Co,Mn,Ni Fe(Cu)	As,Mo,V Cu,Ag,Ni Fe	Sn,Ag	Cr,Ag									
5	Ga,Ti,V Cr,Fe	Pb,Zn	Co,Mn,Ni Fe(Cu)	As,Mo,V Cu,Ag,Ni Fe	Sn,Ag(Cr)										
4	Ga,Ti,V Cr,Fe	Pb,Zn	Co,Mn,Ni Fe,Cu (Sn)	As,Mo,V Cu,Ag,Ni Fe											
3	V,Ga,Ti Fe,Mo,Cu Cr,Ni(As) (Pb)	Zn,Pb, As,Mo, Cu (V) [(Ga)	Co,Mn,Ni Fe,Cu												
2	Fe,Ni V,Ga,Ti Cu,Mn Co,Mo, (As,Cr)	Zn,Pb,As Mo,Ag,Cu (Ni) (Ga)													

LEGEND

Mo,V,(Ni) Order of importance of trace elements in the association. All with loading ≥/02.00/

≠( ) signifies weak loading between /0.200/ and /0.299/.

≠[ ] signifies element antipathetic to the main association.

Table 27.
The element associations indicated by R-Mode factor analysis of the survey of the English Peak District, for all models between 2 and 15 factors.

Factors	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Factor Models															
15	Ga,Ti,V (Cu,Cr, Ni) *	As	Mn	Pb	Ag	Sn	Mo	Fe	Co(Ni)	Cr	Zn	Mo	Ti	V	Ni
14	Ga,Ti,V (Cu,Cr Ni)	As	Mn	Pb	Ag	Sn	Mo	Fe	Co,Ni	Cr	Zn	Cu(Ni)	Ti	V	
13	Ga,Ti,V Cu,Cr,Ni (Co)	As	Mn	Pb	Ag	Sn	Mo,V	Fe	Co,Ni	Cr	Zn	Cu(Ni)	Ti ≠ (Ga)		
12	Ga,Ti,V Cu,Cr,Ni (Co,Fe)	As	Mn	Pb	Ag	Sn	Mo,V	Fe	Co,Ni	Cr	Zn	Cu(Ni) / (Ga)			
11	Ga,Ti,V Cu,Cr,Ni (Co)	As	Mn	Pb	Ag	Sn	Mo,V	Fe	Co,Ni (Cu)	Cr	Zn				
10	Ga,Ti,V Cu,Cr,Ni Co(Fe)	Zn,As	Mn	Pb(Zn)	Ag	Sn	Mo,V,As (Ni,Cu)	Fe	Co,Ni,Zn (Cu)	Cr					
9	Ga,Ti,Cr V,Cu,Ni Co(Fe)	As,Zn	Mn	Pb(Zn)	Ag	Sn	Mo,V,As (Ni,Cu)	Fe	Co,Ni Zn(Cu)						
8	Ga,Ti,Cr V,Cu,Ni Co(Fe)	Zn,As	Mn	Pb(Zn)	Ag	Sn	Mo,As,V (Cu)	Fe,Co Ni (Cu')							
7	Ga,Ti,Cr V,Cu,Ni Fe,Co	As,Zn	Mn(Co)	Pb(Zn)	Ag	Sn	Mo,Fe Ni,V(Co Cu,As)								
6	Ga,Ti,Cr V,Cu Fe,Ni,Co	As,Mo, Ni,Cu Fe Zn	Mn(Co)	Pb,Zn	Ag	Sn									
5	Ga,Ti,Cr V,Fe Cu,Ni,Co Sn(Mo)	As,Mo,Zn V,Ni,Cu Pb(Fe)	Pb,Sn,Zn	Mn(Co,Pb)	Ag										
4	Ga,Ti,Cr, V, Fe, Co,Ni,Cu Sn,Mo)	As,Mo,Zn Ag,Cu,V	Pb,Sn,Zn	Mn(Pb,Co) / Ag											
3	Ga,Ti,V Cr,Fe Ni,Co,Cu Sn,Mo(Mn)	Pb,Zn,As Mo,Ag,Cu (Co)	Sn(Ag) / Mn,Mo(As)												
2	Ga,Ti,V Cr,Fe Cu,Ni,Co Sn(Mo)	Zn,Pb,As Mo,Ag,Ni Cu,Mn(Co)													

LEGEND

* ( ) Elements with factor loadings between /0.200/ and /0.299/.

≠ ___ Elements antipathetically related within one association, the dominant sub-association occurs over the line.

with each other or with other factor associations.

The log-transformed data solutions also revealed the mineralisation association (6 to 10 factor models) but in the lower models (less than 6 factors) combined this with other elements. The black marine shales association does not fully appear until the lower models (less than 6 factors), when it includes other associated elements. The mobile element association is never really formed. The Ga-Ti-Cr-V-Fe association occurs in an incipient form in the 15 factor model and is fully constituted below the 11 factor model. However, it is considerably more complex in these solutions than it is in either the untransformed data or in N. Wales.

It was decided that on balance the untransformed models of the English Peak District regional reconnaissance data provided the best agreement with the known associations.

During the course of follow-up studies in the English Peak District additional drainage sediment samples were collected largely over the lower Namurian bedrocks surrounding the Carboniferous limestone plateau. Data for 70 of these additional samples were included with the reconnaissance data and the data were processed with the R-mode analysis programme. Complete solutions between 15 and 2 factors were obtained from the data both untransformed and log-transformed. The solutions are summarised in tables 28 and 29.

The untransformed data solutions locate all those associations

Table 28.

The trace element associations indicated by R-mode factor analysis of the untransformed trace element data from the reconnaissance and follow-up surveys of the English Peak District, for all models between 2 and 15 factors.

Factors	1	2	3	4	5	6	7
Factor Model							
15	Fe	Pb	Co(Ni)*	Cu	Sn	Ga	Ag
14	Ti,Fe	Pb	Co,Ni(Mn)	Cu	Sn	Ga	Ag
13	Ti,Fe	Pb	Co,Ni,Mn	Cu	Sn	Ga	Ag
12	Fe,Ti	Pb	Co,Mn,Ni	Cu	Sn	Ga(Ti)	Ag
11	V(Mn,As Ti)	Pb	Co,Mn,Ni	Cu,As	Sn	Ga(Ti) / (As) ≠	Ag
10	Fe,Ti (As)	Pb,Zn	Co,Mn,Ni	Cu,As	Sn	Ga(Ti)	Ag
9	Ti,Fe V(As,Mn)	Pb,Zn	Co,Mn,Ni (Fe)	Cu,As	Sn	Ga(Ti,Ni) / (As)	Ag
8	Mo,V,As Fe,Ti,Ni	Pb,Zn	Co,Mn,Ni (Fe)	Cu,As	Sn	Ga,Ti / As	Ag
7	Cr,Ti Fe,V (Cu)	Pb,Zn	Co,Mn,Ni Fe	As,Cu,Mo V,Fe,Ni	Sn	Ga,Ti / (As)	Ag
6	Cr,Ti,V Fe,As,Mo	Pb,Zn	Co,Mn,Ni Fe	Cu,As,Ag Mo,V(Ni)	Sn,Ag	Ga,(Ti) / (As)	
5	Ti,Ga,Cr V,Fe (Ag)	Pb,Zn	Co,Mn,Ni Fe	As,Cu,Mo V,Ag Fe(Ni) / (Ga)	Sn,Ag(Cu)		
4	Ti,Ga,Cr Fe,V Ag	Pb,Zn	Co,Mn,Ni (Fe,Sn)	As,Cu,Mo V,Ag Fe(Ni)			
3	V,Ti Fe,As Cr,Mo,Ga Cu,Ni	Zn,Pb,Ag As,Mo,Cu / (Ga,Ti)	Co,Mn,Ni (Fe,Sn)				
2	Fe,Ni V,Ti,Mn Mo,As,Co Cr,Cu,Ga	Zn,Pb,Ag As,Cu,Mo / Ga(Ti)					

Factors	8	9	10	11	12	13	14	15
Factor Model								
15	Cr	Mo	V	Zn	As	Mn	Ni	Ti
14	Cr	Mo	V	Zn	As	Mn	Fe,Ni	
13	Cr	Mo,Ni (Fe,V)	V(Ti)	Zn	As	Mn		
12	Cr	Mo,Ni (Fe,V)	V(Ti)	Zn	As			
11	Cr	Mo,As,Ni (V,Fe)	Fe_2O_3,Ti / (As)	Zn				
10	Cr	Mo,As,Ni (V,Fe)	V(Mn,As Ti)					
9	Cr	Mo,As,Ni V(Fe)						
8	Cr,Ti / (Mo)							

LEGEND

* ( ); parentheses enclose elements with factor loadings between /0.200/ and /0.299/.

≠ ___; horizontal bar indicates factor constituted of two antipathetic associations, the dominant association on the upper side of the bar.

Table 29

The trace element associations indicated by R-mode factor analysis of the log-transformed trace element data from the reconnaissance and follow-up surveys in the English Peak District, for all models between 2 and 15 factors.

Factor 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Factor Model														
15 Ti	Pb	Ga	Ag	Sn	Co,Ni	Cu	Cr	Mo	Mn	Zn	As	Fe	V	Ni
14 Ti	Pb	Ga	Ag	Sn	Co,Ni	Cu	Cr	Mo	Mn	Zn	As	Fe	V	
13 Fe	Pb	Ga	Ag	Sn	Co,Ni(Mn)	Cu	Cr	Mo,V(Ni)	Mn	Zn(Ni)	As	Ti(V)		
12 Ti,Fe,V	Pb(Zn)	Ga	Ag	Sn	Co,Ni Fe(Mn)	Cu	Cr	Mo,V(Ni)	Mn	Zn(Ni)	As			
11 Ti,Fe*,V	Pb(Zn)	Ga,Ti (V,As)	Ag	Sn	Co,Ni Fe,Mn(Cu)	Mo,As,V Fe (Ni)	Cr	Cu,As	Mn	Zn(Ni)				
10 Ti,Fe,V	Pb,Zn	Ga,(Ti,V Cu,As)	Ag	Sn	Co,Ni Fe,Mn(Zn)	Cu,As (Ni)	Cr(V)	Mo,As, Fe V(Ni)	Mn(Co)					
9 Mo,As,V Fe (Ni)	Pb,Zn	Ga,Ti (As,V, Cu)	Ag	Sn	Mn,Co, Ni Fe	Cu,Zn Ni,Co	Cr	Ti,Fe V(As,Ga)						
8 As,Mo,V Fe (Zn,Ti Cu,Ni)	Pb,Zn	Ga,Ti,V (Fe)	Ag	Sn	Mn,Co, Ni,Fe	Cu,Ni Ga,Cc (Mo,Zn)	Cr(V)							
7 Cr,Ti,V Fe (Ga,Mn)	Pb,Zn	Ga,Cu Ni,Ti (V,Co)	Ag	Sn	Mn,Co, Ni Fe	As,Mo Cu,V,Zn Ni,Fe								
6 Cr,V,As Fe Mo,Ti (Ni,Zn)	Pb,Zn Cu,Mo (As)	Ga,Cu, Ti,Ni (V)	Ag,Cu (As)	Sn	Mn,Co Ni Fe									
5 Fe Cr,V,As Ti,Mn,Mo Ni,Co	Pb,Zn Co,Mn Ni,Cu (Mo)	Ga,Cu Ni,Ti Co(V)	Ag,As Cu,Mo (Sn) ≠ Mn	Sn(Ag Mn,Co)										
4 V,Fe Ti,Cr, Pb,Mo,Ni Mn,Co,Ga Cu,Zn	Pb,Zn, Mn,Co Ni(Mo Cu)	Ga,Sn Cu,Co ____ As	Ag,Cu, As,Mo (Zn,V) Mn											
3 V,Fe Ti,Cr, As,Mo, Ni,Mn, Mo,Ga, (Cu,Zn)	Zn,Pb Ag,As, Mo Cu,Ni Ga(Ti)	Ga,Co,Sn Ni,Cu,Mn Pb(Zn) As												
2 V,Fe Ti,Ni, Cr,Co, Mn,Mo Ga,As Cu,Zn	Pb,Zn, Cu,Ag, Mo,As, Ni (Sn,Co) (Cr,Ga)													

LEGEND

* ( ); parentheses enclose elements with factor loadings between /0.200/ and /0.299/

≠ ____; horizontal bar indicates 2 antipathetic associations within one factor, the dominant association is on top of the bar.

indicated in the reconnaissance data though the order of importance of the elements and the representation of the less significant elements within the factor associations has been modified. Examples of this may be observed in the 5 factor model where Ti-Ga-Cr-V-Fe (factor 1) replaces the equivalent association for the reconnaissance data (Ga-Ti-V-Cr-Fe). The same feature is shown by the association As-Cu-Mo-V-Ag-Fe -(Ni) (cf. As-Mo-V-Cu-Ag-Ni-Fe).

The log-transformed data solutions show significant differences both from their untransformed equivalents and also from the equivalent solutions of the reconnaissance data. The main difference between this data set and that of the reconnaissance data is that the mobile element association is constituted (6 to 12 factor models) whereas that of Cr-Fe -Ga-Ti-V is split or reapportioned to other associations. The lower models (below 7 factors) also reapportion the black marine shales association between other factors.

It was decided that the untransformed data again provided the most potentially useful solutions. Further work was conducted on the data comprised both of the reconnaissance and follow-up drainage sediment data since this constitutes a more complete expression of the geochemistry of the drainage sediments in the English Peak District. The difference between the complete data set and that derived from the reconnaissance survey is probably caused by the collection of the additional samples from over the lower Namurian strata. This introduces a rather different bias to the data than was present in the reconnaissance data alone.

The optimum model from the untransformed data solutions was considered to be that with 5 factors. This is the simplest model indicating all the known trace element associations without exhibiting either their fragmentation or agglomeration. The 4 factor model includes Sn, an immobile element, with the mobile element association; whilst the 6 factor model splits the first factor into two factor associations.

The factor scores for the 5 factor model were generated for all the individual samples. The factor scores have been subjected to moving average analysis in order to identify regional trends.

6.6.2. The results of moving average analysis upon the factor scores derived from the Peak District regional survey drainage sediment data.

The factor scores for factors 1, 2, 3, and 4 from the 5 factor model (untransformed data) have been processed with the moving average analysis programme. The last factor indicates the association, Sn-Ag-(Cu), but in higher models (greater than 6 factors) the principal elements, Sn and Ag, are constituted as unielemental associations. It is considered that the last factor in the 5 factor model is merely composed of elements which are essentially independant entities rather than components of a significant trace element association. This factor association does not appear to have any geochemical or geological significance in this area and consequently has been excluded from the regional analysis.

The results from the moving average are described below and the distributions are displayed in figs. 187-190, vol. 2.

(i) Factor 1: Ti-Ga-Cr-V-Fe, positive factor. (fig. 187, vol. 2)

The Viséan-Namurian (V-N) shale series and the Westphalian outcrops usually underlie the highest concentrations of this association (>0.0), and there are extensive areas of very high values (> +1.0) particularly to the west of the dome. The Namurian sandstone series have generally lower levels (< -0.5), except adjacent to the V-N and Westphalian outcrops. The Permo-Triassic underlies areas with very low concentrations (< -1.0) both in the north-west of the survey area and also along the basal (Bunter) beds of the southern outcrop. The stratigraphically higher Permo-Triassic Keuper beds have marginally higher values (<-0.5).

The higher concentrations occur over the more argillaceous stratigraphic units (V-N series and Westphalian), and the lower levels are found over the more arenaceous units (Namurian sandstone series and Permo-Triassic). This would suggest that these elements, which, except for Fe, are relatively immobile in the secondary environment, are controlled by the presence of minerals common in argillaceous sediments. This impression is strengthened by the increase in the concentration values from the very arenaceous basal (Bunter) Permo-Triassic beds to the more argillaceous bedrocks of the stratigraphically higher Keuper Marls.

(ii) Factor 2; Pb-Zn, positive factor. (fig. 188, vol. 2)

The highest concentrations of this association (>+1.0) occur principally on the northern and eastern flanks of the dome, and are associated with the outcrops of the Visean-Namurian shale series. Extensive areas of higher than average values envelope much of the eastern dome flank, covering most of the Namurian sandstone series outcrop and also extending over onto the Westphalian bedrock. The V-N series outcrop, south and west of the dome are also associated with higher levels (>0.0) particularly over the basal parts of the succession, whilst in the south, the zone of higher values extends over an area of the eastern Permo-Triassic.

The main features of this pattern are controlled by the extensive and intense mining and smelting contamination associated with the mineralisation on the eastern flank of the limestone plateau and in the mineralised inliers on the eastern flank. The extension of the moderately high values over the Namurian and Westphalian are related to the sites of the smelters which were located on the westward facing scarps, formed by these stratigraphic units (Taylor, 1969). The higher values over the eastern part of the southern Permo-Triassic outcrop are related to high Pb and Zn concentrations in the cement of the basal conglomerates of these strata (Taylor, op. cit.). The basal portion of the Visean-Namurian succession also exhibit higher levels. This enhancement may be related to the syngenetic concentration of these elements in the black marine shales. Another explanation of this

feature might be contamination associated with the exploitation of mineralisation within the Carboniferous limestone which is exposed in the cores of minor anticlines on the western and southern flanks of the dome.

(iii) Factor 3; Co-Mn-Fi-Fe, negative factor. (fig.189, vol. 2)

The highest concentrations of this association (<-1.0) occur on the northern and western flanks of the dome, whilst the Viséan-Namurian shale and the Westphalian outcrops are usually associated with only marginally higher levels (<0.0) particularly on the western flank of the dome. The Namurian sandstone series generally exhibit variable concentrations (<+1.0 to >-1.0). The concentration levels over the Permo-Triassic are generally very low (+0.5) both over the north-western and southern outcrops.

The distribution of this factor indicates a certain degree of lithological control in that certain stratigraphic units, for instance the Permo-Triassic, are low in this association, whilst others, notably the Viséan-Namurian series, are high. However, the disposition of the moorland areas, which would be expected to bear higher concentrations of these elements in the drainage channels due to secondary environmental enrichment, shows some correlation with the location of the areas with the highest scores. Moreover, the location of these areas of highest factor scores is predominatly to the west of the dome, and this area has a relatively higher annual rainfall than the eastern flank (see fig. 15).

(4.) Factor iv); As-Cu-Mo-V-Ag-Fe-(Ni), positive factor

(fig. 190 vol. 2)

The areas with the highest concentrations of this factor ($>+1.0$) all overlie the basal portions of the Viséan-Namurian (V-N) shale series outcrop, particularly to the west and south of the limestone plateau. However, all the V-N outcrop areas are associated with higher values (>0.0), except over the drift covered areas in the west which have lower values(<0.0). The remaining stratigraphic units are usually overlain by low concentrations (<0.0), with extensive areas of very low values (<-0.5), notably over the Namurian sandstones series, and also over the Westphalian, particularly to the east and north of the limestone plateau. The southern outcropping Permo-Triassic is usually lower (<0.0) than that in the north-west. A significant feature over the southern Permo-Triassic is that lower values (<-0.5) are found over the stratigraphically higher Keuper Marls than over the more arenaceous Bunter horizons.

The areal distribution of the factor scores evidently indicate a concentration of these elements in the basal part of the V-N succession. The constitution of this factor association is in good agreement with the trace element association which has been shown to be enriched in the V-N black marine shales (Fletcher, 1968), which are more common at the base of this succession.

6.6.3. Discussion

The regional distribution of the factor scores has confirmed

that factors 2, 3, and 4 can be respectively related to areas:

(i) of mining and metallurgical contamination.

(ii) within which secondary environmental effects may be operative.

(iii) underlain by black marine shales.

The regional distribution of factor 1(Ti-Ga-Cr-V-Fe) indicates an enhancement over the dominantly argillaceous relative to the more arenaceous stratigraphic units. A further feature of possible significance is the location of the highest zones for this factor and factor 4 (As-Cu-Mo-V-Ag-Fe-(Ni) over the Viséan-Namurian (V-N) shale series to the west of the limestone plateau. However, to the east of Leek there is an off-set though overlapping relationship, in the location of the areas of peak values for these two factors, which may indicate a change of lithological facies between the basal and upper portions of the V-N succession.

6.7.0. SUMMARY AND CONCLUSIONS.

The factor analysis has in each of the three areas located the major trace element associations known from a priori information. The analysis has in addition indicated a very strong and previously unrecognised association of Cr-Fe -Ga-Ti-V in both N. Wales and the English Peak District and a modified version of this association in S. W. England. The areal dispersion patterns of the scores on this association suggest only a partial control by the incidence of outcropping basic igneous rocks in S.W. England and N. Wales, whilst no such explanation can be advanced for the patterns in the English Peak

District. There are correlations between the regional patterns and the disposition of the stratigraphic units, which suggest that this association may reflect the argillaceous content of the bedrock but this can only be a tentative conclusion at this stage..

The analysis has located within each area an association clearly related to those elements which are mobile in the secondary environment. This feature had not previously been confirmed in the English Peak District. This indicates the general relevance of these secondary environmental effects in their ability to modify geochemical patterns for these elements in Great Britain.

There may be cited against these achievements a number of disadvantages of the method. These are briefly summarised below:

(i) only geochemically pronounced effects are usually located by the technique.

(ii) elements displaying dual, but very unequal allegiances, to two trace element associations may be assigned to that association representing the more geochemically pronounced effect.

(iii) similar but non-identical trace element associations related to similar, but distinct causative agencies tend to be merged by the technique.

(iv) minor geochemical associations displaying subtle geochemical effects are not in general located by the technique.

It is possible that if each trace element distribution was sep-

arately normalised by applying the appropriate transformation, the factor analysis might even more successfully distinguish the trace element associations within the data.

It may be concluded that the technique in indicating all the major known associations and in locating another previously unrecognised association has fulfilled the aims expressed in section 6.2.0. There remains the problem of assessing whether the newly revealed association reflects a geologically relevant feature or whether it represents a mathematical abstraction from the multivariate correlations within the data.

CHAPTER VII

DETAILED INVESTIGATION OF AN R-MODE FACTOR ASSOCIATION

7.1.0. THE PROBLEM TO BE INVESTIGATED

The application of R-mode factor analysis to the drainage sediment data from the three survey areas indicated the presence of a factor association whose principal components were Cr, Fe, Ga, Ti and V. This association was located in N. Wales, the English Peak District and in a modified form in S.W. England. The association had not been recognised previously and it was necessary to establish whether this represented a mathematical abstraction based on the multivariate correlations existing between the trace elements or whether it was a geologically meaningful association.

7.2.0. THE AIM OF THE INVESTIGATION

The aim is to establish whether the factor association of Cr-Fe-Ga-Ti-V is geologically viable. This may be ascertained by determining whether it can be located in soils and bedrocks in an area showing a high contrast in factor scores of this association in the drainage sediments. If the association is located in the bedrock, then it is necessary to establish which mineralogical components, if any, are controlling its presence.

7.3.0. DESCRIPTION OF THE AREA FOR DETAILED INVESTIGATION

7.3.1. Location

The area chosen for the detailed investigation occurs in the English Peak District on the western flanks of the Carboniferous dome, and includes portions of the parishes of Bradnop, Heathylee, Onecote and Tittesworth, all within northern Staffordshire and henceforth referred to as the Onecote area. The National Grid boundary lines of the area are 4000 (west), 4050 (east), 3540 (south) and 3630 (north), see figure 32.

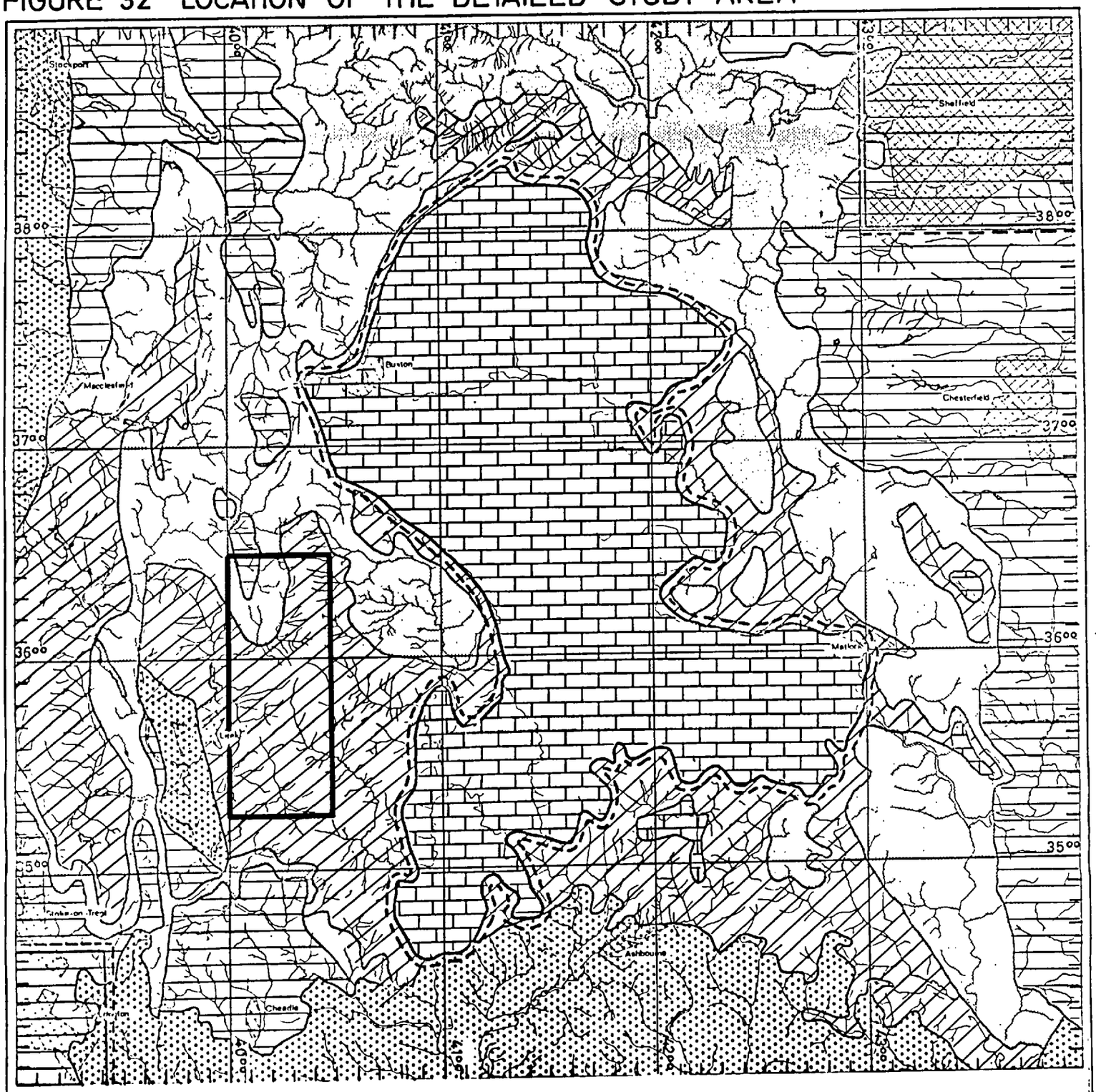
This area was chosen for the following reasons:-

(i) The factor scores for the Cr-Fe-Ga-Ti-V association exhibit a high contrast within the area.

(ii) The factor score patterns for this association and that related to the black shales (As-Mo-Cu-V-etc.) show an areally offset relationship. The lower strata exhibit enhanced levels in both associations, whereas only the Cr-Fe-Ga-Ti-V association exhibits enhanced scores in the higher strata.

(iii) The stratigraphical and sedimentological succession in this area has been investigated by workers at the Department of Geology at Keele University and

FIGURE 32 LOCATION OF THE DETAILED STUDY AREA



REGIONAL GEOCHEMICAL RECONNAISSANCE
STREAM SEDIMENT SURVEY

DERBYSHIRE

Sampled area

Project 65
May 1967
Applied Geochemistry Research Group
Imperial College, London, S.W.7.

N

0 1 2 3 4
miles

GEOLOGICAL KEY

- NEW RED SANDSTONE
- COAL MEASURES
- NAMURIAN WITH MAIN SANDSTONES
- SHALES BELOW MAIN NAMURIAN SANDSTONES
- CARBONIFEROUS LIMESTONE

DETAILED STUDY AREA

Regional Geochemical Survey for N.E.R.C.
(Institute of Geological Sciences)

is relatively well understood.

(iv) The southern part of the area has been subjected to detailed geochemical investigation on drainage sediments, soils and bedrocks in order to establish the validity of the black shale association (Fletcher, 1968). The soil trace element data has confirmed the offset patterns recognised in the reconnaissance stream sediment factor score data for the elements constituting these two associations.

7.3.3. Topography and drainage

The topographical relief is high in the north and east but declines to the west and south. High, poorly drained moorland areas cover the north-eastern portion of the area. (figure 33).

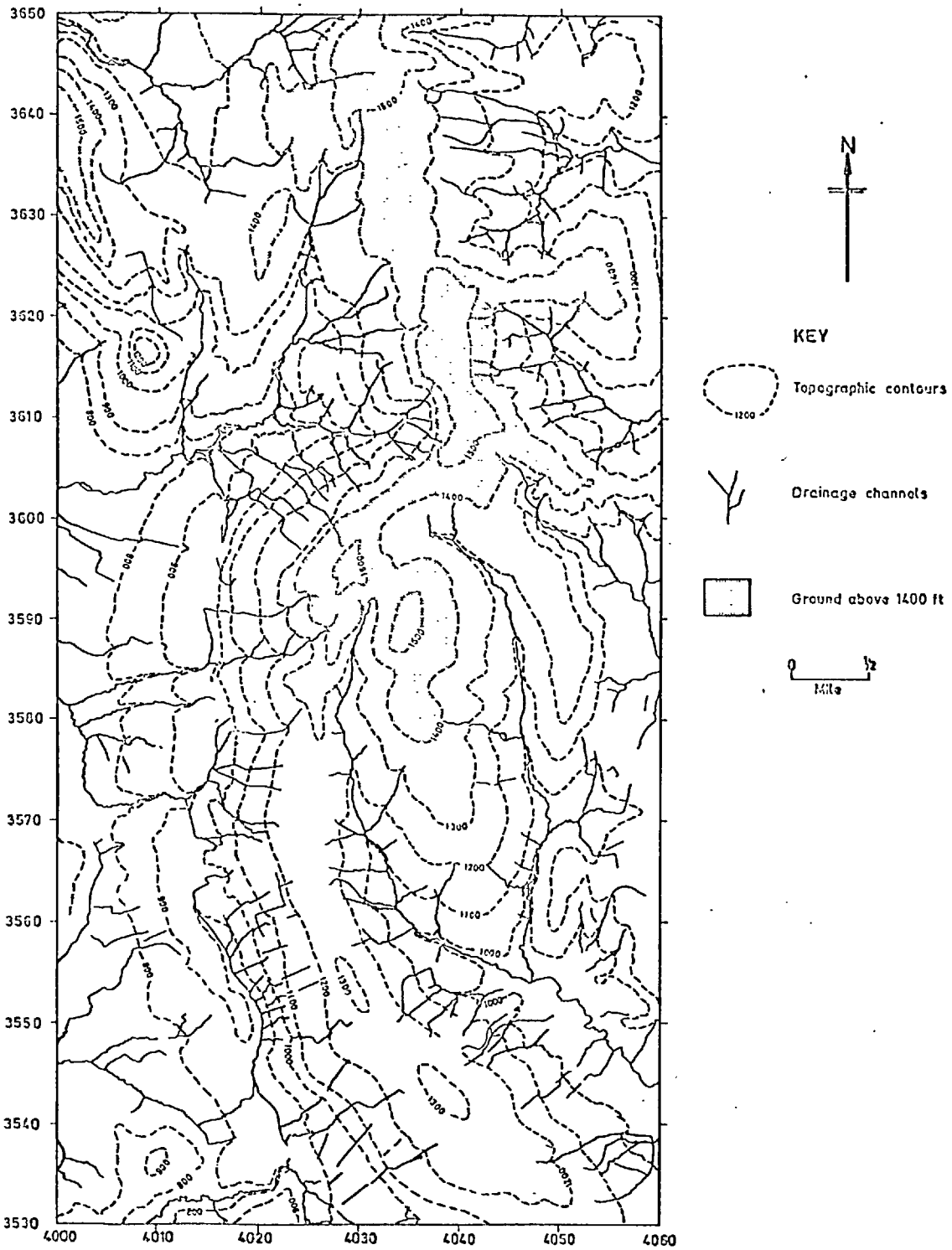
The small drainage channel density is high over the whole area. The larger streams drain principally to the west and south into the Churnet and Hamp rivers respectively.

7.3.4. Geology

Structurally the area lies on the western flank of the Carboniferous dome. Limy shales and shaly limestones of P_1 age, the oldest rocks outcropping in this area, are exposed in the core of the small Mixon anticline in the south-eastern portion of the

FIGURE 33

TOPOGRAPHY OF THE DETAILED STUDY AREA



area. The youngest bedrocks occur in the Goyt syncline in the north-western segment of the area in which Namurian sediments of up to Gastrioceras subcrenatum age are exposed (Cope, 1945). The stratigraphical sequence between these two ends of the time spectrum exhibit a rhythmic sequence of alternating marine bands, shales, calcareous siltstones and protoquartzites. The proportions of these lithological components vary in different parts of the succession. The stratigraphic succession after Holdsworth (pers.comm) is summarised in table 30. For the purpose of this study interest is mainly centred on stratigraphic units 1 to 6, and therefore those between 7 and 11 have been combined to form stratigraphic unit 7-11. The geology is displayed in figure 34.

The area was affected by the Pleistocene glaciation, and there is a drift cover of variable thickness over ground below the 1000 foot contour line (Cazalet, pers.comm. 1968). This restricts the drift cover to the lower areas in the centre-west and south-west of the area

7.3.5. Pedology

Most of the area, except that detailed in the preceding section is covered by residual or locally transported overburden. The drift in the west is considered to be of largely Permo-Triassic derivation. The residual soils form peaty gleys on the exposed moorland, with gleys and brown earths on the better drained slopes and lower ground.

TABLE 30

MAIN STRATIGRAPHIC UNITS EXPOSED IN THE CHECOTE AREA, N. STAFFS.

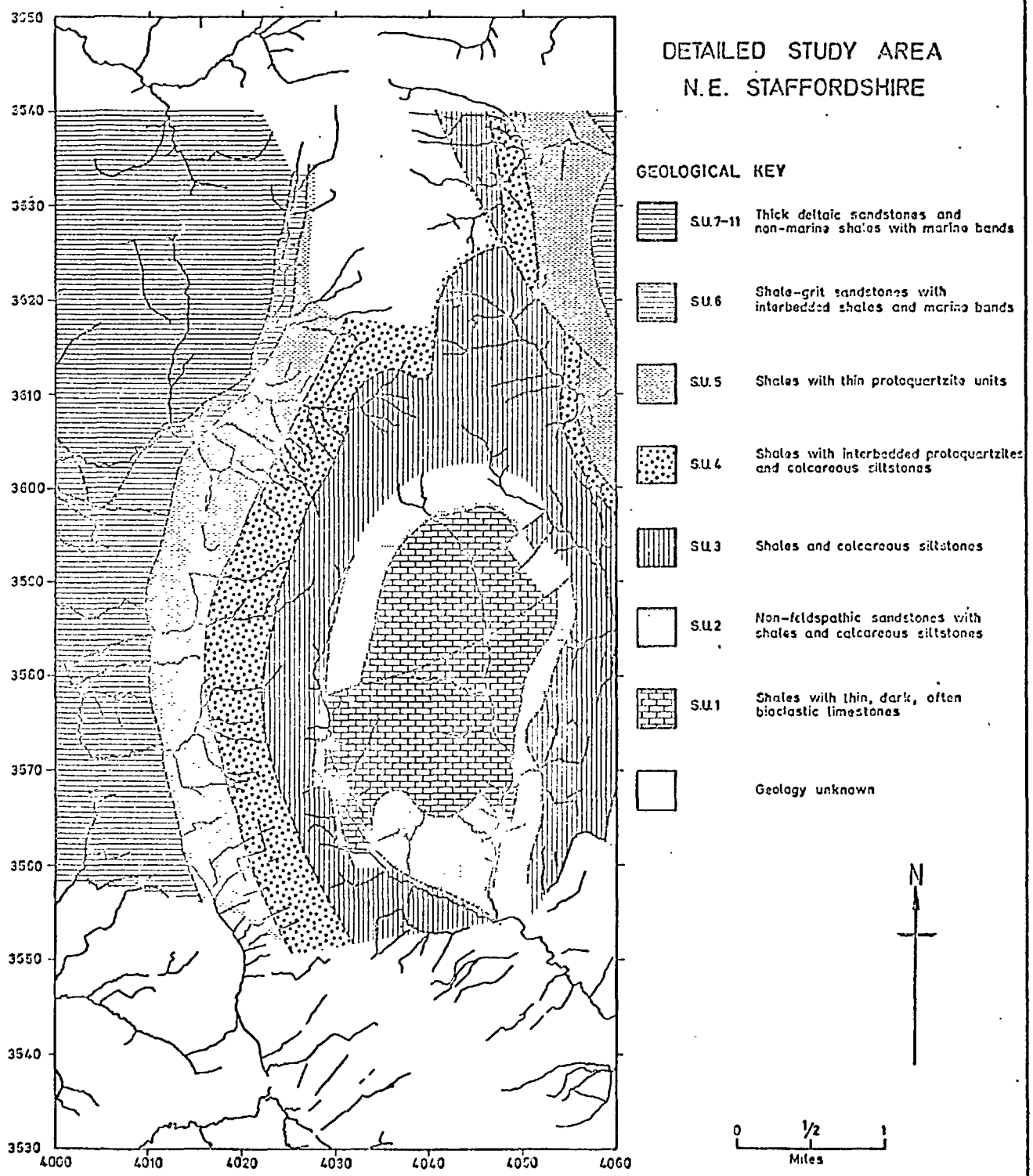
(MOD. AFTER HOLDSWORTH ET.AL., pers. comm., 1968)

Stratigraphic unit	Name	Thickness	Lithology
11	ROUGH ROCK	50 ft.	Sandy shales with iron stones and marine bands.
	Gastrioceras subcrenatum marine band		
	ROUGH ROCK	110 ft.	Lithology as above.
10	HOLCOMBE BROOK	200 ft.	Shaly mudstone interbedded with ironstones and marine bands.
	Gastrioceras cambriense marine band		
	Gastrioceras cancellatum marine band		
	HOLCOMBE BROOK	150 ft.	Massive bedded sandstone
9	ROCHES GRIT	100 ft.	Shaly mudstones interbedded with sandy shale.
		150 ft.	Coarse, feldspathic, cross bedded sandstone.
	Reticuloceras superbilingue marine band		
8			Deltaic deposits, thick beds, coarse sandstones with silty or micaceous shales.
7		175 ft.	Proximal turbiditic deposits, shales with silty mudstones at base, micaceous at top.
		85 ft.	Thick sandstone
	Reticuloceras bilingue marine band		

TABLE 30 (continued).

