Factors Controlling the Surficial Dispersion of Arsenic, Antimony, Bismuth and Selenium from Mineral Deposits in the British Isles

by

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ABSTRACT

This research investigates the cost effective uses of arsenic, antimony, bismuth and selenium as pathfinder elements in geochemical exploration by establishing the controls on their secondary dispersion in soils and drainage sediments. Sensitive and precise determination of these elements in geochemical samples (rapidly and routinely) is made possible by advances in analytical methodology, whereby their volatile hydrides are generated and flushed into an inductively coupled plasma emission spectrometer.

A background study of stream sediments from south-west England confirms that the distribution of arsenic, bismuth and selenium is correlatable with bedrock geology but scavenging, of arsenic by ferric oxides and selenium by organic matter, is locally important. All the elements are relatively enriched in fine grained (reducing) clastic sediments although bismuth is most abundant in granitic intrusives.

Detailed studies of 14 mineral deposits in the British Isles indicate the exploration effectiveness of these pathfinders. Selenium (with arsenic and antimony) is useful in the location of nickel deposits at Arthrath, Scotland. Bismuth and arsenic pick out the tungsten deposits at Ballinglen, Ireland and polymetallic uraniferous veins at Dalbeattie, Scotland. The Kuroko-type deposit at Avoca, Ireland shows distinct zonation from base to top of bismuth, arsenic and antimony with bismuth associated with the copper zone and antimony with the lead-zinc rich zone. Antimony is a good pathfinder for two Irish style base metal deposits (Keel and Mallow, Ireland) and arsenic for vein gold deposits (Clontibret, Ireland).

In the surficial environment, arsenic and selenium

are potentially mobile while bismuth shows limited mobility and antimony is almost immobile. The mobilities of arsenic and selenium are inhibited by accumulation at geochemical barriers: both by ferric oxides; and for selenium by organic matter.

Arsenic can be recommended for regional and detailed geochemical surveys in temperate terrains but care must be taken to note areas of iron scavenging. Antimony and bismuth are best applied in detailed prospecting with deep sampling much more effective for antimony in areas of moderate to thick overburden. Selenium has very restricted utility in temperate terrains as a result of its affinity for organic matter. All four pathfinders are effective in lateritised areas, where transition metals are particularly prone to leaching.

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Part I :
Introduction and Review of Primary Pathfinder Concentrations

CHAPTER 1 INTRODUCTION

1.1 Aims

The objective of this research is to test the cost effective uses of the pathfinder elements arsenic, antimony, bismuth and selenium in geochemical prospecting. This is best achieved by understanding the fundamental controls on their dispersion and concentration.

1.2 'Why Use Pathfinder Geochemistry ?'

A pathfinder element is defined, for the purposes of this thesis, as an element which occurs in close proximity to the ore element(s) sought but which forms a more extensive halo, is concentrated in the surficial environment or is more easily analysed than the ore element(s). The pathfinder elements, arsenic, antimony, bismuth, selenium (the pathfinders), considered in this research are strongly concentrated in a broad spectrum of sulphide deposits (Fig. 1.1).

Successful prospecting requires the discovery of orebodies at minimum cost. The realities of exploration - particularly the attractions of exploring in industrialised countries - dictate that success is often the result of the application of superior, mainly geological, skills. Pathfinder geochemistry has the potential, which will be demonstrated in this thesis, for resolving complex geochemical anomalies and for discovering blind orebodies.

Recent advances in analytical geochemistry have made possible the determination of background levels of the pathfinders, economically and with good precision and accuracy.

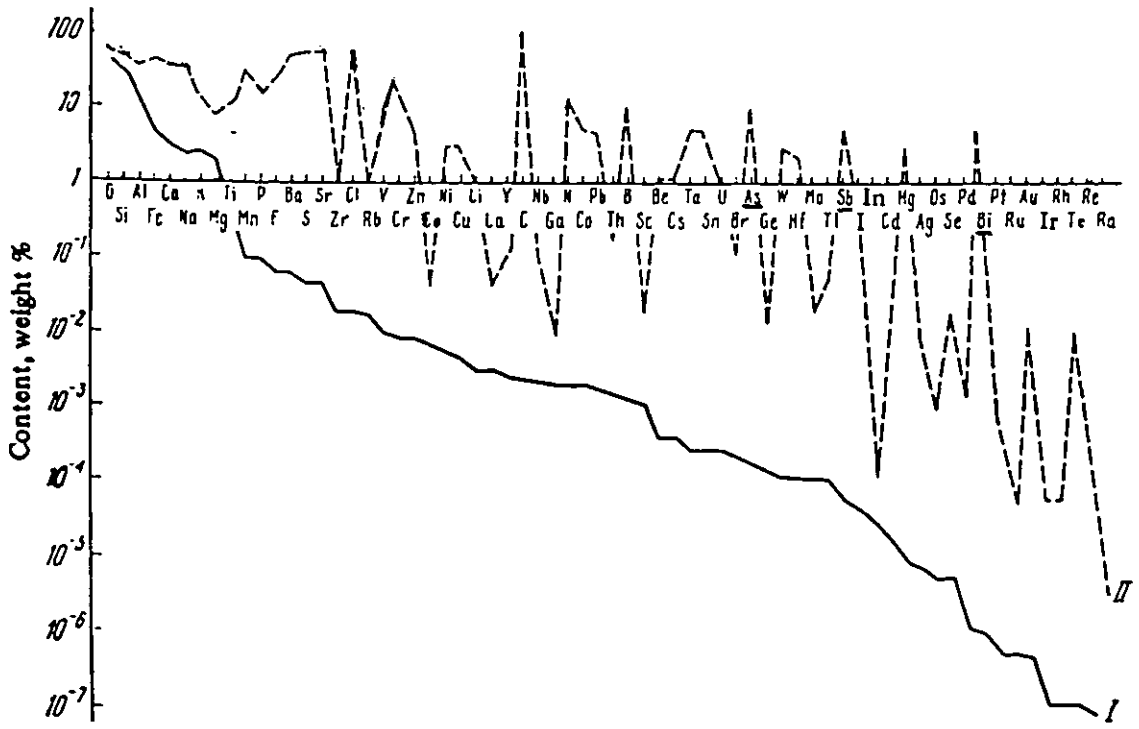


Fig 1.1 Average concentration of elements in the lithosphere (I) and in high grade ores (II) from Perel'man (1977)
Note that Arsenic, Antimony and Bismuth form distinct peaks in curve II

1.3 Approach of this Study

Surficial dispersion involves the interaction of a number of complex variables, both chemical and physical. It is not yet possible to realistically model pathfinder dispersion because of these complexities and the lack of basic data on the aqueous chemistry of some of the elements.

The alternative, and to some extent complementary, approach of detailed studies of areas enriched in pathfinders was therefore adopted. The areas were selected as

(i) having ore grade or close to ore grade concentrations of metals;
(ii) representative of a deposit type;
(iii) known or likely pathfinder concentrations;
(iv) relatively uncontaminated by mining.

In addition a study of a large background area (South West England) is presented. Soils, stream sediments and waters are the main media used in surficial geochemical exploration and in this research. Rock geochemistry is not comprehensively investigated in all of the areas but sufficient information is generally available to make some informed estimate of the extent of primary concentration.

The results from the detailed studies are here collated, summarised and conclusions made. It is then possible to compare these conclusions with the theoretical data, to suggest how the pathfinders may behave in various environments and their most cost effective uses.

1.4 Arrangement of this Thesis

This reflects the approach to the problem and is

divided into three parts:

I Chapters 1-2 : Introduction and a review of primary concentrations

II Chapters 3-7 : Regional and detailed studies - a summary of the type of samples studied is given in Table 1.1 and the locations of the areas are shown in Fig. 1.2

III Chapters 8-9 : Conclusions from the detailed studies, a comparison with theoretical models of surficial dispersion, suggestions for the cost effective use of pathfinder geochemistry and future research.

1.5 Field and Laboratory Procedures

1.5.1 Sampling Methods

Reconnaissance soil sampling was undertaken with hand augers and samples collected in Kraft paper bags. 'Cobra' samples were taken using a Cobra petrol-driven percussion drill fitted with standard (1" diameter) steel rods and a Holman 'thru-flow' sampler. Samples were prised out with a hard steel screw driver. Detailed investigations at Dalbeattie (Chapter 4.1) demonstrate that the -190μm fraction is the most effective practical fraction for maximum anomaly/background contrast and this was used throughout. Samples were sieved through nylon sieves after air drying at 50°C. Any fractions >190μm were crushed in agate pots, using a tema mill.

Active stream sediment was grab sampled with polythene containers and collected in Kraft bags. Preparation was similar to the soils. No systematic attempt was made to compare panned concentrate samples with grab samples.

Water samples (1 litre) were collected in acid rinsed hard polyethylene bottles. The samples were vacuum

Table 1.1 Summary of deposits sampled and sample type

Area (Deposit Type)	Rock	Surface Soil	'Cobra' Till Profiling	Stream Sediments	Stream Water
Arthrath (Ni-Cu)		X	X	O	
Avoca (Cu-pyrite)	O	X	X		
Ballinglen (W-Sn)	O	X	X	X	X
Burley Wood* ((Pb-Zn))		X		O	O
Clontibret (Au)		X		X	
Dalbeattie (U)	O	X			
Glendinning (Sb)		X		X	X
Keel (Zn-Pb)		X	X	O	O
Kilmelford (Cu)	O	X		X	O
Maudlin* (Sn-W)				O	O
Mallow (Cu-Ag)		X			
Marl Slate* ((Zn))	O	X			
Matlock* (Ba-F)		X			
Meall Mor (Cu)	O	X		X	O
South West England (Background)				X	

O Limited Survey X Extensive Survey

* These areas are not discussed in detail due to extensive contamination (Matlock, Maudlin) or low metal grade (Burley Wood, Marl Slate)

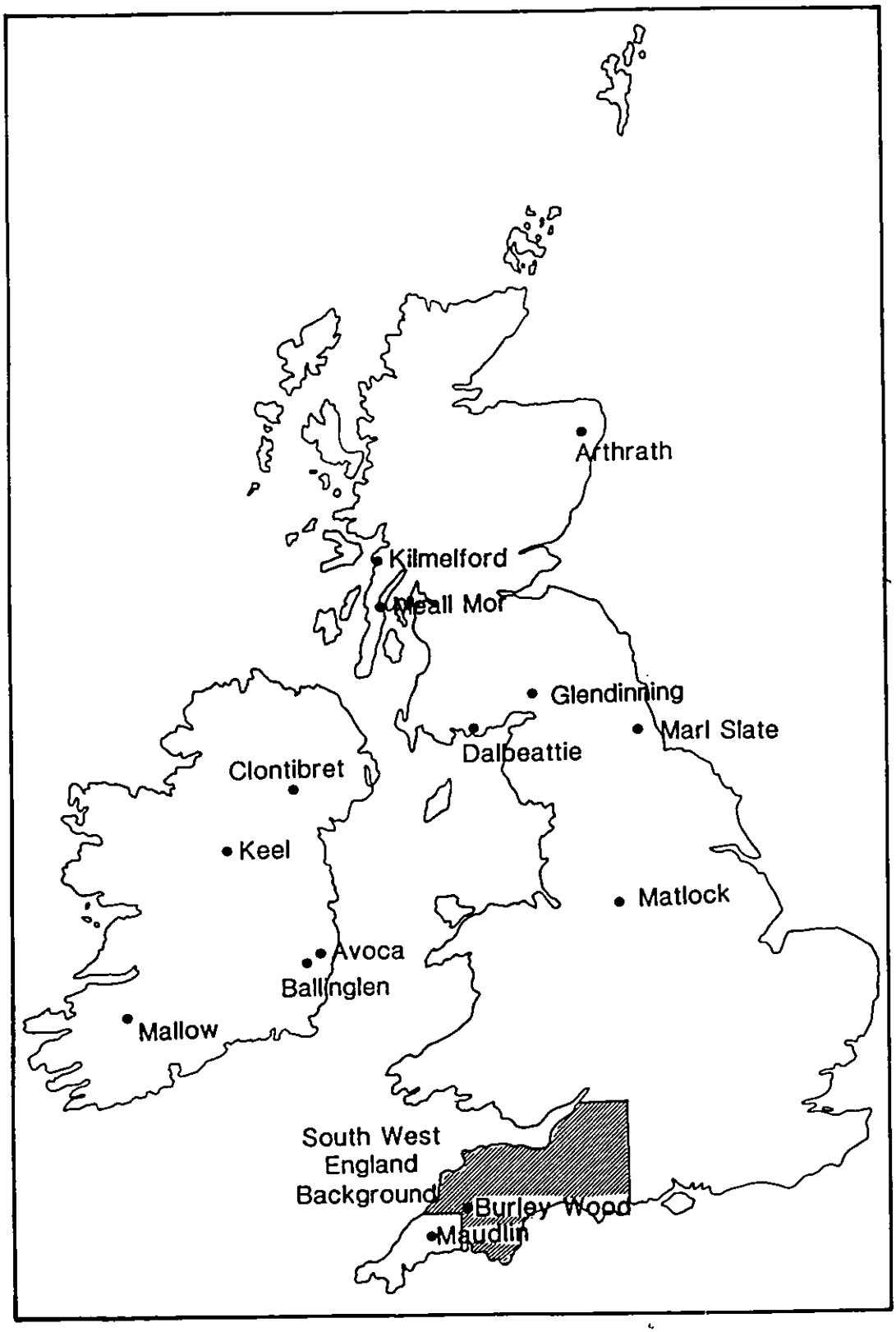


Fig 1.2 Location of field areas in the British Isles

microfiltered through 0.45 μm cellulose nitrate filters within 24 hours of collection. The filtered waters were acidified with 5 ml of Aristar HCl to prevent trace element loss. Other, smaller samples were collected for anion and pH determination in the field.

Rock samples are mainly composite chip samples at outcrop or grab samples of selected rocks. They were broken into small fragments and pulverized in an agate pot (tungsten carbide for sulphides) tema mill.

1.5.2 Analytical Techniques

Samples were analysed for pathfinders, ore metals and elements/anions which were thought to potentially control pathfinder dispersion.

Solid samples were analyzed by two methods (Pahlavanpour et al 1980a, Pahlavanpour et al 1980b). They both involve the generation of pathfinder hydrides from a solution containing the elements in a reduced state (As^{+3}, Sb^{+3}, Bi^{+3}, Se^{+4}). The hydrides are then flushed into an inductively coupled plasma emission spectrometer (ICP) by argon carrier gas.

The first method (magnesium nitrate attack) is accurate and precise for arsenic, antimony and bismuth. The sample pulp is wet ashed with magnesium nitrate at 450°C, taken up in concentrated HCl and reduced with KI (For details see Appendix 1).

In the second method (coprecipitation method), a sample is attacked by 2:1 $HNO_3/HClO_4$, leached into HCl, co-precipitated with ammonia and $La(NO_3)_2$ solution to remove interfering transition metal ions, and reduced with KBr. This is accurate and precise for selenium and precise (although slightly inaccurate, dependent on dissolution temperature) for arsenic and bismuth.

Other elements in solid sediments were determined by nebulisation into the ICP or into an atomic absorption spectrophotometer (AAS) after a 2:1 $HNO_3/HClO_4$ attack followed by uptake in HCl. A few samples, early in the project, were attacked by HNO_3 (specifically noted in the text). Organic carbon was determined as CO_2 by gas chromatography following a chromic acid/sulphuric acid/ hydrogen peroxide attack in a sealed vessel.

Water samples and particulates were analysed for pathfinders in an analagous manner to the solids. Waters were analyzed by lanthanum nitrate/ammonia co-precipitation method and uptake in HCl/KI (Thompson et al, 1981) or by direct introduction of the waters into the ICP with HCl/KI. Particulates were analysed by shaking the filter papers with concentrated HCl and reduction with KI. Water samples were analysed for metals/major elements after concentration by evaporation,and for anions by titration; pH determinations were made with a glass electrode.

1.5.3 Quality Control of Analytical Data

This is vitally important to any geochemical project and was planned according to standard practice guidelines at the Applied Geochemistry Research Group (A.G.R.G.). With solid samples quality was maintained by the incorporation in each batch (usually about 100 samples) of 4% reference materials, 10% duplicates and 4% reagent blanks. Results were carefully monitored and any batches that significantly deviated from acceptable accuracy and/or precision were rejected. Overall precision is 16-20% for the co-precipitation method and 12-15% for the magnesium nitrate attack on solids. Similar precisions were obtained for the determination of general elements. Waters samples were only subject to scrutiny for precision as no reference waters were available: typical precision is 20% for hydrides and 30% for general

elements.

The quality control system has been computerised (10.81) and only quality controlled results are accessible from the system (termed QUTE).

1.6 Data Handling

All data were entered on to the Imperial College mainframe (CDC 6500/Cyber 174) initially by hand from hard copy output from analytical instruments, but subsequently via diskreaders from floppy disks generated by the microcomputer dedicated to the ICP.

The data is stored on magnetic tapes using UPDATE format.

Initial investigation of the data utilised the MINITAB package available at Imperial College; and the GIRAF interactive histogram and distribution dissection programme (written by S. Earle but based on Sinclair 1976). Multivariate data analysis utilised the PCA (Principal Component Analysis) programme written by S. Mancey and R. Howarth. Plotting on microfilm (KPLOT7) and hard copy (KPLOT8) utilised the general purpose plotting programmes written by M. Wheatley.

CHAPTER 2 PRIMARY DISPERSION AND CONCENTRATION - A REVIEW

All the pathfinder metalloids used here are chalcophile (Goldschmidt, 1954) and concentrated in sulphide deposits. Arsenic, antimony and bismuth belong to Group 5 of the Periodic Table. Selenium is significantly different from the other pathfinders as it is a member of Group 6 of the Periodic Table and generally substitutes isomorphously for sulphur rather than forming independent minerals.

The pathfinders have considerable similarities in chemistry, notably their variable valencies (mainly 0, 3^+, 5^+ for Group 5 and 0, 4^+, 6^+, for Group 6). There are systematic variations in the chemistry within the Group 5 pathfinders, particularly increasing metallic and cationic properties with increasing atomic number. These are also reflected in the decreasing stability of higher valency states (Bi^{5+} is probably absent from surficial environments) and anionic complexes (bismuth complexes are not stable in aqueous solution).

The terminology used in this thesis is that propounded by Russian geochemists (Beus and Grigorian, 1977). Dispersion is the deviation from the crustal average (Clarke) toward the lower values as opposed to concentration where values are higher than the Clarke.

2.1 Primary Distribution : Background/Geochemical Cycles

2.1.1 Background Geochemical Cycles

A compilation of data (Table 2.1) gives an empirical idea of the geochemical behaviour of the pathfinders. The quality of these data is variable and that of antimony should be treated with some scepticism.

The main conclusions are the great similarities between the relative abundances of arsenic and antimony

Table 2.1 Average Abundances (ppm) of Pathfinders in Various Lithologies

	As	Sb	Bi	Se
Ultramafic	2.0	0.1	0.02	0.07
Basalt	1.0	0.1	0.03	0.08
Gabbro	1.5	0.1	0.03	0.15
Andesite	2.0	0.2	0.07	0.01
Granite	1.5	0.2	0.2	0.05
Rhyolite	4	-	0.05	0.14
Syenite	-	-	0.04	0.04
Mica Schist	6	1.0	0.14	0.19
Shale	13	1.5	0.13	0.5
Black Shale	30(?)	30 (?)	0.5	5
Limestone	1.0	0.3	0.03	0.03
Sandstone	2.0	1.0	0.05	0.01
Coal	20	<40	3 (?)	5
Clarke	1.8	0.2 (?)	0.08	0.05

- not available.

Based on Wedepohl (1969) with additional data for Se from Koljonnen (1975) and for Bi from Heinrichs et al (1980)

and to some extent selenium, which contrast with those of bismuth. Arsenic and antimony are significantly concentrated in fine grained clastic sediments relative to igneous rocks. This pattern is repeated for selenium but it has a stronger affinity for fine grained sediments than arsenic or antimony (which may be concentrated in coarser clastic sediments). Bismuth, on the other hand, although displaying some concentration in fine grained sediments, is most abundant in granitic rocks.

The overall geochemical balance, with greater amounts of arsenic, antimony and selenium in sediments than could be derived from igneous rocks, has led to the suggestion (Wedepohl, 1969; Onishi and Sandell, 1955) that significant amounts of these elements are contributed from hot springs (which are significantly enriched in these elements). To this might be added the input from the atmosphere. Indeed, fluxes of these pathfinders from the atmosphere are of the same order of magnitude as stream loads (Läntzky and MacKensie, 1979). All three elements are significantly concentrated due to release from volcanic exhalations and, probably, biological methylation (Chapter 8.1).

2.1.2 Background Distribution in Igneous Rocks

The key feature of pathfinder behaviour in magmas is their concentration in residual fluids (Chapter 2.2).

Detailed studies of the behaviour of pathfinders in magmas, particularly in the Skaergaard Complex, show some differences between the elements. The order of increasing concentration in rock forming minerals is Se Bi As Sb. This appears to be mainly controlled by ionic size and, thus, substitutions in different sites in rock forming minerals. As^{3+} probably substitutes for Fe^{3+}, Ti^{4+} and Al^{3+} whereas As^{5+} substitutes for Al^{3+} or Si^{4+} (Esson et al, 1963).

Antimony enters into early stage magnesian olivines and Sb^{3+} can substitute for Fe^{2+} in silicates and oxide minerals (particularly magnetite). It has been hypothesisied that Bi^{3+} substitutes for Ca^{2+} in igneous rocks but is probably associated with minor sulphides in sphene, apatite and rare earth minerals (Greenland et al, 1973; Heinrich et al, 1980).

2.1.3 Background Distribution in Sedimentary Rocks

Background concentrations of all the pathfinders are probably mainly contained in minor sulphides or sorbed on to organic materials (Wedepohl, 1969). Thus, high concentrations are observed in organic rich fine grained clastic sediments and shales. Arsenic and antimony, in addition, may be sorbed by oxidised iron-rich sediment.

The mechanisms involved are the same as those of surficial dispersion and these are discussed in detail in Chapter 8.1.

2.2 Primary Concentration and Ore Deposition

Concentrations of pathfinders occur in a wide variety of ore environments (summary in Table 2.2) as a result of a number of mechanisms. The most important are: segregation from magmas; complexation, transport in, and deposition from hydrothermal fluids; and sorption and reduction from oxy-anionic complexes at low temperatures.

2.2.1 Selenium and the Problem of S/Se Ratios

Significant selenium concentrations are known from six main environments: copper-nickel sulphides associated with basic/ultramafic rocks; precious metal-uranium veins;

Table 2.2 Summary of Pathfinder Occurrences in some Major Ore Types (mainly after Boyle 1974)

	As	Sb	Bi	Se
Magmatic Segregation Ni-Cu-(Pt)	X	O		X
Porphyry Cu-Mo	O		O	O
Greisen Sn-W	X		X	
Skarn (Zn)(W)	X		X	
Massive Sulphide	X	X	X	O
Vein (Ag)(U)	X	X	O	O
Vein Au (Te)	X	X	O	O
Disseminated Au	X	X		O
Vein Hg	X	X		O
Clastic hosted Cu/Pb/Zn	O	O	O	X
Carbonate Pb Zn (Cu)	O	O		
Unconformity U	O			O
Sandstone U	O			X
Conglomerate Au (U)	O			

O May Be Locally Important

X Important Pathfinder Application

massive sulphides (particularly those in ophiolites); stratiform copper-zinc deposits associated with sapropelites; uranium deposits in clastic sediments; and Recent fumaroles/mercury deposits.

Much of the selenium commercially produced at the present is derived from the by-products of nickel smelting. The ores of the gabbroic deposits at Sudbury, Ontario and the Noril'sk region of the U.S.S.R. are particularly enriched. Both these deposits, and most other nickel deposits, are thought to have been formed by the segregation of sulphide rich liquids from magmas. The mineral assemblages, with the predominance of pyrrhotite, suggests a relative deficiency of sulphur in the system.

Investigation of deposits at Noril'sk by Zainullin and Pashinkin (1963) suggests that selenium is directly associated with the nickel (pentlandite) - copper (chalcopyrite) phases and may be present as microinclusions of selenides ($\pm$ Fe, Sb, Bi, Te, Sn) rather than in solid solution. The content in the ore averages 30-200 ppm Se.

Data from Western Australia and Canada (Naldrett, 1981) suggests that nickel deposits associated with ultramafic rocks are also enriched with 15-150 ppm Se.

There is no comprehensive review of selenium in massive sulphides but certain deposits e.g. Boliden, Cyprus are anomalously rich (up to several percent Se in sulphides). Russian investigations (Yushko-Zakharova et al, 1978) suggest that selenium is present as an isomorphous substitution for sulphur.

Selenides are associated with some vein deposits of silver/cobalt/uranium e.g. Freiberg, G.D.R.; Beaverlodge, Canada and Shinkolobwe, Zaire (Rich et al, 1977). These selenides are a minor phase and by no means universally associated with deposits of this type. The type of alteration and controls suggest that they were deposited

under relatively low temperature reducing conditions.

Porphyry copper deposits contain minor concentrations of selenium which are apparently concentrated at the contact of the potassic and phyllic alteration zones (Chaffee, 1981).

Selenium enrichments are a feature of sulphur rich fumaroles with concentrations reaching 5000 ppm Se (Stanton, 1972). Some mercury deposits of epigenetic origin are also enriched (Smirnov, 1977).

The uranium-vanadium deposits of the Colorado Plateau and Wyoming have long been known to have high selenium contents. They are associated with local reducing environments generated by syngenetic organic matter or roll front mechanisms (. Nash et al, 1981). In the latter type selenium is zoned relative to the other metals and is slightly up dip (higher Eh) from uranium and/or vanadium concentrations. The roll front reflects the gradual down dip movement of oxidising alkaline solutions which transport the ore metals and pathfinders as anionic complexes and deposit them according to the requisite oxidation potential. The occurrence of selenium in the deposits is probably also related to a regional enrichment in selenium and by no means all sandstone uranium deposits are enriched. Typical concentrations range up to several thousand ppm Se with the element present as native selenium and ferroselite.

Selenium is concentrated in black shale environments together with other metals. The exact mechanism is unclear (Chapter 8.1) but is probably a combination of organic sorption and reduction with the incorporation of up to 4% Se in the pyrite lattice. High values are reported from Kupferscheifer, particularly the relatively unaltered deposits in East Germany, where selenium is associated with copper (2%), lead and zinc. Typical values are 10-60 ppm Se with concentrations in early phase (?)

syngenetic copper minerals (Jung et al, 1973). Selenium is associated with 'tar' shales in the Polish Lubin deposit (Wojciechowska and Serkies, 1968). High values (20 ppm Se) can also be found in low grade mineralization (0.1% Zn) of the Marl Slate in northern England. There is a strong correlation of copper ore grade with organic matter in the Kupferscheifer but neither this relationship nor the high selenium values is repeated in other deposits (Gustafson and Williams, 1981).

a) Sulphur/Selenium ratios

Sulphur/selenium ratios in sulphides and sulphur have been proposed as an indicator of the temperature of origin of deposits. High ratios are characteristic of deposits of sedimentary origin and low ratios in those of igneous/hydrothermal derivation (Goldschmidt, 1954; Edwards and Carlos, 1954). More recent work, notably that of Stanton (1972) suggests a number of local controls on this ratio, particularly the regional abundance of selenium. Detailed consideration of the thermodynamics of the system (Yamamoto, 1976) demonstrates that the ratio is also controlled by the availability of sulphur and selenium, pH, oxygen fugacity and the presence absence of native selenium. The S/Se ratio is, however, proportional to temperature given fixed pH, absence of native selenium and constant S, Se.

Some indication of background concentration of selenium in sulphides can be recalculated from reported S/Se ratio. Typical values range from 1 ppm Se (ratio 80,000 - 100,000) for sedimentary pyrite through 40 ppm Se (8,000) for magmatic sulphides to 5,000 ppm Se (200) for volcanic sulphur (Stanton, 1972). Typical values of (3,000) for the Kupferscheifer ores indicate the effect that concentration mechanisms may have.

2.2.2 Arsenic - A Universal Pathfinder ?

Arsenic is the most abundant of the four pathfinders and has been recognised in a wide variety of environments.

A key feature of the element's geochemistry is its occurrence in five main mineral types summarised in Table 2.3.

Table 2.3 Grouping of Arsenic Minerals

Mineral Type	Typical Mineral	Association
Native Arsenic		(?) Low Temperature very reducing conditions rare
Arsenides	Lollingite ($FeAs_2$) Niccolite ($Ni_{1\pm x}As$)	Low-Medium Temperature veins/disseminations ? Sulphur Deficient
Iron-Arsenic-sulphides	Arsenopyrite (FeAsS)	Wide range - the main arsenic mineral
Arsenic sulphides	Realgar (AsS) Orpiment (As_2S_3)	Epithermal deposits Fumaroles
Sulphosalts (contain TS_3, T=As, Sb, Bi groups)	Tennantite ($Cu_{12+x}As_{4+y}S_{13}$)	Wide range but later (lower temperature) than arsenopyrite
Arsenates	Scorodite ($Fe(AsO_4).2H_2O$) Erythrite ($Co_3(AsO_4)_2.8H_2O$)	Low temperature oxidising deposits

There seem to be four main (probably overlapping) mechanisms of concentration: segregation into volatile phases from magmas; transport as and deposition from hydrothermal complexes; low temperature reduction and/or

organic sorption; and sorption on to iron oxides/oxy-hydroxides. Few data are available on the form of complexes in hydrothermal solution (Barnes, 1979) and the exact transport mechanisms are a matter of speculation.

Arsenic is concentrated in a similar manner to selenium in basic-ultramafic magmas but forms discrete minerals. Platinum arsenide (sperrylite) is, for example, a minor component of the Merensky Reef mineralization. There is a more consistent enrichment (100 ppm average) in Komatiite-associated nickel deposits than those of gabbroic association, (Naldrett, 1981).

High arsenic concentrations (up to percentages) are associated with mineralization derived from granitic magmas. Anomalous concentrations in tin-tungsten ores and skarns, contrast with the variable concentrations in porphyry copper-molybdenum deposits. It is not clear to what degree this is due to the recycling of high arsenic shales by the anatexis involved in the formation of S-type granites. A well documented example of distribution around mineralised plutons is that of South West England. Arsenic forms broad haloes around the plutons but much higher concentrations are hosted by the discrete vein structures. These veins show considerable temperature-derived zoning with the hypothetical mono-ascendent zonation scheme of Dines (1956) and Hosking (1964) having an extensive arsenic zone, ranging from the lower greisen sheet Sn-W veins to the copper rich structures. The mineralogy is dominantly arsenopyrite with some early stage lollingite. Arsenic concentrations (as arsenides) are also present in lower temperature veins associated with cobalt^{+}-nickel^{+}-uranium. There does not appear to be a specific sulphosalt zone in South West England. A sulphosalt zone is, however, developed at Zeehan, Tasmania (Stanton, 1972).

Volcanic-associated massive sulphides are often enriched in arsenic and it can form extensive haloes (*XOO*m) in sediments and exhalites overlying the deposits (Scott et al, 1982). Again there is evidence of a separation of arsenic into two mineral phases and two zones - an earlier arsenopyrite phase and a later sulphosalt phase (Beus and Grigorian, 1977) and this is discussed in detail in Chapter 6.1 Typical values are several hundred ppm As.

Base metal sulphides in carbonates are often enriched in arsenic which is contained mainly in sulphosalts (e.g. Irish deposits discussed in Chapter 7) but arsenic concentrations in the brecciaform type are not enriched (Boyle and Jonasson, 1973).

The element is concentrated in some types of sandstone uranium deposits, particularly the tabular types where concentrations reach hundreds of ppm As. This is due to sorption by organic matter or reduction by organically produced hydrogen sulphide.

The Kupferscheifer ore shows localised concentration averaging 200 ppm (Fig. 2.1) but concentrations in many stratiform deposits are near the Clarke.

The sorption of arsenic by iron oxides (Chapter 8.1) leads to enrichments in oolitic iron ores, at least locally, with concentrations reaching 500 ppm.

One of the key features of the exploration geochemical application of arsenic is its almost universal enrichment in hypogene gold deposits (Boyle, 1979). It seems possible that the two elements may be transported together in complexes of the $Au(AsS_3)^{2-}$ type but arsenic sulphides (associated with epithermal deposits) are, in any case, very soluble at low temperatures (<200 C) where S^{2-} and HS^- are the dominant ions (Barnes and Czamanske, 1967).

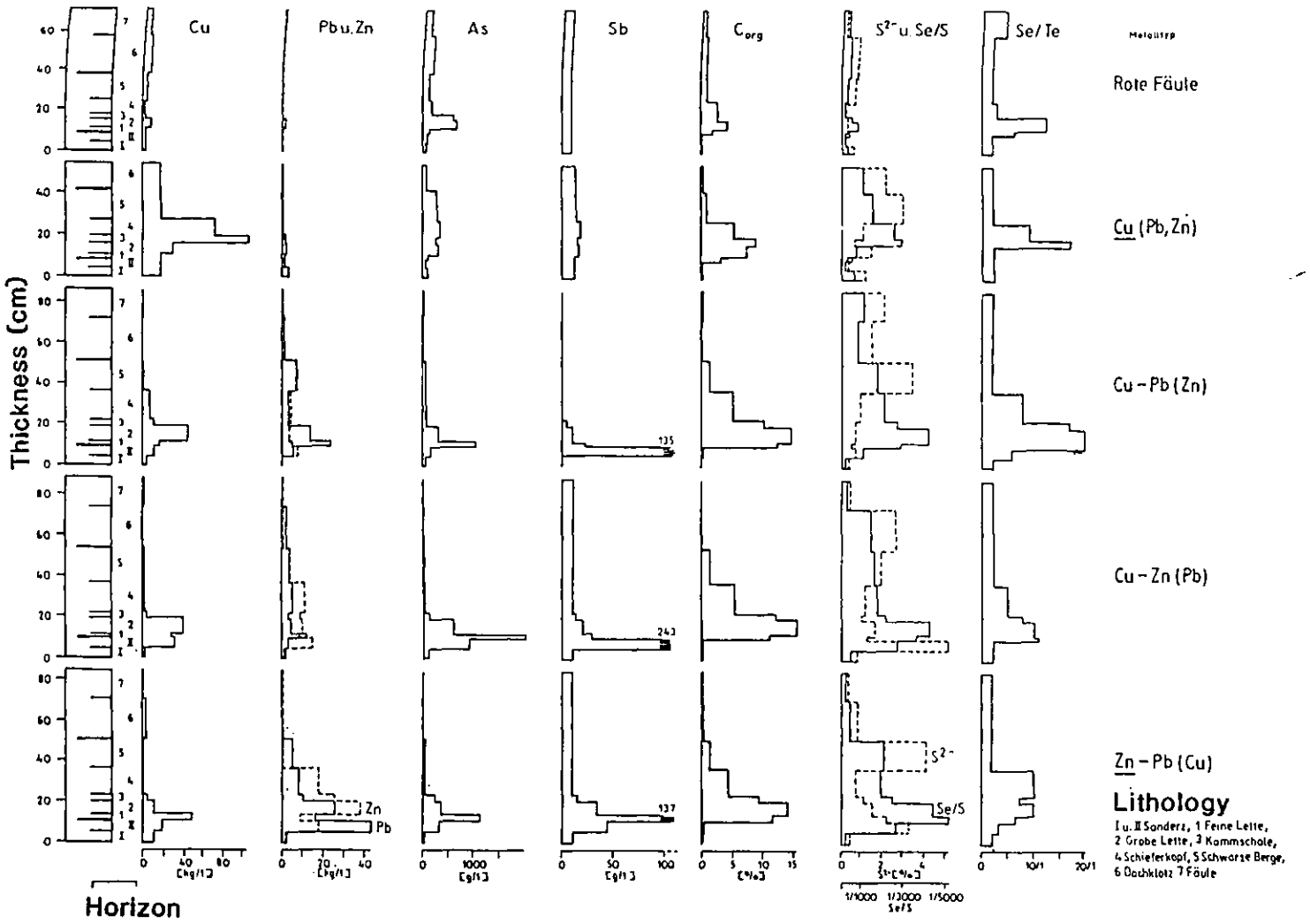


Fig 2.1 Pathfinder concentrations in profiles through the Kupferscheifer enriched in base metals (from Jung et al 1974)

Epithermal processes, which may form gold, arsenic, antimony and mercury deposits are currently active in such geothermal areas as Broadlands, New Zealand (Weissberg et al, 1979). Arsenic and gold (together with antimony, mercury and thallium) are concentrated near the surface whereas base metals (lead and zinc with pyrite) precipitate at depth (>300 m). This suite of elements is observed at other hot spring deposits and is very similar to that from the disseminated gold deposit at Carlin (average 350 ppm As in mineralized rocks, 10 ppm in unmineralized rocks) and other Au deposits in Nevada. It should be pointed out that the exact controls on the formation of ore grade gold and mercury deposits are unknown and it may be that they precipitate at depth, whereas low grade material can form at the surface. Arsenic is present in the simple sulphides realgar and orpiment.

Most arsenic in older vein deposits is present either as arsenopyrite or arsenic-rich pyrite; inclusions of native gold are common. These deposits vary considerably in character but the main economic deposits are in Archean greenstone belts and the arsenic content can be high (up to percents in some ores).

Some enrichment, (30 - 1,000 ppm) is known from Au-U conglomerate deposits, particularly those of the Witwatersrand.

Arsenic is found in significant concentrations in Ag^{+}-C^{+}-Ni^{+}-Co veins mainly as arsenides in such deposits as Freiberg, Germany and Cobalt, Ontario.

2.2.3 Antimony

Antimony is concentrated in most types of mineralization with a high arsenic content: high temperature segre-

gations; massive sulphides, epithermal deposits; and statiform ores formed by reduction. However, antimony is not enriched in high temperature deposits associated with granitic rocks (Boyle, 1974).

The mineralogy of antimony is rather different and less diverse than that of arsenic. The main minerals are stibnite (Sb_2S_3) in epithermal deposits and sulphosalts in more complex and higher temperature deposits - there is no analogue to arsenopyrite. Another dissimilarity is that antimony is the only one of the pathfinders to be mined significantly in its own right.

Comprehensive data on the occurrence of antimony in nickel ores is lacking but there is some evidence of enrichment particularly in Western Australian massive ores (McGoldrick and Keays, 1981) with values of 6 ppm Sb. Minor concentrations occur in the platinum-bearing deposits of the Bushveld and Nor'ilsk (Zainullin and Pashinkin, 1963).

Antimony concentrations in massive sulphide deposits are common especially from the polymetallic Kuroko-type (Chapter 6.1). The average content is about 50 ppm and is mainly associated with late stage lead-zinc ores.

Enrichments of antimony in the zinc bearing skarns are known with the element contained in bournonite or jamesonite. Antimony is the principal ore metal in some Mexican skarns.

Irish-style lead zinc deposits often contain significant concentrations (10 - 100s ppm Sb) but the brecciaform deposits are generally not enriched in antimony.

Polymetallic Ag^{+}-Co^{+}-Ni^{+}-U deposits such as Cobalt and Jachymov have high concentrations (300 - 3,000 ppm Sb) of antimony in the form of native antimony and sulphosalts.

The data for sandstone-type deposits and black shale is almost entirely lacking. Some sandstone deposits

are erratically enriched (up to 60 ppm) and there is some evidence (Boyle, 1975) that black shales are significantly enriched (5-140 ppm Sb). Values from the Kupferscheifer average 15 ppm Sb (Jung et al, 1974). Iron oxide rich sediments are enriched in antimony (up to about 100 ppm) although few details are available.

The best documented antimony enrichments are those associated with gold deposits. These are very similar to, although probably less consistent than, those of arsenic with occurrences in both Tertiary - Recent epithermal deposits and in Archean greenstone belts (Boyle, 1979). The mechanisms of transport are almost certainly similar to those of arsenic. Antimony minerals in gold deposits are dominantly stibnite or sulphosalts (mainly tetrahedrite). In very antimony rich deposits gold may occur as the refractory aurostibite (AuSb).

Some antimony deposits, notably the Consolidated Murchison deposit in South Africa, occur in similar settings to Archean gold deposits. They are stratabound (Viljoen, 1979; Muff and Saager, 1979) and may well have been formed by exhalative/hot spring activity as they have an antimony-mercury-arsenic association.

The other main antimony deposits occur in China and are probably the result of epithermal processes and subsequent clastic transport of the resistant stibnite and sulphosalts into Karstic depressions.

2.2.4 Bismuth - A Pathfinder for Tungsten ?

Major concentrations of bismuth are found in three main settings: high temperature granitic-associated veins and skarns; massive sulphide deposits; and veins and sediments in low temperature reducing conditions.

Bismuth, like arsenic and antimony, shows variation in mineralogy with deposit type and occurs either as

an isomorphous substitution for lead in galena or as discrete bismuth minerals. Native bismuth, which is relatively more common than native arsenic or antimony, is mainly found in vein deposits although it is stable at high temperatures (Kolonin, 1979). Lead-bismuth sulphosalts generally occur in massive sulphides and some hydrothermal veins. Bismuthinite (Bi_2S_3) is more widespread, with sulphur fugacity the main control (Bente, 1982); but is mainly concentrated in greisens.

Minor concentrations of bismuth are known from magmatic deposits such as the Bushveld or Noril'sk with bismuth-platinoid alloys a minor constituent. Contents in ores are unlikely to average more than 10 ppm Bi.

Bismuth distribution in pegmatites is very erratic but concentrations may be high. It is associated with two parageneses (Mintser , 1979): with sulphides (mainly Mo, Fe, Zn, Pb); and with tantalites and rare earth minerals (20-100 ppm).

The abundance of bismuth in greisens is very high with concentrations often reaching several thousand ppm Bi. There is an almost universal association between bismuth and tungsten in this environment (Rundquist, 1982) and deposits probably form at high temperature. Examination of the zonation pattern (Fig. 2.2) shows that bismuth is a relatively early phase and, in my opinion, may well be transported as a sulphide complex that is unstable at lower temperatures. In sub-volcanic deposits such as Chloroque, Bolivia, bismuth is closely associated with tin and zoning is not evident (Grant et al, 1977), probably because of a high temperature gradient. Bismuth in the form of bismuthinite and cosalite is a minor, though significant, component of tungsten and zinc skarns. Smirnov (1977).

Bismuth is concentrated in the high temperature

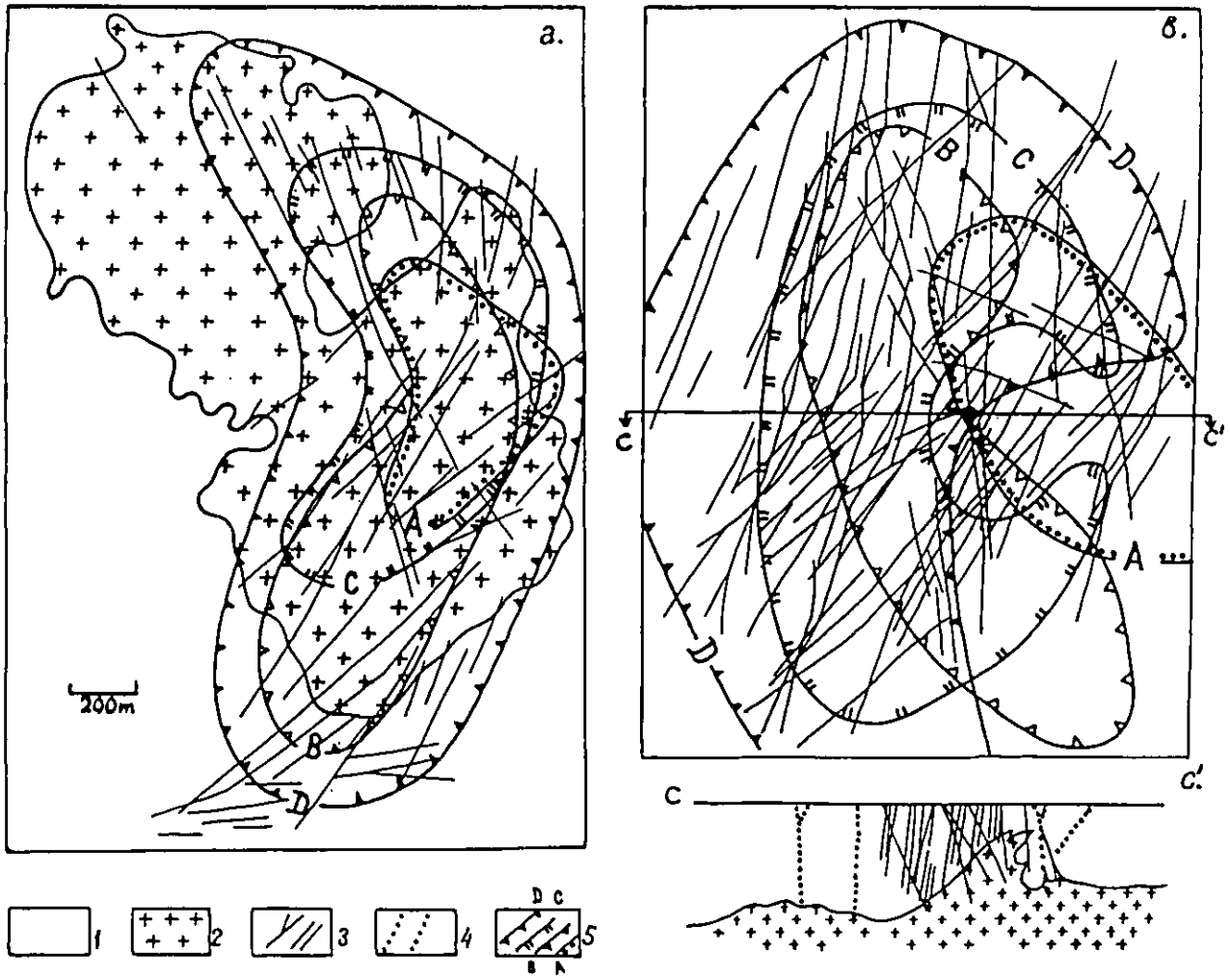


Fig 2.2 Zoning of a vein W deposit of Kazakhstan. (a) Veins within the eroded cupola of the greisenized granites; (b) and (c) veins in the exocontact above the non-eroded cupola (after Rundquist and Nezhensky, 1975). 1, Enclosing schists; 2, granites; 3, quartz-tungsten veins; 4, granite-porphyry and quartz-porphyry dykes; 5, zones of distribution of mineralization: A, Mo mineralization; B, complex rare metal mineralization; C-D, wolframite-sulphide mineralization, C, with bismuthinite, D, with galena, sphalerite and pyrite)

(from Rundquist 1982)

zones of some massive sulphide deposits (Chapter 6.1) and values reach tens of ppm. It is present as bismuthinite, native bismuth, lead-bismuth sulphosalts (aikinite, complectite, galeno-bismutite) and possibly by substitution of Bi for As in tennantite (Yamaoka and Asakura, 1974).

Some gold deposits, such as Tennant Creek, Australia, have significant bismuth concentrations. There is no obvious pattern but it seems likely that they formed at high temperature.

Native bismuth and matildite ($AgBiS_2$) are common associates of the Ag^{+}-Co^{+}-Ni^{+}-U vein deposits. Typical concentrations are 100 ppm.

Bismuth is concentrated in the Kupferscheifer with values of 2-3 ppm Bi (Jung et al, 1974). The content in the Lubin deposits in Poland averages 5 ppm and is thought to occur as bismuthinite (Wojciechowska and Serkies, 1972).

There is some evidence (Picot, 1979) that bismuth concentrations are controlled by structure (major lineaments) rather than by environment.

2.3 Lithogeochemical Applications of the Pathfinders

The usefulness of pathfinders in lithogeochemistry depends on their separation from the ore elements during primary concentration processes. Generalizations of element zonation in three dimensions, such as those proposed by Beus and Gregorian (1977), are a particularly useful guide to selecting pathfinders. There are local effects but the overall controls are the stability (mainly as a result of temperature and pressure in hydrothermal solution and Eh - pH for low temperature deposits) of metalloid bearing complexes or vapours and, thus, generalizations seem permissible.

Substantial differences in terminology exist between English language (Rose et al, 1979) and Russian

descriptions (Beus and Grigorian, 1977) so brief definitions must be given. Haloes around mineral deposits are either additive (i.e. elements are enriched around the deposit) or subtractive, with the former more common and of more practical significance. The additive haloes can be further subdivided into syngenetic or epigenetic (later than the host rocks) types. Epigenetic haloes related to fractures are further divided into leakage or diffusion haloes (Rose et al, 1979): leakage haloes are where ore stage elements are present in mineralizing structures above or below the orebody; diffusion is the movement of solutions into wallrocks. The arrangement of elements (zonality) within these haloes has been quantified in various dimensions (Table 2.4) by Russian workers: transverse zonality for zoning across the ore body and wallrock diffusion; whereas axial or vertical zoning refers to leakage haloes. The size of haloes in epigenetic deposits is dependent on the nature of the solutions, reactivity of the wallrocks and the thermal gradient. In practical terms this means: broad haloes (tens of kilometres) of volatile elements can be produced by large scale intrusion; whereas exhalative solutions at the surface/sea floor can transport mobile metals for hundreds of metres; and wallrock haloes in many hypogene veins are limited to a few metres.

One important application of lithogeochemistry is the recognition of mineralized districts. Most of the successful programmes have been used in the search for lithophile elements, particularly the recognition of mineralized plutons. Pathfinder geochemistry has not been extensively used but a number of examples can be quoted. Arsenic outlines the mineralized district of South West England very effectively (Chapter 3.1) but the effectiveness may be related to the pre-intrusion sedimentary concentrations

of arsenic. There is apparent enrichment of arsenic in metasediments along strike from gold deposits in Sierra Leone (James, 1965; Garrett and Nichol, 1967). Massive sulphide deposits in the Kuroko district of Japan have arsenic anomalies in associated rhyolites (Tono, 1974) but their scale is not clear.

On a deposit scale much more information is available particularly from Russian and, more recently, Canadian workers. The zoning in transverse and axial dimensions is summarized in Table 2.4. Arsenic and antimony are late stage elements although arsenic may be present in two stages, as arsenopyrite and sulphosalts. Bismuth is an earlier phase and of similar width but data on selenium is generally lacking.

The best documented examples of the use of the pathfinder zonation, in non-Communist countries, come from Australia. Arsenic leakage haloes are effective in the search for gold deposits near Kalgoorlie (Mazzucchelli, 1965) persisting updip for hundreds of metres. Haloes in particular sedimentary beds are associated with many stratiform deposits with wide arsenic and antimony concentration in the upper parts of massive sulphide deposits, in exhalites (Scott et al, 1982)or in the vicinity of the sediment/volcanic contact (Chapter 6.1). Sampling of these beds and ratioing of pathfinders to other elements may be an excellent guide to ore, e.g. the use of As/Na ratios in the Rio Tinto area (Möller er al, 1982). Russian work suggests that bismuth may be used as a proximity guide to tungsten deposits (Fig. 2.2)

Pathfinder lithogeochemistry has been successfully used in exploration for the gold deposit at Cortez, Nevada where antimony anomalies led to the discovery of the orebody. In this situation zonation is of little importance (Boyle, 1979).

There is obviously considerable potential for pathfinder lithogeochemistry, particularly as arsenic, antimony (? selenium) can give large haloes. (x00 m) Wide investigation of their potential is merited, particularly the use of ratioing to eliminate the effects of multi-phase mineralization.

Part II :
Detailed Studies

CHAPTER 3 SOUTH WEST ENGLAND BACKGROUND STUDY

3.1 Introduction

Interpretation of detailed surveys and selection of significant anomalies requires a knowledge of background values. As little data was available for the pathfinders, with the exception of arsenic, it was decided to analyse a suite of samples representative of a wide range of provenances and environments.

Samples collected for the Wolfson Geochemical Atlas of England and Wales (Webb et al, 1978) and their corresponding results were available. South West England is a particularly suitable area as there are a wide variety of lithologies, ranging from gneisses to unconsolidated sediments and the geology and mineralization are well understood. Stream sediments are the optimum medium as they approximate a composite sample of the catchment area.

3.1.1 Sample Selection

About 5,000 samples are available from the Wolfson Atlas programme collected at road and stream intersections for an average density of 1 per 2.5 km^2. It was not feasible to analyse all the samples and some form of selection was required.

There seems to be no defined upper limit to satisfactory sample spacing; regional geochemical provinces can be detected by very widely spaced sampling (Armour-Brown and Nichol, 1970). As no particular target size was sought in the South West England background study, no lower limit was defined (Howarth and Martin, 1979). The main constraint was the number of sediments to be analysed. This was, somewhat arbitrarily, set at about 500 (10% of

samples collected). The main requirement of each sample was that it be representative of an area of bedrock; and experience suggests that samples from very large rivers (excessive dilution) and small streams (localised conditions) be omitted.

In order to standardise the size of drainage basin sampled, it is necessary to have some knowledge of the distribution of basin sizes. No information was available so I selected three one-inch sheets of representative areas and calculated basin sizes of all the samples collected for the Atlas project (Fig. 3.1). Basins of 8-15 km^2 were selected to yield about 400 samples (Fig. 3.2).

3.1.2 Elements Determined

The samples were analysed by the co-precipitation method for As, Bi and Se. Antimony was not determined because of time constraints. Determinations for Al, Ba, Ca, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Ni, Pb, Se, Si, Sr, Ti and V by D.C. arc spectroscopy and for As, Mo, Cd, Zn, by wet chemistry were available from the Wolfson Atlas Data.

3.1.3 Data Processing

This was divided into two stages, assessing inter-element association to determine environmental and litho-logical controls, and inspection of individual pathfinder element patterns.

R-mode factor analysis was used, in addition to correlation matrices, for the first stage as the computer programmes are readily available and it had provided useful information for the Wolfson Atlas project (Mancey, 1980). Tin and cadmium are omitted because of the high proportion of values below the detection limit.

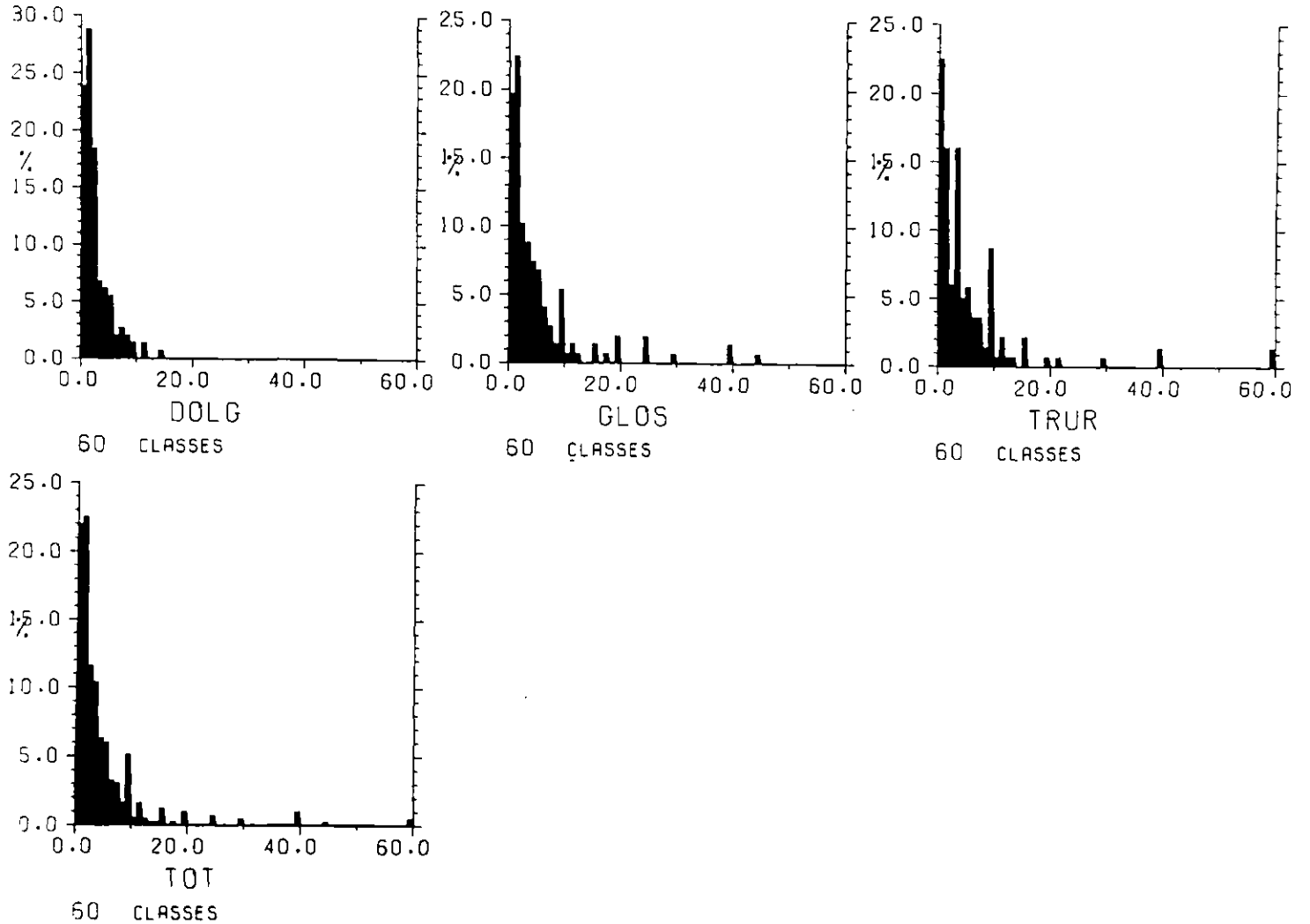


Fig 3.1 HISTOGRAMS OF BASIN SIZES

Basin sizes are in sq. km. DOLG = Dollgellau, GLOS = Gloucester, TRUR = Truro, TOT = Total.

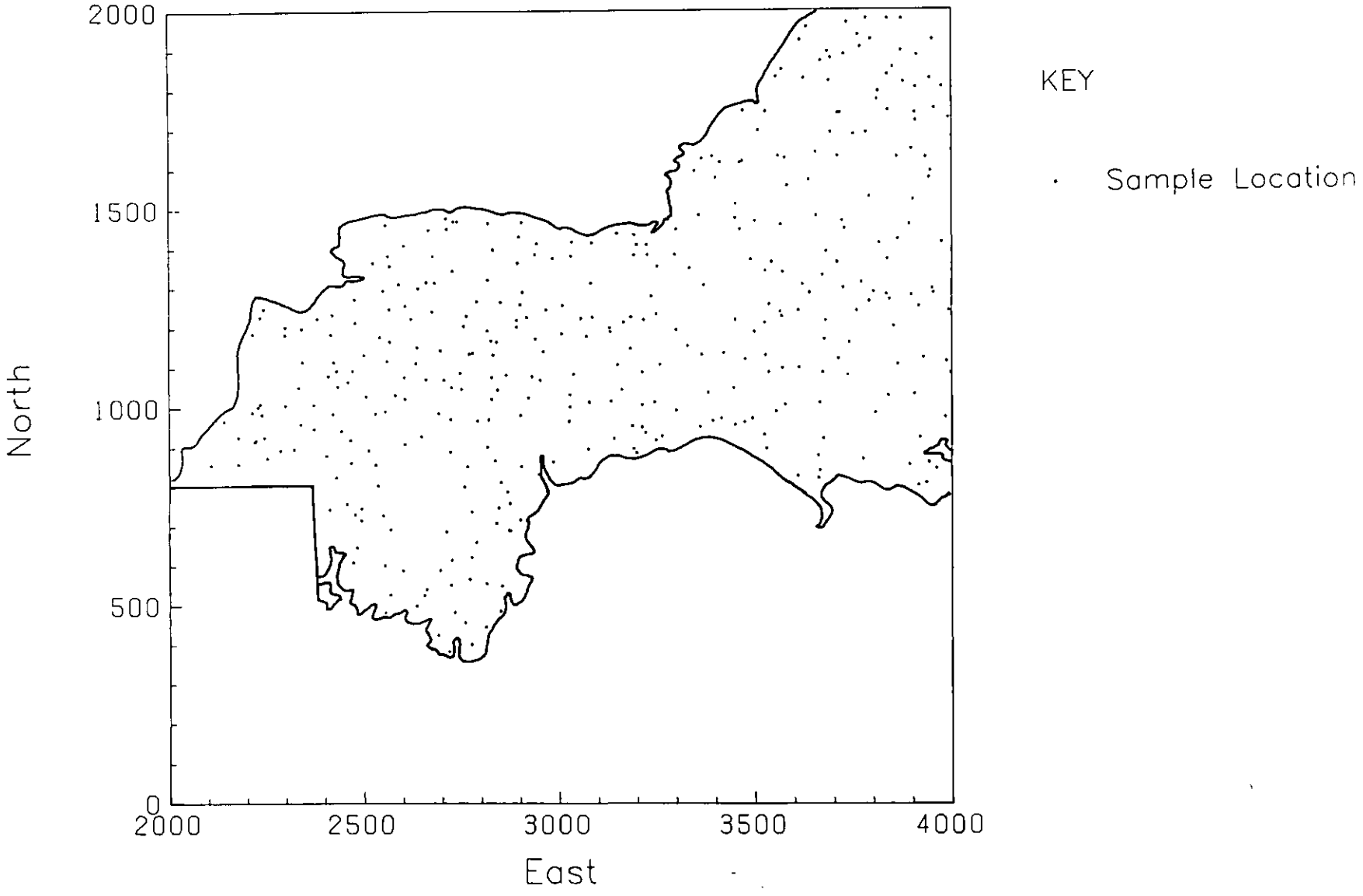


Fig 3.2 South West England: sample location

For the inspection of pathfinder patterns geological data was collated from the relevant one-inch geological sheet (where available). Predominant and secondary bedrock lithology, age and drift type were entered onto the computerised data file (as ordinals) to allow geological controls of the pathfinders to be assessed (Figs. 3.3 - 3.5).

Smoothing of the data was not attempted because of the relatively small number of samples.

3.2 Results

3.2.1 Element Associations

The correlation matrix (Table 3.1) shows that arsenic and bismuth correlate with potassium and to a lesser degree with copper and zinc. Selenium is somewhat correlated with zinc and copper.

Iron and manganese scavenging can considerably influence secondary dispersion of metals. Arsenic shows the highest correlation with iron (and manganese) but scattergrams (Fig. 3.6) suggest that the association is mainly restricted to higher arsenic values. Selenium and bismuth show little correlation with iron and manganese (Figs. 3.7, 3.8) except for the association of higher selenium values with high iron concentrations which may reflect the association of selenium with pyrite in bedrock rather than scavenging. The pathfinder patterns, with the exception of high arsenic values, reflect bedrock geology rather than inorganic environmental effects. Selenium,and possibly bismuth, are scavenged by organic matter although the lack of organic carbon analyses precludes quantification.

Factor loadings for the first 10 factors (Table 3.2) after varimax rotation show that the pathfinders have

	AL	CA	FE	K	MG	SI	GA	SC	CU	PB
AL	1.00000									
CA	-.36433	1.00000								
FE	.39832	-.14207	1.00000							
K	.52179	.04487	.45183	1.00000						
MG	.28090	.32878	.16373	.39438	1.00000					
SI	.50805	-.46557	.06304	-.02359	-.01966	1.00000				
CA	.46332	-.05663	.57242	.65715	.30354	-.06055	1.00000			
SC	.56700	-.59205	.31203	.35501	.11207	.42715	.34551	1.00000		
CU	.36074	-.07227	.49849	.51291	.29938	-.03232	.66012	.37036	1.00000	
PB	.14278	.28175	.62151	.43984	.28366	-.11783	.49764	.04408	.52539	1.00000
V	.48036	-.19254	.50184	.48041	.22533	.17652	.59049	.48786	.51074	.35929
BA	.23001	.18794	.19450	.55221	.39467	-.06140	.33848	.23271	.39398	.43733
CO	.55392	-.58420	.47304	.34517	.07537	.39667	.42320	.77522	.46038	.14825
CR	.58961	-.08408	.39424	.37375	.29364	.29725	.37316	.34527	.31057	.32239
NI	.55882	-.48693	.46435	.39295	.12265	.36982	.46528	.73952	.48792	.20862
MN	.24577	.09270	.75441	.40118	.24192	-.12211	.53260	.16554	.45257	.63023
SR	-.12784	.64272	.24123	.40122	.32189	-.48586	.42667	-.25272	.27248	.58011
LI	.50536	-.60245	.40957	.33904	.01421	.43103	.40031	.81656	.39143	.12562
MO	-.02907	.32248	.02593	.12047	.10082	-.16307	.00386	-.09877	.08052	.19978
ZN	.16694	.33093	.30652	.47200	.45293	-.30229	.41423	.04184	.45198	.48021
AS	.38845	-.05148	.40572	.56971	.25703	-.02843	.46441	.32494	.48587	.35640
BI	.35988	.01494	.31516	.54411	.25119	-.12038	.50221	.26008	.48393	.32532
SE	.24552	.05085	.25391	.34847	.27847	-.11720	.36048	.16173	.42191	.22553

	V	BA	CO	CR	NI	MN	SR	LI	MO	ZN
V	1.00000									
BA	.33859	1.00000								
CO	.53815	.13774	1.00000							
CR	.56686	.32684	.42595	1.00000						
NI	.57060	.23078	.88076	.43549	1.00000					
MN	.42924	.22621	.32740	.21944	.32080	1.00000				
SR	.15969	.46568	-.17443	.09797	-.09410	.45614	1.00000			
LI	.46019	.13309	.80059	.31070	.75094	.22409	-.22691	1.00000		
MO	.02236	.14089	-.07540	.09412	-.06057	.11033	.29017	-.12419	1.00000	
ZN	.28840	.49046	.10697	.26558	.14356	.37493	.49547	.00844	.24063	1.00000
AS	.38520	.33967	.35697	.26811	.34776	.38742	.19395	.29742	.23834	.41415
BI	.30212	.21037	.27580	.16382	.30067	.32753	.22176	.27090	.16590	.39547
SE	.26804	.11384	.27033	.21290	.24309	.25039	.18882	.13474	.29128	.44916

	AS	BI	SE
AS	1.00000		
BI	.68001	1.00000	
SE	.39164	.38676	1.00000

Table 3.1 Correlation matrix of log-transformed data - S.W.England

	FACT 1	FACT 2	FACT 3	FACT 4	FACT 5	FACT 6	FACT 7	FACT 8	FACT 9	FACT10
AL	-.0765	.4168	.0215	-.3691	-.0627	-.4987	.0497	-.2183	-.1341	.4460
CA	-.1300	-.6981	-.2167	.0484	.2913	.0430	.0152	-.3539	-.1373	-.2191
FE	-.8269	.2867	.0041	-.1925	-.0515	-.2319	.0868	.0014	-.0491	.0303
K	-.1896	.2125	-.3342	-.5497	.0353	-.2582	.0298	-.2408	-.4067	-.0304
MG	-.1110	-.0144	-.2168	-.1312	-.0010	-.1123	.1692	-.8867	-.0694	.0506
SI	.0715	.3968	.0779	.1088	-.0312	-.1822	-.1294	-.0332	.0860	.7995
GA	-.3843	.2639	-.1154	-.3336	-.1060	-.2530	.2127	-.0956	-.6291	-.0938
SC	.0140	.8863	-.1098	-.1624	-.0245	-.1182	-.0041	-.0822	-.0343	.1162
CU	-.3570	.3060	-.3600	-.2548	-.0683	-.0175	.5206	.0241	-.3803	.0862
PB	-.7602	-.0666	-.4358	-.1153	.1197	-.0651	.1590	-.0213	-.1786	.0851
V	-.2689	.4321	-.1379	-.1224	-.0158	-.6105	.1134	.0029	-.2730	-.1053
BA	-.0792	.1084	-.8693	-.1606	.0717	-.1742	-.0450	-.1921	-.1099	-.0548
CO	-.1977	.8832	.0062	-.1006	-.0079	-.1910	.1494	-.0175	-.0180	.0595
CR	-.1670	.2033	-.1857	-.0427	.0715	-.8349	.1027	-.1022	-.0064	.1974
NI	-.1938	.8415	-.0875	-.0914	.0067	-.2059	.1201	-.0502	-.1045	.0561
MN	-.8648	.1566	.0089	-.1807	.0522	-.0842	.0284	-.1622	-.0893	-.1665
SR	-.4067	-.3218	-.3827	-.0589	.2550	-.0431	.0068	-.2313	-.4251	-.3855
LI	-.1298	.8795	-.0380	-.1314	-.0363	-.0392	-.0015	.0281	-.1120	.1477
MO	-.0482	-.1104	-.0723	-.1333	.9393	-.0368	.1461	-.0042	.0256	-.0354
ZN	-.2630	-.0621	-.4850	-.2863	.0292	-.1861	.4540	-.2935	.1160	-.2965
AS	-.2273	.2034	-.1819	-.8111	.1334	-.1199	.1464	-.0217	.0657	-.0246
BI	-.1512	.1322	-.0367	-.8339	.0519	.0115	.1962	-.0788	-.1875	-.0428
SE	-.0749	.1180	.0802	-.2377	.2164	-.1314	.8134	-.1730	-.0761	-.0975

Table 3.2 Factor loadings for rotated 10 factor model - S.W.England

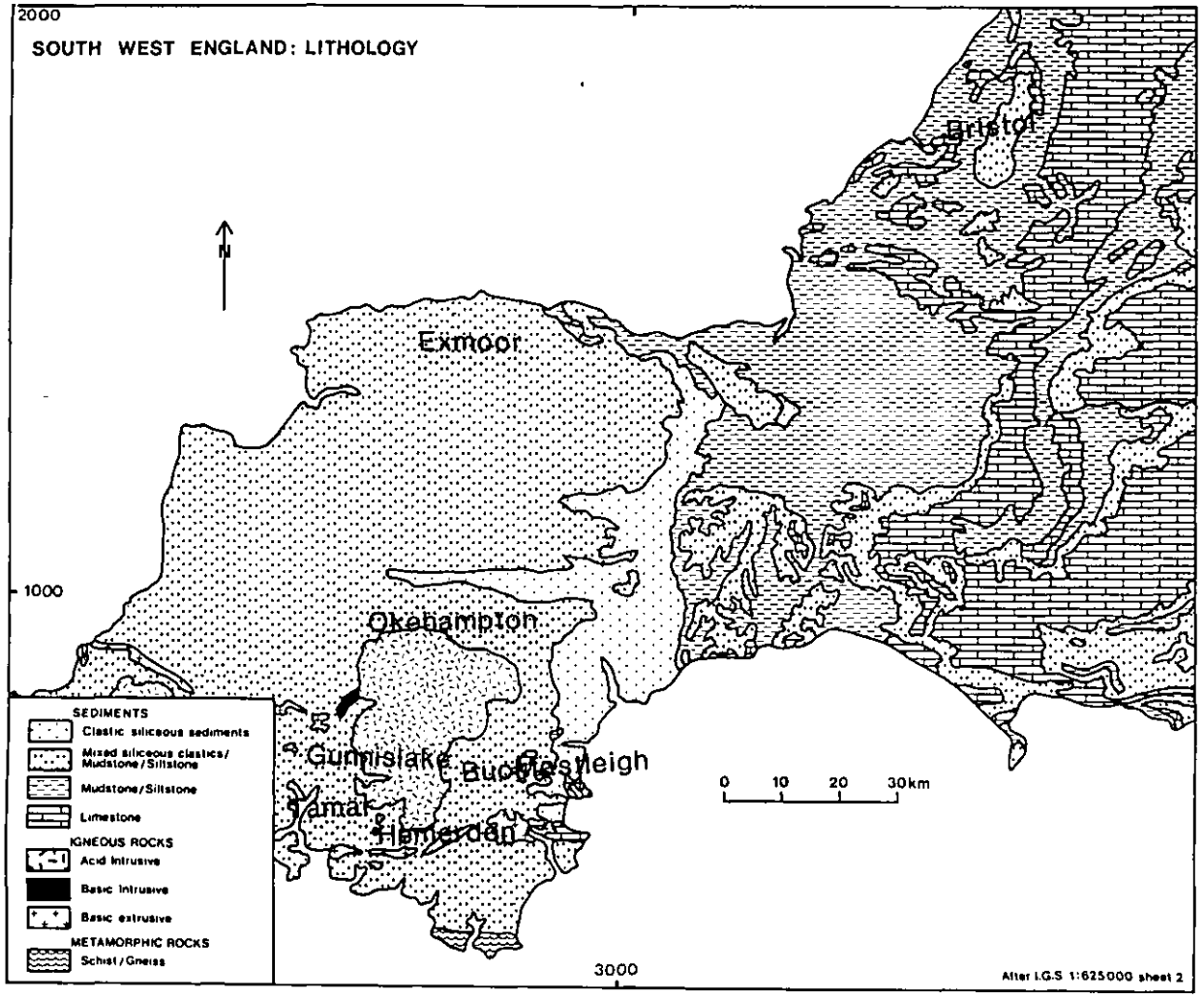


Fig 3.3 South West England: lithology

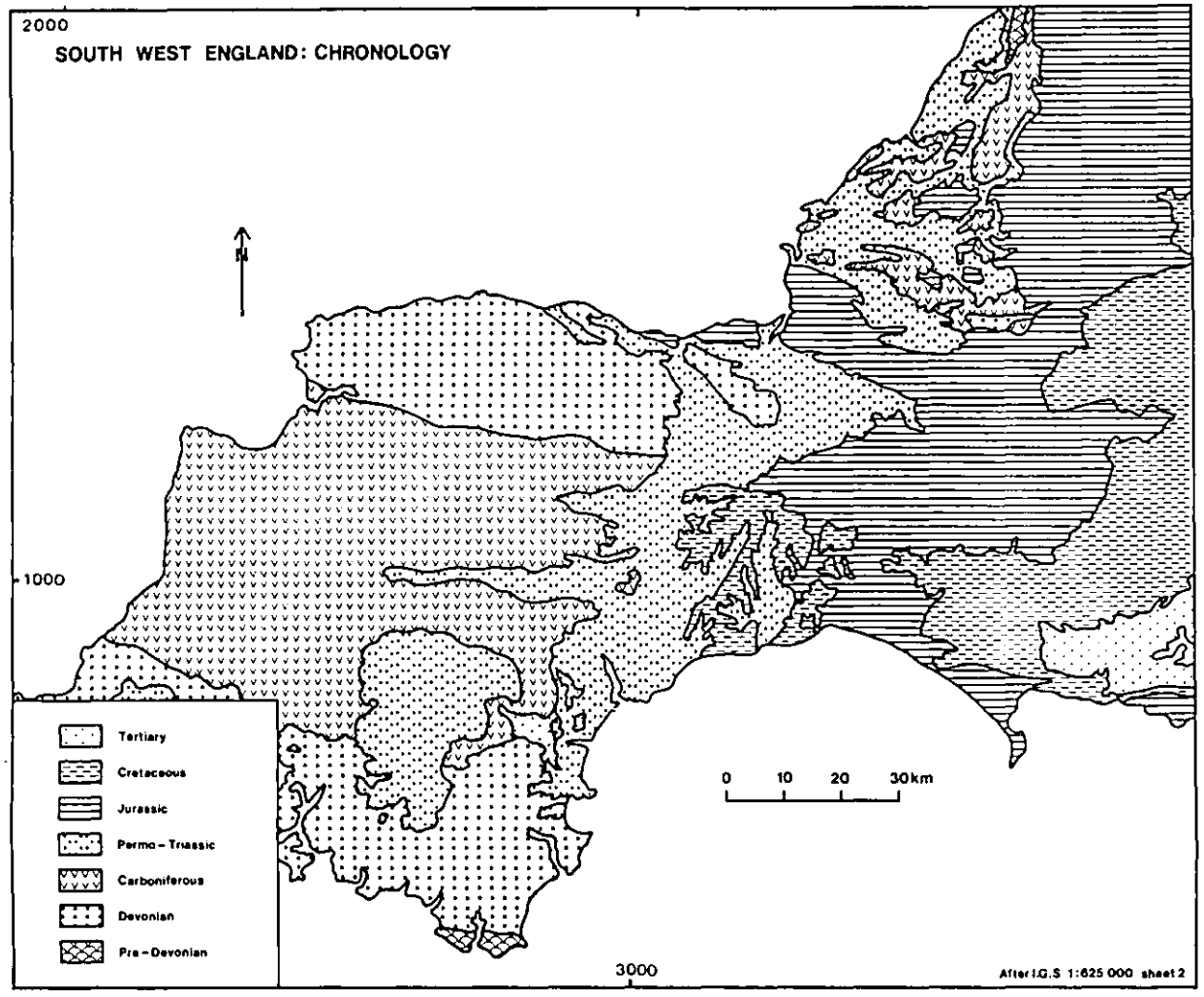


Fig 3.4 South West England: chronology

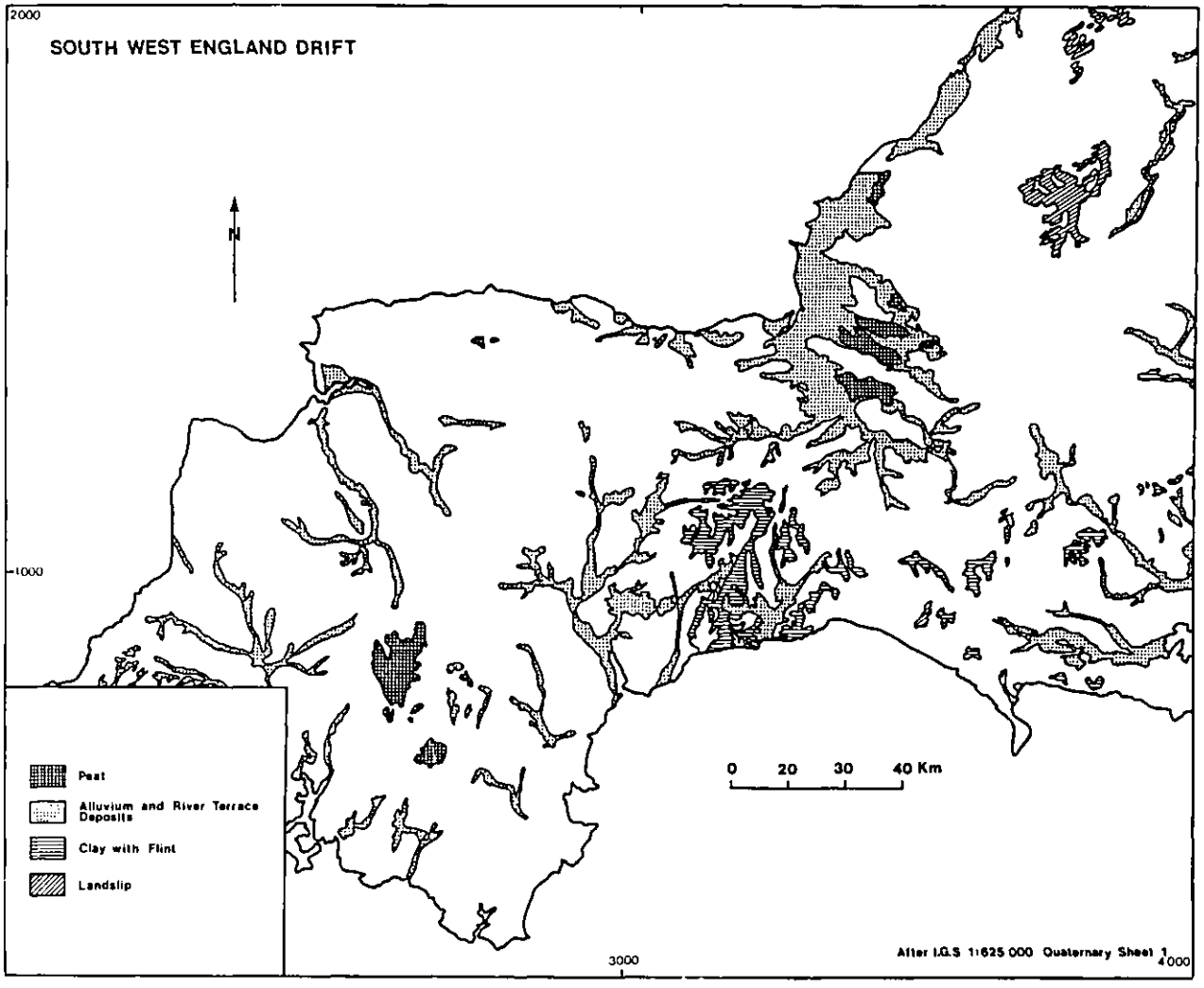
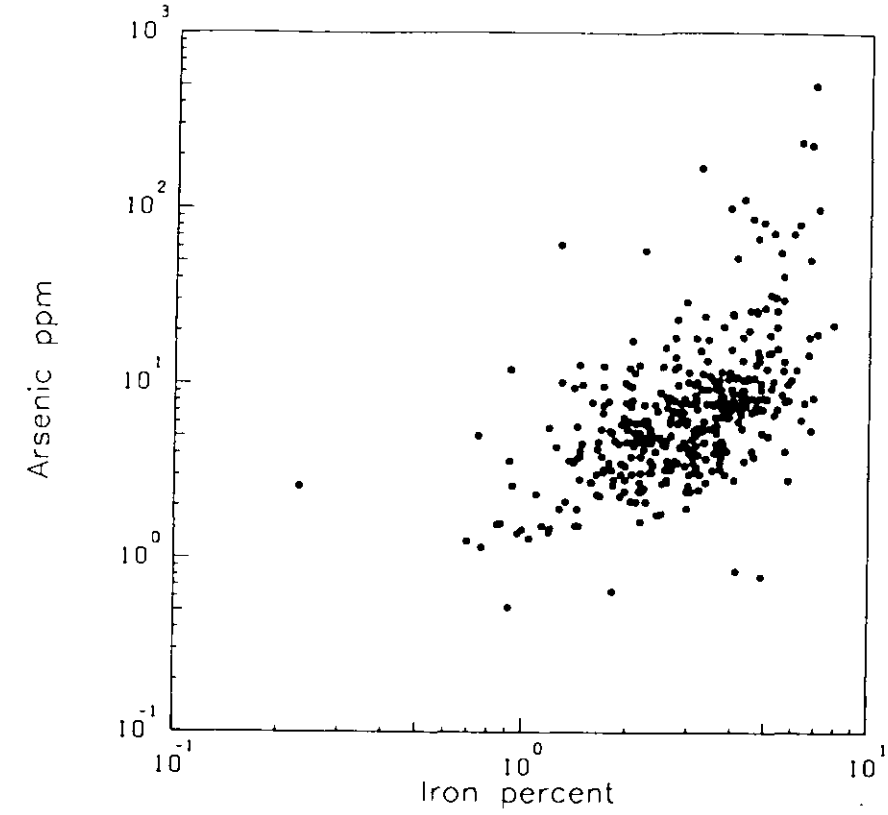