Stratigraphic unit	Name	Thickness	Lithology
6	"LONGNOR SANDSTONE" TYPE		Turbiditic feldspathic sandstone of 'shale-grit' type with interbedded shales.
	Reticuloceras reticulatum s.s. marine band		
5			Predominantly shales with thin protoquartzite units, no calcareous siltstone.
	Cravenoceras edalensis marine band		
4			Mainly shales with alternating units of protoquartzite and calcareous siltstone.
	Cravenoceras malhamense marine band		
3	Gun Hill Siltstones Formation		Alternating shales and calcareous siltstones. No protoquartzites.
	Cravenoceras leion marine band		
2	"ONECOTE" SANDSTONE FORMATION		Interbedded, non-feldspathic, often bioclastic sandstones with interbedded shales and calcareous siltstones.
	Goniatites granosum marine band		
1	MIXON LIMESTONE-SHALE FORMATION		Shales with minor silty layers and thin dark limestones, often bioclastic and graded.

FIGURE 34 GEOLOGY OF THE DETAILED STUDY AREA



7.3.6. Geochemistry

The southern portion of the area had been covered previously by a soil grid. The trace element patterns were used to demonstrate high levels of As, Cu, Mo and V in the east relative to the west of the grid, with a sudden reduction from the eastern zone of enhanced concentrations to the lower levels in the west. It was shown that the high trace element concentrations were due to the presence of sub-outcropping black marine shales (Fletcher, op.cit.)

7.4.0. DESCRIPTION OF TECHNIQUES

7.4.1. Stream sediment sampling

Detailed stream sediments were taken from drainage channels over the whole area. Only actively worked sediments were sampled. These were stored in kraft paper bags, each of which holds about 150 gms of dried sediment. The samples were dried in a Gallenkamp oven at approximately 70°C. The dried material was broken up in a pestle and mortar and sieved to remove the minus 80 mesh fraction, which was retained for analysis.

A total of 198 drainage sediment samples were taken over 24 square miles yielding an average density of approximately 8 samples per square mile.

7.4.2. Soil sampling

The soil grid layed out by Fletcher (op.cit.) was extended to cover the entire area. Samples were collected, using a manual auger, at two depths, 6-12 inches. and 18-24 inches. The soil samples were stored in kraft paper bags and dried at approximately 70°C in a Gallenkamp oven. The 6-12 inch depth samples were ground in a pestle and mortar and were sieved to remove the minus 80 mesh fraction which was retained for analysis.

A total of 287 sites were sampled over 15.6 square miles, at an average density of approximately 18 samples per square mile.

7.4.3. Bedrock sampling

The bedrocks were sampled from the stream sections. Each lithological type, namely, sandstones, calcareous siltstones, limestones, shales and marine bands, represented at each site were separately sampled and stored in large kraft paper bags. An effort was made to take the least weathered material at each site, but unweathered material was rarely available. The samples were dried and broken in a small jaw-crusher. The resulting fragments were dry ground to minus 80 mesh in a motor driven pestle and mortar and retained for analysis.

7.4.4. Analytical methods

The drainage sediment, soils and bedrock samples were

analysed on a Hilger and Watts Large Quartz Spectrograph for the elements Ag, Bi, Cr, Co, Cu, Fe (as Fe_2O_3), Ga, Mn, Mo, Ni, Pb, Sn, Ti and V, by the analytical method described by Nichol and Henderson-Hamilton (1965). The concentrations for all elements, except Ag, Pb and Sn, were determined using a Hilger and Watts L90 microphotometer and standard curves. These were constructed from line intensities of known trace element concentrations on a standard plate. The element concentrations for Ag, Pb and Sn were determined by visual comparison with the lines on the standard plate.

The elements As and Zn were determined by wet chemical methods. The method for As was that detailed by Stanton (1966), involving a potassium bisulphate attack, followed by a weak acid (dilute HCl) leach. The leach solution was used to produce arsine (AsH_3), which is caused to react with $HgCl_2$ paper held in a Gutzeit tube. An aliquot (2.0 mls) of this leach solution was also used to determine the Zn concentration using a Perkin-Elmer Atomic Absorption Spectrophotometer, model 303.

7.5.0. SAMPLING AND ANALYTICAL PRECISION AND ACCURACY

7.5.1. Analytical accuracy

The analytical accuracy was determined by replicate analyses of G_1 and W_1. The mean levels and ranges are shown together with those published by Stevens et al (1960) in table 31.

The analysed results compared to the mean values from the published results (Stevens et.al. op.cit.) are also summarised and shown in table 32.

Table 31 The replicate and mean trace element concentration levels of G_1 and W_1 obtained by spectrographic analysis, compared to some published values. (Stevens et al, 1960)

Analysis	ppm Ag	ppm Cr	ppm Co	ppm Cu	% Fe	ppm Ga	ppm Mn	ppm Mo	ppm Ni	ppm Pb	ppm Sn	ppm Ti	ppm V
G_1 1	<0.2	12	<5	4	1.2	10	146	3	<5	23	<5	2000	15
G_1 2	<0.2	10	<5	4	1.2	11	170	3	<5	26	6	2000	<5
G_1 3	<0.2	9	<5	5	1.3	14	180	2	<5	40	5	1700	<5
G_1 4	<0.2	13	<5	5	1.4	13	140	3	<5	33	8	2200	7
G_1 5	<0.2	8	<5	4	1.3	10	154	3	<5	17	<5	1700	7
MEAN	<0.2	10	<5	4	1.3	12	158	3	<5	28	5 (<5=4)	1880	9 (<5=4)
STEVENS	-	22	2.2	13	-	18	210	7	1.2	50	2-3	1400	21
W_1 1	<0.2	126	29	45	13.6	6	720	<2	48	<5	<5	9800	300
W_1 2	<0.2	160	27	64	16.5	7	650	<2	51	<5	<5	11000	590
W_1 3	<0.2	130	33	52	14.0	6	750	<2	66	<5	<5	9700	400
W_1 4	<0.2	125	29	88	12.6	6	810	<2	47	<5	<5	9800	300
W_1 5	<0.2	134	31	61	13.5	5	810	<2	58	<5	<5	8800	385
MEAN	<0.2	137	30	62	14.0	6	748	<2	54	<5 (<5=4)	<5	10020	375
STEVENS	-	120	51	110	-	16	1300	0.5	82	7	2-3	7400	240

Table 32 Summary of the relative mean concentration levels from the spectrographic analysis compared to some published values (Stevens et al, op.cit.).

Higher		Equal ($\frac{\text{high-low}}{\text{low}}\% \leq 20\%$)		Lower	
G_1	W_1	G_1	W_1	G_1	W_1
Sn	Ti	Co	Cr	Cr V	Co
Ti	V		Sn	Cu	Ga
				Fe	Mn
				Ga	Mo
				Mn	Ni
				Mo	Pb
				Ni	
				Pb	

It is evident that for the bulk of the elements the levels recorded in this study are low compared to the published mean levels. The significance of this to the application of R-mode analysis is not critical since the multielement correlation coefficients should not be grossly affected by a constant analytical bias. The constancy of the bias is confirmed by the levels recorded for the individual G_1 and W_1 samples (table 31), which were homogeneously distributed amongst the other samples analysed. It is important to note that since the major components of G_1 and W_1 differ considerably from most of the samples analysed, so the matrix effects on the trace element levels will vary. Thus conclusions concerning the analytical bias on the collected samples, which are extrapolated from the results of G_1 and W_1, can only be tentative.

7.5.2. Analytical precision

The precisions of the analyses of rocks, soils and drainage sediments were determined from duplicate analyses. The standard methods for establishing the precision from duplicates is not the optimum method for analytical data in which larger absolute deviations are expected at higher concentration levels. This effect will tend to increase the standard deviation relative to the mean level, which will result in overestimates of the precision. A modified procedure has been adopted in this study and is described below:-

$$\text{If} \quad PD = \left[\frac{(X_1 - X_2)}{\left(\frac{X_1 + X_2}{2}\right)} \times 100 \right] \quad \%$$

where PD is the percentage deviation of each of the duplicate analyses from the mean of the two recorded concentration levels, and X_1 and X_2 are the recorded concentration levels of the duplicate analyses

Then $$\bar{X}_{PD} = \frac{\sum_{i=1}^{N} PD_i}{N}$$

where $\bar{X}_{PD}$ is the mean percentage deviation of all the individual percentage deviations,

PD_i is the percentage deviation for the ith duplicate pair, and

N is the number of duplicate pairs.

Let $$\sigma_{PD} = \sqrt{\frac{\sum_{i=1}^{N} (\bar{X}_{PD} - PD_i)^2}{N - 1}}$$

where σ_{PD} is the standard deviation of the individual percentage deviations (PD_i) about the mean percentage deviation ($\bar{X}_{PD}$); and N is the number of duplicate pairs.

If the individual percentage deviations (PD_i) are normally distributed about their mean ($\bar{X}_{PD}$), then only 1 in 40 analyses will yield levels exceeding ($\bar{X}_{PD} + 2\,\sigma_{PD}$) percent above the mean level. The last parameter has been termed D_{MAX} and is defined below

$$D_{MAX} = \bar{X}_{PD} + 2\,\sigma_{PD}$$

The values for $\bar{X}_{PD}$, σ_{PD} and D_{MAX} for each element analysed on the rocks, soils and drainage sediments are displayed in table 33.

The large majority of the D_{MAX} levels fall below 40 per cent. The most extreme exception is As in the soils and drainage sediments which was determined not by the spectrographic method but by a wet chemical method.

Table 33 Analytical precision (%) calculated from duplicate analyses of bedrocks, soils and drainage sediments.

Element	Bedrocks			Soils			Drainage sediments		
	$\bar{X}_{PD}$	O_{PD}	D_{MAX}	$\bar{X}_{PD}$	O_{PD}	D_{MAX}	$\bar{X}_{PD}$	O_{PD}	D_{MAX}
Ag	1.5	5.5	12.5	6.4	18.7	43.8	1.0	3.3	7.6
As	13.5	13.4	40.3	19.0	19.0	57	23.9	26.3	86.5
Co	6.1	5.5	17.1	7.3	6.4	20.1	3.2	3.6	10.4
Cr	8.8	5.7	20.2	7.4	6.3	20.0	4.5	8.7	21.8
Cu	8.7	8.1	24.9	7.7	12.1	31.6	7.1	5.8	18.7
Fe	13.7	15.7	45.1	7.3	5.4	18.1	5.6	4.5	14.6
Ga	6.5	5.8	18.1	8.4	6.3	21.0	3.4	3.5	10.4
Mn	12.1	8.8	29.7	7.5	7.9	23.3	8.0	7.4	22.8
Mo	7.1	8.1	23.3	8.5	10.6	19.7	7.9	9.8	27.5
Ni	12.0	13.4	38.8	10.6	12.2	35.0	3.6	3.7	11.0
Pb	13.3	10.8	34.9	10.6	8.8	28.2	8.3	6.9	22.1
Sn	5.2	12.6	30.4	5.3	6.3	17.9	15.0	23.3	61.6
Ti	6.3	3.8	13.9	10.9	7.6	26.1	4.0	2.9	9.8
V	10.2	8.5	27.2	12.0	10.3	32.6	4.8	4.2	13.2
Zn	15.5	14.2	43.9	7.0	8.2	23.4	12.0	15.0	42.0
No. of duplicates	13			24			11		

7.5.3. Sampling plus analytical precision

The combined errors involved in sampling and analysing soil and drainage sediment samples have been estimated. The analytical data from duplicate stream sediments taken from the same minor drainage channels but not at the same sample site have been used. The duplicate soil samples were taken from proximal, but not identical, sample sites taken on a traverse across the geological strike. The computational procedure was the same as that used in the preceding section. The results are summarised in table 34.

Table 34 Sampling and analytical precision (%) calculated from duplicate analyses of soils and drainage sediments.

Elements	Soil			Drainage Sediment		
	$\bar{X}_{PD}$	σ_{PD}	D_{MAX}	$\bar{X}_{PD}$	σ_{PD}	D_{MAX}
Ag	2.4	9.0	20.4	5.0	17.3	39.6
As	30.1	32.5	95.1	34.2	21.1	76.6
Co	23.4	21.2	65.8	16.5	15.2	46.7
Cr	22.3	12.8	47.9	26.4	23.0	72.4
Cu	35.5	29.6	94.7	17.6	13.8	45.2
Fe	16.3	15.1	46.5	24.7	19.7	64.1
Ga	20.3	15.4	51.1	15.7	9.3	34.3
Mn	42.0	26.0	94.0	27.4	20.0	67.4
Mo	24.0	23.0	70.0	27.3	18.7	64.7
Ni	30.8	23.5	77.8	23.5	16.8	57.1
Pb	30.2	15.6	61.4	27.5	16.8	61.1
Sn	14.1	20.2	54.5	5.0	9.1	23.2
Ti	17.9	13.9	45.7	13.6	10.9	35.4
V	32.0	19.8	71.6	19.5	23.9	67.3
Zn	27.4	22.8	73.0	34.7	25.1	84.9
No. of Duplicates	14			12		

The results shown in table 34 indicate that the large majority of the D_{MAX} values exceed 40 per cent. The increase in these levels, compared to those shown in table 33, depicting analytical precision, may be ascribed to sampling errors. The D_{MAX} values for most elements in both sampling media usually show a minimum two-fold increase due to sampling errors. This is not the case for those elements displaying very poor analytical precision in the drainage sediments, for instance, As.

7.5.4. Discussion

It is evident that the sampling errors are usually at least equal in magnitude to the analytical errors. It may also be recognised that the sampling imprecision will in most cases account for a large proportion of the data variability.

7.6.0. DRAINAGE SEDIMENT DATA

7.6.1. Areal distribution of the trace element concentrations

There is some degree of correlation between the distribution of most elements and the disposition of the underlying stratigraphic units. The distribution of the elements is displayed on symbol maps in figures 194 to 207 in volume 2. Brief descriptions of the salient features of the trace element distributions are given below:

Arsenic (fig. 194, vol.2.)

The samples with lower concentrations ($\leq$ 50 ppm) are

scattered over all stratigraphic units (S. U.). The lower units, notably S.U. 1, 2 and 3 bear the majority of the samples which gave high concentrations. (50 - >100 ppm).

Chromium (fig.195, vol.2)

The pattern is complex, and lower concentrations (<100 ppm) occur over all stratigraphic units (S.U.). However, the proportion of samples with higher concentrations (100- >150) is greater over S.U. 1, 4 and 5.

Cobalt (fig.196 vol.2)

There is apparently little stratigraphic control over the distribution of this element. A high proportion of the samples with relatively enhanced levels of Co occur over the northern area underlain by S.U. 2 and 3. This, it will be recalled, is an area of high, poorly drained moorland.

Copper (fig.197 vol.2)

There is a very marked concentration of samples with enhanced copper levels (50- >200 ppm) over the lower stratigraphic units (S.U. 1, 2 and 3). Elsewhere, the concentration levels are lower (<50 ppm) especially over S.U. 7-11, where the majority of samples contain less than 20 ppm.

Gallium (fig.198 vol.2)

The distribution of concentration levels is complex, but there is a concentration of samples with relatively enhanced levels

(> 8 ppm) in streams draining the moorland area, over the northern portions of S. U. 3. Elsewhere, there are relatively high proportions of samples with enhanced concentration levels over S.U. 4, 6, and 7-11.

Iron (fig.199, vol.2)

The highest concentrations (16- > 20%) occur in those streams draining the northern moorland. Elsewhere levels tend to be highest over S.U. 5, and lowest over units 6 and 7-11.

Lead (fig.200, vol.2)

There is a very high proportion of samples with enhanced concentration levels (70- > 150 ppm) over the lower stratigraphic units (S.U. 1, 2, and 3) and a slight enhancement over S.U. 7-11.

Manganese (fig.201, vol.2)

The distribution indicates enhanced concentrations (1500- > 3000 ppm) over the northern moorland area and over the middle stratigraphic units (S.U. 4 and 5) and also to a lesser extent over the basal unit (S.U. 1).

Molybdenum (fig.202, vol.2)

A strong apparent stratigraphic control is indicated in the distribution of this data. Samples with enhanced concentrations are located on streams mainly draining S.U. 1, 2, 3 and 4. A possibly significant feature over S.U. 1 is the location of these

molybdeniferous samples around the northern and western margins of the outcrop.

Nickel (fig. 203, vol.2)

The samples with the most enhanced concentrations (100-> 200 ppm) occur over the lower stratigraphic units S.U. 1, 2 and 3. It is also noticeable that a high proportion of the samples from streams draining the northern moorlands also bear high levels (usually 50-200 ppm). The lowest concentration levels (usually <50 ppm) are found in streams draining S.U. 7-11.

Tin (fig. 204, vol.2)

The distribution of this element is very complex and appears to be almost random. Slight enhancements over S.U.3, especially in the streams draining the northern moorland may be distinguished.

Titanium (fig. 205, vol.2)

There is an apparent stratigraphic control effecting the distribution of this element, with the greatest enhancements (> 7000 ppm) in samples from streams draining S.U. 4, 5 and 6. There are also marginally higher concentrations (often 5000-7000 ppm) over the northern moorlands portion of S.U. 3.

Vanadium (fig. 206, vol.2)

The stratigraphic control of this element is manifested in the relatively higher concentrations (300-<7000 ppm) found in

samples from streams draining S.U. 1, 2 and 3. Intermediate levels (150-700 ppm) often occur over S.U. 4 and 5 especially in the north, whilst the lowest concentration levels ($\leq$ 150 ppm) are found over S.U. 7-11.

Zinc (fig.207, vol.2)

There is a strong clustering of samples with high concentrations (500-$>$ 1000 ppm) over S.U. 1, 2 and 3, whilst over the upper part of the succession (S.U. 6 and 7-11) levels are considerably lower ($<$ 500 ppm).

The correlation between the trace element concentrations and the underlying stratigraphic units has been further examined by subdividing the drainage sediment data into stratigraphic subsets. The technique employed was to use data from sample sites in streams whose whole catchment area lay within one stratigraphic unit. The geometric means ($\tilde{X}_G$) and the ranges, ANTILOG ($\tilde{X}_G \pm 2\bar{0}$) are shown in the following table for each subset and each element (see table 35).

The extreme variability of the data, as shown by the overlapping ranges between the stratigraphic subsets, may be ascribed to two main causes:

(i) the effect of the variety of lithological types within each stratigraphic unit which may yield drainage sediments varying mineralogically between

dominant carbonate, clay or sand.

(ii) the effects of the large random errors due to the imprecisions inherent in the sampling and analytical techniques (see section 7.5.0)

Table 35 Mean trace element concentrations with concentration ranges for subsets of the drainage sediment data (ppm units unless otherwise specified) based on the underlying stratigraphic unit.

Stratigraphic Unit	No. of samples	As	Co *	Cr *	Cu *	Fe(%) *	Ga	Mn *	Mo	Ni *	Pb *	Sn	Ti *	V *	Zn *
7-11	16	5 <5-12 ≠	15 5-35	70 35-135	10 5-35	5.9 2.5-14.2	9 5-16	365 30-4375	< 2 <2-3	30 10-80	50 20-125	5 <5-12	3930 2480-6225	90 45-175	170 60-475
6	9	8 <5-78	25 10-50	80 35-200	15 5-35	6.9 1.8-26.2	5 <5-8	515 100-2590	3 <2-13	40 15-100	25 10-50	<5 -	4245 1985-9075	90 45-185	120 40-370
5	10	12 <5-135	20 10-35	145 40-520	20 10-55	12.5 4.3-36.4	6 <5-13	1455 205-10350	5 <2-20	35 15-80	25 10-70	5 <5-5	5305 2420-11620	120 20-770	170 55-535
4	10	10 <5-77	25 5-170	130 55-330	30 10-90	11.9 5.5-25.7	7 <5-14	1450 125-17110	7 4-13	60 5-515	50 20-115	5 <5-12	5865 3360-10250	185 65-520	300 45-1965
3	31	18 <5-117	25 5-130	110 60-205	50 10-215	12.7 3.9-42.0	8 <5-14	635 30-13690	10 3-32	65 10-385	65 15-230	5 <5-14	5515 3965-7670	185 80-480	360 55-2235
2	8	14 <5-90	25 10-65	110 80-135	30 10-70	8.90 4.4-18.0	7 <5-13	650 100-4140	6 2-16	60 30-115	55 20-160	5 <5-6	5140 3490-7575	190 75-480	425 175-1015
1	6	28 <5-370	25 15-40	120 110-140	100 30-450	9.8 5.6-17.2	10 7-14	1145 175-7520	5 2-17	90 65-125	115 50-265	7 <5-42	4495 3405-5940	305 205-450	685 260-1795

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* Those elements for which the data values have been rounded off to the nearest 5 (0.1 for Fe).

≠ Range figures represent $\bar{X} - 2\sigma$ and $\bar{X} + 2\sigma$ respectively.

The data of table 35 may be simplified by employing a ranking procedure. The stratigraphic units with the highest and second highest mean concentrations for any element are described as bearing high concentrations for that element, except where there is a large difference $\left(\frac{\text{1st highest} - \text{2nd highest}}{\text{2nd highest}} \% \geqslant 50\% \right)$ between these two; when only the highest concentration is kept in the high class (see table 36).

Table 36 Relative trace element concentrations in the drainage sediment subsets over the different stratigraphic units.

Stratigraphic Unit	High	Intermediate	Low
7-11		Ga, Pb, Sn	As,Co,Cr,Cu,Fe, Mn,Mo,Ni,Ti,V, Zn
6		Co,Ni	As,Cr,Cu,Fe,Ga, Mn,Mo,Pb,Sn,Ti, V,Zn
5	Cr,Fe,Mn	As,Co,Cu,Mo, Ti,V	Ga,Ni,Pb,Sn, Zn
4	Co,Cr,Mn,Ti	As,Cu,Fe,Ga, Mo,Ni,Pb,Sn,Zn	
3	Fe,Mo,Ti	As,Co,Cr,Cu,Ga, Mn,Ni,Pb,Sn,V	
2	Zn	As,Co,Cr,Cu,Fe, Ga,Mn,Mo,Ni,Pb, Ti,V	Sn
1	As,Co,Cu,Ga,Ni,Pb, Sn,V,Zn	Cr,Fe,Mn,Mo,Ti	

The lowest two mean concentration levels are retained in the low class, subject to the converse limitation used in the high class. The remaining elements are placed in the intermediate class.

The striking feature to note in both table 35 and 36 is the decrease in the relative and absolute trace element levels between unit 1 and unit 7-11. Another feature of interest is the change in relative and absolute levels of certain elements, notably Ti, which appears in the high class in units 3 and 4 but elsewhere falls in the intermediate (units 1, 2, 5) or low (units 6, 7-11) classes.

Discussion

There is some variation in concentration levels along the strike of the stratigraphic units for the elements As, Co, Fe, Mn, Ni, and to a considerably lesser extent also for Cr, Ga, V, and Zn. Higher concentration levels more frequently occur in sediments sampled from the moorland drainage channels. Two possible explanations can be advanced:

(i) the lithology of the stratigraphic units sub-outcropping at the surface changes, with a trace element enriched facies underlying the moorland area.

(ii) the secondary environment in the moorland area causes the enhancement of these elements in the drainage channels.

Investigations over the moorland areas of N. Wales

indicated that certain elements, notably, As, Co, Fe, Mn, Ni and Zn, are mobile in the low Eh-pH soil waters occurring in the poorly drained moorland soils (Horsnail, 1968). The mobile elements are leached from the acid moorland soils and when the soil waters enter the higher Eh-pH environment in the drainage channels, these elements are precipitated and coprecipitated. Therefore, this is probably the principal mechanism causing the enhancement in the moorland streams of the elements As, Co, Fe, Mn, Ni and Zn.

However, Horsnails' (op. cit.) researches led him to the conclusion that Cr, Ga and V are amongst the least mobile elements in acid, moorland soils. Thus, unless the mineralogical and chemical forms for Cr, Ga, and V are markedly different in this area compared to the Silurian slates and sandstones underlying the Denbigh moorlands; it must be assumed that some other mechanism is causing the enhanced concentration levels in the Onecote area moorland streams. It is probably that the cause for this feature is a change in the bulk lithology of the stratigraphic units underlying the moorland area.

7.6.2. The results of R-mode analysis upon the stream sediment trace element concentration data.

The trace element data were analysed using the R-mode programme, previously described. The data were log-transformed prior to the analysis because this data mode yielded more meaningful factor

associations. A total of 14 trace elements were included in the analysis, Ag was excepted because few of the samples contained detectable concentrations of this element.

The results of the R-mode analysis have been summarised in table 37. All solutions between the 10 and 2 oblique factor models have been shown. The higher solution, greater than 10 factor models, have not been included since experience with the regional data indicated that these models yielded little additional information concerning the constitution of the trace element associations.

Table 37 Trace element associations indicated by R-mode factor analysis of the log-transformed drainage sediment data from the Onecote area.

Factors	1	2	3	4	5	6	7	8	9	10
Factor Models										
10	Mo,Cu	Mn,Co,Ni,Zn	Cr	Ga	Fe	Sn	Pb,Cu	Ti	As	V
9	Mo,Cu,V	Mn,Co,Ni,Zn	Ti	Pb,Zn,Cu	Fe	Sn	Ga	Cr	As	
8	V,Mo,As,Cu, Ni	Mn,Co,Ni,Zn	Ga	Cr	Fe	Sn	Pb,Zn,Cu	Ti		
7	As,Mo,Fe,V, Cu	Mn,Co,Ni,Zn	Ga	Cr,V,Mo	Ti,Fe,	Sn	Pb,Zh,Cu			
6	As,Mo,Fe,Cu, V	Mn,Co,Ni,Zn	Cr,V,Mo	Pb,Ga,Zn, Cu,V	Ti,Fe,Ga	Sn				
5	Sn,Pb,As,Fe, Cu,Ti	Co,Mn,Ni,Zn	Mo,V,Cr, Cu,As	Ga,Pb,Ti, Zn,V,Cu	Fe,Ti					
4	Mo,Fe, As,V,Cr,Cu	Co,Mn,Ni,Zn	Pb,Sn,As, Cu,(Ti,Cr)	Ga,Ti,V, Pb						
3	Pb,Sn,As,Cu, Fe,Zn,V	Co,Mn,Ni,Zn, Cr	Ti,V,Ga, Mo,Cr,Fe, Cu							
2	Co,Ni,Mn,Zn, Cr,Mo,Cu	Cu,V,Pb,Fe,As, Mo,Ga,Zn								

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( ) indicate that the enclosed element(s) are antipathetic to the remaining elements in the factor association.

The main features of interest from the results are the early constitution of the secondary environment mobile element association of Mn-Co-Ni-Zn (factor 2,10 factor model), though this excludes As and Fe. The black marine shale association (As-Cu-Fe-Mo-V) first fully appears in the 7 factor model (factor 1). A mineralisation association (Pb-Zn-Cu) appears in the 9, 8 and 7 factor models but is destroyed in the lower models. The association, Cr-Fe-Ga-Ti-V, does not appear until the 3 factor model. Higher models indicate dual controls with Cr and V associated with Mo, and Ga-Fe-Ti forming a separate sub-association. The constitution of a Cr-V-Mo association agrees quite well with the regional trace element patterns where the patterns for these elements are quite similar, but does not correspond to the association indicated by R-mode factor analysis of the regional data.

However, the factor associations indicated in the detailed study area are otherwise comparable to those obtained from the Peak District regional data. The differences between the solutions from the two data sets are probably a function of the smaller number of geological environments occurring in the more restricted, detailed study area. Another factor causing modifications of the factor associations may be the change in the numerical proportions of the samples representing each of the environmental and geological controls. Thus the factor analysis of the regional data yielded a very marked Pb-Zn association, largely

related to the effects of mining-metallurgical contamination. The contamination effects are mainly exhibited east of the Derbyshire dome, that is, outside the detailed study area and so this factor does not appear as consistently in the factor solutions from the detailed study area.

The 6-factor model was chosen as the optimum solution in the Onecote area for the following reasons:-

(i) it yields factor associations comparable to those obtained from the regional survey data.

(ii) higher factor solutions have Ga (7-factor model) and successively Cr and Ti (8-factor model) splitting off to form unielemental factors.

(iii) all factor models lower than 7-factors exhibit agglomeration of the associations. Thus the Pb-Zn-Cu association is combined with Ga and V to form the 4th factor in the 6-factor model. Lower factor solutions show this agglomeration tendency to an even greater extent.

(iv) the 6-factor model appears to be the most geochemically feasible solution since it represents a compromise between those models exhibiting

excessive association splitting and association agglomeration.

7.6.3. Geochemical significance of the factor associations

The first factor of the 6 factor model is an association of As-Mo-Fe-Cu-V which has been related to black marine shales (Fletcher, 1968). The second factor association, Mn-Co-Ni-Zn, represents the mobile element association affected by changes in the secondary environment (Horsnail, 1968). This association excludes As and Fe and the most probable reason for this is that due to the stronger affinities exhibited by these elements to the black shales association and, in the case of Fe, also to the fifth factor association (Ti-Fe-Ga) their correlation with the mobile element association has been masked. The third factor includes Cr-V-Mo and the inclusion of Mo highlights the affinities of these elements to Mo and to the black marine shales association. The fourth association, Pb-Ga-Zn-Cu-V, appears to be a mathematical agglomerate between the mineralisation-contamination association, Pb-Zn-Cu, and Ga and V. It appears to be geochemically and geologically meaningless, though this can only be a tentative conclusion. The fifth factor association, Ti-Fe-Ga, represents those elements, notably Ti and Ga, which are enhanced in the higher stratigraphic units. The sixth and final factor is unielemental, representing Sn. The pattern of the Sn concentrations show no clear correlations with

the other trace elements patterns and so its presence as a unielemental factor is quite explicable.

7.6.4. Geochemical meaningfulness of the drainage sediment R-mode factor scores

The trace element data have been subdivided into subsets in order to demonstrate the degree of correlation between the variations in the R-mode factor scores and those of the trace element concentrations. The samples were subdivided on the basis of their factor scores for each factor. The scores vary usually between -2.00 and +2.00 with a few sample scores greater than /0.200/. A factor score interval of 0.25 was chosen and the samples were subdivided into 18 classes. The trace element concentrations for the samples in each class were then used to calculate the geometric mean ($\bar{X}_G$) and the geometric range (ANTILOG ($\bar{X}_G \pm 2\sigma_G$) for each element in each subset. The geometric parameters were computed because a logarithmic transform was employed on the data prior to the R-mode analysis. The results have been tabulated and are presented in tables 38 to 43.

The sequence of the elements in the left-most column indicates their importance in the factor association since they are ranked from the element with the highest factor loading to that with the lowest. The adjacent column to that of the elements gives the loading of the element on the particular factor under examination.

Table 38. The correspondence between factor 1 (As-Mo-Fe-V-Cu) scores and the trace element concentrations of the Onecote drainage sediments.

Sequence	Element	Factor loading	1 -Infinity -2.00	2 -1.75	3 -1.50	4 -1.25	5 -1.00	6 -0.75	7 -0.50	8 -0.25	9 0.00	10 +0.25	11 +0.50	12 +0.75	13 +1.00	14 +1.25	15 +1.50	16 +1.75	17 +2.00	18 +Infinity
1	As	+ .818	<5 -	<5 -	<5 -	5 <5 - 7	< 5 -	7 <5-14	6 <5-10	10 5-20	9 5-17	12 6-25	20 11-34	22 12-40	34 15-80	37 23-62	47 25-91	74 56-96	99 86-113	119 78-180
2	Mo	+ .726	<2 -	<2 -	<2 -	<2 -	3 2 - 5	3 2-6	6 4-8	4 2-8	5 3-11	7 4-11	7 4-12	10 6-16	10 6-17	12 9-16	20 15-26	15 11-21	10 6-15	12 6-22
3	Fe (%)	+ .704	3.25 2.59-4.07	5.33 7.33-9.60	5.29 3.45-8.11	5.58 4.00-7.79	6.19 4.88-7.87	7.24 6.16-850	7.31 5.15-10.38	8.14 5.94-11.16	8.87 6.41-12.27	10.62 7.07-15.96	11.25 7.75-16.34	11.91 7.74-18.32	11.80 7.57-18.41	13.32 8.76-20.25	11.66 7.58-17.94	14.92 10.71-20.79	30.18 28.82-31.60	26.29 18.18-37.97
4	Cu	+ .479	5 3-6	10 6-15	11 7-18	18 11-31	15 7-26	16 7-38	24 15-38	23 13-39	27 18-41	29 16-54	31 20-47	39 20-76	46 21-99	71 30-167	57 53-63	67 26-174	42 26-68	91 23-358
5	V	+ .467	64 50-81	90 58-127	91 67-124	80 34-190	79 35-177	117 75-184	136 96-193	140 88-222	178 125-251	170 111-259	202 121-340	201 139-291	244 125-474	320 203-502	303 257-357	236 171-325	214 132-345	175 110-279
6	Pb	+ .208	32 21-49	46 33-64	43 21-85	30 13-70	32 20-52	40 26-62	27 15-49	30 16-59	38 25-58	45 22-92	40 25-65	51 31-86	52 33-81	68 42-111	67 49-91	80 41-156	43 16-111	72 38-135
7	Zn	+ .111	121 92-157	177 121-258	231 155-365	121 60-247	175 97-318	188 90-393	224 117-430	181 77-426	210 93-474	261 114-596	284 132-615	370 208-660	420 192-922	477 222-1027	472 371-601	595 300-1179	262 167-407	337 148-768
8	Co	+ .109	10 7-13	14 10-20	19 11-31	13 7-27	18 13-24	16 11-23	21 15-31	19 11-32	19 14-27	23 10-52	27 18-40	28 18-45	28 17-45	35 20-62	31 22-44	34 24-49	24 11-54	23 6-85
9	Cr	+ .054	57 45-73	86 66-112	64 45-91	98 68-142	140 51-386	84 67-106	106 87-128	124 66-231	119 85-168	116 84-161	126 90-175	110 101-121	112 140-894	129 91-185	117 116-118	117 110-125	105 93-118	75 50-115
10	Ti	+ .029	3234 2726-4051	4377 3000-6386	4006 3226-4974	4980 3510-7066	4069 2995-5527	3784 2208-6486	4898 3436-6982	4375 2877-6653	5028 3823-6613	4515 2909-7009	4823 3230-7199	4909 4018-5998	4805 3686-6261	4409 3330-5839	2877 1483-5585	5074 4153-6198	6139 5153-7317	3590 1675-7693
11	Sn	+ .014	7 <5-17	<5 -	<5 -	< 5 -	<5 -	5 <5-6	<5 -	<5 -	<5 -	5 <5-9	<5 -	<5 -	<5 -	<5 -	7 6-8	<5 -	6 <5-9	10 6-17
12	Ni	+ .007	31 16-61	40 25-64	42 24-75	32 17-62	37 23-60	34 19-63	48 29-77	46 25-84	50 30-82	60 29-125	60 25-146	82 45-149	64 23-182	115 63-211	116 94-144	84 49-142	35 16-80	43 10-183
13	Mn	- .077	221 90-543	461 207-1030	394 98-158	290 114-740	907 393-2092	507 222-1157	976 478-1994	689 205-2314	479 181-1266	1058 262-4768	999 351-2849	777 299-2015	1086 320-3688	1179 387-3593	722 529-986	1158 438-3059	555 146-2104	512 82-3217
14	Ga	- .211	8 5-12	9 6-12	7 6-10	9 6-13	6 4-9	8 6-10	7 5-10	7 4-10	7 5-9	7 5-11	7 6-9	8 6-10	7 6-10	8 6-9	7 6-8	7 5-9	7 6-9	6 4-9
Numbers of samples			3	6	9	6	8	8	21	21	17	19	20	13	14	15	2	8	3	5

Table 39.
The correspondence between factor 2(Mn-Co-Ni-Zn)scores and the trace element concentrations of the Onecote drainage sediments.