Fig 3.5 South West England: drift



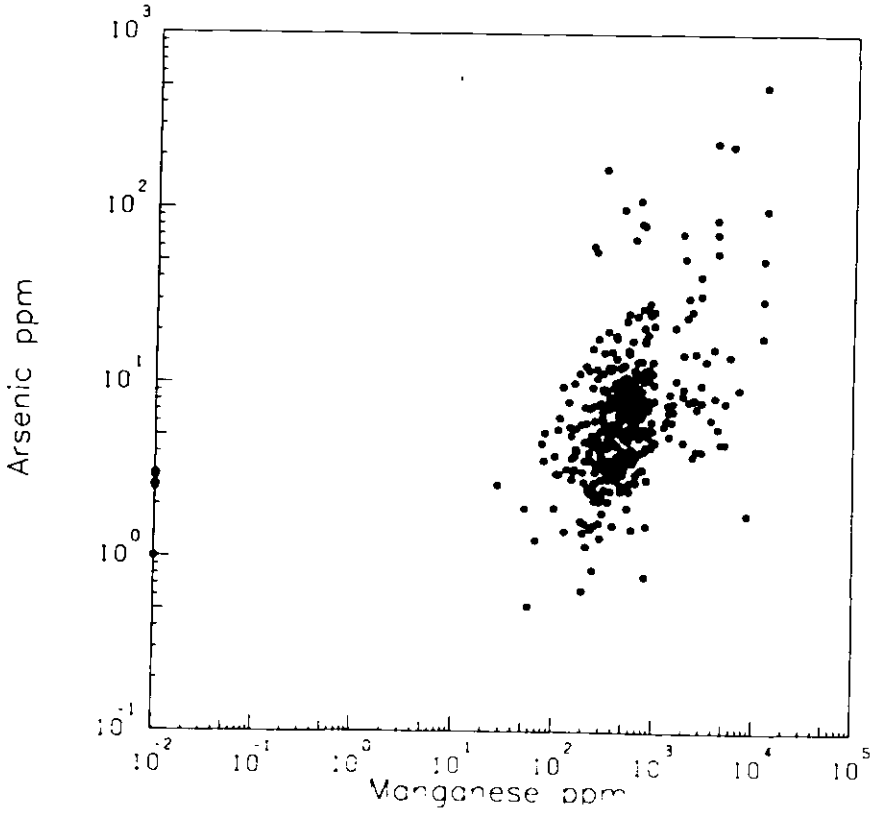


Fig 3.6 Scattergrams of Arsenic against Iron and Manganese
Note that Manganese values less than the detection limit (20 ppm) were coded as 0.01 ppm

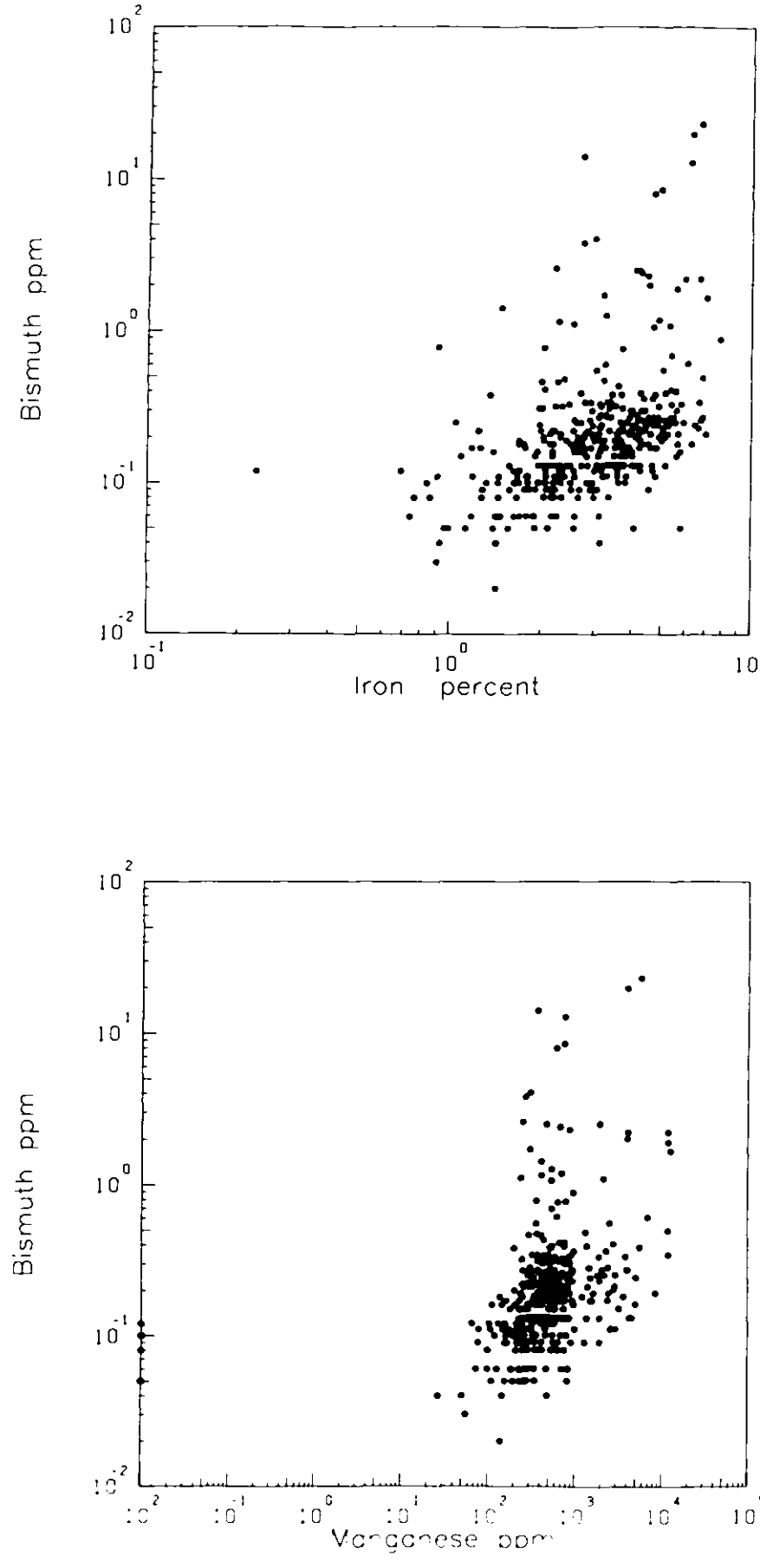
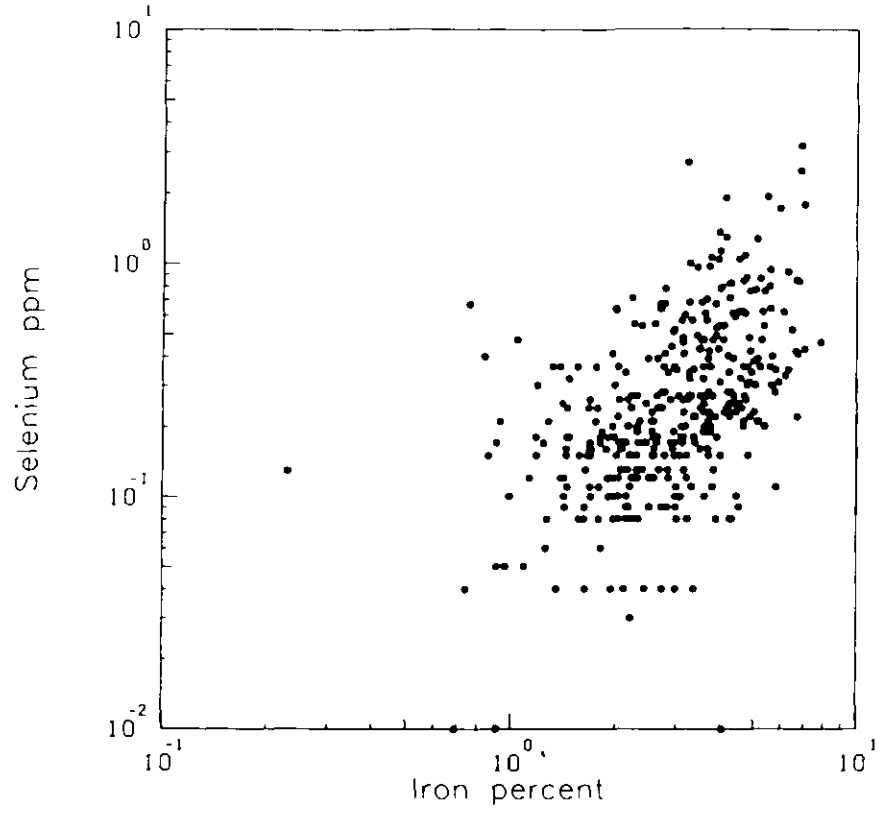


Fig 3.7 Scattergrams of Bismuth against Iron and Manganese. Note that Manganese values less than the detection limit (20 ppm) were coded as 0.01 ppm



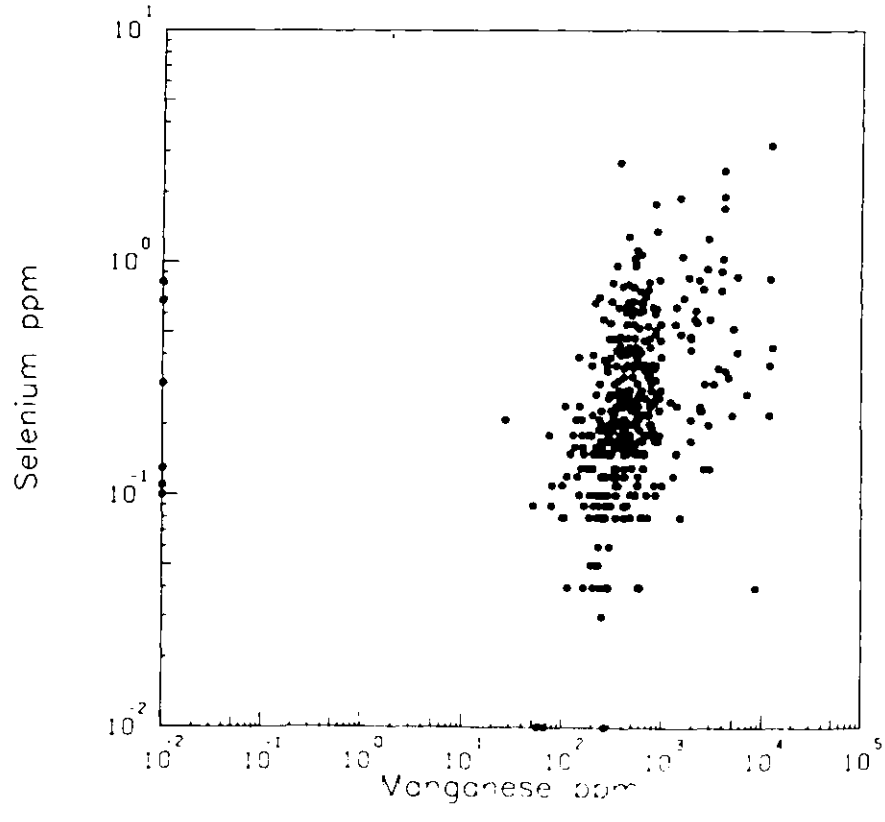


Fig 3.8 Scattergrams of Selenium against Iron and Manganese. Note that values less than the detection limit (20 ppm for Manganese and 0.03 ppm for Selenium) were recoded as 0.01 ppm

high loadings in factors 4 (As Bi) and 7 (Se). Factor 4 has high loadings of As and Bi with somewhat lower loadings of K and high scores show a spatial correlation (Fig. 3.9) with the granitic rocks. Factor 7, which has a high loading of Se and a moderate one of Cu and Zn, has a complex distribution (Fig. 3.10) which is discussed fully in the section 3.2.4. Other factors which have a bearing on pathfinder geochemistry are: factor 1 (Fe Mn Pb) probably reflecting oxide precipitation and mineralization, has little spatial resemblance to pathfinder distribution (Fig. 3.11); factor 2 (-Ca +Li, Ni, Co, Sc) probably indicates lithology and the incidence of limestones (Fig. 3.12) and factor 3 (Ba(Pb, Zn)) which seems to reflect mineralization particularly in the Mendips/Bristol area (Fig. 3.13).

3.2.2 Arsenic Distribution

Arsenic was the only one of the pathfinder elements analysed (by the Gutzeit method) for the Wolfson Atlas and its distribution has been extensively studied.

The prime interest in the area for environmental scientists is the contamination associated with mining and smelting of ores (Aston et al, 1975; Colbourn et al, 1975) particularly in the Upper Tamar Valley. This area is outstanding on the Wolfson Atlas plot (Fig. 3.14) and it is a result of both natural enrichment and contamination (Aguilar,1974). Arsenic is most easily leached from smelter-derived dust and this gives rise to the most intense anomalies (Aston et al, 1975). Only one sample in the present survey was collected from an area of known arsenic smelting.

The other obvious feature of the Wolfson Atlas data, and of the present survey (Fig. 3.15) is the halo of

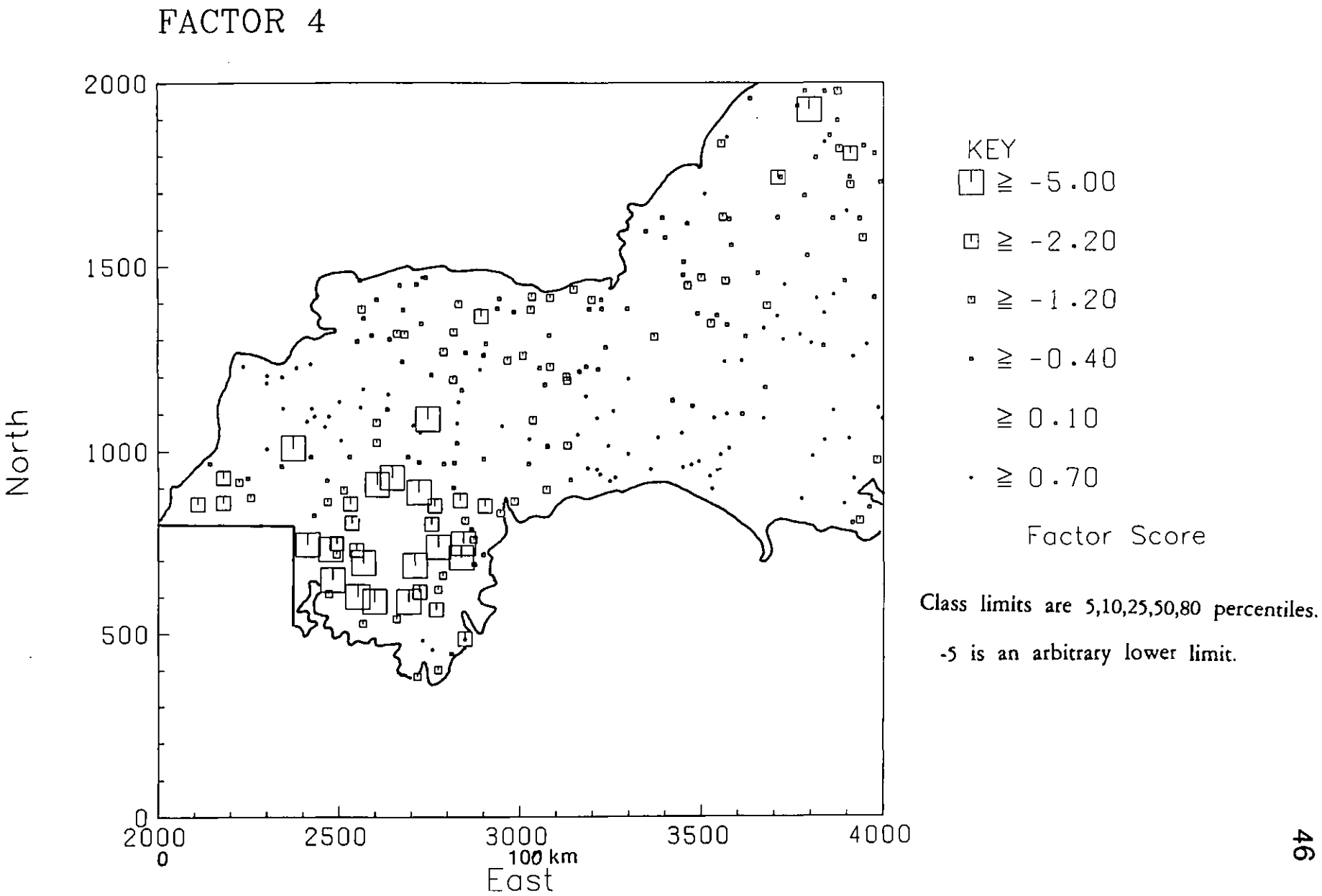


Fig 3.9 Distibution of scores : factor 4

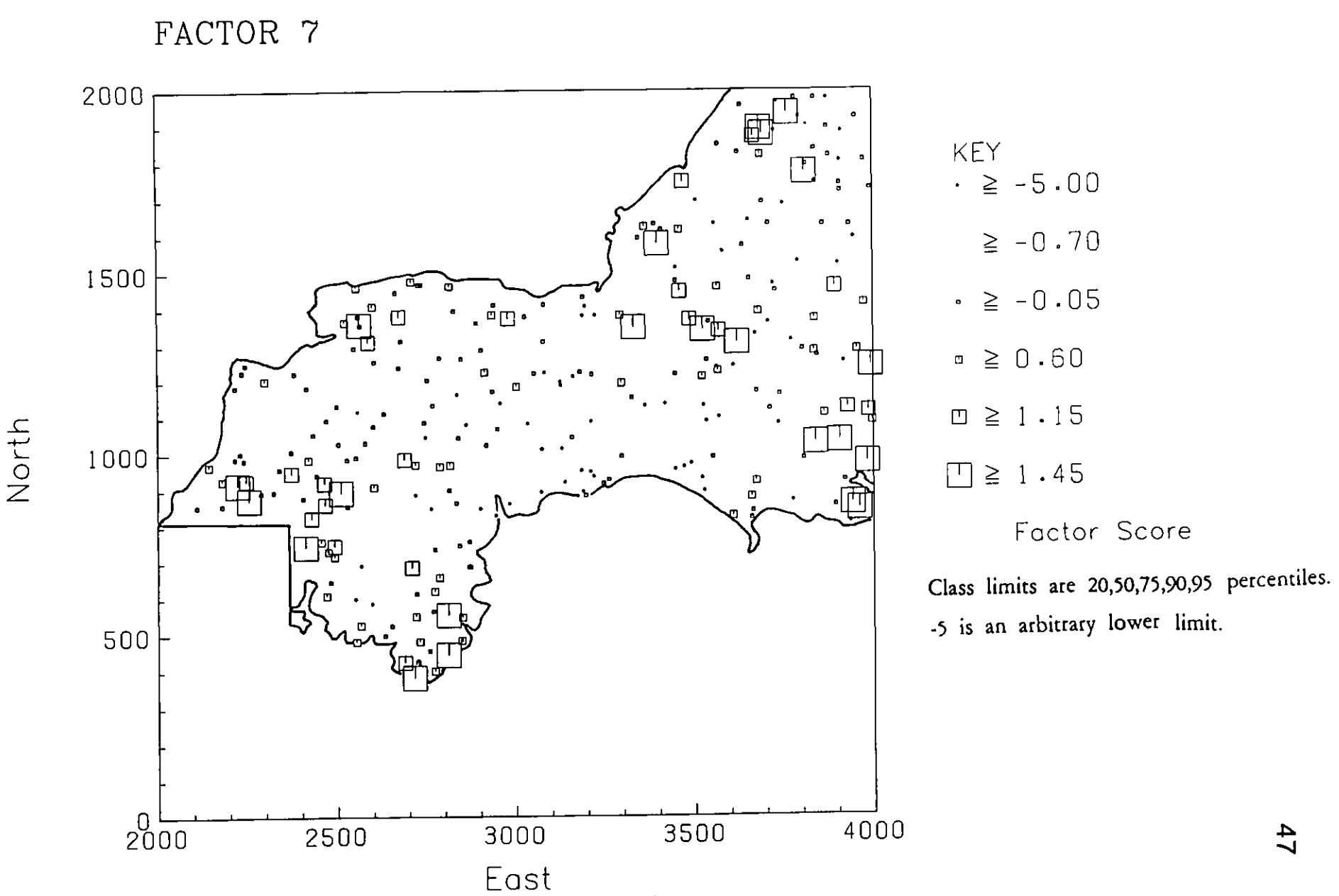


Fig 3.10 Distribution of scores : factor 7

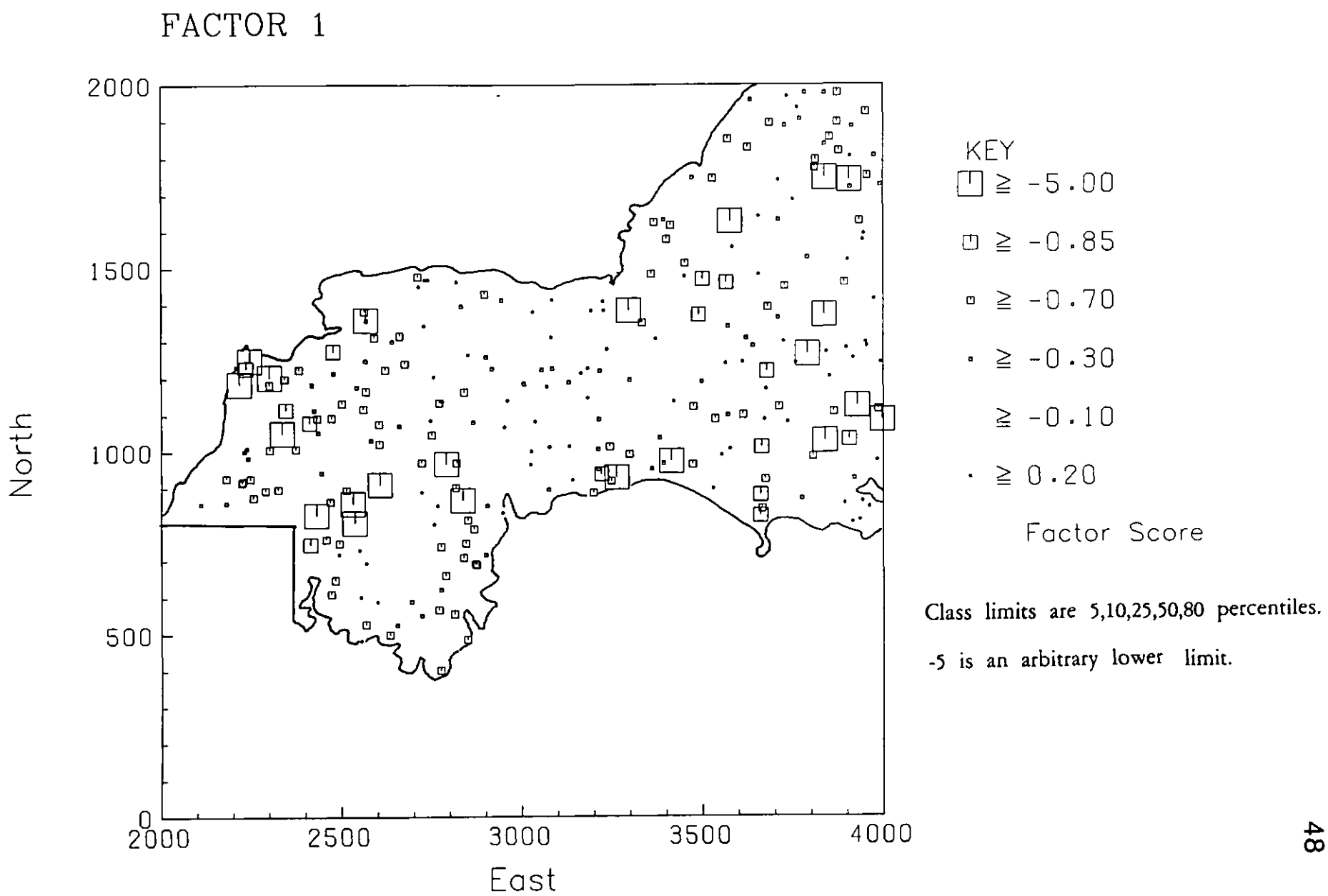
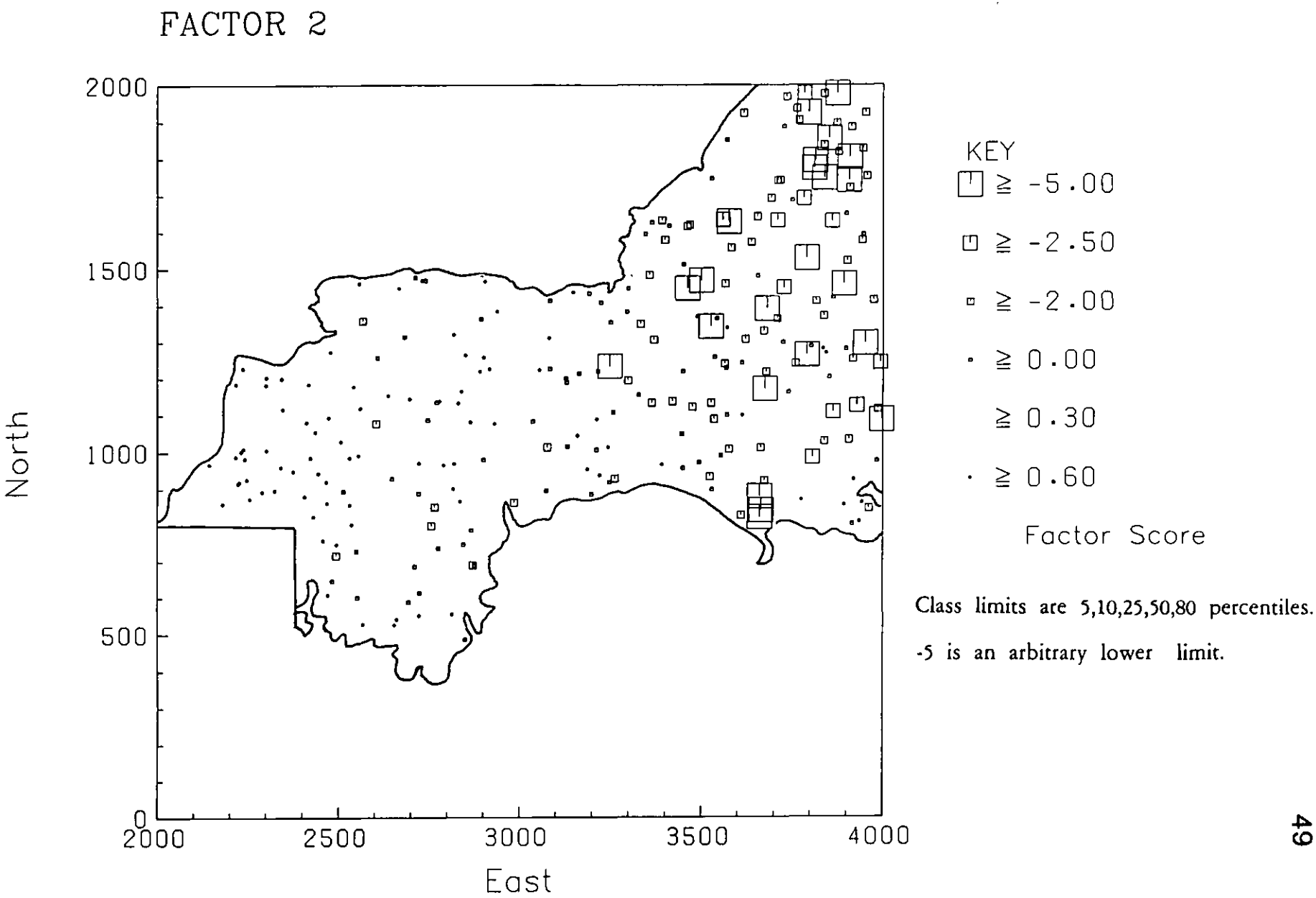


Fig 3.11 Distribution of scores: factor 1



Class limits are 5,10,25,50,80 percentiles.

-5 is an arbitrary lower limit.

Fig 3.12 Distribution of scores: factor 2

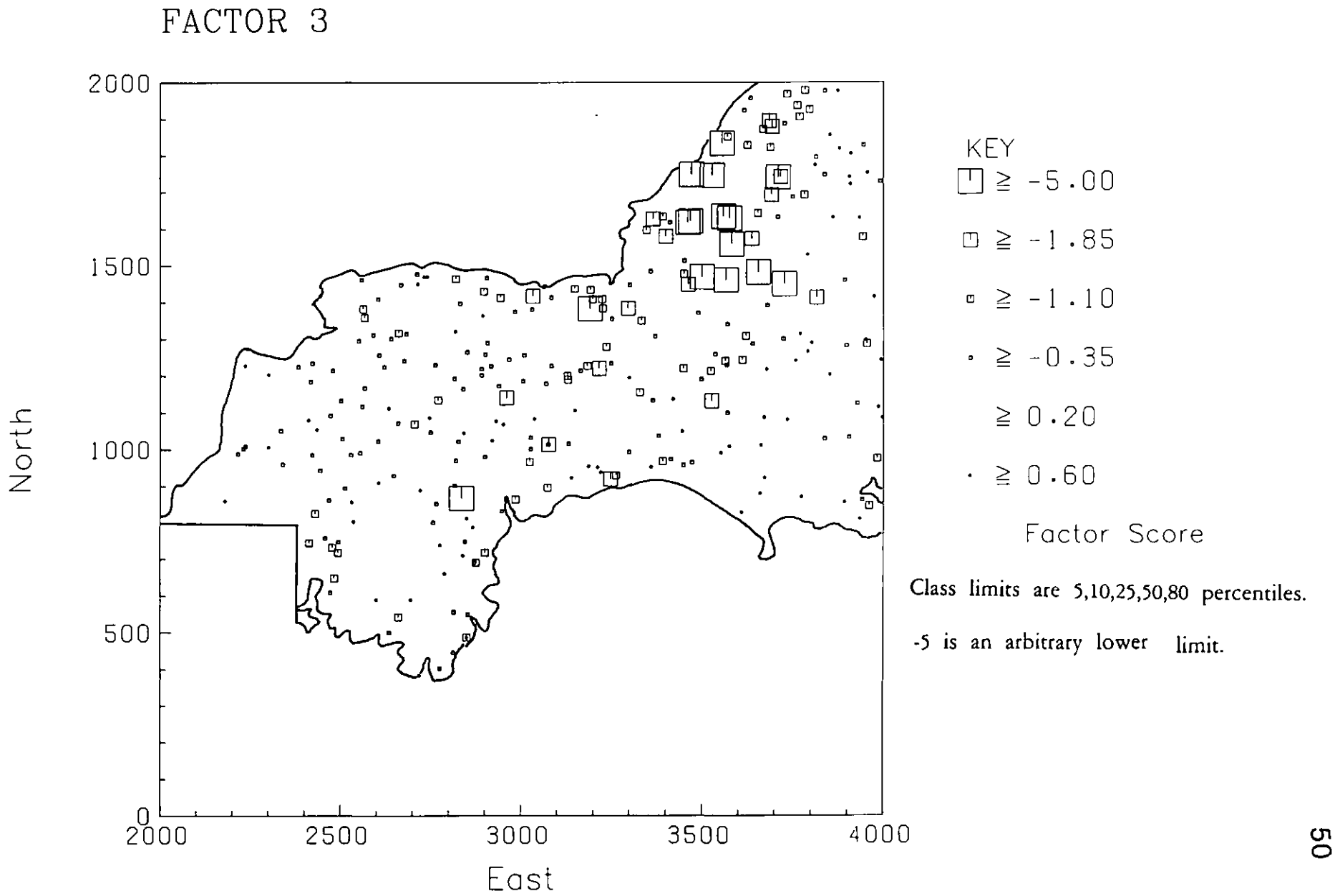


Fig 3.13 Distribution of scores: factor 3

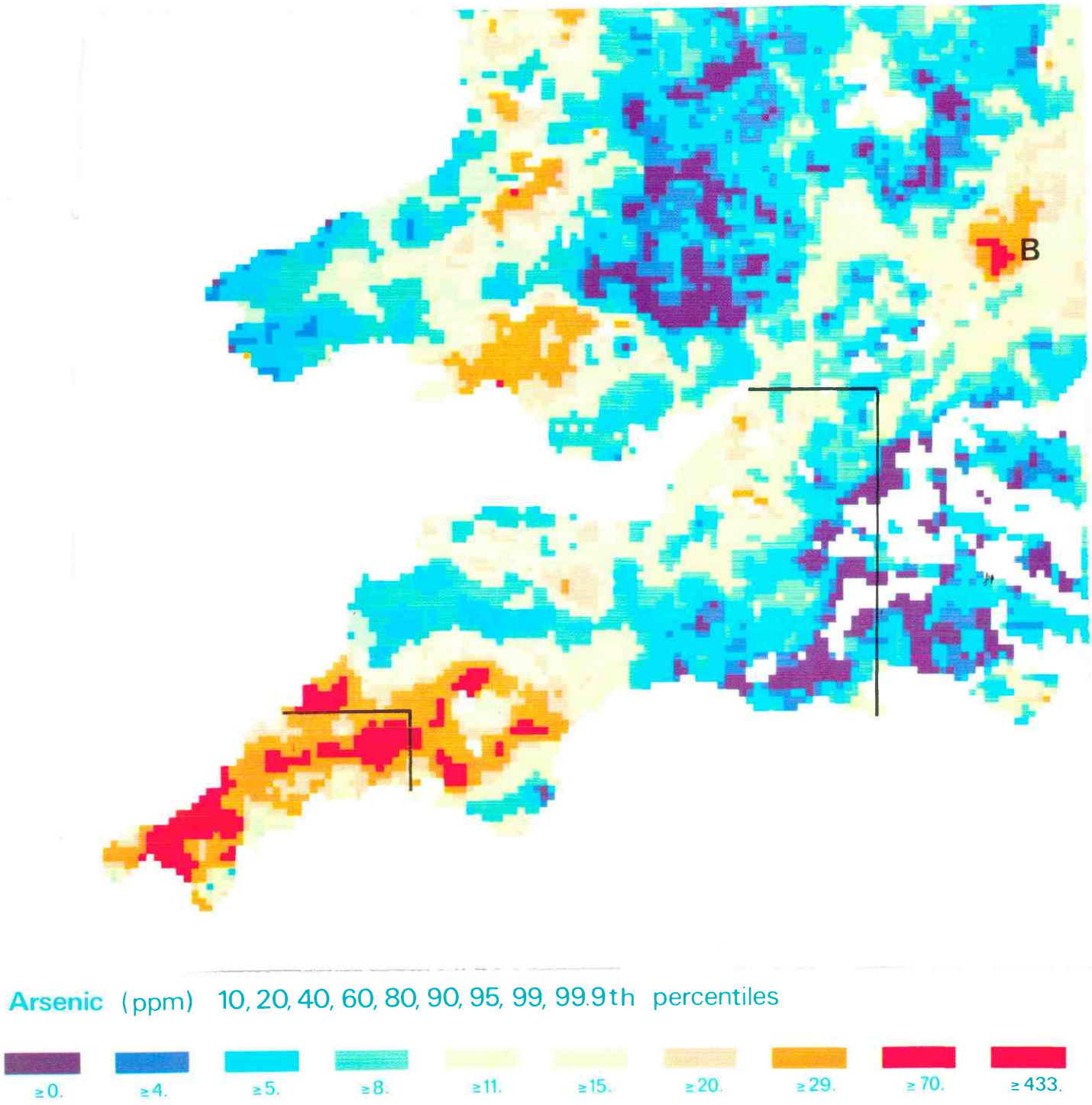


Fig 3.14 Arsenic distribution from the Wolfson geochemical atlas of England and Wales (Webb et al. 1978)
Note the distinct halo around the Dartmoor granite and the anomaly near Banbury (marked B) associated with Jurassic ironstones.

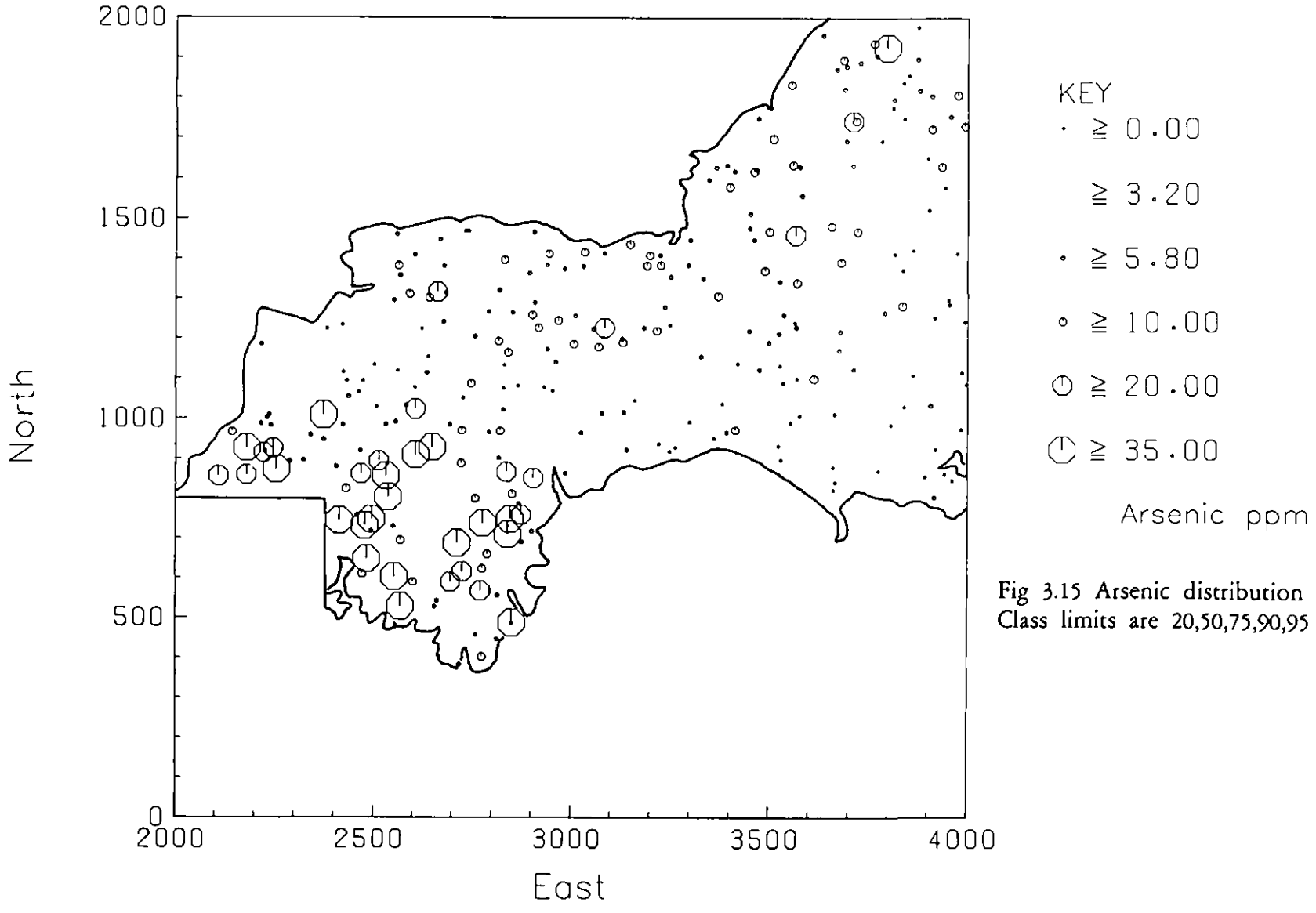


Fig 3.15 Arsenic distribution
Class limits are 20,50,75,90,95 percentiles.

high arsenic values around the Dartmoor and Bodmin Moor granites. The detailed investigations of Aguilar (1974) show that the high values are concentrated in sediments and basic intrusives of the metamorphic aureole, (average 66 ppm compared to 8 ppm in unmetamorphosed rocks). He considered that the enrichment in the aureole was caused by late stage hydrothermal fluids which deposited arsenic in veinlets, analogous to the crackle breccias of porphyry copper deposits.

It is difficult to assess the degree to which the arsenic anomalies are due to vein mineralization but examination of the top ten percent of arsenic values (top five percent shown in Table 3.3) suggests that the arsenic enrichment is only relatable to base metal-Sn-W mineralization in about 50% of the samples. The Wolfson Atlas data can also not be correlated to intensity of known mineralization although the mineralized Hemerdon and Okehampton districts are clearly defined.

This pattern, related to fluids associated with granite intrusion, is superimposed on a subtler pattern caused by other concentrating processes and environmental factors. This is reflected in the frequency distribution of the data (Fig. 3.16). The total data set is further subdivided for examination into histograms by lithology and age (Figs. 3.17, 3.18). Sandstone, shale and mixed siliceous lithology have similar means (Table 3.4) but shale is more positively skewed. Limestone values are slightly lower but there are insufficient samples derived from granite for comparison. Paleozoic strata are particularly enriched relative to the younger rocks with Devonian sediments particularly high. This, to some extent, reflects the development of lithologies which are particularly arsenic rich, e.g. black shales, in the

Table 3.3 Explanation of highest five percent of Arsenic Values

Sample No.	E	N	Conc. As ppm	Geology	Explanation
45599	2840	709	230	Dev sh/dol/gr	Sn-As Min
45829	2846	748	83	Cht/tuff	? No min ? Aureole
49176	2374	1008	52	Carb sh	Lamprophyre Dyke
49338	2255	873	56	Carb Sh/cht	No Min ?
49354	2180	927	72	Carb Sh/cht	No Min ?
50022	2483	647	81	Div sh/gr	Met Aureole
50076	2553	602	57	Dev sh	Met Aureole
50091	2568	528	41	Dev sh	W of Hemerdon Sn-W
50281	2712	687	67	Dev sh	Met Aureole
50343	2850	487	100	Dev Meadfoot Beds	?
51155	2414	744	72	Carb/Dev sh	Contaminated by As smelting
51165	2478	731	112	Dev sh	Cu Min
51174	2495	747	87	Dev sh/dol	Aureole
51183	2532	857	99	Dev sh/gr	Aureole
51259	2537	804	51	Dev sh/gr	Aureole
51471	2607	910	503	Gr	No min ?
51477	2649	929	169	Gr/Dev cht	Cu-As Min
51698	2777	738	239	Carb Sh/granite	No Min Skarn ?
52354	3796	1926	61	Inf. Oolite Jur	Ironstone

Abbreviations

sh - shale
ss - sandstone
cht - chert
Dev - Devonian
Jur - Jurassic
bl - black
lst - limestone
gr - granite
Carb - Carboniferous
met - metamorphic
mdst - mudstone
dol - domerite
Perm - Permian
min - mineralization

Table 3.4 Sample Classified by Predominant Lithological Provenance

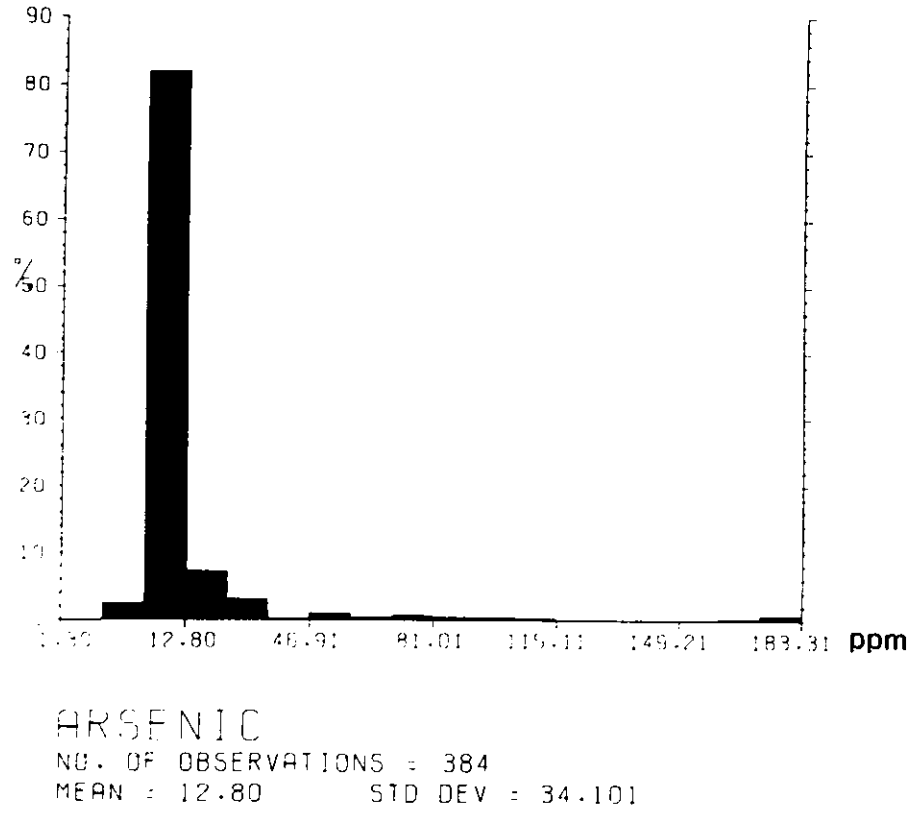
	Arsenic		Bismuth		Selenium	
	Mean (log mean)	Std dev	Mean (log mean)	Std dev	Mean (log mean)	Std dev
Coarse ground sediments (n = 75)	4.8 (0.68)	0.30	0.14 (-.83)	0.25	0.2 (-.7)	0.39
Mixed coarse clastic/firm clastic sediment (n = 55)	6.3 (0.8)	0.31	0.18 (-.73)	0.27	0.21 (-.68)	0.33
Fine grained clastic sediments (n = 197)	7.6 (0.88)	0.40	0.22 (-.66)	0.44	0.27 (-0.57)	0.35
Limestone (n = 44)	4.3 (0.63)	0.43	0.13 (-.86)	0.40	0.20 (-0.69)	0.40
Granite (n = 7)	30.0 (1.48)	0.71	0.81 (-0.09)	0.28	0.25 (-0.61)	0.59

(n = number of samples)

Table 3.5 Samples Classified by Age of Predominant Provenance

	Arsenic		Bismuth		Selenium	
	Mean ppm		Mean ppm		Mean ppm	
	(log mean	Std dev)	(log mean	Std dev)	(log mean	Std dev)
Tertiary (n = 5)	3.5	(0.55 0.59)	0.1	(-1.0 0.49)	0.20	(-0.7 0.55)
Cretaceous (n = 27)	2.4	(0.38 0.25)	0.1	(-1.0 0.24)	0.19	(-0.73 0.34)
Jurassic (n = 95)	5.2	(0.72 0.28)	0.14	(-0.84 0.26)	0.20	(-0.70 0.34)
Permo-Triassic (n = 77)	7.9	(0.90 0.36)	0.20	(-0.69 0.37)	0.21	(-0.68 0.34)
Carboniferous (n = 105)	6.9	(0.84 0.38)	0.19	(-0.72 0.40)	0.25	(-0.60 0.38)
Devonian (n = 67)	10.7	(1.03 0.48)	0.41	(-0.39 0.52)	0.37	(-0.43 0.34)

(n = number of samples)



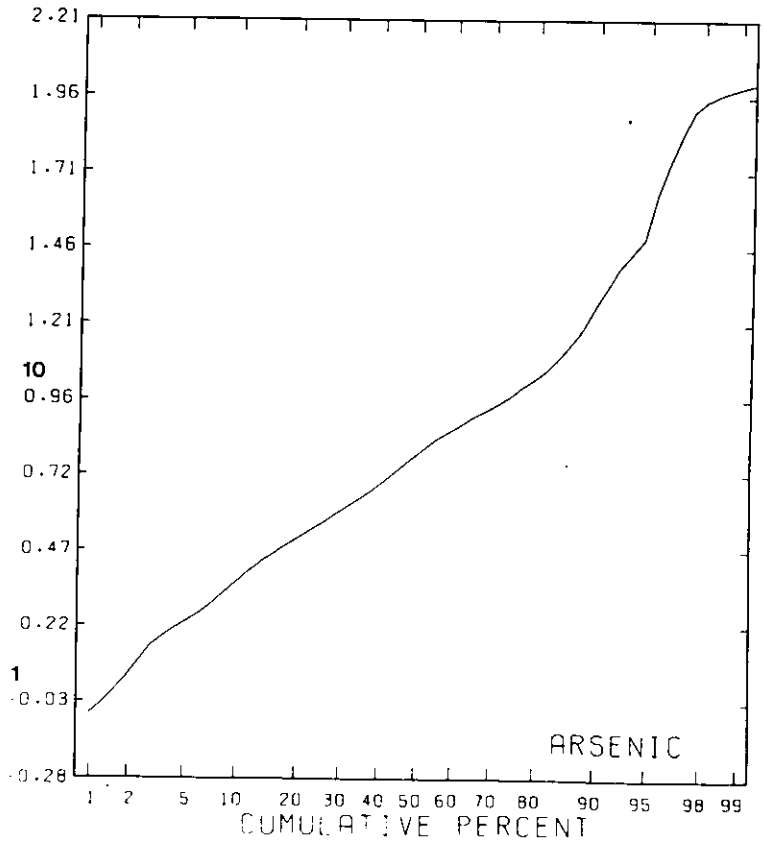


Fig 3.16 Histogram and (log transformed) cumulative frequency plot: arsenic

SS = sandstone, SS/H = mixed sandstone / claystone / mudstone, SH = mudstone / claystone, LST = limestone, GR = granite

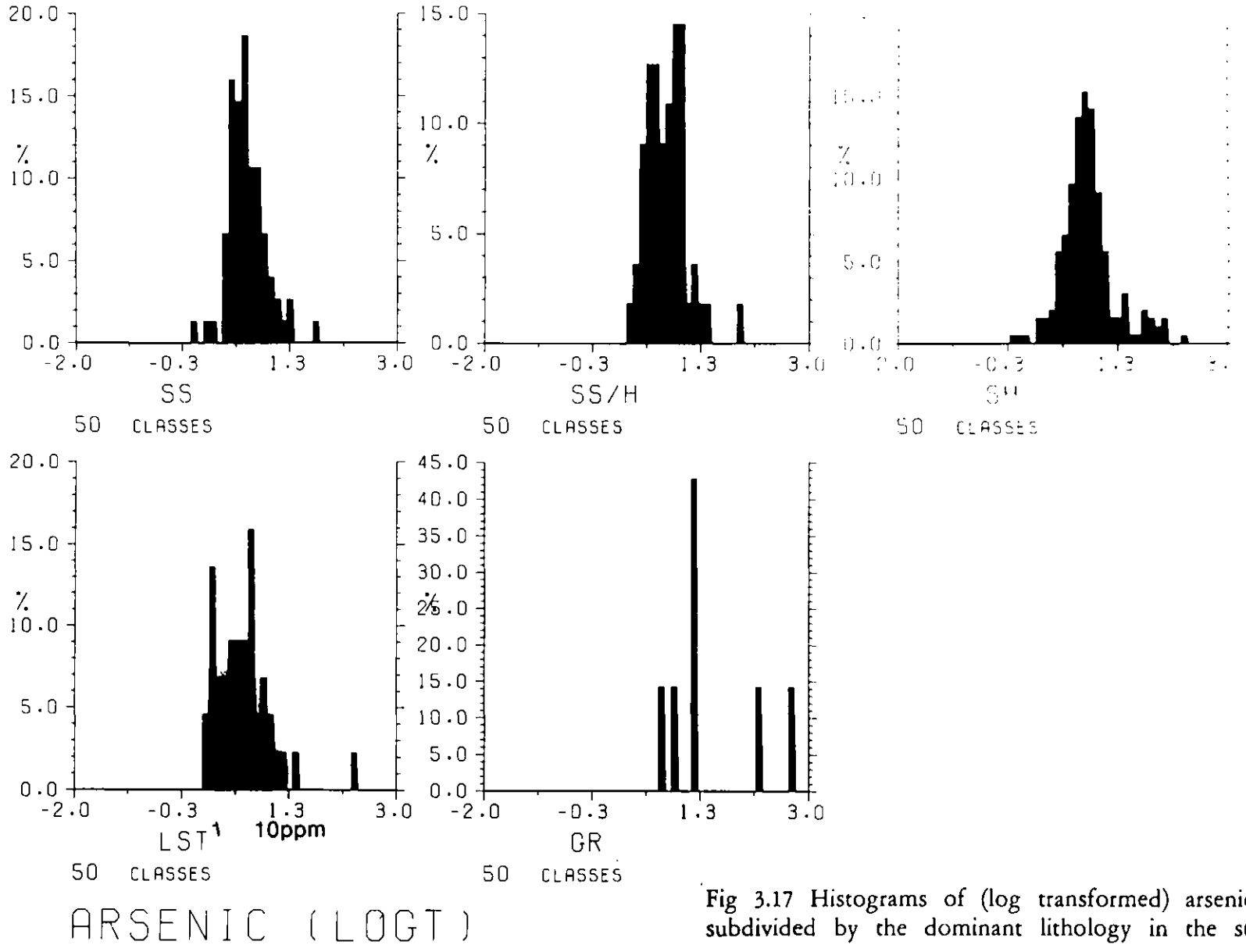


Fig 3.17 Histograms of (log transformed) arsenic concentrations subdivided by the dominant lithology in the stream sediment provenance area.

TERT = Tertiary, CRET = Cretaceous, JUR = Jurassic, P/T = Permo-Triassic, CARB = Carboniferous, DEV = Devonian.

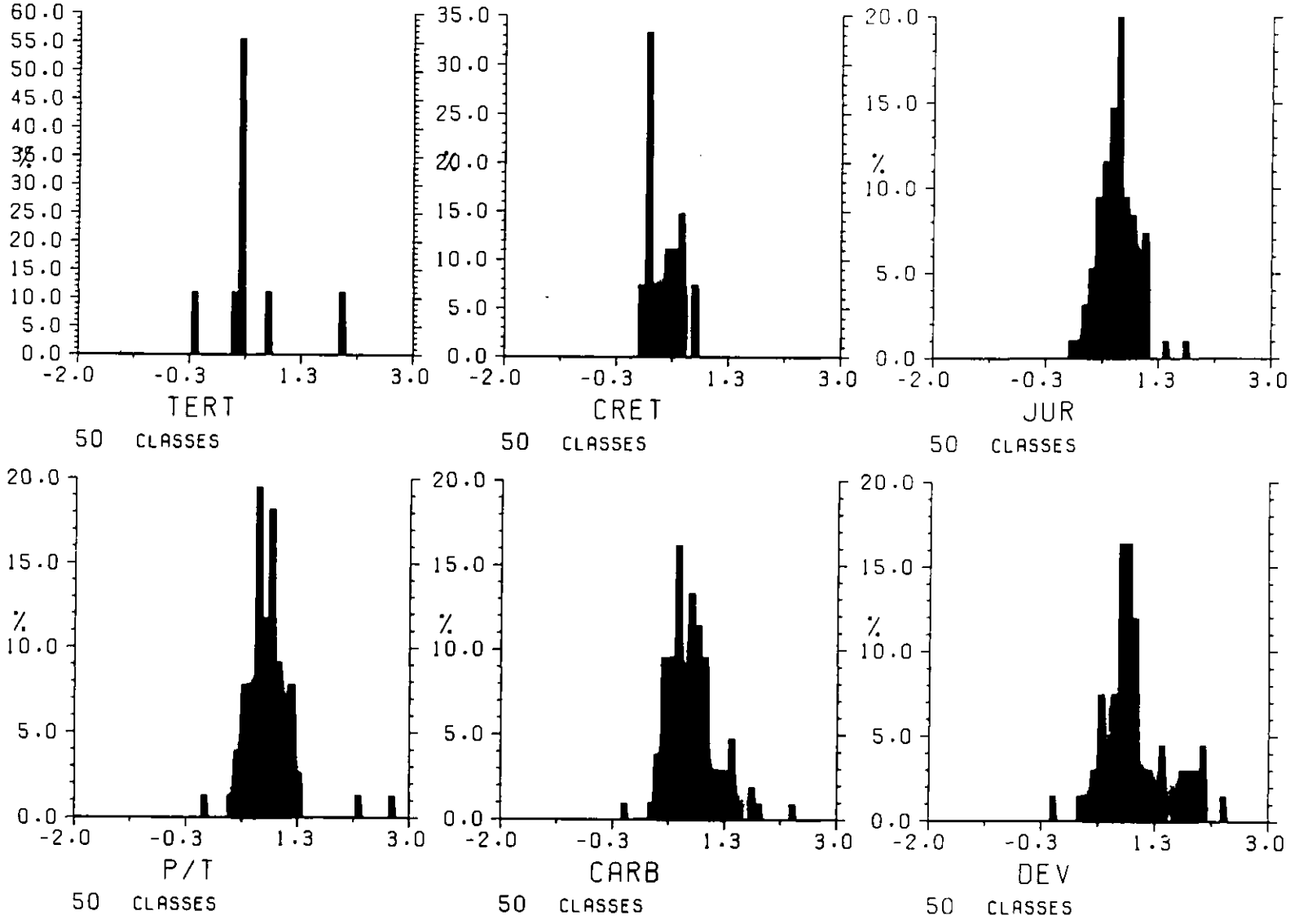


Fig 3.18 Histogram of (log transformed) arsenic concentrations subdivided by the dominant age of bedrock in the stream sediment provenance area.

Paleozoic but, in my opinion, relates to the overall environment of deposition. The high values of geosynclinal deposits in the Devonian and Carboniferous contrasts with the lower values of shelf sediments in the Jurassic and Cretaceous.

High (90 - 95 percentile) arsenic values are common in stream sediments derived from a section of Dinantian age (lowest Carboniferous) in Central West Devon. This consists of a succession of black shales, cherts, limestones, tuffs and thin sandstones (Edmonds et al, 1968), which have been subject to imbricate thrusting (Isaac et al, 1982). High values (51 ppm) are known from the pyritic, molybdeniferous shales and also from the cherts (Aguilar, 1974). Most of the cherts are biogenic in origin but, in my view, the possibility of exhalative activity and mineralization analagous to the pyrrhotite mineralization (MacKeown et al, 1973) at Wilsey Down (2125 0888) should not be ruled out. Less consistently high arsenic values occur on the other main Devonian outcrop, which forms Exmoor. There are occasional sulphide shows and they are dominantly stratiform in character.

Sporadic high values exist in the western part of the Permian red bed molasse sequence and detailed investigations by Aguilar have shown that vulcanism, contemporaneous with the base of the sedimentary section, is enriched in arsenic. These volcanics have also been reworked and arsenic rich clasts deposited in the basal sedimentary units. Poorly exposed lamprophyre dykes, which are probably related to the vulcanism, cause discrete arsenic anomalies within the otherwise low Mid-Carboniferous sediments. Arsenic values in sediments derived from the unroofing of the Dartmoor Granite (e.g. the Crediton conglomerates) are lower than the

underlying sediments, perhaps because they are more distal from the sediment source.

Examination of the distribution of values in the Jurassic shows that high (20 - 40 ppm As) values correlate with the outcrop of the carbonaceous black clay of the Lower Lias (Thomson, 1971) and with ironstones of the Inferior Oolite. This latter unit is associated with major arsenic anomalies on the Wolfson Atlas, particularly near Banbury, Oxfordshire.

Sediments of Cretaceous and Tertiary provenance are low in arsenic.

3.2.3 Bismuth Distribution

High (>90 percentile) bismuth values are more obviously related to the granite intrusives than those of arsenic (Fig. 3.19). In particular there is no halo effect and stream sediments derived from granite are higher than those from the surrounding metamorphic aureole. The very high (>95 percentile) values are 75% relatable to areas of known mineralization (Table 3.6), particularly the tin-arsenic deposits in the Buckfastleigh area and the disseminated tungsten-tin deposit at Hemerdon, north of Plymouth, which is known to be enriched in bismuth (Ball, 1982). A stream draining the Eisen iron ore mine on Exmoor is high as is a sample taken from an area of smelter contamination near Gunnislake, Cornwall. Two anomalous samples are not relatable to mineralization; one is downstream from a Permian lamprophyre dyke but the source of the other anomaly (14.1 ppm) is unknown, although no check analysis has been carried out.

The restricted nature of the high bismuth values allows easier evaluation of background levels. The overall distribution of values (Fig. 3.20) suggest that

Table 3.6 Explanation of highest five percent Bismuth Values

Sample No.	E	N	Conc. Bi ppm	Geology	Explanation
45565	2905	852	2.3	Perm sh	? Near bl sh/cht
45599	2840	709	23.0	Dev lst/dol/gr	Sn-As Mineralization
45767	2837	867	1.9	Dev sh/gr	Mineralized gr
47411	2895	1364	2.5	Dev sh	Eisen Iron Mine Exmoor
49176	2374	1008	2.5	Carb sh	? Lamprophyre Dyke
50022	2483	647	12.8	Dev sh/gr	Extension of Sn vein
50045	2569	694	3.8	Gr	Mineralized gr
50068	2600	589	4.0	Dev sh/gr	Hemerdon Sn-W
50076	2553	602	2.6	Dev sh/gr	Hemerdon Sn-W
50232	2695	589	8.5	Dev sh/gr	Lurton Area-Min
50281	2712	687	8.0	Dev sh	Sn min
51155	2414	744	2.2	Dev sh	? Contamination from As smelting
51165	2478	731	2.4	Dev sh	Cu min
51174	2495	747	2.0	Dev sh/dol	?
51183	2532	857	1.7	Dev sh/gr	? min
51259	2537	804	2.2	Dev sh/gr	? No min
51477	2649	929	1.7	Gr/Dev cht	Cu-As min
51605	2748	1087	14.1	Carb ss/sh	??
51698	2772	738	19.7	Dev sh/gr	Sn-As min

Abbreviations

See Table 3.3

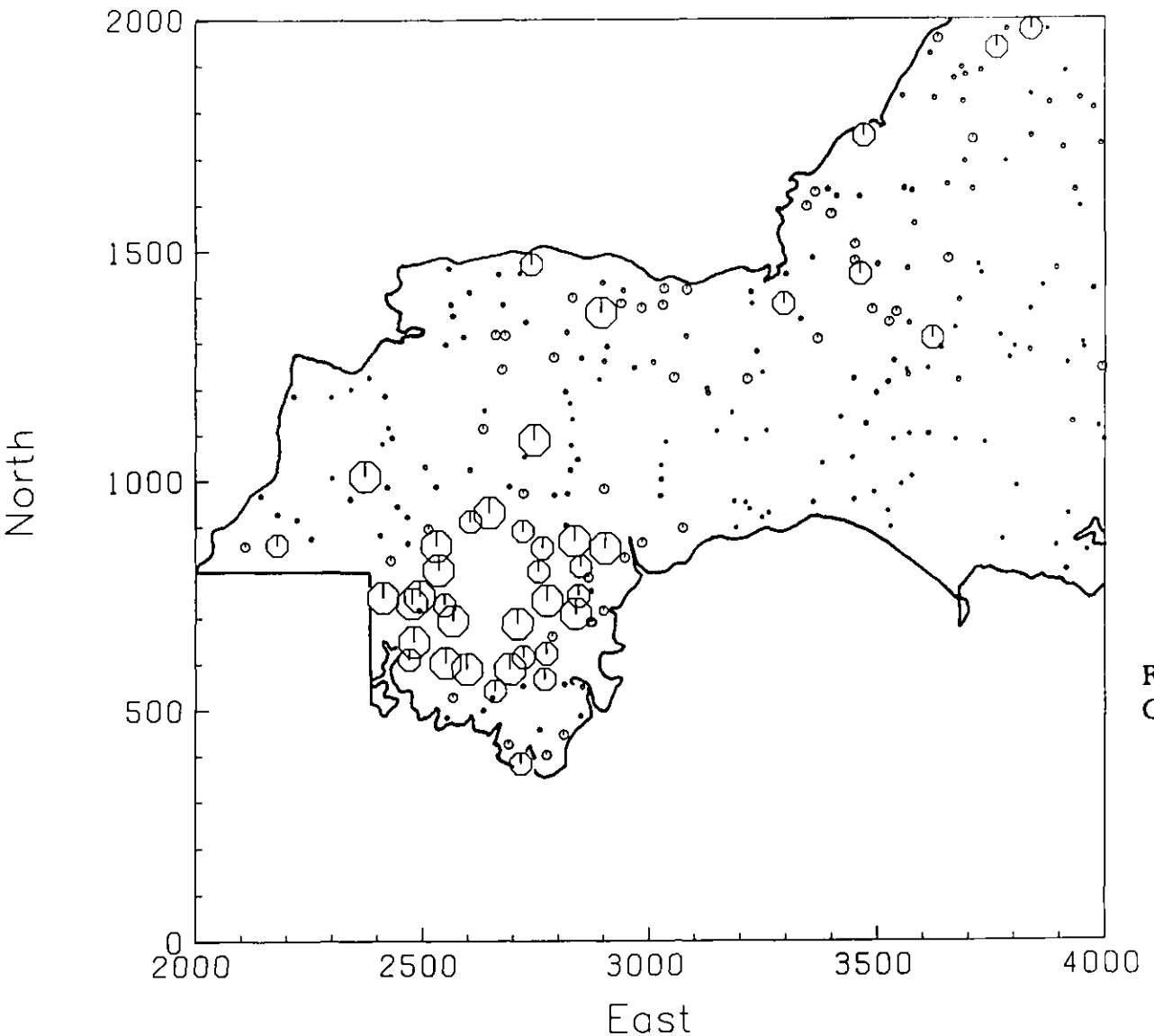
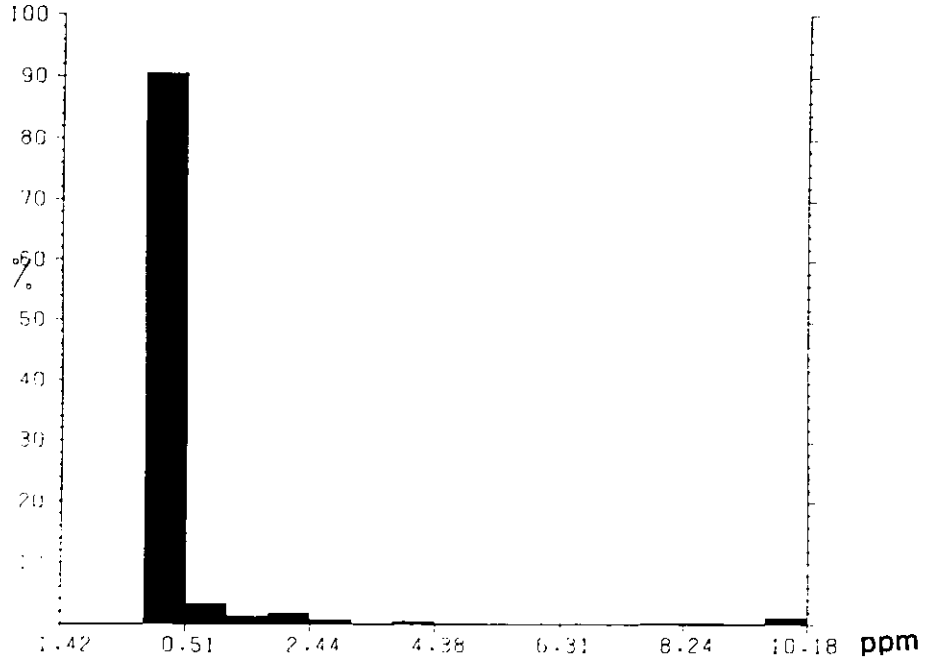


Fig 3.19 Bismuth distribution
Class limits are 20,50,75,90,95 percentiles.



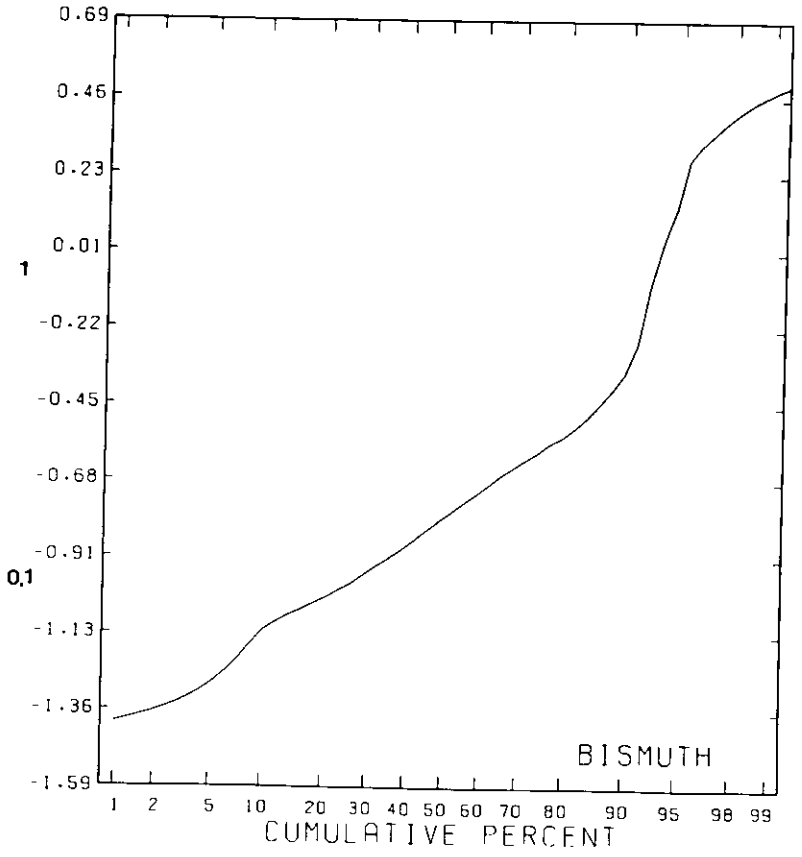


Fig 3.20 Histogram and (log transformed) cumulative frequency plot: bismuth

the uppermost 10 percent of values may be regarded as an anomalous population. Fine grained clastic sediments (Fig. 3.21) are enriched in bismuth relative to their coarser equivalents and there is a positive skew in the shale distribution (although this is partly due to mineralization/granite influences). The bismuth contents of stream sediments derived from limestone are similar to those derived from sandstones. Devonian rocks (Fig. 3.22), with their predominance of shales, are particularly enriched relative to the sediments of other ages with Cretaceous and Tertiary sediments notably low.

There are two main high background, non granite, areas: a belt in the Devonian sediments on Exmoor; and another correlating with the outcrop of the Lower Lias and Triassic marls in central Somerset. Lack of detailed geology prevents accurate evaluation of the Exmoor anomalies but they are probably associated with marine shales of the Ilfracombe Beds. The outcrop of the Lower Lias has been the subject of considerable investigation (e.g Thornton et al, 1969) and the organic rich component of the shales is enriched in metals (Le Riche, 1959), particularly molybdenum, as is the lowest part of the Rhaetic. The main problem in this area is to try to apportion the influence of bedrock and that of the thick organic rich alluvium on pathfinder content. I have attempted to do this by examining the soil survey information for the area (Avery, 1955). Moderately high values are associated with both peat covered areas and gleyed soils, but the highest values are on thick peats. The overall control is not clear.

Other minor enrichments are associated with the Lower Lias and Inferior Oolite, east of Bristol, and are probably related to bedrock enrichment of the type

SS = sandstone, SS/H = mixed sandstone / claystone / mudstone, SH = mudstone / claystone, LST = limestone, GR = granite

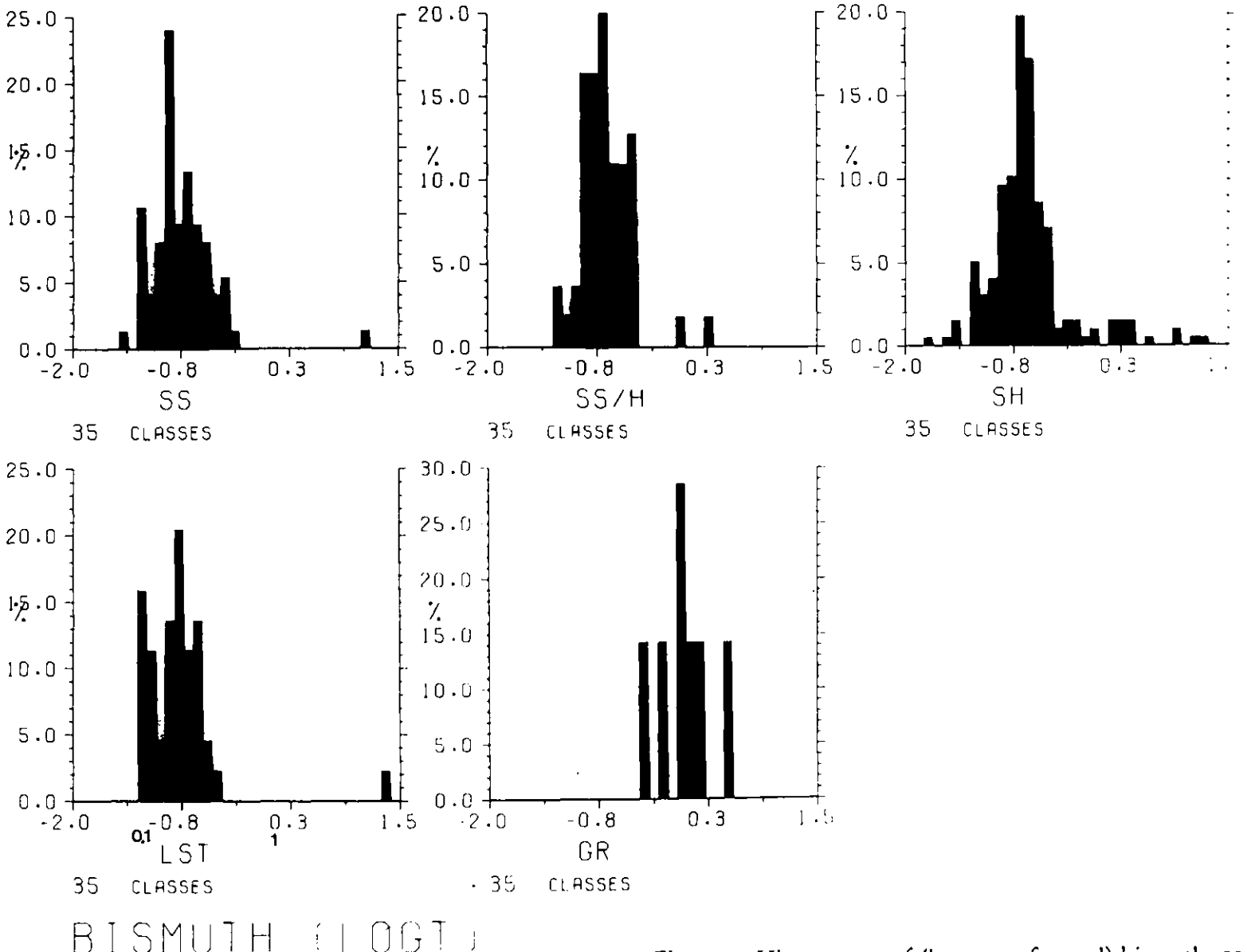


Fig 3.21 Histograms of (log transformed) bismuth concentrations subdivided by the the dominant lithology in the stream sediment provenance area.

TERT = Tertiary, CRET = Cretaceous, JUR = Jurassic,P/T = Permo-Triassic, CARB = Carboniferous, DEV = Devonian.

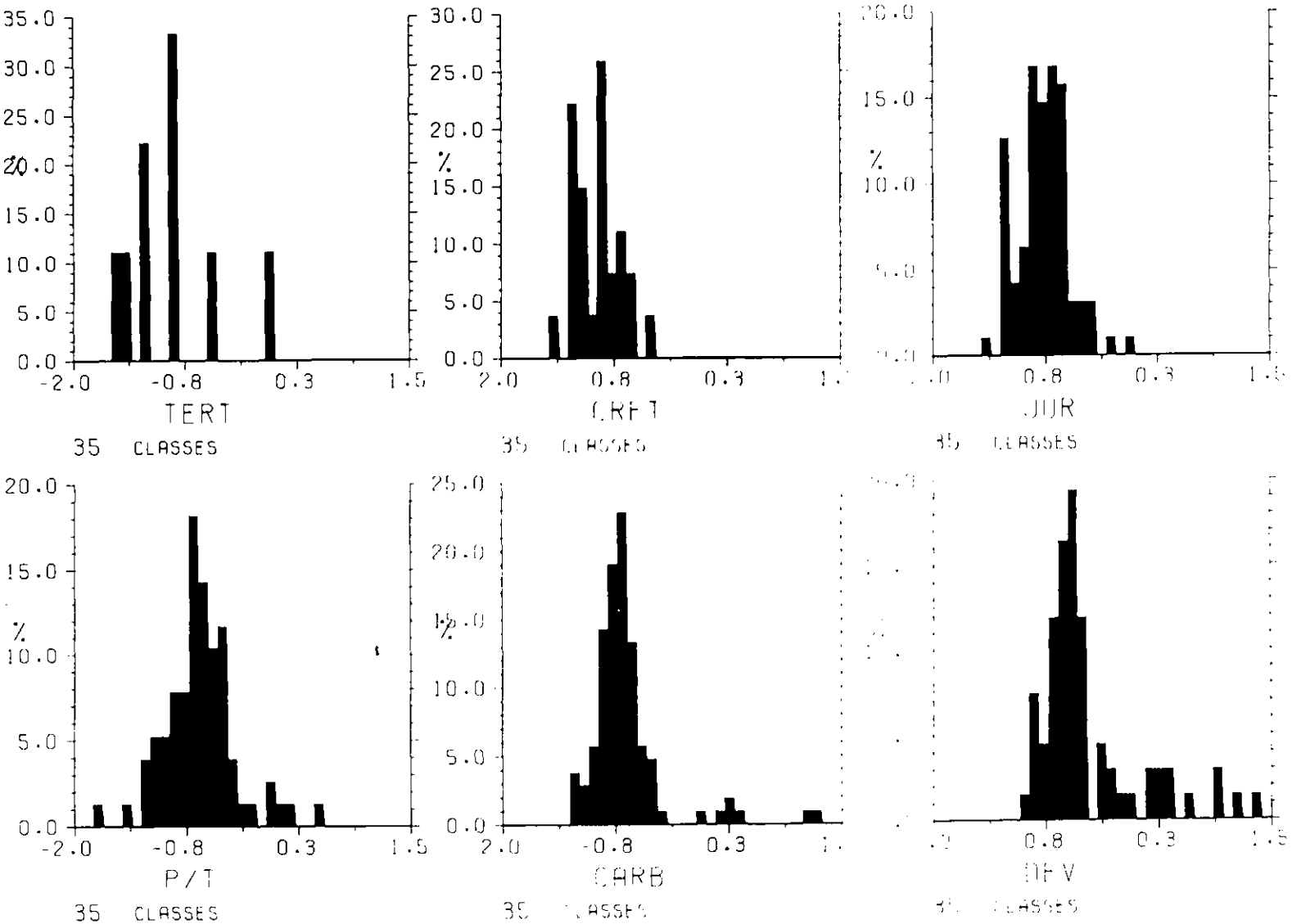


Fig 3.22 Histograms of (log transformed) bismuth concentrations subdivided by the dominant age of bedrock in the stream sediment provenance area.

mentioned above. There is a possibility that a single point high near Avonmouth is a result of contamination from base metal smelting.

3.2.4 Selenium Distribution

Selenium has a very different distribution pattern from those of arsenic and bismuth as it does not reflect the mineralization associated with the granites and there is no anomalous population (Fig. 3.23).

The majority of high values (Fig. 3.24) occur in south Devon and north Cornwall and many are associated with Dinantian black shales which are molybdeniferous. Detailed studies (Webb et al, 1966) show that the pyritic shales range from 2.5 - 6.0 ppm Se. Other stream sediments derived from Devonian shales are enriched, but there is no obvious geological control on their distribution.

Environmental effects appear locally important and selenium can be strongly enriched in peat overlying bedrock, low in selenium, such as granite (Table 3.7).

High values of selenium, correlated with molybdenum, occur in the 'teart pastures' of the Somerset Levels. There is no obvious association with peat and I suggest that the prime controls are bedrock content and fixation in gleyed soils.

The other main area of selenium enrichment is the Forest of Dean coalfield, where high selenium values correlate with coal outcrops. It is not known whether the enrichments are related to smelting or are a primary feature, but the area is worthy of future investigation by environmental geochemists.

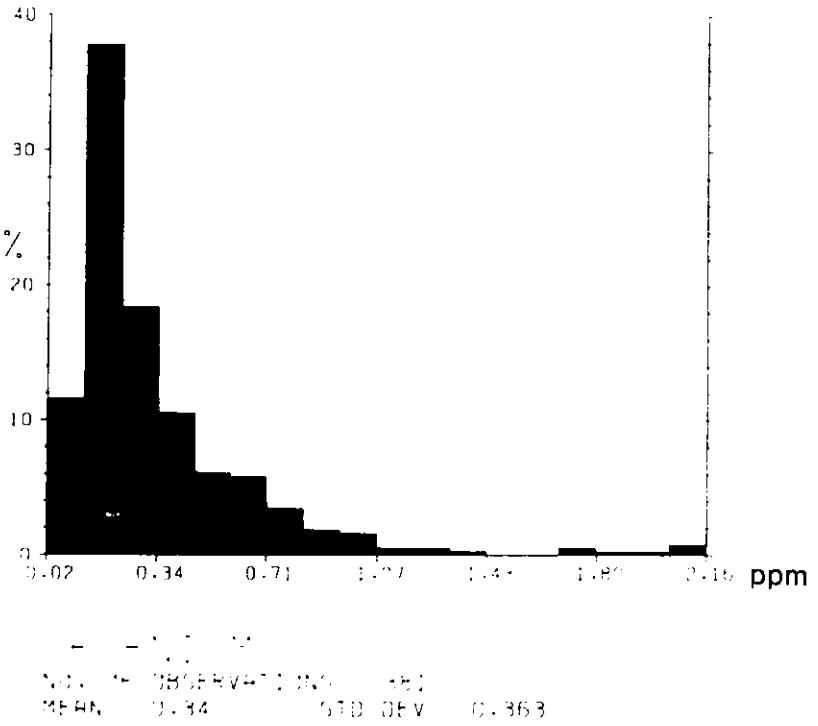
A histogram of provenance lithology (Fig. 3.25) shows that shales are higher and have a more positive skew than the coarser clastic sediments and limestones.