Sequence	Element	Factor Loading	1	2	3	4
			-.00	-2.00	-1.75	-1.50	-1.25
1	Mn	- .925	9453 6000-11000	6025 5500-6600	4023 2250-11000	4007 2250-11000
2	Co	- .918	128 90-170	79 79-80	51 39-62	42 33-50
3	Ni	- .776	229 140-660	131 78-220	129 84-175	116 72-180
4	Zn	- .674	1257 1035-1825	686 600-785	943 900-990	702 500-1010
5	Cu	- .166	67 54-80	32 18-58	45 29-76	35 25-49
6	Cr	- .100	136 54-450	114 100-130	113 100-120	108 86-130
7	Ti	- .045	5938 1035-1825	3652 2300-5800	5250 4300-6600	4391 4000-4600
8	Pb	- .039	95 66-150	62 39-98	64 36-100	45 28-100
9	Fe(%)	- .026	23.3 18.5-30.0	8.6 8.3-8.9	12.4 11.8-12.7	11.1 9.2-13.1
10	Mo	- .019	7 3-10	7 5-10	15 7-30	8 4-21
11	As	- .017	24 <5-90	18 <5-85	21 <5-6	45 30-80
12	Sn	+ .018	9 6-16	7 5-10	5 <5-10	6 <5-10
13	V	+ .042	152 94-270	232 145-370	172 90-245	167 118-245
14	Ga	+ .094	6 3-10	7 7-8	9 8-9	8 7-9
Number of samples 4				2	3	3

5	6	7	8	9	10	11
	-1.00	-0.75	-0.50	-0.25	0.00	+0.25	+0.50
2328 810-9000	1550 900-3200	1320 520-2650	984 460-2200	896 130-4300	722 270-2300	499 220-1240	
42 29-60	37 28-50	30 24-44	25 15-30	23 13-31	20 13-27	19 16-24	
104 38-160	110 53-170	78 46-150	82 37-135	66 24-135	47 26-90	41 20-105	
608 300-1035	502 148-1210	3 3 200-1265	345 84-1460	268 80-785	196 52-660	188 64-425	
70 25-380	43 14-110	34 7->1000	42 20-420	29 21-420	17 6-55	21 5-56	
118 98-170	132 98-880	125 69-900	110 86-128	119 38-440	106 43-420	99 43-142	
4580 1900-7200	4381 1800-6800	4866 2700-8000	4601 3200-6000	4096 1300-8800	5080 2600-8200	4965 3300-7950	
64 15-190	50 15-100	32 15-60	46 16-240	42 17-123	30 14-76	36 15-105	
14.1 6.5->31.0	11.1 7.6-21.5	9.0 4.0-15.7	8.3 4.5-13.7	8.8 2.2-18.0	7.6 4.7-18.0	8.2 3.8-26.6	
10 4-21	10 4-21	7 <2-19	7 <2-15	5 <2-24	3 <2-8	4 <2-12	
42 15-85	24 5-88	15 <5-50	16 <5-88	9 <5-85	7 <5-85	11 <5-35	
5 5-8	<5 <5-6	<5 5-16	<5 5-6	<5 5-25	<5 <5-20	<5 5-10	
230 140-800	247 76-450	153 17-390	195 70-420	160 13-470	135 50-510	156 60-560	
8 5-10	7 3-11	7 5-11	7 4-10	7 4-14	7 4-12	6 4-10	
14	15	15	16	40	20	17	

12	13	14	15	16	17	18
	+0.75	+1.00	+1.25	+1.50	+1.75	+2.00	+00
575 380-1000	272 110-1100	217 100-340	174 140-220	91 46-160	102 96-110	66 28-160	
17 12-27	15 13-18	13 11-16	11 9-13	10 8-11	10 7-13	5 5-11	
42 21-48	31 16-67	28 23-33	23 18-28	28 20-48	11 <5-22	10 5-19	
154 25-420	121 64-275	159 110-235	116 65-160	117 95-135	68 50-115	91 55-140	
22 5-60	24 11-78	19 6-45	26 15-64	14 5-28	8 3-24	20 10-52	
100 34-135	94 57-130	95 47-130	88 54-145	91 64-120	57 43-68	97 80-400	
4637 2000-7600	4189 1900-7300	5691 4400-8600	4699 3150-8200	4409 3400-6000	2990 1800-5500	4042 980-7600	
31 10-87	45 16-125	41 18-96	42 10-97	49 38-71	31 20-50	65 25-150	
10.0 3.3->30.0	11.8 6.3->30.0	6.9 4.3-10.0	7.9 3.1->30.0	7.8 3.7-11.8	9.00 3.7->30.0	10.4 3.7->30.0	
5 <2-24	8 3-27	4 <2-13	<2 <2-6	3 <2-7	<2 <2-5	4 <2-27	
18 <5-240	16 <5-85	6 <5-20	12 <5-88	10 <5-25	7 <5-25	12 5-113	
5 <5-16	5 <5-30	<5 <5-8	6 <5-10	<5 -	<5 <5-5	7 <5-20	
173 54-740	126 68-190	147 92-220	107 56-190	116 82-175	66 63-72	134 66-220	
8 4-10	7 4-9	9 5-12	9 7-12	9 7-11	6 4-9	8 4-12	
14	8	8	4	3	3	9	

TABLE 40. The correspondence between factor 3 (Cr-V-Mo) scores and the trace element concentrations of the Onecote drainage sediments.

Sequence	Element	Loading	1	2	3	4	5	6	7	8	9
			00	-1.75		-.25		-0.75		-0.25	
			-2.00		-1.50		-1.00		-0.50		-0.00
1	Cr	+.918	45 34-64	44 43-47	60 53-65	77 57-100	85 72-100	77 68-96	98 74-123	104 82-123	106 96-130
2	V	+.401	83 63-170	69 50-92	70 56-86	47 13-120	111 72-155	94 63-180	93 17-175	141 62-390	160 84-370
3	Mo	+.332	3 <2-7	<2 -	<2 -	3 2-3	3 <2-6	3 <2-10	4 2-21	5 <2-30	7 <2-19
4	Ni	+.235	18 4-145	47 33-68	22 13-36	14 4-28	45 18-118	33 16-72	47 24-205	52 14-110	44 12-140
5	Cu	+.160	19 6-64	9 5-22	10 5-18	19 14-24	26 6-64	13 5-60	17 7-80	29 8-450	28 6-96
6	Sn	+.106	6 5-20	<5 5-20	5 <5-8	5 5-6	5 5-10	5 5-6	5 <5-16	5 5-30	5 5-13
7	Ga	+.106	4 4-8	6 5-8	7 4-10	6 5-7	7 6-10	7 4-11	6 4-11	7 4-11	7 4-12
8	Ti	+.037	3050 980-6800	4481 4000-5000	3265 2800-3950	3628 2800-5500	3469 1300-5200	3427 1900-5500	4692 2800-7400	4650 2600-7600	4786 3300-6800
9	Mn	+.017	446 96-10,000	297 130-610	219 28-1500	404 53-4300	595 140-1600	640 110-10,000	1240 103-10,000	767 110-10,000	753 72-6500
10	Co.	+.003	17 5-136	14 13-16	12 6-24	13 11-14	23 13-48	18 7-33	95 11-130	23 <5-60	19 5-51
11	As	-.028	16 <5-113	<5 -	6 <5-18	7 5-10	19 5-88	12 5-240	9 <5-85	18 5-115	14 5-95
12	Fe (%)	-.080	12.9 3-30.0	3.5 2.5-4.3	5.20 3.1-7.2	12.2 7.0-30.0	15.2 6.6-30.0	7.3 4.4-30.0	9.3 3.3-25.0	11.6 3.4-30.0	8.6 4.5-28.6
13	Zn	-.100	149 50-1035	175 160-185	123 60-260	100 75-155	229 150-760	181 52-1265	228 84-1240	287 100-1460	319 102-1000
14	Pb	-.291	53 17-150	45 22-96	47 23-84	27 17-38	53 22-100	33 18-87	40 12-190	49 15-240	51 18-120
Numbers of samples			6	3	6	3	4	10	20	26	17

10	11	12	13	14	15	16	17	18
+0.25		+0.75		+1.25		+1.75		+
	+0.50		+1.00		+1.50		+2.00	00
112 98-140	119 100-140	124 100-150	122 110-135	129 113-143	147 130-170	450 -	-	520 400-900
200 135-400	259 150-550	234 143-460	252 144-450	227 140-500	495 190-800	130 -	-	167 76-510
9 2-24	7 3-16	8 3-27	11 5-19	8 5-15	7 2-13	9 -	-	7 4-12
77 19-175	72 14-135	65 10-180	84 29-220	69 38-120	76 28-160	660 -	-	56 19-110
38 19-310	48 21-580	34 11-380	42 20-1000	33 22-76	43 22-150	54 -		24 14-37
5 <5-8	5 <5-25	<5 <5-8	5 <5-16	5 <5-10	5 -	10 -	-	<5 <5-8
7 4-10	8 5-13	8 5-12	8 6-11	10 7-14	7 5-12	10 -	-	6 4-8
4636 1900-7950	5198 3200-8800	5753 3600-8600	4374 2000-7400	5763 2100-8200	4829 3300-8200	4200 -	-	3699 1700-7000
1016 130-6600	598 46-2150	708 24-2250	937 220-6600	846 480-1900	487 220-2300	10,000 -	-	870 80-3200
29 13-90	22 <5-39	21 <5-42	27 11-80	22 17-29	22 11-41	170 -	-	22 7-36
15 <5-88	19 <5-85	13 <5-37	17 <5-113	8 <5-30	11 <5-35	88 -	-	10 <5-35
10.2 2.2-23.0	10.2 6.1-18.0	9.6 4.4-15.8	8.0 4.7-13.6	9.5 7.2-11.8	8.3 5.5-15.0	22.5 -		8.3 5.9-12.7
391 140-1065	336 25-785	263 55-750	294 150-600	189 88-700	208 65-1000	1825 -	-	156 80-320
50 21-100	58 19-123	38 15-80	26 10-54	22 14-50	37 10-98	66 -	-	31 15-70
28	22	16	16	8	5	1	0	7

TABLE 41. The correspondence between factor 4 (Pb-Ga-Zn-Cu-V) scores and the trace element concentrations of the Onecote drainage sediments.

Sequence	Element	Loading	1	2	3	4	5	6	7	8	9
			00	-2.00	-1.75	-1.50	-1.25	-1.00	-0.75	-0.50	-0.25
1	Pb	-.743	18 15-26	25 15-50	22 17-26	36 25-87	24 12-38	28 17-48	23 10-56	27 10-66	35 17-150
2	Ga	-.709	4 3-4	4 4-6	4 4-5	4 3-5	6 4-8	6 4-9	7 5-9	8 4-12	7 4-11
3	Zn	-.515	84 52-148	128 55-305	128 100-155	226 64-1035	162 50-450	130 22-275	190 92-685	260 65-1825	232 80-500
4	Cu	-.513	12 9-18	16 9-25	11 8-19	22 9-64	14 5-35	18 5-25	19 7-28	22 3-54	27 6-52
5	V	-.436	81 70-92	64 13-170	73 62-86	95 60-130	113 68-170	116 70-205	136 59-235	147 17-740	174 110-280
6	Ni	-.209	43 19-60	27 <5-88	33 21-42	67 34-145	36 <5-96	37 16-58	44 20-93	53 19-660	64 <5-180
7	Sn	-.143	<5 -	5 <5-13	<5 -	5 <5-8	<5 <5-6	<5 <5-16	5 <5-20	5 <5-20	5 <5-10
8	Ti	-.129	3608 2600-4600	4243 3100-7200	3263 2600-3800	4677 3400-6800	4856 1800-7400	4786 1900-7950	4366 1300-7300	4706 1900-8200	4377 980-8800
9	Mo	-.075	3 2-4	5 3-12	3 2-4	4 <2-7	3 <2-9	5 <2-24	5 <2-13	5 <2-30	8 <2-21
10	As	-.052	8 5-10	9 <5-115	5 <5-10	9 <5-90	11 <5-85	12 <5-80	10 <5-35	15 <5-88	16 <5-113
11	Co	-0.37	23 15-36	21 13-60	20 17-22	39 22-136	20 10-36	20 13-28	19 12-33	21 7-170	23 <5-51
12	Fe (%)	+.087	9.2 7.0-10.6	11.5 5.3->30.0	6.4 4.3-11.8	9.6 3.8->30.0	9.9 5.9->30.0	9.3 4.0-13.4	7.7 3.3-14.1	9.1 2.5-23.0	10.0 4.9->30.0
13	Cr	+.120	140 69-880	94 64-118	80 34-123	104 53-420	104 43-900	92 43-140	110 76-140	129 43-450	120 43-440
14	Mn	+.143	1157 390-3200	1138 100-4300	819 380-1850	2091 330->10,000	680 53-9000	588 170-2100	986 230->10,000	896 80->10,000	755 100-2250
Numbers of Samples			5	6	4	4	17	12	12	18	17

10	11	12	13	14	15	16	17	18
+0.25	+0.50	+0.75	+1.00	+1.25	+1.50	+1.75	+2.00	+00
50 19-97	52 34-98	62 34-150	58 26-120	93 52-190	73 31-96	91 73-110	98 80-110	172 123-240
7 5-10	8 5-12	8 6-11	8 5-14	9 8-10	9 6-14	10 9-12	9 7-11	11 10-13
261 60-700	291 95-785	273 95-1240	445 125-900	599 180-1065	475 55-1210	481 140-785	735 425-1035	1071 785-1460
30 11-64	22 5-96	39 10-80	53 20->1000	51 40-110	76 25-580	81 31-380	118 56-310	194 84-450
197 74-390	173 56-560	180 66-470	251 140-500	188 92-320	258 140-440	259 120-460	430 280-800	305 270-345
50 13-126	64 20-220	60 14-205	81 14-175	81 33-145	65 10-130	60 12-110	102 62-160	81 78-85
5 <5-16	5 <5-30	6 <5-30	5 <5-13	5 <5-10	5 <5-20	<5 -	<5 <5-8	10 <5-25
4665 2100-7200	4334 2300-8600	4460 1700-7400	4529 1800-8200	5257 4200-6800	4678 3200-6750	4962 4300-6000	5158 4700-6100	4718 4200-5300
9 <2-27	4 <2-21	6 <2-24	9 2-19	7 <2-21	10 3-27	6 3-12	7 3-11	6 4-10
22 <5-240	10 <5-85	12 <5-35	20 <5-113	14 <5-88	17 <5-88	15 <5-85	24 17-70	47 25-88
18 <5-51	25 9-80	21 6-130	26 <5-62	33 13-90	17 <5-35	19 <5-42	30 18-41	25 24-27
12.6 5.4->30.0	7.8 3.1-21.5	10.2 4.9->30.0	9.5 4.7->30.0	10.2 3.4-18.5	8.3 4.5-18.0	7.9 3.7-14.1	9.7 6.5-18.0	13.3 13.0-13.7
108 90-180	99 38-150	116 65-420	114 98-143	102 47-120	109 100-120	119 106-130	131 110-170	122 120-125
506 110-2150	735 160-6600	569 28->10,000	684 49-6500	1021 130-6000	684 24-2200	655 72-2100	1077 370-2300	639 610-670
18	24	14	16	11	8	5	5	2

TABLE 42. The correspondence between factor 5 (Ti-Fe-Ga) scores and the trace element concentrations of the Onecote drainage sediments.

Sequence	Element	Loading	1	2	3	4	5	6	7	8	9
			00	-2.00	-1.75	-1.50	-1.25	-1.00	-0.75	-0.50	-0.25 -0.0
1	Ti	-.863	7600 -	7086 5500-8600	7279 5600-8800	6937 5500-8200	6429 5000-7400	5857 4300-8000	5846 4400-7300	5005 4200-5900	4623 3700-5700
2	Fe (%)	-.525	23.0 -	15.8 7.5- >30.0	14.8 8.9- >30.0	14.7 9.2- >30.0	12.7 7.5- >30.0	13.8 5.3- >30.	10.5 5.6- >30.0	10.6 6.3- >30.0	10.6 6.1- 15.0
3	Ga	-.470	10 -	9 7-12	10 6-12	8 4-11	8 6-11	8 5-11	8 3-14	8 5-13	7 4-11
4	Mn	-.064	1000 -	214 53-530	1043 49- 6000	618 100- 2300	1679 560- >10000	675 150- 2650	612 46- >10000	739 110- 2150	1380 170- >10,000
5	V	-.056	200 -	167 120- 200	214 130- 500	201 63- 380	162 140- 230	162 81- 440	183 92- 550	145 17- 510	167 70- 740
6	Co	-.047	18 -	14 11-19	26 <5-90	21 13-46	29 15-130	20 <5-51	23 7- 136	24 17-36	26 13-45
7	Cr	-.022	135 -	110 80-145	119 100- 143	118 64- 145	120 98-140	104 83- 135	113 54- 400	122 85- 420	106 72-130
8	Mo	-.021	8 -	3 2-9	6 <2-12	7 4-21	4 < 2-9	5 <2-19	7 < 2-18	7 <2-17	7 <2-30
9	Zn	-.018	165 -	98 65-175	273 125- 1065	216 55- 700	338 100- 1240	236 100- 660	275 95- 1035	225 25- 785	354 84- 1000
10	Cu	+.016	25 -	16 9-25	28 6-80	32 21-76	27 11-72	27 10-78	31 6-120	25 7-84	33 6-380
11	Pb	+.034	52 -	25 10-38	38 15-95	31 14-54	38 15-150	53 17- 125	40 12-110	32 17- 123	44 18-190
12	Sn	+.072	<5 -	<5 <5-6	5 < 5-8	<5 <5-5	5 < 5-16	5 <5-30	5 <5-10	5 <5-25	5 <5-10
13	Ni	+.117	19 -	18 <5-34	56 14-140	42 <5-105	64 38- 205	50 14- 126	56 19- 145	60 27- 115	64 20- 140
14	As	+.132	25 -	9 <5-30	12 < 5-115	9 <5-95	10 < 5-85	12 <5-240	14 <5-90	15 5-85	15 6-16
Numbers of samples			1	4	7	11	10	13	23	11	19

10	11	12	13	14	15	16	17	18	+
	+0.25	+0.50	+0.75	+1.00	+1.25	+1.50	+1.75	+2.00	00
4532 3300- 5700	4184 3100- 6400	3822 2800- 4800	3608 2600- 4800	3457 1900- 4700	2880 1900- 4300	2669 2000- 3800	-	1680 980- 3200	
9.7 4.7 - 22.5	6.3 3.7 - 9.6	7.8 5.6 - 13.7	7.1 3.7 - 11.9	6.8 2.5 - 13.6	6.4 3.1 - 12.7	5.3 3.3 - 8.9	-	10.2 2.2 -> 30.0	
7 4-12	7 4-11	6 4-10	6 3-9	6 4-10	6 4-10	6 4-9	-	6 4-8	
920 24- >10,000	499 72 - 4300	850 110 - 6500	586 110- 3200	647 28- 2300	688 165- 6600	1184 470- 6600	-	347 96-1600	
171 78-390	103 13-240	139 64-280	177 63-560	170 50-800	158 56-450	164 59-370	-	140 72-270	
25 <5-170	16 < 5-50	21 7-31	21 7-36	22 6-44	22 9-37	27 12-80	-	11 <5-40	
114 62-450	97 43-440	122 38-900	113 34-880	100 43-170	95 54-130	105 69-130	-	94 43-420	
7 <2-27	3 < 2-11	5 <2-17	6 <2-18	4 < 2-19	6 <2-17	6 < 2-15	-	4 <2-16	
347 52-1825	182 64-1010	328 60- 1460	224 85-745	243 64-1010	265 120-475	294 100- 1265	-	196 50 -560	
33 5-310	20 5-60	28 9-450	23 3-82	34 6->1,000	28 18-42	32 7-580	-	25 6 - 61	
50 18-105	46 16-100	49 21-240	39 15-110	43 18-98	43 26-100	30 10-85	-	59 30-150	
5 <5-10	5 < 5-20	5 <5-8	5 <5-6	6 <5-20	<5 < 5-6	5 < 5-16	-	6 < 5-20	
64 10-660	39 12-120	50 13-92	62 21-150	63 14-160	66 24-170	78 38-220		41 <5-135	
21 <5-88	8 < 5-80	12 <5-88	11 < 5-85	17 < 5-88	14 <5-75	18 < 5-85	-	22 <5-113	
25	16	9	12	15	8	8	0	6	

TABLE.43. The correspondence between factor 6 (Sn) scores and the trace element concentrations of the Onecote drainage sediments.

Sequence	Element	Loading	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
			-00	-2.00		-1.50		-1.00			-0.50		0.00	+0.25			+0.75		+1.25		+1.75		+
				-1.75			-1.25			-0.75			-0.25			+0.50			+1.00		+1.50		+2.00	00
1	Sn	+.958					5 -	5 -	5 -	5 -	5 5-5	5 5-6	5 5-6	5 5-6	6 5-8	8 -	8 6-10	9 8-10	11 9-13	16 10-30
2	Fe (%)	+.203					5.9 2.2-8.9	9.0 5.4-15.0	8.8 3.7-21.5	9.1 3.7-23.0	8.9 3.4-30.0	11.9 6.3- 30.0	9.3 3.3-28.6	7.2 3.1-18.5	18.6 13.1- 30.0	8.3 4.3-13.1	12.6 7.2- 30.0	12.7 7.2- 30.0	14.5 9.2-24.25	12.8 2.5- 30.0
3	Pb	+.173					50 20-98	35 17 96	38 10-110	37 12 240	38 15-190	46 26-105	50 17 96	47 15-95	43 29-54	79 52-100	45 38-60	46 23-87	59 27-100	66 10-150
4	Cr	+.150					120 98-170	121 103-150	111 43-400	105 53-420	100 43-900	119 61-440	113 94-140	126 54-180	86 64-116	88 47-120	163 80-420	84 54-140	108 100-114	105 43-450
5	Cu	+.092					40 21-150	34 21-76	33 5.580	24 3 450	19 5-110	24 9-62	26 7-61	21 10-24	32 24-54	51 20-310	31 14-58	29 11-64	96 18- 1000	42 6-86
6	As	+.079					14 5-98	13 5-75	13 5-85	10 5-88	13 5-115	11 5-85	28 5-95	5 5-8	15 5-30	14 5-70	31 10-85	42 18-90	33 5-113	30 5-240
7	Mn	+.074					389 24-2300	612 230-2250	732 72-2300	822 46- 10,000	793 96-6600	990 110-9000	782 450-2200	911 28-6000	861 100- 10,000	241 49-2200	623 53-6600	1999 110-10,000	600 160-2600	772 140- 10,000
8	Ga	+.063					7 5-11	7 5-14	8 4-12	7 4-11	7 4-12	7 5-11	7 5-9	6 3-10	6 4-8	10 8-12	8 7-8	7 3-11	8 7-9	7 4-13
9	Zn	-.029					341 55-1010	320 125-700	291 65-1265	261 64-1460	195 25-910	230 80-785	228 65-560	217 95-1065	247 55-685	286 125-1035	238 75-600	312 60-1035	374 100-1010	295 102-1825
10	Co	-.030					22 5-41	24 11-50	23 7-62	23 7-54	19 10-60	24 17-79	19 12-40	19 6-90	22 13-33	13 13-41	27 11-80	32 7-136	21 5-50	22 5-170
11	Ni	-0.70					89 10-160	82 29-190	59 12-175	58 19-145	45 16-98	47 19-118	43 16-135	37 14-140	31 5-100	36 14-100	46 5-220	61 13-145	58 14-120	53 5-660
12	Ti	-.139					4579 3200-5900	1 2100-7300	5150 2200-8600	5021 2600-7100	4142 1800-7400	4426 1300-7950	3859 1800-7200	3544 2600-6800	4660 4000-5500	5825 5000-7600	2781 1700-5500	4520 2800-6800	4183 3700-4600	3893 980-6400
13	V	-.147					321 150-800	277 144-740	198 70-550	150 60-510	120 68-320	124 17-370	65 59-370	65 13-270	136 63-340	167 92-280	210 120-370	99 74-155	203 150-350	156 50-345
14	Mo	-.173					10 2-27	12 7-21	8 2-21	4 2-19	3 2-21	5 2-27	6 2-24	2 2-10	9 5-24	3 2-5	6 2-10	7 2-9	8 4-19	5 2-10
Numbers of samples			0	0	0	0	8	16	45	35	31	19	8	6	3	3	3	4	3	13

The loadings may vary between $\pm$1.000. The factor is described as positive or negative depending upon the the sign of the highest factor loading, that is, the loading most closely approaching /1.000/. Thus factors 1, 3 and 4 are positive whilst 2, 5 and 6 are negative.

All the elements bearing the same sign as the factor show a trend of increasing mean concentration values either towards factor loadings of +2.000 (for positive factors) or towards -2.000 (for negative factors). Moreover the gradient of the trend for the principal element (and sometimes the associated elements) increases near the positive or negative extremities for positive and negative factors respectively.

It is usual for the trend of increasing mean values to be interrupted by occasional short reversals, for example, in factor 1 (table 38), As shows a reversal between classes 6 and 7 and again between 8 and 9. The reason for he reversals are that the increasing factor scores represent the sum of the increases of the associated trace element concentrations. The trend is not smooth and regular, and when one element is subject to a large scale increase then one or several of the associated elements may show complementary reversals.

The frequency and duration of the reversals in the gradient of the mean trace element concentrations increases for those elements with factor loadings approaching 0.000. It has been

found that elements with loadings less than 0.200 usually display frequent reversals and only a gradual trend. Those elements with factor loadings greater than 0.300 usually display less frequent reversals and a more intense gradient. Thus in factor 1 (table 38), Pb (factor loading +0.208, positive factor) shows large reversals ($\geqslant$ 25 per cent) between classes 3 and 4, 6 and 7 and 16 and 17; whilst in the same factor V (factor loading +0.467) shows large reversals only between classes 15 and 16. The arbitrary convention has been adopted in this study of considering elements with factor loadings in excess of /0.300/ as being significant members of that factor association, and including elements with loadings between 0.200 and 0.299 as tentative members of the associations.

It is usual when dealing with the imprecise trace element data used in this type of study to regard only contrasts of at least 100 per cent ($\frac{\text{high-low}}{\text{low}}$ % $\geqslant$ 100%) as geochemically significant. This criterion has been used to assess the contrast in factor scores, which may be considered geochemically significant. If those elements with significant factor loadings ($\geqslant$ 0.300) are considered then a contrast of 100 per cent in the mean trace element concentrations is obtained usually with a factor score difference between 1.00 and 2.00. It is frequently the case that this applies also to those elements with factor loadings less than 0.300 . However, because of the frequency and duration of the trend reversals in these elements the geochemical significance of the factor scores

is less certain. Moreover, whilst a difference in factor scores of 1.00 to 2.00 is generally significant for the association as a whole it cannot be relied upon for any one element of that association over the whole factor score range, that is, from -2.000 to +2.000. It may be said that in general the trace element levels for the significant elements in the factor association are significantly different between samples with factor scores less than -1.50, compared to scores between -0.25 and +0.25, and compared to scores greater than +1.50.

7.6.5. Distribution of the R-mode factor scores

The distribution of the factor scores have been displayed as symbol maps (figs. 208 to 212 vol.2) in order to assess the correlations between the factor score levels and the underlying stratigraphic units. The salient features of the factor distributions are described below:-

Factor 1, As-Mo-Fe-Cu-V, positive factor. (fig.208, vol.2)

The higher factor scores ($>$ + 1.0) are concentrated over the lower stratigraphic units (S.U. 1, 2 and 3), whilst the lowest factor scores ($<$ 0.0) occur over the top-most unit (S.U. 7-11).

Factor 2, Mn-Co-Ni-Zn, negative factor (fig.209, vol.2)

The location of the highest concentrations for this association are found predominantly in streams drainage the northern moorland areas, underlain by S.U.3.

Factor 3, Cr-V-Mo, positive factor. (fig.210, vol.2)

The distribution of these scores is very complex, but the lowest scores (< 0.0) occur exclusively over S.U. 7-11. Elsewhere, there are less variable and marginally higher scores over S.U. 1, 4 and 5.

Factor 4, Pb-Ga-Zn-Cu-V, positive factor. (fig.211, vol.2)

A strong stratigraphic control is apparent with the highest scores ($> + 1.0$) concentrated over the lower units (S.U. 1, 2, and 3). There is in addition a marked enhancement in samples from streams draining the northern moorland areas over S.U. 3 and 4.

Factor 5, Ti-Fe-Ga, negative factor. (fig.212, vol.2)

The highest concentration levels for this association (< -1.0) occur in streams draining S.U. 4, 5 and 6. An additional feature is the clustering of similar scores in streams draining the northern moorland overlying S.U. 3.

Factor 6, Sn, positive factor.

This factor exhibits essentially the same patterns as those of the trace element, Sn, and has thus not been included.

Discussion

The maps indicate the dominant stratigraphic control for all factors except factor 2 (Mn-Co-Ni-Fe). This factor exhibits variations in factor score levels along the strike with the highest scores most commonly found in the north-eastern quadrant of the area,

a similar feature to that shown by the maps of the trace element concentrations for the mobile elements.

The sample factor scores have been subdivided into stratigraphic subsets in the same way as was the trace element concentration data. The arithmetic mean ($\bar{X}$) of the factor scores and their ranges ($\bar{X} \pm 2\bar{\sigma}$) for each stratigraphic unit have been tabulated and are presented below (see table 44).

Table 44 Mean factor scores ($\bar{X}$) and ranges ($\bar{X} \pm 2\bar{\sigma}$) for subsets of the drainage sediment data based on the underlying stratigraphic units.

Stratigraphic Unit	No. of Samples	Factor 1 +ve As,Mo Fe,Cu,V	Factor 2 -ve Mn,Co, Ni,Zn	Factor 3 +ve Cr,V Mo	Factor 4 +ve Pb,Ga Zn,Cu,V	Factor 5 -ve Ti,Fe, Ga	Factor 6 +ve Sn
7-11	16	- <u>1.6*</u> -2.6 -0.5	+ <u>0.8</u> -1.1 +2.6	- <u>1.1</u> -2.5 +0.3	+ <u>0.2</u> -0.8 +1.2	+ <u>0.1</u> -1.5 +1.7	+ <u>0.3</u> -1.5 +2.2
6	9	- <u>0.4</u> -2.4 +1.5	+ <u>0.2</u> -1.0 +1.4	- <u>0.7</u> -2.5 +1.2	- <u>1.4</u> -2.5 -0.2	+ <u>0.4</u> -1.9 +2.7	- <u>0.4</u> -0.9 +0.2
5	10	- <u>0.0</u> -2.2 +2.2	- <u>0.0</u> -1.3 +1.2	- <u>0.2</u> -2.2 +2.7	- <u>1.2</u> -3.1 +0.7	- <u>0.7</u> -2.8 +1.4	- <u>0.1</u> -0.8 +1.0
4	10	+ <u>0.1</u> -0.9 +1.1	- <u>0.3</u> -3.4 +2.7	+ <u>0.3</u> -1.3 +1.9	- <u>0.1</u> -1.9 +1.8	- <u>0.7</u> -1.9 +0.6	+ <u>0.3</u> -2.3 +2.8
3	30	+ <u>0.6</u> -1.0 +2.1	- <u>0.0</u> -3.0 +2.9	+ <u>0.0</u> -2.0 +2.1	+ <u>0.5</u> -1.4 +2.5	- <u>0.4</u> -1.8 +1.0	+ <u>0.2</u> -2.5 +2.9
2	8	+ <u>0.0</u> -1.0 +1.1	- 0.1 -1.5 +1.3	- <u>0.0</u> -1.0 +0.9	+ <u>0.4</u> -1.1 +1.9	- <u>0.0</u> -1.7 +1.7	- <u>0.3</u> -1.2 +0.6
1	6	+ <u>0.4</u> -1.6 +2.4	- <u>0.5</u> -1.3 +0.4	+ <u>0.2</u> -0.5 +0.9	+ <u>1.8</u> -0.6 +3.0	+ <u>0.3</u> -0.7 +1.4	+ <u>0.8</u> -3.0 +4.7

* Mean level is underlined.

The tabulated factor scores show a similar stratigraphic relationship for the individual factors to that exhibited by their constituent trace elements (table 35). Thus factor 1 (As-Mo-Fe-Cu-V) exhibits enhanced levels in stratigraphic units (S.U.) 1 and 3, though the trace element data shows Fe and Mo to be relatively higher in S.U.3 than in S.U.1, whilst the converse relationship holds for As, Cu and V. Factor 2 (Mn-Co-Ni-Fe) shows the highest levels in S.U.1 and 4, again the trace element concentration of Mn is relatively higher in S.U.4, whilst Ni and Zn are relatively higher in S.U.1. Factor 3 (Cr-V-Mo) exhibits enhanced levels in S.U.1, 4 and 5, the trace elemental concentrations of Cr are relatively higher in S.U.4 and 5, whilst V is higher in S.U.1. Factor 4 (Pb-Ga-Zn-Cu-V) shows highest scores in S.U.1 with a pronounced decrease up the stratigraphic column; this is in accord with the trace elemental concentrations for the principal elements of this association in the stratigraphic subsets. Factor 5 (Ti-Fe-Ga) has the highest mean scores in S.U.4 and 5, which agrees with the relatively high trace elemental concentrations of Ti in both units and of Fe in S.U.4. Factor 6 (Sn) exhibits the same relative levels up the stratigraphic column as do the trace element concentrations for Sn with highest levels in S.U.1 and successively lower levels in S.U.4 and S.U.7-11.

7.6.6. Geological interpretation of the R-mode factors

The R-mode analysis has reduced the number of

variables from 14 to 6. Two of the factor associations are fairly well understood. Thus factor 1 (As-Mo-Fe-Cu-V) probably reflects trace elements concentrated in sedimentary rock deposited in a reducing environment with the contemporaneous incorporation of organic carbon and sulphides (Fletcher, op.cit.). Factor 2 (Mn-Co-Ni-Zn) reflects trace elements concentrated in the drainage sediments by precipitation and coprecipitation induced by the rise in the Eh-pH environment in the stream waters relative to the ground and soil waters (Horsnail, op.cit.). The stratigraphic behaviour of factor 4 (Pb-Ga-Zn-Cu-V) shows strong affinities with that of factor 1, except that it shows a moderate enhancement in S.U.7-11. This, too, may indicate a reducing environment in the original basin of deposition. The geological controls of factor 6 (Sn) are not well understood, though it shows some correlation in its stratigraphic behaviour with factor 4. The factor association of the regional data, that is, Cr-Ga-Fe-Ti-V, has been split into two factor associations in this model, though they are combined in the 3 factor model together with Mo and Cu. Factor 3 (Cr-V-Mo) shows affinities with factors 1, 4 and 5 (Ti-Fe-Ga) in its stratigraphic distribution, but both factors 3 and 5 show the highest mean factor scores in S.U.4 and 5.

7.7.0. SOIL TRACE ELEMENT CONCENTRATION DATA

7.7.1. Areal distribution patterns of the soil trace element concentration data.

Symbol maps have been prepared for all the soil trace element distributions (figures 213 to 227, vol.2). The salient features of the distribution are briefly described below:

Arsenic (fig.213,vol.2)

There is an apparent stratigraphic control for the distribution of this element with the higher concentrations (20-$>$100 ppm) clustered over the lower stratigraphic units (S.U. 1, 2, 3 and to a lesser extent 4). The concentrations levels are lowest over S.U. 7-11 (usually$<$ 5 ppm). There is a significant reduction in levels (often$<$5 ppm), over the northern outcrop, of S.U. 3, where the leached moorland soils occur.

Chromium (fig.214,vol.2)

Higher concentration levels (200-$>$300 ppm) are scattered over all stratigraphic units except S.U. 7-11 (usually $<$150 ppm). However, these are mainly concentrated over the southern outcrops of S.U. 1, 2, 3, and 4. The northern moorland areas underlain by these units also tend to have lower values ($<$150 ppm).

Cobalt (fig.215,vol.2)

The distribution of this element is complex with higher concentrations (16-$>$30 ppm) scattered over all stratigraphic units, but to a notably greater degree over S.U. 1, 4 and 5. There are lower levels (often$<$5 ppm) over the northern moorland area,

even though S.U. 3 has generally lower concentrations of this element (usually $<$10 ppm).

Copper (fig.216,vol.2)

The basal unit (S.U. 1) has a very high proportion of higher concentration levels (30-$>$70 ppm), though these are scattered over all units. There are marginally higher levels over S.U. 5 and 6, whilst S.U. 7-11 has predominantly lower concentrations (usually $<$7 ppm), except in the north.

Gallium (fig.217,vol.2)

The higher concentrations (16-$>$30 ppm) tend to occur over the higher stratigraphic units (S.U. 6, 7-11 and to a lesser extent S.U.4 and 5), though these values are also scattered over all units.

Iron (fig.218,vol.2)

There seems only a slight stratigraphic control of the iron distribution, though higher concentration levels (8-$>$15%) appear to be slightly more numerous over S.U 1, 5 and 6. Lower levels ($<$ 5%) are more commonly found over the northern moorland area than elsewhere.

Lead (fig.219,vol.2)

Concentration levels are usually low ($<$ 70 ppm) with marked enhancements over S.U. 1 (often 70-$>$300 ppm) and along the northern boundary of the sampled area (often $>$ 300 ppm).

Manganese (fig.220,vol.2)

The distribution of this element is quite complex with

higher concentration levels (500 - >2000 ppm) over all stratigraphic units. These are notably concentrated over S.U. 1 and are significantly absent from S.U. 3. There are apparently lower levels over the northern moorland but this may be due in part to the large portion of this area underlain by S.U. 3.

Molybdenum (fig.221,vol.2)

The higher concentration levels (>6 ppm) occur scattered over all units except S.U. 7-11, but are more common over S.U. 1, where they tend to be located near the junction with S.U. 2.

Nickel (fig.222,vol.2)

The basal unit (S.U. 1) bears a high proportion of enhanced concentration levels (31- >50 ppm), but these are also scattered over the other stratigraphic units. Marginally higher levels (16- >50 ppm) predominate over S.U. 6. A relatively high proportion of very low concentrations (7 ppm) are located over the moorland areas.

Silver (fig.223,vol.2)

The lowest stratigraphic units, especially S.U. 1, underlie the sample locations with the highest concentrations (0.2- >0.5 ppm), but these occasionally occur over the other units.

Tin (fig.224,vol.2)

Higher concentration levels (8- >30 ppm) are sparsely scattered over all stratigraphic units, except S.U. 6. There is an apparent concentration of these enhanced levels over the northern

boundary of the sampled area.

Titanium (fig.225,vol.2)

There is evidence of a stratigraphic control with the higher concentration levels (7000- >10000 ppm) relatively more common over S.U. 5 and 6 and relatively less common over S.U. 1 and 3.