Table 3.7 Explanation of highest five percent of Selenium Values

Sample No.	E	N	Conc. Se ppm	Geology	Explanation
47550	2984	1375	1.0	Mid Devonian	? Marine shales
49271	2247	926	1.1	Culm ss/sh	?
49338	2255	873	1.9	Dev/Carb sh/cht	Black shale
49362	2223	915	1.3	Dev/Carb sh/cht	Black shale
50091	2568	528	0.9	Dev tuff/sh	Black shale
50139	2691	425	1.0	Dev Meadfoot	? Marine shales
50281	2712	687	1.1	Dev shale	? Marine shales
50358	2814	556	2.5	Dev sh/tuff	Black shales
51125	2514	894	1.4	Dev/Carb sh/cht	Black shales
51155	2414	744	1.7	Dev/Carb sh/cht	Black shales
51174	2495	747	1.0	Dev tuff lst	Black shales
51471	2607	910	3.2	Granite	Peat
51698	2777	738	0.9	Dev/Carb shales	? Marine shales
51983	3622	1308	1.0	Jur L.Lias	Marine clay
52358	3763	1937	2.7	Jur L.Lias	Marine clay
52612	3686	1895	1.8	Carb Coal Measures	Coal
52615	3694	1879	1.3	Carb Coal Measures	Coal
52639	3689	1822	1.0	Carb Coal Measures	Coal
52647	3669	1872	1.1	Permian mdst	Peat
75180	2813	446	1.9	Dev sh	Organic rich drift

Abbreviations

See Table 3.3



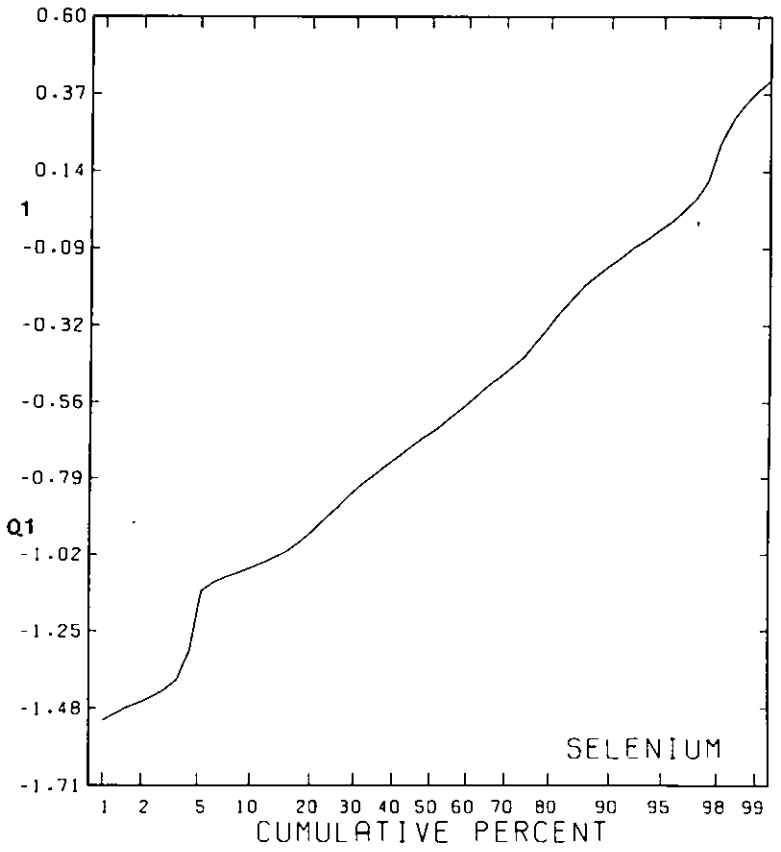


Fig 3.23 Histogram and (log transformed) cumulative frequency plot: selenium

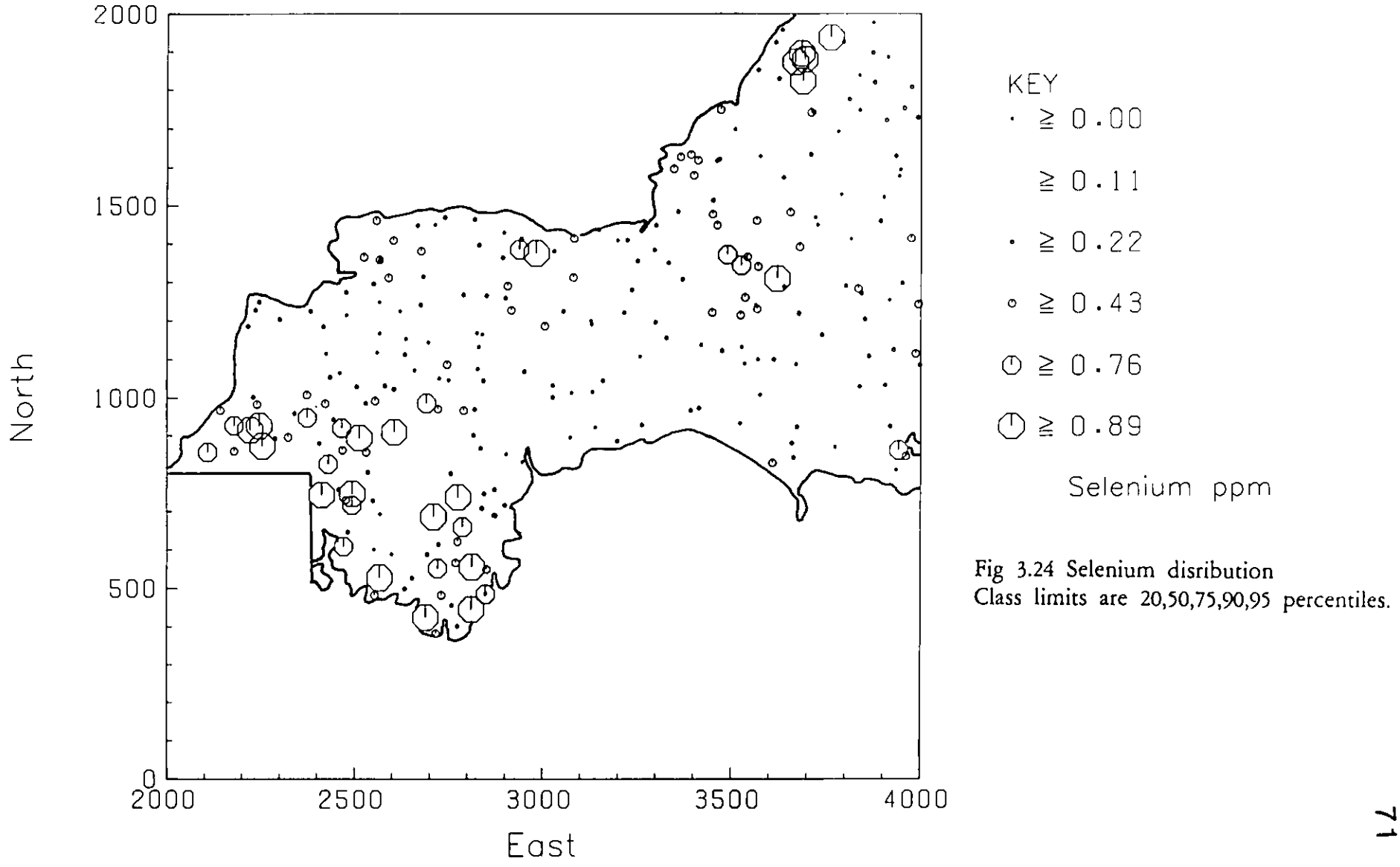


Fig 3.24 Selenium disribution
Class limits are 20,50,75,90,95 percentiles.

SS = sandstone, SS/H = mixed sandstone / claystone / mudstone, SH = mudstone / claystone, LST = limestone, GR = granite

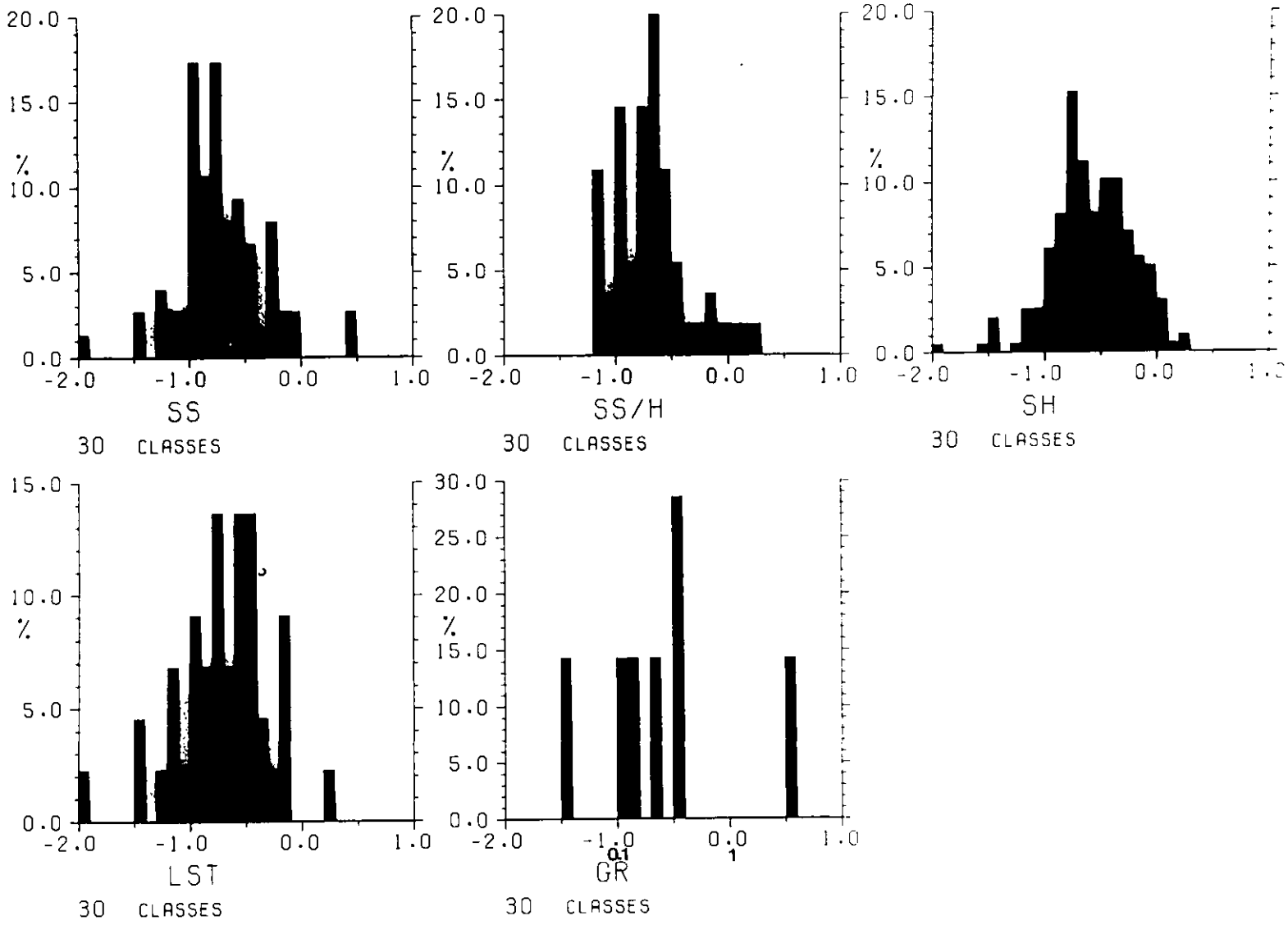


Fig 3.25 Histograms of (log transformed) selenium concentrations subdivided by the dominant lithology in the stream sediment provenance area.

TERT = Tertiary, CRET = Cretaceous, JUR =Jurassic, P/T = Permo-Triassic CARB = Carboniferous, DEV = Devonian.

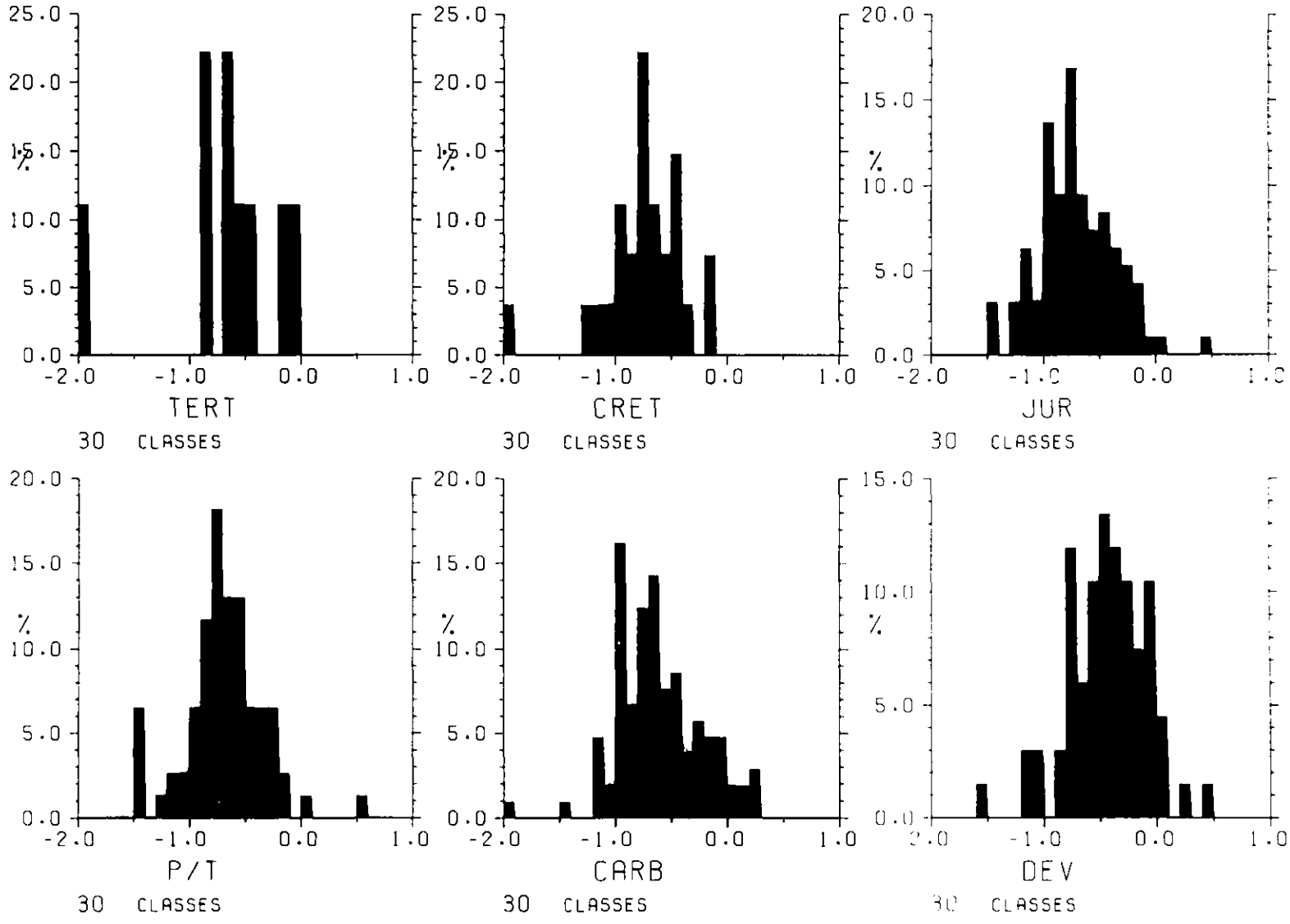


Fig 3.26 Histograms of (log transformed) selenium concentrations subdivided by the the dominant age of bedrock in the stream sediment provenance area

Stream sediments derived from Devonian rocks (Fig. 3.26) are particularly enriched, possibly reflecting the predominance of shales and the deposition of these in relatively deep water. The positive skews of the Carboniferous and, to a lesser extent, Jurassic histograms show the influence of black pyritic shales.

The factor (factor 7) which shows a high loading on selenium with lesser loadings on copper and zinc is, thus, interpreted as a combination of organic scavenging (known elsewhere for copper, Rose et al, 1979) and enrichments in black shales.

3.3 Discussion and Conclusions

The major control on the distribution of pathfinder elements is the provenance of the sediments rather than secondary scavenging. There is some correlation between arsenic (and, to a lesser degree, bismuth and selenium) and iron, but this may reflect bedrock association rather than scavenging. Secondary organic concentration and gleying are locally important for selenium and possibly for bismuth.

The stream sediments show that all three pathfinders are concentrated in black shale environments, whereas arsenic and bismuth are also concentrated in late stage igneous processes.

Very high bismuth values are spatially restricted to the vein deposits whereas arsenic forms broad haloes around the mineralized plutons and discrimination of individual deposits, particularly within the metamorphic aureole, is less obvious. The high bismuth background of the granite may make evaluation of anomalies (possibly related to mineralization) at the granite/sediment contact difficult. Late stage intrusive dykes appear enriched in bismuth and arsenic while comparable

extrusives have enhanced arsenic. The enrichment of arsenic in and around the plutons may, at least in part, be due to anatexis of arsenic rich sediments similar to that suggested for copper by Jackson et al, (1982). The bismuth background is also high in metamorphic gneisses.

The sedimentary provenances highlight the pathfinder associations and in particular the high concentrations in reduced marine shales. Both arsenic and selenium are concentrated in volcanically associated Dinantian shales while probably only selenium is high in their Jurassic (non-volcanic) counterparts. Arsenic is however particularly enriched in some iron-rich (oolitic) sediments and in red beds.

Comparison (Table 3.8) of the stream sediment results with rock data suggest that selenium is concentrated in stream sediments while arsenic and bismuth values in this medium more closely reflect bedrock concentrations. The stream sediment data also show the high degree of inter-mixing of different rock types, and the values given, here, are probably more useful as background values for mineral exploration purposes than the 'pure' rock values available from the literature.

Limited data are available to compare soils with stream sediments but the preliminary data of Thornton (1982 pers. comm.) suggest that soils concentrate selenium relative to stream sediments and rocks.

The stream sediment data demonstrates no evidence of a correlation between rainfall and selenium, as reported in Norway by Lag and Steinnes,(1978).

Table 3.8 Comparison between stream sediment data (this study) and rocks (Table 2.1)

	ARSENIC		BISMUTH		SELENIUM		
	Rock	Stream* Sediment	Rock	Stream* Sediment	Rock	Soils#	Stream Sediment
Sandstone	2.0	4.8	0.05	0.14	0.01	0.36	0.2
Limestone	1.0	4.3	0.03	0.13	0.03	0.35	0.20
Shale	13	7.6	0.13	0.22	0.5	0.46	0.27
Granite	1.5	30	0.2	0.81	0.05	-	0.25
Clarke (Rocks) Median (Stream Seds.) Mean (Soils)	1.8	6.3	0.08	0.16	0.05	0.48	0.22

* Partial Extraction

\# Soil data co-precipitation method Thornton (pers. comm., 1982) approximately 500 analyses in total includes some peats

CHAPTER 4 SECONDARY DISPERSION FROM VEIN HOSTED DEPOSITS

Mineralized veins present the simplest case to investigate secondary dispersion because of their spatially limited primary concentration. Three areas were examined: uranium veins at Dalbeattie, Scotland; tin-tungsten vein swarms at Ballinglen, Ireland; and gold-antimony mineralization near Clontibret, Ireland. Each is sub-economic but of commercial interest.

4.1 Dalbeattie, Dumfries and Galloway, Scotland

The veins present a relatively simple exploration problem with thin surficial cover and a reasonable amount of outcrop. The general problems of uranium exploration caused by that element's mobility, however, remain.

4.1.1 Geology

The vein uranium mineralisation was discovered in cliffs flanking the Solway Firth in 1959 (Miller and Taylor, 1966) and was subsequently investigated by trenching and drilling. I estimate that resources of the most promising vein do not exceed 150,000 kg U_3O_8.

The veins occur on the periphery of the Caledonian Criffel granodiorite. Hornfelsed sediments, which are Silurian in age, are intruded by N.W. trending porphyrite pene-dykes, contemporaneous with the granodiorite and overlain unconformably by Carboniferous sediments. The mineralization is structurally controlled by northwest trending fractures, which cut the major northeasterly striking coastal fault, and is almost entirely confined to the hornfelsed sediments (Fig. 4.1).

Pitchblende is closely associated with hydrocarbon, chalcopyrite, native bismuth, hematite, with minor löllingite,

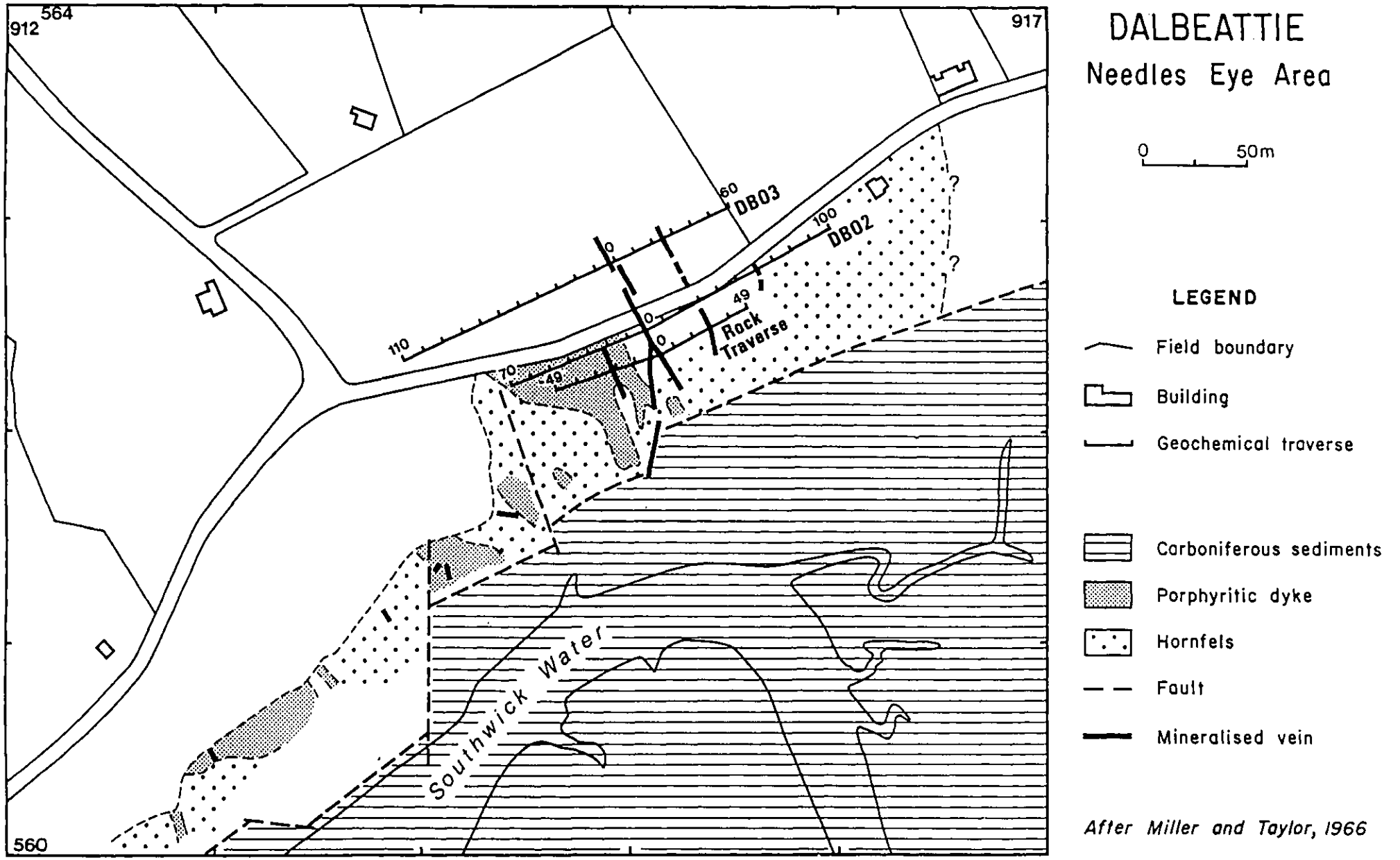


Fig 4.1 Dalbeattie: solid geology

niccolite and sphalerite in a dolomite gangue. Paragenetic studies suggest a later quartz-bismuth-calcite phase. There is a large supergene assemblage developed, including the uranium minerals, boltwoodite, zeunerite and connellite; the copper mineral atacamite ; and the bismuth mierals bismoclite (BiOCl) and mixite ($Cu_{11}Bi(AsO_4)_5(OH)_{10}.6H_2O$) and the arsenates erythrite and annabergite

Uranium-lead dates suggest an age of 180 Ma for the final stage of mineralization but the overall ore genesis, especially the role of the unconformity, is not clear.

The veins are up to 100 m in length, 0.6 m wide and at least 50 m in vertical extent. There is very little wall rock alteration.

a) Surficial Geology

The area was extensively glaciated during the Devensian glacial period, but drift cover is limited to relatively thin boulder clay. Compilation mapping (I.G.S. 1981) suggests that the area north of the road is mainly underlain by bedrock. The soils are mainly brown earths with little podzolisation.

4.1.2 Programme

The Needle's Eye area (915562), about 9 Km south east of Dalbeattie, was selected as high grade mineralization is well described and some veins are bismuth rich. They crop out on cliffs bordering the Solway Firth and can be traced for about 100 m inland (Fig. 4.1).

A lithogeochemical traverse(DB01) along the cliff

(by F.J. Tavora) sampled wallrocks and veins at approximately 7 m intervals. Two soil traverses normal to the veins and of 150-200 m length were taken, one at the top of the cliff in woodland (DB02) and the other in a pasture field 50 m further inland (DB03).

a) Lithogeochemical Traverse DB01

The samples were analyzed by ICP nebulisation, by both pathfinder attacks, and for uranium by ion exchange at Barringer Resources Inc., Denver.

The main feature of the traverse (Figs. 4.2 - 4.5) is the high but very erratic enrichment in the veins of a wide variety of transition metals and pathfinders. The elements enriched strongly are uranium, arsenic, bismuth, copper, lead, silver, molybdenum, cobalt, nickel with relatively lesser enrichements of chromium, vanadium, antimony and selenium.

The content of each element varies considerably from vein to vein and (based on field observations) within each vein. Uranium shows this particularly and radiometric highs are often associated with hydrocarbons, which are patchily seleniferous. Bismuth seems to be one of the more consistent elements but is particularly prominent in the veins around 0 m and in the east of the traverse. Wall rock enrichment in pathfinders is low although there is a high arsenic background in the centre and east of the traverse and,perhaps more significantly, uranium enrichment in the west.

b) Soil Traverse DB02

The object of this traverse is to determine the optimum particle size for analysis with a subsidiary interest in pathfinder response. The soil samples were collected at two depths (0 - 30 cm, and 30 - 60 cm), dry

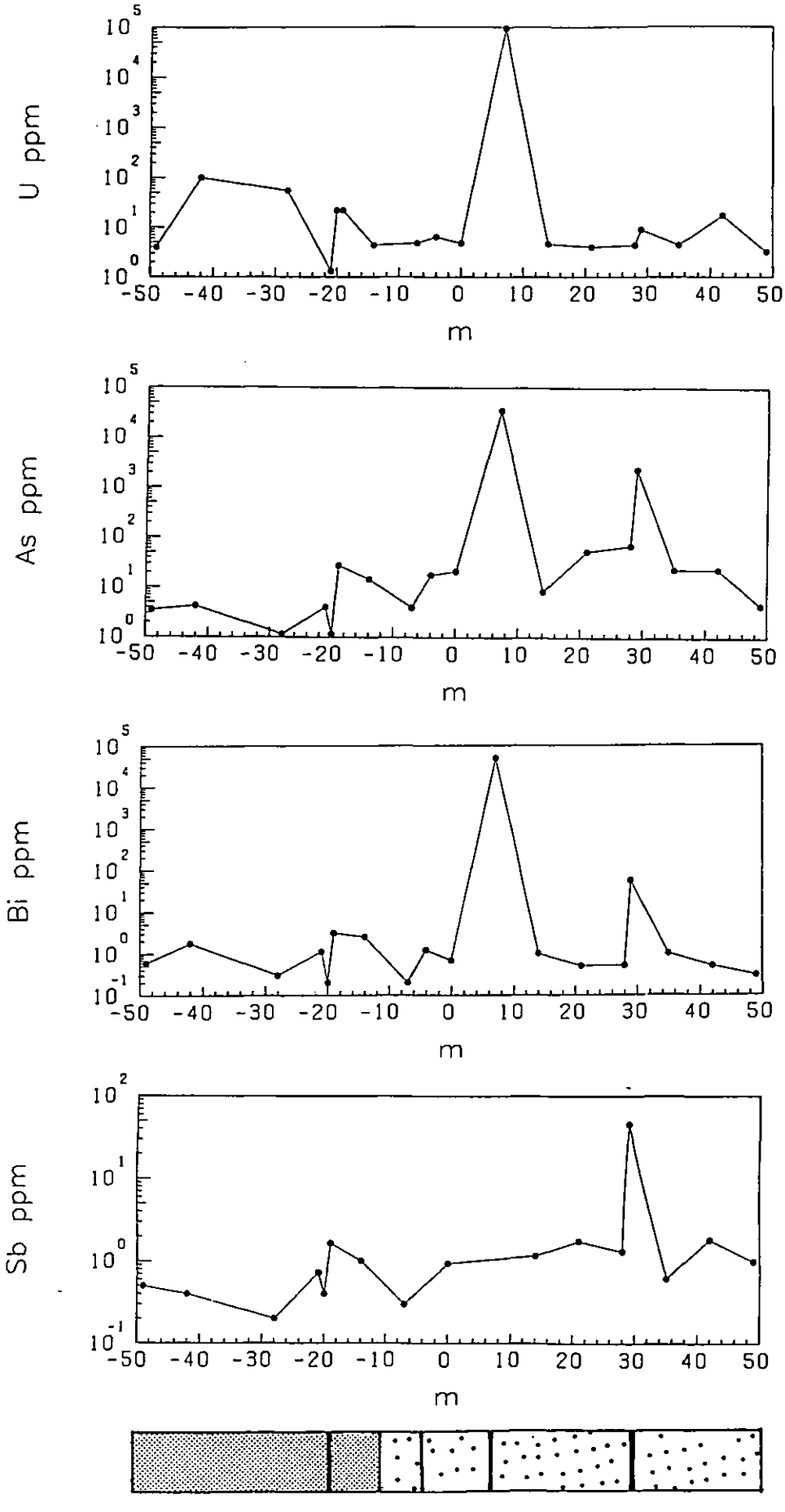


Fig 4.2 Dalbeattie: lithogeochemistry traverse DB01
Geological symbols as Fig 4.1

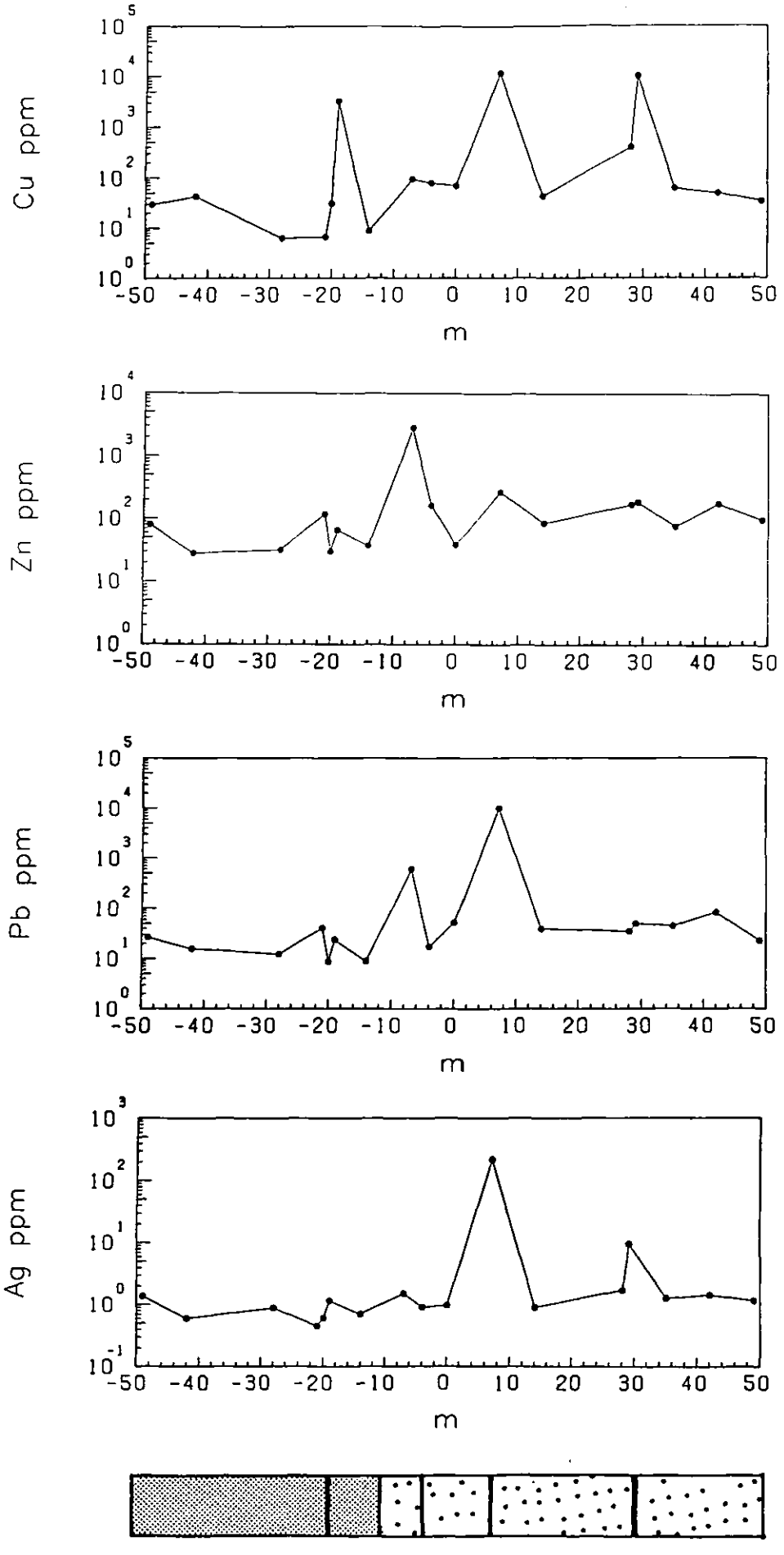


Fig 4.3 Dalbeattie: lithogeochemistry traverse DB01
Geological symbols as for Fig 4.1

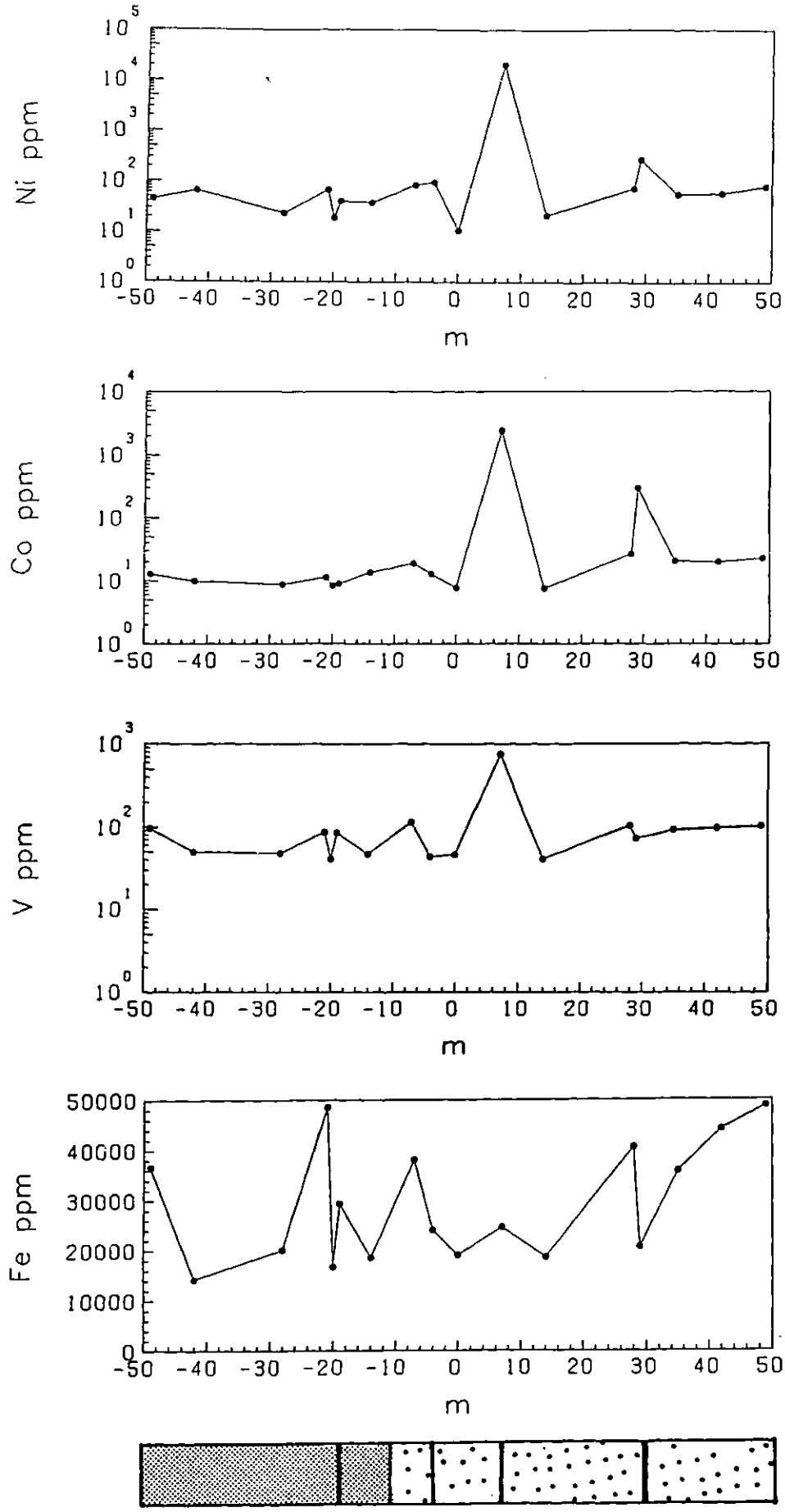


Fig 4.4 Dalbeattie: lithogeochemistry traverse DB01
Geological symbols as for Fig 4.1

sieved into three size fractions (-2,000 μm + 190 μm, -190 μm + 63 μm and -63 μm); and analyzed by atomic absorption following a nitric attack and for pathfinders by the co-precipitation method.

Comparison of the three size fractions (Fig. 4.5) shows that concentrations are similar in each fraction but the highest values, as might be anticipated, are in the finest fraction. A useful measure of the grain size dependency is to ratio the pathfinder content of a particular grain size to the average pathfinder content in the whole sample. This demonstrates (Table 4.1) that all the pathfinders are enriched and most variable in the finest fraction. This is most pronounced in the deeper samples and there is little difference between the two finer fractions. There is no correlation between the ratio and the location of the mineralization.

Plots of the more complete data of the intermediate fraction (-190 μm + 63 μm) give distinct, although narrow, arsenic and bismuth anomalies over the two veins indicated by gamma-ray spectrometry (Fig. 4.6). Bismuth reaches 33ppm relative to background of 2 ppm Bi while comparable figures are 30 ppm and 5 ppm for arsenic (note there is no deep sample at 60 m). Copper is the most useful of the transition metals with a maximum of 280 ppm relative to 10 ppm background. In addition to the major anomalies over the main veins there are minor anomalies: one at -20 m associated with a vein shown on Fig. 4.1 and a smaller anomaly at 15 m of unknown origin.

Minor lead highs occur over the veins, especially in the shallower samples but they are less prominent than the anomaly at -50 m (130 ppm relative to 40 ppm Pb background) of unknown origin. In contrast, selenium is not anomalous.

Table 4.1 Comparison of pathfinder content in various size fractions using the ratio of pathfinder content in each fraction to the mean content in the sample Traverse DBØ2

		Ø–3Ø cm			3Ø–6Øcm		
		−2ØØØμm +19Øμm	−19Øμm +63μm	−63μm	−2ØØØμm +19Øμm	−19Øμm +63μm	−63μm
As	x	Ø.91	1.17	1.22	Ø.91	1.16	1.4Ø
	s	Ø.Ø6	Ø.12	Ø.16	Ø.Ø7	Ø.12	Ø.35
Bi	x	Ø.89	1.2Ø	1.27	Ø.9Ø	1.16	1.41
	s	Ø.Ø6	Ø.12	Ø.19	Ø.Ø7	Ø.13	Ø.31
Se	x	Ø.88	1.24	1.25	Ø.89	1.23	1.36
	s	Ø.Ø8	Ø.17	Ø.22	Ø.Ø8	Ø.2Ø	Ø.36

x = mean of traverse
s =standard deviation

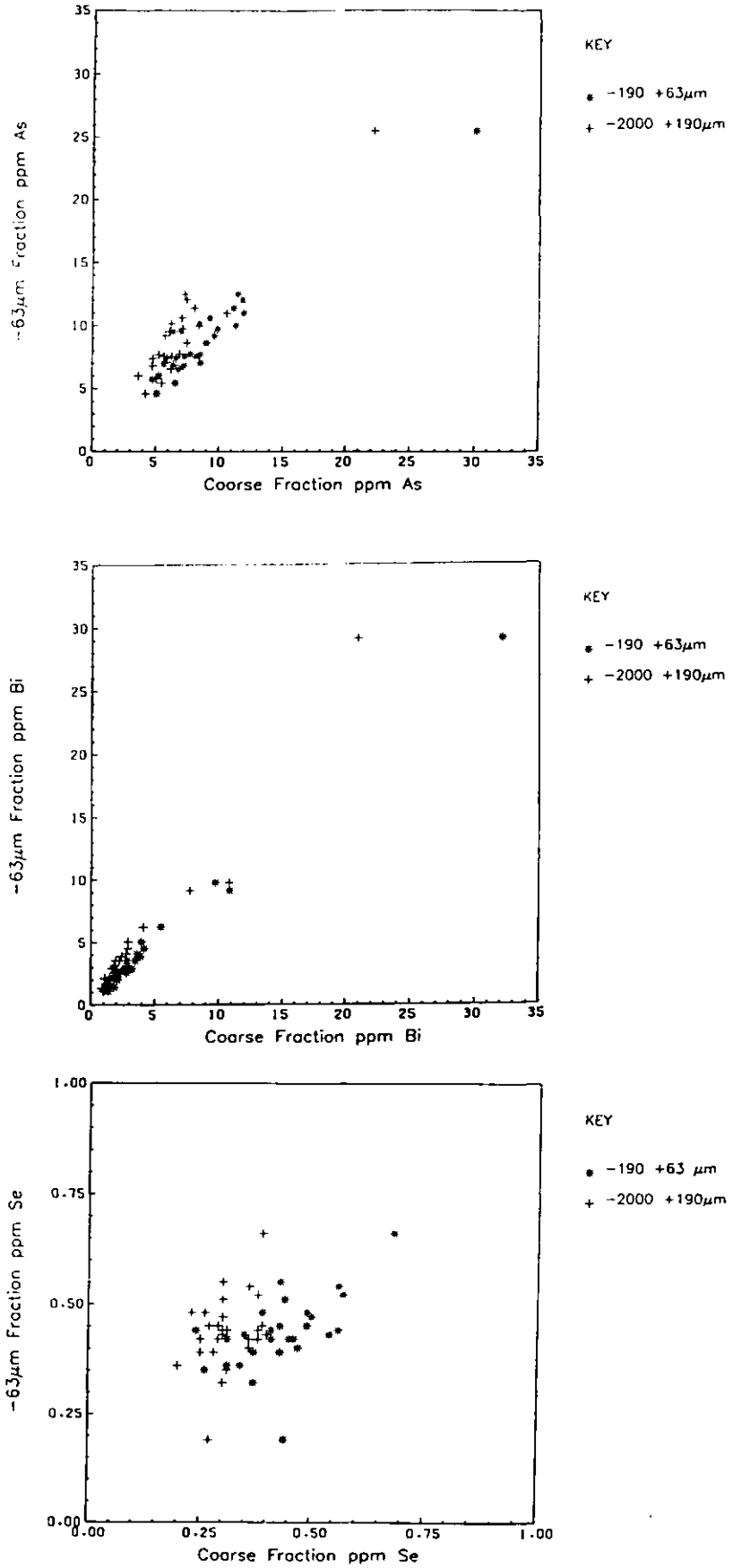


Fig 4.5 Scatter plots of coarser fractions against fine (-63 μ m) fraction: traverse DB02

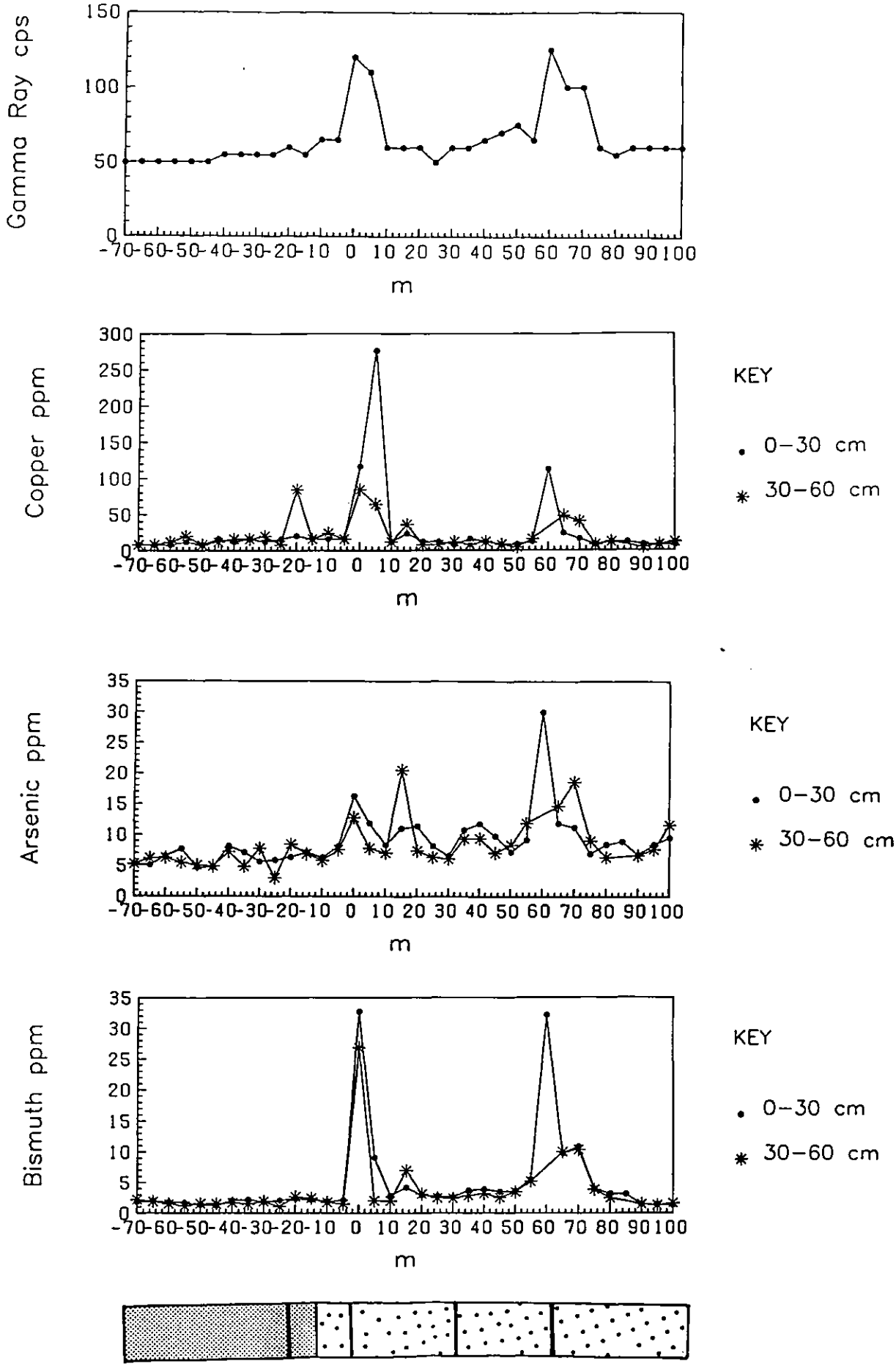


Fig 4.6 Dalbeattie: traverse DB02 -190 μ +63 μ m
Gamma ray data 1m height, geological symbols as for Fig 4.1

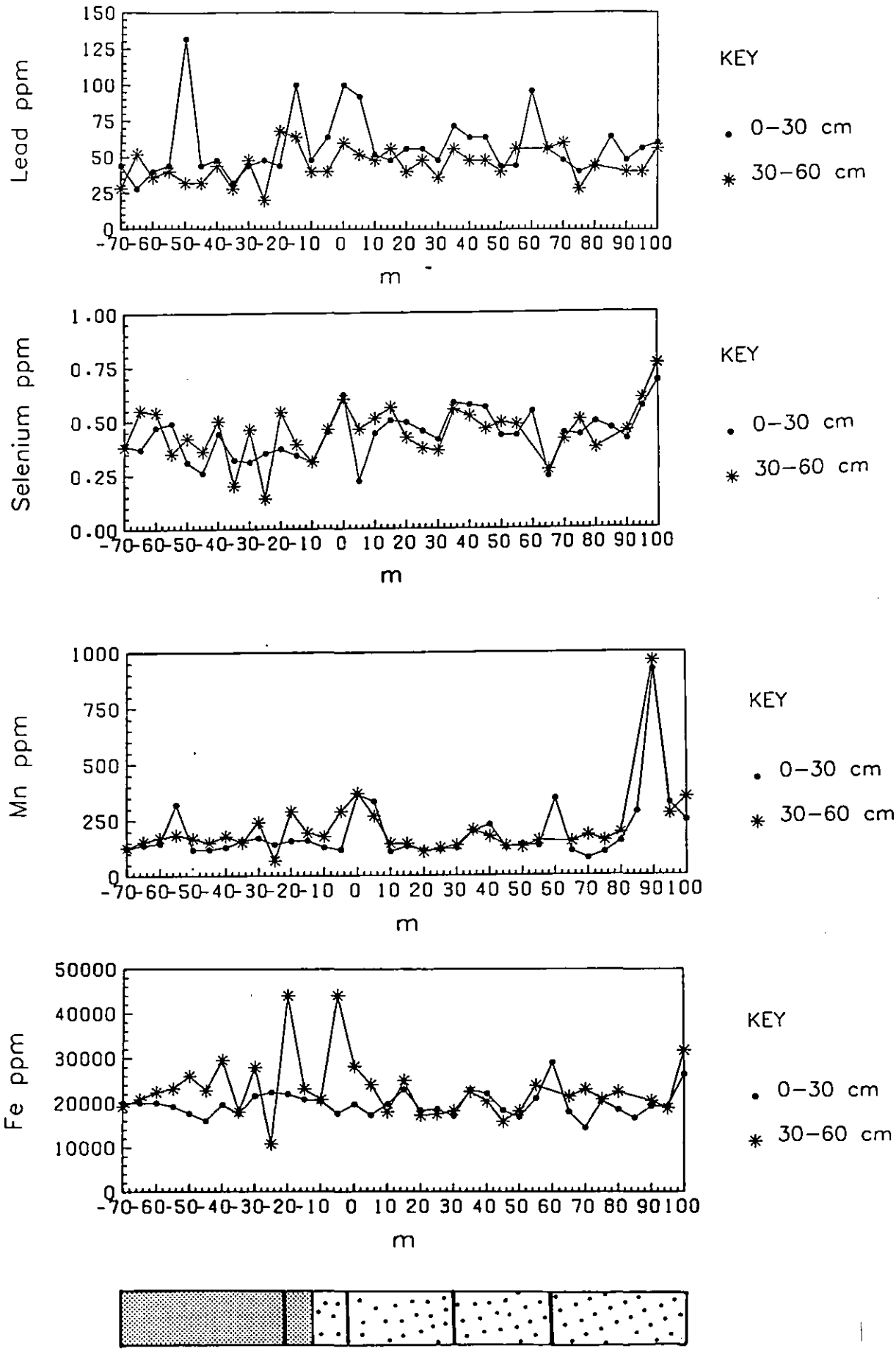


Fig 4.7 Dalbeattie: traverse DB02 -190 μ m +63 μ m fraction
Geological symbols as for Fig 4.1

c) Soil Traverse DB03

A scintillometer survey, conducted at the same time as the soil sampling, shows two main anomalies (Fig. 4.8) at 0 and 30 m with lesser peaks at 50 m and - 30 m. The uranium content of the soils (-190 μm, 0 - 30 cm) is erratic with a high at 30 m of 10 ppm U (relative to background of 2.5 ppm), other single point anomalies of 15 m and 55 m and smaller peaks at -30 m -80 m and -100 m. Arsenic and bismuth (Fig. 4.8) are generally correlatable with the gamma-ray survey and are strongly anomalous at 30 m (300 ppm Bi, 150 ppm As relative to background of 3 ppm Bi and 15 ppm As). In addition bismuth gives minor peak at 50 m (8 ppm Bi) and -30 m (6 ppm Bi).

Transition metals (Fig. 4.9 - 4.10) are not so consistently enriched at the location of the gamma ray peaks. Copper and lead are both high at 30 m but the location of peaks at the western end of the traverse is variable (-70 m for copper, -90 m for lead). The major nickel high is also at - 70 m while antimony is confined to - 30 m. Iron shows little variation along the traverse, in contrast to the manganese peak at 0 m.

4.1.3 Discussion

Multielement soil geochemistry is effective in locating a variety of mineralized structures.

The lithogeochemical data demonstrate that the elemental content of the veins varies considerably, both between and within veins, and an effective exploration programme for uranium probably requires the identification and follow up of all the mineralized structures. The wide variety of elements and lack of wallrock alteration suggest deposition at relatively low temperatures and raises the possibility that permeability contrasts,

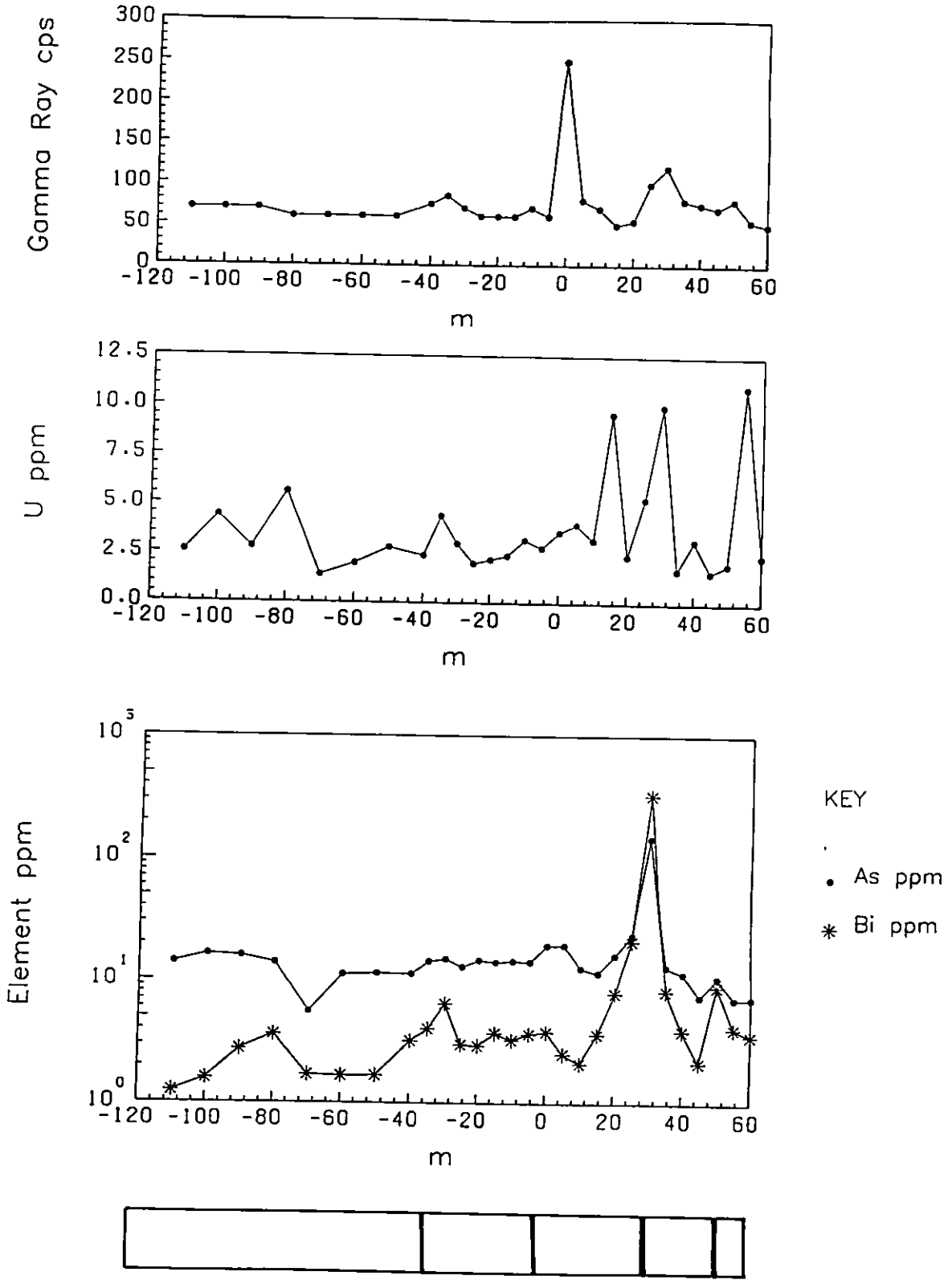


Fig 4.8 Dalbeattie: soil traverse DB03 -190 μ m fraction

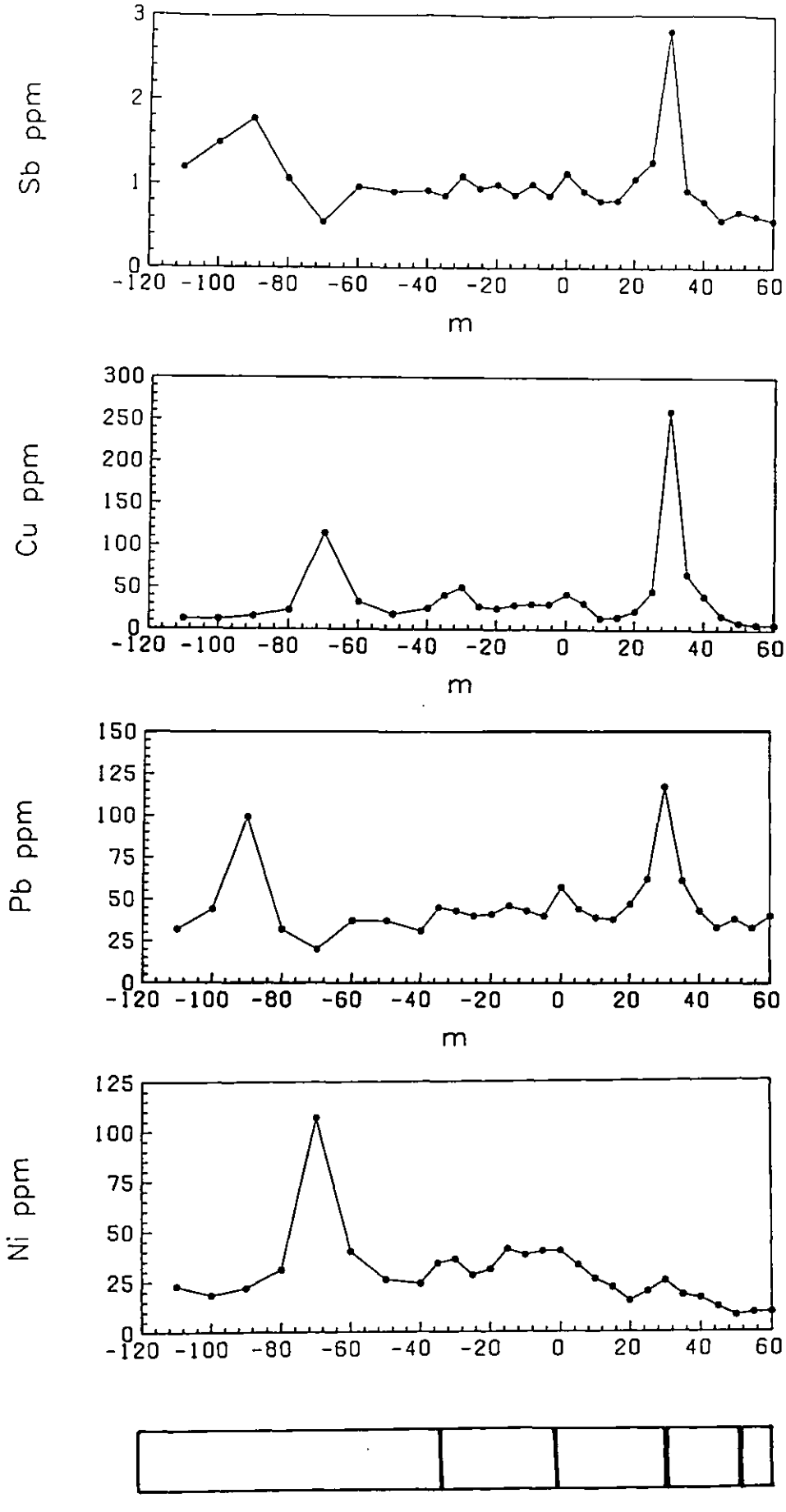


Fig 4.9 Dalbeattie:soil traverse DB03 -190 μ m fraction

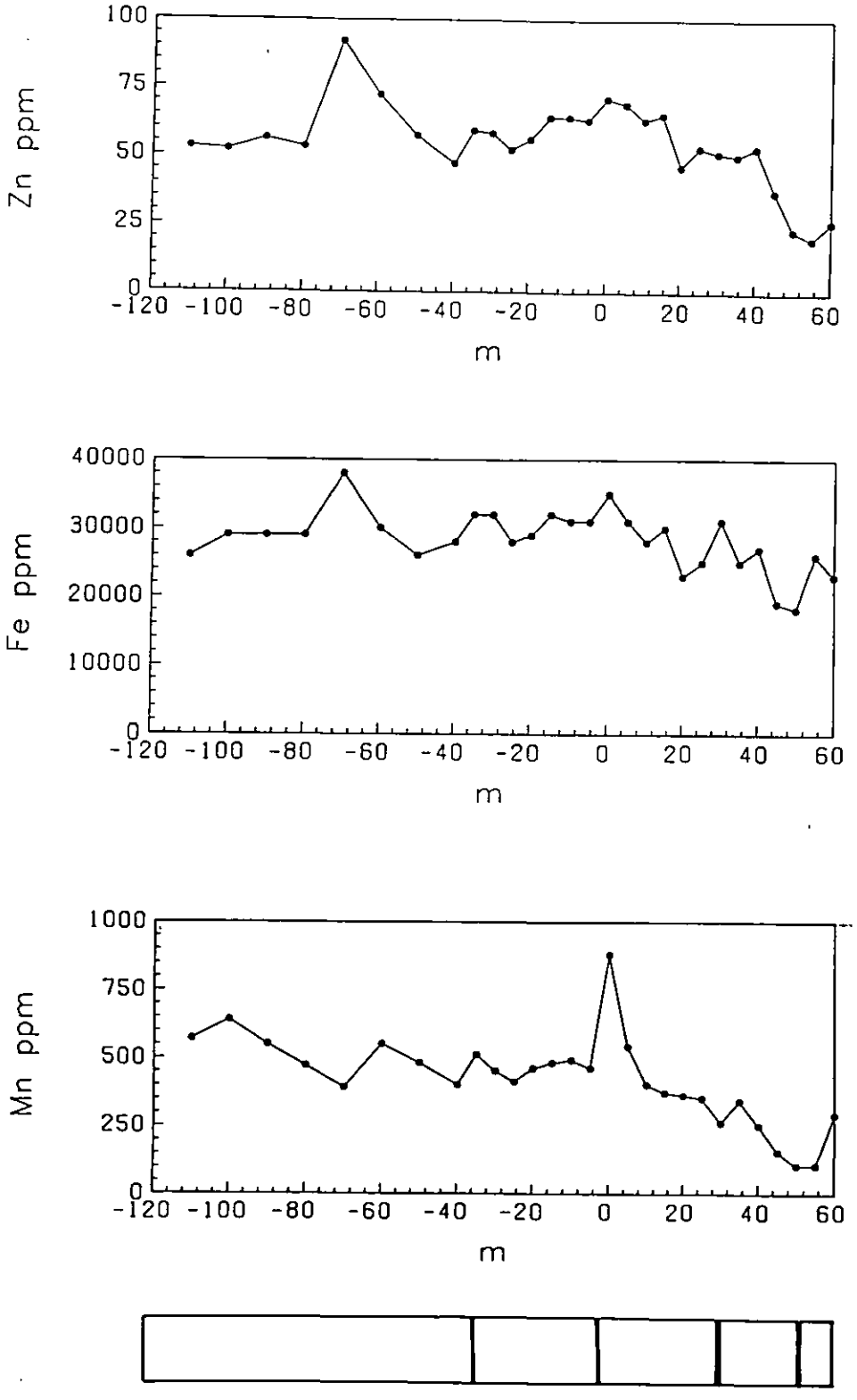


Fig 4.10 Dalbeattie: soil traverse DB03 -190 μ m fraction

such as the unconformity, are important controls in the location of mineralization. This latter feature is not the sole control as weak mineralization is found on the northern side of the batholith (Gallagher et al, 1971), where the unconformity is not present. High uranium values at the western end of the traverse reflect either concentration in granitic dykes or by paleo weathering.

The soil traverse DB02 demonstrates that the anomalies are extremely spatially restricted, mainly giving single point peaks. Copper, bismuth and arsenic are useful in locating veins with bismuth providing the highest contrast anomalies. The shape and intensity of these anomalies are not thought to be seriously affected by minor contamination caused by trenching.

Particle size separations show that the finest fraction (-63 μm) contains the highest concentration of pathfinders and, thus, gives the highest contrast anomalies. The relative paucity of this fraction (average 8% of the sample) limits its general applicability which in turn means that the -190 μm (or similar size) is, in practice, the most effective size for analysis of samples from temperate terrains, and this was used throughout this study.

Soil traverse DB03 again reflects the erratic nature of the base metal and pathfinder anomalies. The subcrop of the main veins is detected by a concentration of arsenic, bismuth and copper, with bismuth the most useful. Uranium is not particularly effective as it is so mobile e.g. the high background values at the western end of the traverse which are probably a result of concentration in a topographic depression. The cause of the nickel/copper anomaly at 70 m is unknown and requires further investigation.

The mobility of the pathfinders arsenic and bismuth in this environment is low and they are no less dispersed

than other transition metals. The relatively high, and consistent, enrichment of bismuth in veins, however, means that it can be recommended as a useful part of a multielement survey, along with copper, arsenic, nickel and lead.

4.2 Ballinglen, Co. Wicklow, Ireland

Tungsten-tin deposits are currently being evaluated, by Irish Base Metals, Ltd. in the area between Tinahely and Aughrim, western County Wicklow (Fig. 4.11). These occurrences are completely undisturbed and provide a good opportunity for the evaluation of pathfinder geochemistry versus indicator elements, which are relatively more difficult to determine.

4.2.1 Geology

a) Solid Geology (Fig. 4.11)

Tin-tungsten deposits are associated with and mainly hosted by acid dyke complexes which intrude sediments of the Cambro-Ordovician Ribband Group (Steiger and Bowden, 1982). The dykes range from granodiorite through microgranite to quartz felsite in composition and are probably genetically associated with, although later than, the Leinster Granite. This Caledonian batholith crops out 4 km northwest of the main dyke complex, which trends subparallel to the granite/sediment contact. Dyke complexes consist of a number of individual dykes separated by country rocks. These country rocks are dominantly pelitic with lesser quartzite, greywacke and volcanics. The regional slatey cleavage is conformable with local hornfels development near the granite.

The mineral assemblage is typical of the greisen association with veins showing hydrothermal alteration

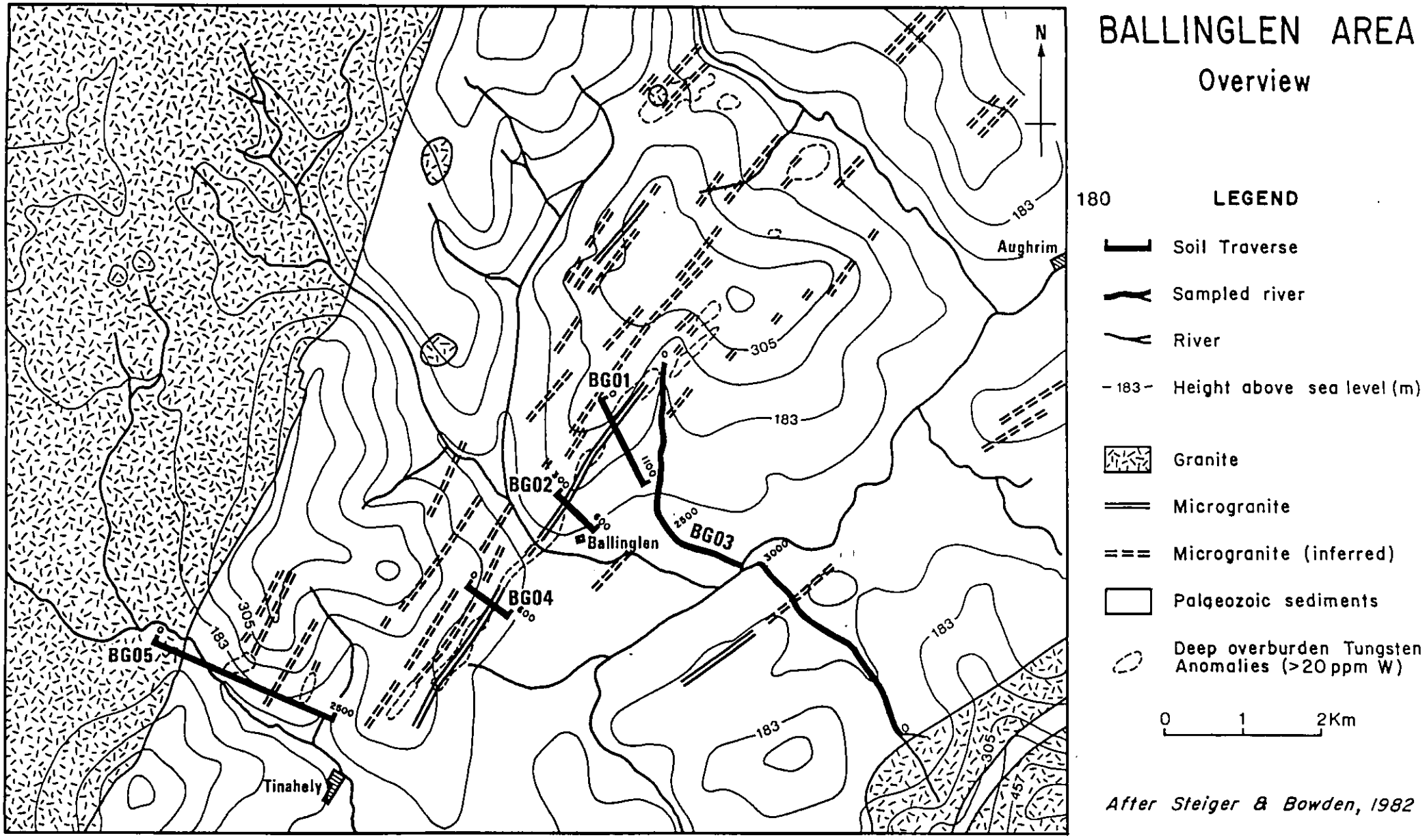


Fig 4.11 Ballinglen: solid geology

(muscovite, sericite), almost exclusively within the microgranite. Scheelite and stannite are the main ore minerals with very minor cassiterite. Scheelite occurs as discrete grains or as intergrowths with sulphides, particularly pyrrhotite. Stannite is often intimately intergrown with chalopyrite, sphalerite and pyrrhotite, and is commonly associated with bismuth minerals. The latter have been identified as native bismuth and the bismuth sulphosalts matildite and ?cosalite (Steed, 1978). Small quantities of ruby silver minerals, mainly proustite occasionally occur. Arsenopyrite is abundant, and is the only arsenic mineral identified. The main gangue minerals are fluorite, tourmaline, sphene, apatite and some carbonates.

b) Surficial Geology

The area has been extensively glaciated but drift is residual or periglacial, generally 2 - 4 m thick, and topped by brown earth soils.

4.2.2 Programme

The main object is to compare pathfinder and indicator element dispersion in soil and deep overburden samples. Three soil sampling traverses were made (BG01, BG02 and BG04) across the strike of the mineralization (Fig. 4.11, 4.12). The most intense anomalies (on BG01) were followed up by deep overburden sampling. In addition, a regional till traverse, collected by Irish Base Metals Ltd., was analyzed. A very limited number of drill core samples were also analyzed.

Stream sediment and water were sampled from rivers draining both a mineralized area (along strike from BG01) and a background area.

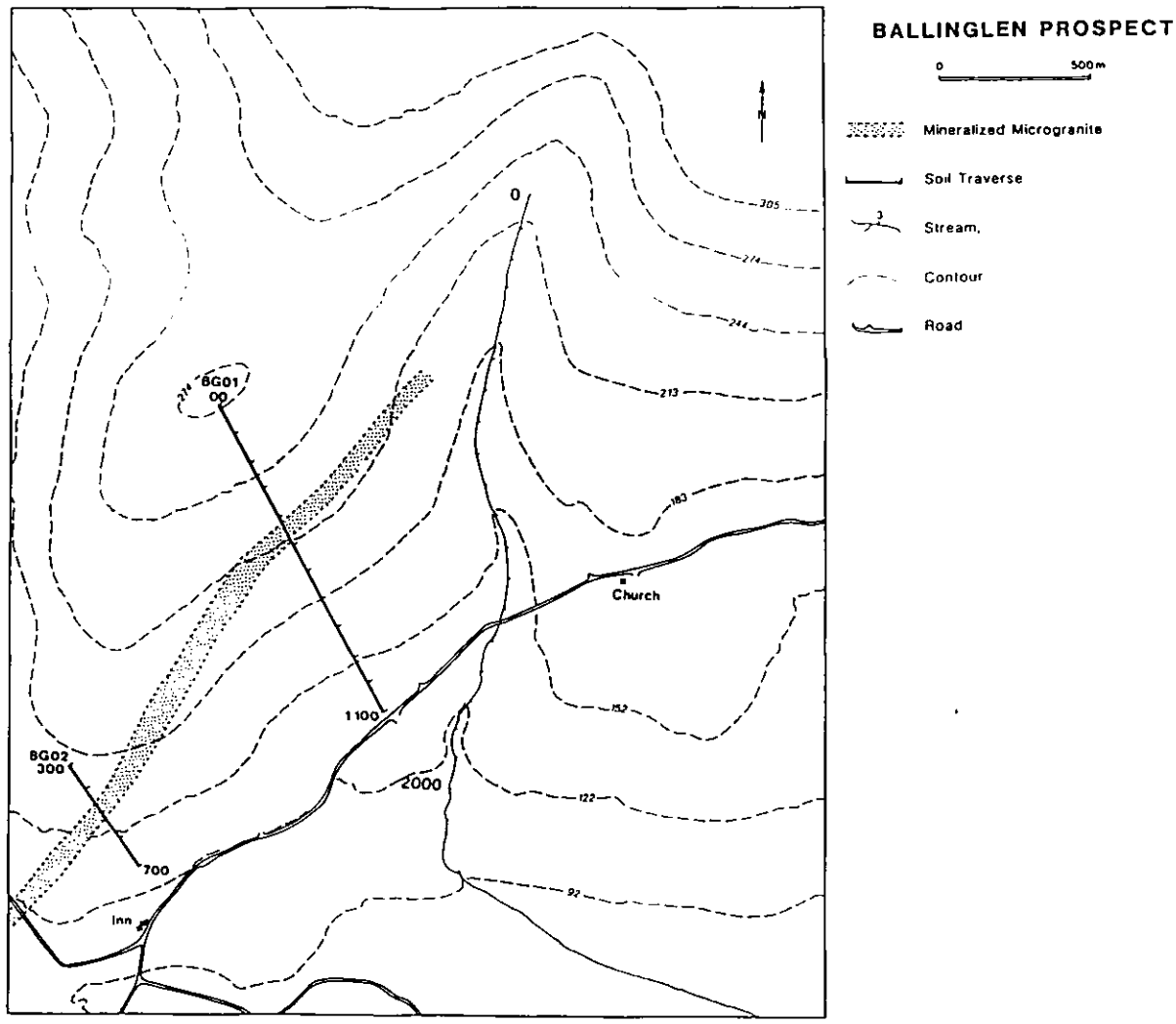


Fig 4.12 Ballinglen: location of traverses BG01 and BG02

a) Lithogeochemistry

Five drillcores (Table 4.2) from diamond drillhole AYBG/13 were selected as representative of mineralized and background sediments and intrusives . their location is shown in Fig. 4.13. Enriched transition metals are copper, zinc and silver with lesser lead ,and these correlate with visual sulphide identification. Arsenic is high in zones of both scheelite and sulphide mineralization, while bismuth is concentrated in the sulphide rich samples.

b) BG01 Soil Traverse

Prominent arsenic and bismuth anomalies occur over and slightly downslope from the suboutcrop of the mineralized microgranite. (All soil samples are collected from the B horizon where soil zonation is developed). Anomalous arsenic values (Fig. 4.14) reach 300 ppm relative to background of 30 ppm while comparable bismuth values are 1.1 ppm maximum and 0.4 ppm background. Copper shows a more spatially limited anomaly of 55 ppm maximum with the interesting feature of enhanced background (30 ppm Cu) downslope from the mineralization.

The other elements determined (by atomic absorption) do not show anomalies around 500 m but there are significant increases in background for zinc and nickel (Fig. 4.15) and to a lesser degree for manganese, from 650m to the southern end of the traverse.

Cobra drill profiling provides detail on the dispersion of the anomalous elements through the overburden. Tungsten values of the deepest overburden samples suggest that the highest values occur in the microgranite with interlaminated hornfels ,(the same lithologies as the tungsten intersections in drill core , Fig. 4.13). Copper, arsenic and bismuth are highly

Table 4.2 Elemental content of drillcores, Ballinglen drillhole AYBG 13

Sample	Li	Na	K	Mg
1.	225.	260.00	14369.0	8980.00
2.	332.	756.00	16732.0	3990.00
3.	159.	1041.00	4775.0	5987.00
4.	138.	1503.00	16172.0	2209.00
5.	73.	263.00	8525.0	2168.00

Ca	Al	Mn	Fe	Co
1763.0	47260.0	1195.00	49000.0	23.0000
13740.0	39850.0	258.00	11860.0	6.5000
5336.0	17800.0	297.00	16150.0	8.0000
35163.0	43390.0	222.00	8680.0	2.9000
2778.0	23860.0	236.00	22170.0	4.0000

Ni	Cu	Zn	Pb	As
48.0000	49.0	93.00	31.000	46.00
9.4000	372.0	181.00	20.000	1380.00
11.0000	98.0	52.00	9.500	8.40
6.9000	5970.0	1960.00	35.000	764.00
10.0000	11900.0	2823.00	400.000	3300.00

Sb	Bi
.18000	.6200
.42000	1.3000
.19000	.1700
-1.00000	4.9000
-1.00000	68.2000

First two digits of data are significant

Sample 1	220'	Pelitic country rock
2	248'	Elvan with quartz vein, scheelite
3	298'	Unmineralized elvan
4	431'	Quartz-veined microgranite with stannite, arsenopyrite and fluorite.
5	448'	Altered microgranite adjacent to quartz vein with galena, sphalerite, chalcopyrite, stannite, cassiterite.