Vanadium (fig.226,vol.2)

This element tends to have higher concentrations (300- >700 ppm) over S.U. 1 and 2, whilst these occur infrequently over S.U. 7-11 (usual levels <150 ppm), and to a lesser extent also over S.U. 6. The northern moorland portion over S.U. 3 is marginally lower with more frequent levels below 150 ppm, than over the southern outcrop.

Zinc (fig.227,vol.2)

A significant contrast is afforded by the clustering of higher concentration levels (>150 ppm) over the basal stratigraphic unit (S.U. 1), than over the remaining units.

Discussion

The symbol maps indicate the basic stratigraphic control for most of the elements but also show the change in the levels along the strike of the mobile elements. This is most marked over S.U. 3 and 4 where in the north over the poorly drained moorland the soils bear relatively low levels which have been ascribed to acid leaching of these elements from the soils

(Horsnail, 1968).

The sample trace element concentration data were subdivided on the basis of the sample site locations with respect to the underlying stratigraphic units. Data have only been used from areas where the stratigraphic unit boundaries can be reasonably placed and have thus not been taken from the extreme north-east and south of the area. The data was log-transformed, since this transformation was applied prior to the R-mode analysis of the data, and the geometric means ($\bar{X}_G$) and ranges (ANTILOG ($\bar{X}_G \pm 2\sigma$)) were computed. The results have been tabulated for all the stratigraphic subsets (see table 45).

The data in table 45 has been further simplified to show the relative levels of the elements over the different stratigraphic units. The ranking procedure was identical with that employed for the drainage sediment data (see section 7.6.1.). The simplified dataare presented in table 46.

Table 45. Mean trace element concentrations (ppm) and ranges (geometric) for subsets of the soil geochemical data based on the underlying stratigraphic units.

Stratigraphic unit	No. of Samples	Ag	As	Co	Cr* rounded to 5	Cu	Fe* (%) rounded to 0.1	Ga	Mn* rounded to 10	Mo	Ni	Pb* rounded to 5	Sn	Ti* rounded to 100	V* rounded to 10	Zn* rounded to 10
7-11	20	<0.2 ≠ -	<5 -	8 <5 - 16	85 35 - 205	2 <2-16	4.9 2.1-11.5	14 7-29	560 40-7200	2 <2-4	14 5-35	45 5-335	5 <5-8	6800 4400-10600	60 30-110	50 30-100
6	38	0.2 <0.2-0.2	5 <5-13	10 <5 - 26	140 75 - 270	4 <2-35	5.6 2.2-14.3	15 7-29	420 40-4340	3 <2-8	17 6-50	30 15-75	5 <5-7	7600 4300-13300	120 40-430	60 <20-260
5	35	<0.2 -	6 <5-22	11 <5 - 38	55 95 - 255	5 <2-75	6.4 2.9-14.3	14 7-28	630 60-6300	4 <2-14	15 5-52	30 10-85	5 <5-10	7600 4100-14100	150 30-610	70 30-190
4	33	<0.2 <0.2-0.2	6 <5-30	9 <5 - 37	160 100 - 360	5 <2-94	5.2 1.8-15.3	15 8-27	290 10-7320	3 <2-11	13 <5-54	35 10-140	5 <5-12	7800 4300-14000	220 40-1070	70 20-180
3	48	<0.2 <0.2-0.2	9 <5-77	6 <5 - 20	140 80 - 250	4 <2-56	4.0 1.2-13.5	12 6-23	100 <10-1780	5 <2-16	8 <5-38	40 10-140	5 <5-13	7600 4400-13300	150 30-740	70 30-200
2	16	<0.2 <0.2-0.6	18 <5-223	10 <5 - 43	180 85 - 380	7 <2-135	5.5 1.2-25.3	12 6-25	320 20-4270	5 <2-33	20 <5-122	60 30-155	5 <5-10	5800 3400-9800	370 50-2530	180 40-750
1	33	0.2 <0.2-1.1	16 <5-149	10 <5 - 33	170 85 - 340	27 3-266	5.3 2.2-13.0	13 8-19	540 40-7040	5 <2-24	23 5-103	95 20-410	5 <5-17	6200 4000-9800	420 100-1810	230 60-860

* Indicate those parameters which have been rounded-off.

≠ Mean values underlined.

Table 46. Summary of the relative mean trace element concentration levels for subsets of the soil geochemical data based on the underlying stratigraphic units.

Stratigraphic Unit.	High	Intermediate	Low
7-11		Mn,Ni,Pb,Sn	Ag,As,Co,Cr,Cu,Fe, Ga,Mo,Ti,V,Zn
6	Ga,Fe	Ag,Co,Cr,Cu,Mn,Mo,Pb, Sn,Ti	As,V,Zn
5	Co,Fe,Mn	As,Cr,Cu,Ga,Mo,Ni,Sn, Ti,V	Ag,Pb
4	Ga,Ti	Ag,As,Co,Cr,Cu,Fe,Mo, Ni,Pb,Sn,V,Zn	Mn
3	Mo,Ti	Ag,As,Cr,Cu,Pb,Sn,V, Zn	Co,Fe,Ga,Mn,Ni
2	As,Cr,Mo,Ni, Pb,V,Zn	Ag,Co,Cu,Fe,Mn,Sn	Ga,Ti
1	Ag,As,Cr,Cu, Mo,Ni,Pb,V, Zn	Co,Fe,Ga,Mn,Sn	Ti

The two preceding tables demonstrate points of similarity and divergence with certain features of the stream sediment data. These are:-

(i) The decrease in relative and absolute levels of the elements Ag,As,Cr,Cu,Mo,Pb,V and Zn between stratigraphic units 1 and 7-11. However, the decline is noticeably more gradual in the soils than in the drainage sediments.

(ii) The increase in the levels of Ti, and with less perfect agreement also Ga, between the lower stratigraphic units (S.U.) and S.U.3 and 4; which is shown more intensely in the soils than in the drainage sediments. The decrease in the Ti levels in S.U.5,6 and 7-11 are also similar to the drainage sediment trend.

(iii) The changes in the level of the mobile elements (As,Co,Fe,Mn,Ni,Zn) exhibit significant divergences from the drainage sediment data. Thus the two principal mobile elements (Mn and Fe) show their highest levels in the drainage sediments collected over S.U.3,4 and 5, whilst the soils exhibit the lowest levels over S.U.3 and 4 and their highest levels over 5 and 6. It

is of interest to note that S.U.3 and 4 sub-outcrop under the high poorly drained moorlands of the north-east quadrant of the area, whose soils would be leached of the mobile elements. The enhancement in the soils over S.U.5 and 6 can be correlated with research in other areas carried out over the interfluves between streams (Horsnail, 1968). These studies showed that along seepage lines, where the water-table intersects the topographical surface, there occurred concentrations of the mobile elements. The concentrating mechanism was postulated as being precipitation of hydroxides and oxides of Fe and Mn with coprecipitation of the other elements induced by the relatively higher Eh-pH environment along the seepage line than in the soil and ground waters. The stratigraphic units 5 and 6 in this area form the lower flanks of the moorland areas and along the shale-sandstone junctions there are frequently seepages. It is considered that the concentration of the mobile elements in these soils is due to the same mechanism as that postulated Horsnail.

The variability of the soil trace element concentrations as shown by the overlapping ranges between the different stratigraphic units can be ascribed both to the variety of bedrock lithologies in each stratigraphic unit and also to random errors caused by the sampling and analytical imprecision. Thus all units include shales and sandstones in varying proportions and whilst the former generally bear high concentrations of many trace elements the latter usually bear much lower levels.

7.7.2 The results of R-mode analysis upon the soil trace element data

The trace element concentration data from the soils was subjected to R mode analysis. All 15 elements were included and the data was log-tranformed prior to the analysis, since this gave the more geochemically feasible factor solutions compared to those from the untransformed data. All models between 2 and 10 factors were examined in order to choose the optimum solution. The 'best' model was that which indicated either those associations which had been confirmed in the drainage sediment data, though it was expected that these would be somewhat modified. The principal elements in each association have been summarised and exhibited for all the models between 2 and 10 factors (see table 47).

Table 47 Summary of the factor associations indicated by R-mode analysis of the log-transformed geochemical data from the soils in the Onecote area.

Factor Model	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Factor 9	Factor 10
10	Cr,V (Ga)*	Mn,Co,Fe,Ni	Ti (Cr)	Sn (Pb)	Mo,Cu,V (Fe)	Zn	As (Fe)	Ge,Fe	Ag,Pb (Cu)	Ni (Co)
9	Cr,V (Ni,Ga)	Co,Mn,Ni,Fe	Ti (Cr)	Sn,Pb	Mo,Cu,V,Fe (Pb)	Zn	As, Fe	Ga,Fe,Ni	Ag,Pg (Cu)	
8	Cr,V (Ti,Ga, Ni)	Co,Mn,Ni,Fe	Ti,Cr(Sn) Sn [Ag] ≠	Pb,Ag,Cu	Mo,Cu,V,Fe Pb	Zn	As,Fe	Ga,Fe(Ni)		
7	Cr,V,Ga (Ni,Cu, Ag)	Co,Mn,Ni,Fe	Ti,Ga,Fe,Cr (Sn)	Sn,Pb,Ag,Cu	Mo,Cu,V,Fe, (Pb)	Zn (Ni)	As,Fe			
6	As,Mo,Fe,V (Cu)	Co,Mn,Ni,Fe	Ti,Ga,Fe,Cr	Sn,Pb,Ag,Cu	Cr,V,Ga,Cu (Ag,Ni,Mo)	Zn (Ni)				
5	Zn,V,Cr,Cu,Ag, Ni	Mn,Co,Ni,Fe	Ti,Ga,Cr,V	Sn,Pb,Ag,Cu	As,Mo,Fe (V,Cu)					
4	V,Zn,As,Mo,Cu Ag,Cr(Pb,Fe)	Co,Mn,Ni,Fe	Ti,Ga,Cr,V	Sn,Pb,Ag,Cu						
3	Pb,Ag,Cu,Mo,V, As,Zn,Sn (Cr,Fe)	Co,Mn,Ni,Fe (V,Cr,Ga)	Ti,Ga,Cr,V (Sn)							
2	Pb,Ag,Cu,Mo,As V,Zn,Sn(Fe) [Ti]	Mn,Co,Ga,Ni, Cr,Fe,Ti,V, (Mo)								

LEGEND

* ( ) signify a factor loading between 0.200 and 0.299

≠[ ] signify an element antipathetic to the principal association of a factor.

The 10 factor model displays most of the known associations in incipient forms. Thus factor 2 (Mn-Co-Ni-Fe) represents the mobile element association, factor 5 (Mo-Cu-V) represents the black marine shales association, and factors 1 (Cr-V), 3 (Ti) and 8 (Ga,Fe) represent the regional factor association, Cr-Fe-Ga-Ti-V. Lower models show progressively more agglomeration but not until the 6 factor model does the black shale association include As (Factor 1) though Cu is now only tentatively included in this association. The mobile element association remains constant down to the 3 factor model but never includes As or Zn. The regional association, Cr-Fe-Ga-Ti-V, is indicated in its most complete form in the 5, 6 and 7 factor models but never includes both V and Fe simultaneously. A possible mineralisation association is represented in the 8 factor model (factor 4, Sn-Pb-Ag-Cu) but this never includes Zn. It was again necessary to subjectively choose the optimum model, and the 5 factor solution was chosen as the most geochemically feasible, especially since this model includes the most completely constituted black marine shales association, As-Mo-Fe-(V-Cu). The disadvantages of this model are that two of the factors (1 and 4) are of dubious value. Factor 1 (Zn-V-Cr-Cu-Ag-Ni) appears to be without any geochemical meaning though this can only be a tentative conclusion, and factor 4 (Sn-Pb-Ag-Cu) may relate to mineralisation but the presence of Sn in such an association in this area was not to be expected, and cannot be accounted for.

7.7.3. Geochemical significance of the soil R-mode factor scores

The factor scores on each sample have been used to assign the samples into 18 classes for each factor. The trace element data for the samples in each class have been used to establish the mean concentration and ranges (applying a log-tranformation to the sample data since this was employed in the factor analysis) for each class. The results have been tabulated in order to establish what variations in factor scores represents a meaningful geochemical contrast. The procedure was identical to that described for the drainage sediments in section 7.6.4. and the results are presented in tables 48 to 52.

The results indicate that in certain cases elements with factor loadings less than /0.300/ may still be significant members of the factor associations. Thus an arbitrary cut-off factor loading to /0.300/ cannot be justified in determining the membership of the factor associations. Several examples may be cited to illustrate this:

(i) Cu in factor 5 (factor loading -0.275, negative factor)

(ii) Pb in factor 5 (factor loading -0.188, negative factor)

Both these elements show few reversals in the trend of increasing trace element concentrations towards -2.000, and a sufficiently steep concentration gradient to qualify as members of the

TABLE 48. The correspondence between factor 1 (Zn-V-Cr - Cu-Ag-Ni) scores and the trace element concentrations of the Onecote soils.

Sequence	Element	R score	1	2	3	4	5	6
			-00	-2.00	-1.75	-1.50	-1.25	-1.00 -0.75
1	Zn	+ .749		<50 -	<50 <50 53	<50 <50 102	<50 <50 92	50 <50 84
2	V	+ .612		35 7 164	60 32 112	83 20 341	73 34 154	83 45 152
3	Cr	+ .552		50 6 405	83 32 217	145 103 205	98 43 225	118 69 218
4	Cu	+ .436		2 <2 14	<2 -	2 <2 10	2 <2 30	2 <2 8
5	Ag	+ .427		<0.2 -	<0.2 -	<0.2 -	<0.2 <0.2-0.4	<0.2 -
6	Ni	+ .417		5 5 5	6 3 12	5 3 11	10 4 23	11 4 27
7	Ga	+ .191		7 5 10	10 4 24	10 4 24	12 6 24	13 6 26
8	Mo	+ .170		2 <2 8	2 <2 4	3 <2 12	2 <2 5	3 <2 7
9	As	+ .163		<5 -	5 <5 10	<5 -	5 <5 18	6 <5 26
10	Pb	+ .129		71 44 117	53 6 479	31 8 115	48 <5 547	31 13 74
11	Co	+ .039		<5 -	9 2 36	6 3 13	7 3 15	8 4 14
12	Mn	- .063		43 8 218	488 6 37528	112 4564	262 4189	382 40 3675
13	Fe (%)	- .171		5.05 51.00 92.51	6.83 2.27 20.55	6.52 1.00 42.60	5.36 1.25 23.01	5.72 2.99 10.95
14	Sn	- .185		<5 <5 6	<5 <5 6	8 <5 77	6 <5 30	5 <5 6
15	Ti	- .311		8150 8010-8292	8149 5014-50244	10144 5601-18371	7764 4137-14572	7961 4252-14907
Numbers of samples			0	2	7	3	14	21

7	8	9	10	11	12	13	14	15	16	17	18
	-0.50	-0.25	0.00	+0.25	+0.50	+0.75	+1.00	+1.25	+1.50	+1.75	+2.00 +00
63 50 124	67 <50 135	72 <50 159	82 50 230	98 <50 233	103 50 326	158 <50 712	136 116 161	254 74 870	226 95 538	353 133 931	401 176 911
99 50 327	104 37 298	162 94 598	199 51 778	219 54 882	346 66 1804	267 75 945	557 201 1543	470 120 1846	543 137 2152	654 367 1165	729 278 1910
121 54 225	136 78 238	147 86 250	152 85 273	163 89 299	178 118 267	155 104 230	217 172 275	203 126 328	200 106 377	161 92 281	246 160 377
2 <2 11	4 <2 75	5 <2 38	8 <2 124	6 <2 45	9 <2 212	24 <2 266	20 2 340	75 5 1292	31 16 59	74 10 531	51 9 288
<0.2 -	0.2 <0.2-1.0	<0.2 <0.2-0.3	<0.2 <0.2-0.4	<0.2 <0.2-0.7	<0.2 <0.2-0.2	0.2 <0.2-0.8	0.2 0.2-0.2	0.3 0.2-0.8	0.3 0.2-0.8	0.4 0.2-0.6	0.4 0.2-0.8
8 2 31	14 4 49	14 4 50	18 6 52	19 3 104	16 4 69	22 3 167	32 15 65	51 13 207	23 11 49	34 12 96	44 15 126
11 5 25	14 7 29	14 8 26	15 9 25	15 9 25	15 8 28	14 8 25	16 11 22	16 8 32	14 9 22	11 5 25	15 10 22
3 <2 12	4 <2 11	4 <2 12	4 <2 18	4 <2 11	5 <2 19	5 <2 29	6 2 32	13 2 203	8 4 14	15 3 77	5 2 16
7 <5 51	6 5 26	6 5 25	7 <5 45	7 <5 33	8 5 56	16 2 240	8 2 59	15 2 388	15 3 68	48 5 902	17 5 131
28 10 77	38 <5 314	35 12 101	47 11 196	38 15 92	43 24 76	46 9 221	55 26 120	120 9 1566	65 24 176	130 12 1384	102 20 521
8 2 26	9 3 27	8 3 21	9 3 23	9 2 44	9 2 39	14 3 81	10 4 26	14 2 87	13 5 36	19 6 66	12 5 24
246 13 4717	416 70 8494	306 24 3955	328 23 4575	314 12 7953	213 11 4086	570 21 15509	314 16 6050	1335 230 7765	778 61 9865	732 172 2992	678 96 4761
4.41 1.45 13.43	4.88 1.62 14.72	5.23 1.95 14.03	5.76 2.10 15.82	4.57 1.60 13.10	4.18 1.17 14.99	6.10 1.67 22.37	6.12 4.30 8.72	6.85 2.84 16.52	6.09 4.49 8.25	10.22 2.74 38.11	5.66 3.55 9.03
5 <5 9	6 <5 20	5 <5 10	5 <5 13	5 <5 9	<5 <5 6	5 <5 8	5 5.9	8 5.94	5 5 7	5 5 9	5 5 18
7297 3933-13539	7471 4268-13077	7549 4532-12561	7620 4589-12654	7142 4770-10808	7122 3637-13945	6377 4040-10068	7302 5811-9176	7988 4429-14407	5678 3460-9318	5174 3411-7849	5536 3555-9621
27	45	55	25	23	19	9	3	4	7	5	15

Table 49.

The correspondence between factor 2 (Mn-Co-Ni-Fe) scores and the trace element concentrations of the Onecote soils.

Sequence	element	R	1	2	3	4
			-00	-2.00	-1.75 -1.50	-1.25
1	Mn	+.893 -	24 -	37 5 295	40 16 99	57 20 163
2	Co	+.892	5 -	5 <2 21	4 3 6	5 3 7
3	Ni	+.676	5 -	5 <2 14	5 3 8	7 3 16
4	Fe(%)	+.483	1.20 -	2.43 1.09 5.39	3.17 1.18 8.55	3.02 1.13 8.03
5	Ga	+.165	8 -	10 4 21	10 6 17	11 6 21
6	Cu	+.113	<2 -	4 <2 164	2 <2 11	4 <2 45
7	Ag	+.039	<0.2 -	<0.2 <0.2-0.8	<0.2 -	<0.2 <0.2-0.2
8	Cr	+.033	115 -	107 38 302	121 66 223	131 72 231
9	Sn	+.013	5 -	5 <5 6	6 <5 25	5 3 7
10	Mo	+.004	3 -	4 <2 12	4 <2 18	4 <2 14
11	Zn	-.019	<50 -	54 25 115	55 30 101	69 34 140
12	As	-.025	<5 -	6 <5 34	6 <5 28	8 <5 63
13	V	-.026	55 -	91 19 437	125 21 747	164 26 1045
14	Pb	-.076	50 -	47 10 232	26 9 79	46 22 97
15	Ti	-.078	7800 -	7216 4128 12616	7219 3580 14557	6924 4171 11493
Number of samples			1	18	7	18

5	6	7	8	9	10	11
-1.00		-0.75	-0.50	-0.25	0.00	+0.25 +0.50
62 26 145	97 22 424	126 21 743	217 71 666	319 55 1839	505 145 1758	686 210 2246
5 4 6	6 4 9	6 4 10	7 5 9	7 4 12	8 5 13	10 7 14
9 3 33	9 3 27	10 3 37	12 5 29	14 5 44	15 6 37	19 8 48
3.38 1.05 10.89	4.60 1.28 16.49	5.16 2.34 11.40	4.91 1.95 12.37	5.57 2.35 13.23	5.14 2.48 10.66	6.16 3.12 [illegible]
12 8 17	12 8 19	13 7 23	15 7 30	13 7 25	13 6 28	15 8 27
3 <2 41	2 <2-16	4 <2 46	3 <2 43	7 <2 110	3 <2 33	7 <2 103
<0.2 -	<0.2 -	<0.2 0.2-0.2	<0.2 -	<0.2 <0.2-0.7	<0.2 <0.2-0.4	<0.2 <0.2-0.6
133 72 247	149 80 279	142 69 291	142 65 312	136 57 325	134 70 259	162 77 342
<5 <5-6	5 <5-6	5 <5 16	5 <5 10	5 5 11	5 5 11	5 <5 12
3 <2 10	2 <2-6	4 <2 11	3 <2 13	4 <2 14	3 <2 9	4 <2 13
76 18 312	63 23 17[illegible]	70 25 193	64 22 186	83 25 268	76 28 209	91 22 383
5 <5 17	7 <5 35	6 <5 32	8 <5 40	8 <5 53	7 <5 34	7 <5 34
150 30 757	.40 62-460	133 20 877	173 23 1281	172 25 1184	124 35 444	203 35 1171
36 28 47	37 13-85	35 11 111	31 15 64	51 8 319	29 9 94	44 8 231
6651 4794 9227	7522 3629 15592	7057 4004 12440	7637 4267 13667	7083 3972 12629	6984 3698 13189	7470 4508 12336
7	12	18	18	40	25	35

12	13	14	15	16	17	18
+0.75		+1.00	+1.25 +1.50	+1.75	+2.00	+00
885 355 2206	1251 601 2605	1463 231 9250	1352 674 2710	1895 942 3811	3604 1082 12000	4507 600-15000
11 6 20	14 8 24	16 9 26	21 13 33	26 12 56	41 28 25	49 42 - 82
25 12 50	21 6 70	31 7 133	39 13 117	40 12 139	37 24 57	39 20 - 74
6.46 3.10 13.49	6.38 3.75 10.92	7.65 2.11 27.67	8.35 4.65 14.99	7.56 3.28 17.45	8.81 1.03-3.30	11.04 6.50-30.00
16 10 25	15 9 25	16 8 34	15 10 23	17 7 39	11 4 32	14 9-16
11 <2 287	7 <2 119	20 <2 3024	10 <2 83	10 <2 284	10 <2 490	7 3-30
0.2 <0.2-0.8	<0.2 <0.2-0.6	0.3 <0.2-1.0	0.2 <0.2-0.8	<0.2 <0.2-0.3	0.3 <0.2-0.6	<0.2 -
167 94 297	144 73 287	154 83 285	178 121 263	182 122 272	164 102 262	75 90-250
5 <5 14	5 5 13	9 <5 76	5 <5 16	5 <5 6	<5 -	5 <5-8
5 <2 23	4 <2 12	6 <2 47	6 2 17	4 2 10	13 <2 163	4 2-9
114 25 528	97 20 474	114 25 520	139 30 840	117 16 852	317 53 1885	148 60-380
10 <5 105	6 <5 25	10 <5 136	12 <5 97	6 <5 20	29 <5 1288	8 <5-75
209 26 1652	131 28 616	216 39 1183	331 134 816	268 64 1121	311 2455 6895	181 75-2275
56 6 545	44 9 209	67 <5 1090	46 10 209	33 10 110	37 6 246	27 20-30
8033 4704 13718	7495 4288 13099	7219 3825 13627	6572 3379 12781	7879 4406 14088	5247 2860 9627	7567 6200-10,000
24	23	13	8	9	3	6

Table 50. The correspondence between factor 3 (Ti-Ga-Cr-V) scores and the trace element concentrations of the Onecote soils.

Sequence	Element	Factor Loading	1	2	3	4
			-.00	-2.00	-1.75 -1.50	-1.25
1	Ti	- .841	12298 9517 15892	11519 9336 14215	11862 8453 16644	8792 4096 18876
2	Ga	- .739	26 21 32	23 19 28	19 10 36	16 7 32
3	Cr	- .674	202 140 293	211 159 281	214 167 275	187 128 272
4	V	- .362	364 82 1607	364 102 1299	192 60 611	360 39 3362
5	Fe(%)	- .765	8.36 1.68 41.48	8.21 6.25 10.78	5.92 2.14 16.38	6.09 2.[illegible]7 17.61
6	Sn	- .127	11 <5 154	<5 <5 5	7 <5 44	<5 <5 6
7	Mo	- .089	6 <2 23	6 2 20	4 <2 24	7 <2 52
8	Ni	- .086	20 6 65	17 <5 76	24 <5 129	12 <5 48
9	Cu	- .032	13 <2 746	11 2 70	9 <2 239	7 <2 284
10	Mn	- .014	503 183 1388	626 108 3645	445 27 7316	170 10 2942
11	Pb	+ .029	111 5 2603	30 17 52	45 5 397	38 13 110
12	Co	+ .060	8 <5 17	9 <5 20	10 <5 38	7 <5 15
13	Zn	+ .073	56 24 131	80 34 186	58 24 139	88 < 20 427
14	Ag	+ .180	0.2 <0.2-1.0	<0.2 -	<0.2 <0.2-0.8	< 0.2 <0.2-0.2
15	As	+ .196	9 <5 94	8 <5 35	5 <5 8	20 < 5 233
Number of samples			6	8	10	7

5	6	7	8	9	10	11
	-1.00	-0.75	-0.50	-0.25	0.00	+0.25 +0.50
37 9144 6864 12182	8731 7095 10744	8249 6020 11802	7810 5300 11510	7636 4058 11762	7024 5215 9354	6631 4944 8893
18 14 24	17 13 23	16 10 24	15 10 21	18 8 22	13 9 20	13 9 19
188 130 272	182 129 258	178 104 307	164 99 271	156 84 291	132 90 196	130 68 251
338 157 731	248 61 1010	225 37 1380	173 33 893	143 30 680	133 31 568	153 26 912
7.86 3.07 20.09	5.80 2.51 13.40	5.73 2.82 11.66	5.97 2.45 14.55	4.58 1.51 13.86	5.61 1.71 18.41	5.05 2.03 12.53
6 <5 19	5 <5 9	5 <5 7	5 <5 16	5 <5 7	6 <5 26	5 <5 12
5 2 18	4 <2 13	4 <2 13	4 <2 12	3 <2 9	4 <2 11	5 <2 16
20 5 75	17 <5 88	16 5 50	18 <5 86	14 <5 45	13 <5 54	14 <5 64
11 <2 358	9 <2 140	4 <2 55	6 <2 103	3 <2 30	4 <2 59	10 <2 184
483 31 7564	627 52 7560	418 17 10059	554 46 6643	270 10 6963	459 25 8476	328 20 5475
55 10 300	38 14 103	37 8 174	41 9 199	36 14 94	39 8 185	52 11 260
12 <5 54	9 <5 43	9 <5 29	10 <5 29	8 <5 26	9 <5 39	8 <5 24
78 31 192	94 26 342	74 <20 304	89 22 363	62 <20 469	81 31 209	95 <20 515
<0.2 <0.2-0.3	<0.2 <0.2-0.6	<0.2 <0.2-0.8	<0.2 <0.2-0.3	<0.2 <0.2-0.4	<0.2 <0.2-0.4	0.2 <0.2-0.8
6 <5 26	6 <5 23	7 <5 40	7 <5 36	6 <5 28	6 <5 42	9 <5 71
13	20	28	24	26	27	36

12	13	14	15	16	17	18
+0.75	+1.00	+1.25	+1.50	+1.75	+2.00	+00
6125 5006 7493	5833 4094 8312	5400 3758 7759	5674 4645 6931	4638 2359 7318	5039 3821 6646	4743 2754 8169
12 8 17	12 7 18	11 6 18	9 5 15	9 5 18	7 4 14	6 6 8
129 67 249	115 62 212	112 62 201	105 70 157	108 72 163	96 58 158	64 24 167
139 26 728	131 20 843	105 24 457	92 24 344	138 22 876	65 45 94	63 9 453
4.29 1.59 11.62	3.99 1.23 12.98	4.21 1.66 10.72	3.88 1.29 11.68	5.72 <1.00 40.50	3.48 1.38 8.79	3.73 <1.00 21.81
5 <5 8	<5 <5 7	<5 <5 5	<5 <5 5	<5 -	5 <5 8	<5 <5 7
3 <2 12	3 <2 15	3 <2 8	3 <2 13	3 <2 50	2 <2 3	3 <2 25
14 <5 63	14 <5 103	13 <5 101	10 <5 55	17 <5 107	9 5 17	8 <5 44
4 <2 55	6 <2 190	4 <2 58	6 <2 252	10 <2 286	4 <2 28	3 <2 30
303 11 8369	214 10 4687	189 22 1655	174 10 2964	483 35 6663	240 31 1869	161 <10 3287
37 14 98	44 8 229	32 13 79	49 7 352	36 <5 342	28 7 106	41 <5 1116
9 <5 29	7 <5 24	8 <5 17	7 <5 19	15 <5 135	5 <5 10	7 <5 32
98 24 396	97 21 459	83 <20 447	86 <20 462	146 21 996	66 <20 236	72 14 368
<0.2 <0.2-0.3	0.2 <0.2-0.8	0.2 <0.2-0.7	0.2 <0.2-0.8	<0.2 <0.2-0.2	<0.2 <0.2-0.2	0.2 <0.2-0.6
6 <5 34	8 <5 63	7 <5 35	9 <5 134	16 <5 434	12 <5 84	8 <5 95
20	23	12	9	4	4	10

Table 51. The correspondence between factor 4(Sn-Pb-Ag-Cu) scores and the trace element concentrations of the Onécote soils.

Sequence	Element	Factor loading	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
			-00	-2.00	-1.75	-1.50	-1.25	-1.00	-0.75	-0.50	-0.25	0.00	+0.25	+0.50	+0.75	+1.00	+1.25	+1.50	+1.75	+2.00 +00
1	Sn	- .880	28 6 147	6 <5 13	13 <5 131	10 <5 45	6 <5 22	5 <5 7	6 <5 13	6 <5 8	5 <5 7	5 <5 7	<5 <5 5	<5 -	<5 -	<5 -	<5 -			
2	Pb	- .792	533 133 2141	294 56 1539	77 5 1133	43 8 224	69 5 897	63 15 272	63 25 163	58 30 111	48 25 92	41 23 73	35 19 64	28 16 49	17 11 26	13 7 26	8 -			
3	Ag	- .574	0.3 <0.2-1.0	0.7 0.6-0.8	0.3 <0.2-0.6	0.2 <0.2-0.4	0.2 <0.2-0.8	0.3 <0.2-0.7	0.2 <0.2 - 0.8	<0.2 <0.2-0.6	<0.2 <0.2-0.3	<0.2 <0.2-0.3	<0.2 -	<0.2 <0.2-0.2	<0.2 -	<0.2 -	<0.2 -			
4	Cu	- .443	80 8 808	57 30 107	18 <2 1390	10 <2 174	8 <2 314	24 <2 412	15 <2 250	11 <2 115	8 <2 127	6 <2 75	4 <2 41	2 <2 17	2 <2 12	<2 <2 6	<2 -			
5	Mo	- .140	9 2 50	8 2 30	3 <2 16	3 2 7	5 2 14	6 2 15	4 <2 13	4 <2 16	4 <2 18	4 <2 18	4 <2 10	4 <2 12	3 <2 8	3 <2 15	<2 <2 2			
6	Ni	- .125	29 5 170	28 10 81	11 5 23	13 <5 92	8 <5 71	28 13 63	22 6 77	15 <5 92	14 <5 47	16 <5 74	13 <5 55	12 <5 55	13 <5 54	16 <5 91	11 6 21			
7	Ga	- .069	16 7 40	16 10 26	12 9 17	11 7 17	12 6 23	14 10 19	13 8 20	13 6 28	14 7 29	14 8 27	14 7 28	13 7 25	12 6 25	13 6 26	7 -			
8	Fe (%)	- .024	8.64 1.91 39.11	7.23 3.17 16.48	3.05 <1.00 20.68	4.84 2.76 8.49	4.78 1.62 14.11	5.79 2.61 12.87	5.69 2.69 12.05	5.66 1.38 23.23	5.23 1.63 16.79	5.62 1.91 16.60	4.56 1.64 12.72	5.02 2.05 12.28	4.98 1.97 12.58	5.66 <1.00-30.00	3.71 1.36 10.16			
9	V	- .009	252 29 2215	710 230 2186	242 9 6396	126 35 456	173 24 1257	287 45 1815	203 35 1176	170 27 1084	150 22 1009	201 35 1144	143 29 713	153 27 861	103 32 327	128 36 455	69 58 83			
10	Mn	- .005	499 123 2015	871 187 4056	164 <10 20167	1132 <10 152268	145 <10 5776	1020 67 13738	464 56 3846	248 13 4570	462 35 6129	411 25 6810	292 12 7341	236 14 3999	304 29 3175	845 80 8969	690 54 8842			
11	Ti	+ .010	7075 3549 14469	6420 4458 9243	9165 2275 36922	6668 4934 9049	6455 5266 7914	7363 3612 15008	6625 4156 10560	6893 4290 11076	7479 4713 11866	7591 4105 14040	7715 4480 13284	7270 4434 11921	7098 3552 14185	6177 3271 11665	4167 1805 9616			
12	As	+ .016	12 <5 160	29 <5 523	12 <5 254	10 <5 88	13 <5 87	10 <5 72	10 <5 100	6 <5 40	7 <5 41	7 <5 54	6 <5 21	7 <5 37	7 <5 32	8 <5 99	9 <5 87			
13	Zn	+ .023	131 30 575	321 90 1143	101 7 1387	24 <20 1743	63 24 163	151 27 829	156 32 764	93 <20 521	78 25 244	88 22 354	74 23 240	68 27 170	64 23 178	82 28 242	63 17 231			
14	Cr	+ .074	140 47 418	221 101 481	210 183 240	113 77 167	119 42 339	174 79 384	162 82 317	150 78 291	131 44 351	157 83 299	141 68 293	143 85 239	128 63 261	131 79 218	88 41 188			
15	Co	+ .082	80 5 27	14 7 27	18 5 12	12 5 136	7 5 33	15 <5 88	10 <5 32	7 <5 25	9 <5 25	9 <5 31	8 <5 24	8 <5 18	9 <5 29	16 <5 86	23 <5 308			
Numbers of samples			11	4	2	4	6	9	15	21	28	50	60	44	24	5	2	0	0	0

Table 52. The correspondence between factor 5 (As-Mo-Fe-(V-Cu)) scores and the trace element concentrations of the Onecote soils.

Sequence	Element	Factor loading	1	2	3	4
			-00 -2.00	-1.75	-1.50	-1.25
1	As	.770	72 23 225	49 28 87	25 5 129	23 5 115
2	Mo	.746	17 7 40	8 2 36	10 6 19	9 5 15
3	Fe(%)	.600	12.92 3.47 68.07	14.90 2.08 107.86	8.20 3.92 17.14	6.79 3.27 14.09
4	V	.388	458 111 1887	423 44 4054	472 110 2031	316 90 1328
5	Cu	.275	34 5 227	63 33 123	19 <2 378	10 <2 136
6	Pb	.188	98 9 1039	490 122 1961	53 14 203	53 5 561
7	Co	.121	12 <5 49	6 <5 23	13 5 34	7 3 15
8	Zn	.088	170 38 761	208 44 983	146 26 814	86 <20 537
9	Ag	.087	0.2 <0.2-1.0	0.4 <0.4-0.5	<0.2 <0.2-0.5	0.2 <0.2-0.8
10	Mn	.042	373 40 3499	642 206 2000	472 414 5016	331 11 9559
11	Ti	.037	6804 3307 13998	6726 4424 10226	7131 4002 12704	9225 4906 17346
12	Cr	.020	144 83 250	120 64 226	176 102 302	177 90 348
13	Ga	+.078	14 5 34	14 11 19	13 9 20	19 9 38
14	Sn	+.089	6 <5 42	18 <5 174	5 <5 5	5 <5 9
15	Ni	+.183	18 <5 122	18 <5 75	15 <5 112	9 <5 43
Numbers of Samples			14	2	10	7

5	6	7	8	9	10	11
-1.00	-0.75	-0.50	-0.25	0.00	+0.25	+0.50
23 <5 140	12 5 70	13 <5 91	7 <5 22	6 <5 22	6 <5 19	5 <5 10
7 3 18	7 3 14	5 2 13	5 <2 18	4 2 8	4 2 7	3 2 6
6.99 2.38 2052	6.12 2.63 14.29	6.85 3.39 13.84	6.98 3.28 14.84	5.41 2.50 11.47	5.22 2.65 10.29	5.37 3.05 9.46
357 47 2740	396 72 2186	263 61 1133	184 53 641	151 33 691	159 32 779	139 26 733
14 <2 376	14 <2 358	6 <2 73	8 <2 195	6 <2 111	7 <2 105	4 <2 36
64 19 209	51 17 151	37 13 106	44 7 292	42 11 167	37 11 128	45 6 336
9 <5 38	8 <5 30	12 <5 52	12 <5 54	8 <5 22	9 <5 37	9 <5 22
113 <20 707	118 32 442	96 <20 533	75 22 256	86 27 274	67 <20 476	79 27 231
0.2 <0.2-0.8	0.2 <0.2-0.8	<0.2 <0.2-0.8	<0.2 <0.2-0.8	<0.2 <0.2-0.8	<0.2 <0.2-0.4	<0.2 <0.2-0.3
411 17 9776	263 12 5617	540 15 19536	509 41 6308	361 17 7728	525 34 8072	368 34 4035
7149 637 11019	7168 829 11870	7260 4613 11427	7865 3991 15497	7870 4324 14322	7439 4002 13828	7332 4239 12680
178 85 375	174 84 359	160 85 300	150 85 265	149 71 311	145 72 289	142 57 357
13 7 24	14 9 22	15 10 22	14 7 31	13 7 23	14 6 29	14 7 28
5 <5 12	5 <5 7	<5 <5 5	6 <5 22	5 <5 13	5 <5 12	5 <5 12
16 <5 83	12 <5 94	24 7 79	16 <5 95	11 <5 50	15 <5 68	18 <5 70
13	11	10	27	25	32	38

12	13	14	15	16	17	18
+0.75		+1.00	+1.25	+1.50	+1.75	+2.00 +00
<5 <5 7	<5 <5 8	<5 <5 5	<5 <5 5	<5 <5 5	<5 -	
3 <2 4	2 <2 4	2 2 3	2 <2 3	2 <2 3	<2 -	
4.26 1.98 9.18	3.83 1.64 8.93	2.73 1.35 5.53	3.10 1.02 9.40	1.64 <1.00 3.44	2.70 -	
122 30 505	87 33 226	92 27 309	97 38 251	73 17 310	58 -	
4 <2 59	2 <2 7	2 <2 32	2 <2 10	2 <2 22	<2 -	
35 13 93	30 12 76	29 9 94	28 11 69	32 13 76	13 -	
7 <5 19	9 <5 24	7 <5 27	7 <5 16	5 <5 9	7 -	
80 20 313	66 28 158	73 <20 334	53 31 89	51 25 104	60 -	
<0.2 <0.2-0.6	<0.2 -	<0.2 <0.2-0.3	<0.2 -	<0.2 -	<0.2 -	
343 15 8081	389 22 6853	131 <10 1953	166 11 2513	43 13 148	105 -	
7405 4556 12037	6768 4267 10734	5471 3653 9758	6624 4327 10139	7806 3812 15984	5500 -	
135 68 268	123 66 231	126 67 238	150 74 306	119 24 590	90 -	
13 7 26	13 7 24	11 5 23	15 9 25	12 5 29	16 -	
5 <5 10	5 <5 8	5 <5 6	5 <5 7	6 <5 29	<5 -	
14 <5 61	12 <5 43	13 <5 58	20 8 47	14 4 57	17 -	
38	29	16	6	6	1	0

5 factor association. However, the same features are not shown by the following:-

(i) Ga in factor 1 (factor loading +0.191, positive factor)

(ii) Ga in factor 2 (factor loading +0.165, positive factor)

(iii) Fe in factor 3 (factor loading -0.165, negative factor)

(iv) Mo in factor 4 (factor loading -0.140, negative factor)

Thus though elements with factor loadings greater than /0.300/ may be assumed to be members of the factor association, those with loadings below /0.200/ may only occasionally be included. Elements with loadings between /0.200/ and /0.300/ must be separately evaluated before they can be accepted as associated elements.

The factor score contrast necessary to ensure a geochemical contrast exceeding 100 per cent $\left(\frac{\text{high-low}}{\text{low}} \% \geqslant 100\%\right)$ is similar to that shown in the drainage sediment data. The safe minimum factor score contrast appears to be approximately 1.50.

7.7.4. Distribution of the R-mode factor scores

The distribution of the factors has been displayed symbolically in figures 228 to 232 (vol.2). The salient features

of the distribution are briefly described below:

Factor 1, Zn-V-Cr-Cu-Ag-Ni, positive factor (figure 228, vol. 2)

The highest factor scores (> + 1.00) are most commonly found over the basal stratigraphic unit (S.U. 1), though these occasionally occur over other units. The lowest scores are relatively most common over S.U. 7-11 except over the base of this unit in the south of the outcrop area.

Factor 2, Mn-Co-Ni-Fe, positive factor (figure 229, vol. 2)

There seems little apparent stratigraphic control governing the distribution of this factor with higher values (+ 1.00 to > + 2.00) scattered over all stratigraphic units. The northern moorland area soils frequently have very low factor scores (-1.00 to < -2.00).

Factor 3, Ti-Ga-Cr-V, negative factor (figure 230, vol. 2)

There are significantly less soil sample sites with high negative scores (-1.00 to < -2.00) over the basal and topmost stratigraphic units (S.U. 1 and 7-11). These higher scores are scattered over the intervening units, with marginally higher levels over S.U. 5 and 6 (often < 0.0).

Factor 4, Sn-Pb-Ag-Cu, negative factor

The highest negative scores (-1.00 to < 2.00) are principally located over the basal stratigraphic unit (S.U. 1) and along the northern margin of the sampled area. Elsewhere, these values occasionally occur over the other units except S.U. 6.

Factor 5, As-Mo-Fe-V, negative factor.

There is an apparent reduction in the number of higher negative scores (-1.00 to < -200) from the basal stratigraphic unit (S.U. 1) towards the topmost (S.U. 7-11). The levels over S.U. 1 are commonly negative whilst those over S.U. 7-11 are usually positive.

The sample factor scores have been subdivided into stratigraphic subsets in the same way as were the soil trace element concentration data (see section 7.7.1.). The arithmetic means ($\bar{X}$) and the ranges ($\bar{X} \pm 2\sigma$) for the factor scores in each stratigraphic subset have been computed and are presented in table 53.

The stratigraphic control is shown most strongly for factor 1 (Zn-V-Cr-Cu-Ag-Ni), factor 4 (Sn-Pb-Ag-Cu) and factor 5 (As-Mo-Fe-V-(Cu)) whose highest levels occur in stratigraphic units (S.U.) 1 and 2. The maximum contrast in the mean factor scores exceed /1.000/ . A maximum contrast in the excess of /1.000/ is also shown by factor 2 (Mn-Co-Ni-Fe) which has its maximum values in S.U.5 and its minimum value in S.U.3, which agrees reasonably well both with the trace element concentration data (see table 45) and also with the disposition of these stratigraphic units with respect to the moorland areas. Thus, S.U.3 underlies most of the moorland area whilst S.U.5 sub-outcrop along the flanks of the moorland and bears seepage lines along its strike. Factor 3 (Ti-Ga-Cr-V) shows the minimum mean factor score contrast (/0.96/) of all the factors. The highest levels occur in S.U.4 and 5 and the lowest levels in S.U.2 and 7-11 both of which include high proportions of arenaceous material. The same features are shown by Ti and Ga though not by Cr and V in the tabulated results of the trace element concentrations (see table 45).

Table 53 Mean factor scores and ranges, for subsets of the soil factor score data based on the underlying stratigraphic units

S.U.	Sample Nos.	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
		+ve Zn,V,Cr Cu,Ag,Ni	+ve Mn,Co Ni,Fe	-ve Ti,Ga Cr,V	-ve Sn,Pb Ag,Cu	-ve As,Mo Fe,V,Cu
7-11	20	* -0.91 ≠ -1.69 -0.12	+ 0.20 -1.20 1.72	+ 0.57 -1.36 2.49	-0.05 -1.89 1.78	+ 0.75 0.04 1.47
6	38	-0.40 -2.67 1.86	+ 0.30 -1.25 1.85	-0.18 -2.27 1.91	+ 0.26 -0.73 1.25	+ 0.24 -1.16 1.64
5	35	-0.20 -1.45 1.05	+ 0.41 -1.10 1.92	-0.22 -2.25 1.82	+ 0.34 -0.78 1.45	-0.02 -1.61 1.56
4	33	-0.03 -1.21 1.14	-0.10 -2.24 2.04	-0.39 -2.12 1.35	+ 0.22 -1.71 2.15	+ 0.10 -1.91 2.11
3	48	-0.23 -1.42 0.97	-0.92 -3.00 1.16	+ 0.05 -1.89 1.99	+ 0.10 -1.62 1.82	-0.14 -2.50 2.22
2	17	+0.99 -1.14 3.12	-0.00 -2.14 2.14	+ 0.44 -1.69 2.56	+ 0.01 -0.84 0.85	-0.52 -3.47 2.42
1	32	+1.41 -0.48 3.30	+0.23 -1.52 1.97	+ 0.37 -1.07 1.80	-0.75 -2.85 1.36	-0.51 -2.81 1.80

* Means are arithmetic ($\bar{X}$) ≠ Ranges are $\bar{X} \pm 2\sigma$

7.7.5. Interpretation of the soil R-mode factors

The relationship between factor 2 (Mn-Co-Ni-Fe) and the drainage status of the soils has been examined. When the soil samples were collected the agricultural status of the area around the sample site was approximately assessed. Three classes of land-usage were discerned, namely, moorland, rough pasture and improved pasture, the last category included land being cultivated. The relationship between the soil drainage status and land usage was such that generally the improved pasture was the best drained whilst the moorland was the poorest; the rough pasture falls between the two categories but was frequently poorly drained. Soil samples with either low (< -1.000) or high ($> +1.000$) scores on factor 2 were separately subdivided on the basis of the agricultural status around the soil sample site. The percentage proportion of both the high and low factor score subsets in each of the agricultural categories were computed and the results are tabulated below (see table 54).

Table 54 The relationship between agricultural status and soil factor scores for Factor 2 (Mn-Co-Ni-Fe)

	Numbers of Samples	Improved pasture (incl.cultivated land)	Rough Pasture	Moorland
Low scores (<-1.000)	48	8.5%	25.0%	66.5%
High scores (>+1.000)	26	38.5%	38.5%	23.1%

The high factor scores represent high soil concentrations of the trace elements in this association, the converse holds for the low scores. It is know that in poorly drained acid soils these mobile elements, constituting the factor association, are leached from the soils. Thus lower scores would be expected in those soils taken from poorly drained areas. It may be seen from table 54 that there is a considerable difference between the proportion of moorland soils with low compared to high scores on this factor association. There is in addition an even more marked discrepancy when the proportion of low and high scores are compared for the improved pasture (including cultivated land) soils. The reason that the contrast is not more intense may be ascribed to bedrock lithological variations since shales and especially black marine shales would be expected to contain far higher concentrations of these elements than would sandstones. Another cause would be due to liming of the agricultural land which has the effect of raising the soil pH and EH and thus partially immobilises or 'fixes' these mobile elements. Thus it would seem reasonable to ascribe the causative control of this factor dominantly to the soil drainage status and only subsidiarily to the bedrock composition.

It may be argued that the variations of factor 2 (Mn-Co-Ni-Fe) are mainly due to the siting of the agricultural land (improved pasture and cultivated land) over bedrocks generally richer in these elements, since due to the exercise of geological and

geomorphological controls stratigraphic units (S.U.) 3 and 4 underlie most of the moorland areas. However, the change in factor scores and trace element concentrations along the strike of S.U.3 with lower levels over the northern moorland and higher levels on the southern better drained upland slopes are quite significant. Moreover, there is little variation in the factor scores between the soils over S.U.1, 2 and 7-11, even though the proportions of black marine shales, shales and sandstones is quite different in these three units. Thus it may be concluded that variations in bedrock lithology are relatively unimportant when considering the distribution of this factor.

The general correspondence between the areal distribution patterns of the sample scores on factors 1 (Zn-V-Cr-Cu-Ag-Ni), 4 (Sn-Pb-Ag-Cu) and 5 (As-Mo-Fe-V-Cu) would indicate similar provenance and controls for these three factors. The relationship of the factor 5 trace element association, As-Mo-Fe-V-Cu to the sub-outcropping of black marine shales has already been established (Fletcher, 1968). It is probable that the other two associations, namely, Zn-V-Cr-Cu-Ag-Ni and Sn-Pb-Ag-Cu, are also, at least partially, under the same control. However, the sudden decrease in the levels of the Sn-Pb-Ag-Cu association between S.U. 1 and 2, suggests that some other causative process is also operating. The most likely answer would seem to be the presence of mining and metallurgical contamination, since mining activity on the Mixon anticline, on the area underlain by the Visean limestones, has ceased only

relatively recently. The areal distribution of the sample scores for the association, Sn-V-Cu-Cn-Ag-Ni, exhibits correlations with the patterns for both factors 4 and 5 and is possibly a function of both contamination due to mining activity and also to syngenetic enrichment of these elements in the black marine shales of stratigraphic unit 1.

Factor 3 (Ti-Ga-Cr-V) shows an areal distrib·tion pattern for the sample factor scores rather similar to the equivalent drainage sediment factor scores. These are generally highest over S.U.4 and 5 which have the highest proportions of argillaceous units (Holdsworth, pers.comm.). Thus the data tends to suggest the hypothesis that this factor represents an argillaceous bedrock trace element association.

7.8.0. GEOCHEMICAL DATA OF THE BEDROCK

7.8.1. Lithological control of the bedrock trace element concentrations

The bedrock analytical data was subdivided on the basis of visually identifiably lithology into 5 categories, namely, sandstones, calcareous siltstones, shaly limestones and limy shales, shales and mudstones, and finally marine band shales. The variation of trace element concentration levels in the different lithologies was investigated and the mean concentration for each

lithological type and element were computed. The results are presented in table 55.

The data in table 55 has been simplified by ranking the elements, employing the same procedure used for the drainage sediments and soils, according to their relative abundances in the various lithologies. The results have been tabulated and are presented in table 56.

Table 55 Mean trace element concentration levels (ppm) of the different bedrock lithologies subcutcropping in the Onecote area.

Lithology	No. of Samples	As	Co	Cr * rounded to 10	Cu	Fe* rounded to 0.1 (%)	Ga	Mn* rounded to 10	Mo	Ni* rounded to 10	Pb	Sn	Ti* rounded to 100	V* rounded to 10	Zn* rounded to 10
Sandstone	27	5	11	80	6	3.4	4	240	< 2	30	7	5	4900	60	60
Calcareous siltstone	12	8	15	80	10	3.9	4	310	5	40	9	5	3900	100	90
Shaly lsts & limy shales	6	9	28	330	22	9.0	7	400	13	120	6	< 5	5700	480	90
Shales and mudstones	43	12	19	170	31	6.7	10	170	8	80	9	< 5	7400	300	90
Marine band shales	16	24	27	210	50	8.2	10	220	24	140	9	< 5	7500	580	140

* Mean levels rounded-off.

Table 56 Summary of the relative mean trace element concentration levels in the different bedrock lithologies suboutcropping in the Onecote area

Lithology	High	Intermediate	Low
Sandstones	Sn	Mn	Pb,Ga,V,Mo,Cu,Zn,Ti, Ni,Co,Cr,As,Fe
Calcareous siltstones	Pb,Sn,Mn	Zn	Ga,V,Mo,Cu,Ti,Ni,Co, Cr,As,Fe
Shaly limestones & limy shales	V,Ni,Co,Mn, Cr,As,Fe	Ga,Mo,Cu,Zn,Ti	Pb,Sn
Shales and mudstones	Pb,Ga,Ti	V,Mo,Cu,Zn,Ni, Co,Cr,As,Fe	Sn,Mn
Marine band shales	Pb,Ga,V,Mo, Cu,Zn,Ti,Ni, Co,Mn,Cr,As, Fe		Sn

The most striking feature observed are the very high concentration levels of all the trace elements, except Sn, in the marine band shales, a feature previously noted in this area by Fletcher (op. cit.). The sandstones have low concentrations for all elements except Mn, whilst the other lithologies generally have intermediate concentrations.

Certain groups of elements display similar relative levels in the different lithological types, for instance Ti-Ga, Cr-V, Mo-As and to a lesser extent Fe,Ni-Co, Cu-Zn; whilst Pb, Sn and to a lesser extent Mn appear to be distributed in a semi-independent manner. These groupings are indicative of the correlations existing between the component elements of these groups. It is possible that the variations of some of these groups are controlled by variations in the mineralogy between these lithological categories.

The Ti-Ga group is most enhanced in the shales, especially the non-calcareous types. This would indicate that the concentration of these elements is perhaps controlled by certain mineralogical phases common in argillaceous sediments. The V-Cr group displays similarities in its relative levels to that of Ti and Ga but correlates even more closely with the Mo-As-Fe group and also the Ni-Co group with the highest levels in the marine band shales and the limy shales-shaly limestone categories, with intermediate levels in the shales and mudstones and with the lowest

levels in the calcareous siltstones and sandstones. A very close correspondence exists between the groups Mo-As-Fe and Ni-Co. The Cu-Zn group is most enhanced in the marine bands; intermediate levels occur in the shales-mudstones and limy shales-shaly limestones, with lower levels in the calcareous siltstones and even lower concentrations in the sandstones. It can only be concluded that all these associations are probably controlled by those mineral phases common in sedimentary rocks comparable to marine band shales, limy shales and shaly limestones. These are rocks considered to have been deposited in marine basins with restricted circulations leading to the establishment of reducing conditions and the consequent formation within these rocks of organic and sulphide mineralogical phases.

Geochemical variations of shales and sandstones in the different stratigraphic units

It is possible that the changing trace element concentrations in the different stratigraphic units are a function of the varying proportions of the different lithological types in each unit. To test this hypothesis both the sandstone and the shale-mudstone samples were separately divided into stratigraphic subsets. If the hypothesis were true it would be expected that there would be only minor variations in the trace element levels between the different stratigraphic subsets for each lithology

compared to the variation between these different types. The arithmetic mean trace element concentrations of each subset have been computed and have been summarised in table 57 (sandstones) and in table 59 (shale-mudstones). The relative levels of the trace elements in the different stratigraphic units have also been tabulated for both sandstonesand shale-mudstones, using the same ranking procedure as employed previously, and these have been summarised in tables 58 and 60 respectively.

The sandstones represent units 2 to 7-11 and show that three of the trace element groupings discerned in the lithological subsets are also recognisable, namely As-Mo-(Fe), Ga-Ti and Co-Ni, though not as clearly, in this data. The As-Mo-(Fe) association is highest in the sandstones of unit 2 and the levels are lower in the higher stratigraphic units. The Ga-Ti association shows increasing enhancement up the stratigraphic column reaching its peak in units 6 and 7-11. The Co-Ni association reaches its highest levels in units 3 and 6, and its lowest levels in units 2, 4 and 7-11.

Table 57. Mean trace element concentrations (ppm) in sandstones from different stratigraphic units.

Stratigraphic Unit	No. of Samples	As	Co	Cr * rounded to 10	Cu	Fe(%)* rounded to 0.1	Ga	Mn * rounded to 10	Mo	Ni * rounded to 10	Pb	Sn	Ti * rounded to 100	V * rounded to 10	Zr* rounded to 10
7-11	7	< 5	10	60	6	3.0	5	200	<2	20	13	6	5400	50	60
6	3	5	13	70	6	4.3	5	320	<2	40	7	< 5	5600	60	80
5	5	6	12	80	9	4.5	2	440	<2	30	3	< 5	4200	70	50
4	6	5	9	110	4	2.5	3	160	<2	30	7	6	4200	40	50
3	2	5	16	120	4	2.6	3	210	<2	60	7	5	4900	60	90
2	2	11	5	70	3	3.2	2	180	4	10	16	6	4200	40	130

* Mean levels rounded-off.

Table 58 Relative mean trace element levels in the sandstones from different stratigraphic units

Stratigraphic Unit	High	Intermediate	Low
7-11	Pb,Sn,Ga,Ti	V,Cu,Co,Mn,Fe	Mo,Zn,Ni,Cr,As
6	Ga,V,Ti,Ni,Co,Mn,Fe	Pb,Cu,Zn,Cr,As	Sn,Mo
5	V,Cu,Mn,Fe	Ti,Ni,Co,Cr,As	Pb,Sn,Ga,Mo,Zn
4	Sn,Cr	Pb,Ga,Ni,As	V,Mo,Cu,Zn,Ti,Co,Mn,Fe
3	Zn,Ni,Co,Cr	Pb,Sn,Ga,V,Ti,Mn,As	Mo,Cu,Fe
2	Pb,Sn,Mo,Zn,As	Cr,Fe	Ga,V,Cu,Ti,Ni,Co,Mn

Table 59. Mean trace element concentrations (ppm) in shales mudstones from different stratigraphic units.

Stratigraphic Unit	No. of Samples	As rounded to 5	Co * rounded to 5	Cr* rounded to 10	Cu* rounded to 10	Fe* rounded to 0.1	Ga	Mn * rounded to 10	Mo	Ni* rounded to 10	Pb	Sn	Ti * rounded to 100	V * rounded to 10	Zn * rounded to 10
7-11	4	5	10	140	20	4.5	13	100	4	40	17	< 5	7100	260	60
6	1	30	40	130	100	13.6	14	370	47	140	12	< 5	9300	300	140
5	17	15	25	150	40	9.6	12	310	7	100	9	< 5	7600	290	90
4	11	10	20	190	30	5.9	10	190	5	80	7	< 5	8100	280	100
3	12	10	15	200	20	5.2	8	110	9	80	9	< 5	7000	350	80
2	3	20	15	120	30	4.6	8	60	23	100	15	< 5	5900	340	150
1	4	30	25	160	30	5.0	9	140	19	90	4	< 5	7100	290	90

* Mean levels rounded-off.

Table 60 Relative mean trace element levels in the shales-mudstones from different stratigraphic units

Stratigraphic Unit	High	Intermediate	Low
7-11	Pb,Ga	Ti	V,Mo,Cu,Zn,Ni,Co,Mn,Cr, As,Fe
6	Ga,Mo,Cu,Zn, Ti,Ni,Co,Mn, As,Fe	Pb,V,Cr	
5	Ni,Mn,Fe	Pb,Ga,V,Mo,Cu,Zn, Ti,Co,Cr,As	
4	Ti,Cr	Ga,V,Cu,Zn,Ni,Co, Mn,As,Fe	Pb,Mo
3	V,Cr	Pb,Mo,As,Fe	Ga,Cu,Zn,Ti,Ni,Co,Mn
2	Pb,V,Mo,Zn	Cu,Ni,Co,As	Ga,Ti,Mn,Cr,Fe
1	Mo,As	Ga,V,Cu,Zn,Ti,Ni, Co,Mn,Cr,Fe	Pb

It is possible to discern certain of those trace element groupings, which have similar relative concentrations in the different stratigraphic units. These are notably As-Mo-(Fe), Ga-Ti, Cr-V, Co-Mn-Ni and Cu-Zn. The As-Mo-(Fe) group reaches its highest levels in units 1 and 6, whilst the lowest levels are recorded in unit 7-11 and to a lesser extent in unit 4. The Ti-Ga group reaches its higher levels in the upper part of the stratigraphic succession especially in unit 6, and the lowest levels in units 2 and 3. The Cr-V group is highest in unit 3 and lowest in unit 7-11. The Co-Mn-Ni group reaches the highest levels in units 5 and 6 and the lowest in units 3 and 7-11. The Cu-Zn group is most enhanced in unit 6 and most depressed in units 3 and 7-11.

Discussion

The units with the most enhanced levels of these trace elements groups recognised in both sandstones and shales are essentially the same. This would indicate that whatever causative processes are controlling these trace element concentrations in the different stratigraphic units these appear to affect both lithological types. This evidence would seem to refute the hypothesis that variations in trace element concentrations between the different stratigraphic units are caused solely by variations in the proportion of the different lithological types in the individual stratigraphic units. The evidence indicate that there is also a change in the geochemistry, and by inference also the mineralogy, of the individual lithological types

in the stratigraphic succession in this area.

7.8.2. R-mode analysis of the bedrock trace element data

The results of the R-mode analysis upon the bedrock trace element data for all models between 2 and 10 factors were examined. Higher models were not examined since they seldom yield extra information. The data was log-transformed prior to the analysis because this gave more geochemically feasible solutions compared to those from the untransformed data. The principal trace elements in the factor associations have been tabulated below (see table 61).

The 10 factor model indicates some of those trace element groups recognised in the trace element data notably Ti-Ca, As-Mo-Fe, Cr-V and Ni-Co in addition to some which were unrecognised, namely, Mn-Fe and Cu-V-Mo. As the number of factors is reduced so the associations combine in different ways. Those elements displaying no affinities form unielemental factors until the 5 factor model in which no such factors occur. Below the 8 factor model the simple element groups begin to be combined, for instance, factor 5 in the 7 factor model combine both Co-Ni and Cu-Zn groups. Successively lower models produce combined groups similar to those recognised after R-mode analysis of the drainage sediment and soil data both on the regional scale and also in the detailed study area. Examples of these are:-

Table 61 Summary of the factor associations indicated by R-mode factor analysis of the log-transformed geochemical data from bedrocks in the Onecote area.

Factor Model	1	2	3	4	5	6	7	8	9	10
10	Ti,Ga	Zn	Pb	As,Mo, Fe	Ga	Sn	Cr,V	Mn,Fe	Ni,Co	Cu,V,Mo
9	Ti,Ga Cu	Mn,Fe	Pb	Cu,Mo, V,Ga	Zn	Sn	Cr,V	As,Mo, Fe	Ni,Co	
8	Ti,Ga	Mn,Fe	Pb	As,Mo, Fe,Cu	Zn	Sn	Cr,V	Ni,Co, Cu,V		
7	Ti,Ga, Cu	Mn,Fe	Pb	Mo,As, Cu,Fe	Zn,Ni, Co,Cu	Sn	Cr,V			
6	Ti,Ga Cr	Ni,Zn, Co,Cr, V,Cu	Pb	Mo,As, Cu,Fe	Mn,Fe	Sn* [V]				
5	Ti,Ga, Cr,Cu, Co	Mn,Fe, Co,As	Pb,Sn	Mo,As, Cu,V, Fe, [Sn]	Zn,Ni, V,Cr, Co,Cu					
4	Ga,Ti, Cr,V, Cu,Ni Mo,Co [Mn] *	Zn,Ni, Co,Mn, Cr	Pb,Sn	As,Fe, Mo,Mn, Cu						
3	Ga,Cu, V,Ti, Mo,Cr, As,Ni, Co,Fe Pb [Sn]	Mn,Zn, Co,Fe, Ni	Pb,Sn							
2	Ga,Cu, V,Ti, Mo,Cr, As,Ni, Co, Fe,Pb [Sn]	Mn,Zn, Co, Fe,Ni [Ti]								

LEGEND

*[ ]; square brackets enclose elements with factor loadings $\geq$/0.300/ of opposite sign to the dominant association in that factor.

(i) the association Mn-Zn-Co-Fe-Ni (factor 2, 3 factor model) representing those elements mobile in the secondary environment.

(ii) the association Ga-Ti-Cr-V-Cu-Ni-Mo-Co (factor 1, 4 factor model) which represents a rather more complex expression of the hypothetical argillaceous association Cr-Ga-Ti-V.

(iii) the association Mo-As-Cu-V-Fe (factor 4, 5 factor model) which is identical, except in the order of the elements, to the black marine shale association.

(iv) the association Zn-Ni-V-Cr-Co-Cu (factor 5, 5 factor model) is very similar to that indicated by the factor analysis of the soil data from this area, namely Zn-V-Cr-Cu-Ag-Ni, though the geochemical significance of this association is not established.

7.8.3. The correlation of the R-mode factor association scores with stratigraphy and bedrock weathering

The association As-Mo-Fe-Cu (factor 4, 8 factor model) has been shown to be related to black marine shales in this area (Fletcher, 1968); and these elements are concentrated either in the organic phase (Le Riche, 1959) or in the sulphide phase (Korolev, 1957, 1958). The variation of scores on this factor in the lithological and stratigraphic subsets will be illustrated later.

The associations Mn-Fe (factor 8, 10 factor model) and Ni-Co (factor 9, 10 factor model) will be considered further. These are the most mobile elements in the secondary environment and would be amongst the first to be leached out of weathered rocks. The bedrock shale samples from one section, that of the River Churnet, were used to test this hypothesis. The scores below -1.000 and greater than +1.000 on these two factors were subdivided according to whether the bedrocks were apparently weathered or unweathered. The results have been tabulated below (see table 62).

If only those samples with low factor scores are considered it is apparent that these are predominantly weathered material. The ratios of weathered to unweathered are 11:1 for the Ni-Co association and nearly 3:1 for the Mn-Fe association. The proportions are reversed for the high factor scores where the proportion of weathered to unweathered material is over 1:2 for the Ni-Co association and is also over 1:2 for the Mn-Fe association. These results show conclusively that the process of weathering leads to the removal of these mobile elements. The same conclusion though not shown here probably applies to some extent also to As and Zn, which are usually also highly mobile in the secondary environment. It is clear that due to the effects of weathering the relationship of these elements to the primary mineralogy of these bedrocks cannot be further elucidated.

Table 62 Illustrating the correlation between the factor scores on the Mn-Fe and Ni-Co factor associations with the degree of weathering in bedrock shales from the Churnet river section in the Onecote area.

Degree of weathering	Low factor scores (< -1.000)		High factor scores (> +1.000)	
	Ni-Co	Mn-Fe	Ni-Co	Mn-Fe
Unweathered	8.52≠ (12)*	26.7% (15)	69.2% (13)	70.0% (10)
Weathered	93.5% (12)	73.3% (15)	30.8% (13)	30.0% (10)

≠ The percentage of samples within each group

* The number of samples within each group.

The sample scores for the 8 factor model associations (Ti-Ga (factor 1), As-Mo-Fe-Cu (factor 4) and Cr-V (factor 7)) will be considered simultaneously since these probably relate to the primary mineralogy of the bedrock samples. All bedrock samples have been subdivided on the basis of their lithology into exactly the same categories as were employed in table 55 namely, sandstones, calcareous siltstones, shaly limestones and limy shales, shales and mudstones and finally marine band shales. The arithmetic mean ($\bar{X}$) of the factor scores and also the ranges of these scores ($\bar{X} \pm 2\sigma$) in each subset have been computed and are summarised in table 63.

The Ti-Ga association is most enhanced in the shales-mudstones and marine band shale groups with the lowest levels in the calcareous siltstones. The association As-Mo-Fe-Cu is most enhanced in the shaly limestones-limy shales and marine band shale groups and are most depressed in the sandstone type. The factor 7 association Cr-V, is most highly enhanced in the marine band shales followed by the shale-mudstones group and least enhanced in the sandstones and to a lesser extent in the calcareous siltstone groups. It is apparent that whilst the distribution of the Ti-Ga association is related to that of factor 4, (As-Mo-Fe-Cu) it is quite distinct from it. Both are shown to a high degree in argillaceous sediments but whereas Ti-Ga appears to bear an antipathetic relationship towards carbonate, the reverse is true for the As-Mo-Fe-Cu association. The

Table 63 Mean factor scores and ranges for three factor associations from the 8 factor model in lithological subsets of the bedrock data

Factor Association		No.1 Ti-Ga	No.4 As-Mo-Fe -Cu	No.7 Cr-V
Lithological Type	Numbers	+ve	+ve	-ve
Sandstone	27	-0.709 (-1.919 0.429)*	-0.900 (-1.526 0.290)	1.084 (-0.774 3.396)
Calcareous siltstone	12	-1.077 (-1.665 0.490)	-0.391 (-1.313 0.202)	0.890 (-0.510 1.463)
Shaly limestones & limy shales	6	-0.093 (-2.887 1.015)	0.996 (-0.344 1.981)	-0.136 (0.248 0.142)
Shales and mud-stones	43	0.464 (-2.143 1.649)	0.201 (-1.478 2.508)	-0.215 (-1.654 2.471)
Marine band shales	16	0.363 (-0.773 1.199)	0.994 (-1.182 2.353)	-0.608 (-2.120 0.504)

* ( ) Ranges displayed by the R scores in each subset.

Cr-V association exhibits behaviour intermediate to that of the other two factor associations, but rather more closely resembles that of Ti-Ga, in that it is hardly exhibited at all by the shaly limestones-limy shales group (c.f. the factor 4 association). Thus it may be concluded that this also exhibits an antipathetic relationship to carbonate, albeit weakly. The degree of overlap exhibited by the factor score ranges between the lithological subsets may be ascribed to the effects of variations in mineralogy within each lithological category, and also to analytical imprecision.

The factor scores of the sandstones and shales-mudstones for the 8 factor model associations 1 (Ti-Ga), 4 (As-Mo-Fe-Cu) and 7 (Cr-V) have been seperately subdivided on the basis of the stratigraphic units (S.U.) from which they were sampled. The arithmetic means of the scores within each unit and also the ranges of score exhibited within each unit have been summarised and are presented in tables 64 and 65.

The tabulated results of the sandstone data confirm those features shown by the trace element data (see table 55). Thus the As-Mo-Fe-Cu association exhibits the most enhanced levels in S.U.2 and much lower levels in the higher units. The Ti-Ga association shows the highest levels in S.U.6 and 7-11, which exhibits some correlation with the shale factor score distributions, which are most enhanced in S.U.4, 5 and 6 (see table 65). The Cr-V association exhibits the most enhanced levels in S.U.3 and 6 which also correlates.

Table 64 Mean factor scores and ranges for three factor associations from the 8 factor model in stratigraphic subsets of the sandstone bedrock data.

Factor Association		No.1 Ti-Ga	No.4 As-Mo-Fe-Cu	No.7 Cr-V
Stratigraphic Unit	Numbers	Positive factor	Positive factor	Negative factor
7-11	6	-0.314 (-1.004 0.338)	-0.900 (-1.509 0.802)	1.084 (-0.774 2.386)
6	3	-0.183 (- .842 .429)	-1.174 (-1.226 -1.167)	0.854 (0.539 1.332)
5	4	-0.901 (-1.673 - 0.534)	-0.672 (-1.240 0.188)	0.946 (-0.567 3.396)
4	5	-0.990 (-1.809 0.253)	-1.081 (-1.526 - .272)	1.141 (0.115 2.474)
3	2	-0.778 (-1.041 -0.514)	-1.205 (-.470 -0.939)	0.716 (0.370 1.062)
2	2	-1.319 (-1.919 -0.719)	0.053 (-0.185 -0.290)	2.446 (2.039 2.852)

to some degree with the shale scores which are most enhanced in S.U.3 and 4 (table 65).

The shales are most enhanced in the Ti-Ga association in S.U.4,5 and 6 (though the last unit is represented only by one sample). This shows good agreement with the trace element data shown in table 55. The Cr-V mean sample scores again confirm the trace element data, exhibiting the highest levels in S.U. 3 and 4. This also shows some degree of agreement with the distribution of the sample scores for the soil factor association Ti-Ga-Cr-V which are most enhanced over S.U.4 and 5 (table 53), though the correlation is of course closer to that of the bedrock Ti-Ga association. The same is also true for the drainage sediment association Ti-Ga-Fe (table 44). The bedrock Cr-V sample score distribution does not fully correlate with the drainage sediment association of Cr-V-Mo which exhibits its peak enhancement in S.U.4 and 5. The reasons for this maybe twofold:-

(i) the stratigraphic unit boundaries are more accurately determined for the stream sections from which the bedrocks were sampled than they were over the drift covered areas. This will lead to a certain amount of incorrect placement of soil samples within the different stratigraphic units.

(ii) stratigraphic unit 3 is frequently thickly covered by peat which would preclude the residual weathered material from being adequately represented in soil samples taken between 6 and 12 inches depth.

Table 65 Mean factor scores and ranges for three factor associations from the 8 factor model in stratigraphic subsets of the shale-mudstone bedrock data.

Factor Association		No.1 Ti-Ga	No.4 As-Mo-Fe-Cu	No.7 Cr-V
Strat-igraphic Unit	Numbers	Positive factor	Positive factor	Negative factor
7-11	3	0.277 *(-0.113 0.833)	-0.522 (-1.168 0.272)	-0.143 (-0.632 0.267)
6	1	0.951 -	1.300 -	0.071 -
5	17	0.678 (-0.737 1.402)	0.328 (-1.336 1.724)	0.049 (-0.715 0.904)
4	11	0.670 (0.076 1.649)	0.112 (-1.478 2.508)	-0.390 (-1.479 0.641)
3	12	0.145 (-2.143 1.395)	0.053 (-1.115 1.248)	-0.593 (-1.654 0.927)
2	3	-0.196 (-0.913 0.724)	0.757 (-0.073 1.777)	-0.274 (2.471 0.869)
1	4	-0.093 (-2.887 1.015)	0.996 (-0.344 1.981)	-0.136 (-0.248 0.142)

* Ranges displayed by the samples in R scores

The association of As-Mo-Fe-Cu exhibits the most enhanced levels in S.U.1 and 2, which correlates very well with the trace element data and also the factor score data for the other two sampling media.

7.8.4. Correlations between the R-mode factor solutions between bedrocks from the detailed study area and other areas

The regional reconnaissance drainage sediment data in the English Peak district yielded the R-mode factor association Cr-Ga-Ti-V-Fe, whilst the detailed study area drainage sediment and bedrock data yielded two sub-associations from this group namely, Cr-V and Ga-Ti-(Fe). To test whether the presence of these two sub-associations was merely a function of the bedrock geochemistry within the study area or whether it was more generally applicable, bedrocks from another area within the same region and within the same stratigraphic range were used. Composite shale samples collected by Fletcher (1968) from the Alport borehole, west of Sheffield, were used for this purpose. These shales were chemically analysed by the same techniques previously employed and the untransformed data was subjected to R-mode analysis. All oblique factor associations for the models between 10 and 2 factors were examined. The factor associations have been summarised in table 66. The factor associations are considerably more complex than for the bedrocks in the detailed study area. The reasons for this may be twofold:

(i) these rocks comprise only shales, thus variations in shale

Table 66.

Summary of the factor associations indicated by R-mode factor analysis of the untransformed geochemical data from the composite shale samples from the Alport borehole, west of Sheffield.