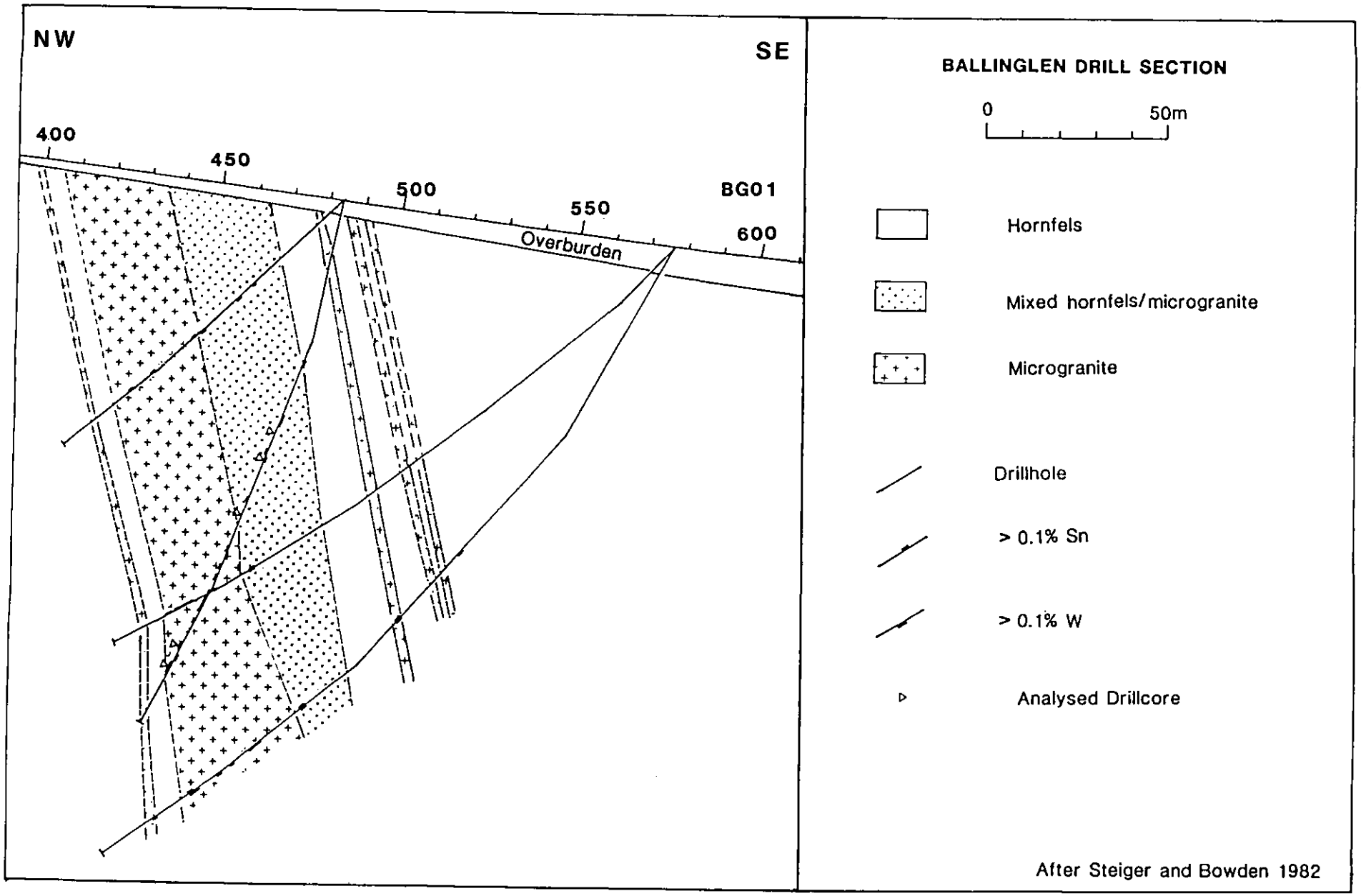


Fig 4.13 Ballinglen: drillsection along traverse BG01

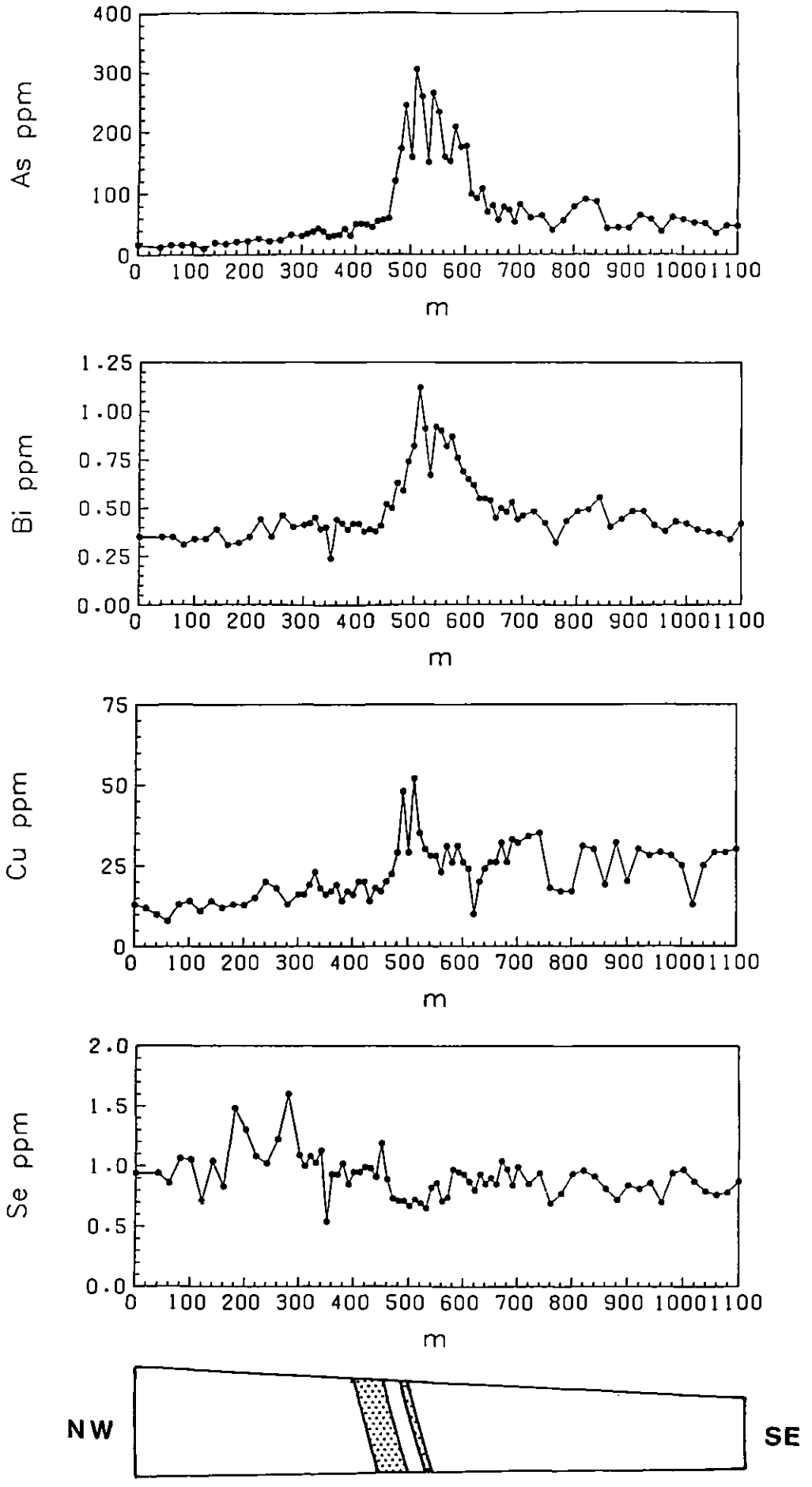


Fig 4.14 Ballinglen: soil traverse BG01
Geological symbols as for Fig 4.12

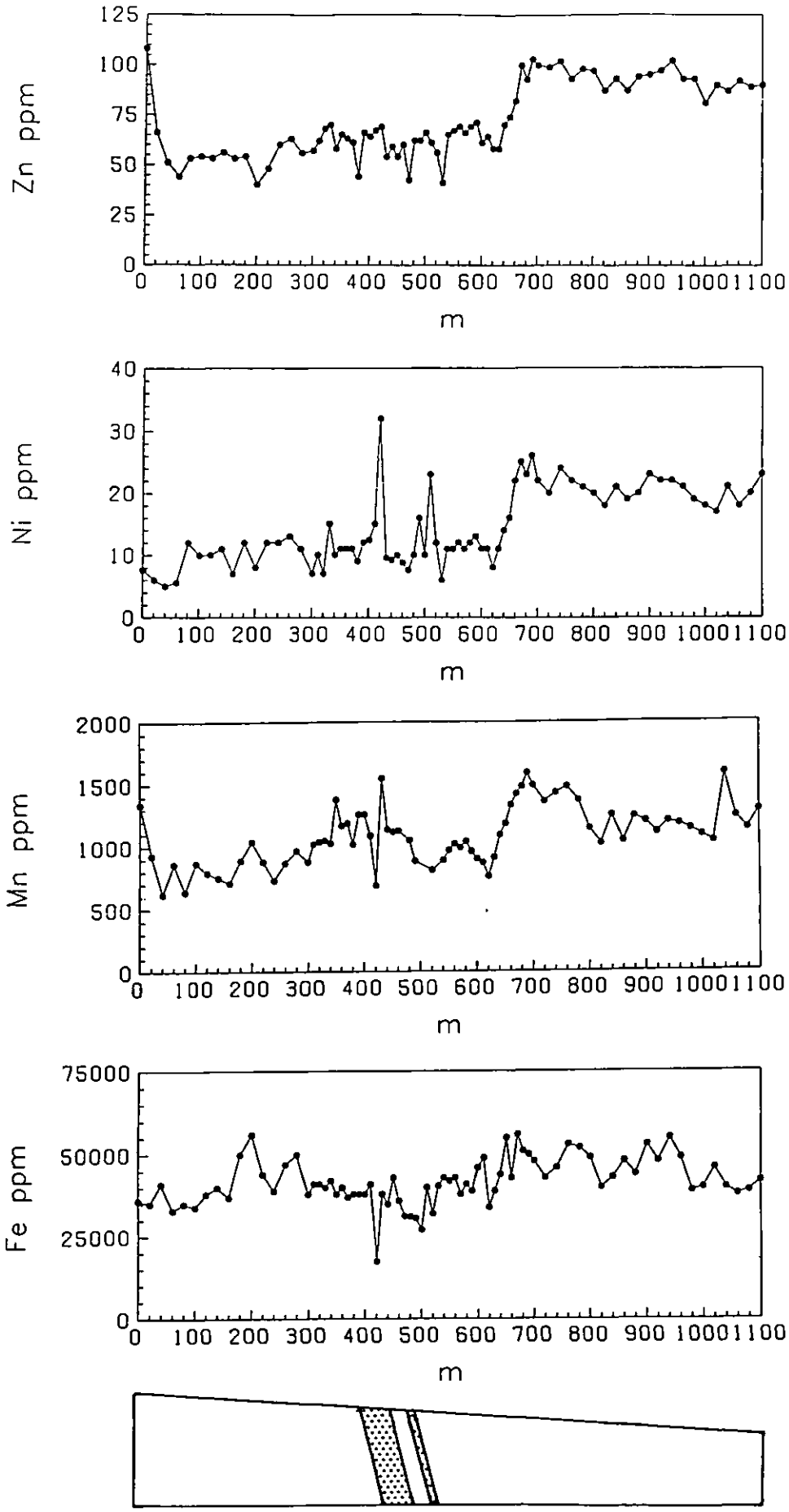


Fig 4.15: Ballinglen soil traverse BG01
Geological symbols as for Fig 4.12

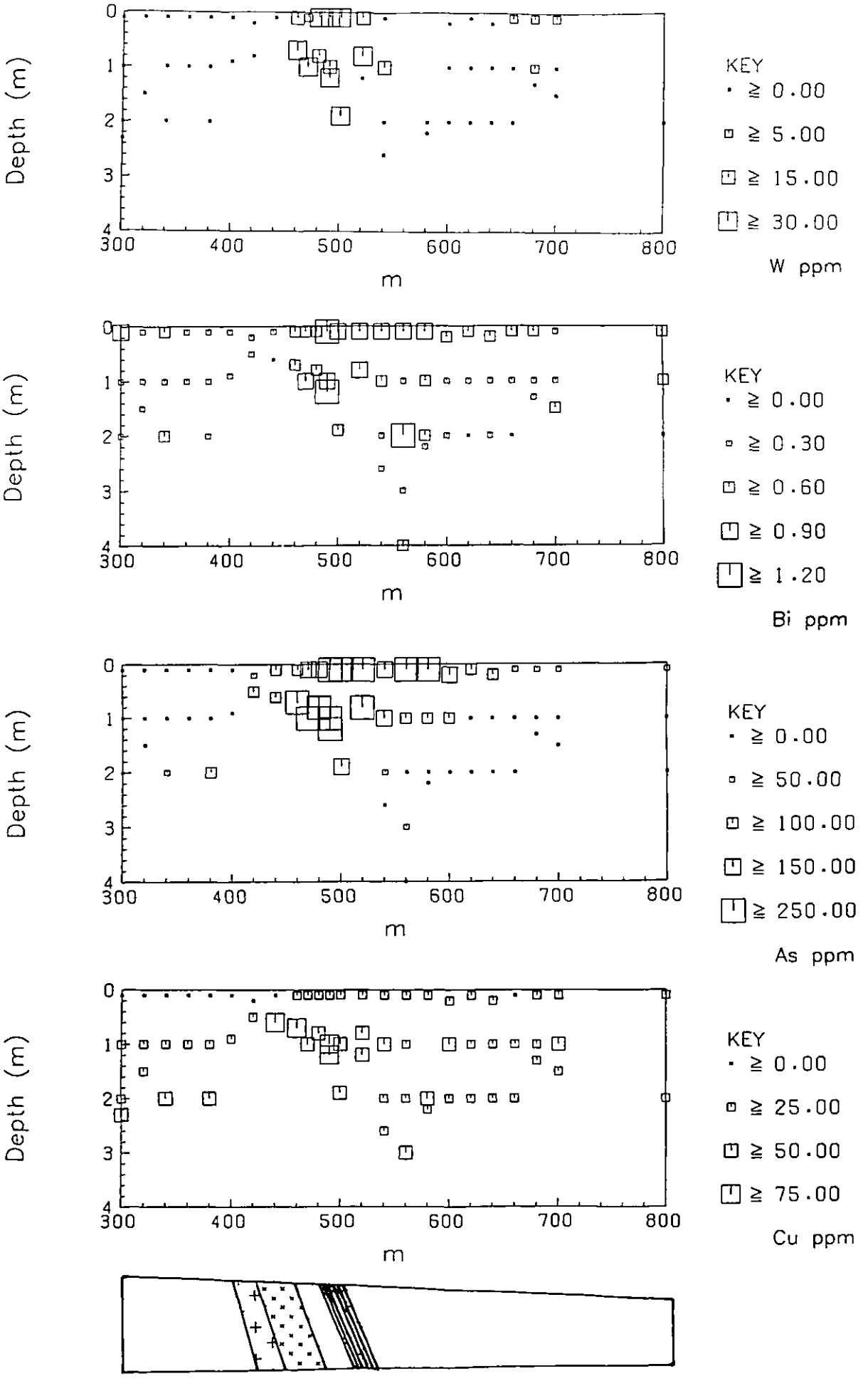


Fig 4.16 Ballinglen: overburden profile BG01
Geological symbols as for Fig 4.13

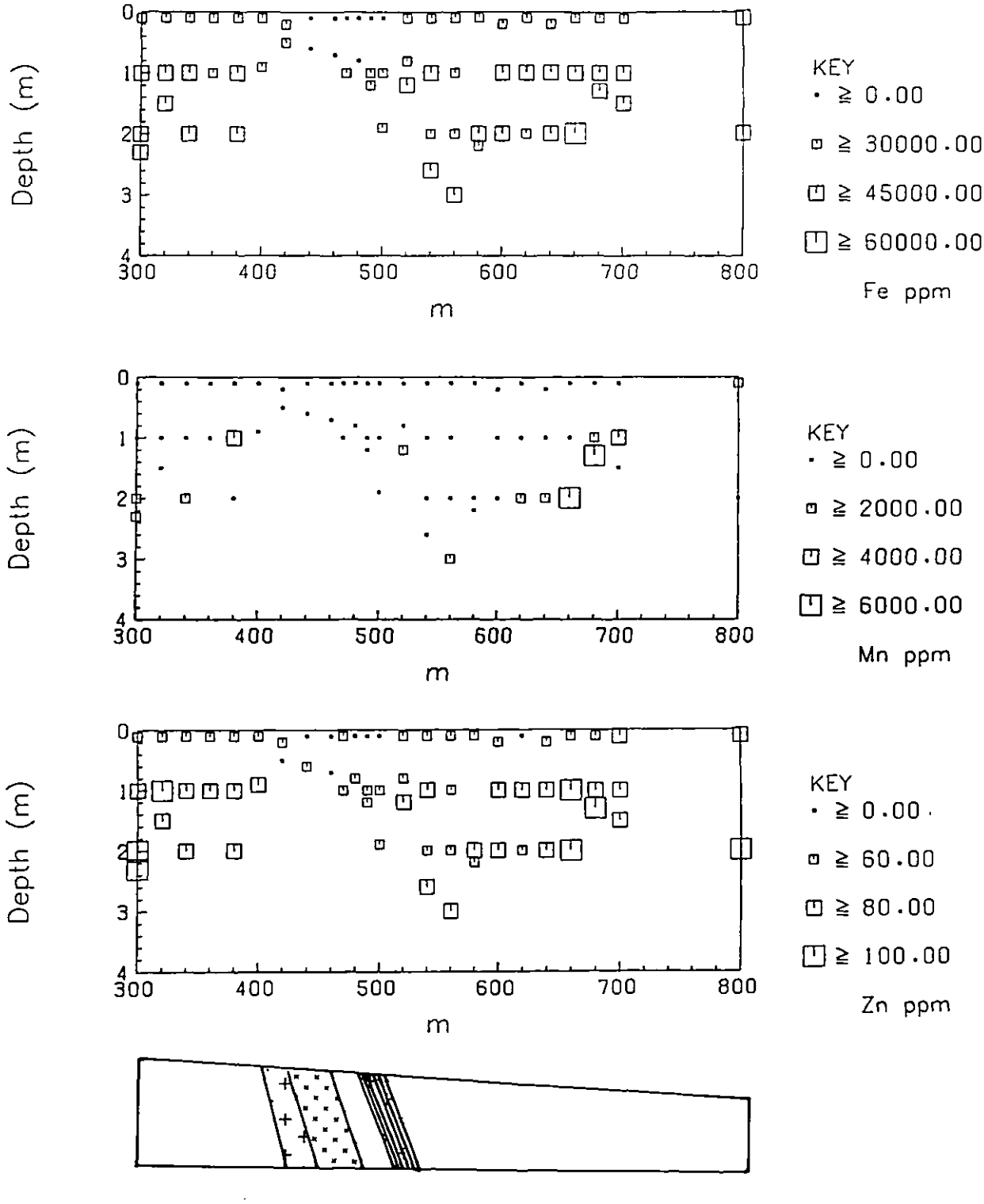


Fig 4.17 Ballinglen: overburden profile BG01
Geological symbols as for Fig 4.13

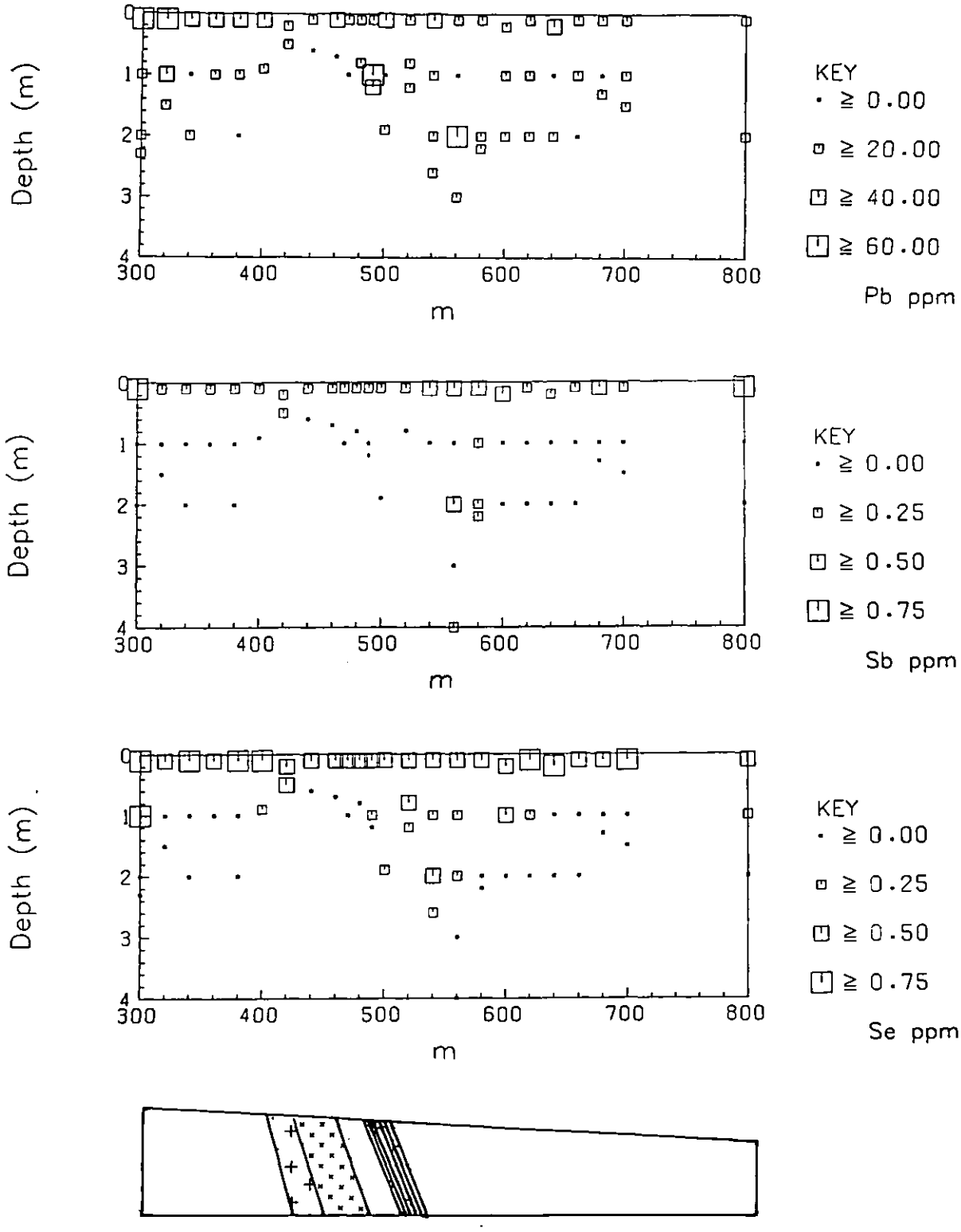


Fig 4.18 Ballinglen: overburden profile BG01
Geological symbols as for Fig 4.13

anomalous in the deepest samples but copper and arsenic highs are slightly broader than those of tungsten because they also reflect the more stanniferous microgranite dyke.

All the elements show downslope (southwards) dispersion, with the order of increasing secondary dispersion:

W Cu Bi As

Copper shows a poor contrast at surface relative to the deep samples unlike the strong contrast in both arsenic and bismuth (Fig. 4.16).

Selenium and antimony give somewhat similar patterns. Selenium is anomalous in deep samples overlying and downslope from mineralized sediments to the south of the main microgranite but this is not reflected at the surface. Indeed, there is a slight low relative to the highly enriched surface samples. Antimony is also significantly enriched at the surface but the anomalous values at depth are very limited and show some spatial correlation with bismuth and lead.

Iron (Fig. 4.17) is low in the deepest samples over the mineralization but is concentrated at intermediate depth. Manganese, zinc and cobalt are concentrated in the deepest samples at the southern end of the traverse and this is reflected in high surface values slightly further down slope.

c) Soil Traverse BG02

This traverse is located some 1.1 km from BG01, along strike of the mineralized dyke complex, and is much shorter (400 m).

The geochemical responses, however, are similar, with arsenic, bismuth and copper anomalies in soil samples slightly downslope from the subcrop of the mineralization (460 - 510 m). Arsenic values (Fig. 4.19)

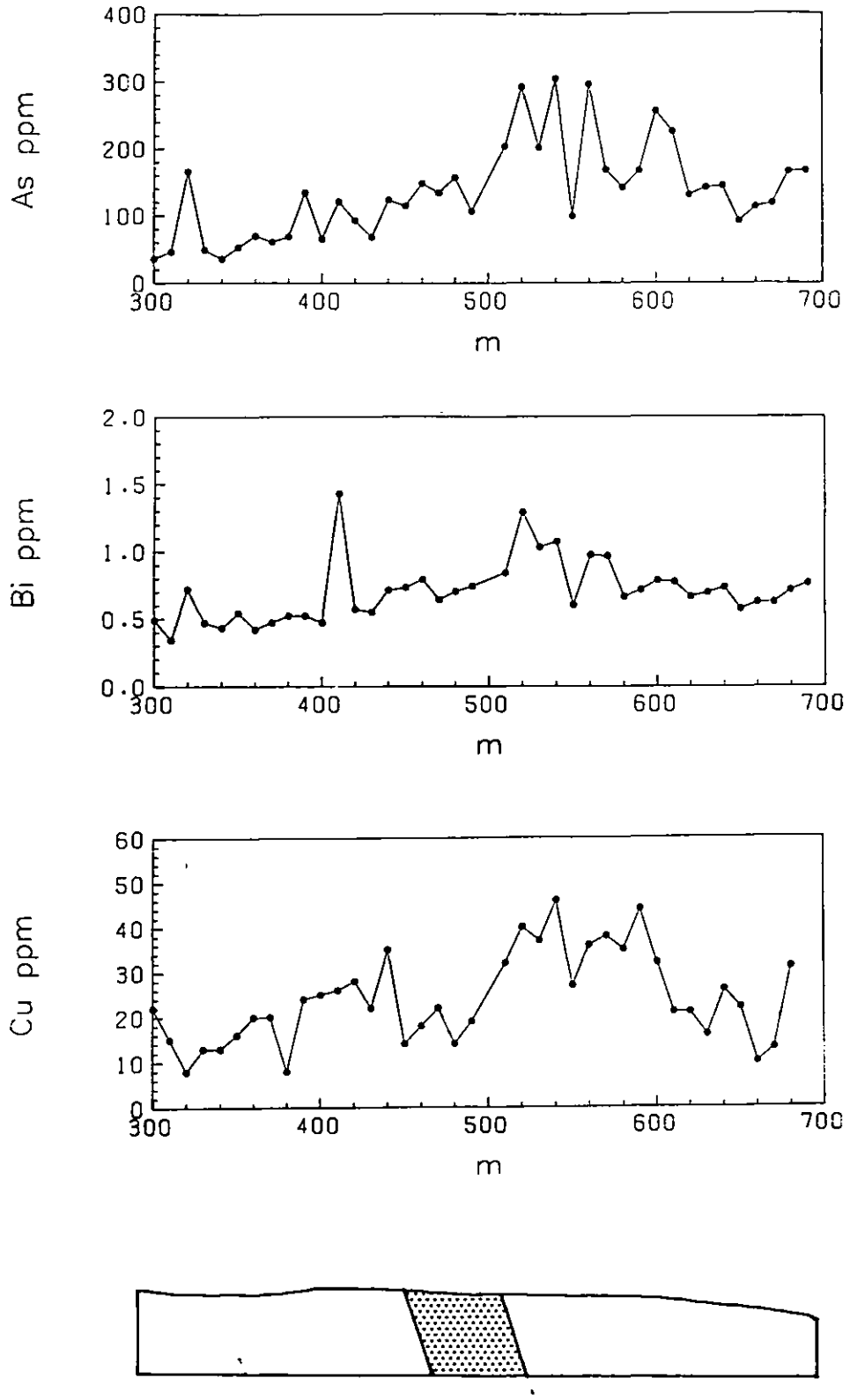


Fig 4.19 Ballinglen: soil traverse BG02
Geological symbols as for Fig 4.12

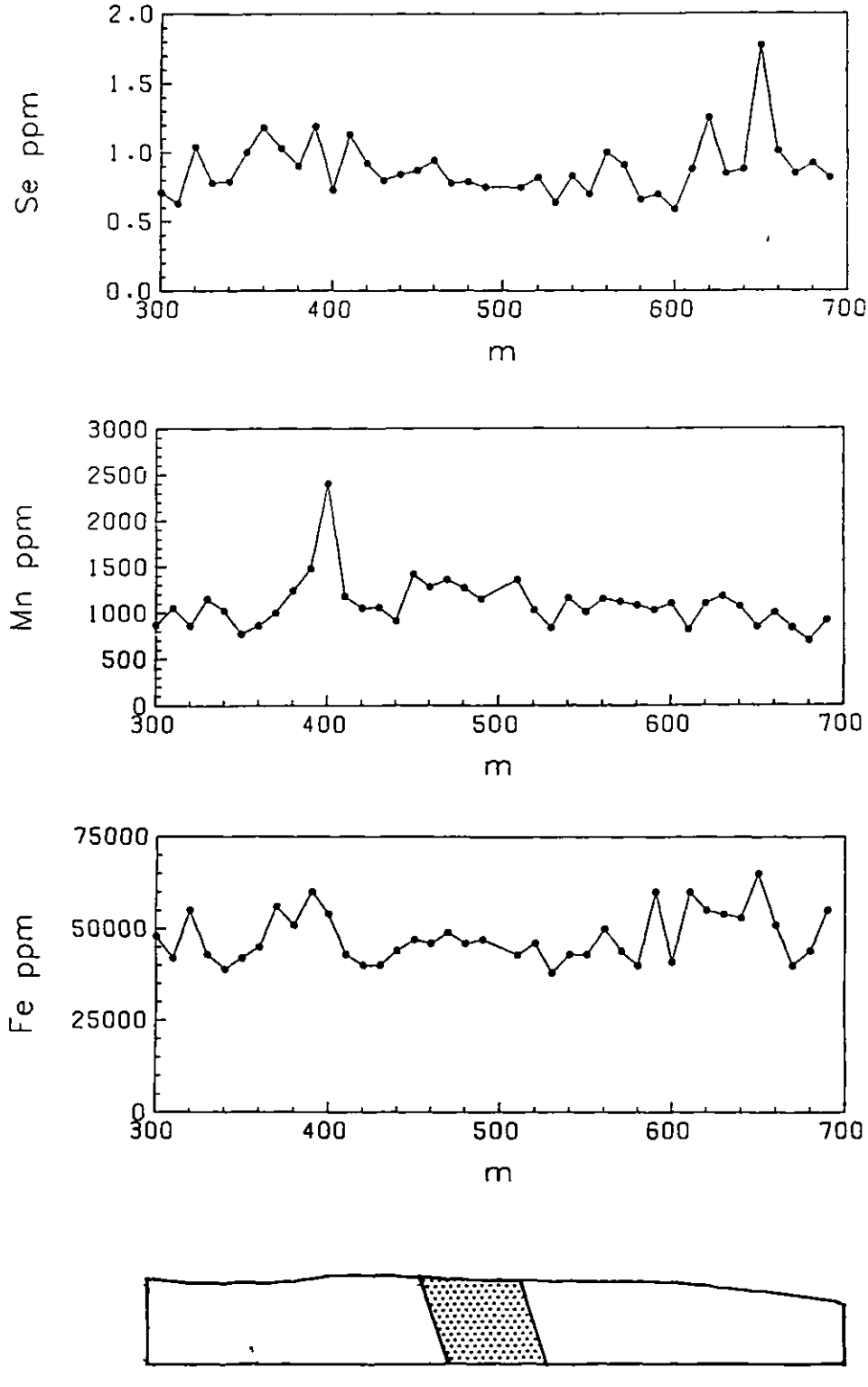


Fig 4.20 Ballinglen: soil traverse BG02
Geological symbols as for Fig 4.12

reach 300 ppm relative to a background of 60 ppm As. The main bismuth high (1.3 ppm relative to background of 0.5 ppm) is located at 500 m but there is also an unchecked single point anomaly at 410 m. Copper reaches 45 ppm relative to 25 ppm background.

The other elements determined (Pb, Zn, Ni, Fe, Mn, Ca, Se) generally show little variation (Fig. 4.20) with the exception of rather erratic lead values, which are anomalous at 460 m, and a distinct manganese peak at 390 m.

d) Soil Traverse BG04

This is designed to transect a deep sampling arsenic anomaly associated with the mineralized microgranite, which is exposed in Ballybeg Quarry (200 m to the north east). Tungsten values in the deep samples (Irish Base Metals, pers. comm.) are only slightly anomalous.

Analyses (by I.C.P. nebulisation and magnesium nitrate method) of soil samples give only minor anomalies in copper and arsenic (Fig.4.21). They have maxima slightly downslope from the subcrop of the dyke complex (320 - 400 m) of 125 ppm As and 35 ppm Cu relative to 60 ppm As and 25 ppm Cu background.

None of the other elements show significant variations.

e) Overburden Traverse BG05

This regional traverse extends from the granite/sediment contact and transects four microgranite dykes (Fig. 4.11), to the north of the main mineralized dyke complex. The samples were analyzed by ICP nebulisation and for pathfinders by the magnesium nitrate method.

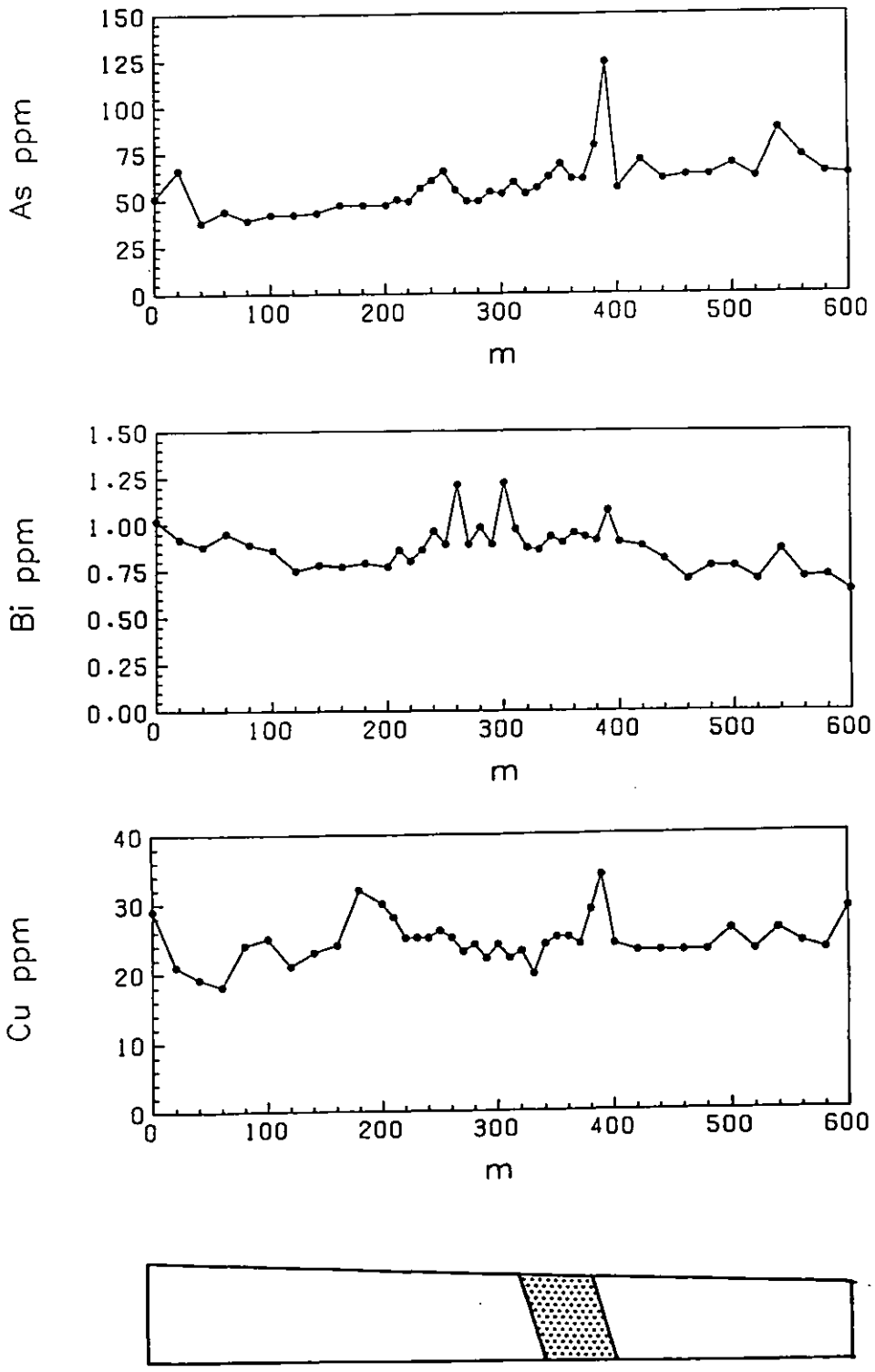


Fig 4.21 Ballinglen: soil traverse BG04
Geological symbols as for Fig 4.12

Arsenic and bismuth (Fig. 4.22) show a high degree of inter correlation and six anomalies are developed. The most prominent of these, between 750 m and 1,000 m, has maxima of 950 ppm As and 2.7 ppm Bi relative to background of 50 ppm As and 0.5 ppm Bi. These anomalies show a strong correlation with tin (and to a lesser extent, tungsten) values determined for Irish Base Metals Limited.

Sodium anomalies (Fig. 4.24) are associated with the main arsenic and bismuth anomaly but the relationship at the southern end of the traverse is less pronounced. There is an antimony anomaly (0.8 ppm relative to 0.1 background) at 1550 m.

Base metal concentrations (copper, lead, zinc) and manganese are particularly high at the northern part of the traverse overlying the granite. Lithium is enriched over the granite but not over the microgranite dykes.

f) Stream Sediments: (BG03)

The two rivers sampled show the distinct contrast between the rivers draining mineralization from those draining background.

Tungsten, bismuth and arsenic are anomalous in the stream draining the mineralization (Fig. 4.12). Tungsten data (Fig. 4.25) reflect the input of mineralized material at 300 m, as might be expected from the extrapolation along strike of the mineralized dyke complex (Fig. 4.12). Arsenic on the other hand indicates the additional input at the head of the river and the maximum (105 ppm As) is developed there. Deep overburden sampling at the head of the river indicates bedrock arsenic enrichment with low tungsten values. Arsenic is strongly correlated with stream

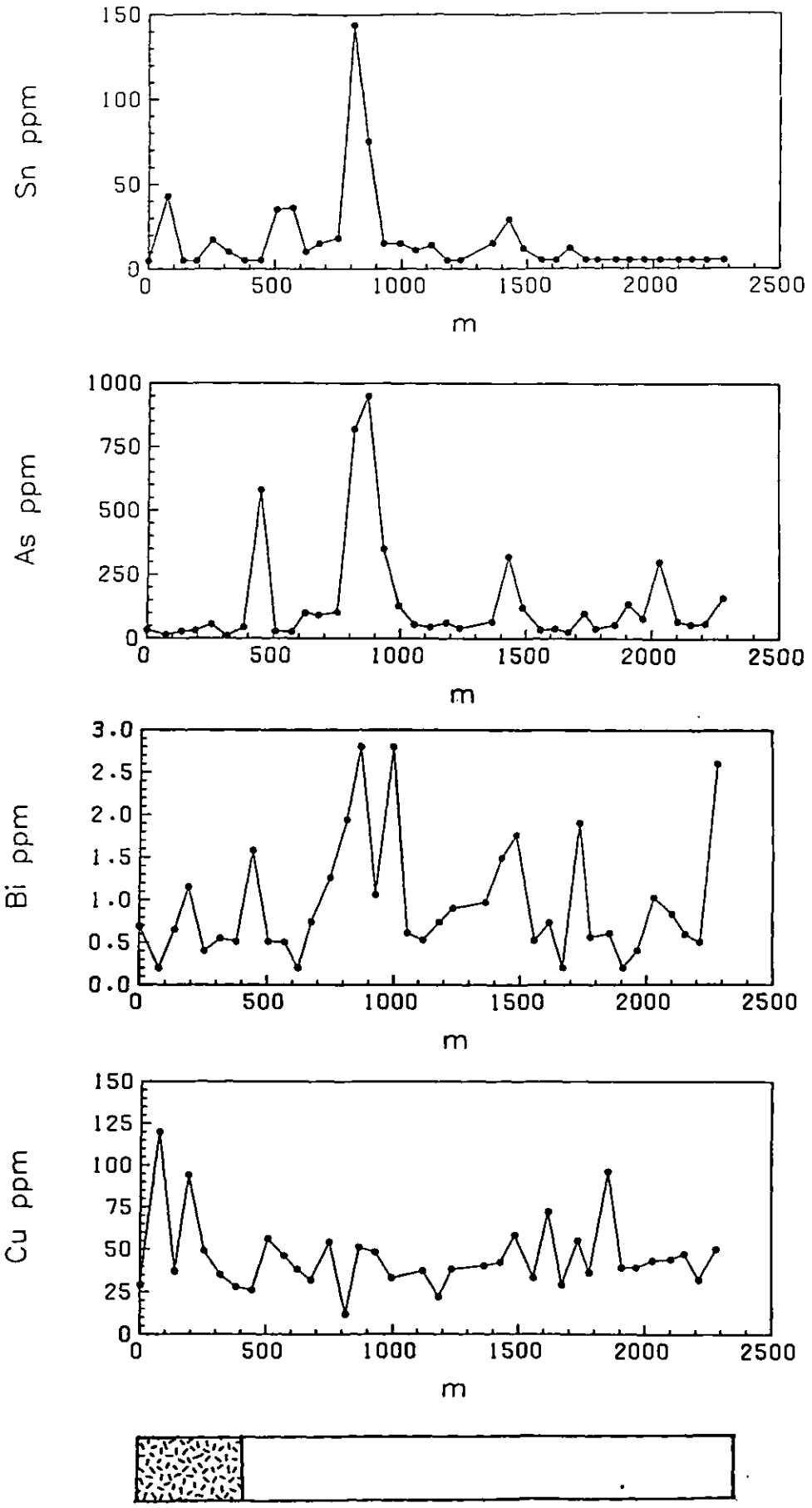


Fig 4.22 Ballinglen: basal overburden traverse BG05
Geological symbols as for Fig 4.11; location of dykes can be gauged from this figure

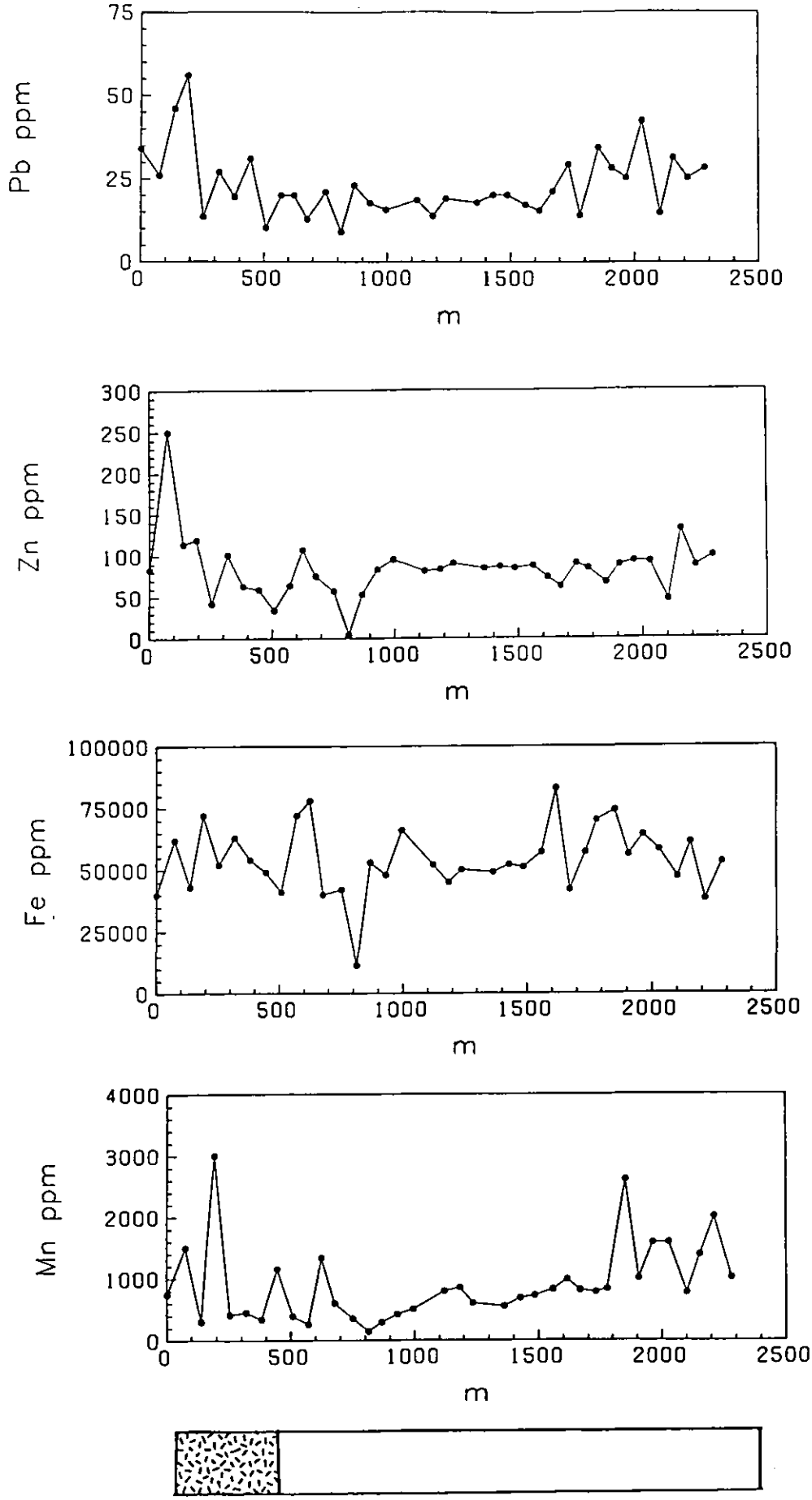


Fig 4.23 Ballinglen: basal overburden traverse BG05
Geological symbols as for Fig 4.11; location of dykes can be gauged from this figure

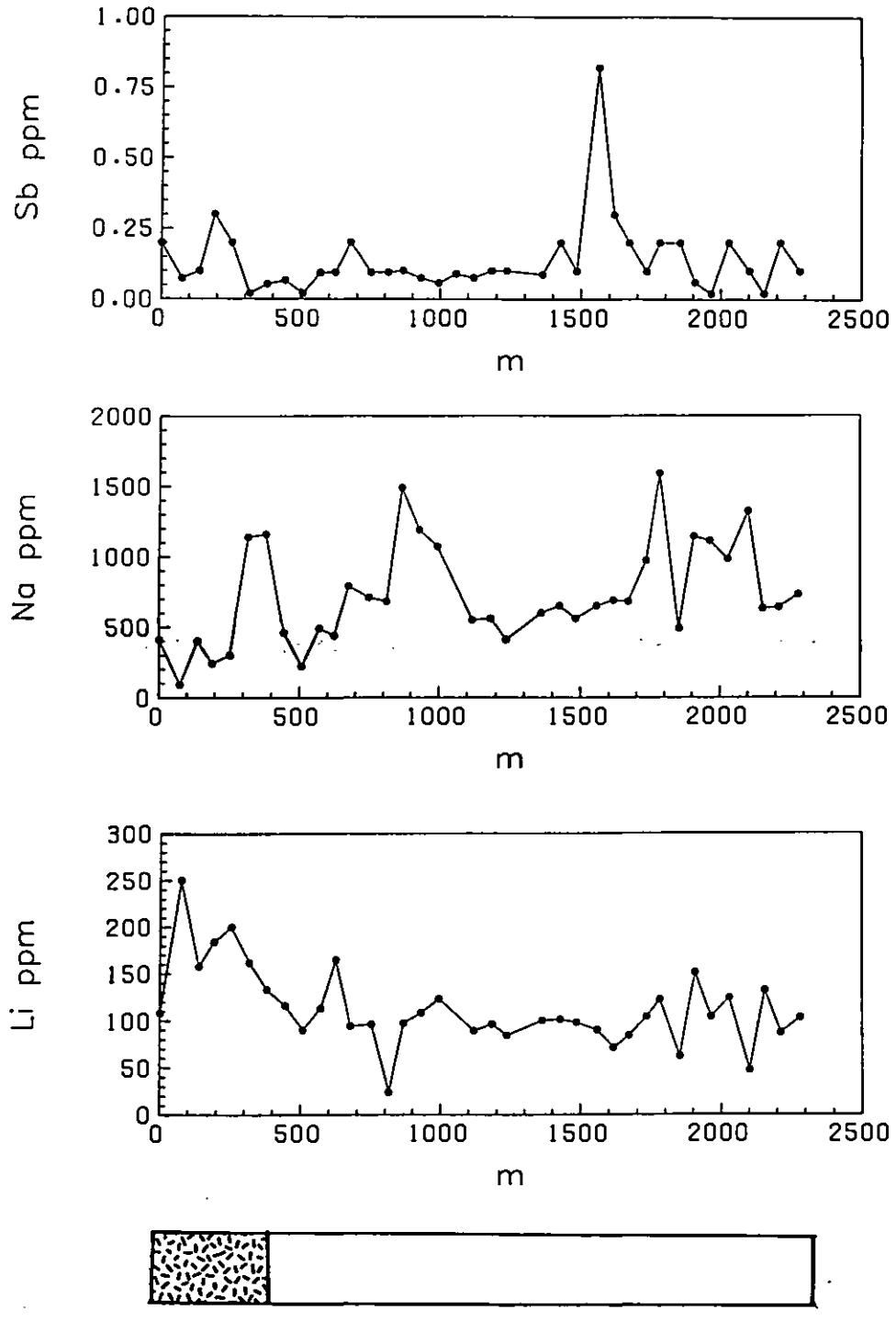


Fig 4.24 Ballinglen: basal overburden traverse BG05
Geological symbols as for Fig 4.11; location of dykes can be gauged from this figure

sediment iron (Fig. 4.34) in both rivers. Bismuth concentrations correlate with tungsten and show the lower mineralized input with an erratic decline downstream relative to the more steady decrease in arsenic. Copper anomalies are even more erratic but probably reflect mineralized material.

Selenium shows some correlation with arsenic in the stream sediment. It is enriched near the head of the stream whereas downstream dispersion is erratic. In contrast antimony has background values at the top of the river, rising downstream to a single point peak near 2,000 m. The other elements show little decrease downstream (iron and zinc), or increase at about 1000 m (calcium and manganese).

There is little variation in the background river (Fig. 4.29) and the elements enriched in the mineralization are not anomalous, with the exception of tungsten. This element is high at 2500 m but the relation to bedrock is not known.

Copper and selenium are erratic with single point anomalies of twice background. Calcium and antimony show some correlation near the head of the rivers but calcium declines downstream thereafter.

g) Waters (BG03)

Water samples were collected at about half of the sediment sample sites, providing an opportunity to further examine the aqueous dispersion of arsenic. Bismuth and antimony are below the instrumental limit of detection in waters and particulates. Water sampling involves the separation into two physical phases: soluble arsenic ($<0.45\ \mu m$) and particulate arsenic ($>0.45\mu m$). The water samples were analyzed for pathfinders by co-precipitation and for general elements by I.C.P. nebulisation following evaporation.

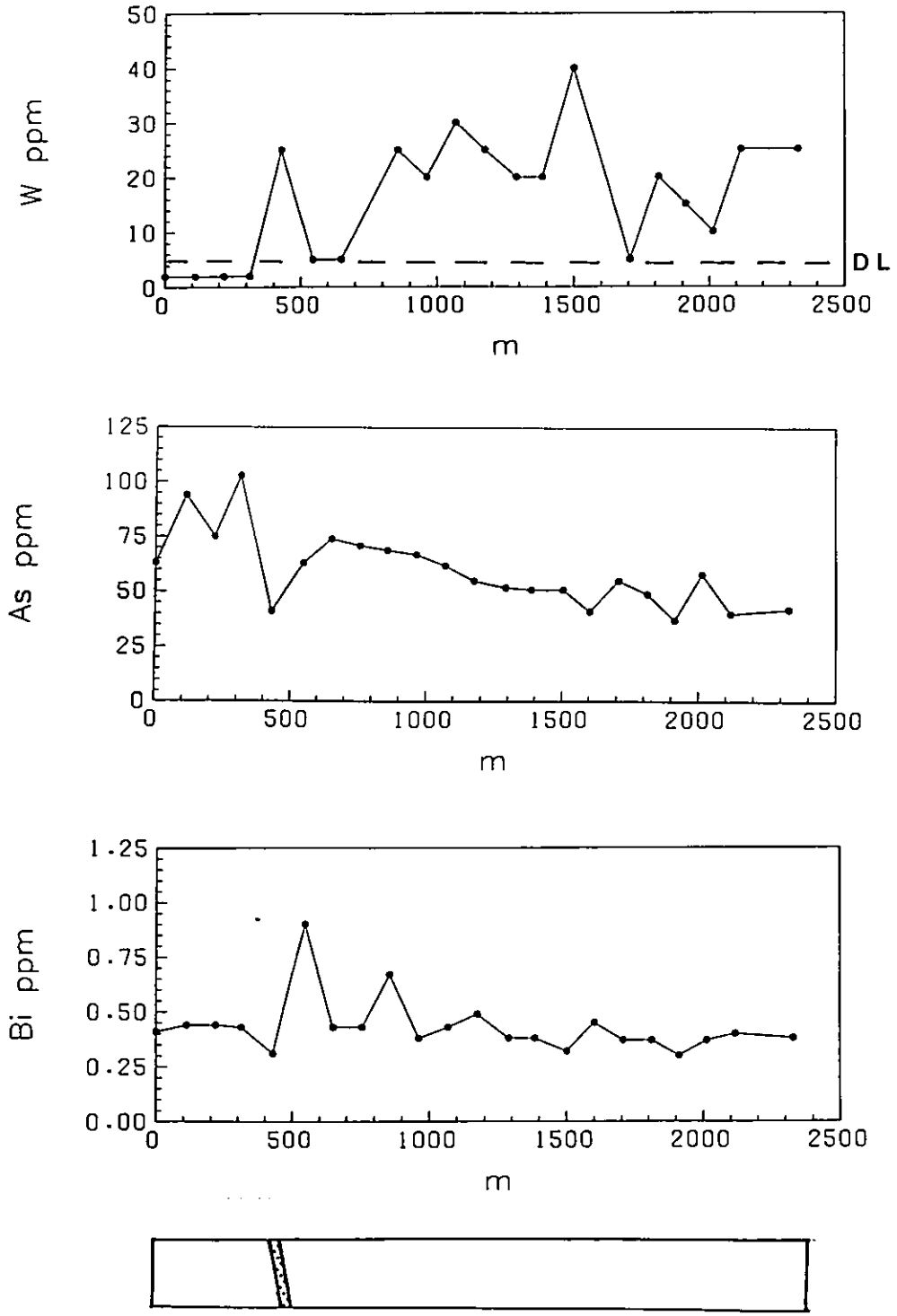


Fig 4.25 Ballinglen: stream sediments, anomalous stream BG03
Geological symbols as for Fig 4.12

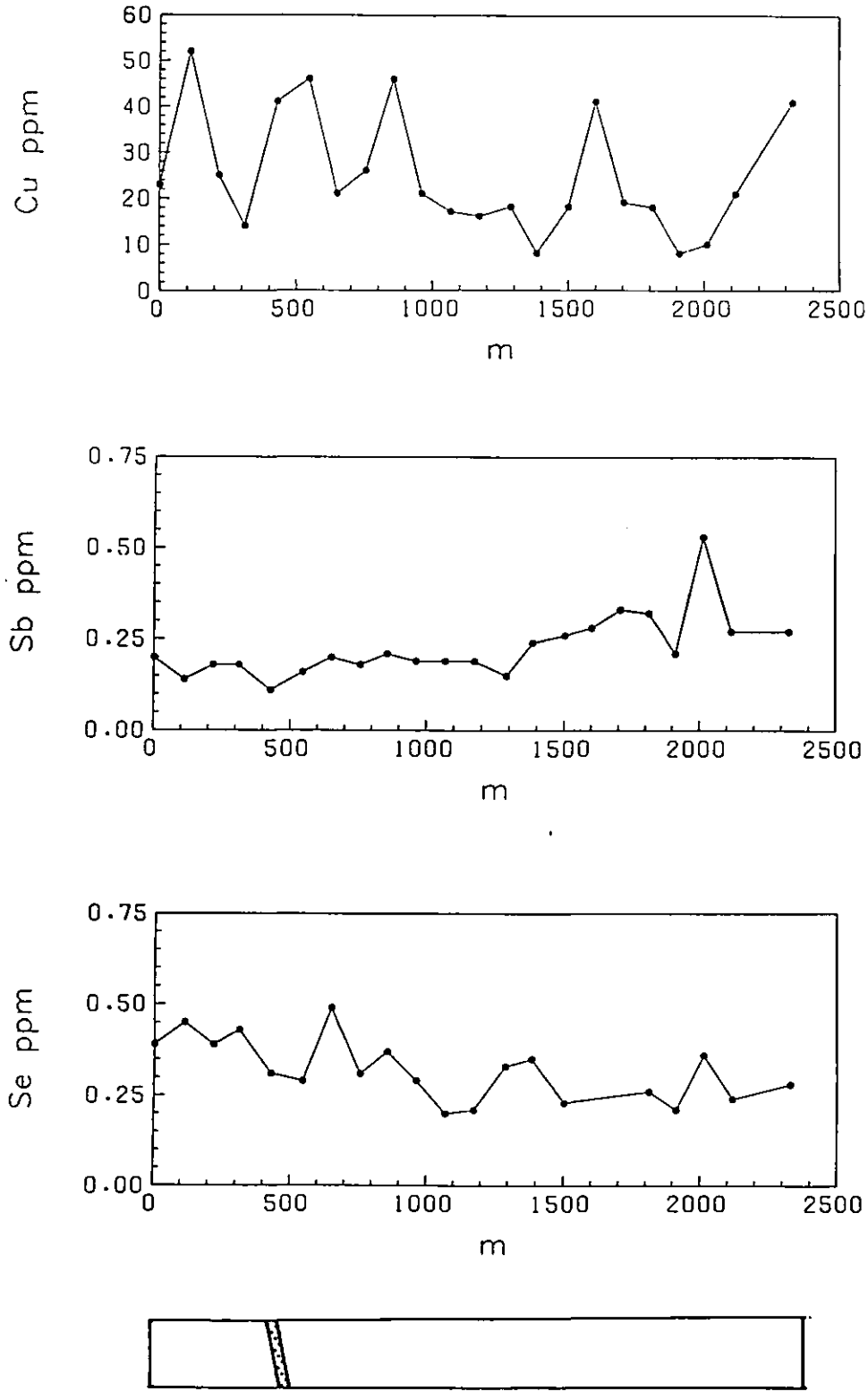


Fig 4.26 Balllinglen: stream sediments, anomalous stream BG03
Geological symbols as for Fig 4.12

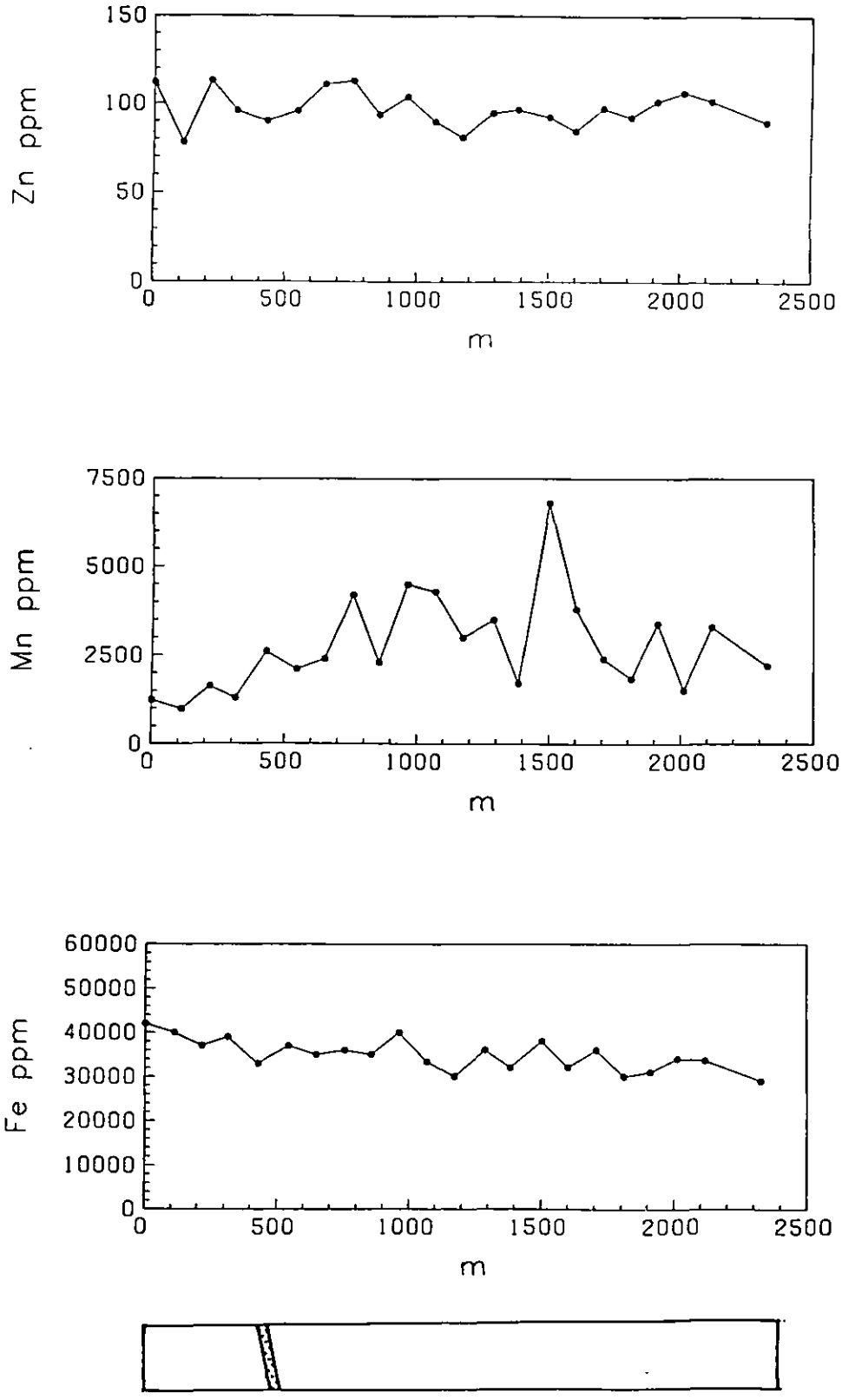


Fig 4.27 Ballinglen: stream sediments, anomalous stream BG03
Geological symbols as for Fig 4.12

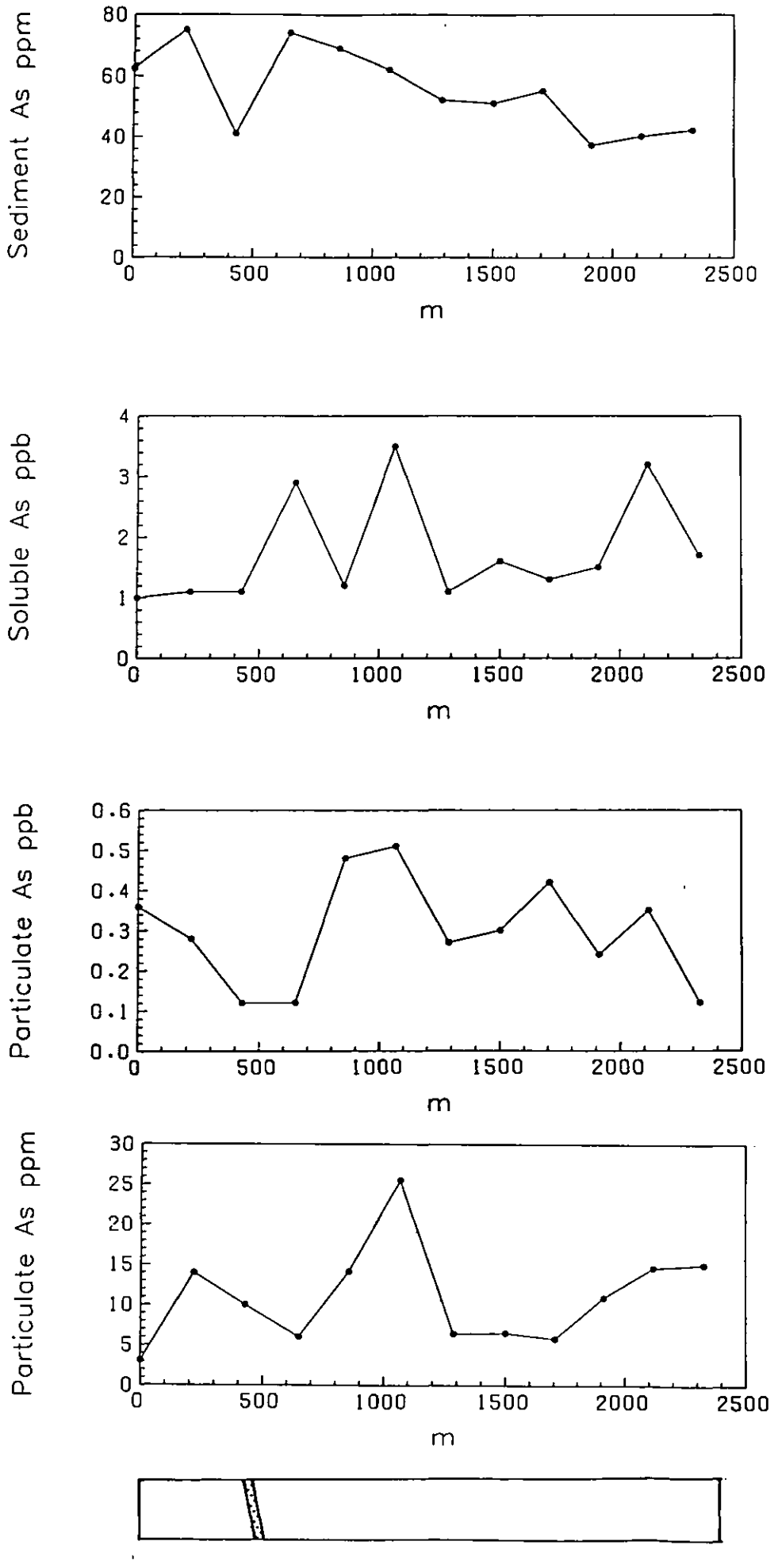


Fig 4.28 Ballinglen: anomalous stream BG03
Geological symbols as for Fig 4.12

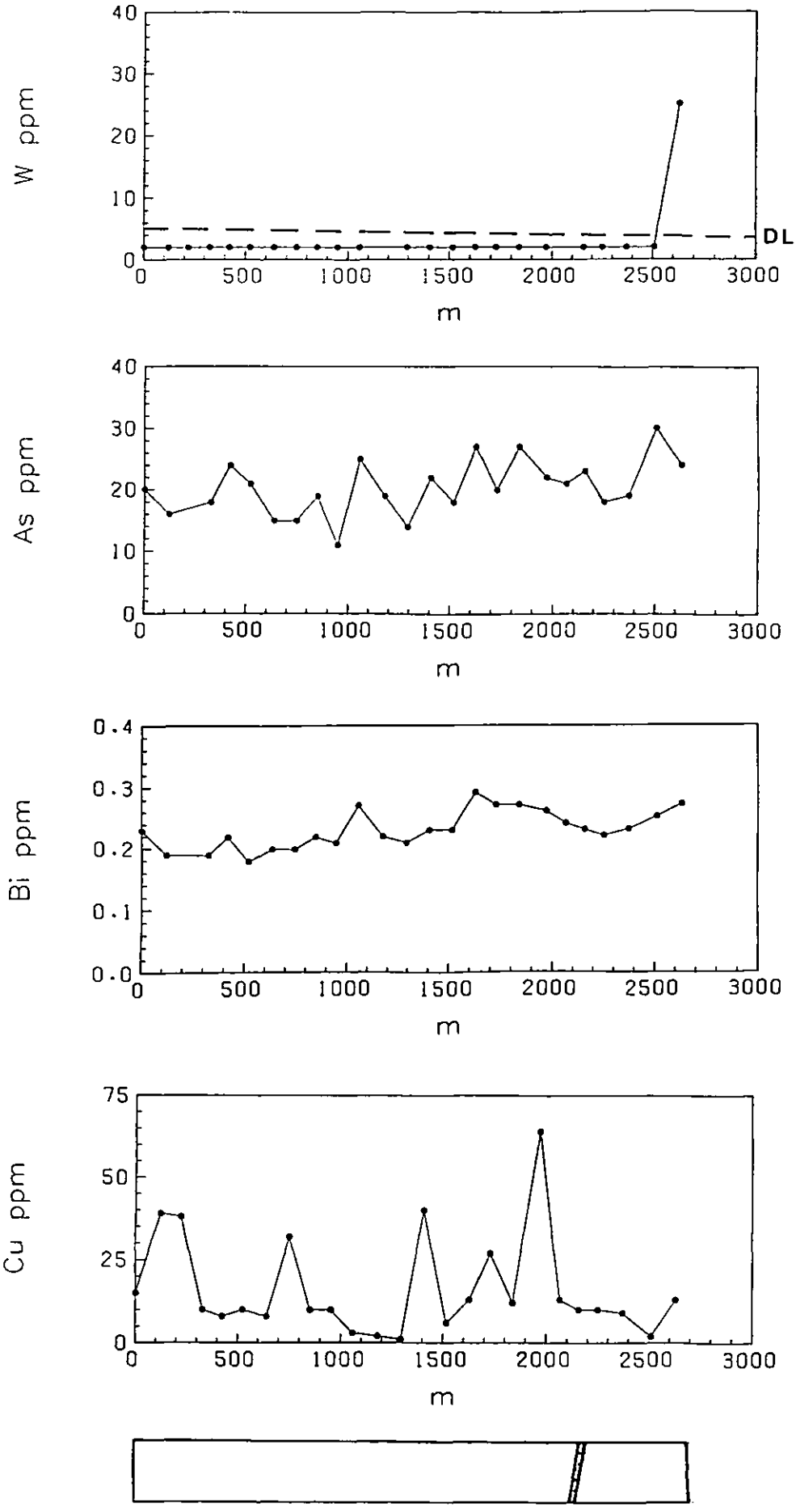


Fig 4.29 Ballinglen: stream sediments, background stream BG03
Geological symbols as for Fig 4.12

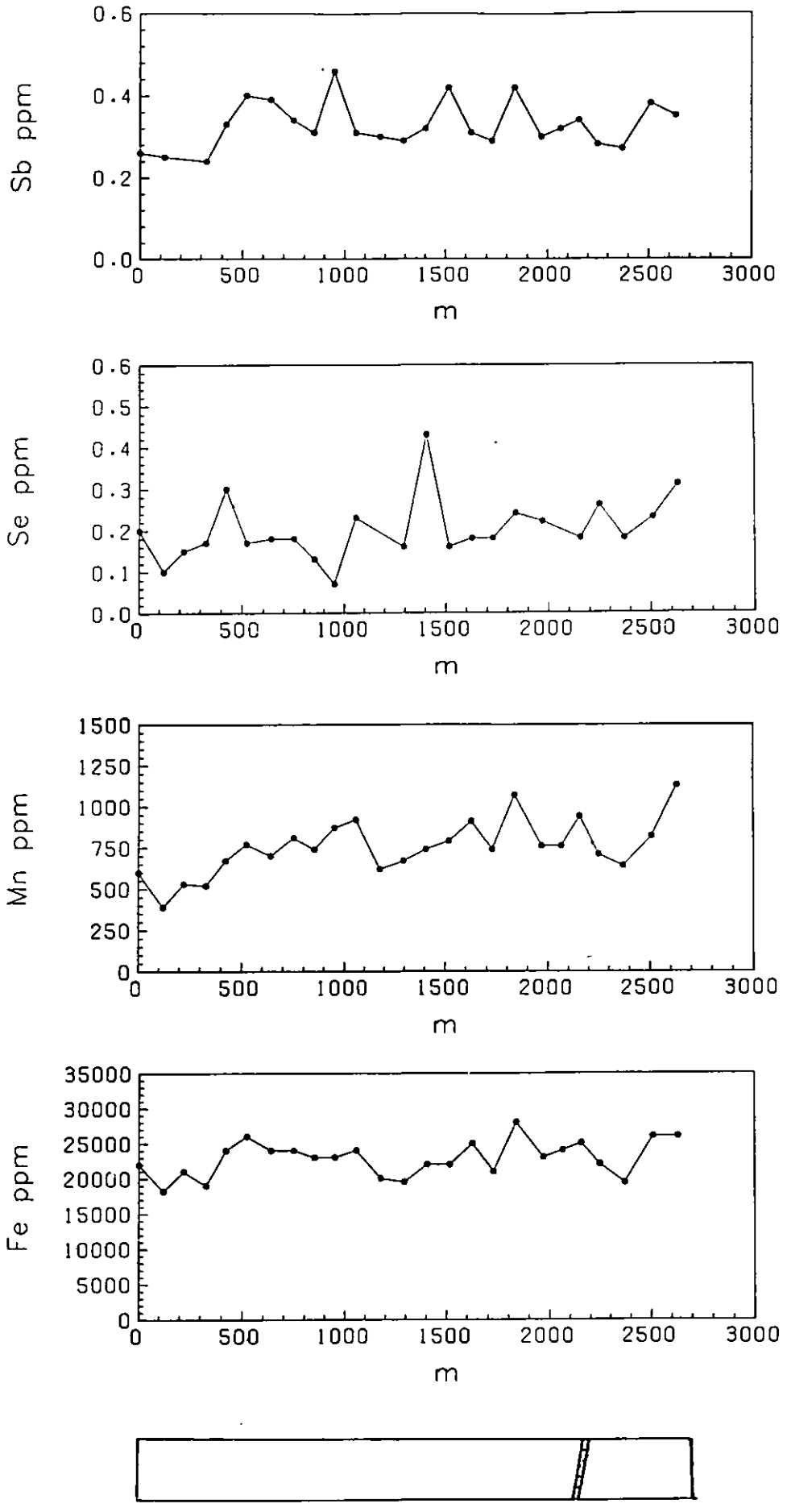


Fig 4.30 Ballinglen: stream sediments, background stream BG03
Geological symbols as for Fig 4.12

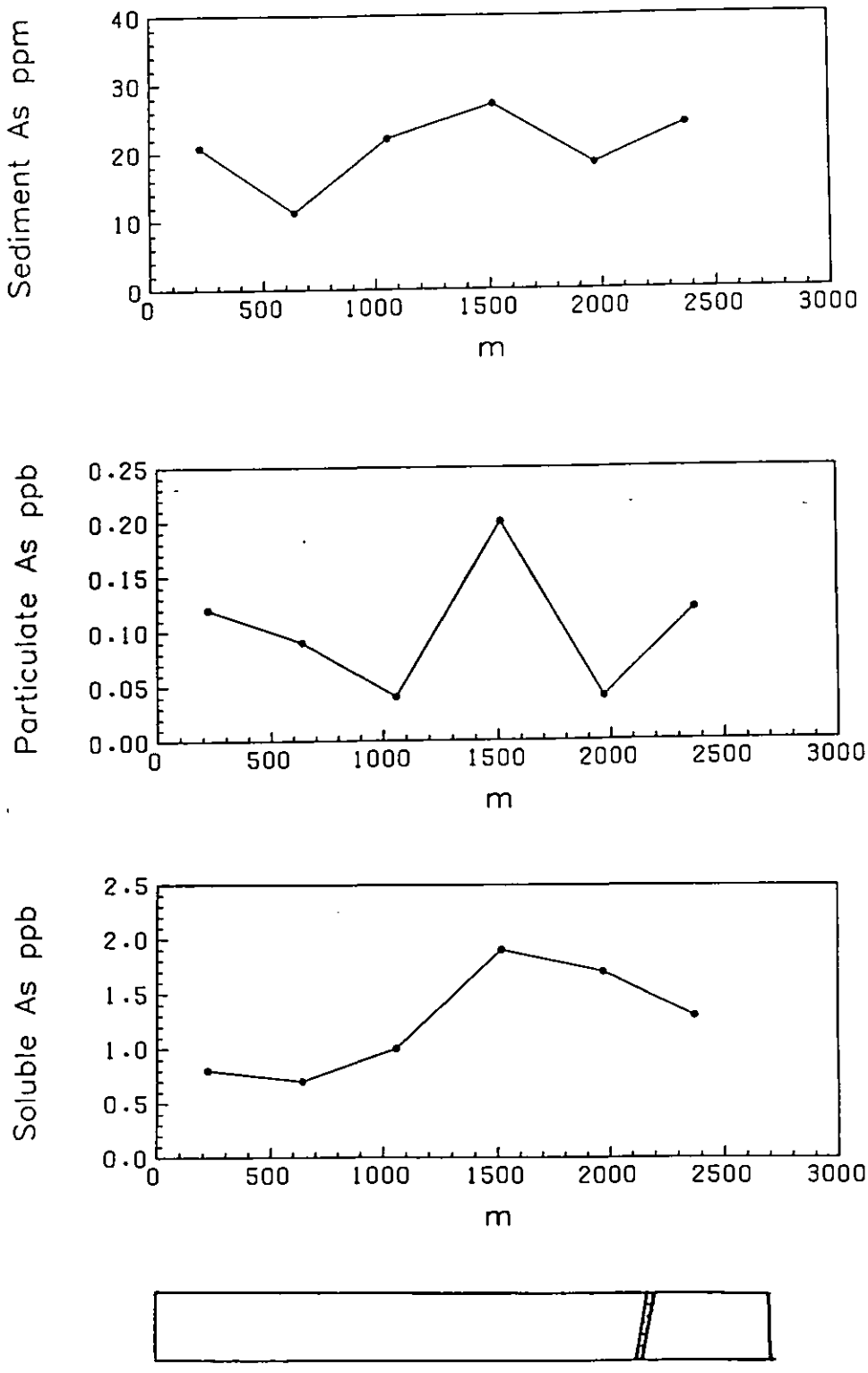


Fig 4.31 Ballinglen: background stream BG03
Geological symbols as for Fig 4.12

The quantity of particulate and soluble arsenic differs between the two inputs of mineralized material (Fig. 4.28). The upper input is reflected in the particulates (expressed in terms of a volume of water) but not in the soluble phase. Both phases, however, peak immediately downstream from the lower input. Soluble arsenic is more erratic and only single point highs are present; whereas the particulate arsenic anomaly is more persistent with a gradual, though somewhat erratic decrease downstream. Recalculation of particulate phase arsenic (Fig. 4.28) as the arsenic concentrations in that phase reveals even more consistent anomalies. This is because the sampling effects at the head of the river are eliminated. Soluble arsenic is stongly correlated with major ions in the water (Na, K, Ca), which themselves show strong intercorrelation (Fig. 4.32). Dissolved arsenic and the majors are, however, independent of pH, which shows rapid decrease at the lower reaches of the traverse due to an influx of farmyard sewage.

Particulate arsenic in the background stream (Fig. 4.31) is more erratic than soluble arsenic, which gives a peak at nearly 1,500 m. Soluble major elements again show strong correlation with arsenic and are uncorrelated with pH (Fig. 4.33).

Scattergrams demonstrate that particulate arsenic in the mineralized streams is significantly higher than in the background stream (Fig. 4.34), while the contrast is not pronounced for soluble arsenic.

4.2.3 Discussion

Conclusions on the primary concentration mechanisms and zonation of pathfinders relative to tin and tungsten are not derivable from the limited data. The data available indicate that, at Ballinglen, very high bismuth values

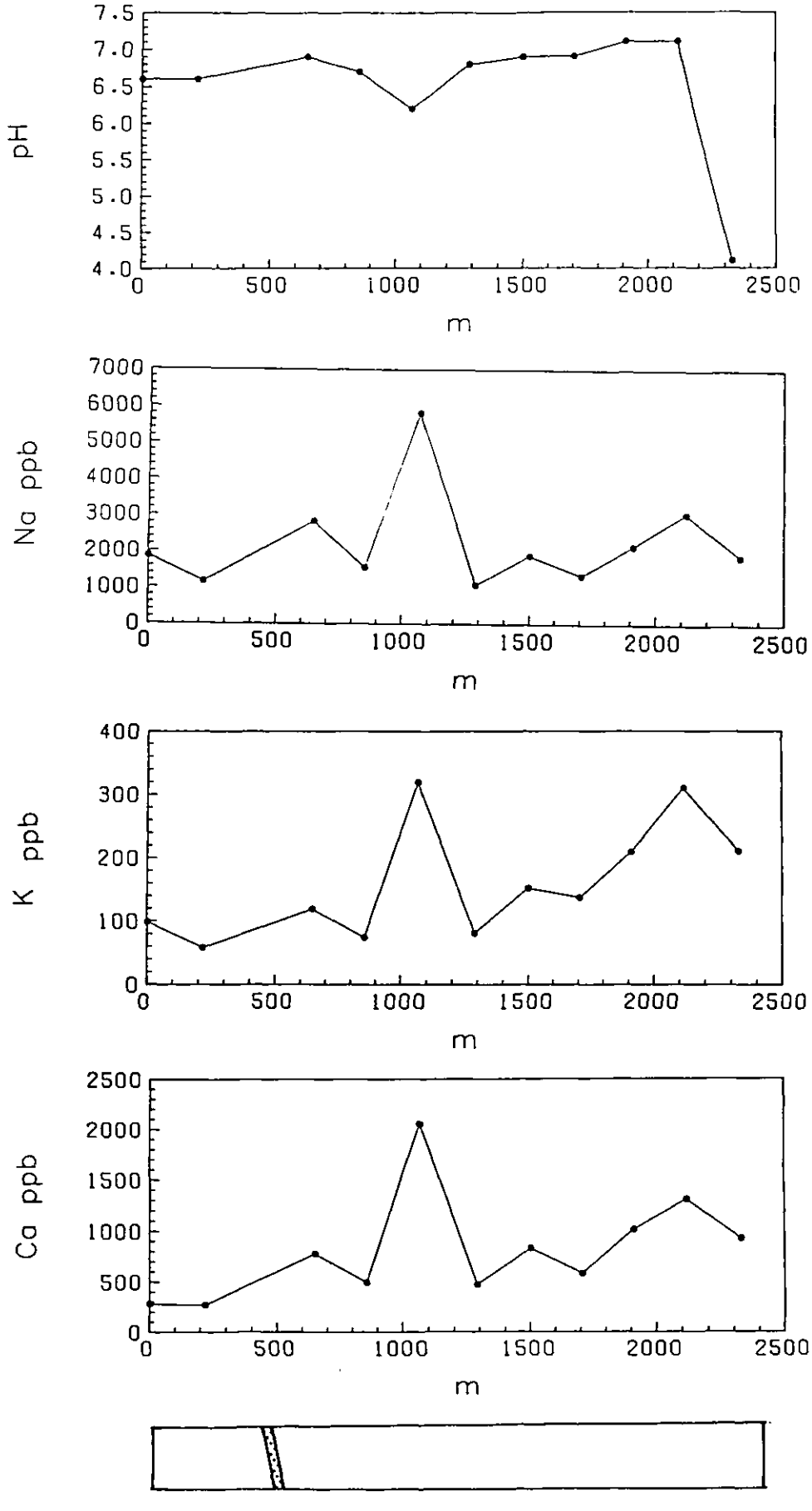


Fig 4.32 Ballinglen: stream waters, anomalous stream BG03
Geological symbols as for Fig 4.12

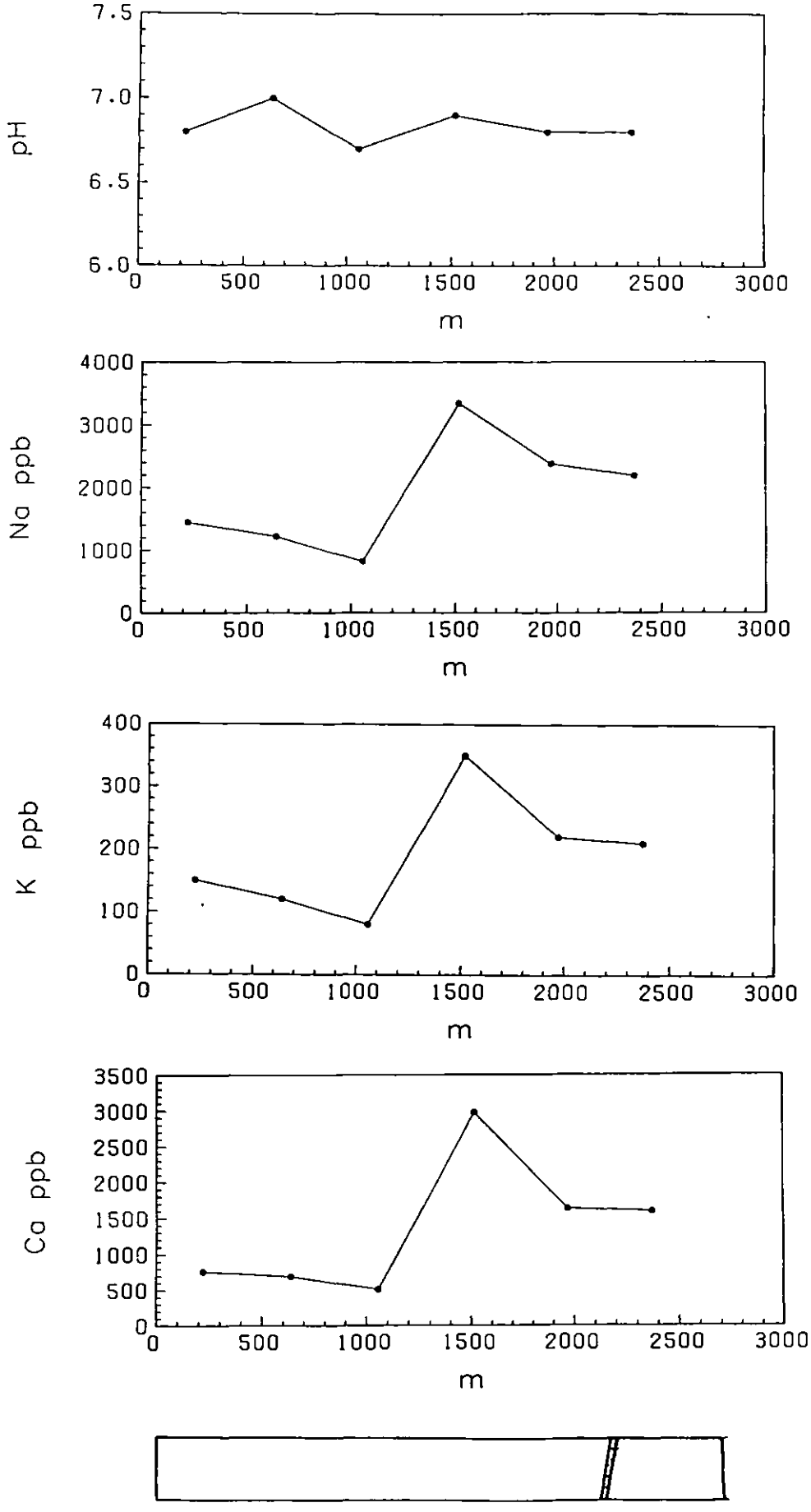


Fig 4.33 Ballinglen: stream waters, background stream BG03
Geological symbols as for Fig 4.12

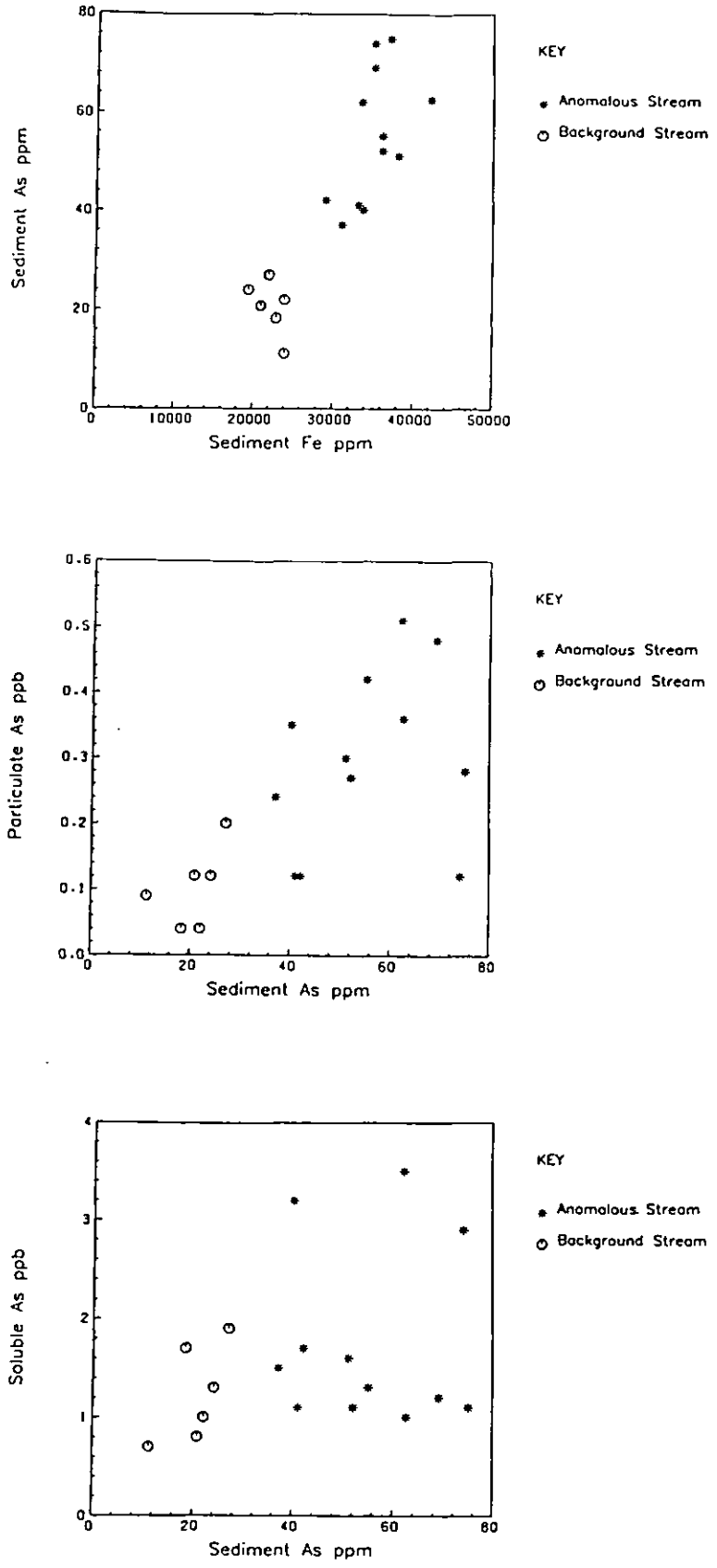


Fig 4.34 Ballinglen: scattergrams for stream sediments and waters

are associated with sulphide development; while arsenic is strongly enriched in zones of both scheelite mineralization and sulphides, with lesser concentrations in phyllites near the mineralization. Bismuth in the only unmineralized microgranite sample analyzed is lower than in phyllite suggesting that bismuth enrichment is related to alteration rather than lithology.

Variations in the primary concentrations of the ore elements and pathfinders probably account for the differences in anomaly/background contrast between the four soil and till traverses. The intense soil anomalies of BG01 reflect the higher grade of the underlying mineralization compared to BG02 and BG04. Thus BG01 can be taken as a model for element dispersion. Little is known of the subsurface geology along BG05 although the same ore/pathfinder associations seem tenable. High lead and zinc values at the margin of the granite are probable associated with mineralization similar to that found further north along the granite/sediment contact (Kennan, 1978).

The till profiles of BG01 demonstrate that tungsten, arsenic and bismuth are dispersed from bedrock through to the surface while high copper concentrations are more restricted to the deeper parts of the profile. Scheelite is virtually insoluble under surficial conditions, indeed scheelite grains can be panned from the soils (Steiger, 1977) and its distribution approximates to clastic dispersion. Bismuth and arsenic form wider haloes than tungsten, as a result of a combination of hydromorphic and clastic dispersion, with arsenic more soluble than bismuth. The near surface concentration of these elements is particularly noticeable.

Research by Ruan (1981) is complementary to the present investigations. He collected samples and undertook gas sampling at the same time as the original traverse

BG 01 was sampled. Soil gas arsenic anomalies (partition coefficient relative to solid $\simeq 10^{-10}$) occur erratically over the subcrop of the mineralization but the most prominent anomaly ($25\,\mu g/m^3$) is downslope between 600 - 700 m. This latter anomaly suggests to Ruan that it is the result of the development of more reduced organo-arsenic compounds, as physical desorption methods reveal only the upslope anomaly. The lower anomaly correlates with the sharp decrease in surface arsenic values and probably seepage of mineralized ground waters. This suggests that organo-arsenic compounds or at least volatile arsenic compounds are generated at the expense of arsenic in solution.

Drift profiling demonstrates that the increases in manganese and zinc to the south of the arsenic anomaly are caused by variations in their primary distribution rather than by variations in the secondary environment.

The other pathfinder elements show distributions that give insight into their surficial behaviour. Very restricted antimony anomalies, possibly reflecting sulpho-salt concentrations, are found only in deep samples. Selenium, in contrast, is more mobile and disperses from bedrock through the lower and intermediate parts of the profile. The lack of surface selenium anomalies poses a considerable problem with two obvious alternative explanations: (i) the element is concentrated at intermediate depth by adsorption or co-precipitation; or (ii) the surface is saturated with respect to selenium and input from depth is removed in solution or, less plausibly, by volatilisation. The lack of correlation between iron and selenium suggests that removal in solution is more likely.

Aqueous dispersion of arsenic and bismuth is well demonstrated in the river draining mineralization, and can

be compared with that of tungsten, which approximates clastic dispersion. The strong correlation of arsenic with iron,and gradual decline of arsenic downstream from the main anomaly,suggest that adsorption/co-precipitation of arsenic by iron is the most important process. The interaction of arsenic in groundwater with dissolved and particulate phase arsenic in the river water is, however, less clear. The correlation of arsenic in solution with major elements suggests that seepage of groundwaters is important in providing arsenic to the stream, and the correlation of particulate and stream sediment arsenic anomalies implies that adsorption/co-precipitation of arsenic onto iron takes place near the seepage of anomalous groundwaters. Most arsenic is transported in the dissolved phase, but the interaction of this phase with anomalous arsenic concentrations in stream sediments and particulates cannot be determined from data available. Bismuth forms very weak anomalies downstream from the mineralization and comparison with tungsten data suggest that its transport is probably clastic.

Arsenic and bismuth are effective pathfinders in soil with arsenic giving the higher contrast. The occurrence of spurious arsenic anomalies (Irish Base Metals, pers. comm.) is worrying and further research on primary concentration patterns is required to solve this problem. Bismuth may be useful in detailed geochemistry as enrichment seems restricted to the mineralized dyke with the background in the Leinster Granite low relative to the South West England granites. Basal drift sampling is the optimum technique for determining drill targets.

Arsenic is useful in regional stream sediment surveys as it reflects groundwater movement as well as clastic dispersion. Stream sediment geochemistry proved a useful reconnaissance technique in the original exploration

of this area (Steiger, 1977).

4.3 Clontibret, Co. Monaghan, Ireland

Gold and antimony mineralization occurs in the Paleozoic sediments of the Southern Uplands (e.g. Glendinning, Chapter 6.3) and the northern part of Ireland. The Clontibret area is the only location of this association within the Irish Longford-Down massif, but base metal veins have been sporadically worked. Clontibret is currently being explored by Anglo-United Ltd. and most of the background data is derived from their work and that of the Irish Geological Survey.

The key exploration problem in the area is the thick glacial overburden, which takes the form of drumlin swarms. These drumlins cover much of the landsurface (Fig. 4.36) and effective geochemistry is limited to the interdrumlin areas.

4.3.1 Geology (Fig. 4.35)

The previously exploited mineralization is hosted by N.N.E. trending shears which cut a Silurian turbidite sequence. Alteration is limited with bleaching near the vein (as found in the stream bed around the old workings near traverse CT03). Minor stibnite can also be seen in this stream bed.

4.3.2 Programme

Two soil traverses, each of 150-200 m, cross the outcrop of the known vein (Clontibret, CT03) and an undrilled deep overburden anomaly (Bryanlitter, CT02). A detailed study of soils from an area of enriched arsenic (Ballygreany, CT01) was made to examine arsenic scavenging.

A small number of stream sediment samples were collected from rivers draining both the Clontibret and Bryanlitter areas (CT04).

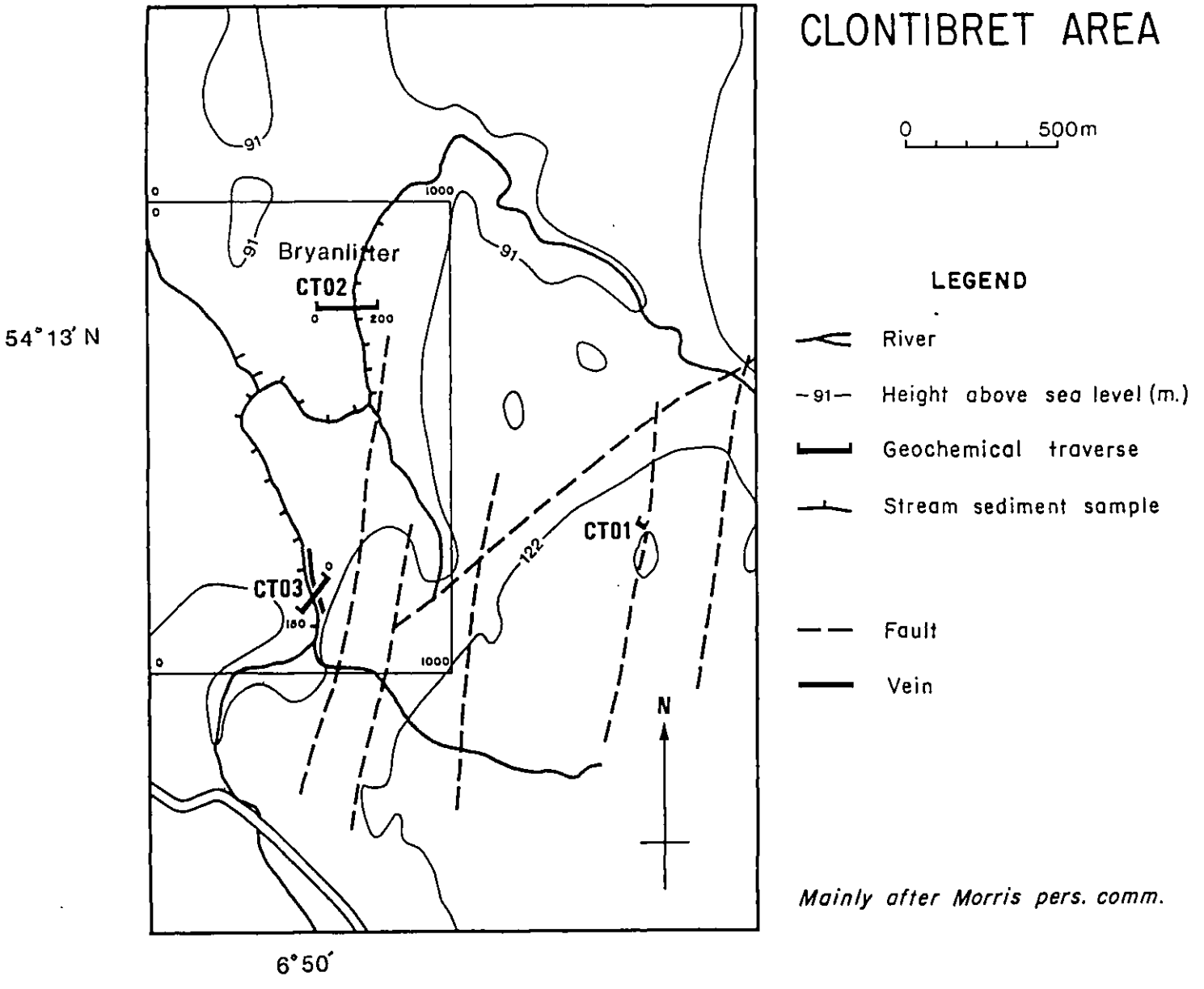


Fig 4.35 Clontibret: location plan

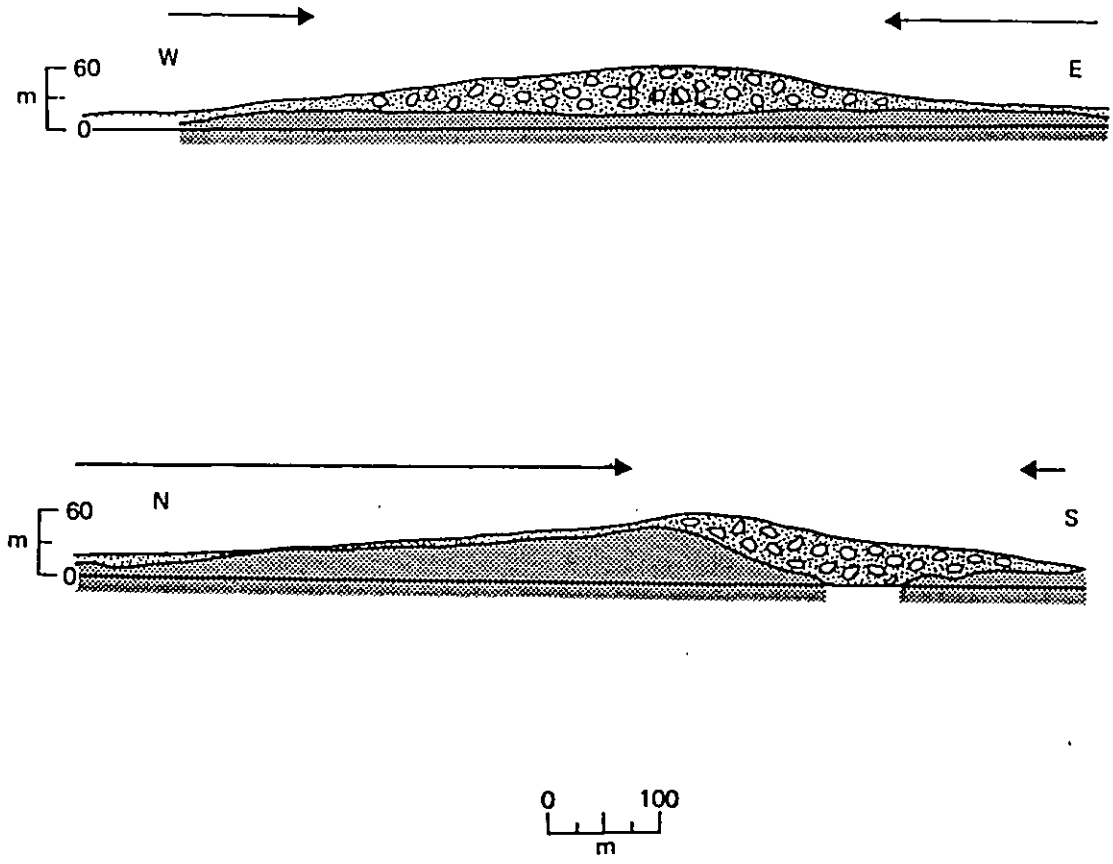


Fig 4.36 Cross section of typical drumlins (from Flint 1971). Arrowed areas are amenable to shallow overburden / soil sampling.

a) Clontibret Soil Traverse CT03

This traverse is parallel to the stratigraphy but approximately perpendicular to the vein, which was discovered in the inter-drumlin valley (Fig. 4.37). The traverse starts and finishes on the tops of drumlin and was sampled at 5 metre intervals. The samples were analysed for pathfinders by the magnesium nitrate method and for general elements by I.C.P. nebulisation (as were the samples from the other three traverses).

Prominent arsenic and antimony anomalies (Fig. 4.38) are developed,with lesser lead highs. Antimony has a maximum of 450 ppm relative to background of 9 ppm while arsenic values are up to 90 ppm with 20 ppm background. The major anomalies are on the valley floor and may be the result of contamination. Extrapolation of the vein outcrop in the stream suggests that its subcrop should be at 80 m as indicated by the eastern end of the anomaly. The subcrop is defined by arsenic and antimony but not by lead. Both arsenic and antimony show a gradual decrease in background eastward (upslope) from the vein subcrop suggesting primary enrichment or drift movement to the east.

Manganese and zinc are also enriched (Fig. 4.39) in the valley floor.

b) Bryanlitter Soil Traverse CT02

Commercial evaluation of this area (Fig. 4.40) is not complete so no details of the geology are available. The traverse runs perpendicular to a shallow valley and transects significant Munster Base Metals deep sampling arsenic and antimony anomalies (Fig. 4.40). These have a similar strike and are close to the north-south trending river. The area between 80 and 160 m is ill drained and

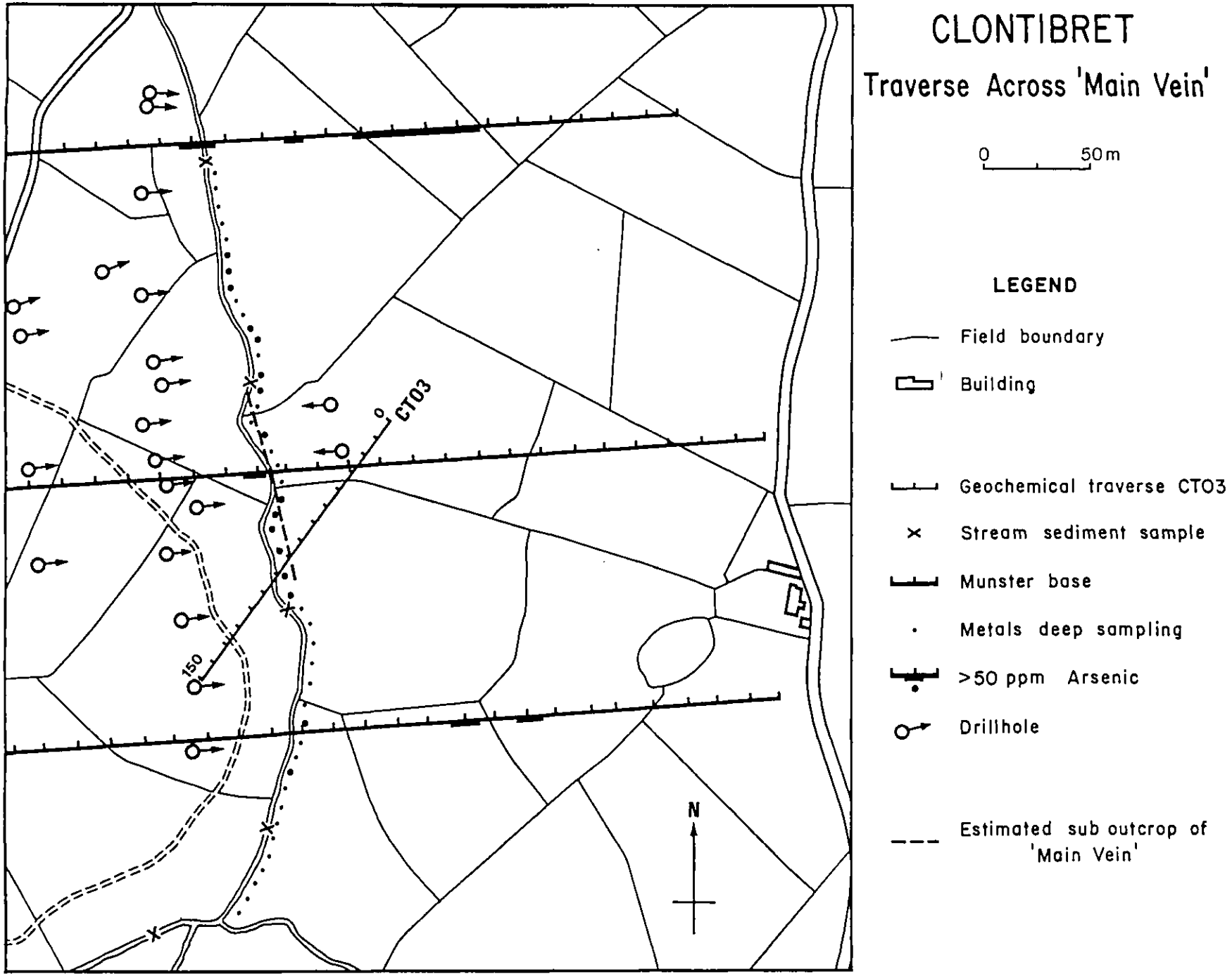


Fig 4.37 Clontibret: location of traverse CT03

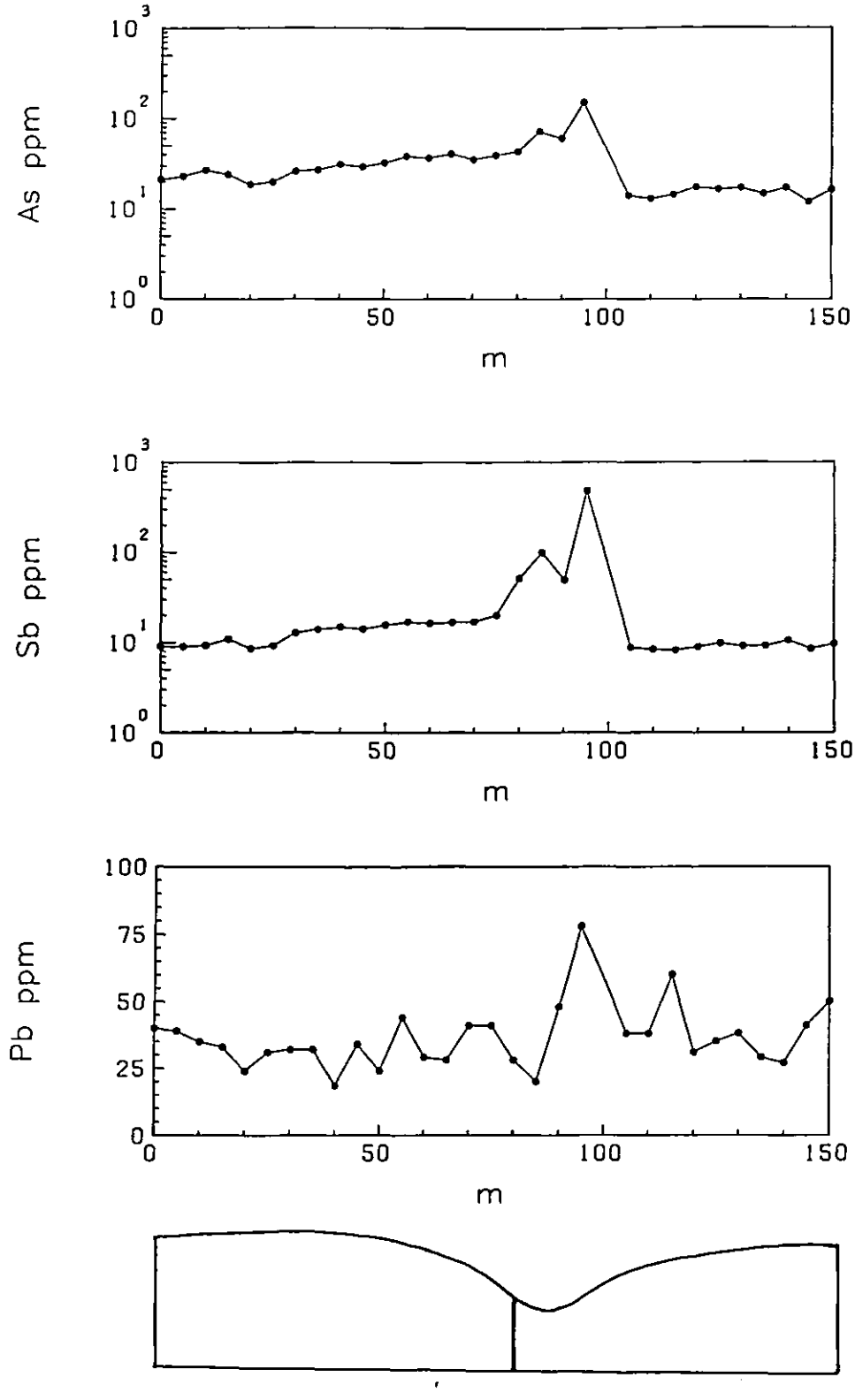


Fig 4.38 Clontibret: soil traverse CT03
Geological symbols as for Fig 4.37

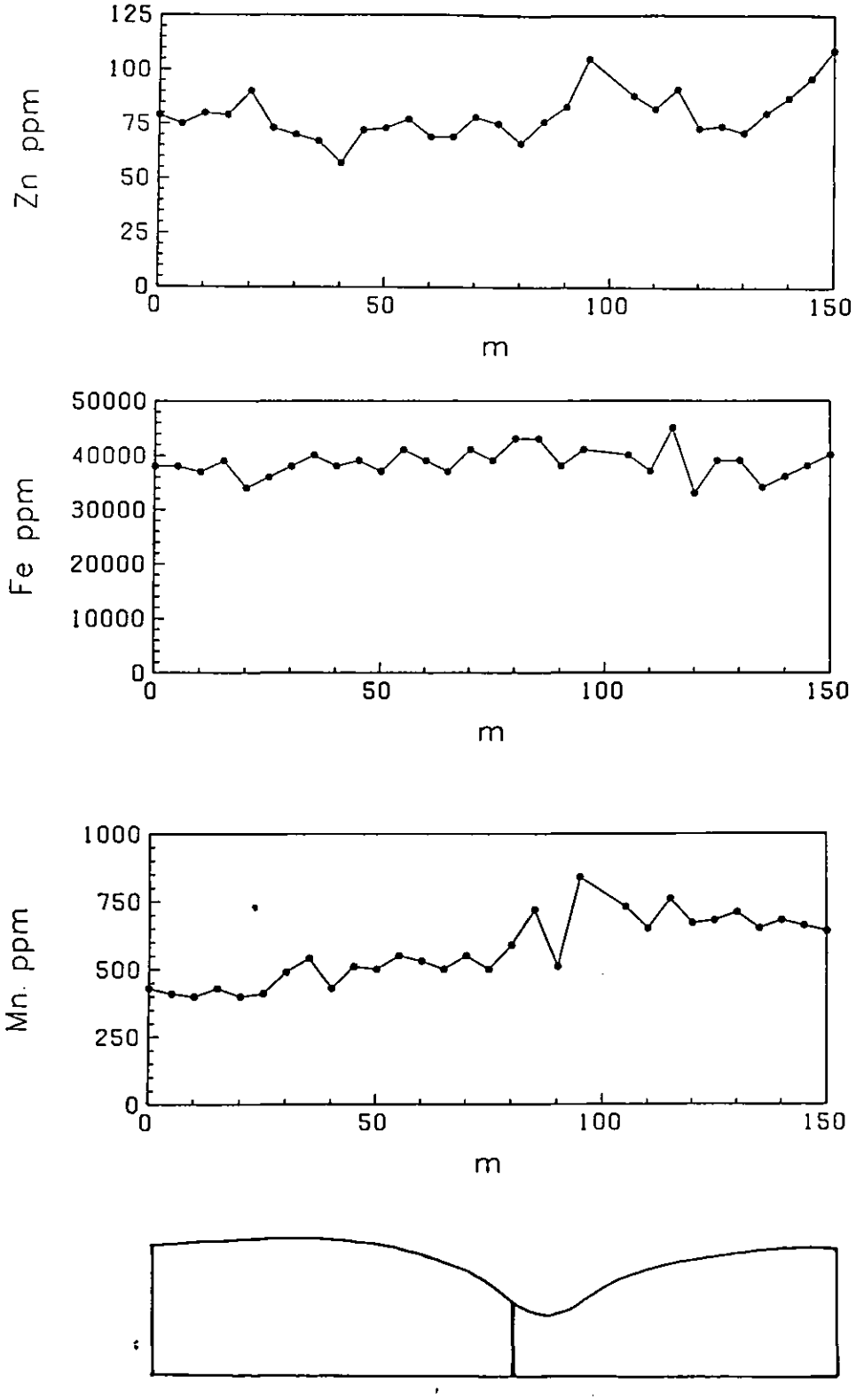


Fig 4.39 Clontibret: soil traverse CT03
Geological symbols as for Fig 4.37

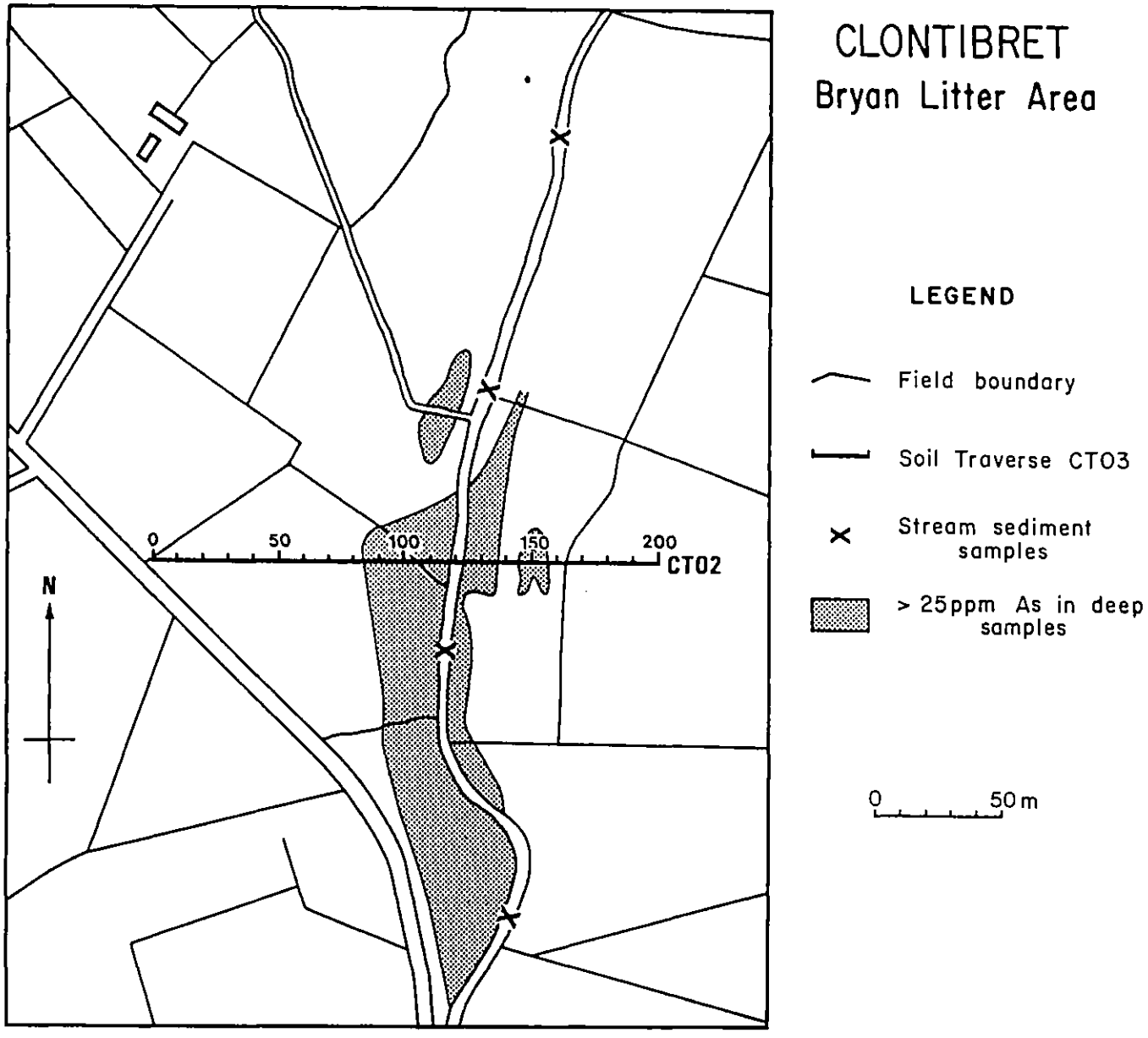


Fig 4.40 Clontibret: location of traverse CT02

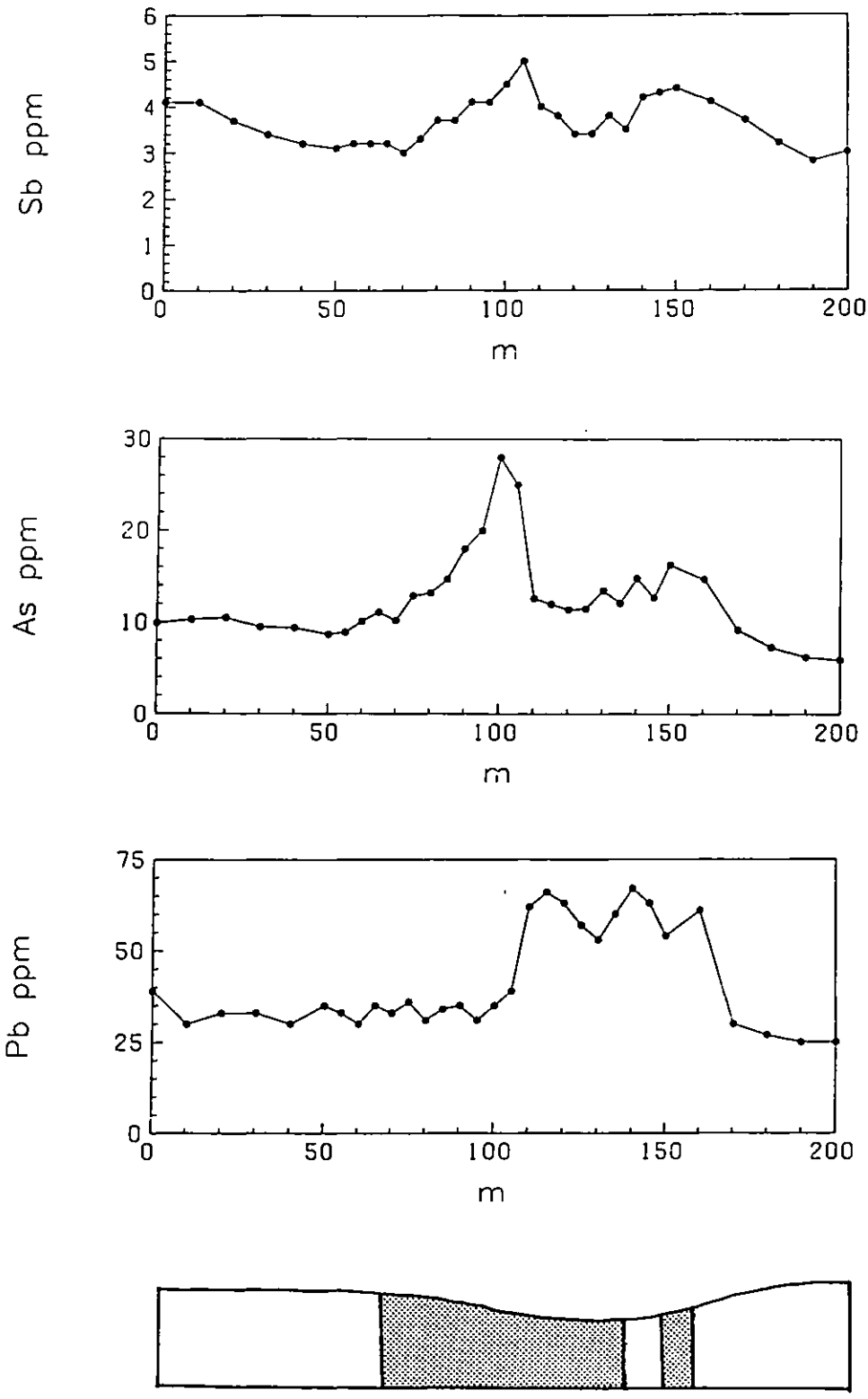


Fig 4.41 Clontibret: soil traverse CT02
Deep anomaly indicated as for Fig 4.40

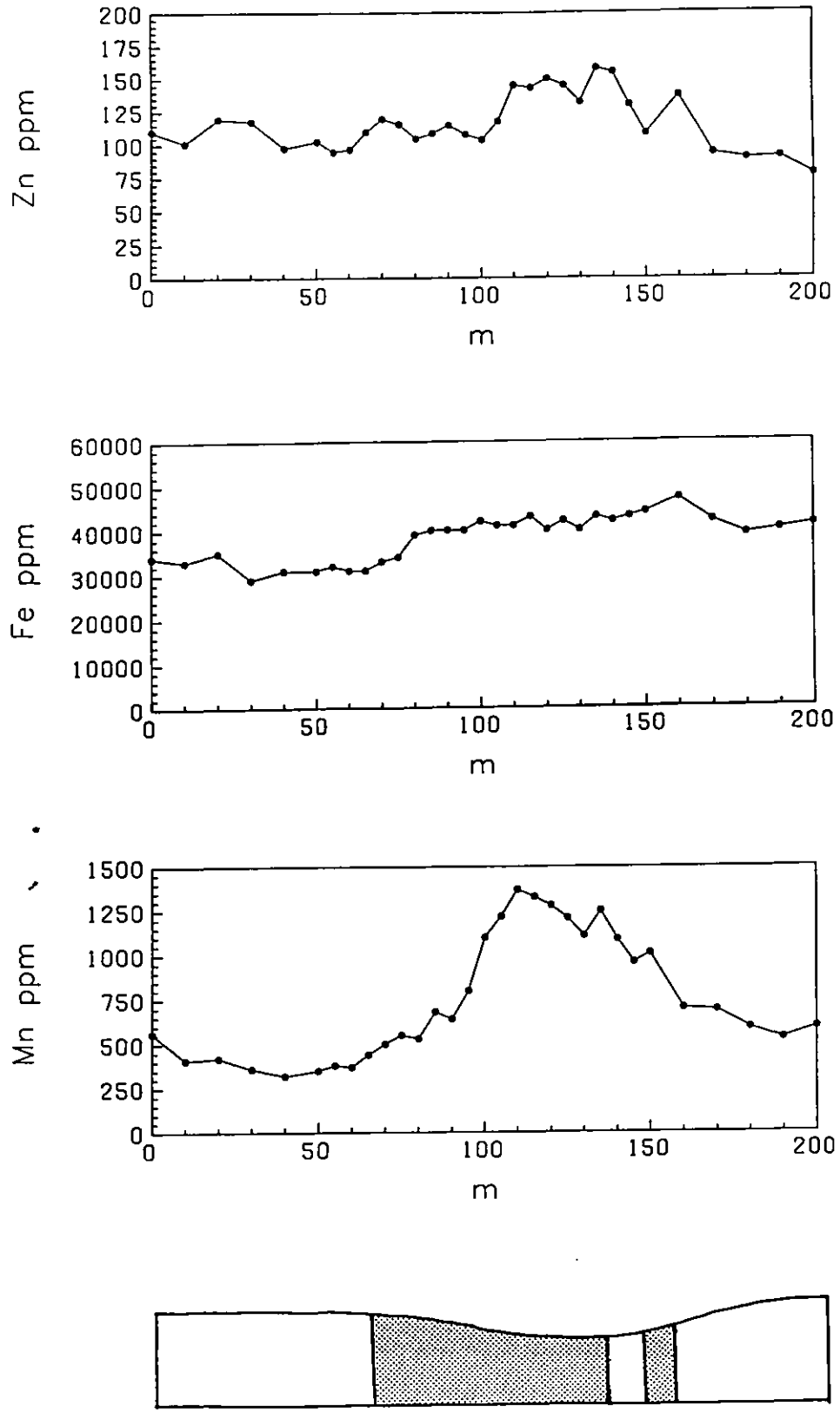


Fig 4.42 Clontibret: soil traverse CT02
Deep anomaly indicated as for Fig 4.40

boggy while the rest of the traverse is moderately drained farmland.

Arsenic gives a soil sample peak (Fig. 4.41) over the deep anomaly with a maximum of 28 ppm relative to a background of 10 ppm As. The antimony high, in contrast, is not significant.

Lead, manganese and, to a lesser degree, zinc (Fig. 4.42) are high over the boggy ground reaching twice the background of the better drained soils.

c) Ballygreany Soil Traverse (CT01)

This traverse is designed to investigate the detailed dispersion of high arsenic and antimony regionally associated with auriferous quartz veins sub-parallel to the regional strike. This area has been trenched (Munster Base Metals) and the highest bedrock arsenic values are found in a major fault (Fig. 4.43) at 18 m. Antimony is particularly enriched at the western end of the fault induced depression, while gold enrichment occurs in the centre of the traverse.

The results from the soil traverse are not encouraging and do not pinpoint the mineralization. The two point arsenic and antimony anomalies (Fig. 4.44) probably reflect contamination of surface soils from trenching soil, but the background throughout the traverse is high (100 ppm As, 4 ppm Sb). No other intersting anomalies were found.

d) Stream Sediments (CT04)

Arsenic and antimony (Fig. 4.45) form prominent anomalies downstream from the outcrop of the main vein. Antimony declines from 300 ppm immediately below the input to 12 ppm below the confluence of the two rivers, while the comparable figures are 120 ppm and 30 ppm for arsenic.

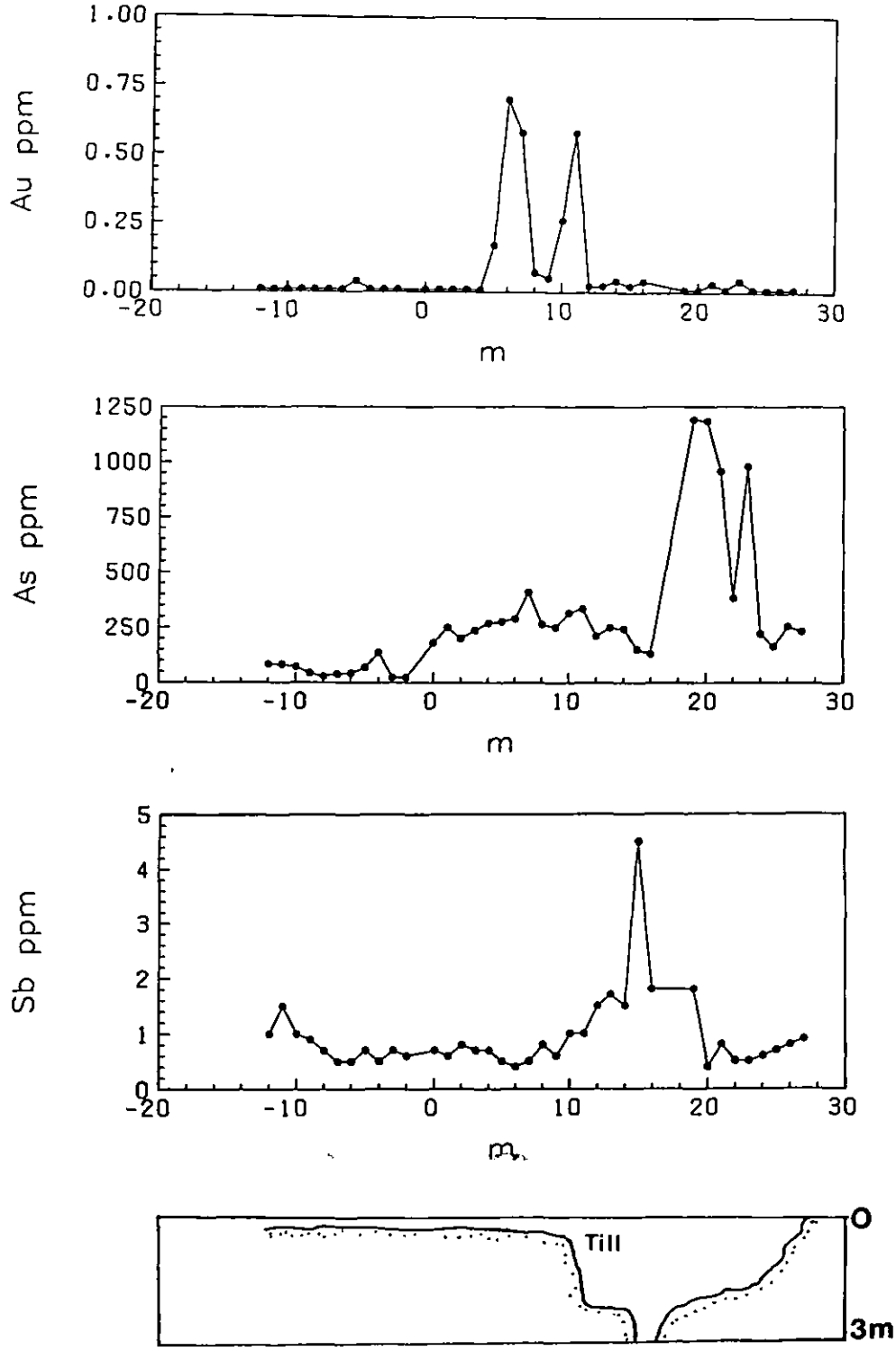


Fig 4.43 Clontibret: bedrock samples along CT01
Data from Anglo-United Ltd.

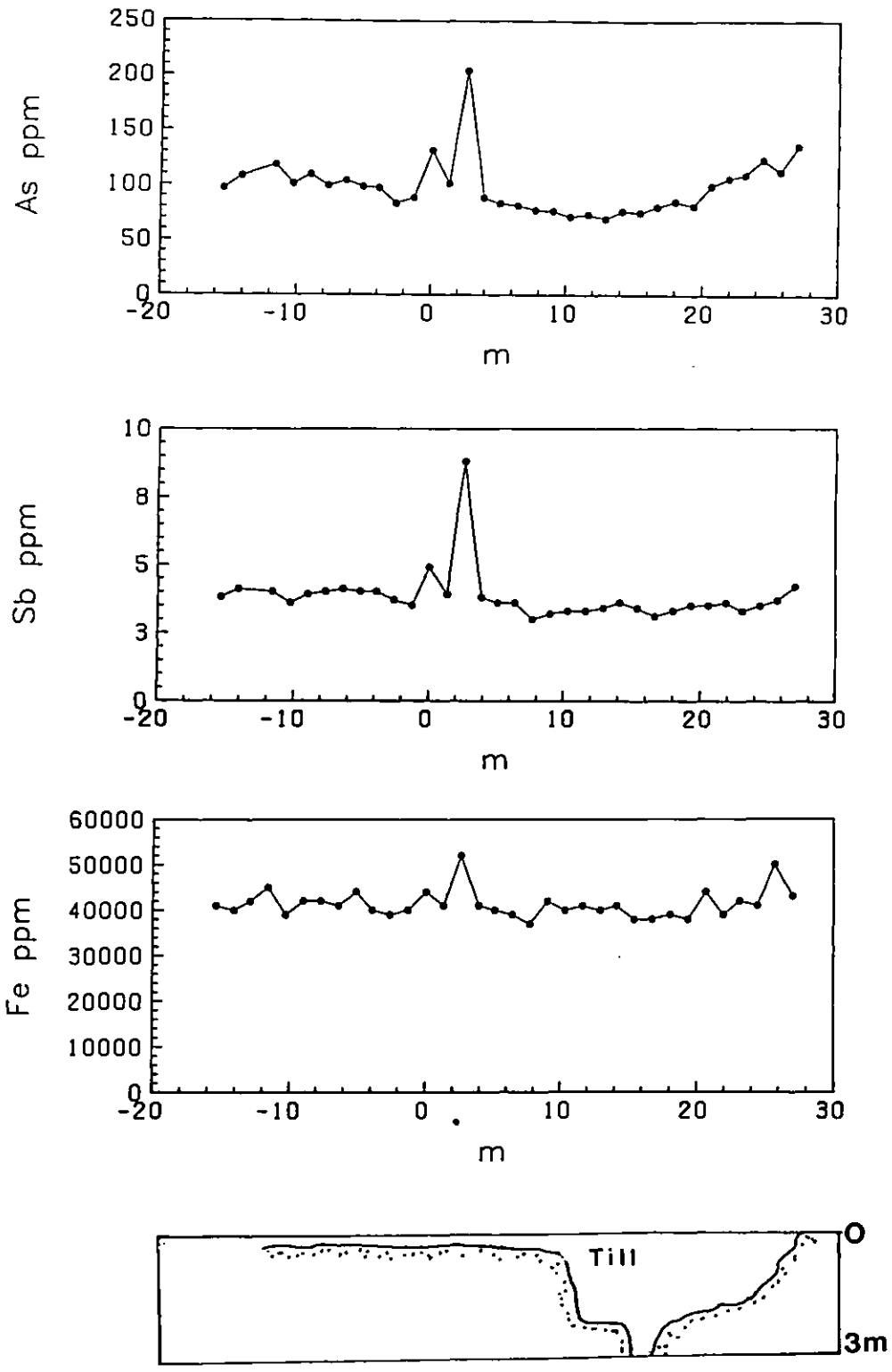
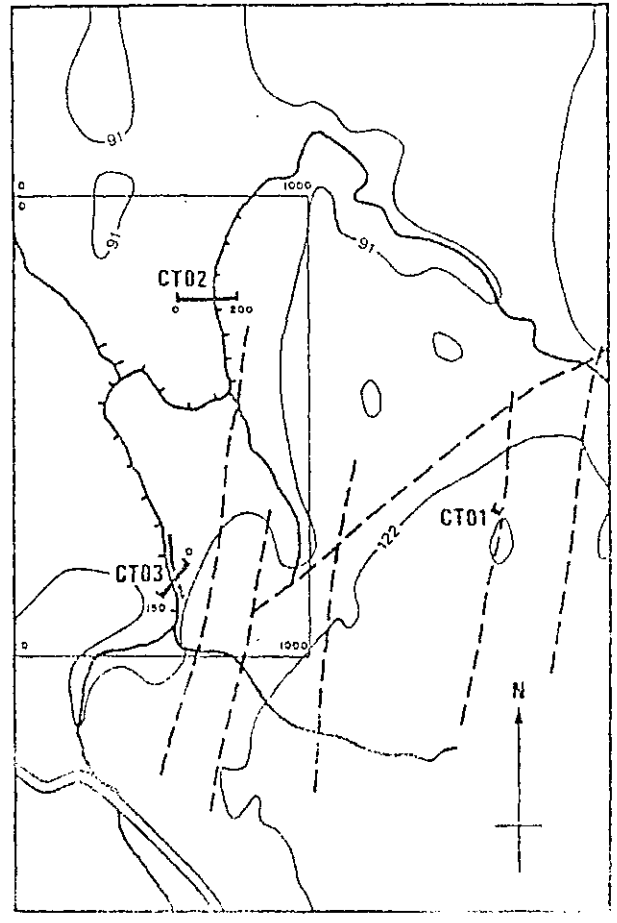


Fig 4.44 Clontibret: soil traverse CT01



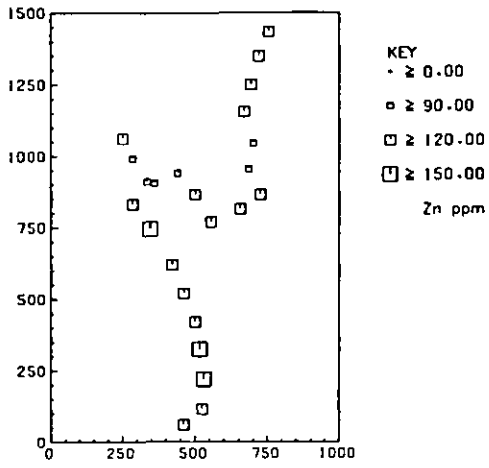
CLONTIBRET AREA

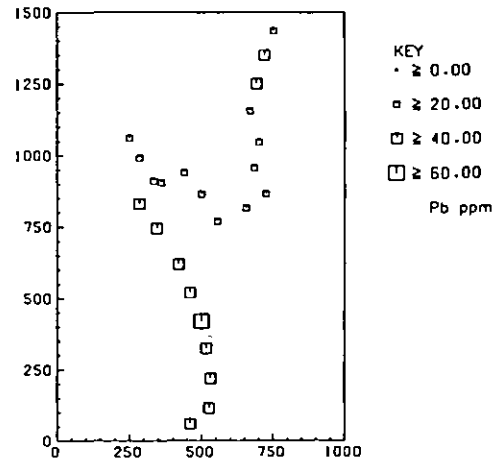
0 500m

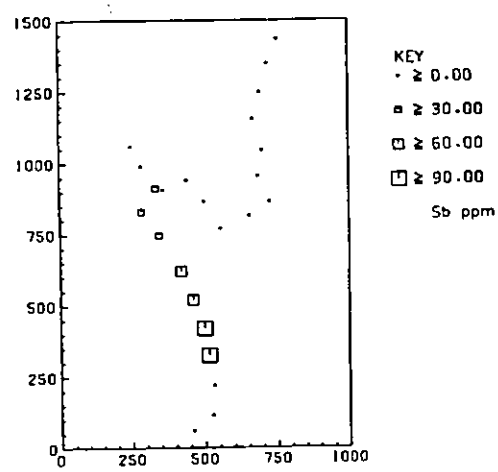
LEGEND

- River
- 91 — Height above sea level (m)
- Geochemical traverse
- Stream sediment sample
- Fault
- Vein

Mainly after Morris pers. comm.







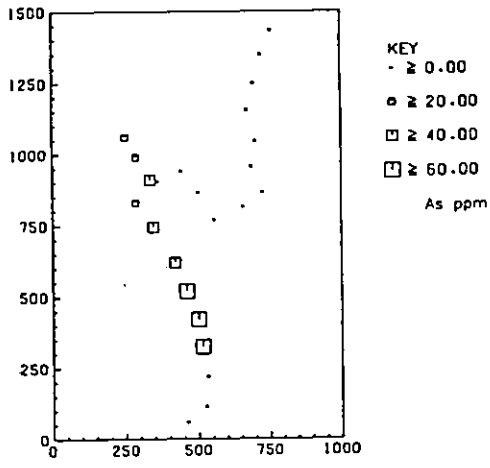


Fig 4.45 Clontibret: stream sediments
Overlay of geology opposite

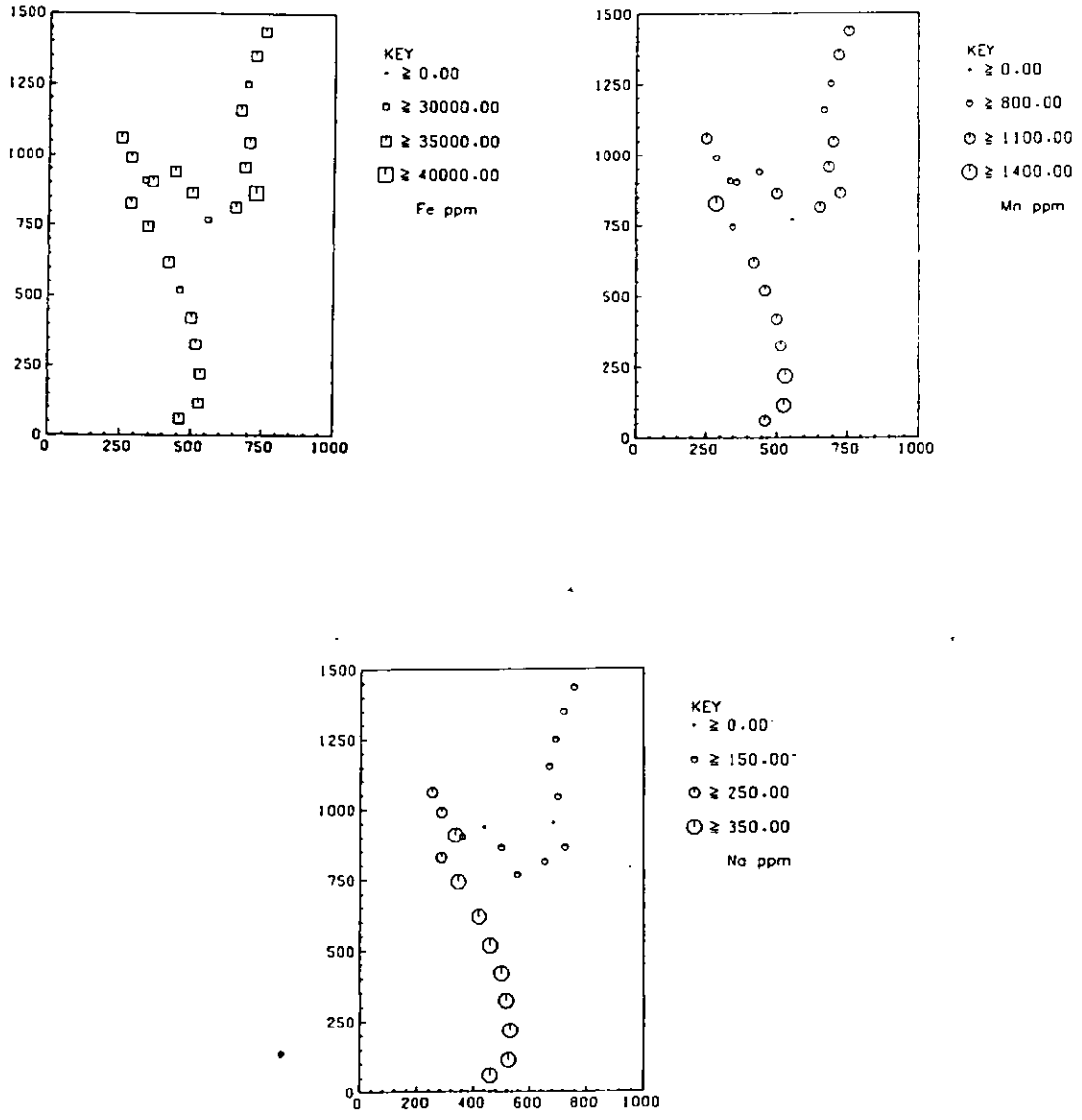


Fig 4.46 Clontibret: stream sediments
Geology is shown in the overlay

Thus arsenic declines less rapidly downstream than antimony and anomalies extend past the confluence.

Lead is enriched downstream from the old mine and also possibly from the soil highs around traverse CT02. There is a clear division in sodium values with high values along the whole length of the river draining the old mine area, and even upstream from it.

Iron, manganese and zinc are erratically high (Fig. 4.46) and there is little association with the known mineralization.

4.3.3 Discussion

The lack of detailed geological information and likelihood of contamination around the old mine workings (CT03) make firm conclusions difficult.

The ubiquity of the drift and lack of subsurface investigations means that few data are available on the primary concentrations of arsenic and antimony but they do seem to be closely associated with known vein gold mineralization. Their enrichment in particular stratigraphic units is much more speculative although it is perhaps indicated for arsenic in the consistently high surface values of CT01 and a regional stream sediment anomaly over Silurian- Ordovician sediments north east of Clontibret in Northern Ireland (Webb et al, 1973). The till traverse of CT03 also has particularly high backgrounds in both arsenic and antimony, the origin of which is unknown.

Arsenic and antimony are effective in locating the sub-outcrop of the vein near the old mine workings, where till is thin. The cause of the downslope dispersion is unclear but is probably a combination of clastic dispersion from the vein and contamination from the old workings. Where the inter-drumlin till is thicker, as at CT03, the surface expression of bedrock arsenic anomalies is poor. It is, however, more mobile than antimony which gives no surface indication of these primary anomalies. Surface geochemistry is thus, not recommended but deep overburden sampling is generally effective in areas not covered by drumlins.

Arsenic and antimony give prominent stream sediment anomalies downstream from the vein outcrop. Regression of arsenic and antimony on iron and manganese give very similar and high residuals (Fig. 4.47) and their distribution suggests that dispersion is dominantly clastic. The origin of the anomalous elements is at least in part due to weathering of fresh stibnite exposed in the river bed, although contamination may be an important factor. The absence of arsenic and antimony anomalies downstream from the deep sampling anomaly at CT02 is due to the lack of a surface anomaly and the impervious nature of the till. Stream sediment sampling is probably ineffective due to the thickness of impervious till and the restrictions this imposes on aqueous dispersion.

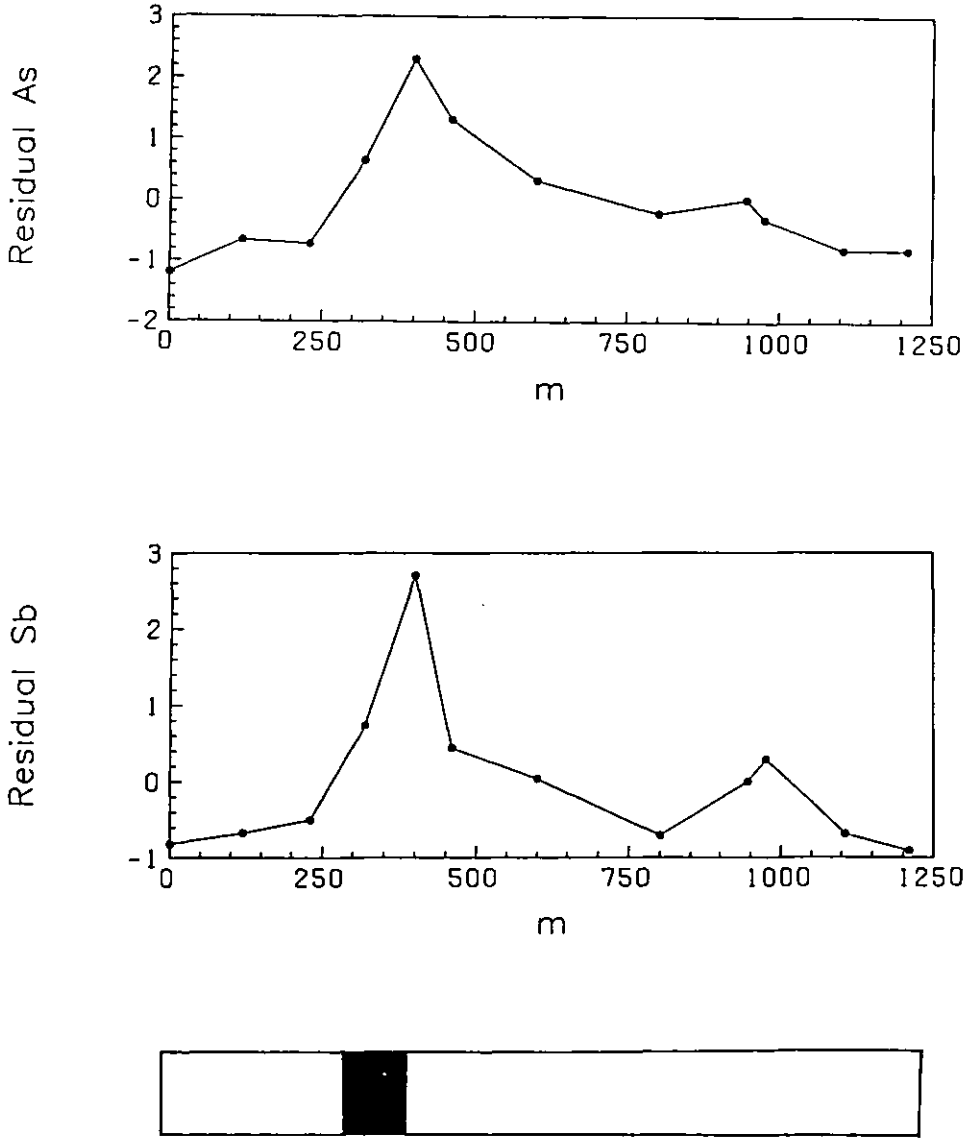


Fig 4.47 Clontibret: residuals after regression on iron and manganese in the stream draining the old mine area. Vein shown by the heavy line.

CHAPTER 5 DEPOSITS ASSOCIATED WITH IGNEOUS INTRUSIONS IN GLACIATED AREAS

The deposits investigated are representative of two of the major types of metalliferous deposits in igneous rocks: copper-nickel sulphides in mafic intrusives (Arthrath) and disseminated copper-molybdenum sulphides in porphyritic acid intrusives (Kilmelford).

5.1 Arthrath, Grampian, Scotland

Exploration geochemistry is one of the most useful techniques in the search for nickel sulphide deposits. Nickel has a high background in mafic rocks as a lattice constituent of rock forming minerals, and the major problem is the discrimination of this form of occurrence from nickel sulphide ore. The simple use of nickel geochemistry is insufficient and various other approaches notably using primary S (Hale, 1978), Cr/Ni and Cu/Ni ratios have been utilised. More recent work in the lateritised areas of Western Australia has emphasised the effectiveness of multi-element geochemistry (McGoldrick and Keays, 1981, Travis et al, 1976). Arsenic, antimony and selenium together with platinoid elements can successfully be employed in the discrimination of gossans overlying nickel sulphides from barren ironstones.

5.1.1 Geology

Mineralization at Arthrath (6 km north of Ellon) was discovered during commercial prospecting by Riofinex in 1967 (Rice, 1975). The sulphides are sub-economic with nickel and copper grades not exceeding 0.5%. The attractions of the occurrences as a study area are that they are completely undisturbed by mining and are covered by variable thicknesses of drift.

a) Solid Geology

A variety of basic and ultramafic rocks host the

nickel sulphides: dunites, pyroxenites, norites and contaminated norites (Rice, 1975). There is no outcrop of the intrusive rocks in the Arthrath area but they are comparable to the intrusives that crop out to the west in the Arnage area (Gribble, 1967, Read and Farquhar, 1951). The intrusives are Caledonian in age and form part of a much larger body of basic rocks in north east Scotland.

Host metasediments to the intrusives are Dalradian and predominantly siliceous, although minor limestones occur. Detailed mapping (Rice, 1975) of the intrusives (Fig. 5.1) revealed extensive faulting but it is not clear how this is related to the intrusive processes. The sequence in the Arthrath area is cut by a Permo-Carboniferous quartz dolerite dyke.

b) Surficial Geology

North east Scotland was glaciated on several occasions during the Pleistocene with the bulk of the drift relating to the last (Devensian) glaciation. The Arthrath area was probably peripheral to the major centres of the ice-sheet, and till cover is of variable thickness but is generally thin (Clapperton and Sugden, 1977).

Detailed drift mapping by Ross (in Merritt, 1981) suggests that much of the area has cryoturbated bedrock near to surface, or thin till (Fig. 5.2). These tills are generally reddish and sandy in the Arthrath area. Meltwater water channels have been mapped along many present day river valleys and evidence from the area immediately south of Ellon shows that most are filled with fluvio-glacial sediments. Although those sediments have not been mapped in the Arthrath area, pits at Muirtack (993375) indicate that they may fill some of the meltwater channels shown in Fig. 5.2 (Merritt, 1981, 1982 pers. comm.)

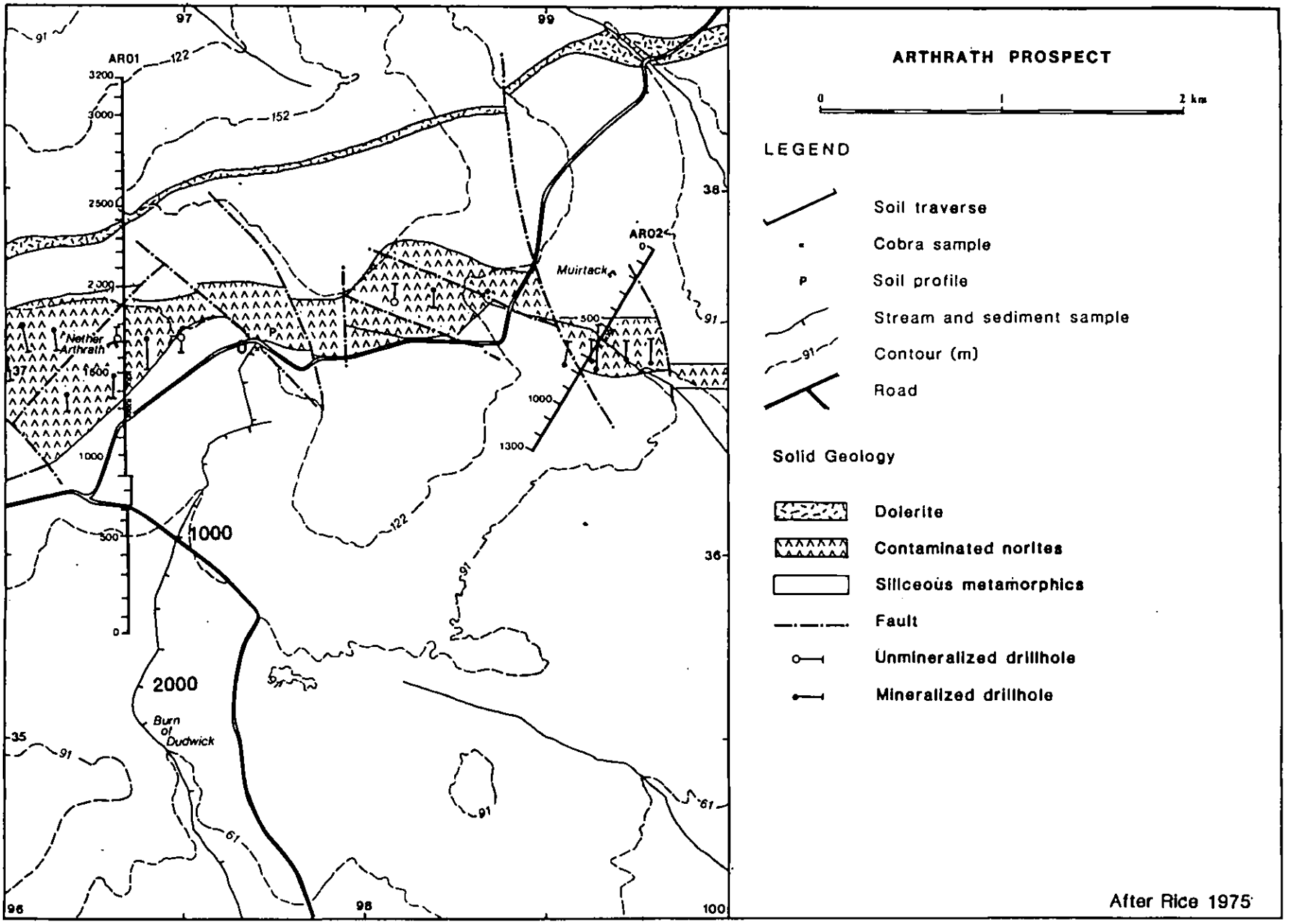


Fig 5.1 Arthrath: solid geology

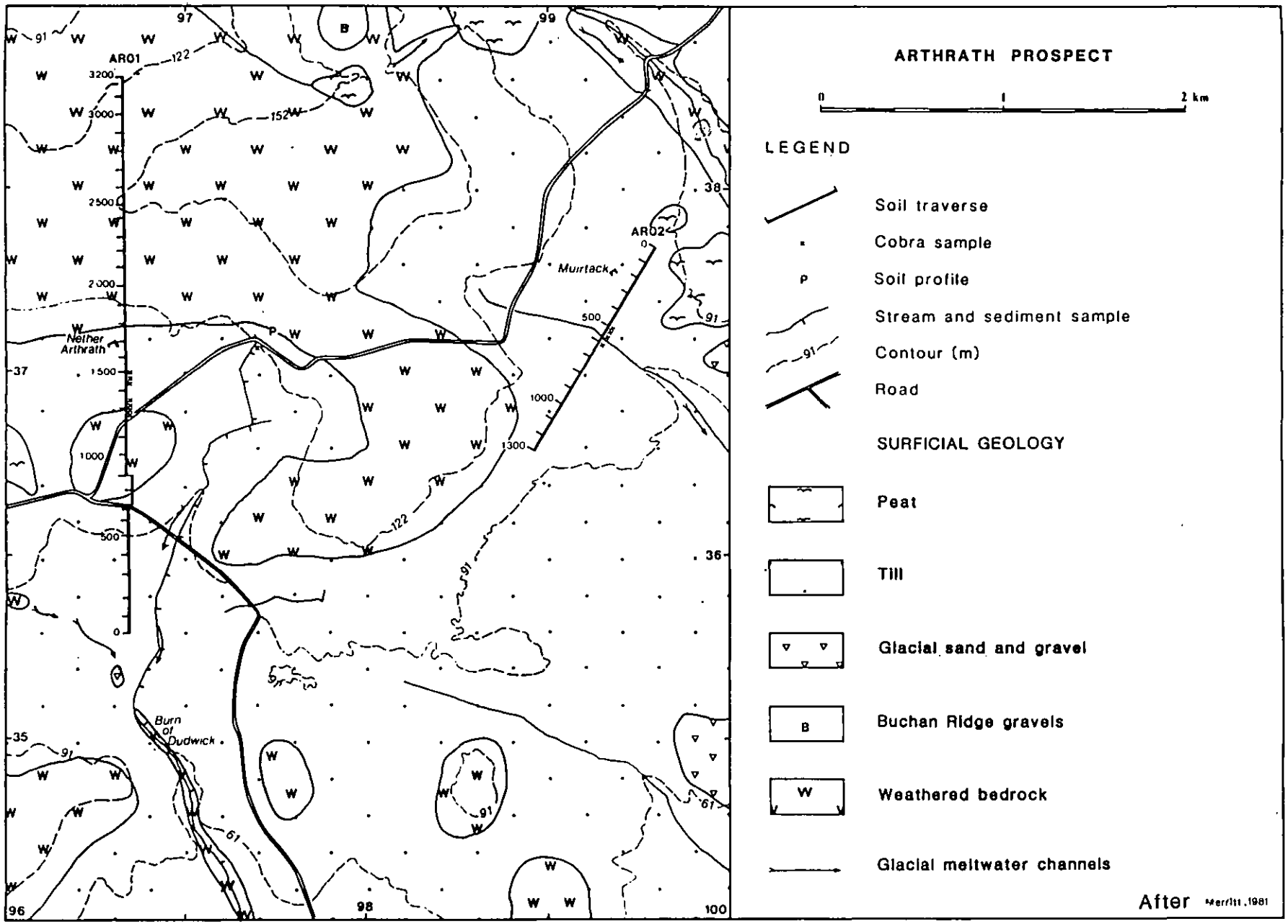


Fig 5.2 Arthrath: surficial geology

Pre-glacial (Tertiary) weathering during a period of warm and humid climate, is thought to be extensive (Basham, 1974). Minor ?Pliocene gravels top some of the hills in the area.

A variety of soils are developed in the area (Glentworth and Muir, 1963). Ill drained gleysols are formed on the tills while weathered bedrock is covered by podzols or brown earths. Localised basin peats occur on higher ground. The soils have been considerably disturbed by grain farming and stock rearing.

c) Regional Geochemistry

Nickel and copper determinations on soil samples, coupled with geophysics, delineated diamond drill targets during the Riofinex exploration programme. Soil geochemistry (Fig. 5.3) outlines the targets in the Nether Arthrath (967373) area but fails to do so at Muirtack (994372), where bedrock copper and nickel grades are higher. The contrast between the two areas suggested the location of the two soil traverses undertaken during the present work.

5.1.2 Programme

Soil samples (approximately 0.3 m depth) were collected across the Nether Arthrath (AR01) and Muirtack (AR02) areas and analyzed for transition metals by atomic absorption spectrophotometry and pathfinders by the co-precipitation method. Shallow sampling was followed up by limited Cobra drill till profiling over the anomalies. The follow up samples were analyzed by both pathfinder attacks and by ICP nebulisation.

A small selection of stream sediments, from the Burn of Dudwick (Fig. 5.1), were analyzed by the co-precipitation method and for general elements.