Factor Models	Factors 1	2	3	4	5
10	Ga,Fe,Ti (Co,Mo) ≠	Zn [Cr,Ti] *	As,Ni (Cr, Ga)	Mn,Mo,Ni,Co (Fe)	Ag,Cr
9	Ga,Fe,Ti (Co, Mo) / [Zn]	Zn [Ti,Cr,(Pb)]	As,Ni (Cr,Ga)	Mn,Mo,Co,Ni (Fe)	Ag,Cr [(Mn,Pb)]
8	Ga,Fe,Ti (Co,Mo) / [(Zn)]	Cr,Ti(Pb) / [(Zn)]	As,Ni (Cr,Ga)	Mn,Mo,Co,Ni (Fe)	Ag(Cr) / [(Pb,Mn)]
7	Ti,Ga,Fe Cr / [Zn]	V,Cr,Pb (Ni,Cu) / [Ga,Zn,Fe]	As,Ni (Ga,Cr)	Mo,Mn,Co,Ni Fe	Ag,Cr / Ga,Pb,Mn
6	Ti,Ga,Fe, Pb,(Cr,Co,Cu) / [Zn]	V,Cr,Pb (Ni) / [Zn(Fe,Ga)]	Ni,As,Mo Co,Cr,Ga, Fe,Cu,Pb)	Mn,Mo(Co, Fe / [As (Pb)]	Ag,Cr [Pb,(Co)]
5	Ti,Fe,Ga Cu,Co / [Zn,(V)]	Cr,V,Pb,Ti (Ni) / [Zn]	As,Ni,Co Mo,Cu,Ga Cr (Zn)	Mn,Mo,Co,Ni Fe / [(As,Pb)]	Ag,Cr [Pb (Ga,Co Ti,V)]
4	Ti,Ga,Fe Pb,Co,Cu / [Ag,Zn]	Cr,V,Pb,Ti (Ni) / [Zn]	As,Ni,Cu Co,Mo,Ga Fe,Cr / [(V)]	Mn,Mo,Co,Ni Fe / [(As,Pb)]	
3	As,Ni,Co,Mo Cu,Ga,Fe Cr / [(V)]	V,Pb,Cr,Ti / [Zn(Ag,Mn)]	Fe,Mn, Ti,Ga,Co,Mo / [Ag,Cr,As,Zn]		
2	Co,Fe,Mo Ga,Ni,Cu,As Ti,Mn / [V,Ag]	Pb,Ti,V,Cr / [Zn,Ag(As)]			

6	7	8	9	10
Cu,Co	Pb(Cr)	V(Cr)	(Ti) / [(Fe)]	Mo(Co)
Cu,Co	Pb(Co) / [(Mn)]	V,Cr	(Mo,Ti) / [Fe]	
Cu,Co	Pb(Co,Cr,Mo) / [(Mn,Ag)]	V(Cr)		
Cu,Co Fe Ga	Pb(Co) / [Mn]			
Cu,As Co Fe / [Pb]				

LEGEND

≠ ( ) indicate factor loading between /0.200/ and /0.299/.

* ____ indicates negative correlation with the dominant association over the dash.

mineralogy will be the main cause of trace element concentration variations rather than the presence of predominant argillaceous or arenaceous minerals.

(ii) these rocks sampled from borehole coreshave not been subjected to surface weathering and thus the mobile elements would be expected to recombine into different associations.

The main feature of interest is the presence in the 8, 9 and 10 factor models of relatively simple associations essentially comprising Ga-Fe-Ti and V-Cr. The presence of these associations in a sample set comprised wholly of shales both confirms the general validity of these associations and also lends credence to the hypothesis that these associations are controlled by individual mineral phases present in variable concentrations in these argillaceous bedrocks.

Another feature of interest is the presence in all models between 4 and 10 factors of the association Mn-Mo-Ni-Co-Fe. It is not expected that these rocks have been subjected to supergene leaching effects, other than those caused by borehole drilling, which are assumed to be insignificant, therefore it must be presumed that this association represents some feature of the primary shale mineralogy.

7.8.5. <u>The mineralogical controls of the trace elements Cr,Fe,Ga, Ti and V.</u>

The Alport shale samples were further employed to

establish the mineralogical controls of the Ga-Fe-Ti and V-Cr associations. These rocks were used in preference to those from the detailed study area because they were fresh and thus the primary mineralogy was presumably unaltered by weathering processes.

The composite shale samples from the Alport borehole were subjected to mineralogical analysis by infra-red spectroscopy This method was employed because it is rapid, though only semi-quantitative, compared to X-ray diffraction techniques.

The technique of infra-red spectroscopy involves the measurement of the absorbance by materials of electromagnetic radiation in the infrared region of the spectrum.

Molecular vibrations cause the periodic displacement of atoms with respect to each other. The consequent variation in the interatomic distances will, when combined with changing dipole moments, lead to absorbance of infra-red radiation.

The analysis relies on the absorption of characteristic ranges of infra-red radiation by particular atomic groups in different mineral phases. The absorbance is recorded on continuous chart recording equipment. The results are presented as a series of graphically recorded peaks, each of which corresponds to the absorption of one band of infra-red radiation. Certain of the peaks have been identified as caused by the molecular vibrations of Si-O and C-O pairs in the chemical phases SiO_2 and CO_3^{2-} (Chester and

Green, 1968; Chester and Elderfield, 1967).

It is possible to convert the peak heights recorded on the charts into percentage composition of these phases employing the "baseline" method used by Chester (op.cit) and applying Beer's Law. The procedure adopted was to measure the height of the base (T_B) and apex (T_P) of the SiO_2 and CO_3 peaks. The absorbance due to the individual chemical phases is then given by the relationship

$$A = \log_{10} T_B - \log_{10} T_P = abc$$

where A is the absorbance.

a, the absorbtivity } both constant
b, the path length }
c, the concentration

The absorbance is then used to read off the percentage concentration of the chemical phases using standard concentration curves. The standard concentration curves used for SiO_2 were those published by Chester and Green (op.cit) and Chester and Elderfield (op.cit.); the curve for CO_3^{2-} was drawn using data supplied by Elderfield (pers.comm.).

The infrared analyses were used to establish the quartz and carbonate contents of the shale samples. It was assumed that the shales were composed of three mineralogical phases, clay minerals, quartz and carbonate, that is,

Quartz + Clay minerals + Carbonate minerals = 100%

Employing this relationship, and the percentages of quartz and carbonate determined by analysis of the samples, it was possible to

calculate the percentage of clay minerals.

The mineralogical data was combined with the trace element data and subjected to R-mode analysis, the data was run both with and without a prior log-transformation. The results of all oblique factor solutions for the untransformed and log-transformed data between 10 and 2 factor models have been summarised in tables 67 and 68 respectively.

The results of both R-mode analyses reveal an association in the 10 factor model and all lower factor models between the elements Cr, Fe, Ga and Ti and the clay minerals. This is most clearly shown in the R-mode analysis of the untransformed data in which the association Clay-Ti-Fe-Ga-Cr is shown to be antipathetically related to the association Zn-Carbonate. This antipathetic relationship is not shown by the log-transformed data. The negative correlation between Ti-Ga and carbonate, which is exhibited to a lesser extent by Cr-V, had already been shown qualitatively in section 7.8.3. The results of the R-mode analysis upon the untransformed data also yields an independent V-Cr association, for instance, in factor 7 in the 9 and 10 factor models. Lower models, for instance, the 7 and 8 factor models exhibit the association V-Cr-Ti as being antipathetically related to clay minerals.

It is considered that these results indicate that the concentration of the elements Cr, Fe, Ga and Ti are predominantly

Table 67.

Summary of the factor associations indicated by R-mode factor analysis of the untransformed geochemical and mineralogical data from the composite shale samples from the Alport borehole, west of Sheffield.

Factor Models	Factors 1	2	3	4	5	6	7	8	9	10
10	Zn,CO_3 * Clay, Ti,Fe Ga,Cr.	Qtz(Cr) / Fe,Clay Ga	As,Ni,Cr,Ga	Mo,Mn,Co,Ni Fe	Ag(Cr) ≠ Mn,Pb	Cu,Co	V,Cr	Pb / Mn	Ga / Mn	Fe / Cr
9	Zn,CO_3 Clay,Ti,Fe Ga,Cr	Qtz,Cr / Fe,Clay, Ga	As,Ni,Cr,Ga	Mo,Mn,Ni,Co Fe	Ag,Cr / Pb,Mn	Cu,Co	V,Cr	Pb / Mn	Ga,Ti / Mn	
8	Zn,CO_3 Ti,Clay,Fe Ga,Cr(Cu)	Qtz,Cr / Ga,Fe, Clay (Ti)	As,Ni,(Cr,Ga Cu)	Mo,Mn,Ni,Co Fe	Ag,Cr / Mn,Pb	Cu,Co Clay	V,Cr,Ti / (Clay,As)	Pb,Co / Mn		
7	CO_3,Zn Clay,Ti,Fe, Ga,Cr(Cu,Pb,Co)	Qtz,Cr,Pb (V,Ag) / Ga,Fe, CO_3(Clay,Zn)	Ni,As,Mo,Co Cr,Ga,Fe Ca	Mn,Mo,Co, Fe / As,Pb	Ag Pb,Co,Ti	Cu (Co,As)	V,Cr(Ti) / (Clay, Zn)			
6	CO_3,Zn Clay,Ti,Fe Ga,Cu,Cr (Co,Pb)	V,Qtz,Cr, Pb(Ni) / Zn,Ga,Fe (Clay)	Ni,As,Mo,Co Cr,Ga,Cu Fe	Mn,Mo(Co, Fe) / As(Pb)	Ag Pb,Ti,V, Ga,(Co)	Cu,V (Pb,Qtz)				
5	CO_3,Zn Clay,Ti,Fe Ga,Cu,Co(Cr)	Qtz,Cr,V, Pb(Ni,Ti) / Zn,Fe, (Clay CO_3)	As,Ni,Co,Mo Ga,Cr,Fe	Mn,Mo,Co,Ni Fe / As,Pb	Pb,V,Ti Ga(Co) / Ag					
4	Ti,Clay,Ga Fe,Pb,Co,Cu Zn,Ag,CO_3,Qtz	Cr,Qtz,Pb,V CO_3,Ti(Ni) / Zn(Fe)	As,Ni,Co,Mo Cu,Cr,Ga, Fe	Mn,Mo,Co (Fe,Clay Ni) / As,CO_3,Pb						
3	Clay,Ti,Fe Ga,Co,Mn,Cu, Mo,(Pb)	Cr,Qtz,V, Pb,Ti(Ni) / Zn,CO_3 (Fe)	Ni,As,Mo,Co Cu,Cr,Ga, Fe							
2	Fe,Co,Ga Clay,Mo,Cu,Ti Ni,As,Mn / CO_3,Qtz,Ag,Zn(V)	Cr,V,Qtz,Pb Ti / Zn,CO_3(As)								

LEGEND

* ___ Antipathetic relationship between two associations. Dominant association on top of dash.

≠ ( ) Brackets indicate factor loadings between /0.200/ and /0.299/.

Table 68.

Summary of the factor associations indicated by R-mode factor analysis of the log-transformed geochemical and mineralogical data from the composite shale samples from the Alport borehole, west of Sheffield.

Factor Models	Factors 1	2	3	4	5	6	7	8	9	10
10	As,Ni,Mo,Co,Cu Ga,Fe,Cr,Ti (Clay)*	Qtz,V,Cr(Ti)≠ Fe(Ga)	Mn(Fe) Pb(As)	Ag Pb(Co)	CO_3,Zn Clay,Co,Ti,Co (Cr,Fe,Pb,Mo)	Pb,Mo Cu,As	V,Cu	Zn	Ga,Ti	(Cr)
9	As,Ni,Mo,Co,Cu Ga,Cr,Fe,Ti (Clay, Pb)	Qtz,V,Cr(Ti Pb) Fe,(Ga)	Mn(Fe,Mo) Pb(As)	Ag Pb(Co)	CO_3,Zn Clay,Ti,Cu, Co,(Cr,Fe, Pb,Mo)	Pb,Mo Cu,(As)	V,Cu	Zn	Ga,Ti	
8	As,Ni,Mo,Cu,Co Ga,Cr,Fe,Ti Clay, Pb	Qtz,V,Cr(Ni Pb) Fe,Ga	Mn(Fe,Mo) Pb(As)	Ag Pb,(Co)	CO_3,Zn Clay,Ti (Cu,Co,Cr Fe)	Pb,Mo As(Cu)	V,Cu	Zn Ti(Cr,Ga,V)		
7	As,Ni,Mo,Cu,Co Ga,Fe,Cr,Ti (Clay)	Qtz,V,Cr,Ni Pb,Ti,Mo Fe(Ga,Zn,Mo)	Mn,(Fe,Mo) Pb(As)	Ag Pb(Ga,Co,Ti)	CO_3,ZN(As) Clay,Ti Fe,Cr,Mo, Pb,Ga(Co,Cu)	Zn,(Mo) (Ti)	V,Cu			
6	As,Ni,Cu,Mo,Co Ga,Fe,Cr,Ti Clay (Pb)	Qtz,V,Cr(Pb,Ti) Fe,Ga(Zn, Clay)	Mn(Fe,Mo) Pb,As	Ag Pb(Ga,Ti)	CO_3Zn(As) Clay,Ti,Cr Fe,Ga (Pb,Cu)	Zn,(Mo,Pb) (V,Cu)				
5	As,Ni,Mo,Co,Cu Ga,Fe,Cr,Ti Clay(Pb)	Qtz,V,Cr,Pb,Ni (Ti,Mo) Fe,Ga(As,Zn)	Mn(Fe,Mo) As,Pb	Ag(Co) Pb,Ga(V,Ti)	CO_3Zn(As) Clay,Ti,Cr Fe,(Ga,Pb, Cu)					
4	As,Ni,Cu,Mo,Co Ga,Fe,Cr,Ti, Clay,Pb (CO_3)	V,Qtz,Cr,Pb,Ti Ni Zn,CO_3,Fe_2O_3, As	Mn,Clay,Fe Mo(Cu,Co) CO_3,As,Zn (Pb)	Ag,Zn(Qtz) Pb,Ga (Ti,Co)						
3	As,Ni,Co,Cu,Ga Mo,Fe,Cr,Ti Clay,Pb (Qtz)	V=Qtz,Cr,Pb,Ti Ni,Mo,Cu Zn,CO_3(As,Fe)	Mn,Clay,Fe Ti,Ga,Co(Mo,Cu) CO_3,Zn,Ag,As, Qtz							
2	Fe,Ga,Co,Clay, Mo,Cu,Ni,As,Ti Mn,Cr Qtz,CO_3,Ag	V,Cr,Qtz,Pb,Ti Ni,Mo,Cu,Co (Clay) Zn,CO_3								

LEGEND

* ( ) Brackets enclose variables with factor loadings between /0.200/ and /0.299/.

≠ ___ Antipathetic associations within the same factor. The dominant association is placed over the horizontal bar.

controlled by the clay content of the material. However, the results also indicate that V, and to a lesser extent Cr and Ti, are also controlled by other causative agencies, possibly some other mineral phase.

It may be postulated that these correlations revealed by the R-mode analysis are due to analytical bias induced by the clay mineral content of these samples, such that high clay concentrations induced higher levels of Cr, Fe, Ga and Ti; or conversely high carbonate levels depressed these concentrations. This hypothesis was tested by employing R-mode analysis upon comparable published data employing a different spectrographic analytical technique.

The monograph by J.R. Moore (1968) includes published analyses of 21 Cambrian and Ordovician shales and sandstones taken from the I.G.S. collection of Welsh reference rocks. The analyses included minerals X-ray), major and mino- elements (spectrography), a list of those components analysed is given below (see table 69).

The analytical data for all these variables were subjected to R-mode analysis without prior transformation of the data. The 9 factor model has been chosen because it demonstrates the relationship between Cr, Fe, Ga, Ti, V and the mineralogy most strongly. The factor 1 association is summarised in table 70.

Table 69 The elements and minerals for which the Welsh reference rocks had been analysed

Minerals	Calcite, chlorite, dolomite, mica, orthoclase, plagioclase, quartz
Majors	Al, Ca, Fe, Mg, Na, K
Minors	B, Ba, Co, Cr, Cu, Ga, Mn, Ni, Pb, Sc, Sr, Ti, V, Zr.

Table 70 Summary of the factor 1 association from the 9 factor model derived by R-mode analysis of the geochemical and mineralogical data of the Welsh reference rocks

Minerals		Minor and Major elements	
+ve	-ve	+ve	-ve
chlorite	plagioclase	V, Cr, Ti, Fe, B, Mg, Ni	Zr, Na
mica	quartz	Cu, Ga, Sc, Sr, Co, K	
	orthoclase		

Those minerals and elements of similar sign are positively associated, whilst those of opposite sign are negatively correlated. This reveals that the elements Cr, Fe, Ga, Ti and V are associated with the minerals chlorite and mica, both common mineralogical constituents of argillaceous sedimentary rocks.

Thus it may be concluded that where the elements Cr, Fe, Ga, Ti and V form an association this is indicative of the argillaceous content of sedimentary bedrocks. Moreover, the association is not coherent since it frequently subdivides into two sub-associations Fe-Ga-Ti and Cr-V. It is postulated that each of these sub-associations is related to different mineralogical components common in argillaceous sedimentary rocks.

7.9.0. DISCUSSION

7.9.1. The relevance of the argillaceous trace element association to the geology of the detailed study area

It has been established that within the sedimentary bedrocks of the Onecote area a number of trace element associations indicate different mineral phases. Thus:-

(i) As-Mo-Fe-Cu indicates mineralogical phases common in black marine shales and also carbonate rich shales.

(ii) Ti-Ga and to a lesser extent Cr and Fe represent the clay mineral content within these rocks.

(iii) Cr-V and to a lesser extent Ti indicate the presence of a mineral phase as yet unidentified but common in argillaceous rocks.

These associations are most enhanced within the shale bedrock samples in different stratigraphic units (S.U.). Thus As-Mo-Fe-Cu are highest in S.U.1 and 2, Cr-V are highest in S.U.3 and 4 and Ti-Ga is highest in S.U.4, 5 and 6. This indicates a progressive change in the mineralogy of these shales from the basal shales deposited in a basin in which a restricted circulation led to the establishment of reducing conditions (Fletcher, 1968) up to the predominantly unfossiliferous, and thus presumably non-marine, shales of S.U.6 and 7-11 (Holdsworth, pers.comm. 1968).

The change in the levels of the Ti-Ga association in the sandstones of different stratigraphic units in the detailed study area are indicative of a progressive increase of the argillaceous content of this facies. This correlates with the change from the very arenaceous protoquartzites and calcareous siltstones of units 2,3,4 and 5 to the more argillaceous deltaic sandstones of units 6 and 7-11. It is in the last two units that the sandstones bear the highest levels of the association Ti-Ga.

The drainage sediment and soil sample data both indicated the presence of associations including Cr,Fe,Ga,Ti and V. However, the soil data yielded the association as Ti-Ga-Cr-V (factor

3, 5 factor model) whilst the drainage sediment data indicated the presence of two associations namely, Cr-V-Mo (factor 3, 6 factor model) and Ti-Fe-Ga (factor 5, 6 factor model). The drainage sediment data thus yielded a closer approximation to the bedrock trace element associations than did the soil data.

7.9.2. The relevance of the argillaceous trace element association to the geology of the regional reconnaissance survey areas.

The association Cr-Fe-Ga-Ti-V was indicated by R-mode analysis of the regional geochemical reconnaissance data in both the English Peak district and N. Wales areas.

The English Peak district exhibited generally higher factor scores for this association over the sedimentary strata of lower Namurian, Westphalian and Keuper ages; whilst lower scores generally occured over strata of upper Namurian and Bunter ages. This agrees quite well with the stratigraphic position of the main arenaceous phases of sedimentation during the Carboniferous and Permo-Triassic periods. The remaining sedimentary rocks represent either periods of dominantly argillaceous (lower Namurian and Keuper) or cyclic (Westphalian) sedimentation.

The N. Wales area exhibits a distribution of factor scores on this association which indicate a sudden lowering of these scores over the Carboniferous and later sediments. It has not been

established whether this is due solely to a change in the mineralogy of these sedimentary rocks or whether the exotic glacial drift cloaking appreciable areas of the Westphalian and Permo-Triassic is also an important contributory factor. Certainly, the carbonate-rich Dinantian sediments would not be expected to contain high concentrations of the elements of this association, if the antipathetic relationship between them in the detailed study area also exists in this area.

The regional geochemical data from S.W. England yielded an R-mode factor association, which, though similar to those indicated in the other survey areas, was also significantly modified. The mean differences were the inclusion of Ni (inter alia) and the exclusion of Ga from the factor association. It was considered that the regional patterns indicated that this association represented both the occurrence of basic igneous rocks and also facies changes in the sedimentary bedrocks. The distribution of this association over the Namurian strata indicated a facies variation, with more arenaceous bedrock outcropping in the west than in the centre and east of the survey area This conclusion has some support from recent mapping in this area (Moore, pers.comm., 1969).

7.10.0. SUMMARY AND CONCLUSIONS

7.10.1. Summary

(i) A detailed investigation was made of the geochemistry of a small area in the Onecote district of NE.Staffordshire on the western flanks of the Derbyshire dome.

(ii) The investigation included the geochemical analysis of drainage sediments, soils, and associated bedrock samples.

(iii) The analytical data relating to each sampling medium was subjected to R-mode factor analysis, with the following results:

(a) the association As-Cu-Fe-Mo was confirmed in all three media. It has been shown that in this area these elements are controlled by the sub-outcropping of black marine shales (Fletcher, 1968)

(b) the association Co-Fe-Mn-Ni-Zn was indicated in slightly modified forms in the drainage sediment, soil and bedrock data. It was confirmed by the results obtained on the soils and bedrocks that these were elements mobile in the secondary environment, and were thus only partially related to the primary mineralogy of the sampled material.

(c) the association Cr-Fe-Ga-Ti-V was indicated in the soil data but within the drainage sediment and bedrock data it was split into essentially two associations, namely Cr-V and Ga-Ti with Fe.

(iv) the trace element data and the factor scores indicated that the elements Cr, Fe, Ga, Ti and V were apparently largely controlled by the argillaceous content of the bedrocks. It was also evident that the elements Ga and Ti were concentrated antipathetically with respect to the bedrock carbonate content.

(v) R-mode analysis of the trace element concentrations of stratigraphically equivalent shales from the Alport borehole, west of Sheffield, confirmed within this data the presence of the associations Ga-Fe-Ti and also Cr-V (8, 9, and 10 factor models, table 66).

(vi) Mineralogical analysis of the Alport borehole shales and consequent R-mode analysis of the combined mineralogical and trace element data revealed the presence of the associations, Cr-Fe-Ga-Ti-Clay minerals and V-Cr with Ti.

(vii) Published mineralogical and chemical data of Ordovician sandstones and shales were subjected to R-mode analysis, which indicated an association between mica, chlorite and the elements Cr, Fe, Ga, Ti and V (inter alia).

(viii) the results from the Onecote drainage sediments and

bedrocks and the Alport borehole were interpreted as indicating that two associations of essentially Cr-V and Fe-Ga-Ti both represented distinct mineralogical phases common in argillaceous sedimentary rocks.

(ix) the enhancement of the association, As-Mo-Fe-Cu over the black marine shales and limestones of S.U.1 and 2 in the detailed study area, the similar enhancement of Cr-V over the shales-mudstones, calcareous siltstones and protoquartzites of S.U.3 and 4, and that of Ti-Ga over the shales-mudstones and protoquartzites of S.U.4.5 and 6 was interpreted as indicating a change in the mineralogy of the sedimentary facies, and notably the shales, in this basin of deposition between upper Viséan and middle Namurian times.

(x) The enhancement of the Ti-Ga association in the sandstones of S.U.6 and 7-11 was interpreted as representing an increase in the clay content of these arenaceous sediments with the onset of deltaic conditions in mid-Namurian times.

(xi) The regional reconnaissance areal patterns for the factor scores of the associations, Cr-Fe-Ga-Ti-V, were shown to be enhanced in the English Peak District and

in N. Wales over the more argillaceous sedimentary rocks.

(x) The regional patterns of a similar association in S.W. England indicated a facies change from argillaceous to arenaceous in the western outcrop of the Namurian strata.

7.10.2. CONCLUSIONS

(i) The association Cr-Fe-Ga-Ti-V indicated by R-mode analysis of the regional reconnaissance survey data has been shown to be geologically valid and not a mere mathematical abstraction.

(ii) The association has been shown to be composed of two parts Cr-V and Fe-Ga-Ti.

(iii) It is considered that each of the sub-associations is related to a distinct mineralogical phase common in argillaceous sedimentary rocks.

(iv) Thus R-mode factor analysis of the regional reconnaissance geochemical survey data has revealed a previously unrecognised association.

(v) The identification of this association may allow the results of regional geochemical surveys to be used to establish the relative argillaceous status of major sedimentary units within the survey area.

SUMMARY, CONCLUSIONS AND FUTURE RESEARCH

8.1.0. SUMMARY

8.1.1. Previous work in Regional Geochemistry.

Regional geochemical surveys based on the analysis of drainage sediment samples in tropical and temperate climatic regions have given trace element data which exhibited areal dispersion patterns frequently related to the underlying bedrock lithology.

An examination of the interaction of bedrock lithology, mineralisation, secondary environmental variations, and human contamination, especially that caused by mining and metallurgical activities, upon regional multielement data based on drainage sediments was initiated in the U.K. Three areas in S.W.England, N. Wales and the English Peak District, totalling 2700 square miles, were sampled at an average density of 1 sample per square mile. The analytical results were investigated and interpreted by conventional techniques and a number of trace element associations were identified together with their dominant controls. The most important of these were:

(i) Pb-Zn and to a lesser extent Cu, caused by contamination related to mining and metallurgical extraction and also by mineralisation in N.Wales, and the Peak District.

(ii) As-Mo-Cu-V, which are enhanced in areas underlain by black marine shales in the English Peak District.

(iii) Mn-Co-As-Fe-Ni-Zn are higher in stream channels draining poorly drained areas covered by acid soils. These elements

are leached from the soils and precipitated or coprecipitated from the ground waters, when they enter the drainage channels.

Applications of factor analytical techniques to multivariate geological and geochemical data have indicated the potentiality of these techniques as interpretative aids when dealing with complex data (Garrett, 1966). The technique of R-mode factor analysis can be used to resolve multivarariate data into a lesser number of factors, each comprised of a number of associated variables. The Q-mode technique expresses the similarity of the samples to end-members, which have extreme characteristics with respect to the measured variables.

8.1.2. Problem investigated.

Multielement regional geochemical surveys produce large volumes of data. The quantity of data poses considerable problems in its handling and manipulation in order that it may be interpreted.

8.1.3. Aim of investigation.

The purpose of this research was to examine the applicability of various computerised procedures for data handling and as interpretative aids in regional geochemical surveys.

8.1.4. The presentation of the data in map form.

A computer programme was written for the purpose of employing the Calcomp incremental digital plotter in order to compile scale maps bearing the numerical data for the individual trace

elements. This was found to be an efficient and, providing the computer time was available without charge, an economic method of quickly producing unsophisticated maps of the raw data.

Another, more sophisticated mode of presentation involved the representation of the trace element data in symbolic form. This was achieved by dividing the concentration range of the individual elements into a maximum of 5 classes. Each class was characterised by a coloured symbol (yellow, green, blue, small red, large red).

A computer programme was used to classify the data in terms of the concentration classes and to generate the appropriate plotting instructions for a Stromberg-Carlson 4020 computer recorder. The output was in the form of a number of hard-copy plates, eight inches square, bearing circular black symbols. Each plate represented those sample sites falling within one concentration class for a specific element. Thus the total data for each element was displayed on a minimum of four or five plates.

The photographic output was used in the production of off-set litho printing plates. Maps were then produced on an offset litho machine by over-printing the symbol plates onto base maps in different colours, appropriate to the concentration range. The final product included the base map information (black legend and frame, grey urban areas and drainage, sepia geology, blue National grid) as well as the trace element data (yellow, green, blue and red symbols).

The visual impact of these coloured maps was good and they allowed the correlation between trace element concentration and bedrock geology to be rapidly assessed.

8.1.5. Areal analysis of trace element data.

Two modes of areal analysis were employed, that involving the symbolic representation of the data, previously considered, and in addition, the moving average technique. The latter is a smoothing technique, which was used to reveal the underlying trends within the regional distributions of the trace element data. The computer programme employed for the analysis produces maps of the smoothed data values by use of the Calcomp incremental plotter. The resulting maps were subjectively contoured in order to bring out the correlation of the trace element patterns with the disposition of the major bedrock lithological units.

The technique provided results which were largely comparable to those from the symbol maps. The patterns were detailed but at the same time heightened the underlying trends. The major disadvantage of this technique is that the individual sample locations are lost during the analysis. The map output is however very flexible and can be used as an overlay with geological, pedological, climatic and topographic maps.

8.1.6. Comparison of factor analysis techniques.

An initial comparison of Q- and R-mode analyses was made upon three subsets of the N. Wales regional data, using the Manson-Imbrie computer programme. The results indicated that:

(i) R-mode solutions are simpler to interpret than the equivalent Q-mode solutions;

(ii) known trace element associations were clearly indicated in the R-mode, but were not in the Q-mode solutions.

(iii) the R-mode solutions for three subsets were usually closely comparable, whereas the Q-mode solutions were not.

It was concluded that R-mode was the more appropriate technique for the analysis of the regional multielement geochemical survey data.

The R-mode solutions for the unrotated orthogonal, rotated orthogonal and oblique non-orthogonal axes for three subsets were compared. The subset solutions were again evaluated with respect to the comparability of the factor associations both to each other and also to the known trace element associations. The rotated axis solutions were marginally preferable to those of the oblique axes, whilst these two were both markedly superior to the unrotated axis solution.

An extension to this study involved the comparison of the oblique solutions from the different procedures employed in the Manson-Imbrie (1964) and Garrett (1967) computer programmes. The results indicated that the Garrett programme yielded factor associations for the subsets which bore a marginally closer resemblance both to each other and to the known associations. It was decided on this basis to employ the oblique solutions from the Garrett programme when analysing the regional data.

8.1.7. <u>The application of R-mode factor analysis to the regional multielement data</u>.

The Garrett R-mode factor analysis programme was used for the

analysis of the regional multielement data. All oblique factor solutions for log-transformed and untransformed data were obtained for each of the three survey areas. A subjective choice of the best models was made and these are summarised below (see table 71). The factors include all those trace element associations already recognised in the data. However, in addition, the first factor for the N. Wales and Peak District data consists of a previously unrecognised association, Fe-Ga-Ti-V usually with Cr. A modified form of this association also appears in the S.W.England data.

The individual sample factor scores for the selected factor model were computed using the Garrett R-mode programme. The areal dispersion patterns were analysed by means of the moving average technique. The areal patterns indicated that the new trace element association might be related to the argillaceous content of the sedimentary rocks, since higher scores for this factor occurred over the more argillaceous bedrock units.

8.1.8. The evaluation of the trace element association, Cr-Fe-Ga-Ti-V.

A detailed study was made on the western flanks of the Derbyshire dome, in the Onecote area, N. E. Staffordshire. The geology of this area consists of Viséan and Namurian sedimentary rocks comprised of a rhythmic sequence of shales, sandstones and calcareous siltstones. The sedimentological sequence indicates an evolution from a marine basin with a restricted circulation and reducing conditions to a littoral basin in which deltaic sediments were deposited.

Drainage sediments, soils and bedrocks were sampled and chemically analysed. The analytical data were subjected to R-mode

Table 71

Summary of the subjectively chosen oblique factor models from the regional multielement survey data.

Factors	S.W.England	N. Wales		English Peak District
	log-transformed	log-transformed	untransformed	untransformed
1	Cr V,Ti,Ni, Cu,Zn(Fe).	V,Ga,Ti Cr,Fe,Ni, Cu,Co.	Ga,V,Ti,Fe (Ni).	Ti,Ga,Cr,V,Fe
2	Ga,Sn(Ti , Fe)	Zn,Pb,Cu	Ag,Pb,Zn	Pb,Zn
3	Co,Mn,Fe, Ni,(Zn).	Mn,As,Co, Fe.	Mn,Co,As, Fe,(Ni).	Co,Mn,Ni,Fe.
4	Mo,Cu,(Fe).	Sn,Cu.	Cr,Ni,Cu.	As,Cu,Mo,V,Ag, Fe,(Ni).
5	As,Sn,(Cu).	Mo,As.	Mo,Ag,Zn,Cu, Fe,(Ag).	Sn,Ag,(Cu).
6	Pb,Zn,Cu,(Sn).	Ag.	Sn.	———

factor analysis and the results indicated the existence of the association Cr-Fe-Ga-Ti-V in all three media, though it is split into two parts in the drainage sediment data and the bedrock data.

The factor score distribution for these factors indicated that the earlier sediments, possibly deposited in a basin characterised by reducing conditions, are enhanced in As-Cu-Mo-V (inter alia). The later sedimentary bedrocks, deposited prior to the onset of the deltaic stage, are characterised by higher levels of the Cr-Fe-Ga-Ti-V association.

Composite shale samples of equivalent age to those in the detailed study area, but taken from the Alport borehole, west of Sheffield, were subjected to chemical and mineralogical analysis. R-mode factor analysis of the chemical data revealed the trace element association Cr-Fe-Ga-Ti-V. When the mineralogical data was included for an R-mode factor analysis, the same trace elements were associated with the clay minerals. It was concluded that this trace element association was largely controlled by the clay content of these sedimentary rocks.

8.2.0. CONCLUSIONS

The evaluation of the computerised techniques considered in this study have indicated that:

(i) computerised data handling procedures for the purpose of compiling geochemical maps may allow considerable economies to be effected in terms of time and personnel usage.

(ii) analysis of the areal patterns displayed by the data can be

efficiently conducted, without employing a priori assumptions, by using the moving average technique.

(iii) R-mode factor analysis is a suitable technique for analysing multielement geochemical data, when the purpose is to define geochemical associations.

(iv) the correct application of the R-mode analysis to regional multielement geochemical data will define geochemically meaningful trace element associations.

(v) factor scores on geologically controlled trace element associations derived from drainage sediment geochemical data may be used to compile simplified lithological maps.

It can now be claimed that the application of appropriate computerised techniques may be used on multielement geochemical data to indicate features, which are not evident from detailed examination of the initial data. Thus it is advisable to apply computerised data handling, mathematical and statistical procedures as interpretative aids for complex multielement geochemical data.

8.3.0. FUTURE RESEARCH

8.3.1. Data handling and map production

The data used in this study were punched onto computer cards and these were used for the various computational procedures employed. When a very large number of samples have been subjected to multielement analysis, the quantity of data generated will be very large and unwieldy. The routine use of data on computer cards for computations will not be feasible, and it will be far easier to use the data written onto magnetic tapes, which can then be used for data processing

procedures. It is frequently necessary to classify the data in terms of the underlying bedrock either employing lithological or stratigraphic criteria. It is probable that as further controls acting upon the data are elucidated, so it will be necessary to record other relevant data together with that pertaining to the sample geochemistry. It would be advisable to code this information and to include it with the geochemical data for each sample on magnetic tape. The possible methods of data storage and retrieval have not yet been evaluated for this type of data and this will require some further work. The relevant features to be included with the geochemical data are not yet fully known and it will be necessary to revise and up-date the data set as this information becomes available. Appropriate programmes to revise the data must also be devised and written.

One use of the punched card data discussed in this study has been the compilation of geochemical maps. It is likely that improved methods of data display together with other necessary information will be devised both with respect to visual impact and to production efficiency, on a cost and time basis. Further work on this front is already being undertaken especially with the symbolic representation of geochemical data (Howarth, pers.comm.). Certain problems which have been defined in this study and discussed below will also require further work for their solution.

The production of Calcomp maps is limited by the number of data points which may be plotted onto the scale charts. The maximum number of data which can be plotted varies between 500 to 1000 depending on the type of data to be displayed (see the discussion in

chapter 3). The limiting factor is the length of the magnetic tape, which carries the data together with the plotting instructions, for the off-line use of the Calcomp plotter. Two methods by which this could be improved are by using:-

(i) larger magnetic tape reels.

(ii) the Calcomp plotter directly connected to the computer(on-line) rather than by carrying the instructions on magnetic tape.

The first option is very expensive since the magnetic tape deck on the machine has to be modified, an improvement which may cost approximately £30,000 (Mitchell pers.comm.). The second option may lower the efficiency of the computer, since the plotter operates at a much slower speed than that at which the data and plotting instructions can be generated. It is apparent, in order to avoid these two undesirable side-effects, that major improvements depend upon maximum conservation of the magnetic tape. An approach towards this solution has been made in this study by ordering the data from the most westerly to the most easterly. Further improvements are still necessary and one possible solution would be for the data to be plotted for those locations which are most closely adjacent. The computer would be used to calculate the data location with minimum distance to any starting point and would then compute the next nearest point, and so continue until all the points are plotted. An approach to this has already been made (Howarth pers. comm.), however whether this will yield a minimum distance of travel for the plotting pen with respect to the paper has not been ascertained. Ideally, it should be possible to programme the computer to calculate a number of plotting paths. It would then compare their efficiency with respect to the amount of dis-

tance the Calcomp pen will travel, relative to the chart paper. The final stage will then be to choose the best of these options in order to generate the instructions for plotting the data.

The use of the Stromberg-Carlsan(S-C) 4020 computer recorder indicated a number of problems which were mainly connected with:-

(i) inadequate flexibility in the scaling due to the small number of raster points (1024^2) comprising the cathode ray image and also small size (8 $inches^2$) of the image. One result of this was that the data from the larger areas (N.Wales and S. W. England) could not be generated onto a single image but had to be divided into two separate adjoining images.

(ii) colour inhomogeneity of the black symbols produced on the output, so that a central cruciform area was darker than the margins.

(iii) shrinkage and stretching effects caused by the wet development of the photographic paper output from the recorder.

The first problem can only be overcome by using a recorder with a larger cathode ray screen, comprised of a larger number of raster points. It may be possible to utilise the SC-4060 which includes both these characteristics to allow large areas to be completely plotted onto a single image.

The colour inhomogeneity of the black symbols relates in part to poor machine performance but also to the mode of constructing the 'circular' symbols. This last is achieved by aligning short vectors to form a polygonal black image which appears circular, due to blurring effects on the image. The use of this technique not only

gives rise to colour inhomogeneity, due to differences over the symbol area of the number of overlaid vectors, but also allows little flexibility in the choice of symbol size. The solution to this rests in the development of computer programmes (soft-ware), which generate the plotting instructions in order to produce circular symbols of variable size. Further work requires to be performed on choosing the optimum symbol size, since those used in this study are rather too large. It is necessary to balance the decrease in size, allowing closely adposed points to be clearly perceived, against the decrease in visual impact caused by the use of smaller symbols.