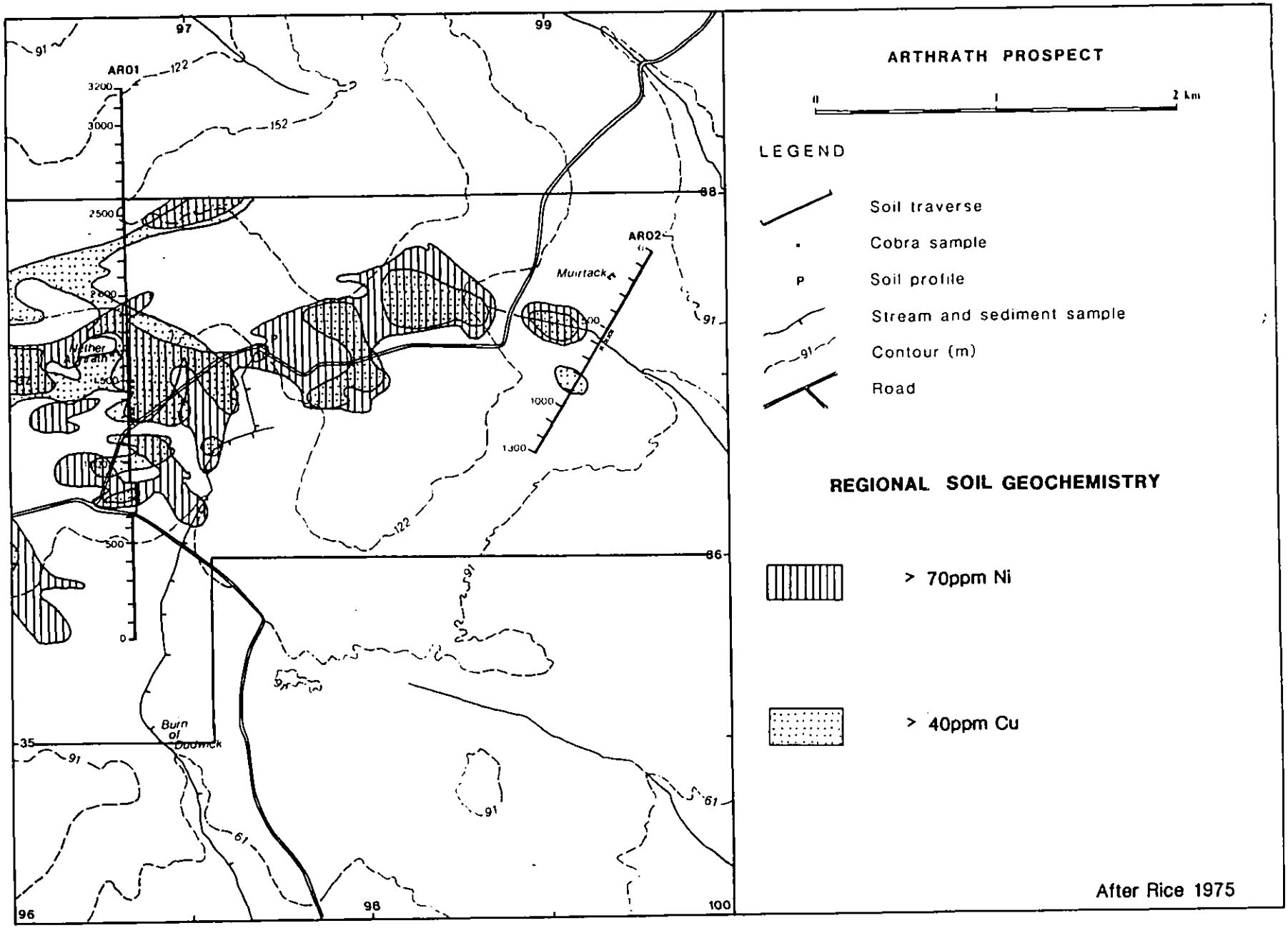


Fig 5.3 Arthrath: regional soil geochemistry

a) Soil Traverse AR01

Nickel and copper show prominent anomalies (Fig. 5.4) over the mineralized area delineated by drilling. Nickel is high (background 150 ppm) over the southern part of the intrusion relative to the siliceous metasediments (background 50 ppm). Over the mineralization nickel reaches 700 ppm while copper has a maximum of 370 ppm relative to a background of 20 ppm on the metasediments and 100 ppm Cu over the intrusives. Copper and nickel are slightly enriched over shallow weathered bedrock from 600 - 700 m, as is copper over the quartz-dolerite dyke at 2,400 m. The other transition metals determined give no anomaly across the mineralization and anomalies, such as that of manganese at 1,000 m can be explained by the occurrence of shallow bedrock beneath the soil.

Arsenic and selenium display high contrast anomalies over the mineralization (Fig. 5.5). Arsenic values read 27 ppm relative to a background of 3 ppm while comparable selenium concentrations are 3.7 ppm relative to 0.4 ppm background. Lesser anomalies occur at other parts of the traverse: for arsenic at 250 m (10 ppm As); and for selenium at 100 m (1.8 ppm) and 1,950 m (1.6 ppm Se). Restrictions on time meant that these anomalies were not followed up. The southern selenium anomaly, however, possibly reflects concentration in organic material around a drainage channel. There is a minor bismuth high over the mineralization (0.3 relative to 0.2 background) but it is not particularly prominent, (Fig. 5.5).

Till profiling detailed part of the area between 1,200 and 1,500 m and includes background and anomalous areas. Both nickel and copper show very high concentrations (2,400 ppm Ni, 3,150 ppm Cu) at depth on the northern part of the traverse. Values decrease upwards and nickel

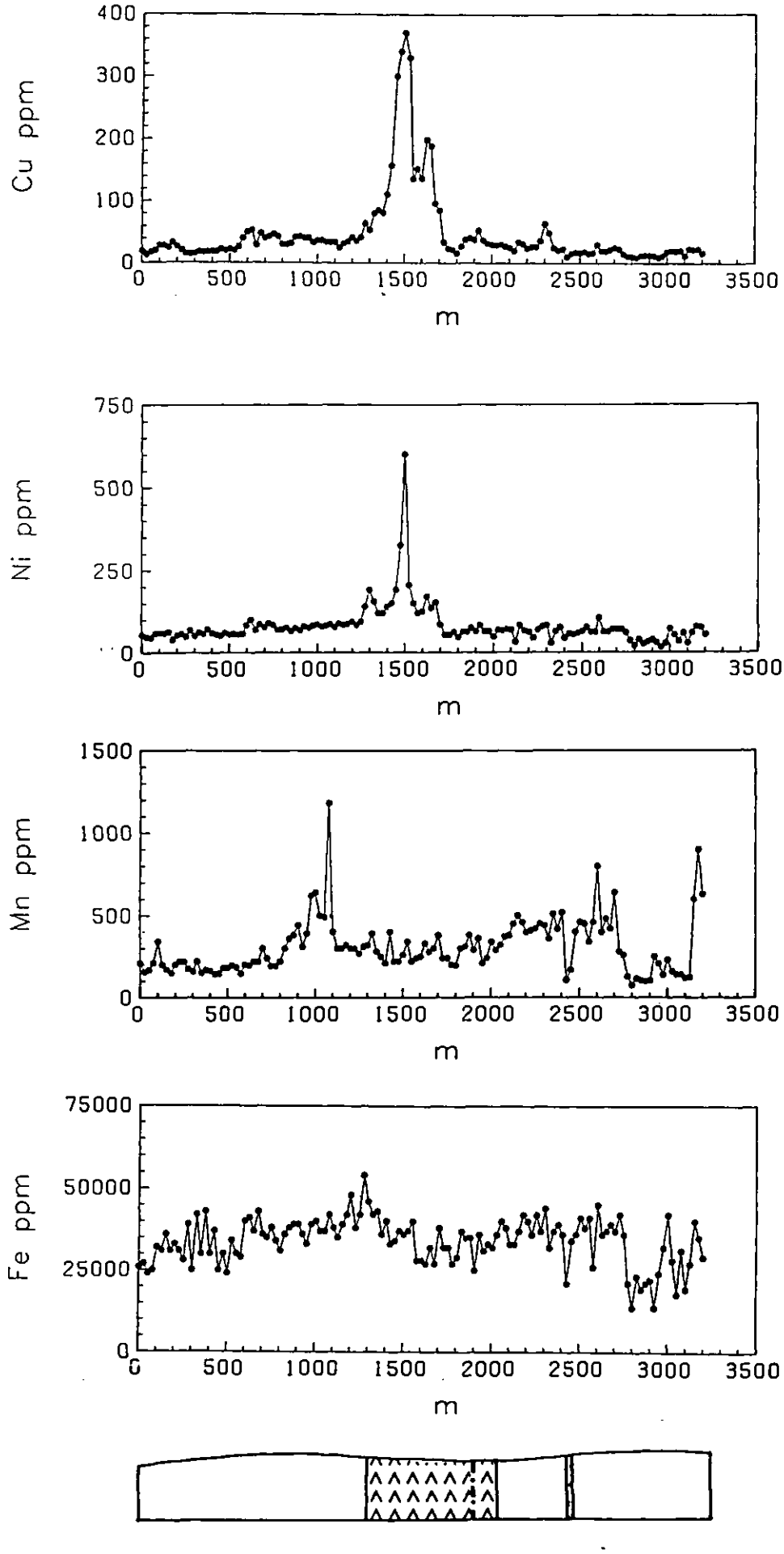


Fig 5.4 Arthrath: soil traverse AR01
Geological symbols as for Fig 5.1

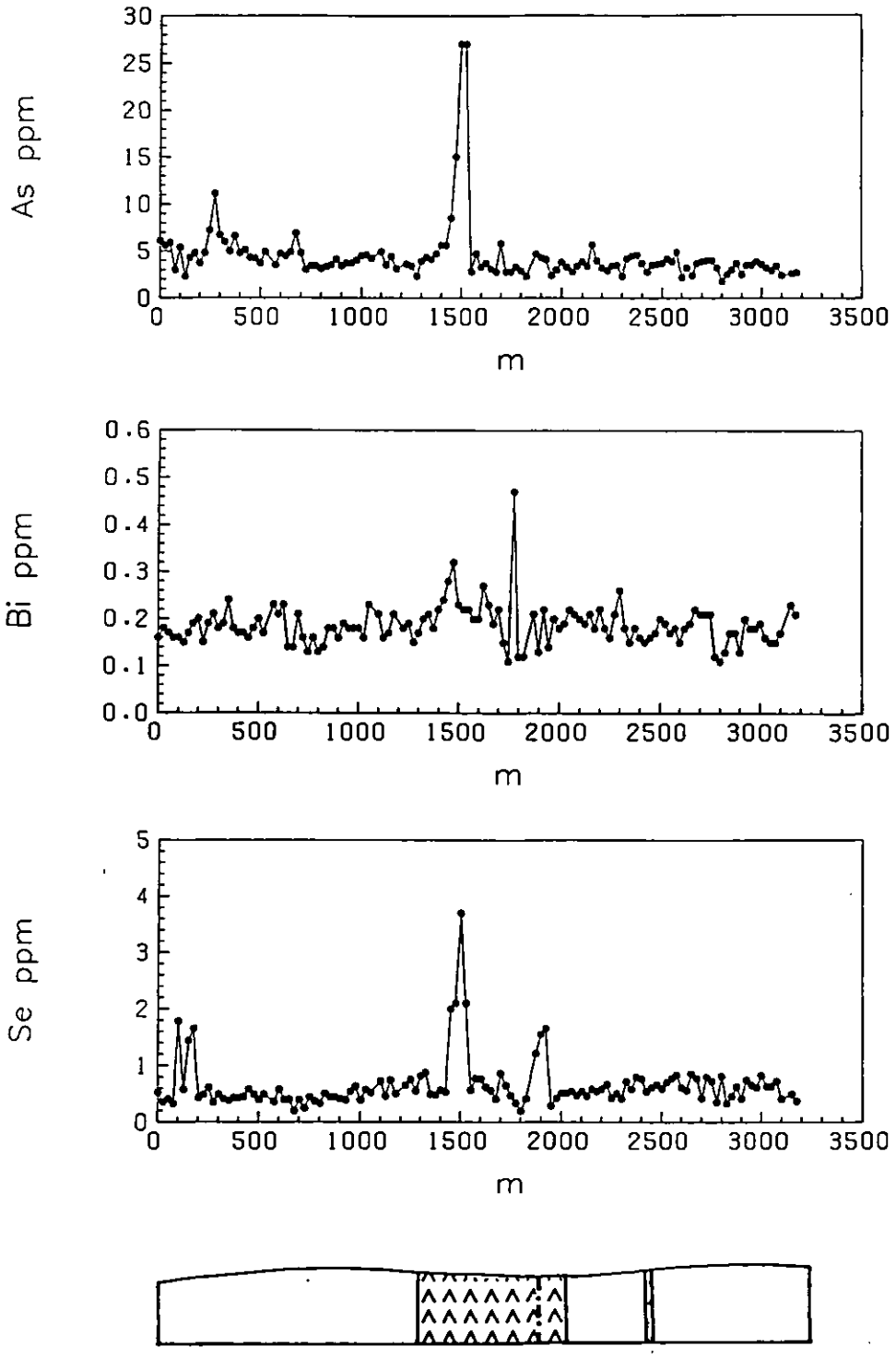


Fig 5.5 Arthrath: soil traverse AR01
Geological symbols as for Fig 5.1

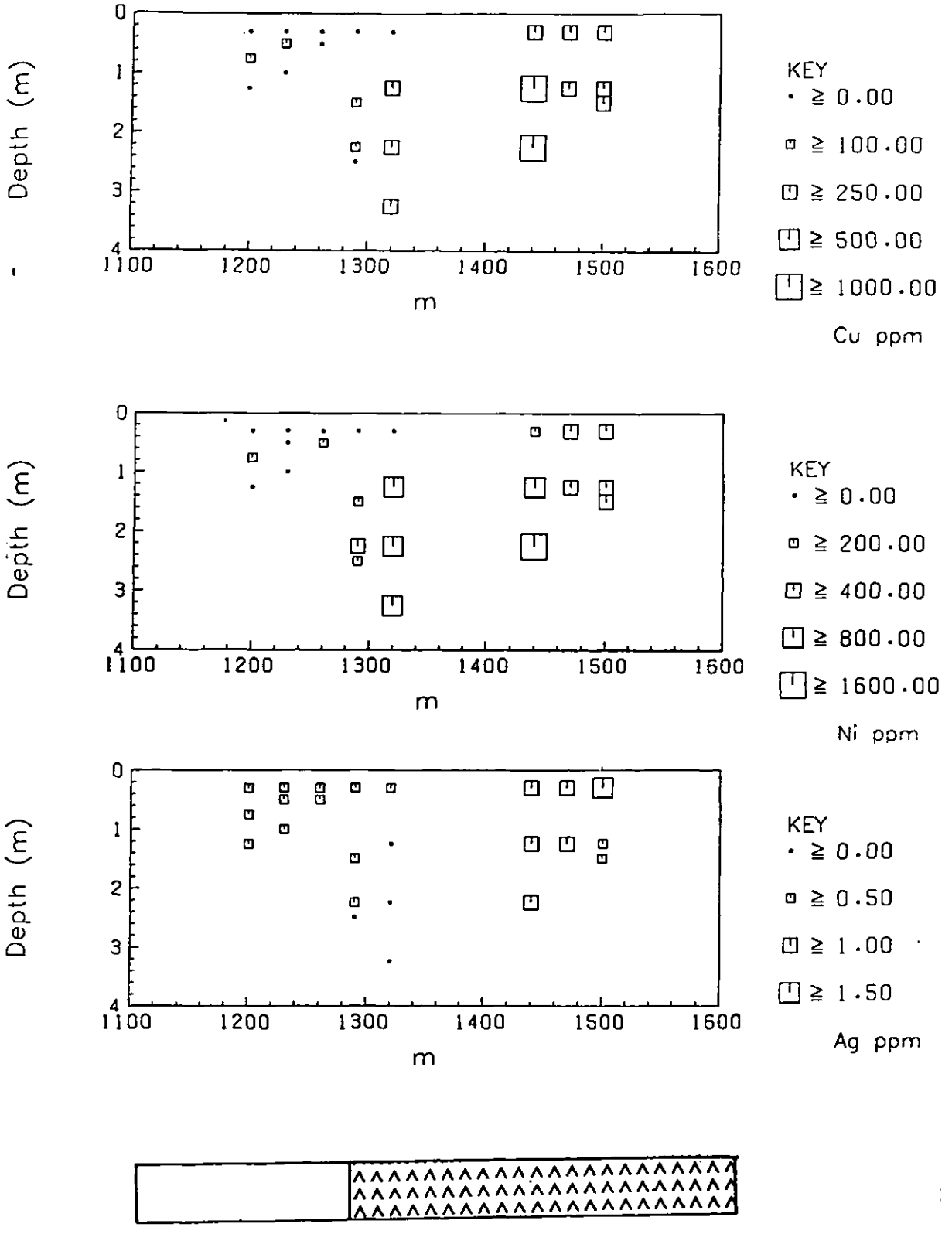


Fig 5.6 Arthrath: till profile AR01
Geological symbols as for Fig 5.1

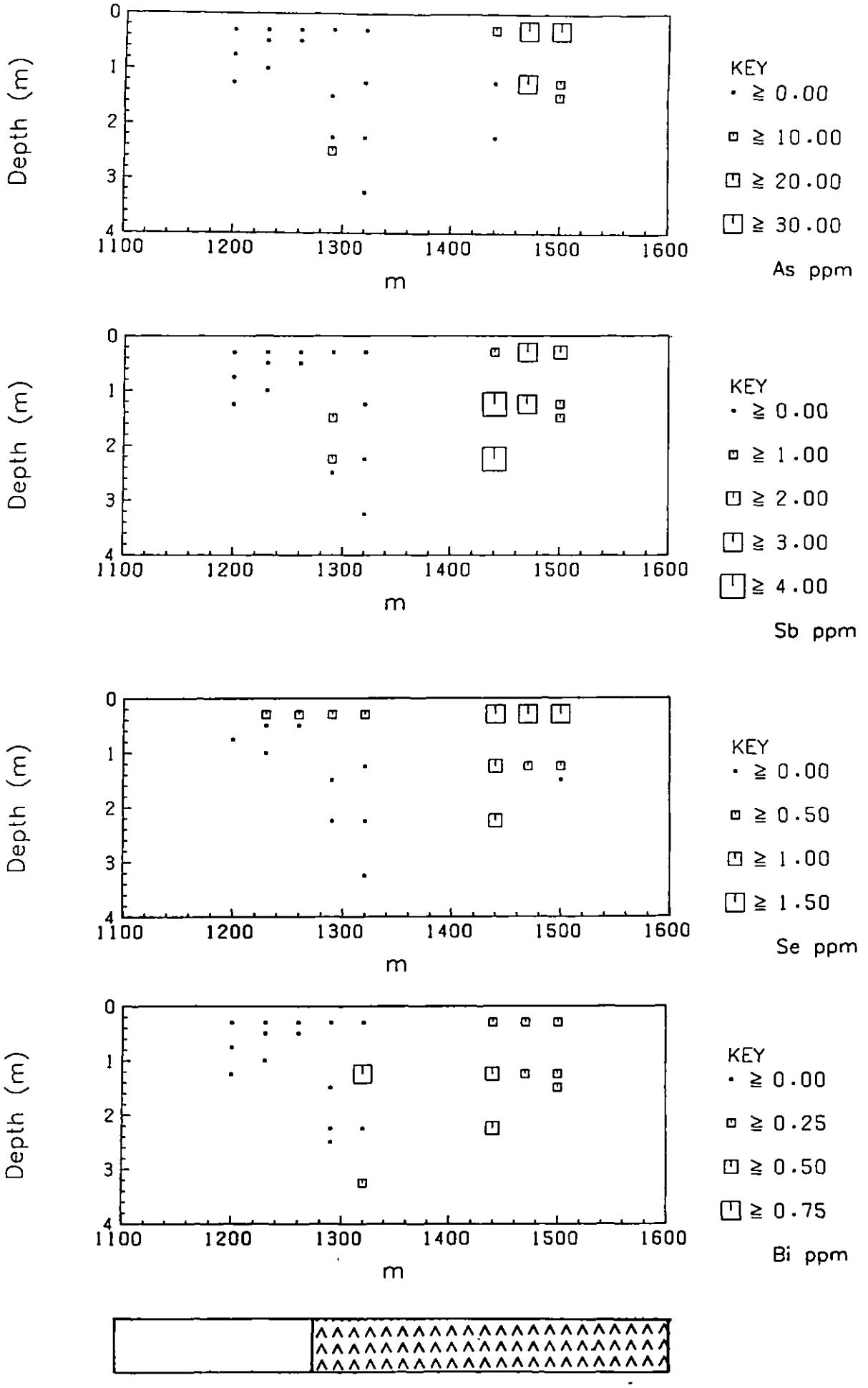


Fig 5.7 Arthrath: till profile AR01
Geological symbols as for Fig 5.1

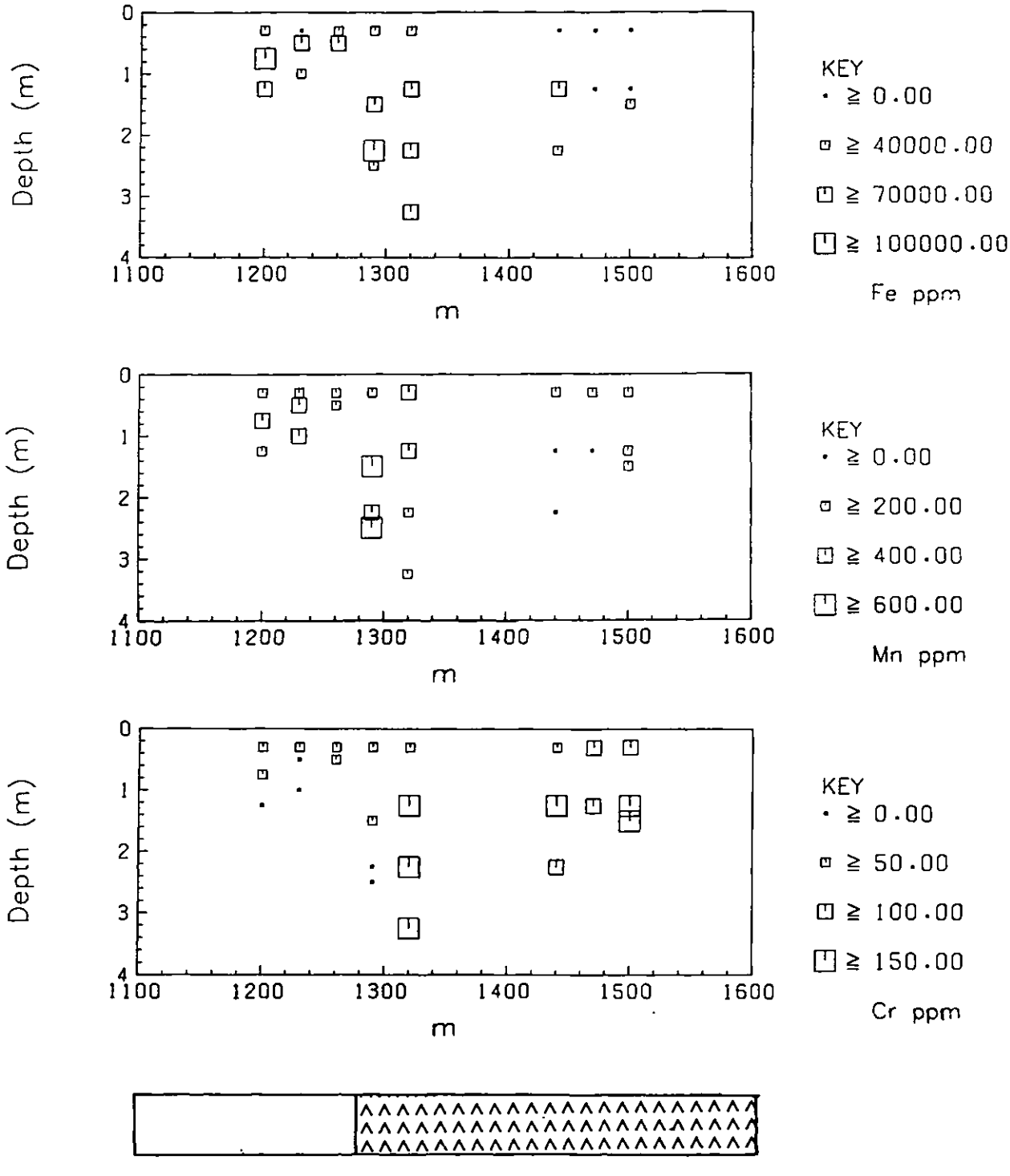


Fig 5.8 Arthrath: till profile AR01
Geological symbols as for Fig 5.1

moves northwards (downslope)

Examination of chromium data (Fig. 5.7) and rock fragments from the Cobra core barrel reveal that the intrusive contact is located at 1,300 m slightly further north than indicated in Fig. 5.1. Thus the nickel high at 1,320 is interpreted as background in the intrusive. Silver is enriched over the mineralization and seems to be enriched downslope and at surface relative to the subcrop of the highest nickel and copper values. In contrast, iron and manganese are enriched at depth over the siliceous metasediments.

Arsenic, antimony and selenium (Fig. 5.8) have very distinct enrichments between 1,420 and 1,500 m but display contrasting dispersion through the drift. Highest antimony values (6.8 ppm) are at depth at 1,440 m, as for nickel and copper, while arsenic highs are at intermediate depth and near surface at 1,470 and 1,500 m. Selenium is enriched absolutely in the surface samples but the selenium in the deep samples is strongly enriched in the northern part particularly in profile 1,440 m. Bismuth is weakly concentrated in the northern part of a traverse.

b) Soil Traverse AR02

The geochemical responses for nickel and copper (Fig. 5.9) are poor, as anticipated from the regional geochemistry. Both elements give lows over the subcrop of the intrusive (500 - 850 m) but within these are single point anomalies (at 575m, 120 ppm Ni, background 40 ppm; and 80 ppm Cu, background 30 ppm Cu). The area from 850 - 1,050 m is slightly enhanced in both elements possibly reflecting weathered bedrock beneath soil. Iron and manganese, in contrast, show depletion from 400 to 800 m.

Arsenic and selenium (Fig. 5.10) also are relatively low from 400 to 750 m but single points over the subcrop of the intrusive (550 m), within the low, reach levels recorded over shallow bedrock. The most intense anomalies are at 1,125 m for arsenic (40 ppm As relative to 15 ppm background) and at 0 m for selenium (1.4 ppm Se, background 0.7). This latter anomaly is immediately explicable as it was the only sample taken in a basin peat, emphasising once again the association of selenium with organic matter.

Cobra drill sampling was used to profile the drift across the central part of the traverse and to decide whether the single point anomalies are a reflection of mineralization at depth. There is a sharp contrast between the thin stony drift encountered on AR01 with that along AR02 which is sandy, and where bedrock was not intersected.

The geochemistry of the profile is also very different from AR01 and there is a general decrease in transition metal concentrations with depth. High values for both nickel and copper (Fig. 5.11) are restricted to profile 570 close to a river, with maximum concentration at 1 m. Iron and manganese (Fig. 5.12) show similar patterns with slightly larger areas of enrichment. Chromium (Fig. 5.11) is strongly concentrated near the surface.

Arsenic and antimony also show decrease with depth. Arsenic is particularly concentrated near the surface while antimony is high at 1 m depth on 570 m. Selenium highs are restricted to deeper samples on profile 570. The bismuth pattern (Fig. 5.12) probably represents variation in background.

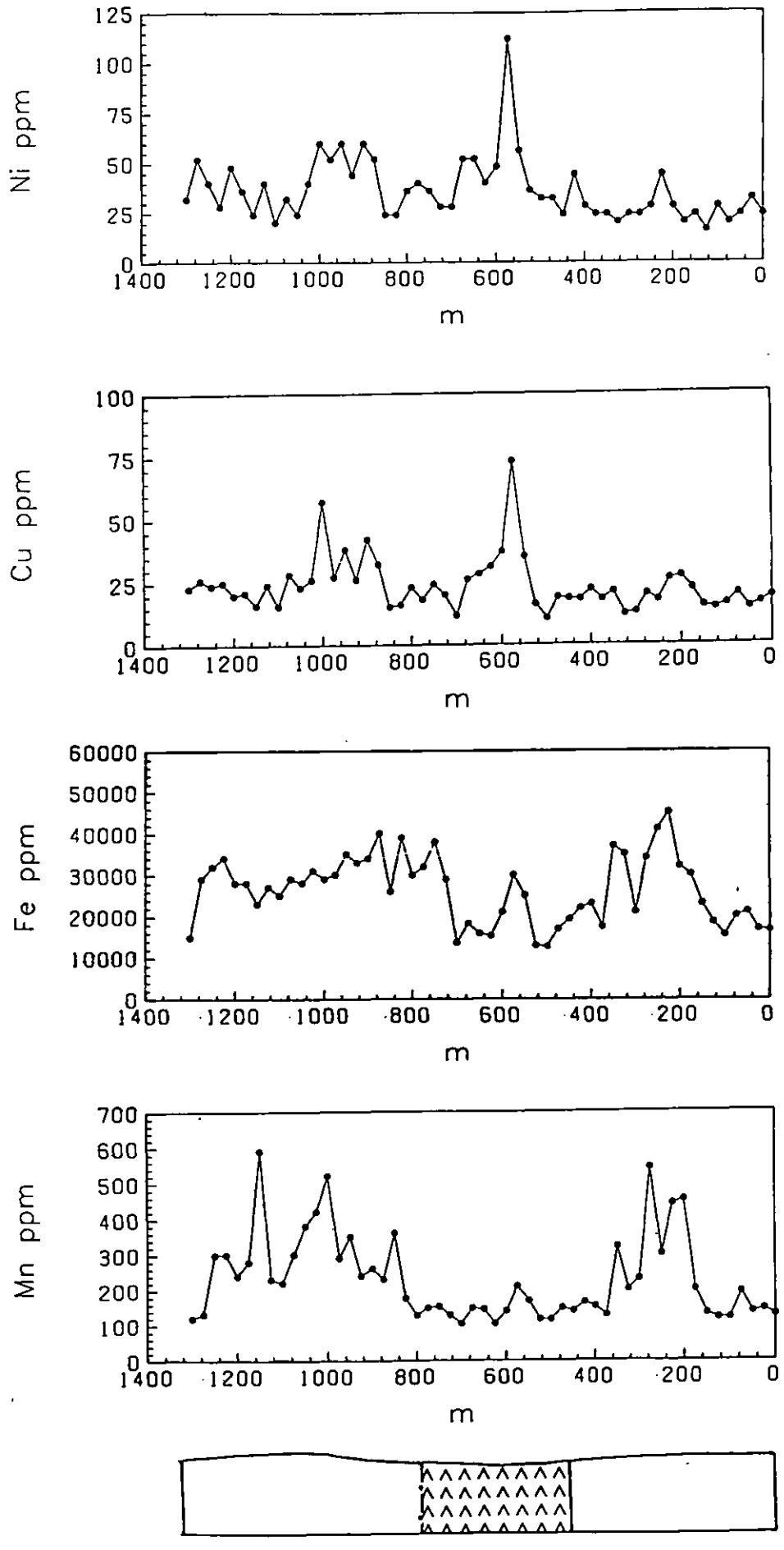


Fig 5.9 Arthrath: soil traverse AR02
Geological symbols as for Fig 5.1

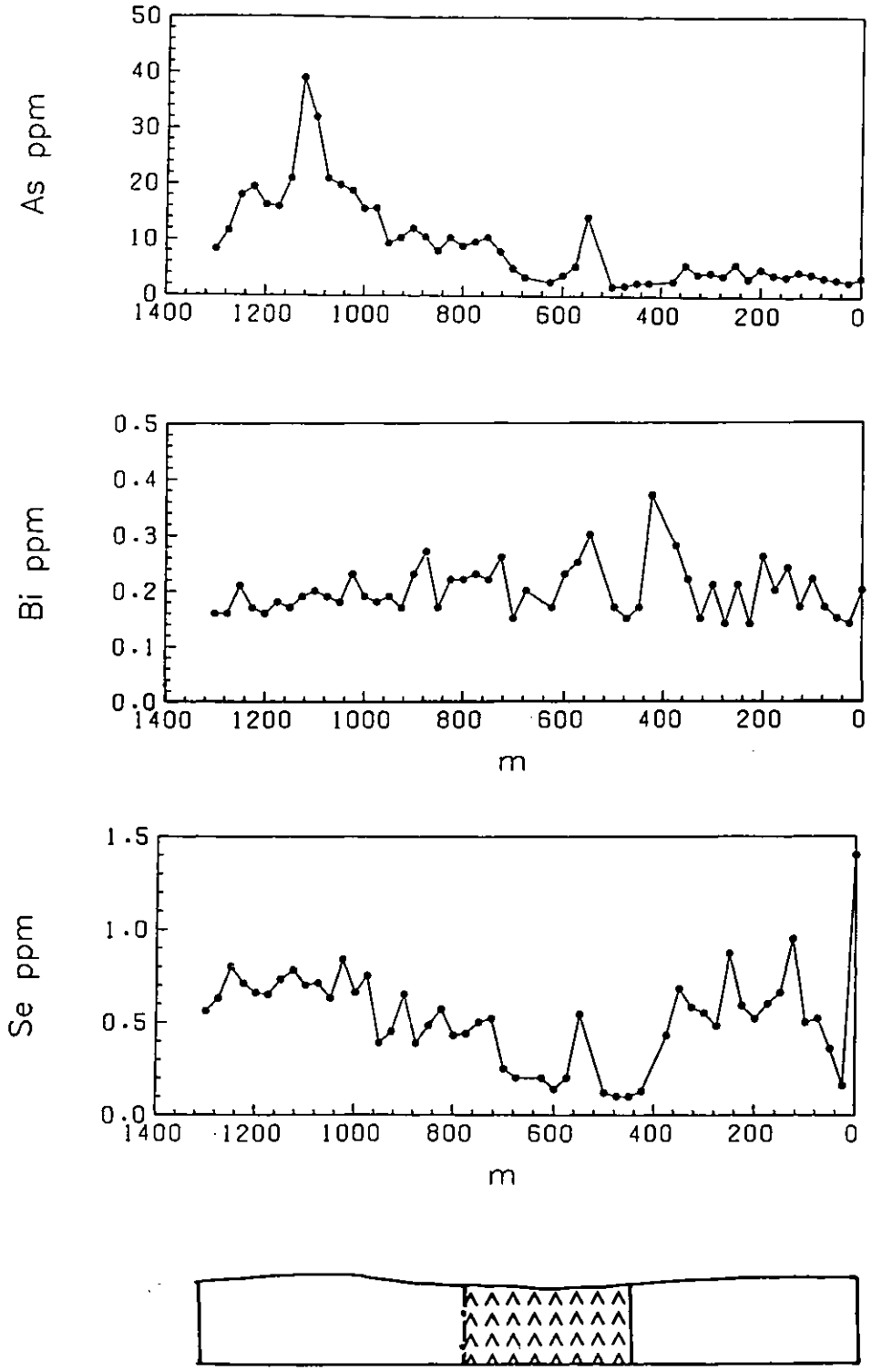


Fig 5.10 Arthrath: soil traverse AR02
Geological symbols as for Fig 5.1

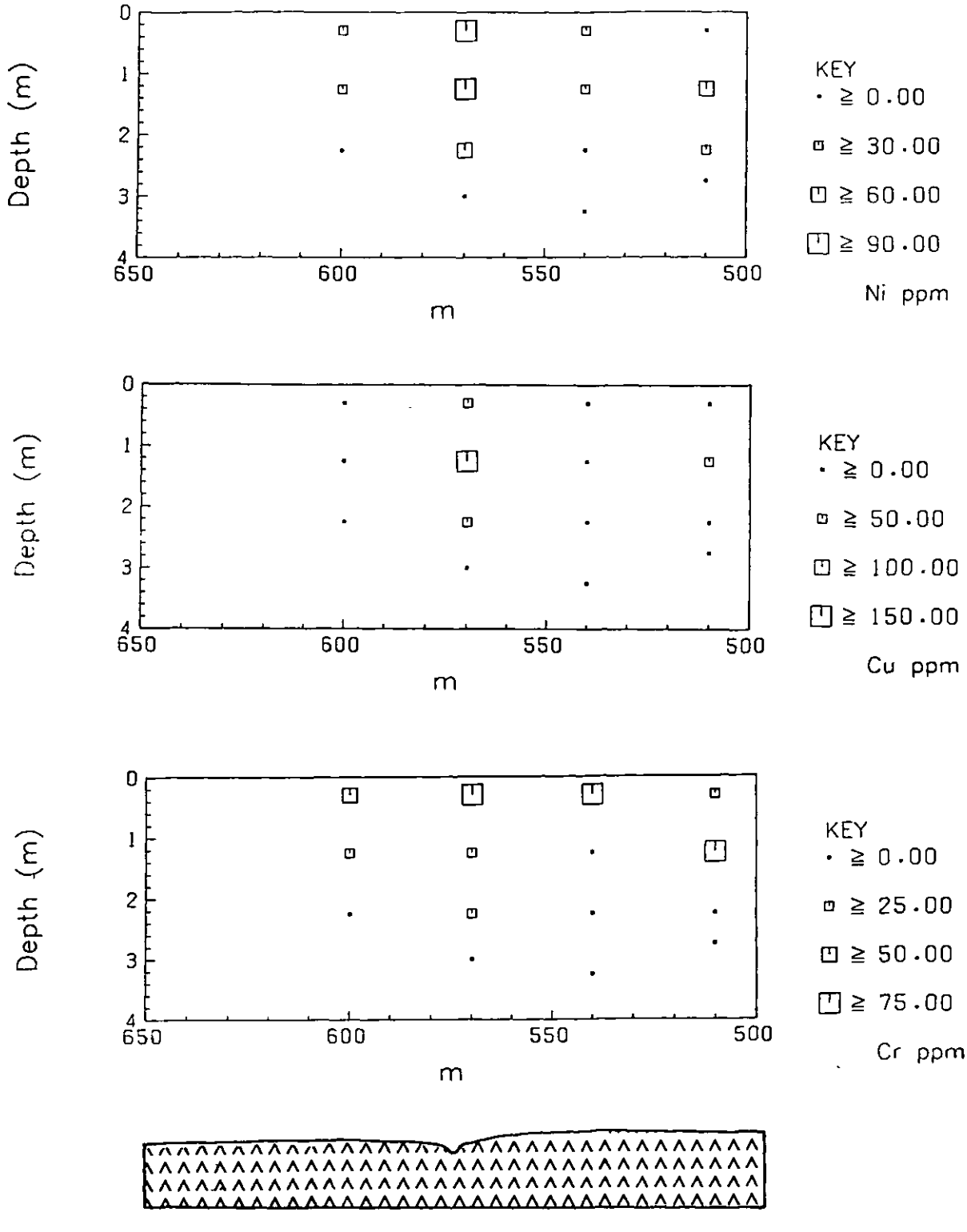


Fig 5.11 Arthrath: till profile AR02
Geological symbols as for Fig 5.1

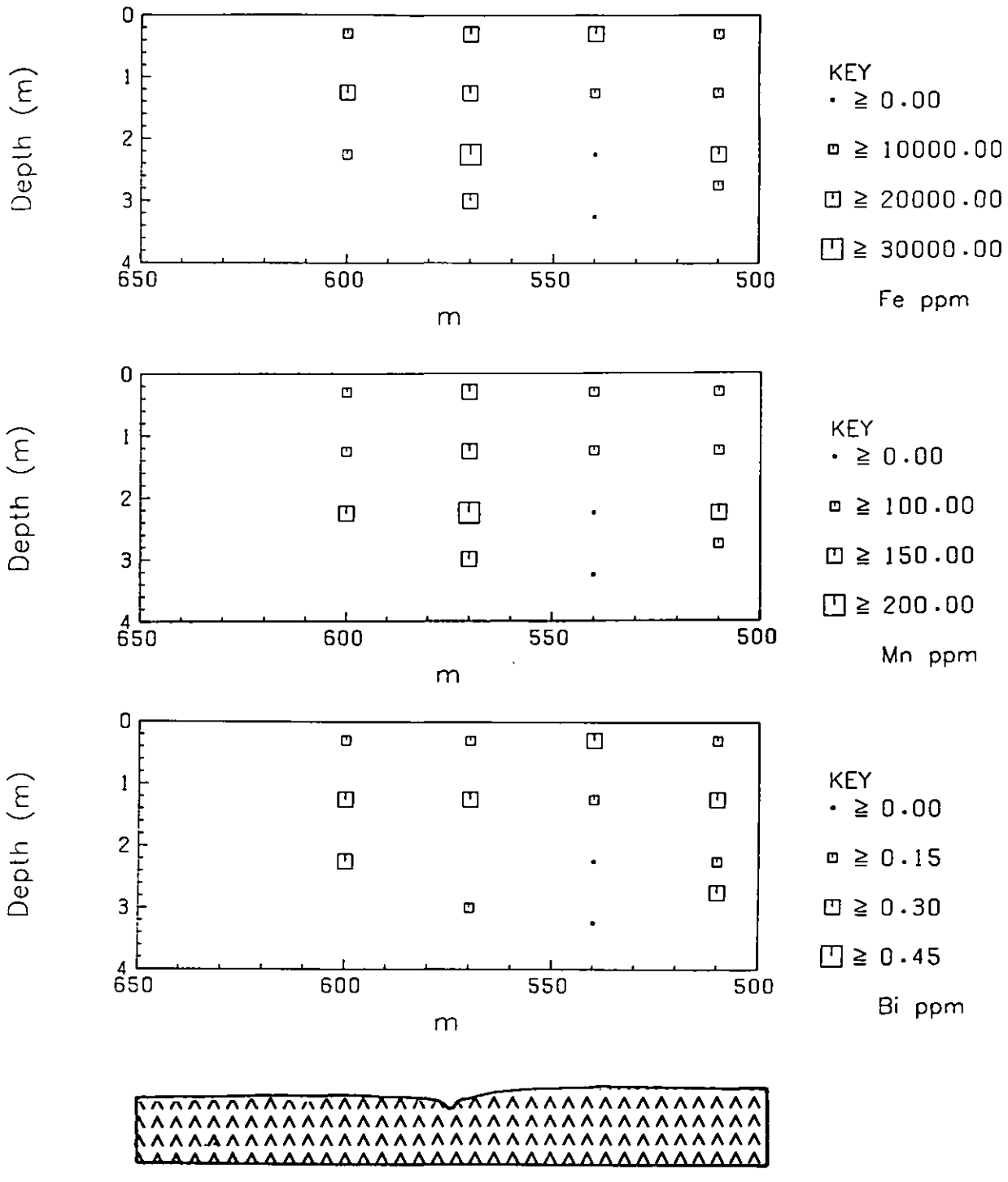


Fig 5.12 Arthrath: till profile AR02
Geological symbols as for Fig 5.1

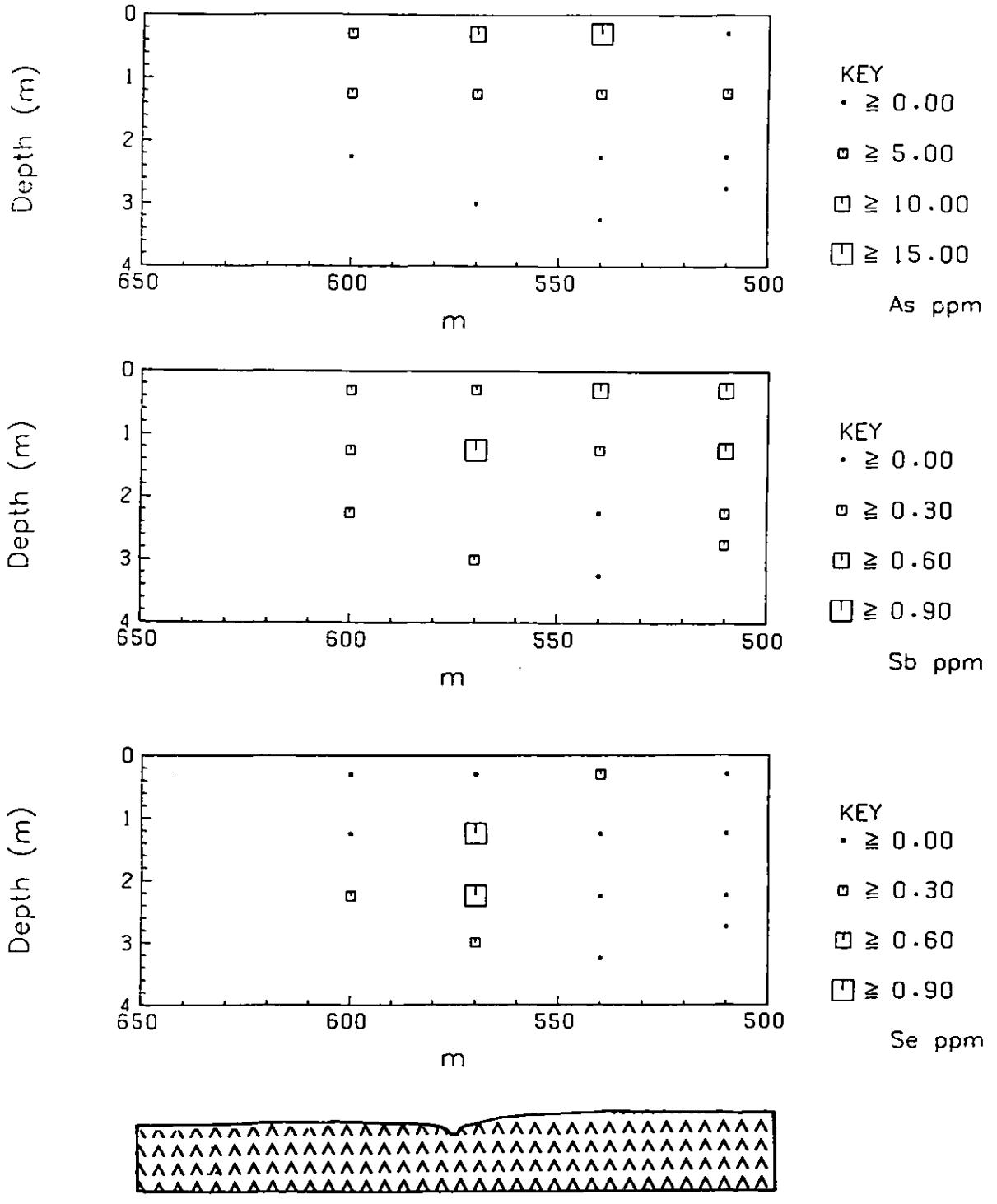


Fig 5.13 Arthrath: till profile AR02
Geological symbols as for Fig 5.1

c) Stream Sediments (AR03)

The sampled drainage does not cross mineralization but the headwaters drain an area of nickel and copper enrichment in soils.

Nickel and copper (Fig. 5.14) reflect the single input of ultramafic material, and decline steadily downstream, as does iron. Manganese, in contrast, shows localised highs downstream.

Arsenic declines very rapidly from the head of the stream while selenium values are high at the top of the stream and at its confluence with a minor sluggish tributary. Bismuth shows similar highs but the background is too near the detection limit to draw conclusions about the element's dispersion.

5.1.3 Discussion

The contrast in geochemistry between the two soil traverses is startling, considering that both are underlain by mineralized intrusives and the bedrock metal grades under AR02 are higher than those under AR01.

Drift type is, in my view, the key to understanding these differences. Observations during Cobra drill sampling, reinforced by those of Merritt (1981 and 1982 pers. comm.), show that the anomalous area of AR01 is underlain by cryoturbated bedrock or till of local derivation. Fluvioglacial material fills a meltwater channel under the centre of AR02 and is partly covered by a thin veneer of till.

An alternative viewpoint, proposed by Rice (1975) is that the pre-glacial weathering is important. He interprets the shattered bedrock at Arthrath as a result of this weathering and its absence at Muirtack as the cause of the lack of geochemical expression.

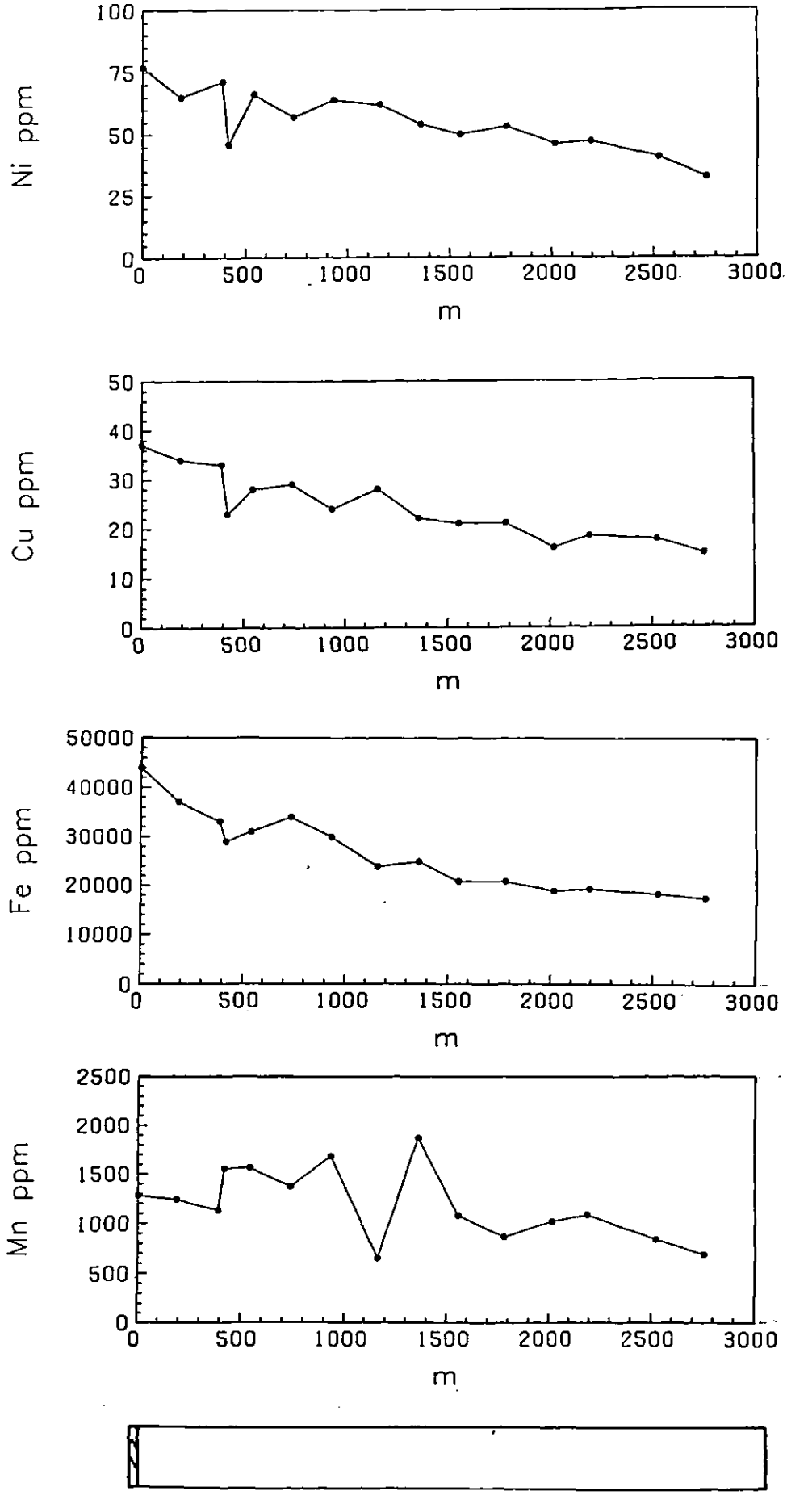


Fig 5.14 Arthrath: stream sediments AR03
Geological symbols as for Fig 5.1

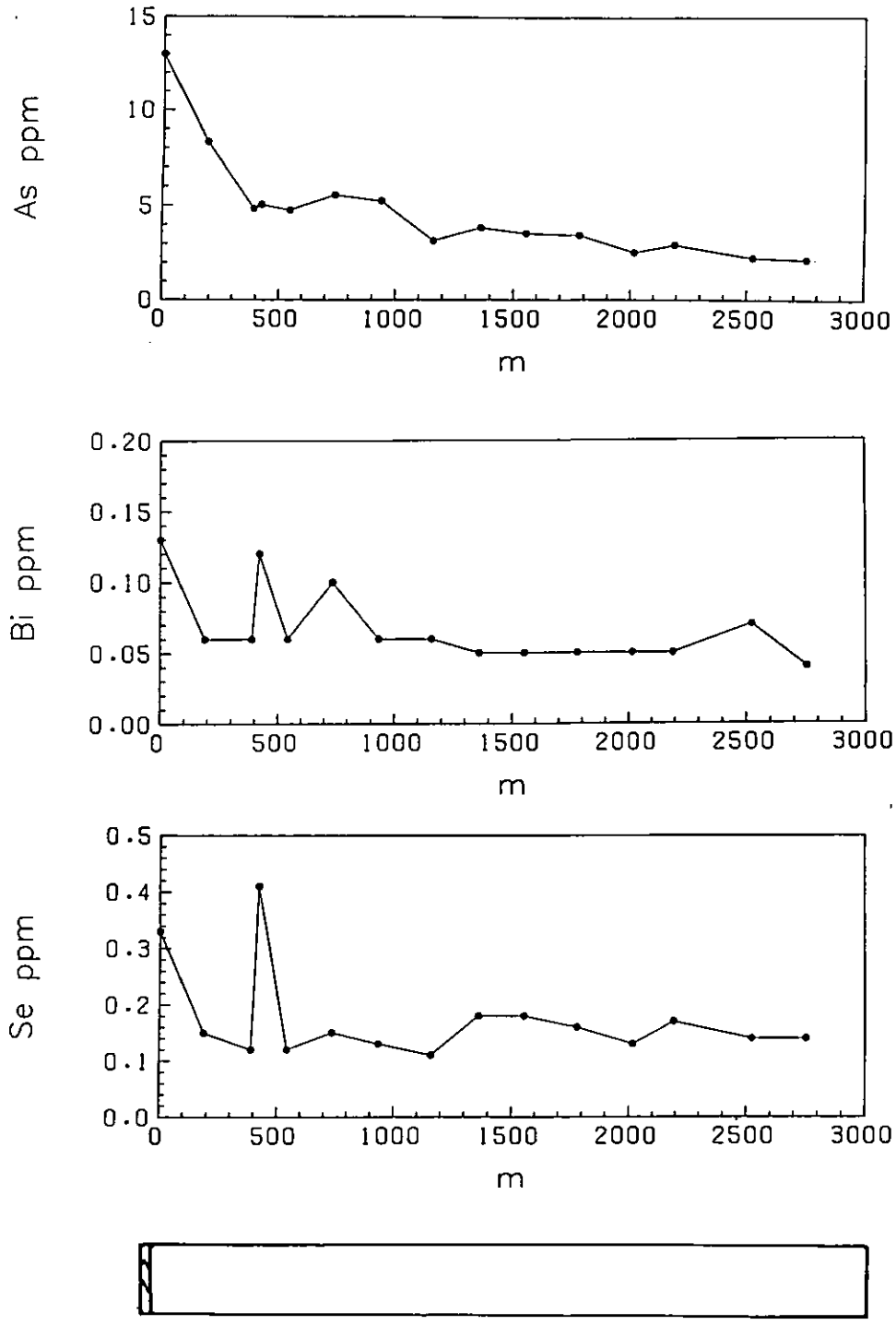


Fig 5.15 Arthrath: stream sediments AR03
Geological symbols as for Fig 5.1

Indurated permafrost horizons, which would dam up-flowing fluids, are also hypothesised for Muirtack.

The traverse AR01 provides a good opportunity to examine the mobility and transport mechanisms of the pathfinders. Gossanous fragments, which represent the weathered mineralization, were collected at the surface and a series of bulk soil samples were analyzed (by M. Hale) for their elemental pore water content. The pore waters give strong nickel and sulphur anomalies with lesser arsenic and copper highs (Table 5.1). In contrast the gossanous fragments contained relatively high concentrations of copper and antimony with intermediate selenium (Table 5.2). Quantification between the two processes is difficult but it seems likely that nickel and arsenic are transported mainly in solution whereas antimony and copper are clastically dispersed. This agrees with the location of the anomalies in the till profile, with maximum antimony and copper anomalies at depth. The selenium anomalies are probably derived from clastically dispersed material, but the evidence is less satisfactory.

The origin of the shallow anomalies on AR02 is equivocal but their decrease with depth seems to represent anomalous material introduced by the river flowing immediately to the south of sample location 570 m. The mechanism of transport is not obvious but the element association suggests mainly clastic transport.

No conclusions on the usefulness of stream sediments can be derived due to the paucity of drainage. The results however emphasise the relatively short dispersion trains of arsenic and selenium due to scavenging.

Pathfinder geochemistry can be a valuable additional tool (to nickel and copper geochemistry) where drift permits secondary dispersion. Selenium, arsenic and probably antimony define well the sub-outcrop of the

Table 5.1 Elemental Content of Pore Waters in ppm (Hale and Wheatley pers. comm., 1982)

	Ni	Cu	S	Na	K	Mg	As	Sb	Bi	Se
1200	<0.03	<0.01	2.4	20	3	12.7	-	-	-	-
1300	<0.03	0.01	6.5	21	80	6.3	0.0006	0.0006	<0.0004	<0.0002
1400	<0.03	0.01	6.1	14	8.5	2.6	-	-	-	-
1500	0.41	0.03	12.5	26	6.7	12.5	0.0038	<0.0002	<0.0004	<0.0002
1600	0.21	0.03	11.4	23	6.1	16.5	0.0007	<0.0002	<0.0004	<0.0002
1700	<0.03	0.01	9.2	11.5	3.0	1.9	0.0013	0.0005	<0.0004	<0.0002
Detection Limit	0.03	0.01	0.01	0.01	0.01	0.01	0.0002	0.0002	0.0004	0.0002

- not analysed

Method Pore waters displaced by centrifuging with Arklone

Ni, Cu, S, Na, K, Mg by ICP nebulisation

As, Sb, Bi, Se by hydride generation ICP

Table 5.2 Elemental content of gossanous fragments 1500m ARØ1

Na	K	Mg	Ca	Ba
8Ø.	3Ø.	86ØØ.Ø	8ØØ.	45Ø.
Al	**Cr**	**Mn**	**Fe**	**Co**
3ØØØØ.Ø	14Ø.	37Ø.	9ØØØØ.Ø	7Ø.
Ni	**Cu**	**Ag**	**Zn**	**Pb**
34Ø.	2ØØØ.ØØ	14.	13Ø.	36.
As	**Sb**	**Bi**	**Se**	
.6Ø	15.	.Ø1	.43	

mineralization. The till profiles suggest that antimony is best used at depth with arsenic more useful in soil samples. Selenium gives good discrimination but environmental scavenging by organic matter is a major constraint on its use.

5.2 Kilmelford, Strathclyde, Scotland

Porphyry copper deposits are the source of much of the world's supplies of this metal. Pathfinder geochemistry has a subsidary role to play in their exploration, notably aiding in the discrimination of leached cappings overlying deposits and of finding occurrences under overburden.

5.2.1 Geology

The Kilmelford deposit is one of a number of sub-economic occurrences in the British Caledonides. It has resources of only a few tens of millions of tons better than 0.05% Cu.

Oban is situated about ·25 km from the mineralization, which crops out in a rugged area on the west coast of Scotland.

a) Solid Geology (Ellis et al, 1977; Rickard, 1979)

Mineralization is generally confined to dacitic porphyrys (porphyrites) of Caledonian age (approximately 400 Ma), and which are probably sub-volcanic in character. Later alteration obscures most of the primary features of the porphyrites but they are probably emplaced as vertical sheets. The porphyrites form a relatively small proportion of the Caledonian igneous rocks (Fig. 5.16), which are

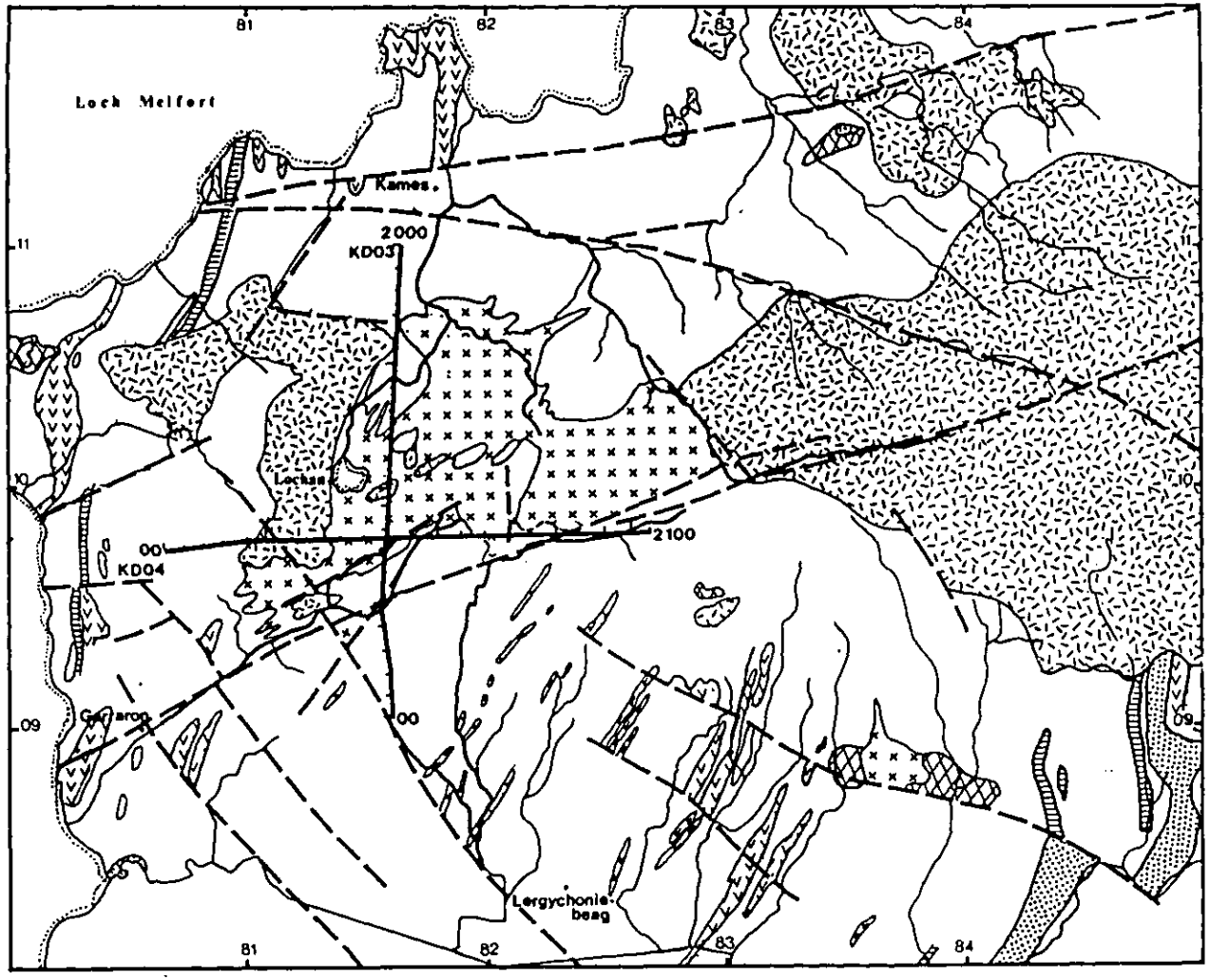


Fig 5.16 Kilmelford: solid geology

predominantly granodioritic in composition. These granodiorite plutons are earlier than, but probably genetically related to, the porphyrites as are the extensive Lorne lavas, which crop out to the north.

The sediments, which have been extensively hornfelsed near the intrusives, are part of the ? Cambrian Middle Argyll Group. They are believed to be of shallow marine origin and are dominantly fine grained siliceous clastics (CraignishPhyllites) with minor coarser clastics (Crinan Grits) and limestones. Skarns form locally near the intrusives.

Faults and lineaments are prominent features in the area. Their dominant orientations are ENE and NW. Relations between the faults and the intrusives are unclear but faults form the southern boundary of the porphyry. Brecciation along the faults is common but distinct from intrusive breccias. The present topography and drainage is greatly influenced by the faulting with, for example, the Garraron River (81000950) flowing along a fault trace for much of its length.

Tertiary dolerite dykes intrude much of the area.

Copper-molybdenum mineralization is generally confined by the porphyry boundaries although disseminations extend into the surrounding hornfels. There is a broad mineralogical zoning but the classical porphyry alteration is absent (Ellis et al, 1977). Two zones are recognized: an early sericitic phase with silicification and pyrite development; and a later kaolinitic zone with chalcopyrite, molybdenite and pyrite. Still later kaolinitic alteration is associated with pyrite and molybdenite. Arsenopyrite accompanies the early phase pyrite but the paragenesses of the minor galena and sphalerite are unclear.

Base metal veins with lead/copper/zinc occur in the hornfels (Ellis et al, 1977) and diorite (Rickard, 1979).

Their controls and significance are ill-understood.

b) Surficial Geology

The area is underlain by relatively thin (generally 0.5 - 1.0 m) till, which is mainly of very local origin except for a limited development of lacustrine clay at 817105

Overlying the till is peat of variable thickness, usually 0.5 - 1.0 m, but reaching 5 m in topographic depressions, (Fig. 5.17).

c) Rock Geochemistry

The primary distribution of major and trace elements is well understood as a result of comprehensive rock sampling exercises by both the I.G.S. (Ellis et al, 1977) and over a larger area by Rickard (1979).

High copper and molybdenum whole rock values are mainly confined to the porphyry although there are very occasional high values (without alteration) in the granodiorite. Anomalous copper values (Fig. 5.18) are concentrated at both the northern and southern margins of the porphyry. Limited arsenic data suggest (Ellis et al, 1977) that the element may form a halo around the main copper anomalies. Microprobe determinations demonstrate that chalcopyrite contains up to 400 ppm Se and 0.5% As (Rickard, 1979).

There is little lead or zinc enrichment in the porphyry and high values are restricted to veins or skarns. The veins have enrichment of up to 40 ppm Sb (Rickard, 1979).

5.2.2 Programme

Two perpendicular soil traverses (KD03 and KD04)

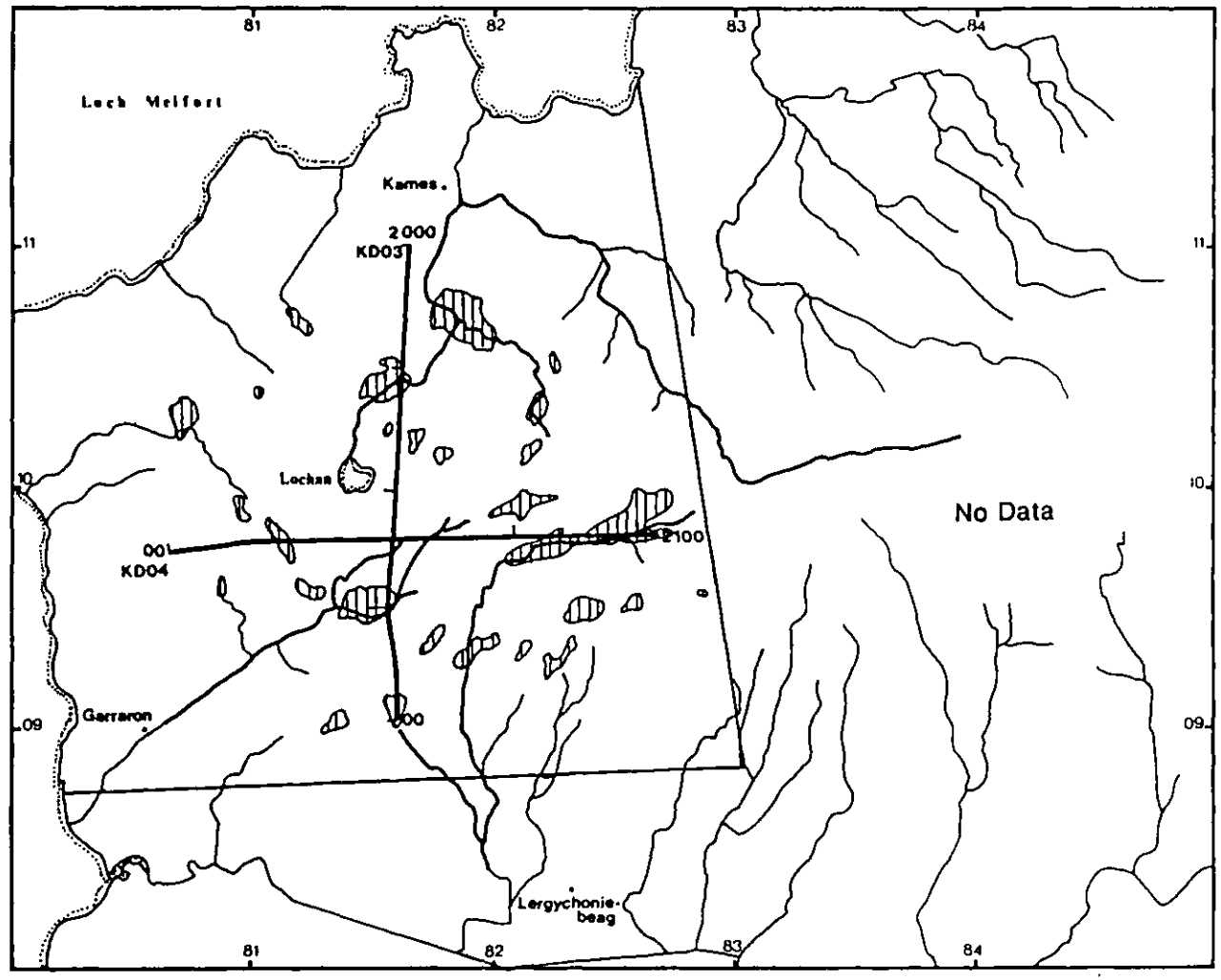


Fig 5.17 Kilmelford: surficial geology

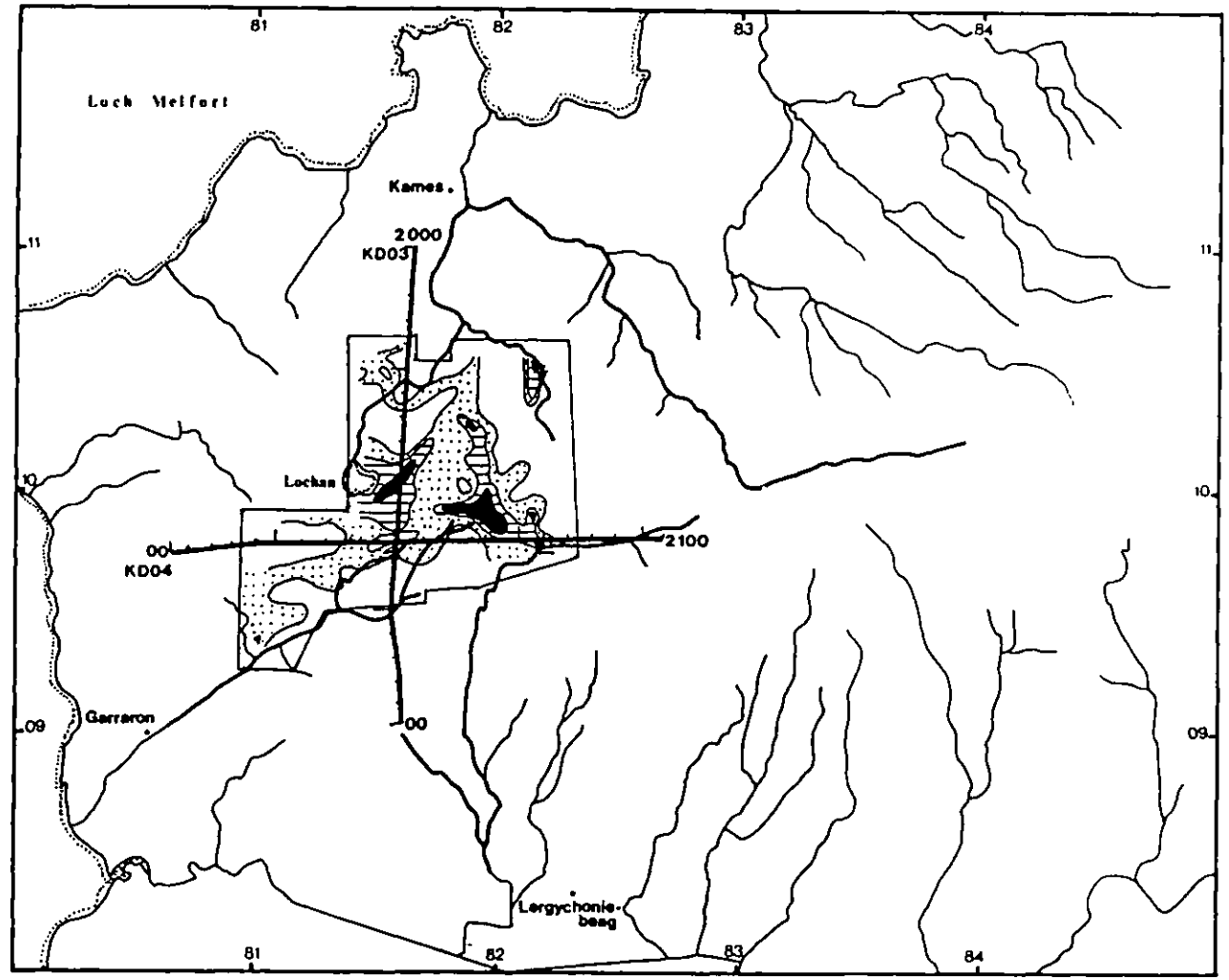


Fig 5.18 Kilmelford: copper rock geochemistry

were designed to cross the mineralized porphyry (Fig. 5.19). Both till and peat were collected although it was not always possible to collect both at each sample site.

Stream sediment samples were taken from three drainages, each of which drain the porphyry to some degree. They were known to be anomalous from I.G.S. data (Ellis et al, 1977).

The surficial sampling was complemented by a limited rock sampling programme (undertaken by F.J. Tavora).

a) Rock Geochemistry (KD02)

The sampling is largely limited to the porphyry, and copper concentrations are evident within it although there are highs in the granodiorite (814108). Copper correlates strongly with molybdenum and to a lesser degree with selenium and antimony. Molybdenum (and selenium) are also enriched in the pyrite rich breccias which crop out in the south west of the sampled area (808094). Antimony is slightly enriched within the porphyry while arsenic values are erratic. Concentrations of bismuth are particularly high on the southern side of the porphyry but within the hornfels (Figs. 5.20 - 5.22).

Lead is not enriched over the porphyry but there is some indication of a zinc halo around it. Little correlation exists between the indicator elements and those associated with alteration, e.g. potassium, rubidium.

b) Soil Traverses (KD03 and KD04)

Copper anomalies are prominent in both soil traverses (Figs. 5.24, 5.27) reaching a maximum of 800 ppm relative to background of 50 ppm Cu. These largely agree with the

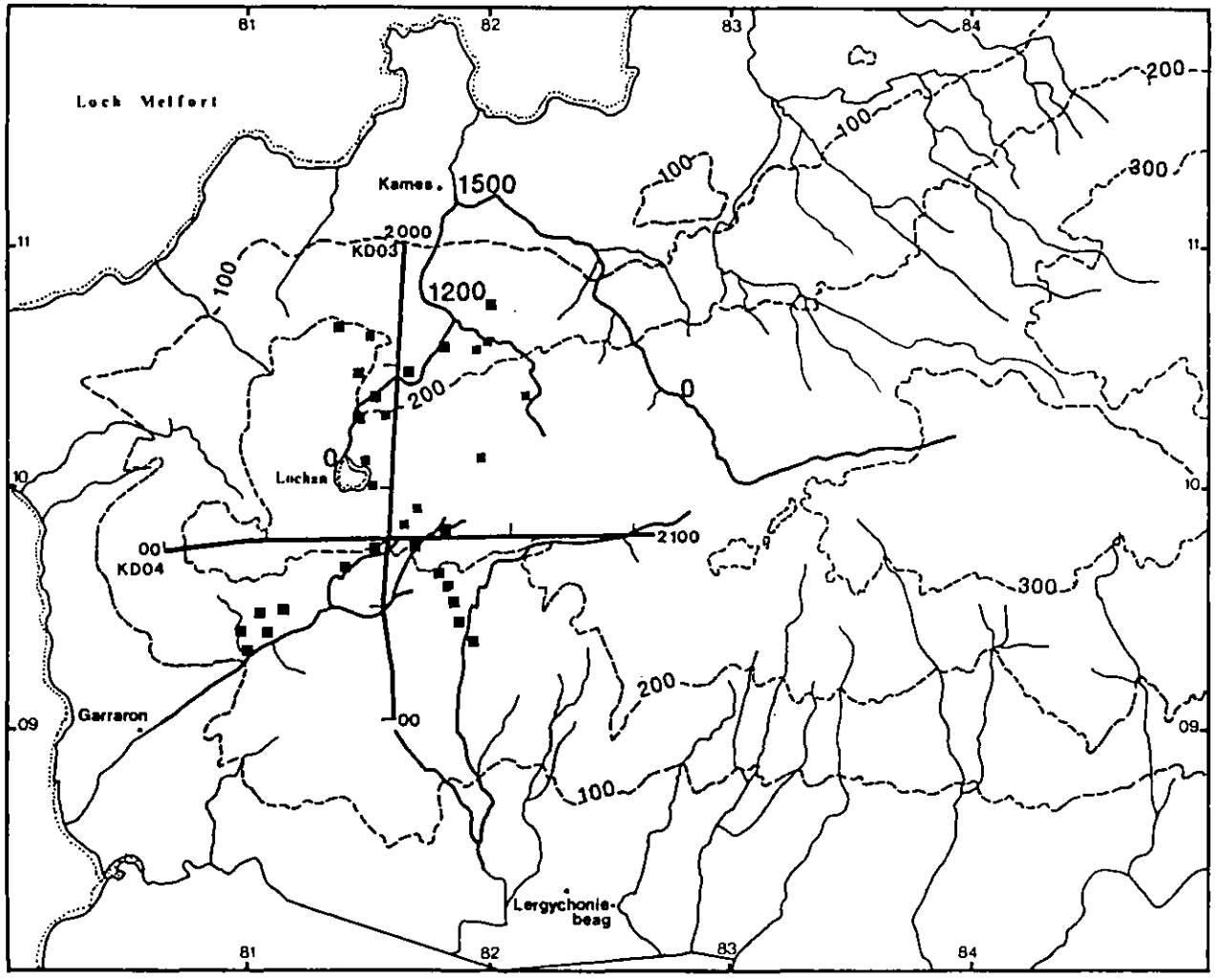


Fig 5.19 Kilmelford: sampling plan

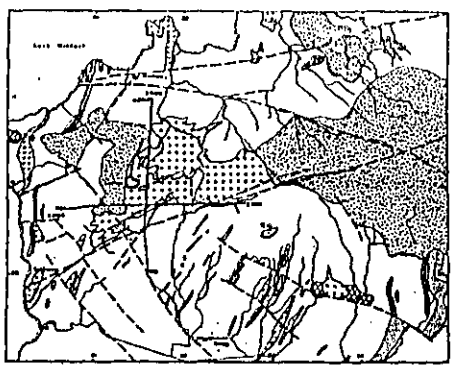


Fig 3.16 Kilmelford: solid geology

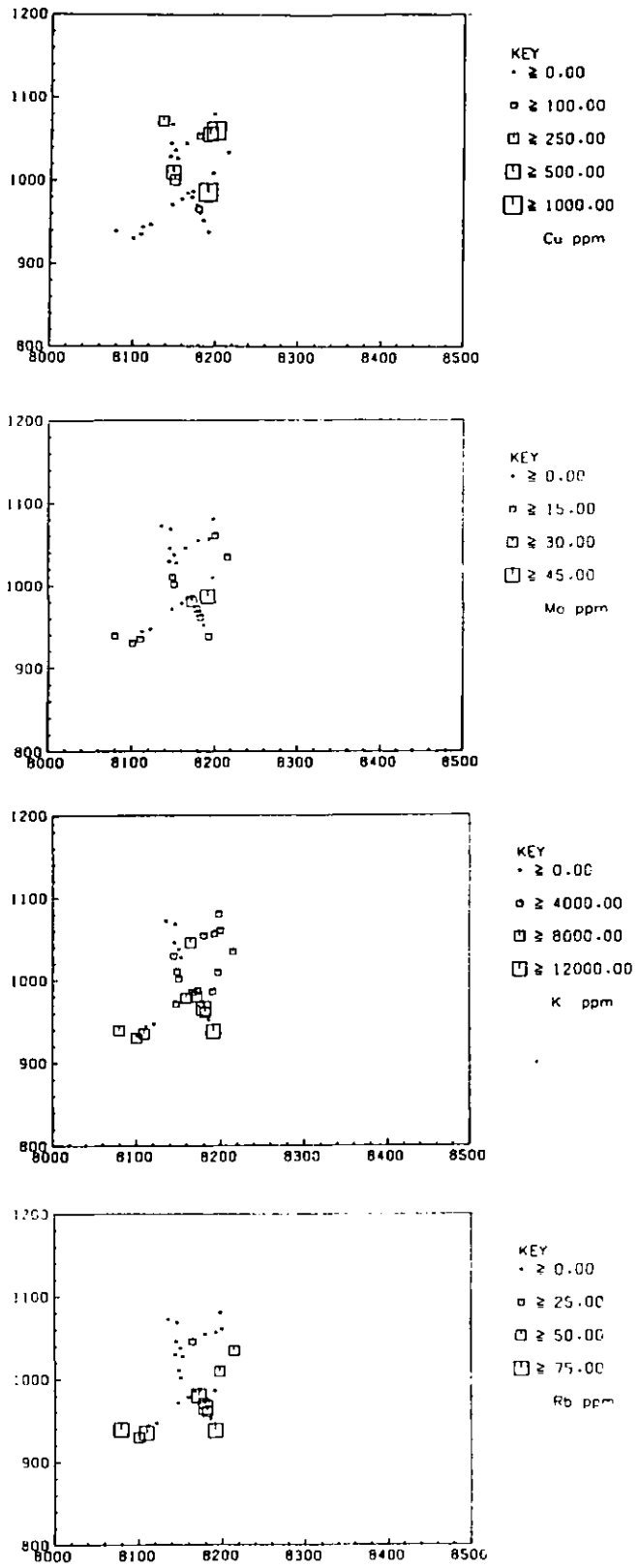


Fig 5.20 Kilmelford: lithogeochemistry KD02
Overlay of geology on opposite page

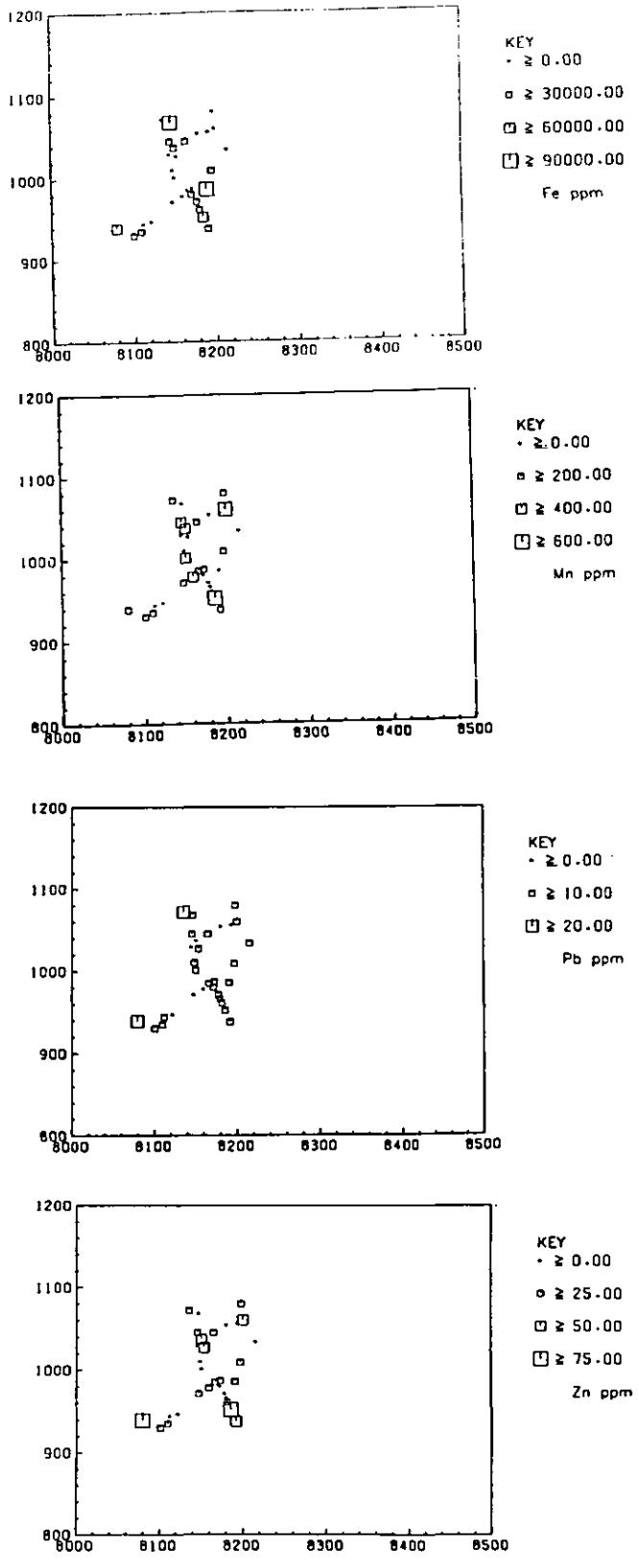


Fig 5.21 Kilmelford: lithogeochemistry KD02

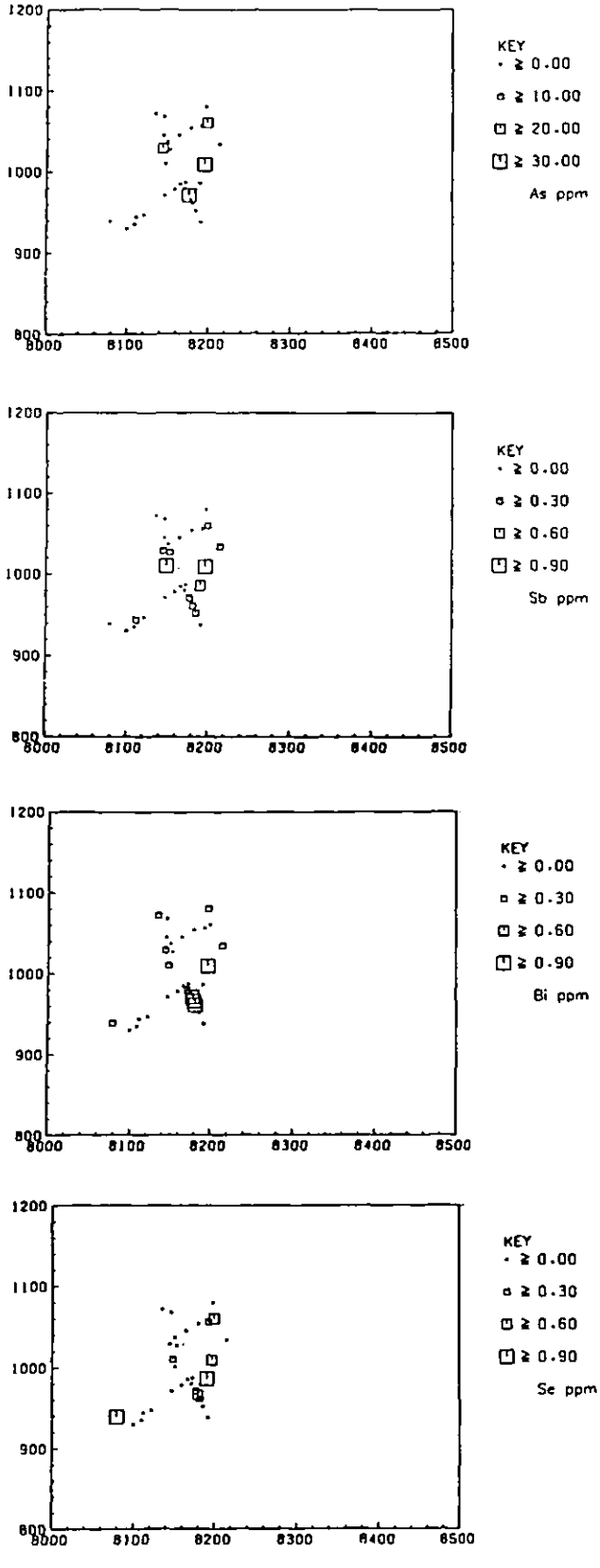


Fig 5.22 Kilmelford: lithogeochemistry KD02

rock copper data (Fig. 5.18) except that there is no anomaly at around 1,000 m on KD03 and an anomaly is developed at 600 m on the same traverse.

The behaviour of selenium relative to copper is elucidated by the use of principal component analysis. Both elements have high loadings on component 2 (Table 5.3) but there are two other components on which copper (component 4) and selenium (component 5) have high loadings. Inspection of component scores and element plots (Figs. 5.25, 5.28) show that the two elements are associated at the base of slopes with copper mineralization and especially in peat flats. High copper without selenium occurs over copper anomalies in rocks on high ground, while selenium without copper is found in peaty areas distant from the mineralization. Analysis of peat samples from KD03 (Fig. 5.29) shows that broad selenium highs are found in peat flats, emphasising the importance of organic matter.

The principal component analysis also shows the association between iron, manganese, arsenic and zinc (component 1) and high scores form a halo around the mineralized porphyry. Peat values for arsenic are particularly low from 900 - 1,000 m on KD03 (the highest ground) and arsenic values are more erratic than those of selenium.

Bismuth and lead are also correlated, with high values around the periphery of the mineralized intrusive. High lead values are found over a possible minor skarn at the east end of KD04 while bismuth enrichment (1.2 ppm relative to 0.4 ppm background) is noticeable over the faulting on the south side of the porphyry. Broad bismuth highs are also evident over this faulting in the peat analyses of KD03 (Fig. 5.29).

Table 5.3 Factor loadings unrotated 5-factor model - Kilmelford soils

	fact 1	fact 2	fact 3	fact 4	fact 5
Cu	-.4333	.5724	-.2569	.5773	.1569
Pb	-.2480	-.4622	.6626	.3101	-.2963
Zn	-.7753	-.3440	-.2327	.2240	-.1194
Fe	-.7532	.1438	-.3452	-.3724	-.0715
Mn	-.7279	-.3928	-.2536	-.0326	.2174
Ca	-.3677	-.7616	-.0169	-.0876	-.0831
As	-.7479	.3057	.3072	-.0575	.0986
Bi	-.4408	.2202	.7069	-.1615	.3616
Se	-.4007	.6620	.0920	-.1252	-.5214

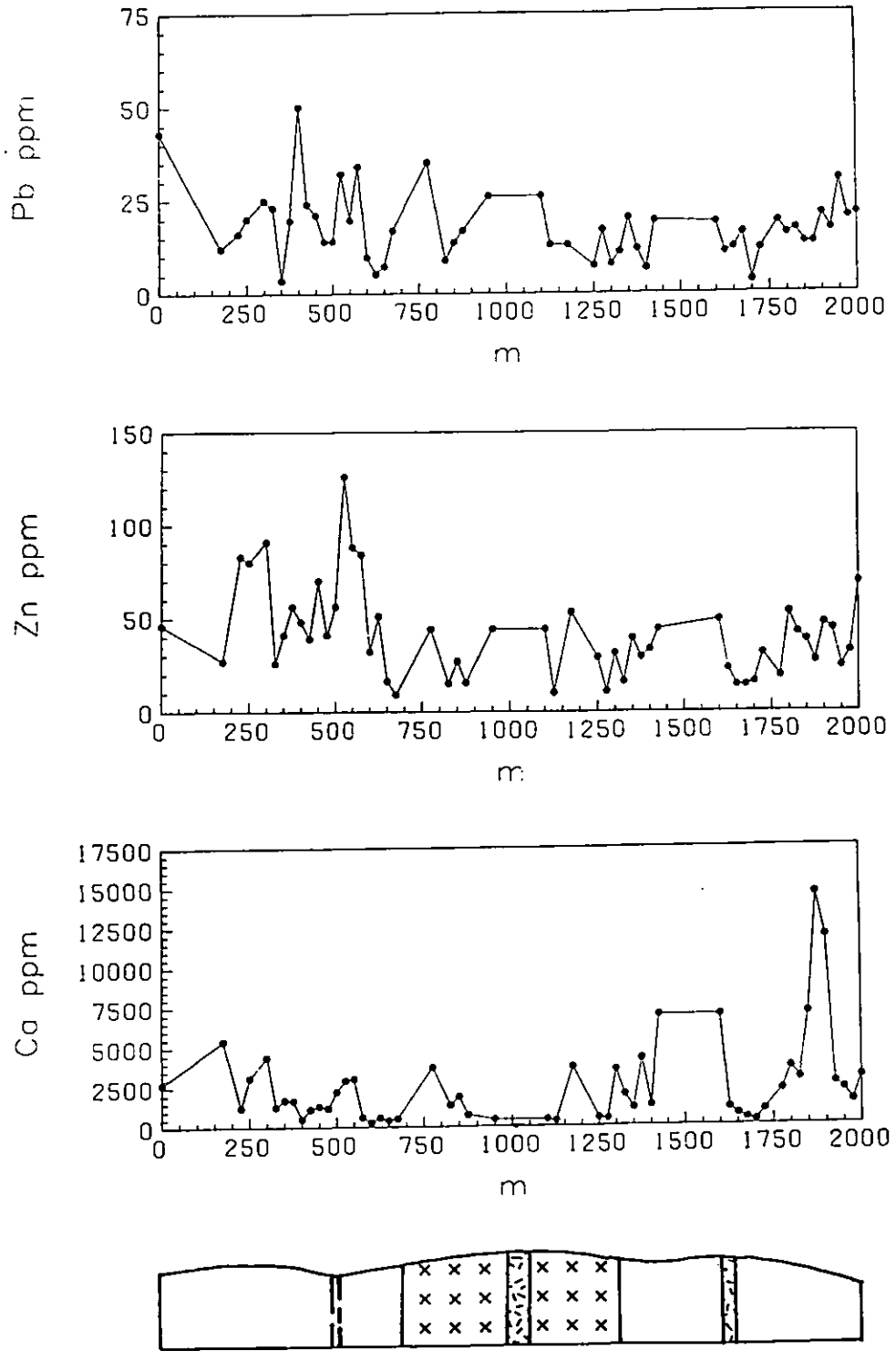


Fig 5.23 Kilmelford: soil traverse KD03
Geological symbols as for Fig 5.16

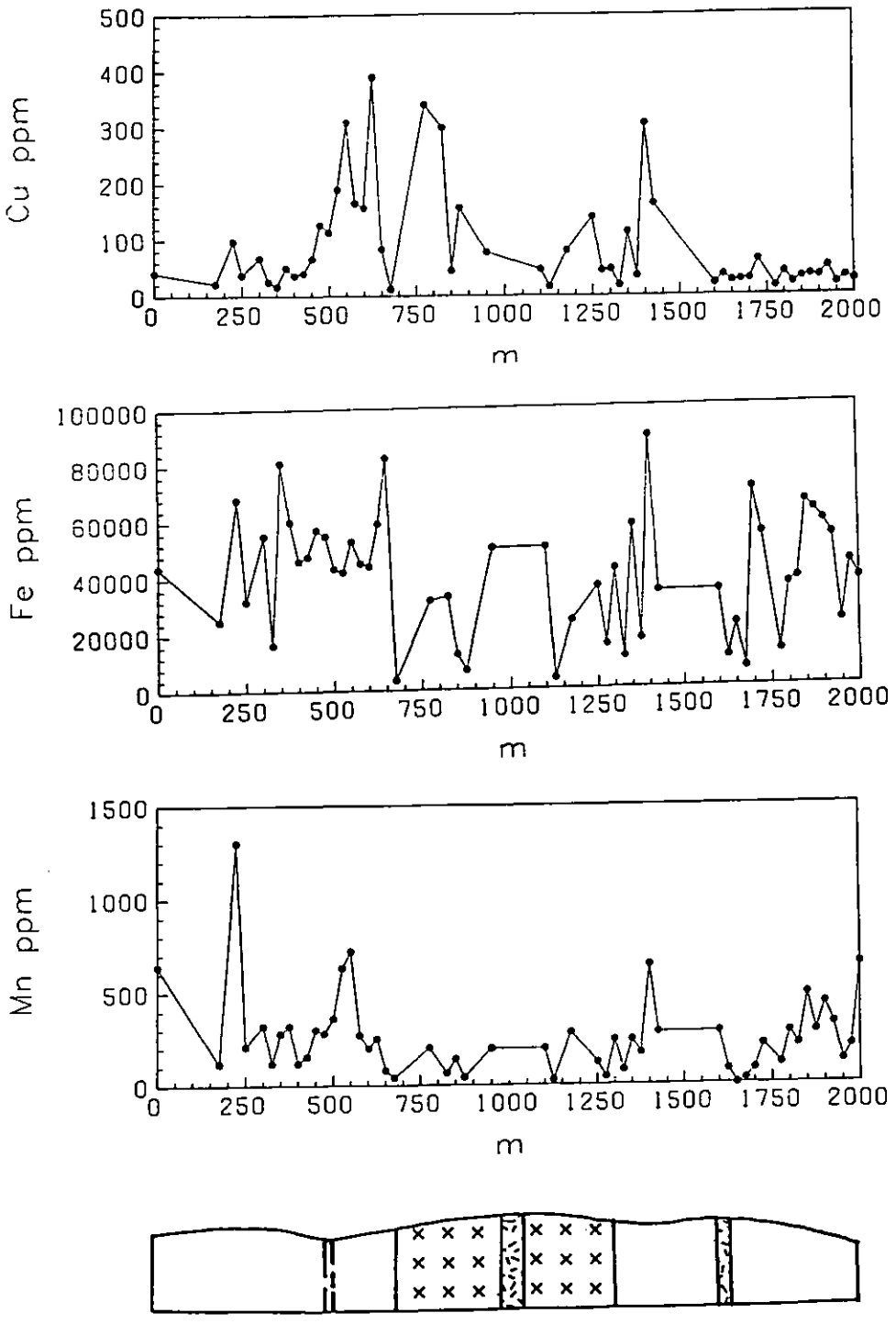


Fig 5.24 Kilmelford: soil traverse KD03
Geological symbols as for Fig 5.16

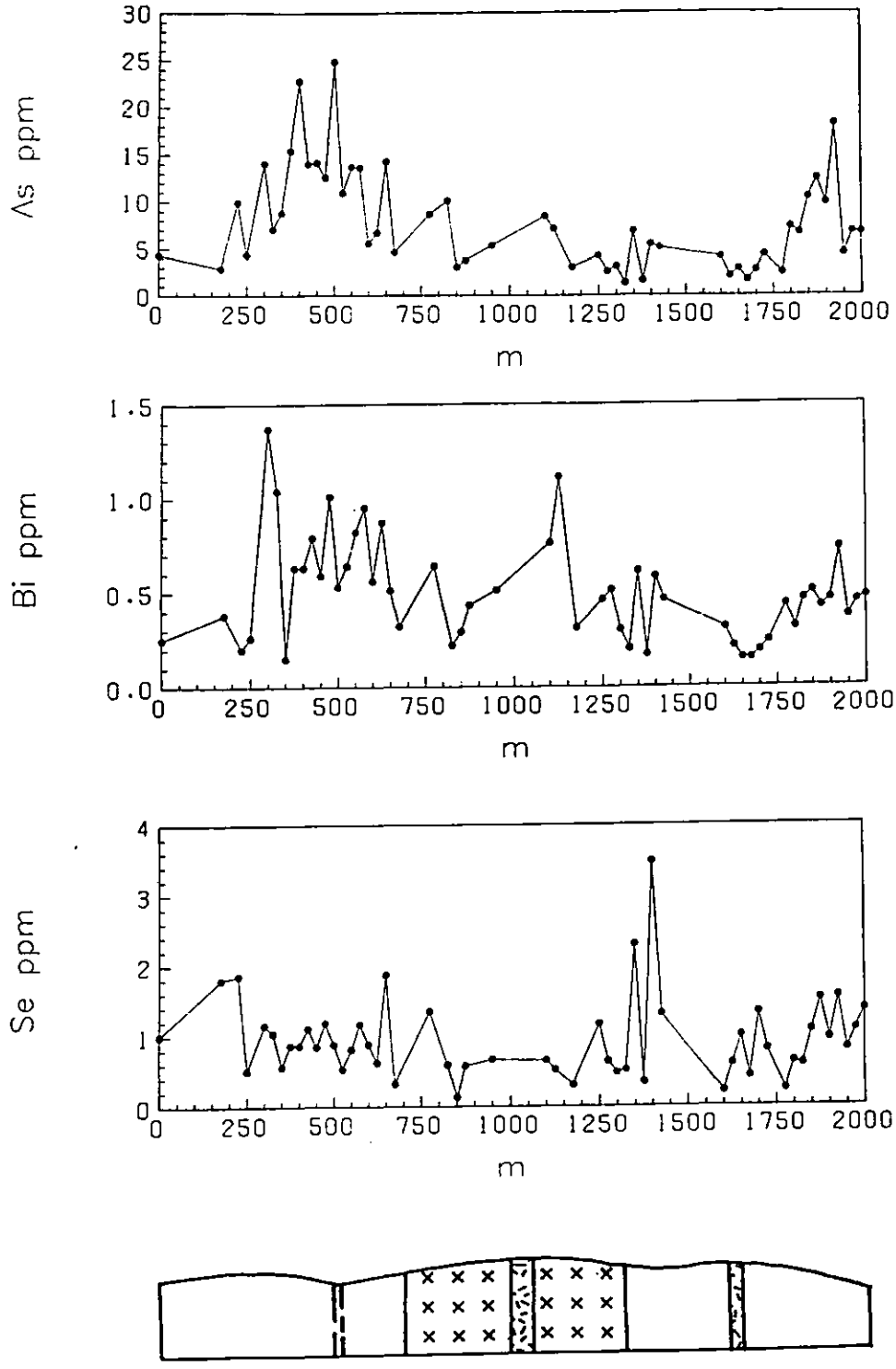


Fig 5.25 Kilmelford: soil traverse KD03
Geological symbols as for Fig 5.16

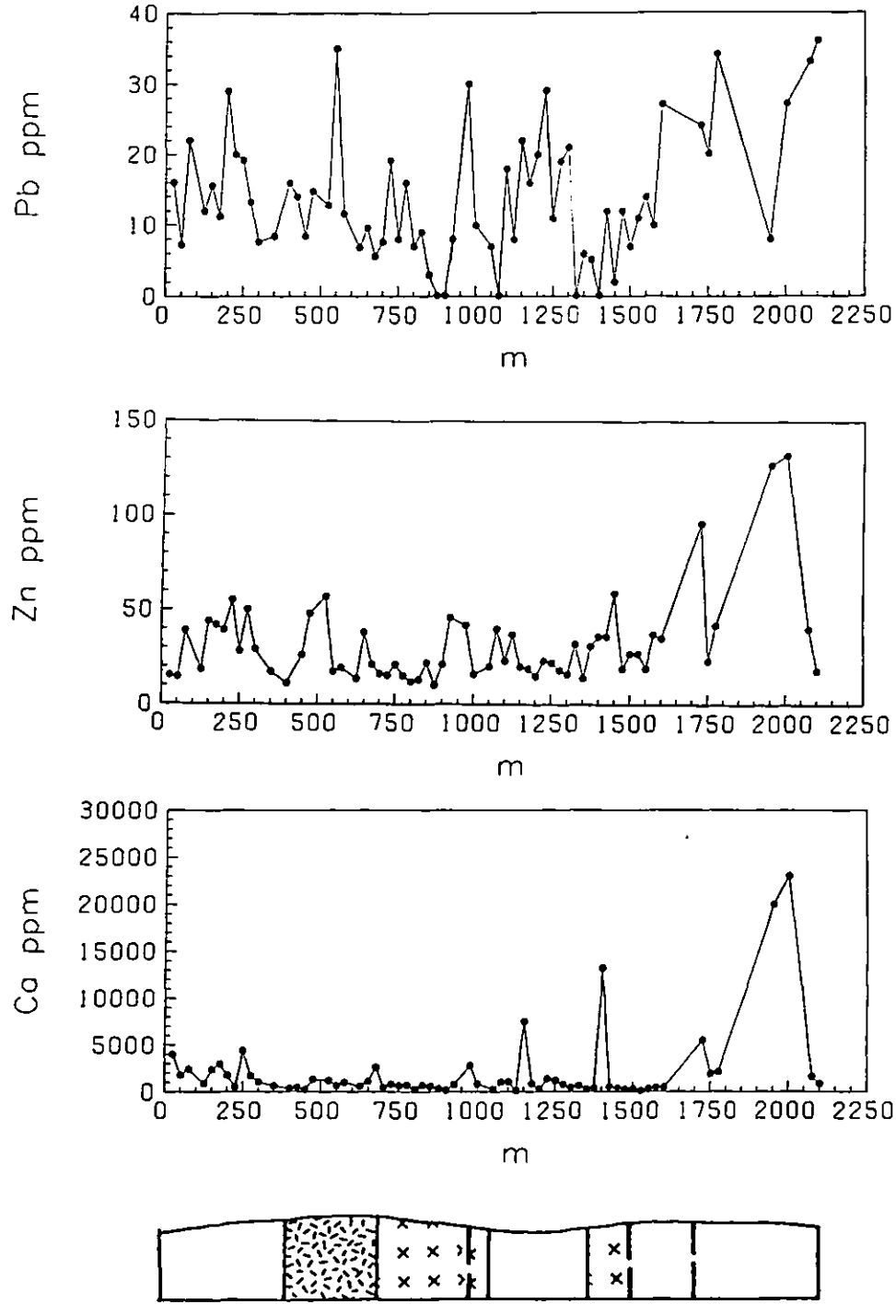


Fig 5.26 Kilmelford: soil traverse KD04
Geological symbols as for Fig 5.16

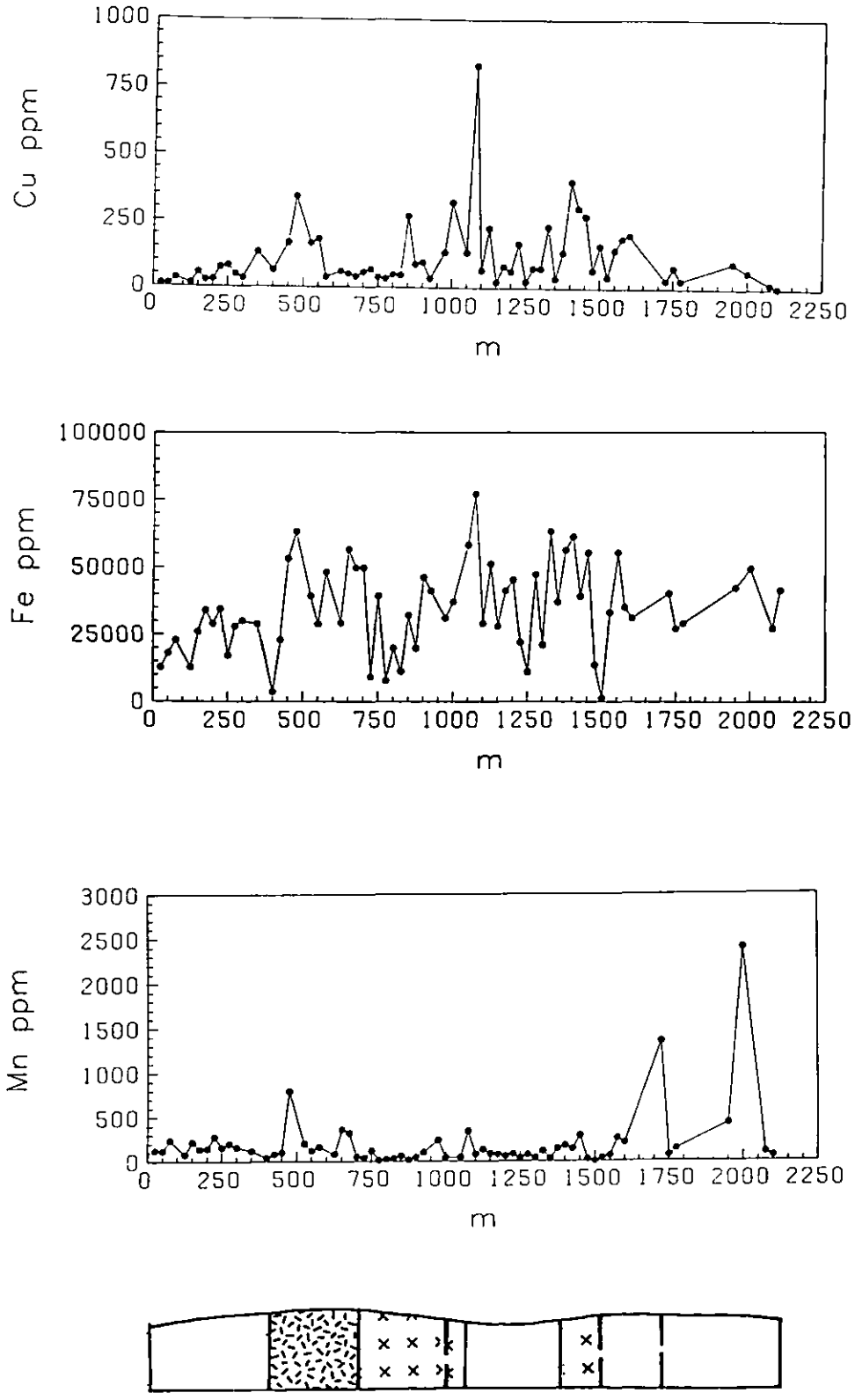


Fig 5.27 Kilmelford: soil traverse KD04
Geological symbols as for Fig 5.16

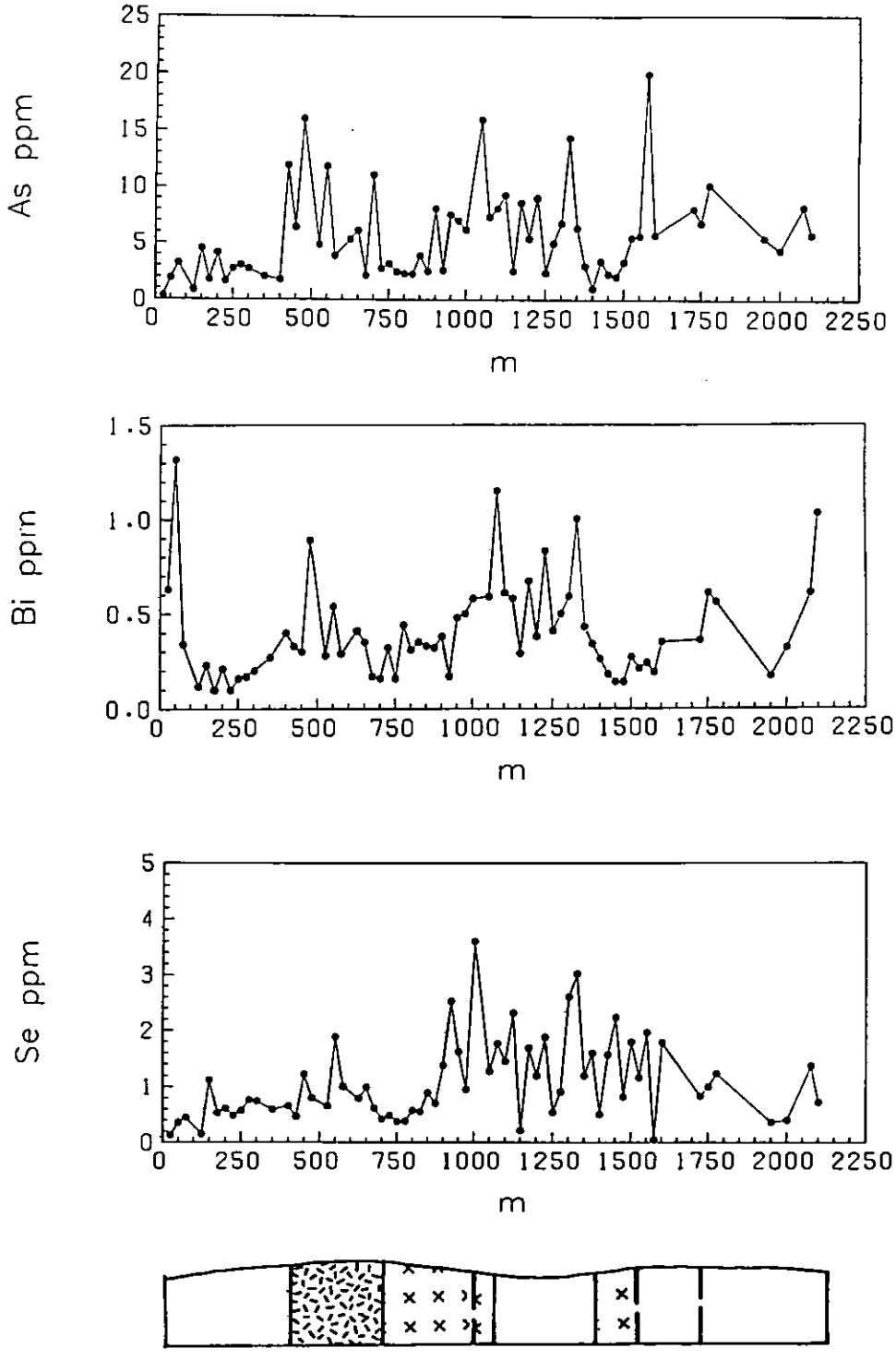


Fig 5.28 Kilmelford: soil traverse KD04
Geolgical symbols as for Fig 5.16

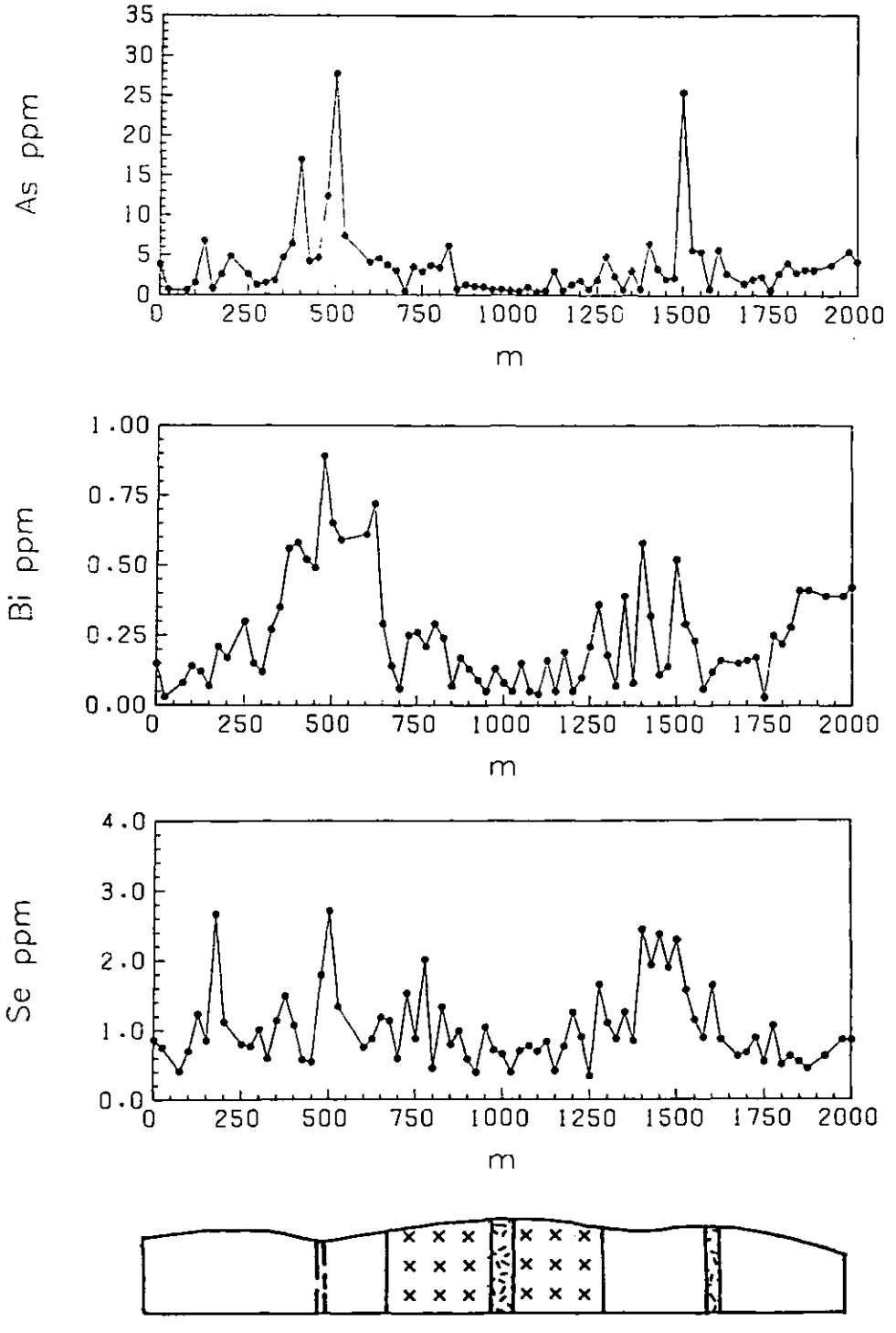


Fig 5.29 Kilmelford: peat traverse KD03
Geological symbols as for Fig 5.16

c) Stream Sediments

Copper anomalies are developed in five streams draining the mineralized porphyry but the most prominent are those flowing toward the south west (Garraron River). Anomalous values reach 250 ppm Cu relative to a background of 20 ppm (Figs. 5.30 - 5.32).

Multivariate analysis of the data shows that there are several distinct elemental associations. The major division is between the sluggish upland part of the streams and the faster flowing portions, where they descend the escarpments. The highland streams show high loadings (Table 5.4, Fig. 5.33) on component 1 (Zn, Fe, As, Mn).

Copper with minor selenium is found in component 3 and probably reflects dispersion downstream from the mineralized prophyry. High loadings on an almost pure localised selenium component (component 4) represent very localised selenium accumulations which are spatially correlatable with peat flats. Limited water data show that selenium in solution is relatively high in the Kilmelford rivers (averaging 0.8 ppb immediately downstream from mineralization in the Garraron river) but declines rapidly downstream (Fig. 5.34) from the small lake (Lochan).

High lead and bismuth concentrations are almost entirely confined to the stream draining northwest toward Kames. Examination of indicator values suggests that unmapped mineralization is present within the catchment of this river, but its nature is not clear. The evidence of peak copper anomalies 200 m upstream from those of lead indicates that the source of the anomalies is complex, possibly with both minor skarns and lead-zinc veins. Panned concentrate studies of the I.G.S.

	FACT 1	FACT 2	FACT 3	FACT 4	FACT 5
CU	-.3475	.6145	-.5041	.1229	-.2445
PB	.0484	.5937	.6237	-.0531	-.2237
ZN	.7716	.2054	.1407	-.2705	-.2368
NI	.2348	.7528	-.3838	-.2265	-.1350
FE	.7139	-.4404	-.2372	.0856	-.0169
MN	.8021	-.1572	-.2336	-.2033	-.2236
CA	.3974	.5179	-.1477	-.3023	.6548
AS	.7139	-.0795	.3628	.3819	.0739
BI	.1065	.6946	.3498	.2932	.0706
SE	.2973	.2255	-.3517	.7585	.0377

Table 5.4 Factor loadings for unrotated 5 factor model : Kilmelford stream sediments

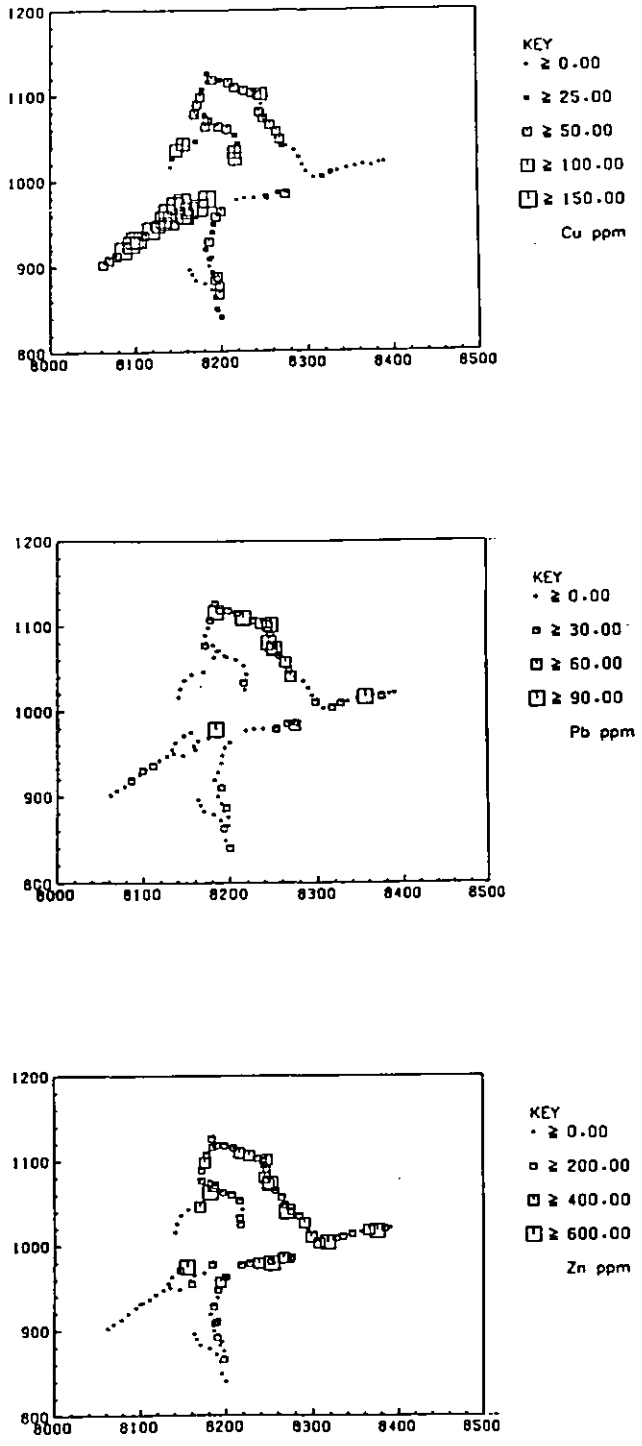


Fig 5.30 Kilmelford: stream sediments KD01
Overlay facing Fig 5.20

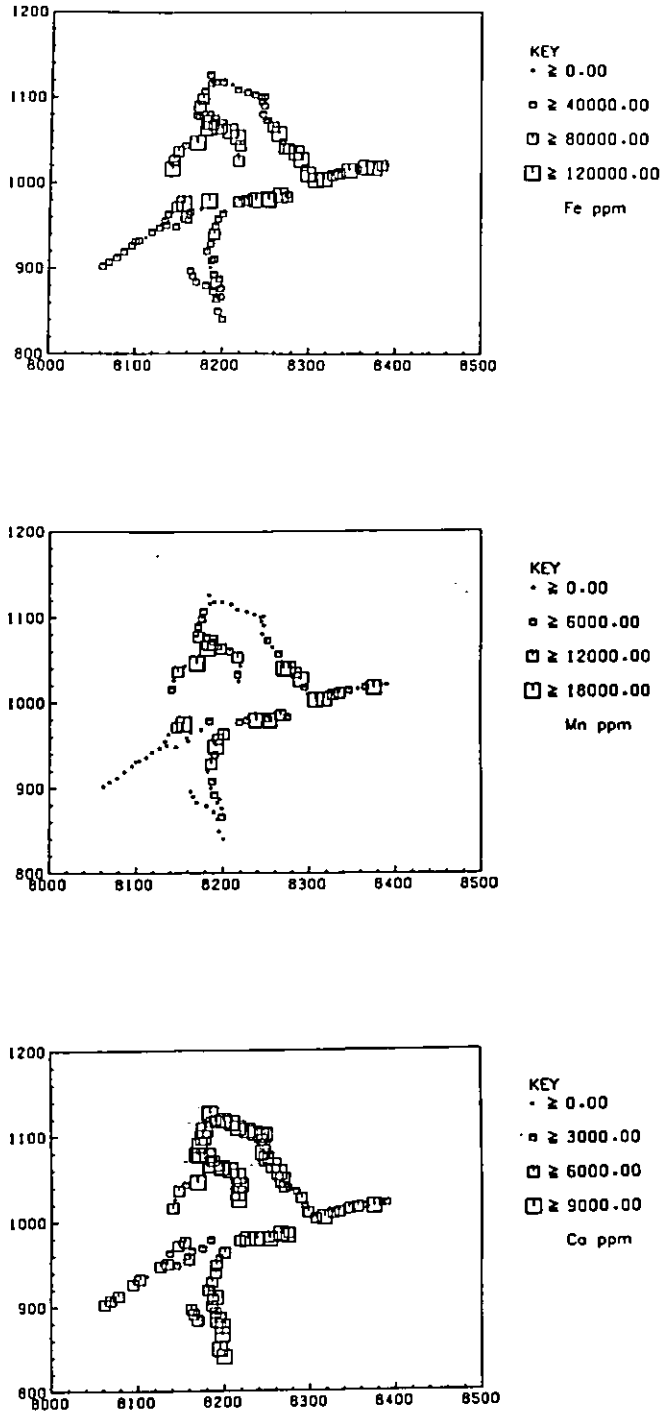


Fig 5.31 Kilmelford: stream sediments KD01

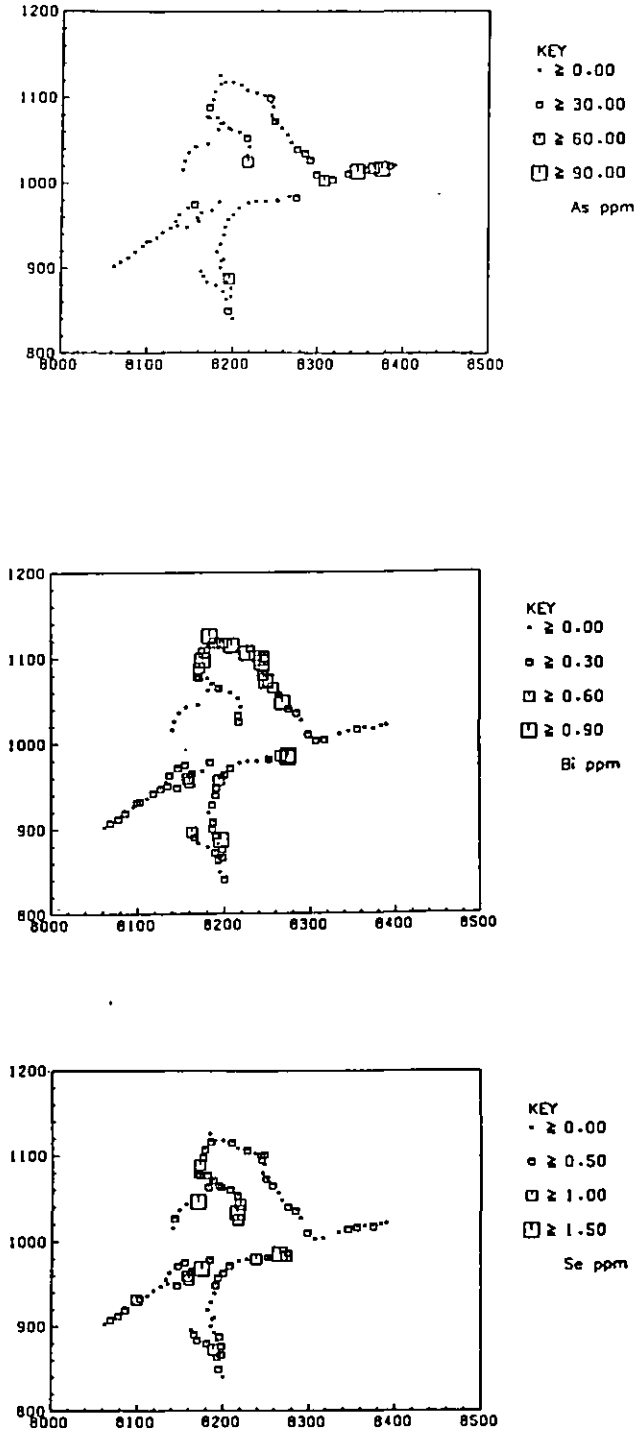
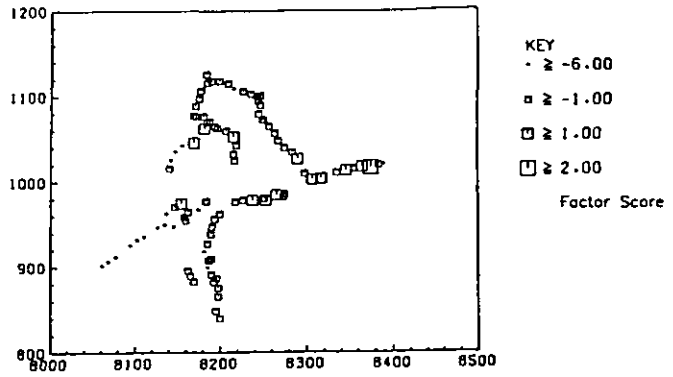
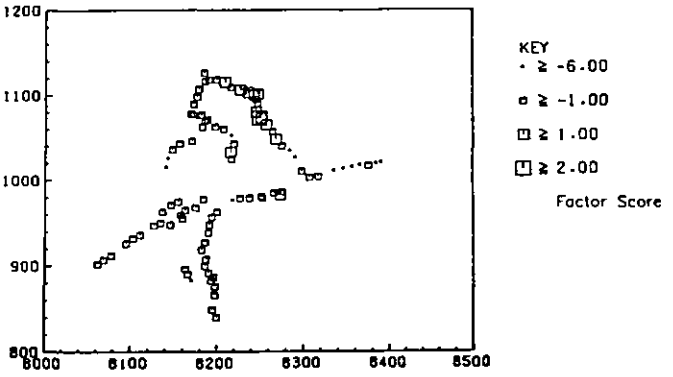


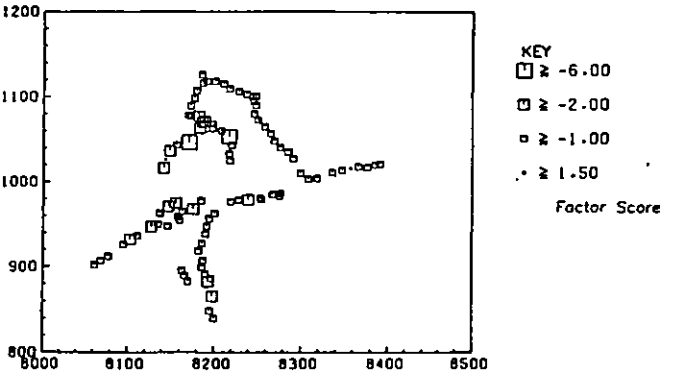
Fig 5.32 Kilmelford: stream sediments KD01



FACTOR 2



FACTOR 3



FACTOR 4

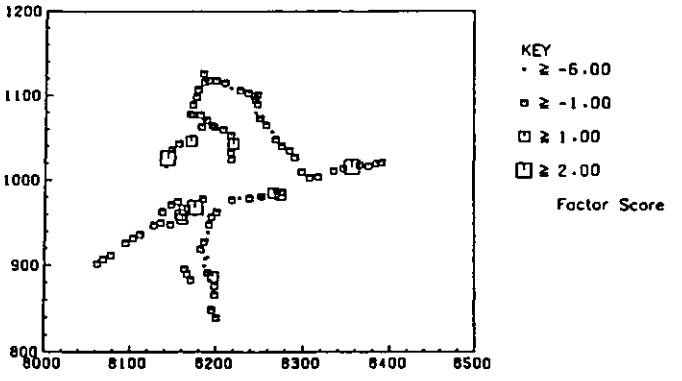


Fig 5.33 Kilmelford: factor score distribution KD01
Overlay facing Fig 5.20

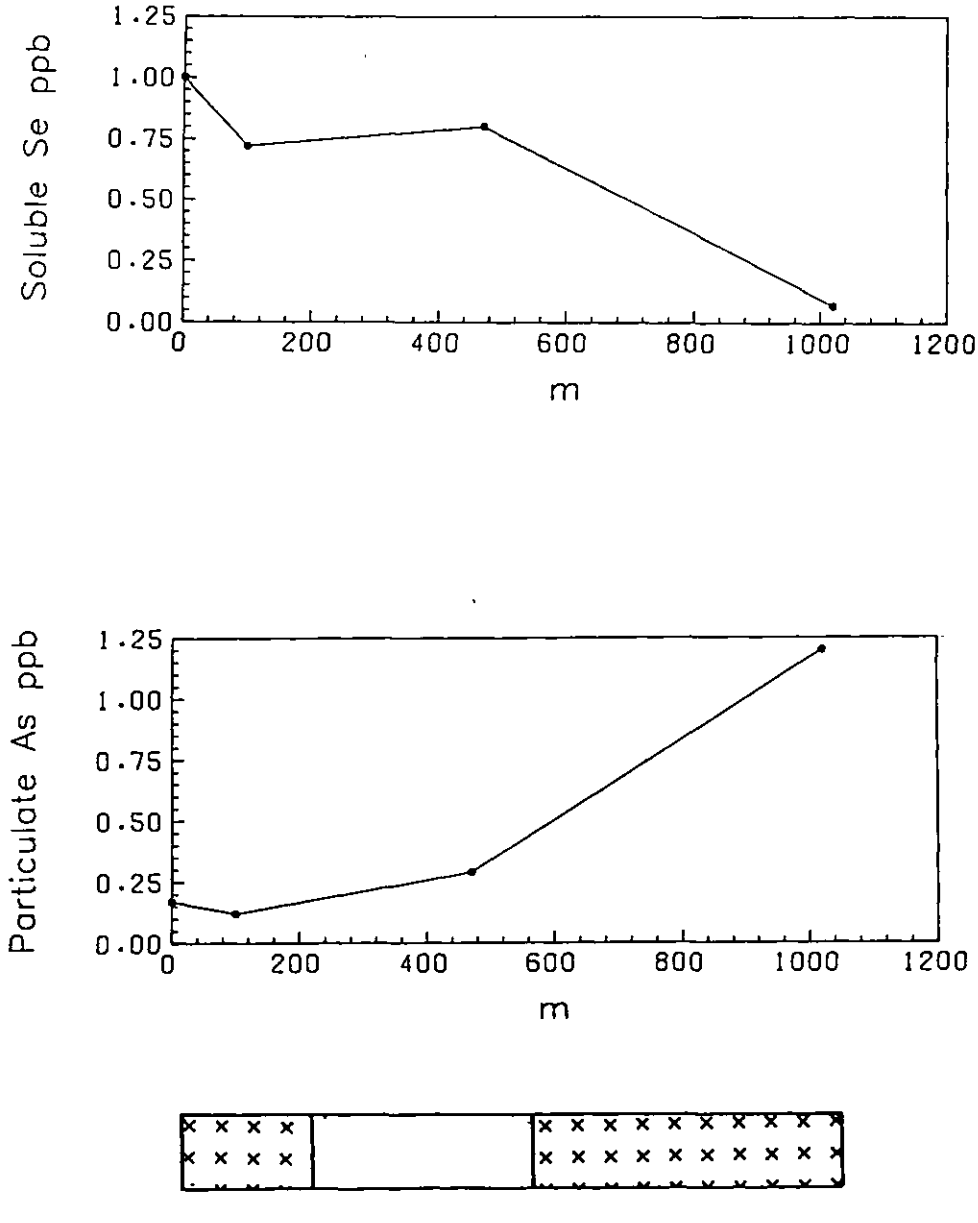


Fig 5.34 Kilmelford: water data from stream draining lochan
Geological symbols as for Fig 5.16 (location Fig 5.19)

have found cerussite grains associated with similar anomalies immediately to the east. Comparison of the lead and zinc patterns (Fig. 5.35) shows the erratic decline of lead downstream, with some input from tributaries, whilst zinc decreases more steadily. Bismuth is not directly comparable with either indicator element possibly reflecting considerable imput from tributaries and association with both postulated types of mineralization. Arsenic, iron and manganese demonstrate the contrast between the two physiographic zones with the two northern samples taken on the highland area.

5.2.3 Discussion

Pathfinder anomalies in surficial material are derived from two bedrock associations: selenium with disseminated copper minerals in the porphyry and bismuth with peripheral lead-zinc-copper veins and minor skarns.

The copper-selenium association persists into the till. Relative depletion of selenium on high ground suggests that it is leached toward the peat filled depressions, whereas copper is less mobile and till copper anomalies have a closer relation to bedrock highs. The major anomalies in depressions are not simply the result of slope wash of copper and selenium but are also partly derived from stream transport of the more mobile copper (q.v.). Selenium anomalies also occur in depressions >1 km distant from the porphyry demonstrating that the magnitude of the mineralization related anomalies is no greater than those formed by organic concentration from waters with background selenium levels.

Copper in stream sediments discriminates the mineralized porphyry but anomalies vary considerably in magnitude, probably as a result of contrast in the rate of output of mineralized material. Selenium highs are spatially

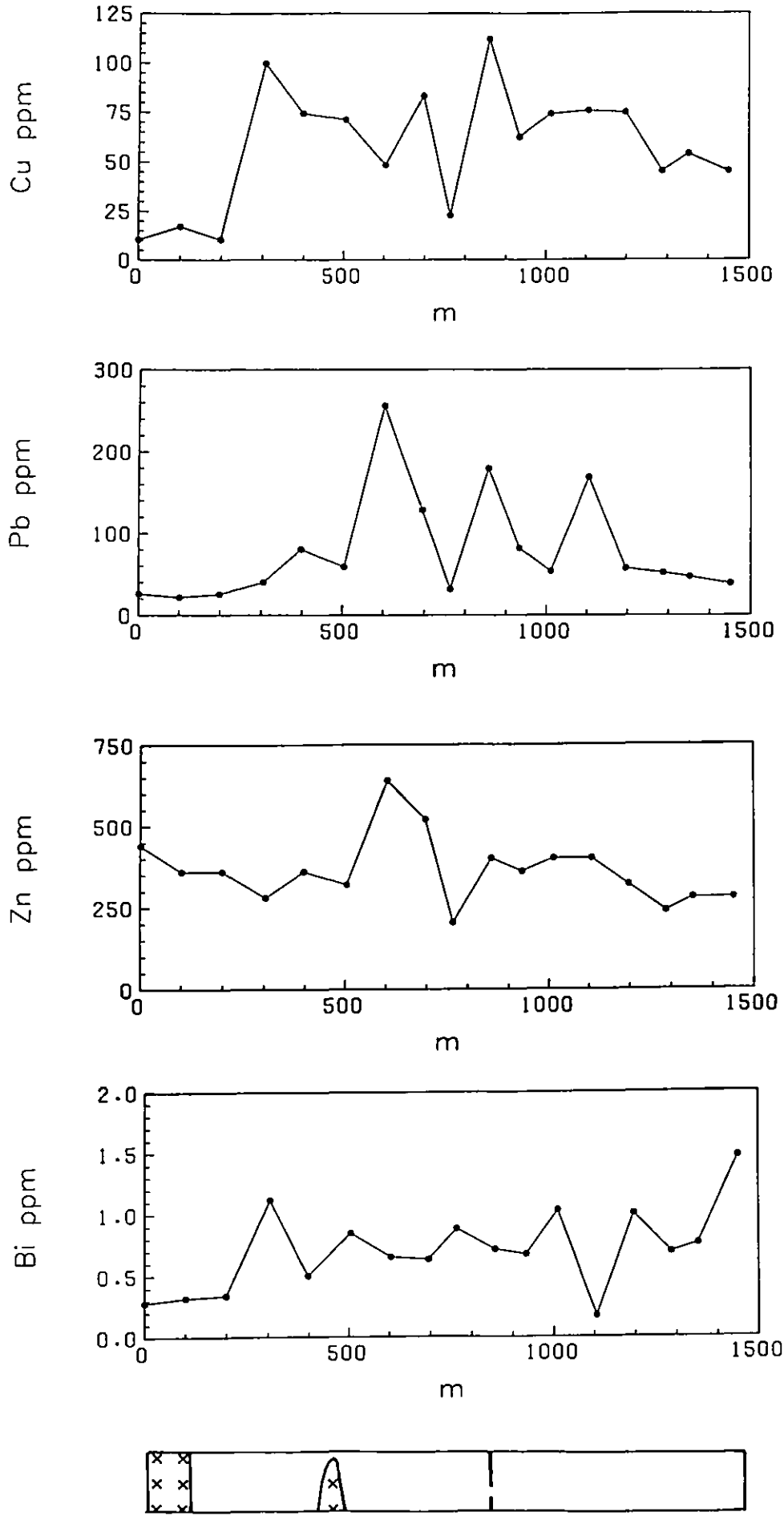


Fig 5.35 Kilmelford: stream sediments Kames river (location Fig 5.19)
Geological symbols as for Fig 5.16

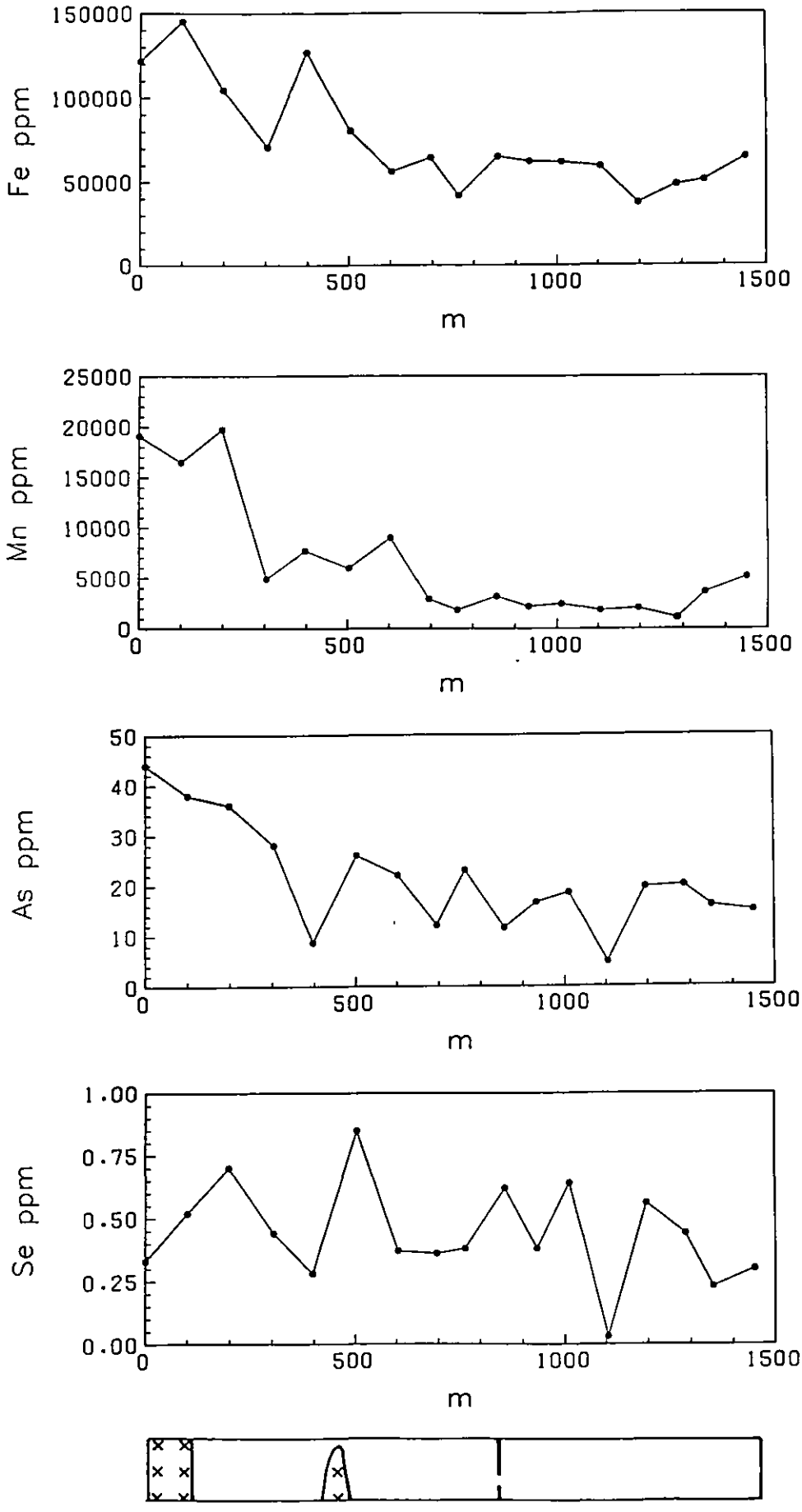


Fig 5.36 Kilmelford: stream sediments Kames river (location Fig 5.19)
Geological symbols as for Fig 5.16

very limited to the organic rich portions of the 'mineralized' streams. Selenium stream sediment values in the more active parts of streams draining the mineralization are more consistent but only slightly enriched. This observation when combined with water determination suggests that much of the selenium is transported in solution and fixed by organic matter.

The lead-bismuth association is much less pronounced but is evident in tills overlying skarns and veins on the periphery of the porphyry. Bismuth anomalies on the southern edge of the porphyry correlate with major faulting. The association persists into the stream sediments and both elements are probably mainly clastically despersed. The extensive nature of the anomalies at823110 is best explained as the result of multiple input of mineralized material.

Arsenic is of little practical use as concentrations are more closely related to the velocity of stream flow than bedrock concentration(which is poorly understood).

The overall exploration significance of this study is limited as the deposit is distinctly sub-economic and extrapolation of conclusions to economic deposits depends on many uncertain relationships - the main one being the correlation between pathfinder concentration and ore grade. Pathfinders are unlikely to find great application to the search for porphyries in temperate terrains as anomalous copper values are invariably found at the surface overlying economic (i.e. mineable by open cut techniques) deposits. The situation in intensely weathered (tropical and arid) areas is very different, and copper is often leached from the near surface.

Comparison with limited information (Wraith, 1982) from the giant Chuquicamata porphyry in Chile shows it

contains significantly higher pathfinder values than Kilmelford. Concentrations in its gossan are 1,420 ppm As, 7.4 ppm Bi, 59 ppm Se relative to 43 ppm As, 17 ppm Bi, 0.07 ppm Se in the enriched primary ore. Some arsenic is also transported to the secondary Exotica orebody. This suggests that pathfinders are potentially effective in these more intensely weathered areas.

CHAPTER 6 STRATABOUND DEPOSITS HOSTED BY CLASTIC SEDIMENTS

Three deposits in this category were investigated. They occur in the British and Irish Paleozoic, are diverse and formed in very different environments. The Avoca deposit is a Kuroko-type massive sulphide deposit associated with calc-alkaline volcanics; the Meall Mor copper show is at the western end of a series of stratiform and remobilised base metal occurrences scattered through the southern part of the Scottish Highlands; while the Glendinning antimony deposit,in the Southern Uplands, is of enigmatic origin and spatially isolated. All the areas have been glaciated and are overlain by variable thicknesses of till.

The exploration problems posed by the deposits are also contrasting. Geochemical recognition of volcanogenic massive sulphide deposits involves the discrimination of the mineralized part of the sequence and the location, within it, of sulphide pods and stockworks. Surficial geochemistry is often used on both regional and local scales to locate the mineralized sequence and hopefully the sulphides. Detailed lithogeochemistry within the mineralized sequence is being increasingly used in the search for sulphides and recent work, both in Spain and Canada, suggests that pathfinder/alkali ratios are good proximity indicators (Møller et al, 1982; Scott et al, 1982).

The location of economic pods of clastically hosted stratiform mineralization is generally an easier problem, and surficial geochemistry has been responsible for many successes, particularly in Africa. The discovery of large blind orebodies (e.g. Lubin, Poland) suggests that multielement techniques may have a considerable role to play.

Arsenic and antimony dispersion patterns are obviously of prime importance in locating deposits in which arsenic and antimony are present as ore metalloids.

6.1 Avoca, Co. Wicklow, Ireland

This deposit was selected for investigation as it was the only working volcanogenic massive sulphide mine in the British Isles, and good access (courtesy of Avoca Mines Limited and the Geological Survey of Ireland) coupled with detailed geological and mineralogical studies were available. A drawback is the large scale mining contamination of much of the area of interest, which precludes assessment of the subcrop of the main orebodies. The object of research of Avoca was to study the primary concentration and secondary dispersion of a variety of elements, but highlighting the pathfinders.

6.1.1 Geology

The Avoca mineralization is hosted in synclinal inliers of Ordovician calc-alkaline volcanics and sediments, which form part of a sequence about 1000m thick, of probable island arc origin (Platt, 1977). The basal unit exposed is the marine clastic Ribband Group, which is overlain by flows, shales and then tuffs of the East Wicklow Volcanic Formation (Sheppard, 1980a). Siliceous tuffs forms the footwall of the mineralization. The hangingwall comprises sericitic tuffs and shales while the uppermost unit present is interpreted by Sheppard (1980a) as an intermediate flow but is at least in part equivalent to the dolomitic tuffs of Platt (1977). Domes and sills of rhyolite intrude the upper part of the sequence. The sediments have been isoclinally folded and thrust, with later normal faulting and minor dioritic intrusion (Fig. 6.1).

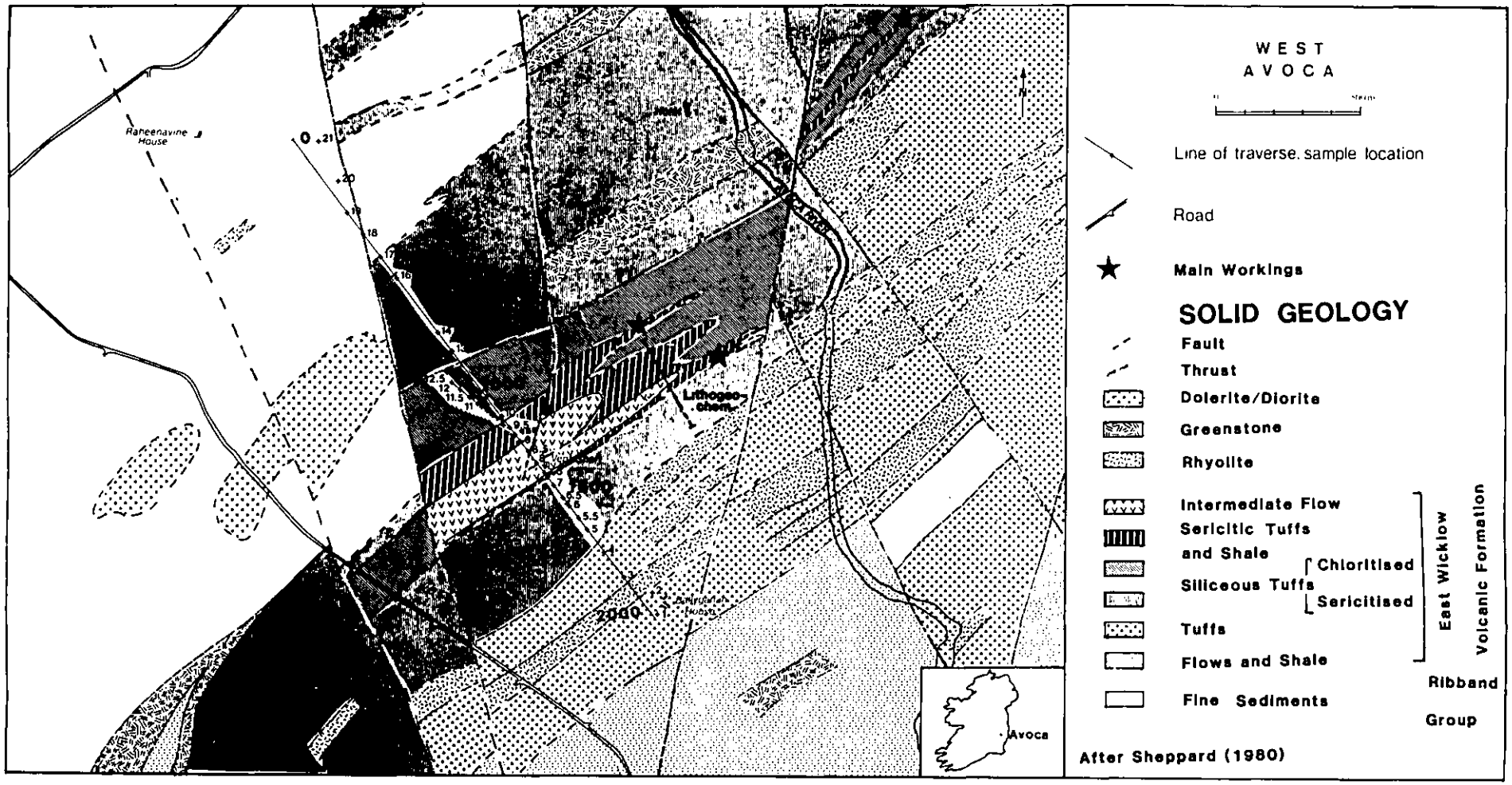


Fig 6.1 Avoca: solid geology

Three distinct types of mineralization are recognised at Avoca: (a) massive cupriferous pyrite (pyritite) grading 1.1% Cu, 0.6% Zn and 0.2% Pb; (b) massive galena-sphalerite grading 7% Zn, 3.5% Pb and 0.3% Cu; and (c) highly siliceous (stringer) ore comprising disseminated pyrite, chalcopyrite and minor sphalerite grading 0.6% Cu, 0.4% Zn and 0.15% Pb. Recent remapping by Sheppard (1980a) and by Pointon (1980) suggests that the pyritite is mainly located at the contact between the siliceous tuffs and the sericitic tuffs while the galena/sphalerite is generally slightly higher in the sequence (Fig. 6.2). The siliceous (stringer) mineralization, which is developed in the footwall siliceous tuffs, is thought to be mainly the product of remobilisation of the massive pyrite and not merely a stockwork zone (Sheppard, 1980a).

The massive sulphides and stringer zones were worked with reserves of about 19 million tons. Reserves of lead zinc ores are estimated at about 2 M tons.

Extensive alteration is a feature of the deposit. The footwall tuffs exhibit widespread sericitization, plus chloritisation close to the pyritite. The hangingwall tuffs are sericitized and dolomotised.

The area has been glaciated but the present overburden is thought to be non-exotic and is generally 2 - 3 m thick.

6.1.2 Programme

a) Sampling

This study was confined to the western part of the deposit, which has escaped the otherwise extensive mining contamination.

Primary dispersion patterns were first examined. A picture of lithogeochemistry was gained from a representative traverse collected by Wheatley (1971), and in addition a

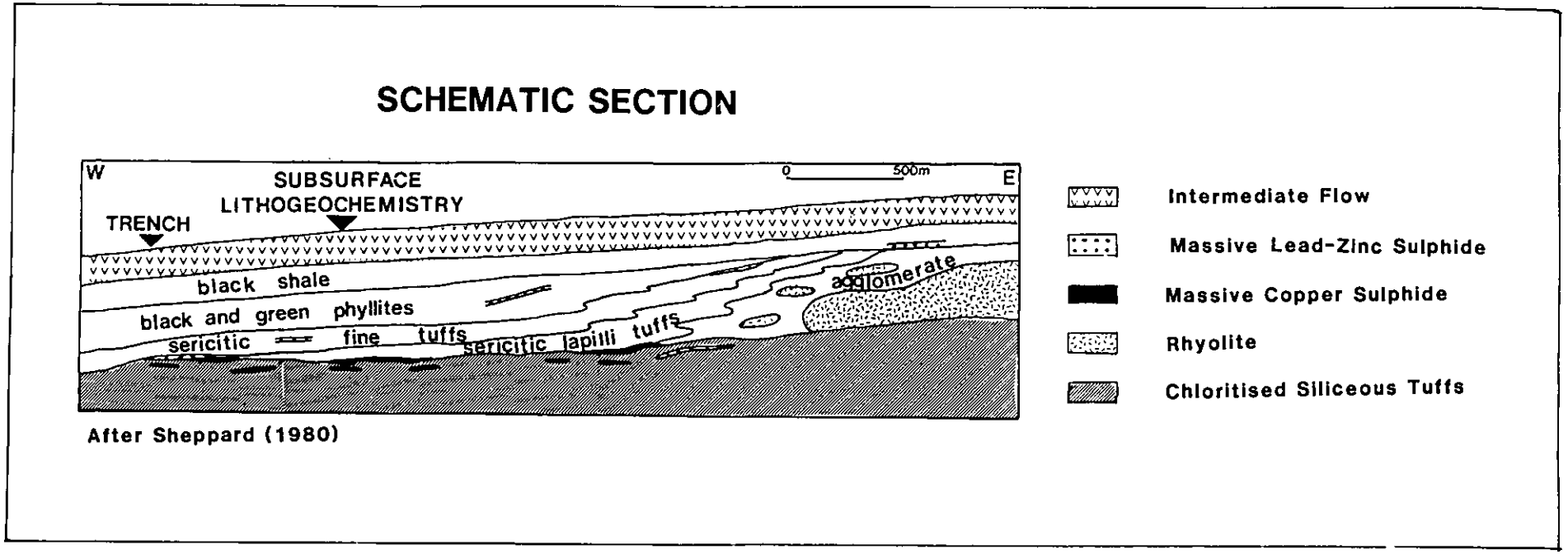


Fig 6.2 Avoca: reconstructed section

a number of ore samples from West Avoca were analysed.

The surface sampling was based on a two kilometre basal till traverse collected by the Geological Survey of Ireland. This crosses the main units of Avoca stratigraphy and parallels a trench excavated across the subcrop of the lateral extension of the massive sulphide orebody. The basal till sampling was followed up by Cobra profiling (by the author) of the anomalous area and the collection of soil samples along the whole traverse.

b) Lithogeochemistry

Comprehensive mineralogical and XRF data for the samples are available (Table 6.1) from the previous work of Wheatley (1971) The traverse represents a composite idealised section of wallrocks across the West Avoca orebody, and intersects the ore horizon twice as the structure is synclinal (Fig. 6.3, Fig. 6.7).

Comparison of XRF and ICP data ($HNO_3/HClO_4$ attack) show that there is significant correlation between the results from the two methods, although the ICP values are, of course, lower.

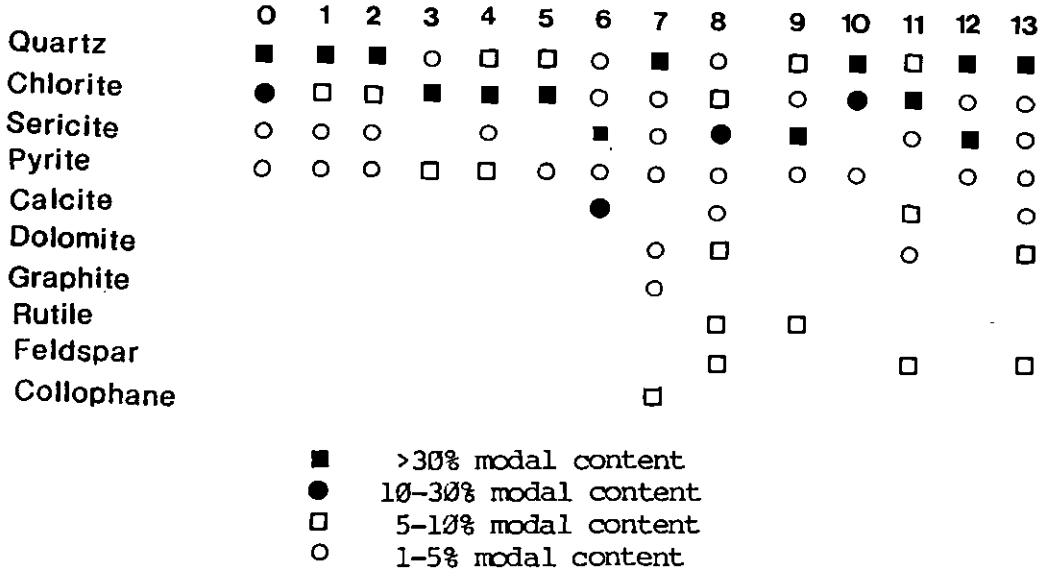
Useful major element patterns are the depletion in sodium and potassium near the orebody with significant enrichments in iron and magnesium (Fig. 6.4).

Of the transition metals, copper , is enriched erratically in the footwall siliceous tuffs (Fig. 6.3) but concentrations are also present in the overlying sericitic tuffs. This contrasts with lead and zinc which are particularly high in the sericitic tuffs but with enrichment also in the northern siliceous tuffs. Manganese is high near both ore zones while barium is enriched in the supra-ore units.