8.3.2. Areal analysis.

The two methods of analysing the trace element data in order to illustrate areal trends over the surveyed region are to either use symbols, representing classes of trace element concentrations, or to contour the data. Problems arising from the first mode have already been considered, but those related to data contouring will now be discussed.

Automatic computerised contouring of data has already been achieved for data distributed over a regular grid. Inhomogeneously distributed data can also be contoured but only after a prior analysis employing polynomials or related mathematical models to approximate the data distribution and then to generate values on a regular grid about which the contours are fitted. The use of such techniques places certain constraints upon the data, which have been discussed in chapter 4, often leading to an oversimplification of the areal

trends. It would be a valuable piece of research to devise an automatic contouring programme which could be used to objectively contour irregularly spaced data. These contour maps could then be compared with those compiled by subjective, conventional methods in order to examine the validity of the interpretations based on the latter.

The use in this study of the moving average technique as a method of areal analysis revealed a small number of features which require further investigation.

The S.W.England data included several previously unrecognised features:-

(i) slightly enhanced levels for the elements As,Co,Cu,Fe, Mn, Mo,Ni,Pb,Sn,Ti and Zn over the Sticklepath fault. This feature may possibly be due to lithological bedrock types associated with the fault;

(ii) low Cr levels along the Namurian - Westphalian junction may also be lithologically controlled;

(iii) enhanced levels of Ag and also Ga are observed over the granites.

All these features could be examined by means of soil sampling along traverses which extend from background control areas across the anomalous area. The soil samples, together with bedrock samples from the available exposures, along the traverse lines should be analysed in order to determine whether these geochemical effects are controlled by the bedrock geochemistry.

The N. Wales data indicated the following features:

(i) enhanced levels of Ga over the areas underlain by lower Palaeozoic compared to upper Palaeozoic strata;

(ii) enhanced levels of Ag and Mo over the Halkyn-Minera mineralised zone.

The first feature might be tested by analysis of representative soil the bedrock samples collected along traverses across the lower and upper Palaeozoic junction. The second feature may be associated with the Pb-Zn mineralisation or with the contamination derived from the slag and mine-waste produced by previous mining and smelting of these ores. Analysis of samples from mine tips and slags derived from smelters could be analysed to indicate whether these elements are enhanced compared to representative soil samples taken in traverses across areas underlain by unmineralised Silesian strata. Another possible explanation is that the Namurian strataare themselves marginally enriched in Mo compared to the Westphalian and Permo-Triassic bedrocks. The occurrence of similar enhancements in the Namurian and older strata in the other two survey areas lends some credibility to the hypothesis.

The English Peak District region indicated a regional distribution for Ga, which exhibited lower levels over the Triassic, south of the Derbyshire dome. It would be possible to examine whether this was controlled by the subcropping bedrock lithology by the collection of soil and bedrock samples along traverses across from those areas underlain by Carboniferous to those underlain by Triassic strata.

8.3.3. R-mode factor analysis.

The results of this study have indicated that R-mode factor analysis can be used to extract geologically meaningful associations from complex multielement geochemical data. The interpretation of the results relies on the field and laboratory assessment of the meaningfulness of the factor associations in terms of the environment from which the samples were taken, or whether they represent mathematical abstractions based on correlations induced by analytical bias inherent in the data. When a large number of factor associations have been identified with the geochemistry of specific bedrock lithologies, it should be possible to compile simplified geological maps from regional multielement geochemical survey data.

The technique of R-mode analysis may be used for all arrays of quantitive or semi-quantitative numerical data in order to determine the associated variables. The modern techniques of mineral exploration frequently involve the collection of geochemical data, usually related to a few elements of commercial significance, together with data derived from a number of geophysical techniques. It may well be practicable to apply R-mode factor analysis to mixed geochemical and geophysical data in order to determine areas of maximum mineralisation potential. Such an approach might be calibrated over a known ore deposit in comparison with a barren area in order to determine a characteristic mineralisation association of geochemical and geophysical variables. This knowledge might

then be used to interpret the R-mode analysis results from over prospect areas.

The relevance of this technique to future mineral exploration surveys probably rests on its potential ability to distinguish associated chemical and physical (sensu lato) properties of mineralised areas from combined geochemical, geophysical, and geological data. Mineral exploration has for some time relied on airborne reconnaissance surveys, particularly for geophysical data. Research has been initiated in order to semi-continuously analyse the air above the ground for the most volatile elements associated with sulphide ore deposits, notably mercury (Barringer, pers.comm). Such surveys will be conducted initially from low flying aircraft, which will at the same time collect a whole array of geophysical data. Further advances await the invention of new instrumentation capable of recording a whole array of chemical and physical characteristics of the surface of the earth. Eventually such instruments may be mounted on satellites revolving round the earth. The volume of data will be enormous and the large number of variables will pose a considerable interpretative problem. It should be possible by subjecting to R-mode analysis, those data arrays from over known barren areas and also from those which surround economic ore deposits of a specific type, to determine which associated variables are indicative of a particular type of ore deposit. Such information can then be used to locate areas which yield chemical and physical responses appropriate to mineralisation.

These areas may be surveyed by conventional air-borne techniques in order to locate the areas of highest potential. The final exploration stage may then be constituted by ground geological, geochemical,and geophysical surveys in order to locate the mineralised zones.

The utility of the technique as an aid to geological mapping from geochemical data has already been outlined. However, there seems no reason why whole arrays of chemical and physical measurements, possibly gained from satellites, could not be used for this purpose. Thus features or associations from known bedrock types might be extrapolated to lesser known areas, particularly those covered by thick overburden. Another possibility is that it might be possible to construct a geological map of the moon by extrapollating terrestrial satellite chemical and physical associations from specific bedrock types to these associations yielded by R-mode analysis of lunar satellite data.

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A P P E N D I X 1

```
C     PROGRAMME PLOTCC (INPUT=TAPE 5,OUTPUT=TAPE 6,CALCOMP TAPE=A8)
C     PLOTCC
C     TITLE-
C        EXECUTIVE PROGRAMME FOR PRODUCING SINGLE VARIABLE MAPS ON THE
C        CALCOMP PLOTTER
C     KEY WORDS
C        COMPUTER GRAPHICS
C     LANGUAGE,COMPUTER,DATE
C        FORTRAN IV IBM026 48 CHAR SET,IMPERIAL COLLEGE IBM 7094,JUN1969
C     AUTHOR-
C        J,KHALEELEE,APPLIED GEOCHEMISTRY RESEARCH GROUP,IMPERIAL COLL
C     PURPOSE
C        THE DATA CONSISTS OF A DEPENDANT VARIABLE AT A NUMBER OF
C        IRREGULARLY SPACED SAMPLE LOCATIONS REFERENCED BY MEANS OF A
C        TWO DIMENSIONAL CARTESIAN FRAME,THE DATA POINTS FALLING WITHIN
C        THE BOUNDS OF A PREDETERMINED MAP AREA ARE REPRESENTED BY THEIR
C        NUMERICAL VALUES ROUNDED OFF TO A PREDETERMINED NUMBER OF
C        SIGNIFICANT FIGURES,THE DATA ARE PLOTTED TOGETHER WITH TITLE
C        INFORMATION ON CALCOMP CHARTS,MAXIMUM HEIGHT(Y-AXIS) OF 29.50
C        INCHES AND UNLIMITED LENGTH(X-AXIS) UP TO 120 FEET.
C     DATA SET UP-
C        FOR EACH SET OF DATA TO BE MAPPED,THE FOLLOWING DATA MUST BE
C        GIVEN
C        FIRST CARD-
C             COL 1-6,INTEGER NUMBER OF DECKS TO BE PROCESSED
C        SECOND CARD-
C             7 VARIABLES WITH F6.1 FORMAT,THAT IS,7F6.1
C             VARIABLE 1-XORIJN OF CALCOMP CHART
C             VARIABLE 2-YORIJN OF CALCOMP CHART
C             VARIABLE 3-OPTION FOR PERCENTAGE RANGE TRANSFORMATION
C                        1 TO EXERCISE,0 OR BLANK NOT TO
C             VARIABLE 4-MINIMUM DATA VALUE FOR PERC RANGE TRANSFORM
C             VARIABLE 5-MAXIMUM DATA VALUE FOR PERC RANGE TRANSFORM
C             VARIABLE 6-RECIPROCAL VALUE TRANSFORM OPTION(1 YES,0 NO)
C             VARIABLE 7-STANDARD VALUE TRANSFORM OPTION (1=YES,0=NO).
C        THIRD CARD-
C             13A6 FORMAT-VARIABLE FORMAT CARD-FMT
C        DATA DECK-
C             INTEGER DATA NUMBER,REAL X- Y- COORDINATES,REAL DATA VALUE
C        LAST CARD-
C             9999 IN THE FIELD RESERVED FOR DATA NUMBER
C        FOURTH CARD-
C             13 CONTROL VARIABLES FOR CALCOMP PLOTTING
C             FORMAT(8F6.2,2I6,2F6.1,F6.2)
C             VARIABLE 1-X-AXIS LENGTH IN INCHES(AXISE),
C             VARIABLE 2,Y-AXIS LENGTH IN INCHES(AXISN),
C             VARIABLE 3,MINIMUM X-COORDINATE VALUE(XMIN),
```

```
C               VARIABLE 4,X-COORDINATE INCREMENT OVER 1 INCH OF X-AXIS.
C               (XINT)
C               VARIABLE 5,MINIMUM Y-COORDINATE VALUE(YMIN).
C               VARIABLE 6,Y-COORDINATE INCREMENT OVER 1 INCH OF Y-AXIS
C               (YINT)
C               VARIABLE 7,SIZE OF TITLE CHARACTERS(SIZET).
C               VARIABLE 8,SIZE OF NUMERICAL CHARACTERS(SIZEN).
C               VARIABLE 9,NUMBER OF TITLE CHARACTERS(INCL BLANKS)- NUMLET
C               VARIABLE 10,NUMBER OF DECIMAL PLACES(NUMDEC).
C               VARIABLE 11,X-COORDINATE(INCHES)OF FIRST TITLE CHARACTER
                (XPOS)
C               VARIABLE 12,Y-COORDINATE(INCHES)OF FIRST TITLE CHARACTER
                (YPOS)
                VARIABLE 13,INCREMENT TO NUMERICAL DATA(IF ANY)-PLUS.
C          FIFTH CARD-
C               CALCOMP CHART TITLE-FORMAT(13A6)
C     SUBPROGRAMS USED-
C               ASORT  FORTRAN IV
C               ZSCORE  FORTRAN IV
C     LIMITATIONS AND ACCURACY-
C               NO MORE THAN 2000 DATA POINTS ARE ALLOWED IN ANY DATA DECK
C               DATA LOCATIONS OCCUR AT THE BOTTOM LEFT HAND CORNER OF
C               THE PLOTTED NUMERIC DATA.
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *

      DIMENSION FMT(13),TITLE(13)
      COMMON N(2000),X(2000),Y(2000),Z(2000)
C
C               ALL NUMERIC DATA HELD IN COMMON AREA OF MEMORY CORE
C
      READ(5,1)NUMJOB
C
C               READ IN NUMBER OF DATA DECKS
C
    1 FORMAT(I6)
      CALL START
      DO 100 NN=1,NUMJOB
C
C               READ IN PLOT ORIGIN AND TRANSFORMATION OPTIONS
C
      READ(5,101)XORIJN,YORIJN,PERC,VALMAX,VALMIN,RECIP,ZVAL
  101 FORMAT(7F6.1)
      CALL PLOT(XORIJN,YORIJN,-3)
C
C               READ VARIABLE FORMAT CARD
C
      READ(5,2) (FMT(I),I=1,13)
    2 FORMAT(13A6)
      WRITE(6,104)
  104 FORMAT(1H1,10HRAW DATA . )
      L=0
    3 L=L+1
C
C             READ DATA CARDS CHECKING FOR LAST (9999) CARD
C
      READ(5,FMT)N(L),X(L),Y(L),Z(L)
      IF(N(L).EQ.9999)GO TO 4
```

```
      WRITE(6,103)N(L),X(L),Y(L),Z(L)
  103 FORMAT(1H ,I10,2F10.0,F10.3)
C
C             DETERMINING MAXIMUM AND MINIMUM DATA VALUES
C
      IF(Z(L).LT.VALMAX)VALMAX=Z(L)
      IF(Z(L).GT.VALMIN)VALMIN=Z(L)
      GO TO 3
    4 IMAX=L-1
      M=IMAX
      WRITE(6,102)VALMAX,VALMIN
  102 FORMAT(1H1,7HVALMAX=,F7.3,7HVALMIN=,F7.3)
C
C             CHECKING IF PERCENTAGE RANGE TRANSFORMATION IS REQUIRED
C
      IF(PERC)10,10,11
   11 WRITE(6,105)
  105 FORMAT(1H1,28HPERCENTAGE TRANSFORMED DATA.)
C
C             CALCULATING PERCENTAGE RANGE TRANSFORM VALUES
C
      DO 12 I=1,M
      Z(I)=(((Z(I)-VALMAX)/(VALMIN-VALMAX))*100.)
      WRITE(6,103)I,X(I),Y(I),Z(I)
   12 CONTINUE
C
C             CHECKING IF RECIPROCAL TRANSFORMATION IS REQUIRED
C
   10 IF(REC(P)13,13,14
   14 WRITE(6,106)
  106 FORMAT(1H1,27HRECIPROCAL PERCENTAGE DATA.)
C
C             CALCULATING RECIPROCAL TRANSFORM VALUES
C
      DO 15 I=1,M
      Z(I)=Z(I)-100.
      Z(I)=ABS(Z(I))
   15 CONTINUE
C
C             CHECKING IF STANDARD VALUE TRANSFORM IS REQUIRED
C
   13 IF(ZVAL)20,20,21
   21 CALL ZSCORE(IMAX)
   20 CALL XSORT(M)
C
C             READING IN CALCOMP CONTROL PARAMETERS
C
      READ(5,9)AXISE,AXISN,XMIN,XINT,YMIN,YINT,SIZET,SIZEN,NUMLET,NUMDEC
     1,XPOS,YPOS,PLUS
    9 FORMAT(8F6.2,2I6,2F5.1,F6.2)
C
C             CALCULATING MAXIMUM X- AND Y- COORDINATES OF  PLOT AREA
```

```
C
      XMAX=(AXISE*XINT)+XMIN
      YMAX=(AXISN*YINT)+YMIN
C
C             STORING  MINIMUM X- AND Y- COORDINATE VALUES
C
      X(IMAX+1)=XMIN
      Y(IMAX+1)=YMIN
C
C             STORING 1 INCH X- AND Y- AXIS INCREMENTS
C
      X(IMAX+2)=XINT
      Y(IMAX+2)=YINT
C
C             CALCULATING ROUND OFF INCREMENT FOR DATA VALUES
C
      XUMDEC=NUMDEC
      FACTOR=0.5/(10.0**XUMDEC)
C
C             DRAWING X AND Y AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,X(IMAX+1),
     1X(IMAX+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,Y(IMAX+1),
     1Y(IMAX+2))
C
C             READ IN CALCOMP PLOT TITLE
C
      READ(5,5)(TITLE(I),I=1,13)
    5 FORMAT(13A6)
C
C             WRITING OUT CHART TITLE
C
      CALL SYMBOL(XPOS,YPOS,SIZET,TITLE,0.0,NUMLET)
C
C             CHECKING IF DATA FALL WITHIN PLOT AREA
C
      DO 7 I=1,IMAX
        IF(X(I).LT.XMIN.OR.X(I).GT.XMAX)GO TO 7
      IF(Y(I).LT.YMIN.OR.Y(I).GT.YMAX)GO TO 7
C
C             SCALING DATA LOCATIONS FOR PLOTTING ON CALCOMP CHART
C
      YY=((Y(I)-Y(IMAX+1))/Y(IMAX+2))
      XX=((X (I)-X ((IMAX+1))/X (IMAX+2))
C
C             ROUNDING OFF DATA VALUES
C
      FPN=Z(I)+FACTOR +PLUS
C
C             PLOTTING ROUNDED OFF  DATA
C
      CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDECI
    7 CONTINUE
C
C             MOVING CALCOMP TO NEXT MAP ORIGIN
C
      ORIGIN=AXISE+4.
      CALL PLOT(ORIGIN,0.0,-3)
```

```
  100 CONTINUE
      STOP
      END
C
C
C
C
C
$IBFTC SUBI     DECK
C     XSORT
C     TITLE-
C        SORTS DATA FROM MINIMUM TO MAXIMUM X-COORDINATE VALUES
C     KEY WORDS-
C        COMPUTER GRAPHICS
C     LANGUAGE,COMPUTER,DATE
C        FORTRAN IV IBM026 48 CHAR SET,IMPERIAL COLLEGE IBM 7094,JUN1964
C     AUTHOR-
C        J.KHALEELEE,APPLIED GEOCHEMISTRY RESEARCH GROUP,IMPERIAL COLLEGE
C     PURPOSE-
C        TO SORT THE DATA FROM EAST TO WEST IN ORDER TO MINIMISE THE
C        CALCOMP MAGNETIC TAPE LENGTH REQUIRED,AND THE PLOTTING TIME
C     USAGE-
C        CALL XSORT(M)
C     ARGUMENTS-
C        M      =TOTAL NUMBER OF DATA
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      SUBROUTINE XSORT(M)
C
C              USES COMMON BLOCK DATA
C
      COMMON N(2000),X(2000),Y(2000),Z(2000)
C
C              SORTS DATA FROM MINIMUM TO MAXIMUM X-COORDINATES
C
C              A IS DUMMY STORE FOR X-COORDINATES
C              B IS DUMMY STORE FOR Y-COORDINATES
C              C IS DUMMY STORE FOR DATA VALUES
C              M IS A DO LOOP PARAMETER STORE
C
C
C              COMPARISON COMMENCES WITH M=NUMBER OF DATA,BUT M IS
C              SEQUENTIALLY REDUCED BY 1,UNTIL M=0
C
      M=M-1
   21 DO 22 I=1,M
      IF(X(I).LE.X(I+1))GOTO 22
      A=X(I+1)
      X(I+1)=X(I)
      X(I)=A
      B=Y(I+1)
      Y(I+1)=Y(I)
      Y(I)=B
      C=Z(I+1)
      Z(I+1)=Z(I)
      Z(I)=C
   22 CONTINUE
      M=M-1
      IF(M.LE.1)GO TO 30
```

```
      GOTO21
   30 RETURN
      END
C
C
C
C
C
$IBFTC SUB2    DECK
C       ZSCORE
C       TITLE-
C          RE-EXPRESSES DATA IN TERMS OF THE POPULATION STANDARD DEVIATIONS
C          ABOUT THE POPULATION MEAN
C       KEY WORDS-
C          COMPUTER GRAPHICS
C       LANGUAGE,COMPUTER,DATE
C          FORTRAN IV IBM026 48 CHAR SET,IMPERIAL COLLEGE IBM 7094,JUN1969

C       AUTHOR-
C          J.KHALEELEE,APPLIED GEOCHEMISTRY RESEARCH GROUP,IMPERIAL COLL
C       PURPOSE-
C       USAGE-
C          CALL ZSCORE(IMAX)
C       ARGUMENTS-
C          IMAX    =TOTAL NUMBER OF DATA
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      SUBROUTINE ZSCORE(IMAX)
C
C              USES COMMON BLOCK DATA
C
      COMMON N(2000),X(2000),Y(2000),Z(2000)
C
C              CUMULATIVE PARAMETERS ARE ZEROED
C
      SUMZ=0.0
      SUMZSQ=0.0
C
C              ACCUMULATE SUMS AND SUMS OF SQUARES
C
      DO 1 I=1,IMAX
      SUMZ=SUMZ+Z(I)
      SUMZSQ=SUMZSQ+(Z(I)**2)
    1 CONTINUE
C
C              CALCULATE STATISTICAL PARAMETERS
C
C              IMAX=NUMBER OF DATA
C              ZMEAN IS THE POPULATION MEAN
C              ZVAR IS THE POPULATION  VARIANCE
C              ZSIGMA IS THE POPULATION  STANDARD DEVIATION
C
      XIMAX=IMAX
      ZMEAN=SUMZ/XIMEAN
      ZVAR=(SUMZSQ-((ZMEAN**2)*XIMAX)/XIMAX-1.)
      ZSIGMA=SQRT(ZVAR)
C
C              WRITE OUT STATISTICAL PARAMETERS
C
```

```
      WRITE(6,5)ZMEAN,ZVAR,ZSIGMA
    5 FORMAT(1H0,5HMEAN=,F6.3,9HVARIANCE=,F6.3,20HSTANDARD DEVIATIONS=,
     1F6.3)
C               TRANSFORM DATA TO STANDARD VALUES(Z-VALES)
C               TRANSFORM DATA TO STANDARD VALUES(Z-VALUES)
C
      DO 2 I=1,IMAX
      ZZ=((Z(I)-ZMEAN)/ZSIGMA)
C
C               WRITE OUT Z-VALUES
C
      WRITE(6,3)N(I),X(I),Y(I),Z(I),ZZ
    3 FORMAT(1H ,I10,2F10.0,2F10.3)
    2 CONTINUE
      RETURN
      END
```

APPENDIX 2

```
C     PROGRAMME ROLLER(INPUT=TAPE 5,OUTPUT=TAPE 6,CALCOMP=TAPEA8,SCRATCH
C     =TAPE 1)
C     ROLLER
C     TITLE-
C        EXECUTIVE PROGRAMME FOR MOVING AVERAGE ANALYSIS OF IRREGULARLY
C        DISTRIBUTED NUMERIC MAP DATA.OUTPUT IS PRODUCED BOTH AS NUMERIC
C        LISTS AND ALSO AS CALCOMP MAPS.
C     KEY WORDS-
C        MAP ANALYSIS
C     LANGUAGE,COMPUTER,DATE-
C        FORTRAN IV IBM026 48 CHAR SET,IMPERIAL COLLEGE IBM7094,JUN1969
C     AUTHOR-
C        J.KHALEELEE,APPLIED GEOCHEMISTRY RESEARCH GROUP,IMPERIAL COLL
C     PURPOSE-
C        THE DATA CONSISTS OF VALUES OF A DEPENDANT VARIABLE AT A NUMBER
C        OF IRREGULARLY SPACED SAMPLE LOCATIONS.THE AREA ENCLOSING THE
C        DATA IS SUBDIVIDED INTO RECTANGULAR OVERLAPPING SUB-AREAS OF
C        PREDETERMINED SHAPE AND SIZE,AND WHICH OVERLAP BY A PREDETERMI-
C        NED AMOUNT.THE DATA WITHIN EACH SUB-AREA IS USED TO CALCULATE
C        THE MEAN,VARIANCE,STANDARD DEVIATION,RATIO OF THE SUB-AREA
C        VARIANCE TO THAT OF THE TOTAL AREA,AND THE DEVIATION OF THE
C        SUB-AREA MEAN FROM THE TOTAL MEAN IN TOTAL AREA STANDARD DEVIA-
C        TION UNITS..EACH OF THESE PARAMETERS IS STORED IN THE MEMORY
C        AND  MAY BE PLOTTED AS SEPERATE PARAMETER MAPS USING THE CAL-
C        COMP PLOTTER.THE COMPUTED PARAMETERS ARE ALSO LISTED  IN THE
C        PROGRAMME OUTPUT.
C        THE INDIVIDUAL SAMPLE DEVIATIONS FROM THE MOVING AVERAGE IN
C        MOVING STANDARD DEVIATION UNITS MAY ALSO BE COMPUTED AND OUTPUT
C        AS CALCOMP PLOTS.
C     DATA SET-UP
C        FOR EACH SET OF MAP DATA TO BE ANALYSED,THE FOLLOWING INFORMAT-
C        ION MUST BE GIVEN
C
C        CONTROL CARD 1-
C             CARD FORMAT (I6,5F6.0,7F2.0),ANALYSIS PARAMETERS.
C             PARAMETER 1-LOG OPTION(1=YES,0=NO)
C             PARAMETER 2-EAST-WEST SIZE OF SUB-AREA IN GRID COORDINATE
C                        UNITS.
C             PARAMETER 3-REQUIRED EAST-WEST OVERLAP IN GRID COORDINATE
C                        UNITS.
C             PARAMETER 4-NORTH-SOUTH DIMENSION OF SUB-AREA IN GRID COO-
C                        RDINATE  UNITS
C             PARAMETER 5-NORTH-SOUTH SUB-AREA OVERLAP IN GRID COORDINATE
C                        UNITS.
C             PARAMETER 6-RAW DATA CALCOMP PLOT OPTION(1=YES,0=NO).
C             PARAMETER 7-ANY MOVING AVERAGE PARAMETERS TO BE CALCOMP
C                        PLOTTED(1=YES,0=NO).
C             PARAMETER 8-MOVING AVERAGE CALCOMP PLOT OPTION(1=YES,0=NO).
```

```
C                       VARIANCE RATIO CALCOMP PLOT PARAMETERS(REPEAT
C                       CONTROL CARD 4)
C        CONTROL CARD 13-
C                       VARIANCE RATIO CALCOMP PLOT TITLE(REPEAT CONTROL
C                       CARD 5)
C        CONTROL CARD 14-
C                       Z- VALUE CALCOMP PLOT CONTROL PARAMETERS(REPEAT
C                       CONTROL CARD 4)
C        CONTROL CARD 15-
C                       Z-VALUE CALCOMP PLOT TITLE(REPEAT CONTROL CARD 5)
C        CONTROL CARD 16-
C                       RESIDUALS CALCOMP PLOT CONTROL PARAMETERS(REPEAT
C                       CONTROL CARD  4)
C        CONTROL CARD 17-
C                       RESIDUE CALCOMP PLOT TITLE(REPEAT CONTROL CARD5)
C     SUBPROGRAMMES USED-
C        XSORT  FORTRAN IV
C        YSORT  FORTRAN IV
C        RESIDU  FORTRAN IV
C     LIMITATIONS AND ACCURACY-
C        NO MORE THAN 1800 DATA MAY BE PROCESSED IN EACH  DATA DECK
C        THE QUOTIENTS (GAPE/ENTE) AND (GAPN/ENTN) MUST BE INTEGERS

C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
      SUBROUTINE ROLLER
C
C              COMMON BLOCK ARRAY IDENTIFICATION
C              XE=ORIGINAL DATA X COORDINATES
C              XXE=X COORDINATES OF DATA IN EACH NORTH-SOUTH STRIP
C              XXXE=X COORDINATES OF SAMPLES IN EACH SUB AREA
C              XLOCE=X COORDINATES OF MOVING AVERAGE
C              XN=ORIGINAL DATA Y COORDINATES
C              XXN=Y COORDINATES OF DATA IN EACH NORTH-SOUTH STRIP
C              XXXN=Y COORDINATES OF SAMPLES IN EACH SUB AREA
C             YLOCN=Y COORDINATES OF MOVING AVERAGES
C               CO=ORIGINAL DATA VALUES
C               CCO=DATA VALUES IN EACH NORTH-SOUTH STRIP
C               CCCO=DATA VALUES IN EACH SUB AREA
C               RMEAN=MEAN VALUE OF DATA IN SUB AREAS
C               RVAR=VARIANCE OF DATA IN SUB AREAS
C               RSD=STANDARD DEVIATION OF DATA IN SUB AREAS
C               VRAT=RATIO OF SUB AREA VARIANCES TO TOTAL DATA VARIANCE
C               ANOM=MOVING AVERAGE EXPRESSED IN TOTAL DATA STANDARD DEV-
C                    IATIONS ABOUT THE TOTAL DATA MEAN
C               II=CUMULATIVE SUM OF TOTAL SAMPLES  OCCURRING IN EACH
C                  NORTH-SOUTH STRIP
C               JJ=CUMULATIVE SUM OF NORTH-SOUTH STRIP DATA OCCURRING
C                  WITHIN EACH SUB AREA
C
      COMMON XE(1800),XXE(800),XXXE(200),XLOCE(1000),XN(1800),XXN(800),X
     1XXN(200),YLOCN(1000),CO(1800),CCO(800),CCCO(200),RMEAN(1000),RVAR(
     21000),RSD(1000),VRAT(1000),ANOM(1000),II(200),JJ(200)
C
C              DIMENSION ARRAY CODE
C              PLOTP=CALCOMP PLOT OPTIONS FOR MOVING AVERAGE PARAMETERS
C              FMT=VARIABLE FORMAT
C              TITLE=DATA TITLE
```

```
C          PARAMETER 9-MOVING VARIANCE CALCOMP PLOT OPTION(1=YES,0=NO).
C          PARAMETER 10-MOVING STANDARD DEVIATION PLOT OPTION(1=YES,
C                0=NO).
C          PARAMETER 11-VARIANCE RATIO CALCOMP PLOT OPTION(1=YES,0=NO)
C          PARAMETER 12-Z-VALUE CALCOMP PLOT OPTION(1=YES,0=NO)
C          PARAMETER 13-SAMPLE DEVIATION VALUES FROM THE MOVING
C            AVERAGE CALCOMP PLOT OPTION(1=YES,0=NO).
C     CONTROL CARD 2-
C          TITLE  72 CHAR (12A6)
C     CONTROL CARD 3-
C          VARIABLE FORMAT(FMT)-(12A6)
C     DATA DECK-
C          DATA INCLUDES SAMPLE NUMBER(INTEGER),X- AND Y- COORDINATES
C          AND DATA VALUES FOR ONE VARIABLE
C     LAST CARD OF NUMERIC  DATA DECK-
C          BEARS 9999 IN COLUMNS  RESERVED FOR SAMPLE NUMBER.
C     CONTROL CARD 4-
C          RAW DATA CALCOMP PLOTTING CONTROL PARAMETERS-
C          CONTROL CARD FORMAT(11F6.2,2I6)
C          PARAMETER 1- EAST-WEST (X) AXIS LENGTH IN INCHES.(AXISE)
C          PARAMETER 2-NORTH-SOUTH(Y) AXIS LENGTH IN INCHES.(AXISN)
C          PARAMETER 3-SIZE OF NUMERIC CHARACTERS IN INCHES.(SIZEN)
C          PARAMETER 4-SIZE OF TITLE CHARACTERS IN INCHES.(SIZET)
C          PARAMETER 5-X-COORDINATE LOCATION IN INCHES OF FIRST TITLE
C            CHARACTER.(TITLEX)
C          PARAMETER 6- Y-COORDINATE LOCATION IN INCHES OF THE TITLE
C            CHARACTERS(TITLEY)
C          PARAMETER 7-EASTING (X) COORDINATE OF MAP ORIGIN (XMIN)
C          PARAMETER 8-GRID COORDINATE INCREMENT EQUIVALENT TO 1 INCH
C            ALONG EASTING (X) AXIS.(XINT)
C          PARAMETER 9- NORTHING (Y) COORDINATE OF MAP ORIGIN.(YMIN)
C          PARAMETER 10-GRID COORDINATE INCREMENT EQUIVALENT TO 1
C            INCH ALONG THE NORTHING (Y) AXIS.(YINT)
C          PARAMETER 11-NUMERIC INCREMENT (IF ANY) TO PLOTTED DATA
C            VALUES.(PLUS)
C          PARAMETER 12-NUMBER OF CHARACTERS (INCL BLANKS) IN TITLE
C            (NUMLET)
C          PARAMETER 13- NUMBER OF DECIMAL PLACES REQUIRED.(NUMDEC)
C     CONTROL CARD 5-
C          RAW DATA CALCOMP PLOT TITLE
C          78 CHARACTERS(INCL.BLANKS)-FORMAT(13A6)
C     CONTROL CARD 6-
C          MOVING AVERAGE CALCOMP PLOT CONTROL  PARAMETERS(REPEAT
C          CONTROL CARD 4).
C     CONTROL CARD 7-
C          MOVING AVERAGE CALCOMP PLOT TITLE (REPEAT CONTROL CARD 5)
C     CONTROL CARD 8-
C                MOVING VARIANCE CALCOMP PLOT CONTROL PARAMETERS
C                REPEAT CONTROL CARD 4)
C     CONTROL CARD 9-
C                MOVING VARIANCE CALCOMP PLOT TITLE(REPEAT CON-
C                TROL CARD 5)
C     CONTROL CARD 10-
C                MOVING STANDARD DEVIATION CALCOMP PLOT CONTROL
C                PARAMETERS(REPEAT CONTROL CARD 4)
C     CONTROL CARD 11-
C                MOVING STANDARD DEVIATION CALCOMP PLOT TITLE
C                (REPEAT CONTROL CARD 5)
C     CONTROL CARD 12-
```

```
C
      DIMENSION PLOIP(6),FMT(13) ,TITLE(13)
      REWIND 1
C
C               READ IN ANALYSIS CONTROL PARAMETERS
C
      READ(5,1)LOG,GAPE,ENTE,GAPN,ENTN,PLOIR,(PLOIP(I),I=1,6),PLOID
    1 FORMAT(I6,5F6.0,7F2.0)
C
C               READ IN TITLE
C
       READ(5,2)(TITLE(I),I=1,13)
    2 FORMAT(13A6)
C
C               READ IN VARIABLE FORMAT
C
      READ(5,4)(FMT(I),I=1,12)
    4 FORMAT(12A6)
C
C               WRITE OUT TITLE
C
       WRITE(6,3)TITLE
    3 FORMAT(1H1,13A6)
C
C               WRITE OUT OUTPUT HEADINGS
C
      WRITE(6,27)
   27 FORMAT(1H1,3X,5HEASTS,2X,6HNORTHS,5X,7HROLLING,9X,7HROLLING,5X,15H
     1ROLLINGVARIANCE,1X,7HROLLING,1X,7HNUMBERS,10X,2HKK,10X,2HMM,10X,2H
     2NN,/23X,5HMEANS,7X,9HVARIANCES,6X,6HSIGMAS,4X,5HRATIO,1X,7HZVALUES
     4,//)
  800 FORMAT(1H ,80X,2HK=,I3,3X,2HM=,I3,3X,2HN=,I3,3X,6HJMAX=,I5//)
  902 I=1
      JK=0
      IGAPE=GAPE/ENTE
      IGAPN=GAPN/ENTN
C
C               ZERO PARAMETERS TO BE USED,AND SET VALUES OF QUOTIENT
C               SEARCH AREA SIZE /OVERLAP
C
      COSUM=0.0
      SUMSQ=0.0
      RMSMSQ=0.0
      VARRED=0.0
      SCOUNT=0.0
      SAVAR=0.0
      SASUM=0.0
      NUMRES=0
C               CHECK FOR LOG OPTION
C
   19 IF(LOG)5,5,7
C
C               READ IN DATA ,CALCULATE SUMS AND SUMS OF SQUARES
C
    5 READ(5,FMT)N,A,B,C
      IF(N.EQ.9999)GO TO 8
      IF(A.LT.1..OR.B.LT.1.)GOTO5
   55 XE(I)=A
      XN(I)=B
```

```
      CO(I)=C
      COSUM=COSUM+CO(I)
      SUMSQ=SUMSQ+CO(I)**2
   51 I=I+1
      GOTO5
C
C             LOG TRANSFORM DATA IF REQUIRED . CALCULATE SUM AND SUM OF
C             SQUARES
C
    7 READ(5,FMT)N,A,B,C
      IF(N.EQ.9999)GO TO 8
      IF(A.LT.1..OR.B.LT.1.)GOTO7
   77 XE(I)=A
      XN(I)=B
      IF(CO(I))300,301,302
  300 CO(I)=-(ALOG10(ABS(C)))
      GO TO 99
  301 CO(I)=0.000
      GO TO 99
  302 CO(I)=ALOG10(C)
   99 COSUM=COSUM+CO(I)
      SUMSQ=SUMSQ+CO(I)**2
   53 I=I+1
      GOTO7
    8 XIMAX=I-1
C
C             CALCULATE TOTAL DATA SET STATISTICAL PARAMETERS
C             XIMAX=IMAX=TOTAL NUMBER OF SAMPLES
C             COMEAN=TOTAL DATA SET MEAN
C             VAR=TOTAL DATA SET VARIANCE
C             SD=TOTAL DATA SET STANDARD DEVIATION
C
      IMAX=XIMAX
      COMEAN=COSUM/XIMAX
      VAR=(SUMSQ-XIMAX*(COMEAN**2))/(XIMAX-1.)
      SD=SQRT(VAR)
      SDLOG=SD
      CLGMN=COMEAN
      VARLOG=VAR
      IF(LOG)610,610,650
  650 IF(COMEAN)305,306,307
C
C             OBTAIN ANTILOG OF TOTAL DATA SET MEAN
C
  305 COMEAN=-(EXP((ABS(COMEAN))*2.3026))
      GO TO 610
  306 COMEAN=1.000
      GO TO 610
  307 COMEAN=EXP(COMEAN*2.3026)
  610 WRITE(6,40) COMEAN,VAR,SD
  400FORMAT(1H ,1HTOTAL MEAN=,F6.2,15HTOTAL VARIANCE=,F6.4,25HTOTAL STA
     1NDARD DEVIATION=,F6.4)
      WRITE(6,27)
      IAMAX=IMAX-1
C
C             CALL SUBROUTINE TO SORT DATA FROM WEST TO EAST
C
      CALL XSORT(XE,XN,CO,IAMAX)
C
```

```
C               CHECK FOR CALCOMP PLOT OPTIONS
C
      IF(PLOTR.LT.1..AND.PLOTP(1).LT.1.) GO TO 208
C
C               CALL IN CALCOMP SUB ROUTINES
C
      CALL START
      CALL PLOT(2.0,2.0,-3)
      IF(PLOTR)208,208,209
C
C               READ IN RAW DATA CALCOMP PLOT CONTROL PARAMETERS
C
  209 READ(5,213)AXISE,AXISN,SIZEN,SIZET,TITLEX,TITLEY,XMIN,XINT,YMIN,YI
     INT,PLUS,NUMLET,NUMDEC
  213 FORMAT(11F6.2,2I6)
C
C               READ IN RAW DATA CALCOMP PLOT TITLE
C
      READ(5,2)(TITLE(I),I=1,13)
      XUMDEC=NUMDEC
C
C               CALCULATE ROUND OFF INCREMENT
C
      FACTOR=0.5/(10.0**XUMDEC)
C
C               STORE ORIGIN AND SCALE VALUES
C
      XE(IMAX+1)=XMIN
      XE(IMAX+2)=XINT
      XN(IMAX+1)=YMIN
      XN(IMAX+2)=YINT
C
C               DRAW CALCOMP PLOT AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,XE(IMAX+1),
     1XE(IMAX+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,XN(IMAX+1)
     1,XN(IMAX+2))
      CALL SYMBOL(TITLEX,TITLEY,SIZET,TITLE,0.0,NUMLET)
C
C               CHECK IF SAMPLES FALL WITHIN PLOT AREA
C
      DO 200 I=1,IMAX
      IF(XE(I).LE.XE(IMAX+1))GOTO 200
      IF(XN(I).LE.XN(IMAX+1))GOTO 200
C
C               CONVERT MAP  TO PLOT COORDINATES
C
      XX=((XE(I)-XE(IMAX+1))/XE(IMAX+2))
      YY=((XN(I)-XN(IMAX+1))/XN(IMAX+2))
C
C               CHECK FOR LOG OPTION
C
  201 IF(LOG)202,202,203
  203 IF(CO(I))308,309,310
C
C               ANTILOG DATA VALUES
C
  308 FPN=-(EXP((ABS(CO(I)))*2.3026))+FACTOR
```

```
      GO TO 204
  309 FPN=1.000
      GO TO 204
  310 FPN=EXP(CO(I)*2.3026)+FACTOR
      GO TO 204
C
C             ROUND OFF DATA VALUES AND PLOT
C
  202 FPN=CO(I)+FACTOR
  204 CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDEC)
  200 CONTINUE
C
C             MOVE CALCOMP TO NEXT MAP ORIGIN
C
      ORIGIN=AXISE+4.0
      CALL PLOT(ORIGIN,0.0,-3)
C
C             CALCULATE WESTERN BOUNDARY OF SAMPLED AREA
C
  208 STARTE=ENTE*(FLOAT(IFIX(XE(1)/ENTE)))
      II(1)=0
      K=2
      END=ENTE
      IG=1
  717 IC=0
C
C             DIVIDE UP DATA INTO NORTH-SOUTH STRIPS
C
      DO 10 I=IG,IMAX
      IF((XE(I)-STARTE).LE.END)GOTO10
      IF((XE(I)-STARTE).LE.(END+ENTE))GO TO 713
      GO TO 714
  713 IF(XE(I+1).EQ.XE(I))GO TO 10
C
C             KEEP RECORD OF NUMBERS IN EACH STRIP
C
      II(K)=I-1
      K=K+1
      END=END+ENTE
   10 CONTINUE
      GO TO 718
  714 K=K+1
      END=END+ENTE
      IC=IC+1
      IF((XE(I)-STARTE).LE.(END+ENTE))GO TO 715
      GO TO 714
  715 II(K)=I-1
      NIG=K-IC
      NOG=K-1
      DO 716 KO=NIG,NOG
      II(KO)=II(K)
  716 CONTINUE
      END=END+ENTE
      K=K+1
      IG=I+1
      GO TO 717
  718 II(K)=IMAX
      NUMII=K+1
      K=0
```

```
      GO TO 719
   11 K=K+1
   29 M=II(K)+1
      KC=K+IGAPE
      N=II(KC)
      IF(M.GT.N)GO TO 719
      J=1
C
C              TAKE DATA FROM ONE STRIP AND STORE IT IN SEPARATE STORE
C
      DO12 I=M,N
      CCO(J)=CO(I)
      XXE(J)=XE(I)
      XXN(J)=XN(I)
      J=J+1
   12 CONTINUE
      JMAX=J-1
      JAMAX=JMAX-1
      WRITE(6,800)K,M,N,JMAX
C
C              CALL SUBROUTINE TO SORT STRIP DATA FROM NORTH TO SOUTH
C
      CALL YSORT(XXN,XXE,CCO,JAMAX)
C
C              SET NORTHERN LIMIT OF SAMPLED STRIP
C
      STARTN=ENTN*(FLOAT(IFIX((XXN(1)+ENTN)/ENTN)))
      JJ(1)=0
      KK=2
      EEND=ENTN
      JIG=1
  617 ID=0
C
C              SUBDIVIDE NORTH-SOUTH STRIP INTO SUB AREAS
C
      DO 13 J=JIG,JMAX
      IF((STARTN-XXN(J)).LE.EEND)GO TO 13
      IF((STARTN-XXN(J)).LE.(EEND+ENTN))GOTO613
      GOTO614
  613 IF(XXN(J+1).EQ.XXN(J))GO TO 13
      JJ(KK)=J-1
      KK=KK+1
      EEND=EEND+ENTN
   13 CONTINUE
      GOTO618
  614 KK=KK+1
      EEND=EEND+ENTN
      ID=ID+1
      IF((STARTN-XXN(J)).LE.(EEND+ENTN))GOTO615
      GOTO614
  615 JJ(KK)=J-1
      NIM=KK-ID
      NOM=KK-1
      DO616 KA=NIM,NOM
      JJ(KA)=JJ(KK)
  616 CONTINUE
      EEND=EEND+ENTN
      KK=KK+1
      JIG=J+1
```

```
      GOTO617
  618 JJ(KK)=JMAX
      NUMJJ=KK+1
      KK=0
      GO TO 619
   28 KK=KK+1
      MM=JJ(KK)+1
      KB=KK+IGAPN
      NN=JJ(KB)
      IF(MM.GT.NN)GO TO 619
C
C             ZERO MOVING AVERAGE PARAMETERS
C
      MAXLL=0
      COUNT=0.0
      RSUM=0.0
      RSUMSQ=0.0
      SUME=0.0
      SUMN=0.0
      LL=1
C
C             STORE SUB AREA DATA IN SEPERATE STORE
C
      DO15 L=MM,NN
      CCCO(LL)=CCO(L)
      XXXE(LL)=XXE(L)
      XXXN(LL)=XXN(L)
      LL=LL+1
   15 CONTINUE
C
C             CALCULATE SUMS,SUMS OF SQUARES,EASTING AND NORTHING SUMS
C             AND COUNT NUMBER OF DATA IN THE SUB AREA
C
      MAXLL=LL-1
      DO 60 LL=1,MAXLL
      RSUM=RSUM+CCCO(LL)
      IF(CCCO(LL).EQ.0.)GOTO54
      RSUMSQ=RSUMSQ+(CCCO(LL)**2)
   54 SUME=SUME+XXXE(LL)
      SUMN=SUMN+XXXN(LL)
      COUNT=COUNT+1.
   60 CONTINUE
C
C             CALCULATE MOVING AVERAGE AND SUB AREA CENTROID LOCATION
C
      SCOUNT=SCOUNT+1.0
      JK=JK+1
      IF(COUNT.LT.1.)GOTO 619
      IF(COUNT.EQ.1.)GOTO66
      RMEAN(JK)=RSUM/COUNT
      XLOCE(JK)=SUME/COUNT
      YLOCN(JK)=SUMN/COUNT
C
C             CALCULATE SUM AND SUM OF SQUARES OF MOVING AVERAGES
C
      SASUM=SASUM+RMEAN(JK)
      IF(RMEAN(JK).EQ.0.)GOTO666
      RMSMSQ=RMSMSQ+(RMEAN(JK)**2)
C
```

```
C               CHECK IF ALL  NORTH - SOUTH STRIPS HAVE BEEN INCLUDED
C
  619 NUMJJ=NUMJJ-1
      IF(NUMJJ.GT.IGAPN)GOTO28
  719 NUMII=NUMII-1
      IF(NUMII.GT.IGAPE)GOTO11
C
C               CALCULATE REDUCTION OF VARIANCE ATTRIBUTABLE TO MOVING
C               AVERAGE ANALYSIS
C
      MAXS=SCOUNT
      SAMEAN=SASUM/SCOUNT
      SAVAR=(RMSMSQ-((SAMEAN**2)*SCOUNT))/(SCOUNT-1.)
      VARRED=((SAVAR/VARLOG)*100.)-100.
      RSSRED=(((SUMSQ-RMSMSQ)/SUMSQ)*100.)
      CSSRED=100.*((SAVAR*(SCOUNT-1.))-(VARLOG*(XIMAX-1.)))/(VARLOG*(XIM
     1AX-1.))
C
C               WRITE OUT REDUCTION OF VARIANCE
C
      WRITE(6,1202)MAXS,SAMEAN,SAVAR,VARRED,RSSRED,CSSRED,RMSMSQ
 1202 FORMAT(1H ,2H**,I6,6F15.4)
      WRITE(6,901)VARRED,RSSRED,CSSRED
  901 FORMAT(1H ,19H VARIANCE INCREASE=,F7.2,/,30H RAW SUM OF SQUARES RE
     1DUCTION=,F7.2,/,35H CORRECTED SUM OF SQUARES INCREASE=,F7.2)
      REWIND 1
C
C               CHECK FOR ANY MOVING AVERAGE PARAMETERS PLOT OPTIONS.
C
      IF(PLOTP(1))1020,1020,1021
 1021 DO 1000 KK=1,5
      GO TO(1001,1002,1003,1004,1005),KK
C
C               CHECK FOR MOVING AVERAGE CALCOMP PLOT OPTION
C
 1001 IF(PLOTP(2))1000,1000,1111
C
C               READ IN MOVING AVERAGE CALCOMP PLOT CONTROL PARAMETERS
C
 1111 READ(5,213)AXISE,AXISN,SIZEN,SIZET,TITLEX,TITLEY,XMIN,XINT,YMIN,YI
     1NT,PLUS,NUMLET,NUMDEC
C
C               READ IN MOVING AVERAGE CALCOMP PLOT TITLE
C
      READ(5,2)(TITLE(I),I=1,13)
C
C               STORE MAP ORIGIN AND SCALE DATA
C
      XLOCE(MAXS+1)=XMIN
      XLOCE(MAXS+2)=XINT
      YLOCN(MAXS+1)=YMIN
      YLOCN(MAXS+2)=YINT
C
C               DRAW MAP AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,XLOCE(MAXS+
     11),XLOCE(MAXS+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,YLOCN(MAXS
     1+1),YLOCN(MAXS+2))
```

```
C               CALCULATE MOVING VARIANCE,MOVING STANDARD DEVIATION,
C               VARIANCE RATIO
C
      RVAR(JK)=(RSUMSQ-(RMEAN(JK)**2)*COUNT)/(COUNT-1.)
      IF(RVAR(JK).LE.0.0001)GOTO666
      RSD(JK)=SQRT(RVAR(JK))
      IF(RSD(JK).LE.0.0001)GOTO666
      VRAT(JK)=RVAR(JK)/VARLOG
      GOTO 666
   66 RMEAN(JK)=RSUM
      XLOCE(JK)=SUME
      YLOCN(JK*=SUMN
C
C               CALCULATE Z-VALUES
C
  666 ANOM(JK)=(RMEAN(JK)-CLGMN)/SDLOG
C
C               CALCULATE SAMPLE DEVIATIONS FROM MOVING AVERAGE AND DEV-
C               IATIONS SQUARED,CONDENSE X- AND Y- COORDINATES(COORD) OF
C               SAMPLES
C
      DO 1200 LL=1,MAXLL
      NUMRES=NUMRES+1
      RESIDU=CCCO(LL)-RMEAN(JK)
      RESSQ=(ABS(RESIDU)**2.)
C
C               CONDENCE X- AND Y- COORDINATES INTO A SINGLE 8- FIGURE
C               NUMBER(COORD)
C
      COORD=(XXXE(LL)*10000.)+XXXN(LL)
C
C               WRITE COORDINATES , DEVIATION,AND DEVIATION SQUARED ONTO
C               TAPE UNIT 1
C
      WRITE(1)COORD,RESIDU,RESSQ
      WRITE(6,1201)NUMRES,COORD,RESIDU,RESSQ
 1201 FORMAT(1H ,1H*,I6,3F20.4)
 1200 CONTINUE
C
C               ANTILOG MOVING AVERAGE VALUES
C
      IF(LOG)56,56,600
  600 IF(RMEAN(JK))311,312,313
  311 RMEAN(JK)=-(EXP((ABS(RMEAN(JK)))*2.3026))
      GO TO 56
  312 RMEAN(JK)=1.000
      GO TO 56
  313 RMEAN(JK)=EXP(RMEAN(JK)*2.3026)
C
C               WRITE OUT MOVING AVERAGE PARAMETERS
C
  560WRITE(6,16)XLOCE(JK),YLOCN(JK),RMEAN(JK),RVAR(JK),RSD(JK),VRAT(JK)
     1,ANOM(JK),COUNT,KK,MM,NN
   16 FORMAT(1H ,2F8.0,F12.0,F16.2,F12.2,2F8.2,F8.0,3I12)
C
C               CALCULATE IF ALL SUB AREAS IN NORTH-SOUTH STRIP HAVE
C               BEEN INCLUDED
C
C
```

```
C
C               WRITE MOVING AVERAGE CALCOMP PLOT TITLE
C
      CALL SYMBOL(TITLEX,TITLEY,SIZET,TITLE,0.0,NUMLET)
C
C               ESTABLISH LIMITS OF MAP AREA
C
      XMAX=(AXISE*XINT)+XMIN
      YMAX=(AXISN*YINT)+YMIN
C
C               CALCULATE ROUND OFF INCREMENT
C
      XUMDEC=NUMDEC
      FACTOR=0.5/(10.0**XUMDEC)
C
C               ESTABLISH IF VALUES PLOT WITHIN THE MAP AREA
C
C
      DO 1006 I=1,MAXS
      IF(XLOCE(I).LE.XMIN.OR.XLOCE(I).GT.XMAX)GO TO 1006
      IF(YLOCN(I).LE.YMIN.OR.YLOCN(I).GT.YMAX)GO TO 1006
      XX=((XLOCE(I)-XLOCE(MAXS+1))/XLOCE(MAXS+2))
      YY=((YLOCN(I)-YLOCN(MAXS+1))/YLOCN(MAXS+2))
C               ROUND OFF AND PLOT MOVING AVERAGE VALUES
C
      IF(RMEAN(I))1067,1068,1068
 1067 FACTOR=-FACTOR
 1068 FPN=RMEAN(I)+FACTOR
 1066 CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDEC)
 1006 CONTINUE
      GO TO 1011
C
C               CHECK FOR MOVING VARIANCE CALCOMP PLOT OPTION
C
 1002 IF(PLOTP(3))1000,1000,1112
C
C               READ IN MOVING VARIANCE CALCOMP PLOT CONTROL PARAMETERS
C
 1112 READ(5,213)AXISE,AXISN,SIZEN,SIZET,TITLEX,TITLEY,XMIN,XINT,YMIN,YI
     1NT,PLUS,NUMLET,NUMDEC
C
C               READ IN MOVING VARIANCE CALCOMP PLOT TITLE
C
      READ(5,2)(TITLE(I),I=1,13)
C
C               STORE MAP ORIGIN AND SCALE DATA
C
      XLOCE(MAXS+1)=XMIN
      XLOCE(MAXS+2)=XINT
      YLOCN(MAXS+1)=YMIN
      YLOCN(MAXS+2)=YINT
C
C               DRAW AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,XLOCE(MAXS+
     1 1),XLOCE(MAXS+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,YLOCN(MAXS
     1+1),YLOCN(MAXS+2))
C
```

```
C               WRITE MOVING VARIANCE CALCOMP PLOT TITLE
C
      CALL SYMBOL(TITLEX,TITLEY,SIZET,TITLE,0.0,NUMLET)
C
C               ESTABLISH LIMITS OF MAP AREA
C
      XMAX=(AXISE*XINT)+XMIN
      YMAX=(AXISN*YINT)+YMIN
C
C               CALCULATE ROUND OFF INCREMENT
C
      XNUMDEC=NUMDEC
      FACTOR=0.5/(10.0**XNUMDEC)
C
C               ESTABLISH IF VALUES PLOT WITHIN THE MAP AREA
C
      DO 1007 I=1,MAXS
      IF(XLOCE(I).LT.XMIN.OR.XLOCE(I).GT.XMAX)GO TO 1007
      IF(YLOCN(I).LT.YMIN.OR.YLOCN(I).GT.YMAX)GO TO 1007
      XX=((XLOCE(I)-XLOCE(MAXS+1))/XLOCE(MAXS+2))
      YY=((YLOCN(I)-YLOCN(MAXS+1))/YLOCN(MAXS+2))
C
C               ROUND OFF AND PLOT MOVING VARIANCE VALUES
C
      FPN=RVAR(I)+FACTOR
      IF(RVAR(I))1007,1007,1077
 1077 CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDEC)
 1007 CONTINUE
      GO TO 1011
C
C               CHECK FOR MOVING STANDARD DEVIATION CALCOMP PLOT OPTION
C
 1003 IF(PLOTP(4))1000,1000,1113
C
C               READ IN MOVING STANDARD DEVIATION CALCOMP PLOT CONTROL
C               PARAMETERS
C
 1113 READ(5,213)AXISE,AXISN,SIZEN,SIZET,TITLEX,TITLEY,XMIN,XINT,YMIN,Y
     1INT,PLUS,NUMLET,NUMDEC
C
C               READ IN MOVING STANDARD DEVIATION CALCOMP PLOT TITLE
C
      READ(5,2)(TITLE(I),I=1,13)
C
C               STORE MAP ORIGIN AND SCALE DATA
C
      XLOCE(MAXS+1)=XMIN
      XLOCE(MAXS+2)=XINT
      YLOCN(MAXS+1)=YMIN
      YLOCN(MAXS+2)=YINT
C
C               DRAW MAP AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,XLOCE(MAXS+
     11),XLOCE(MAXS+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,YLOCN(MAXS
     1+1),YLOCN(MAXS+2))
C
C               WRITE MOVING STANDARD DEVIATION CALCOMP PLOT TITLE
```

```
C
      CALL SYMBOL(TITLEX,TITLEY,SIZET,TITLE,0.0,NUMLET)
C
C               ESTABLISH LIMITS OF MAP AREA
C
      XMAX=(AXISE*XINT)+XMIN
      YMAX=(AXISN*YINT)+YMIN
C
C               CALCULATE ROUND OFF INCREMENT
C
      XUMDEC=NUMDEC
      FACTOR=0.5/(10.0**XUMDEC)
C
C               ESTABLISH IF VALUES FALL WITHIN THE MAP AREA
C
      DO 1008 I=1,MAXS
      IF(XLOCE(I).LT.XMIN.OR.XLOCE(I).GT.XMAX)GO TO 1008
      IF(YLOCN(I).LT.YMIN.OR.YLOCN(I).GT.YMAX)GO TO 1008
      XX=((XLOCE(I)-XLOCE(MAXS+1))/XLOCE(MAXS+2))
      YY=((YLOCN(I)-YLOCN(MAXS+1))/YLOCN(MAXS+2))
C
C               ROUND OFF AND PLOT THE MOVING STANDARD DEVIATION  VALUES
C
      FPN=RSD(I)+FACTOR
      IF(RSD(I))1008,1008,1088
 1088 CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDEC)
 1008 CONTINUE
      GO TO 1011
C
C               CHECK FOR VARIANCE RATIO CALCOMP PLOT OPTION
C
 1004 IF(PLOTP(5))1000,1000,1114
C
C               READ IN VARIANCE RATIO CALCOMP PLOT CONTROL PARAMETERS
C
 1114 READ(5,213)AXISE,AXISN,SIZEN,SIZET,TITLEX,TITLEY,XMIN,XINT,YMIN,YI
     1NT,PLUS,NUMLET,NUMDEC
C
C               READ IN VARIANCE RATIO CALCOMP PLOT TITLE
C
      READ(5,2)(TITLE(I),I=1,13)
C
C               STORE MAP ORIGIN AND SCALE DATA
C
      XLOCE(MAXS+1)=XMIN
      XLOCE(MAXS+2)=XINT
      YLOCN(MAXS+1)=YMIN
      YLOCN(MAXS+2)=YINT
C
C               DRAW MAP AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,XLOCE(MAXS+
     11),XLOCE(MAXS+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,YLOCN(MAXS
     1+1),YLOCN(MAXS+2))
C
C               WRITE VARIANCE RATIO CALCOMP PLOT TITLE
C
      CALL SYMBOL(TITLEX,TITLEY,SIZET,TITLE,0.0,NUMLET)
```

```
C
C               ESTABLISH LIMITS OF MAP AREA
C
      XMAX=(AXISE*XINT)+XMIN
      YMAX=(AXISN*YINT)+YMIN
C
C               CALCULATE ROUND OFF INCREMENT
C
      XUMDEC=NUMDEC
      FACTOR=0.5/(10.0**XUMDEC)
C
C               ESTABLISH IF VALUES FALL WITHIN THE MAP AREA
C
      DO 1009 I=1,MAXS
      IF(XLOCE(I).LT.XMIN.OR.XLOCE(I).GT.XMAX)GOTO 1009
      IF(YLOCN(I).LT.YMIN.OR.YLOCN(I).GT.YMAX)GO TO 1009
      XX=((XLOCE(I)-XLOCE(MAXS+1))/XLOCE(MAXS+2))
      YY=((YLOCN(I)-YLOCN(MAXS+1))/YLOCN(MAXS+2))
C
C               ROUND OFF AND PLOT THE VARIANCE  RATIO VALUES
C
      FPN=VRAT(I)+FACTOR
      IF(VRAT(I))1009,1009,1099
 1099 CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDEC)
 1009 CONTINUE
      GO TO 1011
C
C               CHECK FOR Z-VALUES CALCOMP PLOT OPTION
C
 1005 IF(PLOTP(6))1000,1000,1115
C
C               READ IN ZVALUE CALCOMP PLOT CONTROL PARAMETERS
C
 1115 READ(5,213)AXISE,AXISN,SIZEN,SIZET,TITLEX,TITLEY,XMIN,XINT,YMIN,YI
     (NT,PLUS,NUMLET,NUMDEC
C
C               READ IN ZVALUE CALCOMP PLOT TITLE
C
      READ(5,2)(TITLE(I),I=1,13)
C
C               STORE MAP ORIGIN AND SCALE DATA
C
      XLOCE(MAXS+1)=XMIN
      XLOCE(MAXS+2)=XINT
      YLOCN(MAXS+1)=YMIN
      YLOCN(MAXS+2)=YINT
C
C               DRAW MAP AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,XLOCE(MAXS+
     11),XLOCE(MAXS+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,YLOCN(MAXS
     1+1),YLOCN(MAXS+2))
C
C               WRITE ZVALUE CALCOMP PLOT TITLE
C
      CALL SYMBOL(TITLEX,TITLEY,SIZET,TITLE,0.0,NUMLET)
C
C               ESTABLISH LIMITS OF MAP AREA
```

```
C
      XMAX=(AXISE*XINT)+XMIN
      YMAX=(AXISN*YINT)+YMIN
C
C               CALCULATE ROUND OFF INCREMENT
C
      XUMDEC=NUMDEC
      FACTOR=0.5/(10.0**XUMDEC)
C
C               ESTABLISH IF VALUES FALL WITHIN THE MAP AREA
C
      DO 1010 I=1,MAXS
      IF(XLOCE(I).LT.XMIN.OR.XLOCE(I).GT.XMAX)GOTO 1010
      IF(YLOCN(I).LT.YMIN.OR.YLOCN(I).GT.YMAX)GO TO 1010
      XX=((XLOCE(I)-XLOCE(MAXS+1))/XLOCE(MAXS+2))
      YY=((YLOCN(I)-YLOCN(MAXS+1))/YLOCN(MAXS+2))
C
C               ROUND OFF AND PLOT ZVALUES
C
      IF(ANOM(I))1013,1013,1014
 1013 FACTOR=-FACTOR
 1014 FPN=ANOM(I)+FACTOR
 1100 CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDEC)
 1010 CONTINUE
C
C               MOVE CALCOMP TO NEXT MAP ORIGIN
C
 1011 ORIGIN=AXISE+4.0
      CALL PLOT(ORIGIN,0.0,-3)
 1000 CONTINUE
C
C               WRITE TOTAL NUMBER OF RESIDUE VALUES
C
 1020 MAXRES=NUMRES
      WRITE(6,1101)MAXRES,NUMRES
 1101 FORMAT(1H ,3H***,7HMAXRES=,I10,7HNUMRES=,I10)
C
C               CALL SUBROUTINE TO CALCULATE THE MEAN RESIDUAL VALUE FOR
C               EACH OF THE ORIGINAL SAMPLE DATA
C
      CALL RESID(MAXRES,PLOTD,IMAX)
C
C               PLACE END OF FILE ON CALCOMP TAPE
C
      CALL ENPLOT(0,0)
  900 STOP
      END
C
C
C
C
C
C     XSORT
C     TITLE-
C        SORT DATA FROM MOST WESTERLY (MINIMUM X-COORDINATE) TO MOST
C        EASTERLY (MAXIMUM X-COORDINATE)
C     KEY WORDS
C        DATA SORTING
C     LANGUAGE,COMPUTER,DATE -
```

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C        FORTRAN IV   IBM026 48 CHAR SET*IMPERIAL COLLEGE IBM 7094*JUN69
C     AUTHOR -
C        J*KHALEELEE*APPLIED GEOCHEMISTRY RESEARCH GROUP*IMPERIAL COLL
C     USAGE -
C        CALL XSORT(XE*XN*CO*IAMAX)
C     ARGUMENTS -
C        XE - EASTING (X) COORDINATES
C        XN - NORTHING (Y) COORDINATES
C        CO - DATA VALUES
C        IAMAX - NUMBER OF DATA
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
$IBFTC SUB1     DECK
      SUBROUTINE  ASORT(XE*XN*CO*N)
      COMMON XE(1800)*XXE(800)*XXXE(200)*XLOCE(1000)*XN(1800)*XXN(800)*X
     1XXN(200)*YLOCN(1000)*C0(1800)*CC0(800)*CCCO(200)*RMEAN(1000)*RVAR(
     21000)*RSD(1000)*VRAT(1000)*ANCM(1000)*II(200)*JJ(200)
C
C              X- COORDINATES ARRANGED IN ASCENDING ORDER WITH ACCOMPANY-
C              ING Y-COORDINATES AND DATA VALUES
C              COMPARISON COMMENCES WITH N=IAMAX BUT N IS SEQUENTIALLY
C              REDUCED BY 1 UNTIL N=0
C
   21 DO22 I=1*N
      IF(XE(I)*LE*XE(I+1))GOTO 22
      A=XE(I+1)
      XE(I+1)=XE(I)
      XE(I)=A
      B=XN(I+1)
      XN(I+1)=XN(I)
      XN(I)=B
      Z=CO(I+1)
      CO(I+1)=CO(I)
      CO(I)=Z
   22 CONTINUE
      N=N-1
      IF(N*LE*1)GOTO30
      GOTO21
   30 RETURN
      END
C
C
C
C
C
C     YSORT
C     TITLE -
C        SORTS DATA FROM EACH NORTH-SOUTH STRIP IN TURN FROM MOST NORTH-
C        ERLY (MAXIMUM Y-COORDINATE) TO MOST SOUTHERLY (MINIMUM Y-COORD-
C        INATE
C     KEY WORDS -
C        DATA SORTING
C     LANGUAGE*COMPUTER*DATE -
C        FORTRAN IV   IBM026   48 CHAR SET*IMPERIAL COLLEGE IBM 7094*JUN69
C     AUTHOR -
C        J*KHALEELEE*APPLIED GEOCHEMISTRY RESEARCH GROUP*IMPERIAL COLL
C     USAGE -
C        CALL YSORT(XXN*XXE*CCO*JAMAX)
C     ARGUMENTS -
```

```
C        XXN - NORTHING (Y) COORDINATES OF DATA IN EACH N-S STRIP
C        XXE - EASTING (X) COORDINATES OF DATA IN EACH N-S STRIP
C        CCO - DATA VALUES OF SAMPLES IN EACH N-S STRIP
C        JAMAX - NUMBER OF SAMPLES IN EACH N-S STRIP
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
$IBFTC SUB2     DECK
      SUBROUTINE BSORT (XXN,XXE,CCO,N)
      COMMON XE(1800),XXE(800),XXXE(200),XLOCE(1000),XN(1800),XXN(800),X
     1XXN(200),YLOCN(1000),CO(1800),CCO(800),CCCO(200),RMEAN(1000),RVAR(
     21000),RSD(1000),VRAT(1000),ANOM(1000),II(200),JJ(200)
C
C              ARRANGES SAMPLES IN EACH NORTH-SOUTH STRIP FROM MOST NOR-
C              THERLY (MAXIMUM Y-COORDINATE) TO MOST SOUTHERLY (MINIMUM
C              Y COORDINATE)
C              COMPARISON BEGINS WITH  N=JAMAX , BUT N IS SEQUENTIALLY
C              REDUCED BY 1 UNTIL N=0
C
  722 DO721 I=1,N
      IF(XXN(I).GE.XXN(I+1))GOTO 721
      A=XXN(I+1)
      XXN(I+1)=XXN(I)
      XXN(I)=A
      B=XXE(I+1)
      XXE(I+1)=XXE(I)
      XXE(I)=B
      Z=CCO(I+1)
      CCO(I+1)=CCO(I)
      CCO(I)=Z
  721 CONTINUE
      N=N-1
      IF(N.LE.1)GOTO730
      GOTO722
  730 RETURN
      END
C
C
C
C
C
C     RESID
C     TITLE -
C        TAKES THE ALL THE DEVIATIONS  OF THE INDIVIDUAL SAMPLES FROM
C        THOSE MOVING AVERAGES  WHOSE COMPOSITION THEY INFLUENCED,AND
C        CALCULATE THE MEAN DEVIATION EXPRESSED IN SUB AREA STANDARD
C        DEVIATION UNITS
C     KEY WORDS -
C        MAP ANALYSIS
C     LANGUAGE,COMPUTER,DATE -
C        FORTRAN IV  IBM026 48CHAR SET,IMPERIAL COLLEGE IBM 7094,JUN1969

C     AUTHOR -
C        J.KHALEELEE,APPLIED GEOCHEMISTRY RESEARCH GROUP,IMPERIAL COLL
C     USAGE -
C        CALL RESID(MAXRES,PLOTD,IMAX)
C     ARGUMENTS -
C        MAXRES - TOTAL NUMBER OF SAMPLE DEVIATIONS FROM MOVING ACERAGES
C        PLOTD - CALCOMP PLOT OPTION FOR RESIDUAL VALUES
C        IMAX - TOTAL NUMBER OF SAMPLES
```

```
C
C * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * * *
$IBFTC SUB3     DECK
      SUBROUTINE RESID(MAXRES,PLOTD,IMAX)
      COMMON XE(1800),XXE(800),XXXE(200),XLOCE(1000),XN(1800),XXN(800),X
     1XXN(200),YLOCN(1000),CO(1800),CCO(800),CCCO(200),RMEAN(1000),RVAR(
     21000),RSD(1000),VRAT(1000),ANOM(1000),II(200),JJ(200)
C
C     DIMENSION ARRAY CODING -
C         COORD - CONDENCED X- AND Y- COORDINATES FORMED INTO AN 8 DIGIT
C                 NUMBER
C         RESIDU - RESIDUAL VALUES FOR ALL SAMPLES AND ALL MOVING AVERAGES
C         X - X-COORDINATE LOCATIONS FOR CONDENSED RESIDUALS
C         Y - Y-COORDINATE LOCATIONS FOR CONDENSED RESIDUALS
C         D - CONDENSED RESIDUAL VALUES
C         TITLE - RESIDUAL CALCOMP PLOT TITLE
C
      DIMENSION COORD(7000),RESIDU(7000)
      DIMENSION X(2500),Y(2500),D(2500)
      DIMENSION TITLE(13)
      EQUIVALENCE(COORD(1),XE(1)),(RESIDU(1),CO(1))
      EQUIVALENCE (X(1),COORD(1)),(Y(1),COORD(3501)),(D(1),RESIDU(1))
C
C              ZERO SUMMATION REGISTERS
C
      SUMD=C.00000000
      SUMDSQ=0.00000000
      TOPNUM=MAXRES
      WRITE(6,1000)IMAX,MAXRES
 1000 FORMAT(1H1,5HIMAX=,I6,10X,7HMAXRES=,I6)
C
C              READ IN RESIDUAL DATA FROM TAPE UNIT 1
C
      DO 1 I=1,MAXRES
      READ(1) COORD(I),RESIDU(I),RESSQ
      WRITE(6,16)COORD(I),RESIDU(I),RESSQ
   16 FORMAT(1H ,3F15.4)
C
C              COMPUTE SUMS AND SUMS OF SQUARES OF RESIDUALS
C
      SUMDSQ=SUMDSQ+RESSQ
    1 SUMD=SUMD+RESIDU(I)
      REWIND 1
C
C              CALCULATE RESIDUAL VARIANCE
C
      RESVAR=SUMDSQ/TOPNUM
      WRITE(6,2)SUMD,SUMDSQ,TOPNUM,RESVAR
    2 FORMAT(1H1,18HSUM OF DEVIATIONS=,F12.4,/1X,15HSUM OF SQUARES=,F12.
     14,/1X,26HTOTAL NUMBER OF RESIDUALS=,F6.0,/1X,18HRESIDUAL VARIANCE=
     2,F10.3)
C
C              AVERAGE RESIDUALS PERTAINING TO EACH  SAMPLE
C
      DO 5 I=1,MAXRES
      DUP=1.
      M=I+1
      DO 4 J=M,MAXRES
      IF(COORD(I).EQ.COORD(J))DUP=DUP+1.
```

```
      IF(COORD(I).EQ.COORD(J))RESIDU(I)=RESIDU(I)+RESIDU(J)
      IF(COORD(I).EQ.COORD(J))RESIDU(J)=0.0000
      IF(COORD(I).EQ.COORD(J))COORD(J)=0.0000
    4 CONTINUE
      RESIDU(I)=RESIDU(I)/DUP
    5 CONTINUE
      K=0
      DO 6 I=1,MAXRES
      IF(COORD(I).LE.0.)GO TO 6
      K=K+1
      COORD(K)=COORD(I)
      RESIDU(K)=RESIDU(I)
    6 CONTINUE
      COUNT=K
      WRITE(6,18)IMAX,COUNT
   18 FORMAT(1H1,33HTOTAL NUMBER OF SAMPLE LOCATIONS=,I6,25HCONDENSED RE
     1SIDUE NUMBER=,F6.0)
C
C               CHECK FOR RESIDUAL CALCOMP PLOT OPTION
C
      IF(PLOTD)8,8,9
C
C               READ IN CALCOMP PLOT CONTROL PARAMETERS
C
    9 READ(5, 10)AXISE,AXISN,SIZEN,SIZET,TITLEX,TITLEY,XMIN,XINT,YMIN,YI
     1NT,PLUS,NUMLET,NUMDEC
   10 FORMAT(11F6.2,2I6)
C
C               SET MAP AREA LIMITS
C
      XMAX=(AXISE*XINT)+XMIN
      YMAX=(AXISN*YINT)+YMIN
C
C               STORE MAP ORIGIN AND SCALE DATA
C
      X(IMAX+1)=XMIN
      X(IMAX+2)=XINT
      Y(IMAX+1)=YMIN
      Y(IMAX+2)=YINT
C
C               CALCULATE ROUND OFF INCREMENT
C
      XUMDEC=NUMDEC
      FACTOR=0.5/(10.0**XUMDEC)
C
C               DRAW MAP AXES
C
      CALL AXIS(0.0,0.0,19HEASTING COORDINATES,-19,AXISE,0.0,X(IMAX+1),X
     1(IMAX+2))
      CALL AXIS(0.0,0.0,20HNORTHING COORDINATES,20,AXISN,90.0,Y(IMAX+1),
     1Y(IMAX+2))
C
C               READ RESIDUAL CALCOMP PLOT TITLE
C
      READ(5,11)(TITLE(I),I=1,13)
   11 FORMAT(13A6)
C
C               WRITE RESIDUAL CALCOMP PLOT TITLE
C
```

```
      CALL SYMBOL(TITLEX,TITLEY,SIZET,TITLE,0.0,NUMLET)
C
C             DIVIDE COORD VALUES INTO THE TWO CONSTITUENT X- AND Y-
C             COORDINATES
C
      DO 12 I=1,K
      COSTOR=COORD(I)
      IPOS=COORD(I)/10000.
      X(I)=IPOS
      Y(I)=COSTOR-(X(I)*10000.)
      WRITE(6,616)X(I),Y(I),D(I),COSTOR
  616 FORMAT(1H ,4F15.4)
   12 CONTINUE
C
C             CHECK RESIDUALS FALL WITHIN MAP AREA
C
      DO 13 I=1,K
      IF(X(I).LT.XMIN.OR.X(I).GT.XMAX)GO TO 13
      IF(Y(I).LT.YMIN.OR.Y(I).GT.YMAX)GO TO 13
      XX=((X(I)-X(IMAX+1))/X(IMAX+2))
      YY=((Y(I)-Y(IMAX+1))/Y(IMAX+2))
      IF(D(I))14,14,15
C
C             ROUND OFF AND PLOT RESIDUAL VALUES
C
   14 FACTOR=-FACTOR
   15 FPN =D(I)+FACTOR+PLUS
      CALL NUMBER(XX,YY,SIZEN,FPN,0.0,NUMDEC)
   13 CONTINUE
C
C             MOVE CALCOMP TO NEXT MAP ORIGIN
C
      ORIGIN=AXISE+4.
      CALL PLOT(ORIGIN,0.0,-3)
    8 RETURN
      END
```