The pathfinder elements display very differing associations (Fig. 6.6). Bismuth correlates with magnesium

Table 6.1 Mineralogy and location of lithogeochemical samples : Avoca

Mineral Composition



Desription of samples :

Ø	ddh 1340-10'	Dark grey siliceous brecciated chlorite schist
1	ddh 1332-8'	Dark grey siliceous chlorite schist
2	ddh 1332-16'	Light grey siliceous chlorite schist
3	ddh 1331-49'	Green-black chlorite schist
4	ddh 1343-67'	Blue-black chlorite schist
5	ddh 1353-114'	Greeen chlorite schist
6	ddh 1331-136'	Black sericite schist
7	ddh 1332-147'	Graphite schist
8	7201,hw	Light grey siliceous chlorite schist
9	ddh 1650-900'	Light brown siliceous ash
10	ddh 1644-304'	Dark grey siliceous chlorite schist
11	ddh 1644-236'	Light grey sericite chlorite schist
12	ddh 1632-210'	Light grey siliceous sericite schist
13	ddh 1644-15'	Rhyolite

after Wheatley 1971

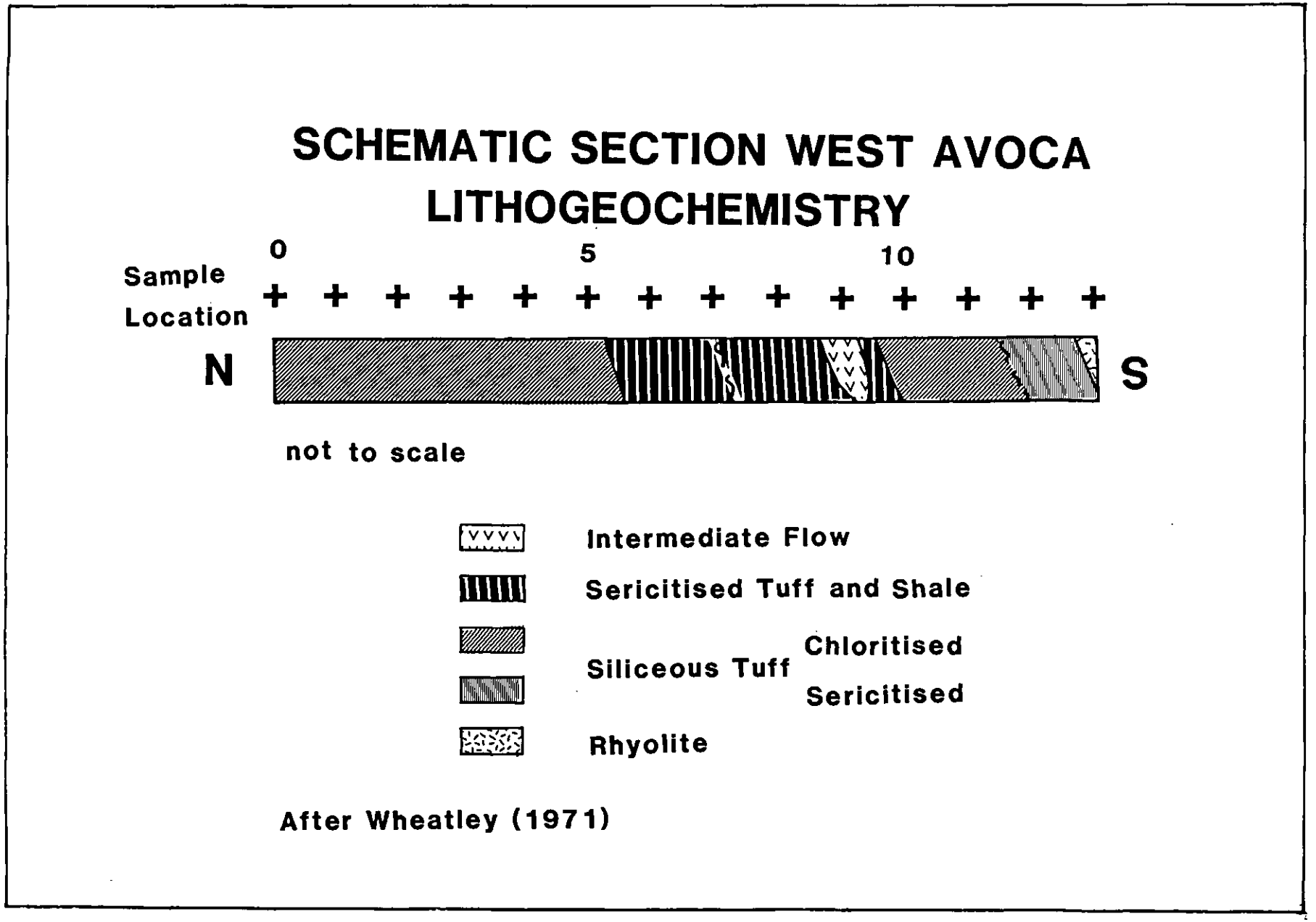


Fig 6.3 Avoca: schematic location of subsurface lithogeochemical samples

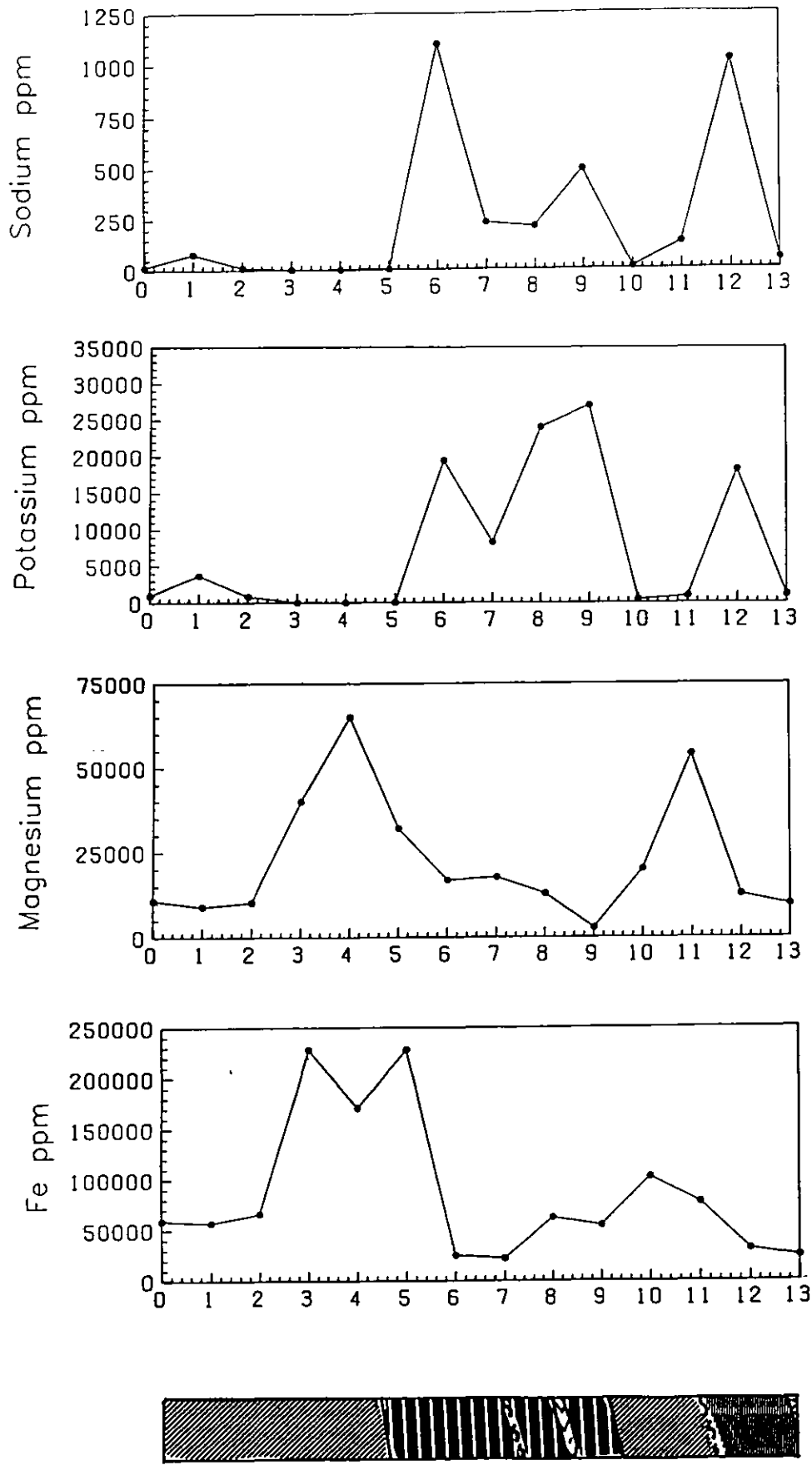


Fig 6.4 Avoca: subsurface lithogeochemical section
Geological symbols as for Fig 6.1

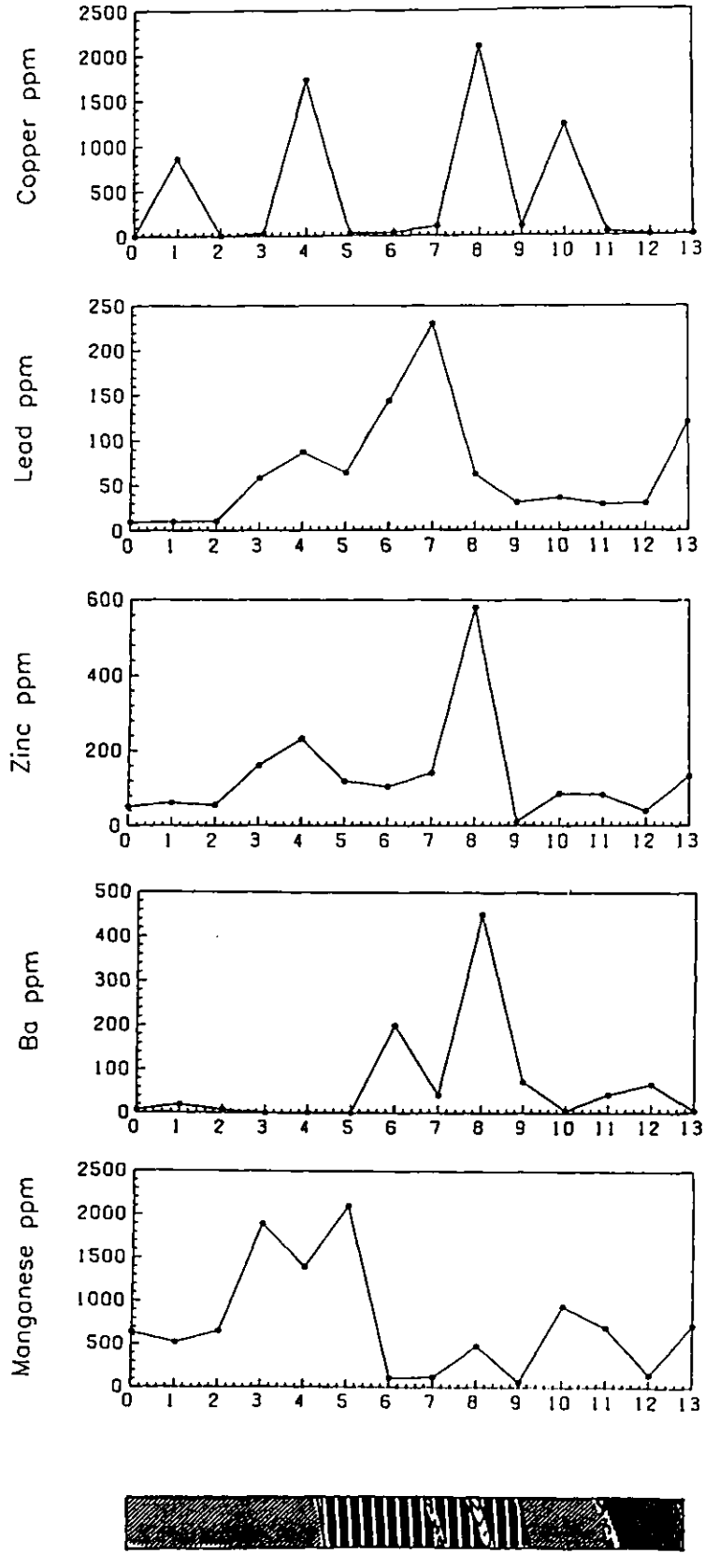


Fig 6.5 Avoca: subsurface lithogeochemical section
Geological symbols as for Fig 6.1

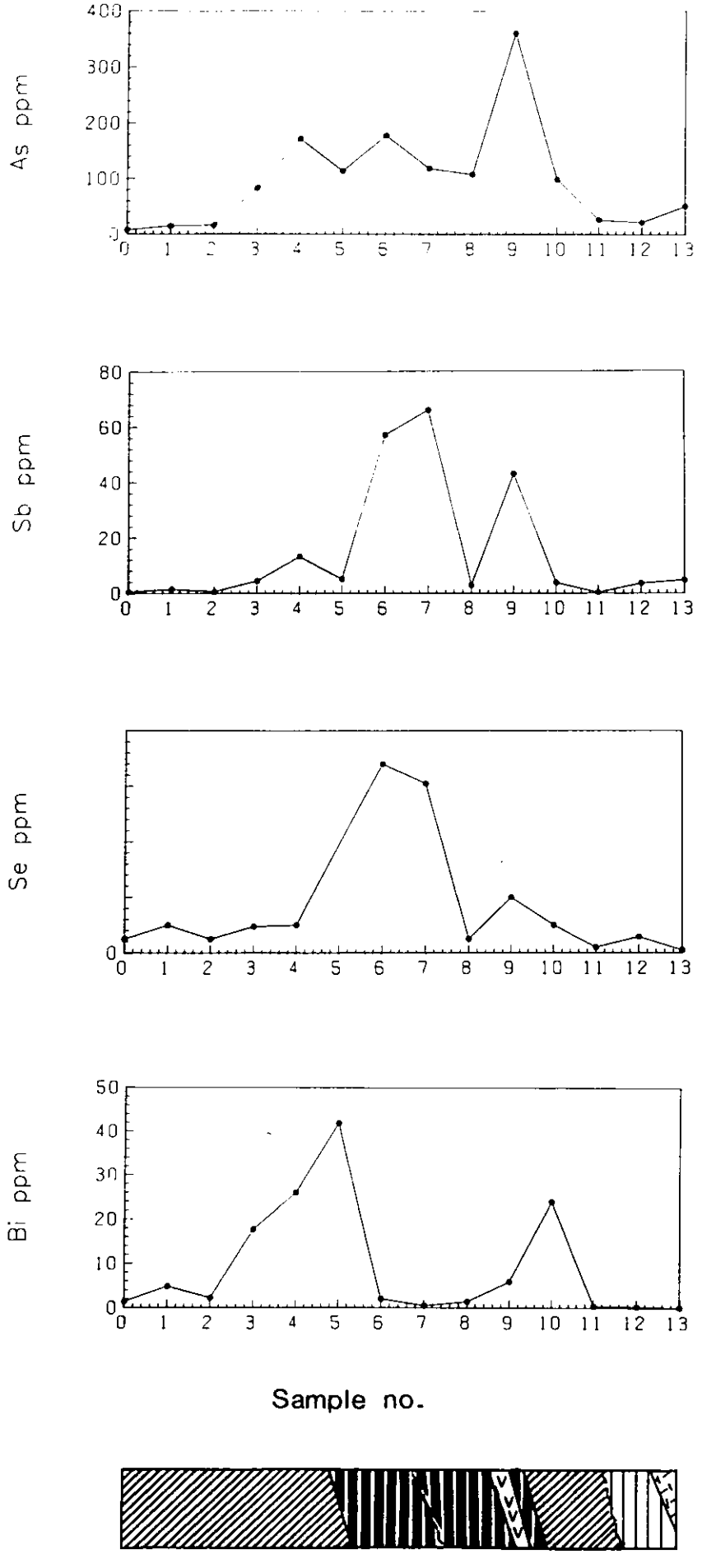


Fig 6.6 Avoca: subsurface lithogeochemical section
Geological symbols as for Fig 6.1

and is strongly enriched near the ore, while arsenic is high both in footwall and hangingwall sediments. Lower amplitude selenium anomalies occur near the ore but mainly in the hangingwall; high antimony values are restricted to the hangingwall sediments.

Analyses of ten copper ore samples (0.2 - 10% Cu) from West Avoca, kindly supplied by Mr. P. McArdle, show that they contain consistently high bismuth values (usually 30 - 300 ppm Bi), more erratic arsenic highs (13 - 300 ppm with occasional values up to 6000 ppm) and low antimony values (4 - 50 ppm), although arsenic and antimony are high in samples enriched in lead and zinc.

c) Surficial Dispersion: Till Profiles

The till profile is 650 m in length with samples collected at 25 or 50 m horizontal and 1 m vertical intervals. It crosses the subcrop of the stratigraphic equivalent of the mineralized units although the main ore-body is only present at depth (Fig. 6.7). The profile parallels a trench (Merrigan's Farm trench) excavated and mapped by Avoca Mines to investigate the complex surface geology and is approximately 300 m west of the composite lithogeochemical traverse. My re-interpretation of this geology, based on the units described by Sheppard and his subsurface interpretation, must be regarded as somewhat tentative (as I did not log any drillcore), but has the merit of fitting the available evidence.

(i) Trench Geochemistry

The geology of the area is a thrust syncline (Fig. 6.7) with both limbs overturned. Transition metal data from the trench (Fig. 6.8) highlight the occurrence of anomalous copper concentrations (750 ppm , background 20 ppm) with erratic high values in the footwall siliceous tuffs

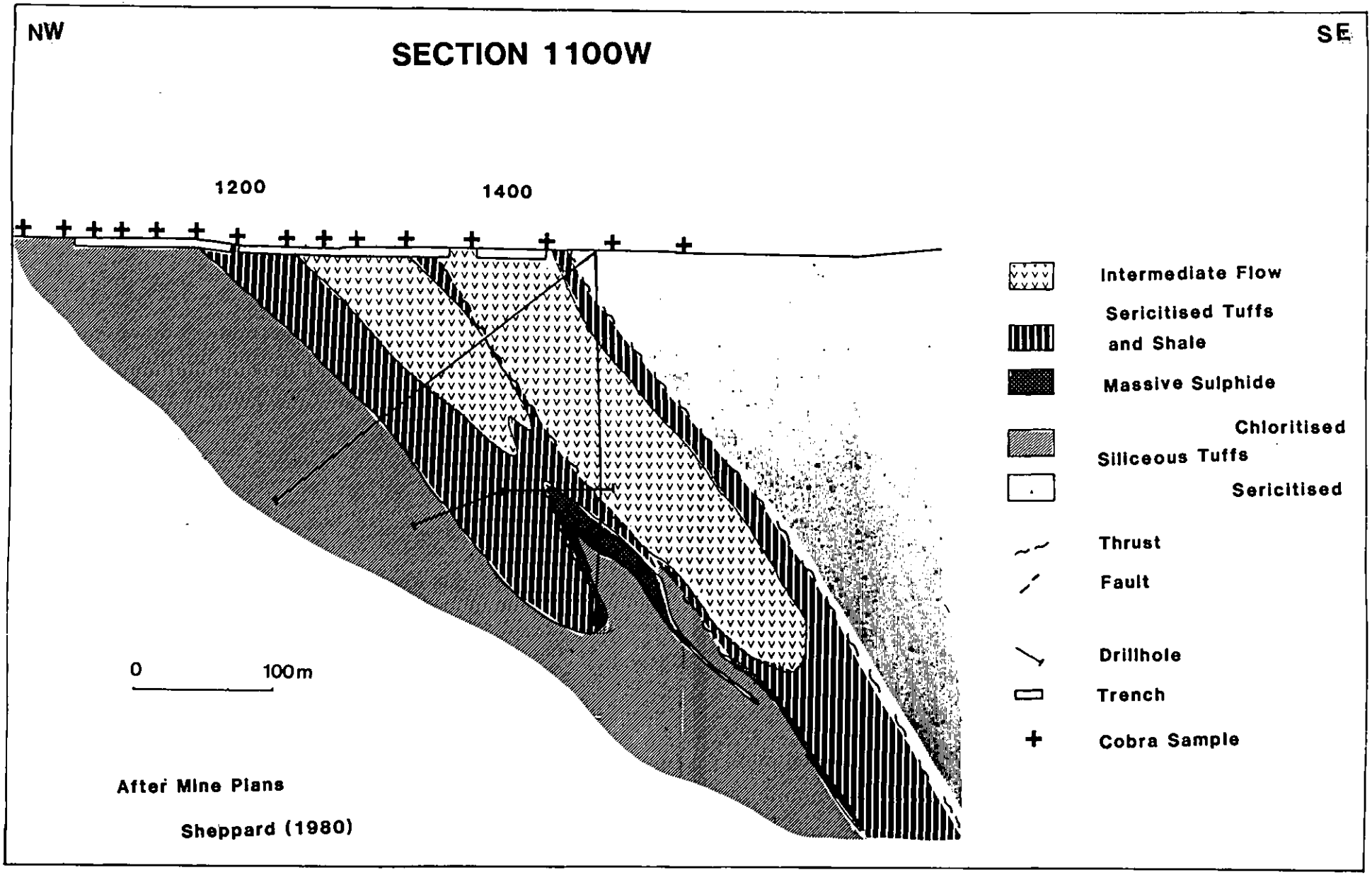


Fig 6.7 Avoca: drill section under surface traverse / trench

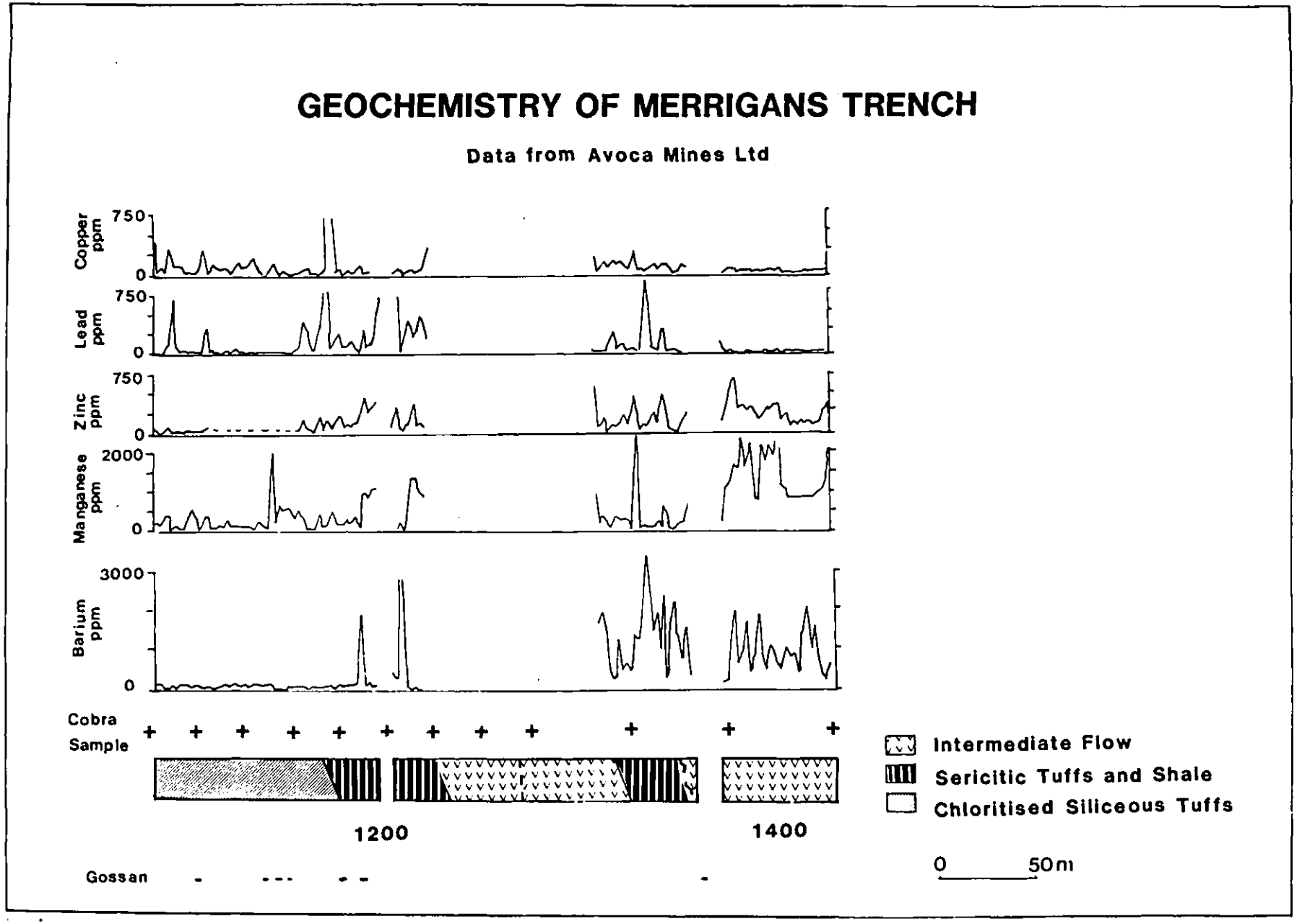


Fig 6.8 Avoca: lithology and bedrock geochemistry of Merrigan's trench

(stringer zone). High lead values (up to 750 ppm., background 10 ppm) occur at the contact with a high background in the overlying tuffs and occasional high values in the footwall. Anomalous zinc values occur within the sericitic tuff and intermediate flow unit as do high barium concentrations. Manganese, although giving a sharp peak at the siliceous tuff/sericitic tuff contact, is particularly enriched in the intermediate flow.

(ii) Basal Till Cobra Samples

The Cobra samples at the base of the till are comparable with the trench samples, although they are discrete samples rather than the continuous sampling of the trench.

The transition metal data (Fig. 6.9) is very similar to that of the trench although the high lead values can be seen to extend to the base of the intermediate flow unit.

Examination of major element data (Fig. 6.10) clearly indicates the high magnesium concentrations associated with the main copper anomaly at the siliceous tuff/sericitic tuff contact. There is also depletion in potassium and sodium at the contact while lanthanum is distinctly enriched in the ore footwall, sericitic tuff and basal intermediate flow.

The pattern of the pathfinders in the basal till are clearly developed (Fig. 6.11) with high arsenic values in the siliceous tuff (stringer zone) and, to a much lesser degree, the top of the sericitic tuff unit. Bismuth enrichment is almost entirely restricted to the stringer zone as is selenium. Antimony enrichments in contrast are confined exclusively to the upper units.

(iii) Dispersion Through the Till

Major element patterns do not persist through the

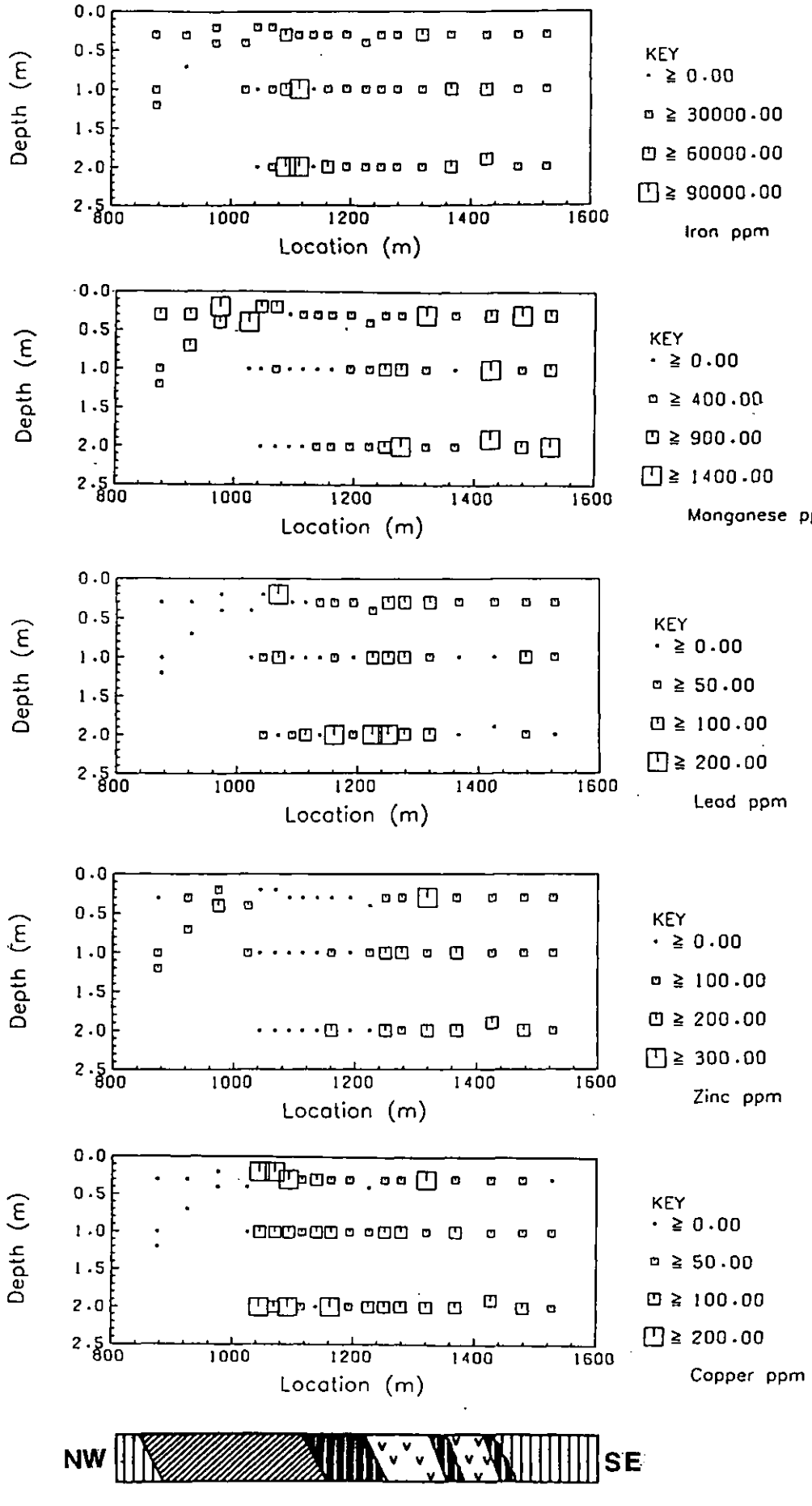


Fig 6.9 Avoca: till profile of Merrigan's trench area
Geological symbols as for Fig 6.8

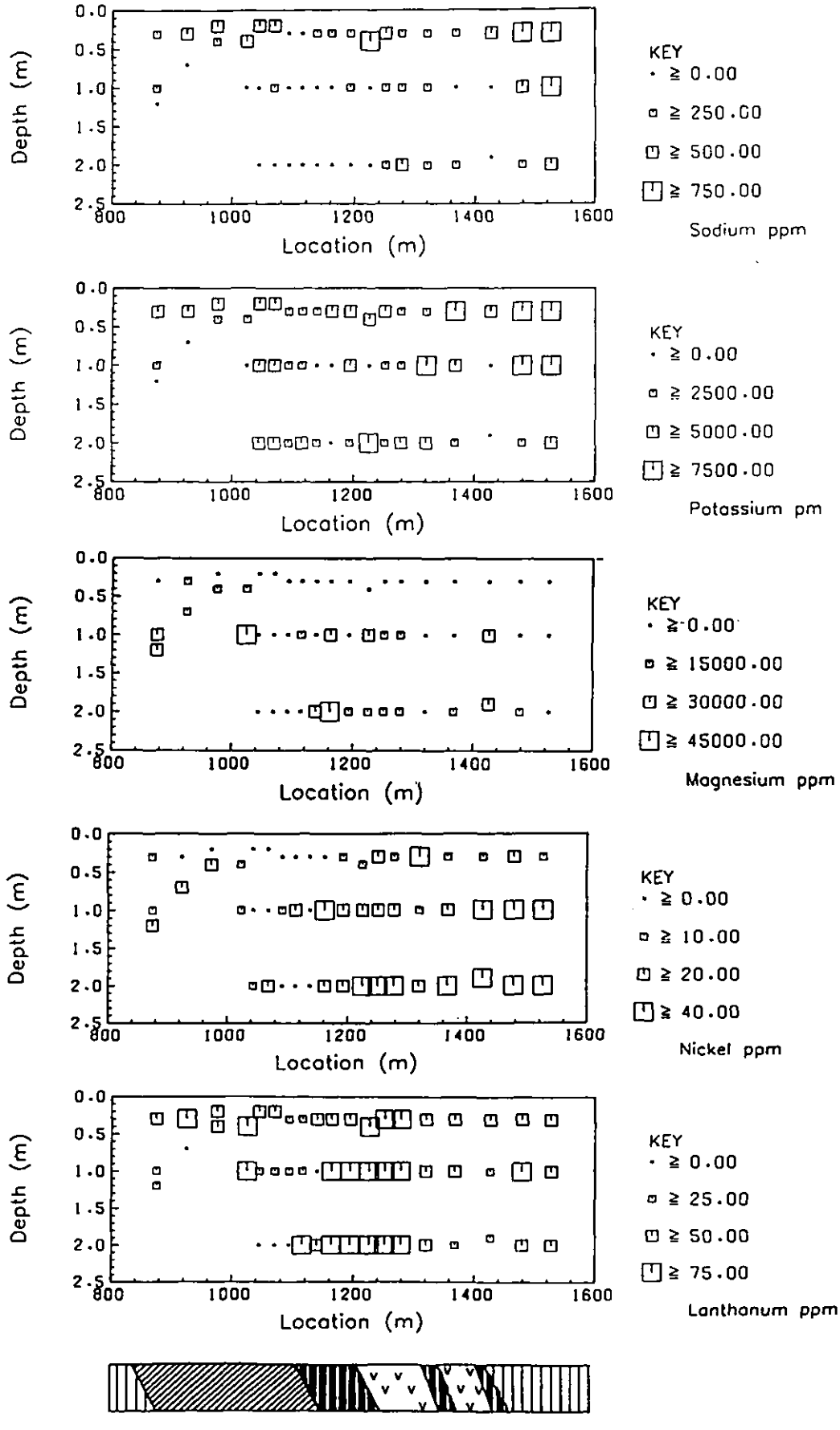


Fig 6.10 Avoca: till profile of Merrigan's trench area
Geological symbols as for Fig 6.8

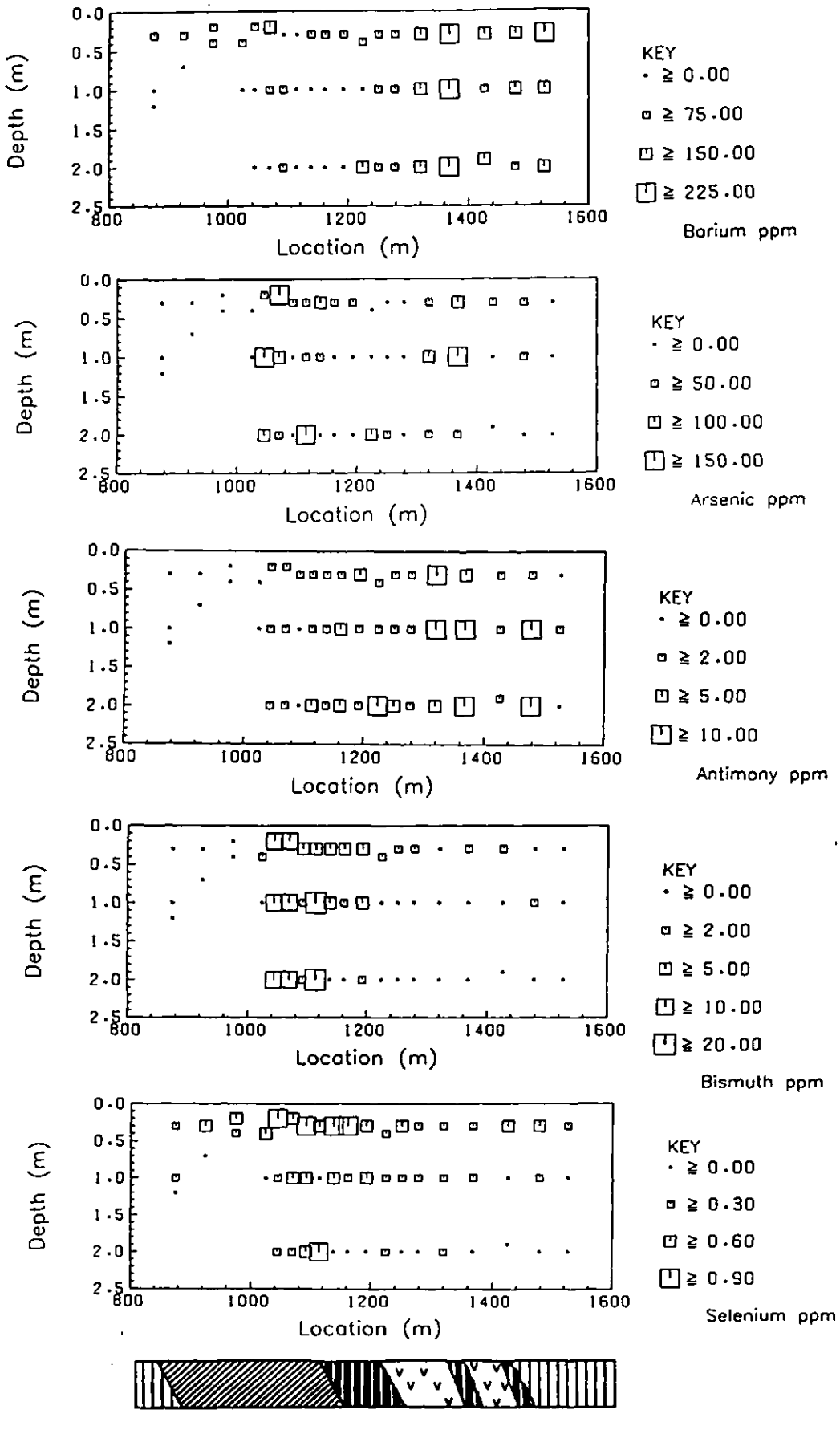


Fig 6.11 Avoca: till profile of Merrigan's trench area
Geological symbols as for Fig 6.8

till and there is no significant magnesium or potassium anomaly at surface.

The transition metals disperse to varying degrees although patterns represented may be altered slightly by contamination from a (filled in) small settling pond at 1320 m. Copper values are concentrated at surface immediately overlying the stringer zone while zinc shows a general depletion upward although there is still a zone of higher values at surface over the enriched bedrock. Lead anomalies show the gradual diminution and movement southward as one ascends the profile. Barium concentrations, in contrast, appear remarkably consistent through the profile.

Iron shows little evidence of concentration at intermediate depth while there are erratic high surface manganese values comparable to those at depth.

Arsenic values higher in the profile generally reflect bedrock concentrations although there is some southward movement and concentration at intermediate depth. The high contrast bismuth basal till anomalies broaden and become less intense with decreasing depth while basal till antimony patterns are evident at the surface although there is some enrichment at intermediate depth, as for arsenic. Selenium is very different, with the surface enriched relative to the underlying basal till and not reflecting the basal till (stringer zone) anomalies.

d) Regional Traverse

This provides some measure of the applicability of specific element anomalies recognised over the subcrop of the mineralization: data for both basal till and soil samples are available.

Major elements are useful only for basal till samples, (Fig. 6.12). Both sodium and potassium are low over the footwall of the mineralization (2000 ppm K, average

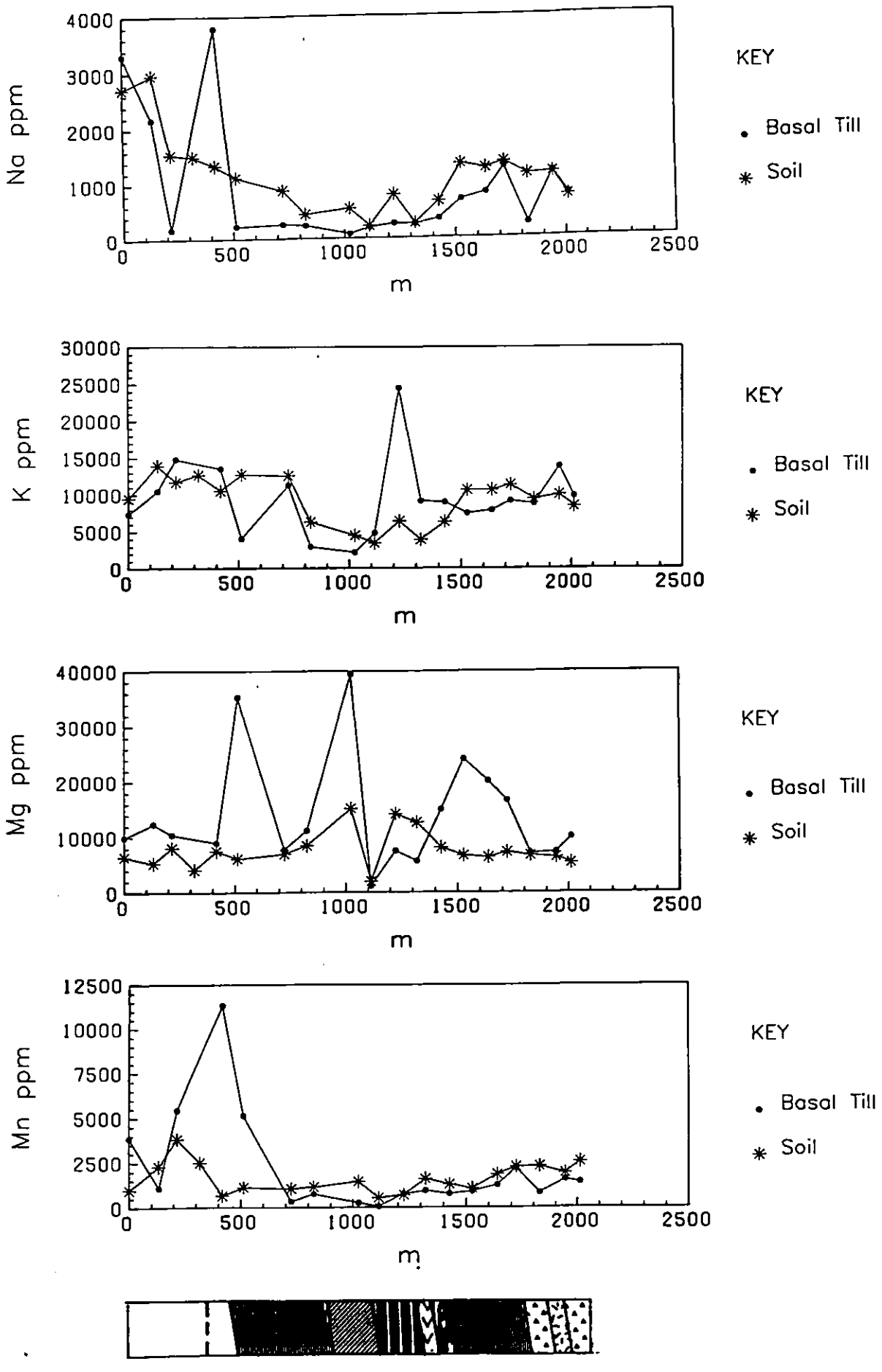


Fig 6.12 Avoca: regional soil-till traverse
Geological symbols as for Fig 6.1

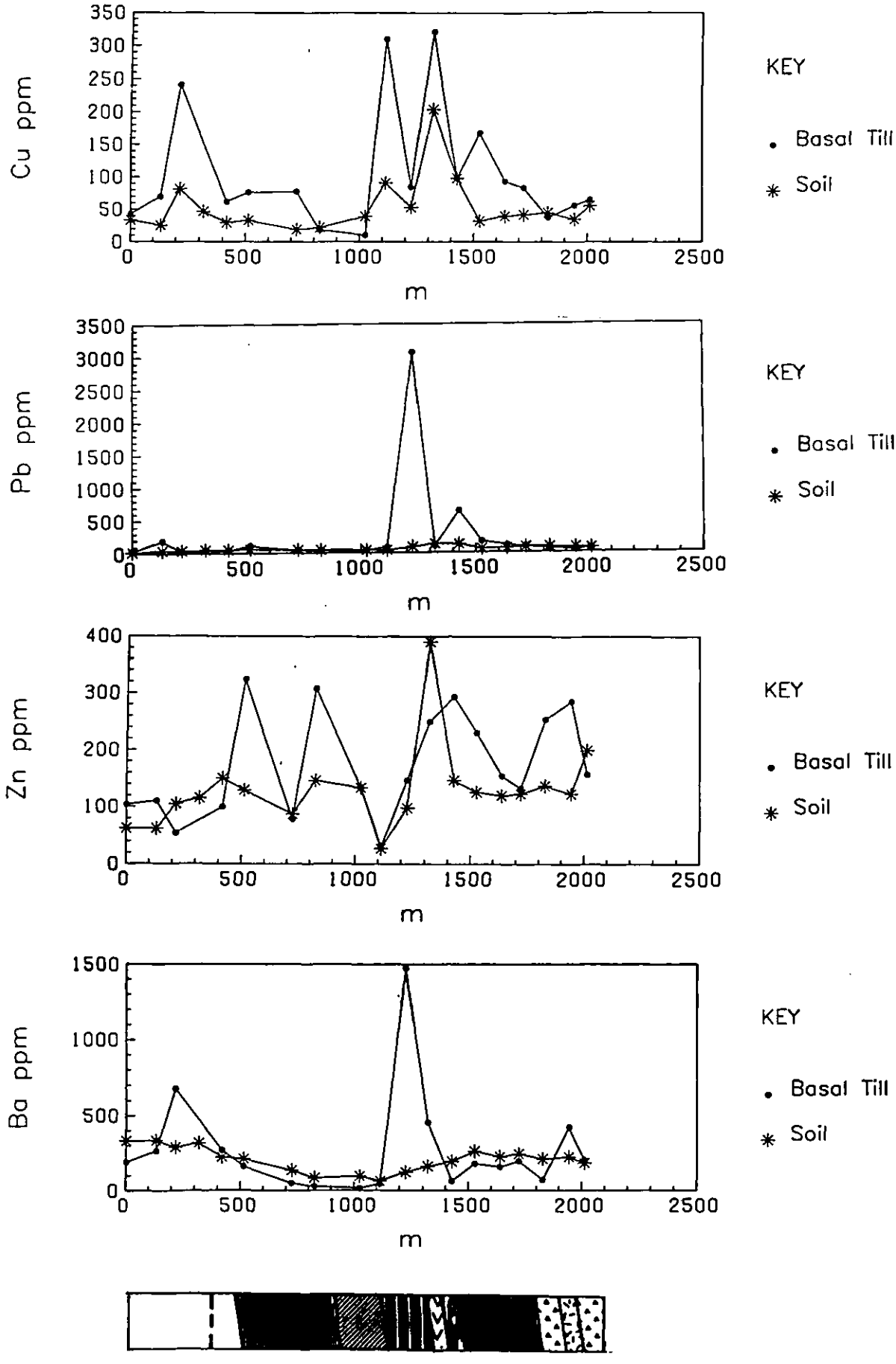


Fig 6.13 Avoca: regional soil-till traverse
Geological symbols as for Fig 6.1

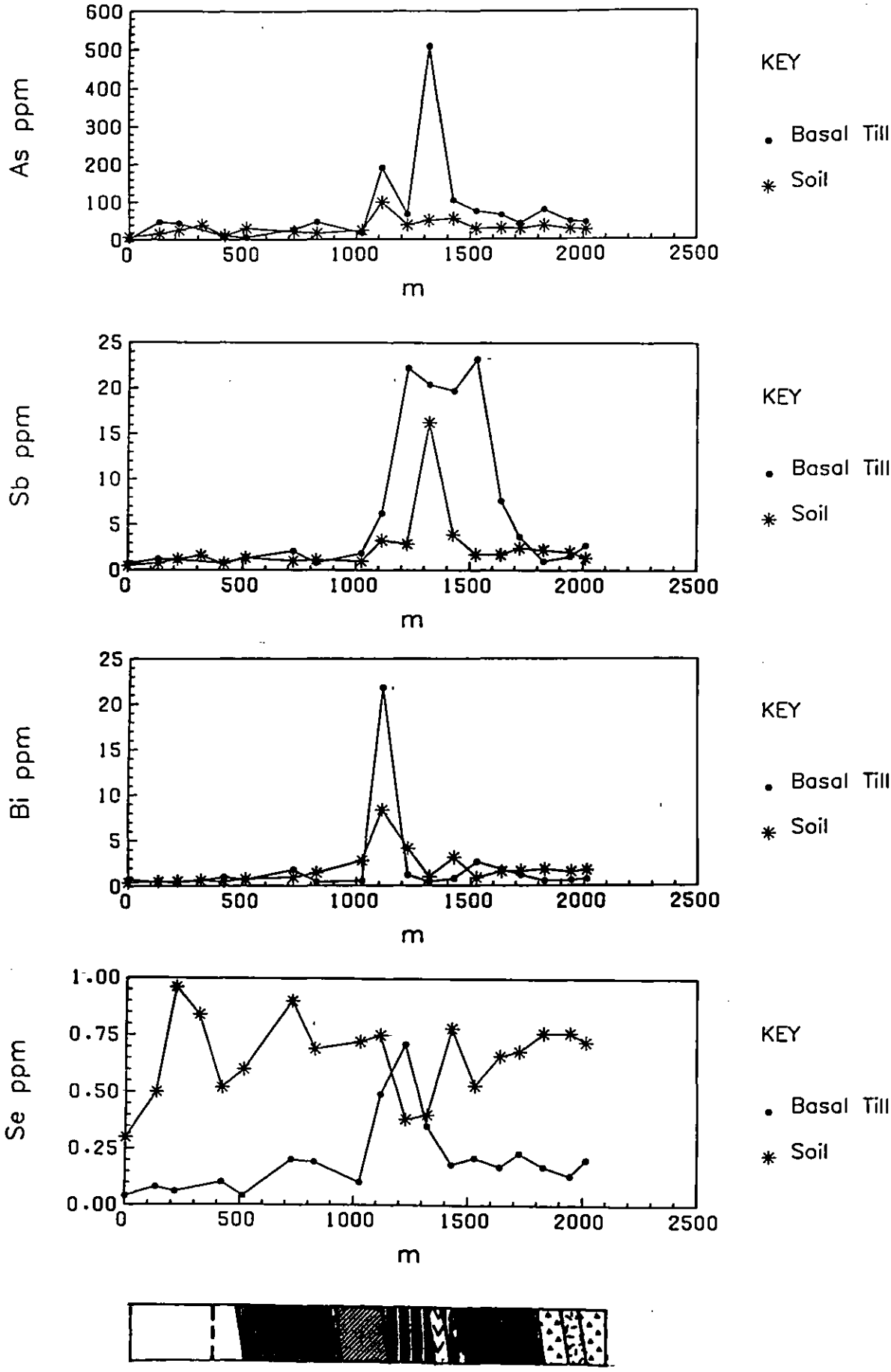


Fig 6.14 Avoca: regional soil-till traverse
Geological symbols as for Fig 6.1

8000 ppm K; and 100 ppm Na average 500 ppm Na in basal till) but the depletions are broad and hardly definitive. Magnesium is high near the ore (40000 ppm Mg peak, 13000 ppm Mg background) but the patterns are rather erratic, as are those of basal till lanthanum with the southern high correlatable with rhyolite. In the surface soils, no major element patterns of significance can be recognized.

The transition metal data does, however, indicate the mineralization. Copper has peaks of 300 ppm in basal till samples compared with a background of 70 ppm. There is a secondary peak of 250 ppm at 250 m, where bed rock is mapped as sediments of the Ribband Group. Soil samples have the same overall pattern although the anomalies are of low amplitude. Lead has particularly a strong single point anomaly of thirty times anomaly/background contrast compared with the broad surface highs. Barium has high contrast anomalies in basal till samples which are not preserved at the surface, while there is no zinc anomaly at depth but a single point high at surface.

The pathfinder concentrations generally define the subcrop of the mineralization (Fig. 6.14). Arsenic has discrete anomalies, of up to 500 ppm As versus a background of 40 ppm As for basal till, with a high background in the south of the traverse; and a similar pattern in the soil samples. There is a broad and high contrast basal till antimony anomaly (20 ppm peak, 1 ppm background) over the sericitic tuff/intermediate flow and part of the sericitic siliceous tuffs. Soil sample anomalies are less well developed. Bismuth has a sharp, single point high in the basal till (anomaly 20 ppm Bi, background 0.5 ppm Bi) with a much broader soil high. Selenium shows a very different pattern with a distinct but low contrast basal till high (0.8 ppm Se anomaly, 0.1 ppm Se background) but the surface samples are low over the suboutcrop of

the copper mineralization.

6.1.3 Discussion

(a) Primary Concentration/Lithogeochemistry

Both the basal till and subsurface samples show a distinct zonation in majors, transition metals and pathfinders. These are summarised in Table 6.2 and are a combination of enrichment and depletion.

The depletion in sodium and potassium and enrichment in iron, magnesium and manganese are consistent with the larger study of Sheppard (1980a) who also recognised barium and manganese enrichment in the hangingwall sediments. These patterns are similar to those observed from many other massive sulphide deposits (Franklin et al, 1981).

The transition metal patterns are of copper enrichments in the footwall and at the (copper) ore horizon while lead and zinc concentrations are stratigraphically higher in the sequence and more distal from the source of the mineralizing fluids (Sheppard, 1980). The data presented also suggest that much zinc (and barium) is dispersed through the overlying sequence rather than concentrated in sulphide deposits. These patterns are similar to those described in classic Kuroko area of Japan (Shimazaki, 1974).

The novelty of the present study is the description of pathfinder zonation. Bismuth is correlatable with magnesium and is concentrated in the footwall (stringer) and pyritite zones while arsenic is present throughout the mineralized sequence and antimony in a position similar to that of zinc and barium. Selenium has a rather ambiguous concentration, in the stringer zone at surface and in the hangingwall sediments in the subsurface.

This zonation correlates well with the qualitative mineralogical studies of Wheatley(1971) in which arsenopyrite is concentrated in the upper part of the sequence

Table 6.2 Summary: Zonation Avoca

	Stringer Zone	Pyritite	Lead-Zinc Zone
Na	—	—	
K	—	—	
Mg	+	+ +	
Mn	+	+	+ +
Fe	+	+ +	
Cu	+	+ +	+
Pb		+	+ +
Zn		+	+ +
As	+	+	+
Sb		+	+ +
Bi	+	+ +	
Se	+	+	

— Depleted

\+ Enriched

\+ + Strongly Enriched

(Table 6.3) while antimony sulphosalts are present in the stringer and massive sulphides. Native bismuth and bismuth sulphosalts (aikinite, kobellite and lillianite) are restricted to the lower part of the mineralized succession. The occurrence of antimony sulphosalts in the stringer zone is probably explained by the occasional occurrence of lead and zinc in that zone in the eastern part of the mine. The pathfinder distribution has considerable similarity to the limited data available from the Kuroko type area in Japan. Typically concentrations are 180 ppm Bi, 230 ppm Sb and 350 ppm As in the massive pyrite; 140 ppm Bi, 80 ppm Sb and 170 ppm As in the stockwork zone and 20 ppm Bi, 290 ppm Sb and 1030 ppm As with the black (sphalerite-galena) ore (Shimazaki, 1974). The mineralogy is also similar to that described at Avoca.

The pathfinder zonation, thus, seems to fit into an overall pattern which has emerged over the last ten years. I consider this to be caused by the relative thermal stability of the metal/pathfinder complexes. However this zonation is by no means universal (cf Petersen and Lambert, 1979) and other factors which may control it are paleo-water depth (Finlow-Bates, 1980), and source area, element availability (Franklin et al, 1981). The problem of the quantity of magmatic input, as opposed to leaching of sediment/volcanics, into mineralizing solutions is by no means resolved and may, considering the geochemistry of bismuth, have an important bearing on its content in ores.

Pathfinder zonation and, in particular, ratios of arsenic and antimony to major elements such as sodium are beginning to find application in lithogeochemistry (Møller et al, 1982; Scott et al, 1982). These studies show that widespread supra-ore arsenic and antimony haloes are developed around some massive sulphide deposits.

DISTRIBUTION OF ORE MINERALS

	Mineralized Zones		
	Siliceous	Pyritite	Lead-Zinc
Pyrite	●	●	●
Chalcopyrite	●	●	✪
Sphalerite	✪	✪	●
Galena	✪	✪	●
Magnetite	○	★	○
Pyrrhotite	☆	☆	○
Cobaltite	☆	○	○
Arsenopyrite	☆	★	✪
Tetrahedrite	☆	○	☆
Bournonite	☆	○	☆
Native Bismuth	☆	☆	○
Galenobismutite	○	☆	○
Aikinite	○	☆	○
Kobellite	☆	○	○
Lillianite	☆	○	○
Gold	○	☆	○

● Major ☆ Trace

✪ Minor ○ Absent

★ Accessory

After Wheatley (1971)

Table 6.3 Ore mineralogy : Avoca

Another recent study in Fiji (Rugless, 1982) confirms the restriction of bismuth to the mineralization.

The zonation/regional distribution of pathfinder and of other elements, notably mercury, gold, molybdenum and tin, merits considerable further research.

b) Secondary Dispersion

Dispersion through the till seems largely hydromorphic. The major element patterns are rapidly diluted with decreasing depth and elements such as magnesium are leached from the near surface. The transition metals appear to reflect their surficial mobilities with limited dispersion of lead and barium downslope (and downice). Copper and zinc are widely dispersed with zinc probably leached from the surface.

By comparison with the transition metals arsenic is mobile and is concentrated to some extent in iron accumulations at intermediate depth. Antimony is relatively insoluble and its behaviour is comparable with lead although there is some association with iron at intermediate depth. Smearing of the restricted bismuth basal till anomalies suggests that it is somewhat mobile. The behaviour of selenium is enigmatic although dispersion is masked by its concentration in near surface organic rich material. The low over the orebody in the surface layer could reflect the increased concentration of inorganic selenium near sulphide mineralization and thus the increased availability for volatilisation (Zeive and Peterson, 1981).

The high contrast bismuth and antimony anomalies are a substantial addition to the low contrast copper and lead data. Overall, surveys within South East Ireland should utilise basal till samples and be analysed for Cu, Pb, As, Bi with Zn and Sb as useful additions. A spacing of 50m. is indicated for detailed sampling

6.2 Meall Mor, Strathclyde, Scotland

This mineralization is part of a belt of sulphide occurrences in the lower Cambrian Argyll Group that stretches throughout the Southern Highlands (Willan, 1980). Further east this belt includes the barite deposit at Aberfeldy. At Meall Mor the mineralization is copper sulphides within a broad pyritiferous zone. The known association of antimony with the copper mineralization suggested the investigation (Smith et al, 1978).

6.2.1 Geology (Smith et al, 1978)

a) Solid Geology

The host unit to the mineralization is the Upper Erins Quartzite (Fig. 6.15), which although dominantly quartzitic shows gradation from orthoquartzite to mica schist. This unit overlies the Stronchullin Phyllite, which is similar to Upper Erins Quartzite, except that it contains minor black shales. The Upper Erins Quartzite also contains minor limestone units and a considerable volume of amphibolite. This amphibolite probably mainly represents metamorphosed basic sills (epidiorite) but some material may be synsedimentary in origin.

The whole sequence has been subject to polyphase Caledonian deformation and green schist facies metamorphism. The sediments strike NNE in general and are inverted, forming the root anticline of the major Tay Nappe. This complex deformation means that detailed stratigraphy is largely unknown.

The zone of weak pyrite enrichment is about 10 km in length and 200 - 800 m in width (less than 200 m true thickness): pyrite forms up to 10% of the pelite and 20% of the quartzites. Disseminated copper sulphides occur throughout the pyritiferous zone as discrete trails

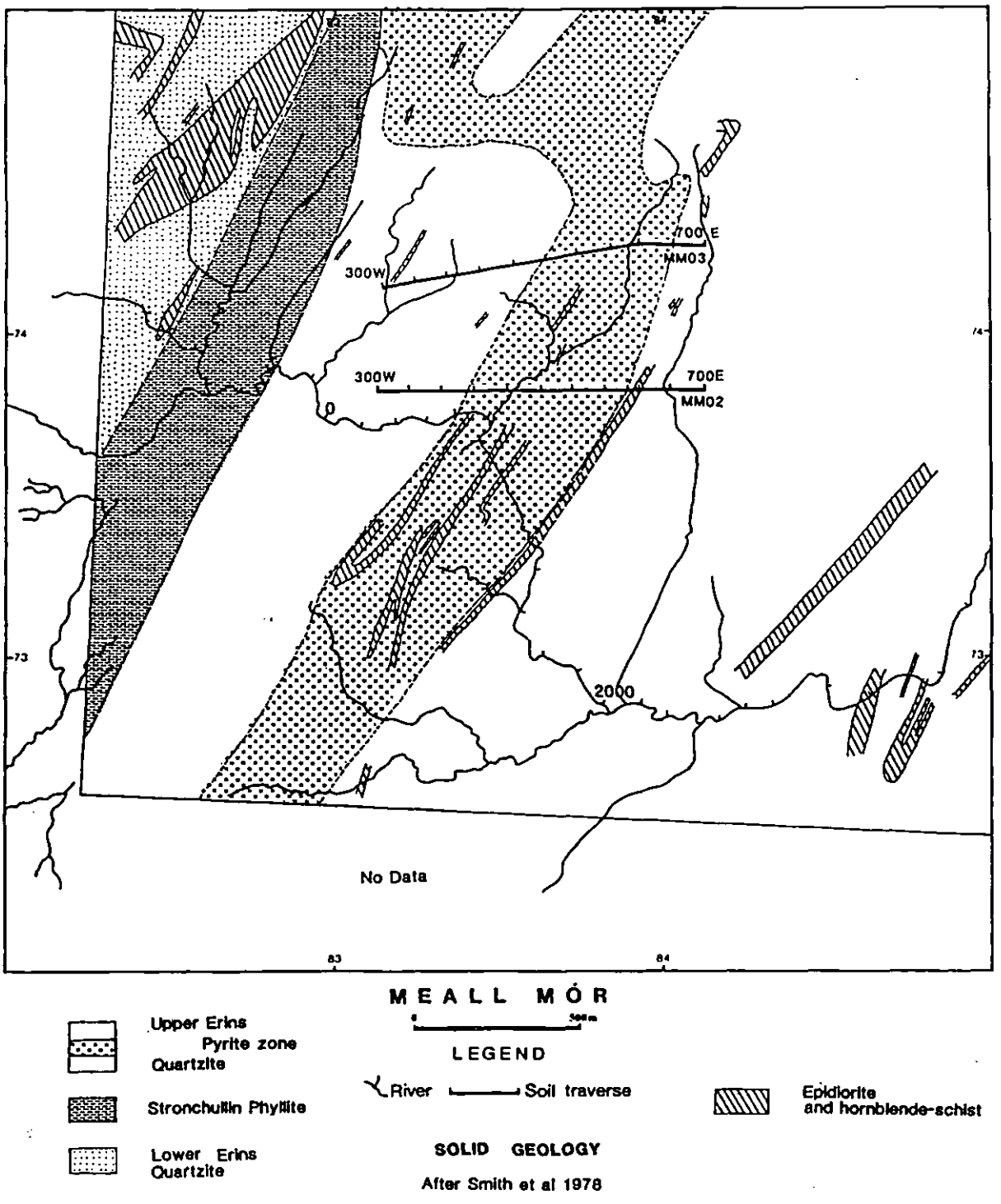


Fig 6.15 Meall Mor: solid geology

which parallel the early schistosity/bedding. The main chalcopyrite/bornite occurrences (including those in the area investigated in detail) are cross-cutting, associated with epidotisation and probably formed by remobilisation. Minor (mainly microscopic) amounts of sphalerite and stibnite are associated with the mineralization. The distribution of galena is not understood but may be associated with quartz-feldspar veins as well as stratiform mineralization.

b) Surficial Geology

The area has been glaciated but the drift is thin and probably non-exotic in origin. An extensive thin peat cover overlies the till with thicker peat accumulations in hollows.

6.2.2 Programme

The investigation was restricted to the area of the old Abhainn Strathain mines, where the most intense copper soil anomalies are developed (Smith et al, 1978).

Two soil traverses (MM02 and MM03) transect the pyrite zone and roughly parallel deep sampling traverses of the I.G.S. Both till and peat samples were collected, where possible.

The main river, and its tributaries, draining the mineralization were sampled for stream sediments. These sediments draining the area anomalous in antimony were separated into several size factors. In addition, a limited number of water samples were collected along the anomalous stretch of river.

Flavio Tavora undertook a limited amount of rock sampling around the main mineralized area and results are presented here.

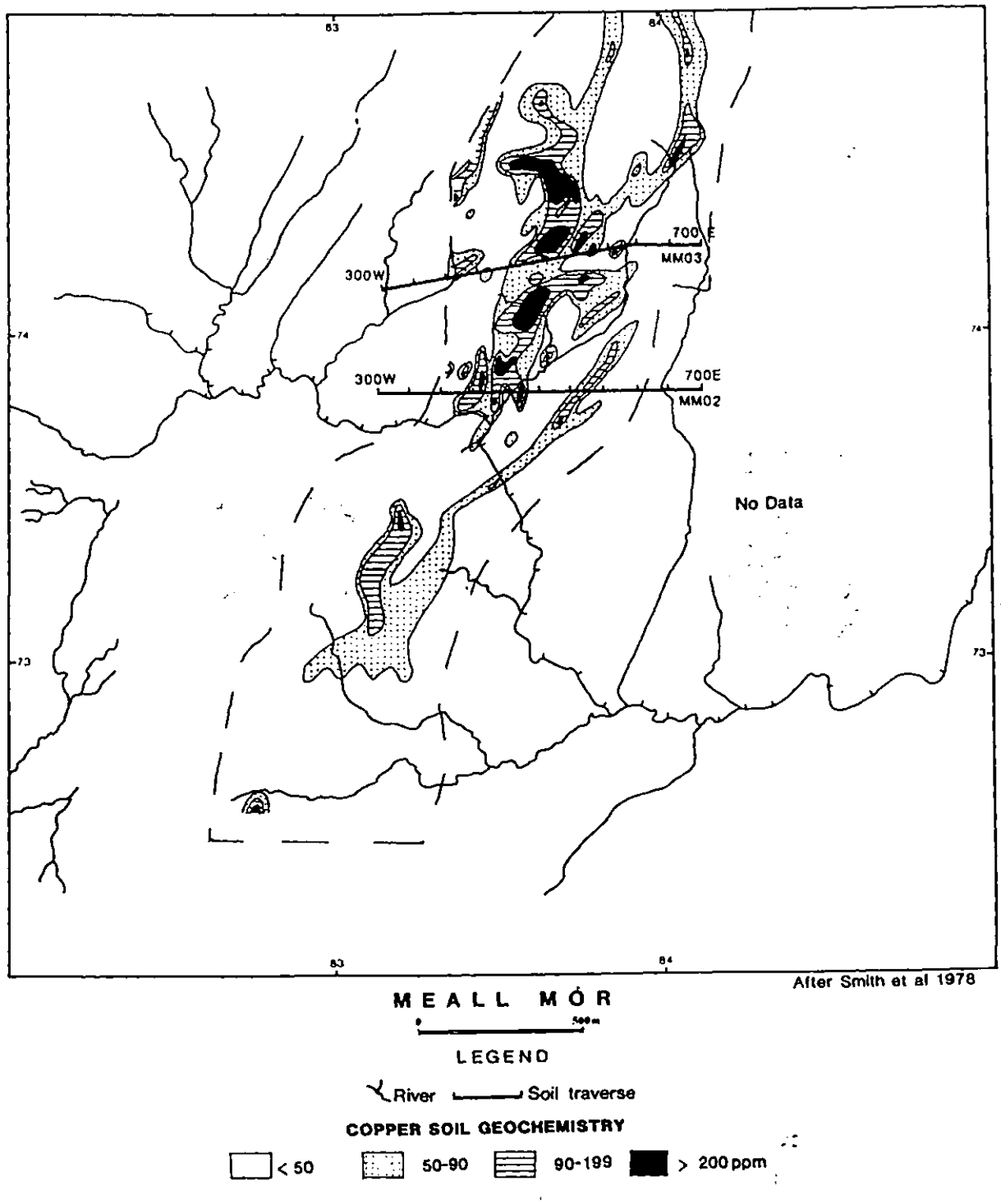


Fig 6.16 Meall Mor: regional copper soil geochemistry

a) Lithogeochemistry (Traverse MM04)

The thirteen samples transect the pyritiferous zone and both copper and zinc highlight the northern part of the main mineralization (Fig. 6.17) as indicated by mineralized outcrops. The copper and zinc highs occur within the broader iron high of the pyritiferous quartzite which also has more spatially restricted manganese enrichments. The copper and zinc high correlates with high selenium values (Fig. 6.18). Antimony is strongly anomalous with high values both in some of the copper rich samples and in arsenic rich quartzites on the southern edge of the pyritiferous zone. The bismuth pattern is much more regular with no definite anomaly.

b) Soil Traverses MM02 and MM03

The traverses transect two different types of mineralization. The main soil copper anomaly on MM03 is thought to be relatively homogenous and underlies quartzite hosted mineralization while the linear south eastern anomaly (Fig. 6.16) is associated with epidiorite and is probably veinlike, (Smith et al, 1978).

Examination of unzoned till traverses (Figs 6.19 - 6.22) confirms the regional copper distribution obtained by I.G.S. and the general association of zinc with copper. The more consistent anomalies of MM03 (reaching 600 ppm Cu and 1400 ppm Zn relative to backgrounds of 20 and 50 ppm) occur within the pyrite rich zone (200 - 500 m), as indicated by iron and similar manganese distribution. The distribution of copper on MM02 is more erratic perhaps reflecting the veinlike nature of some of the mineralization.

The distinction between the two traverses also applies to the pathfinders. Selenium correlates strongly with

MEALL MÓR
LEGEND
SOLID GEOLOGY

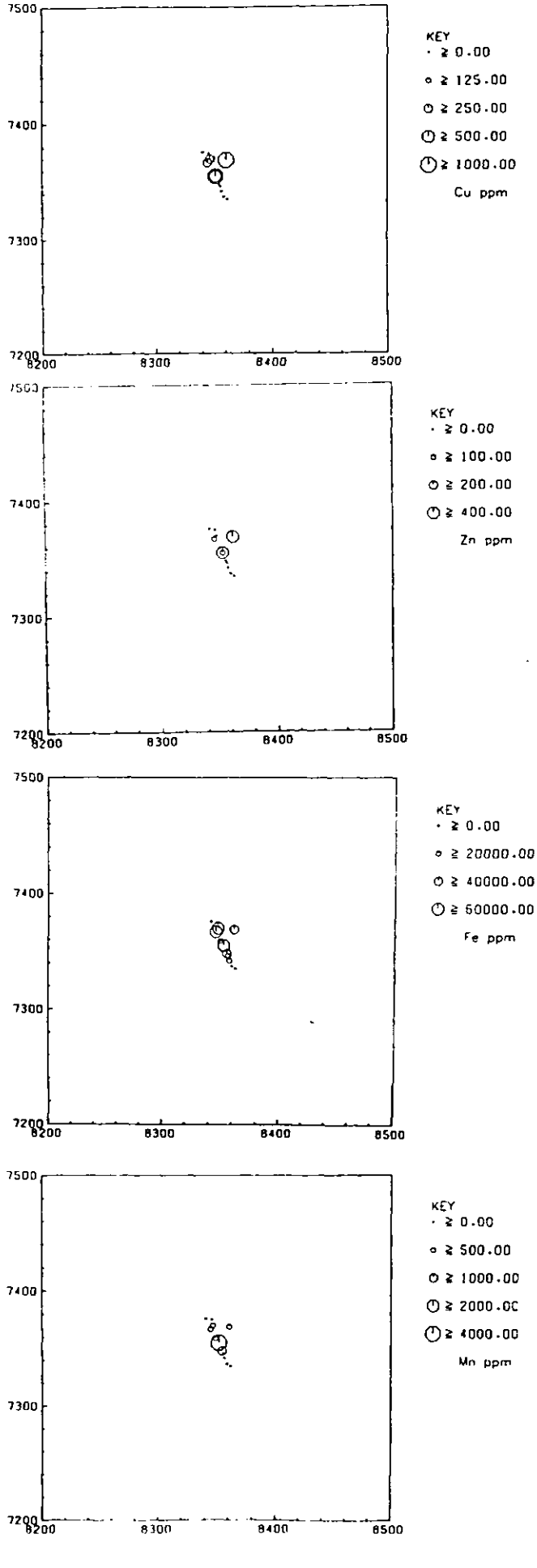


Fig 6.17 Meall Mor: lithogeochemistry MM04
Overlay of geology opposite

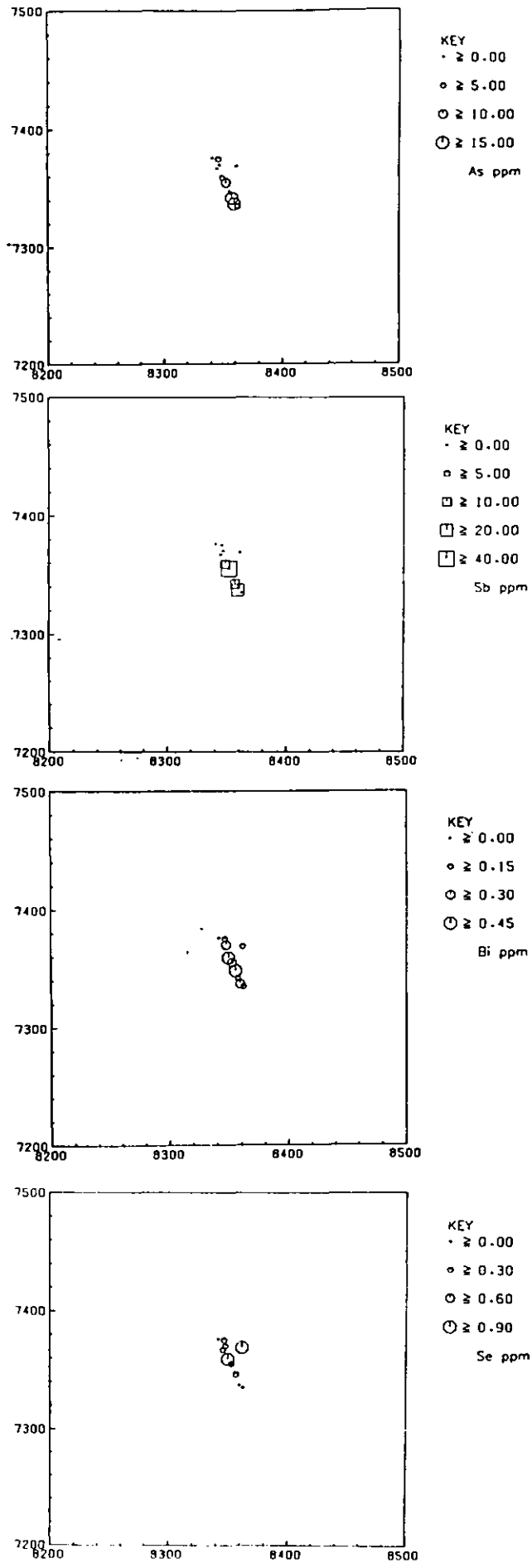


Fig 6.18 Meall Mor: lithogeochemistry MM04

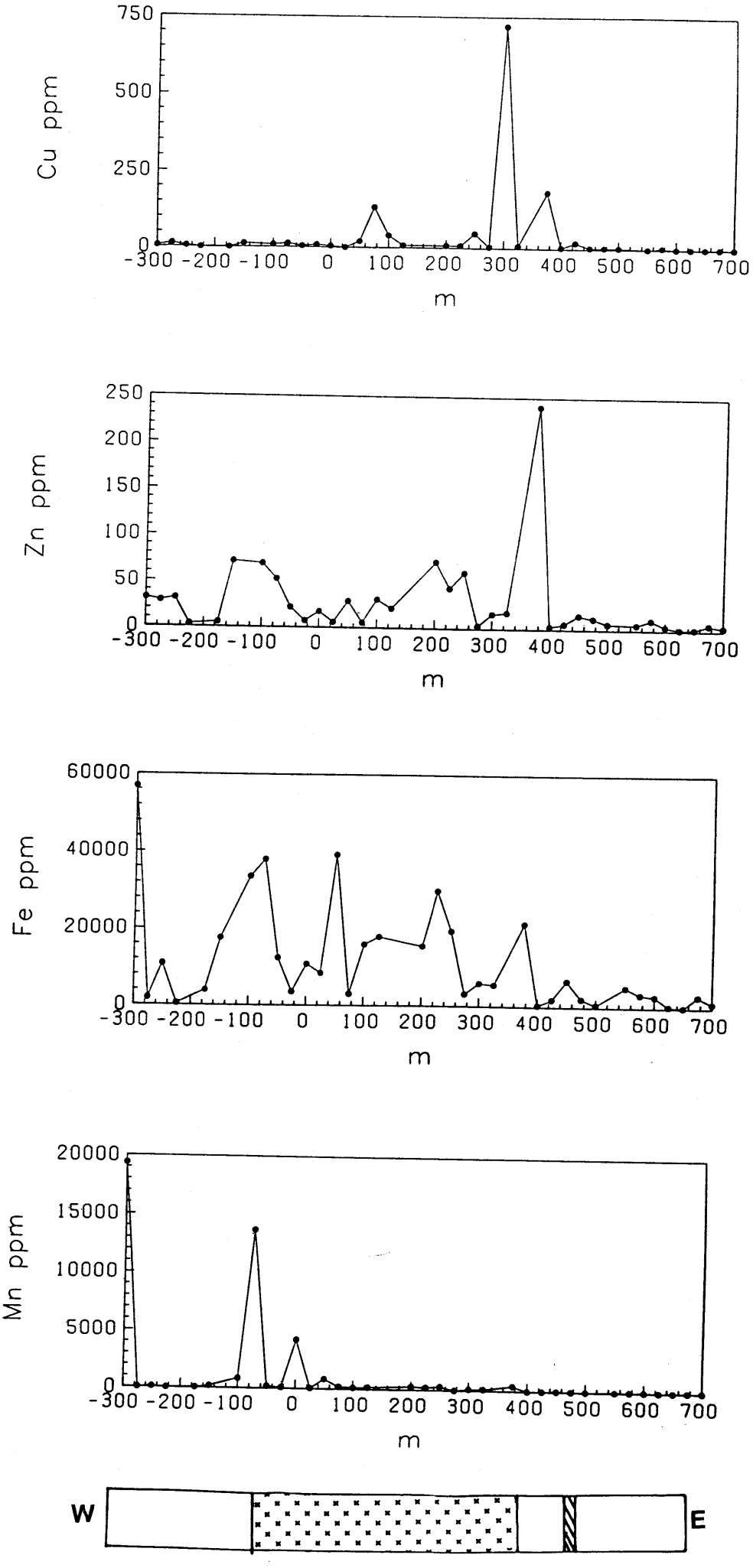


Fig 6.19 Meall Mor: till traverse MM02
Geological symbols as for Fig 6.15

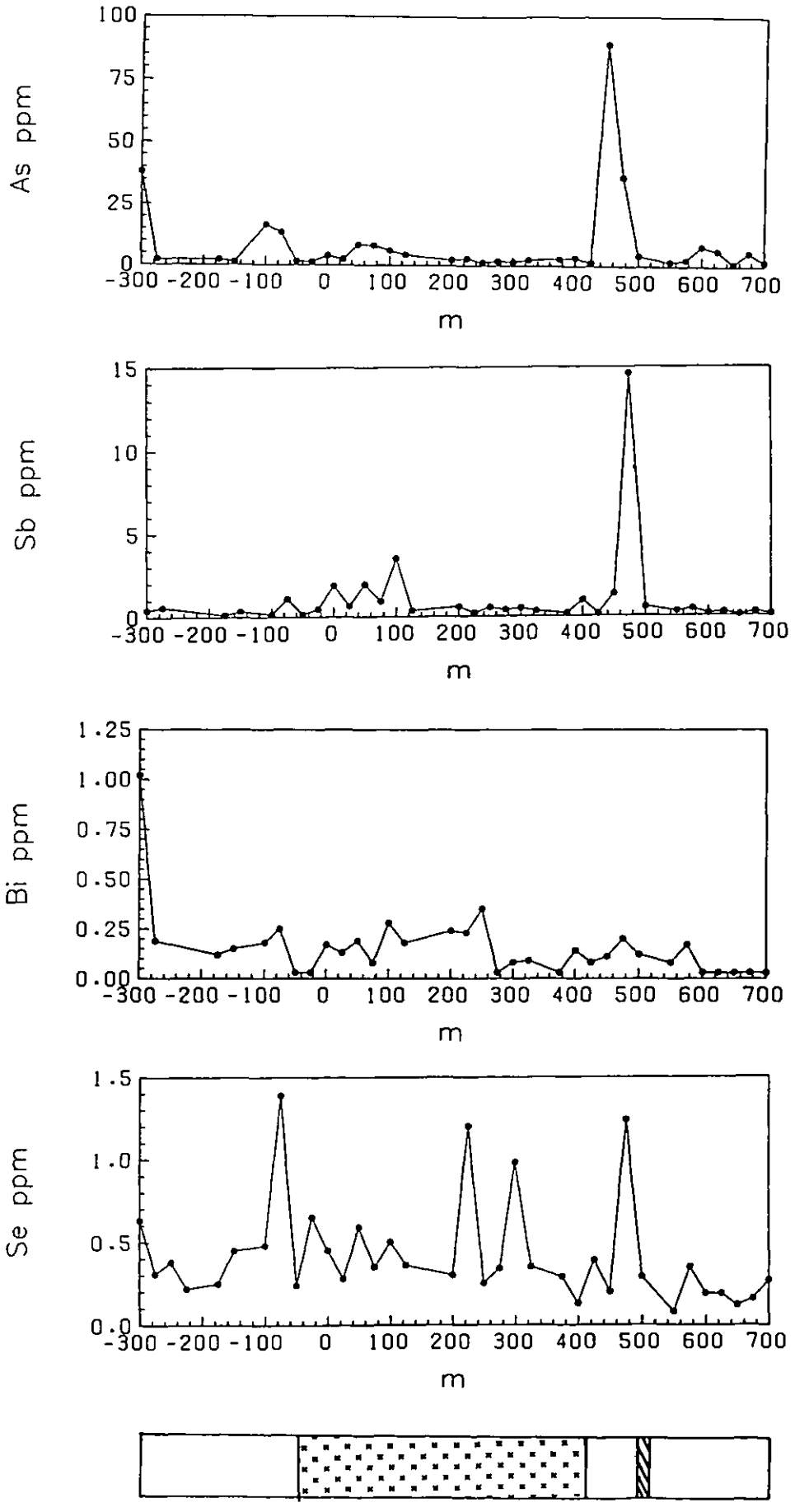
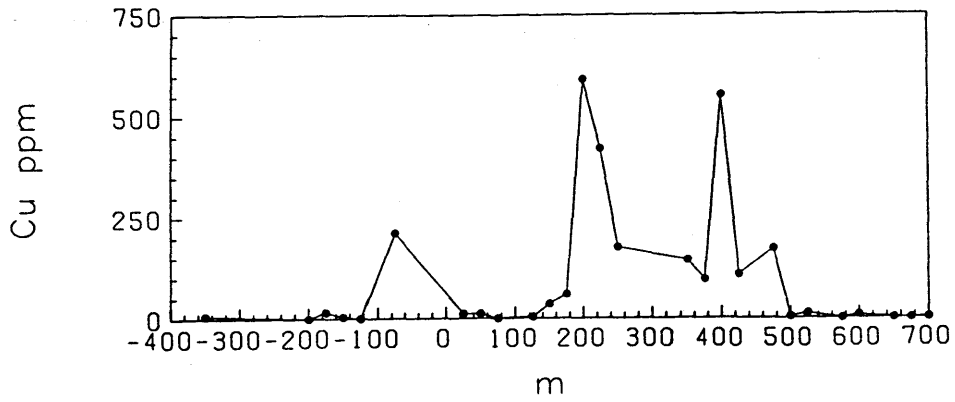
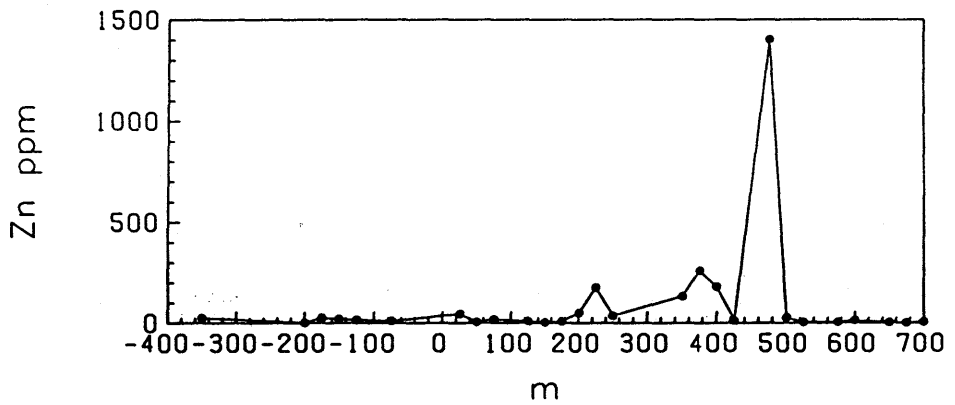
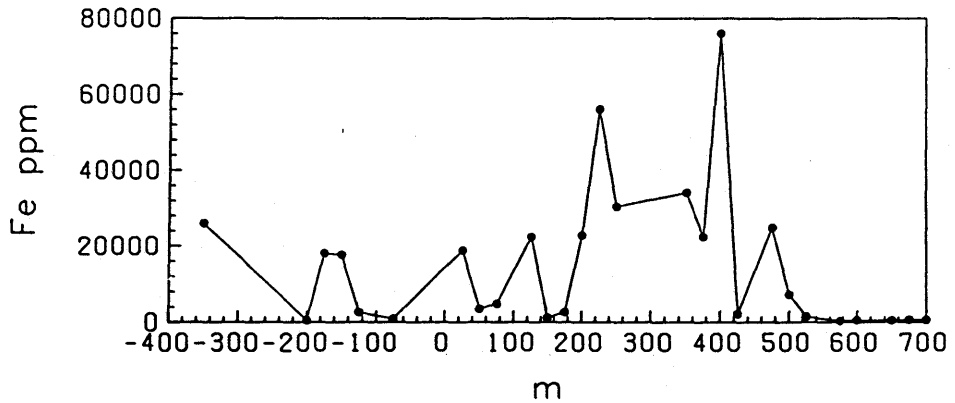
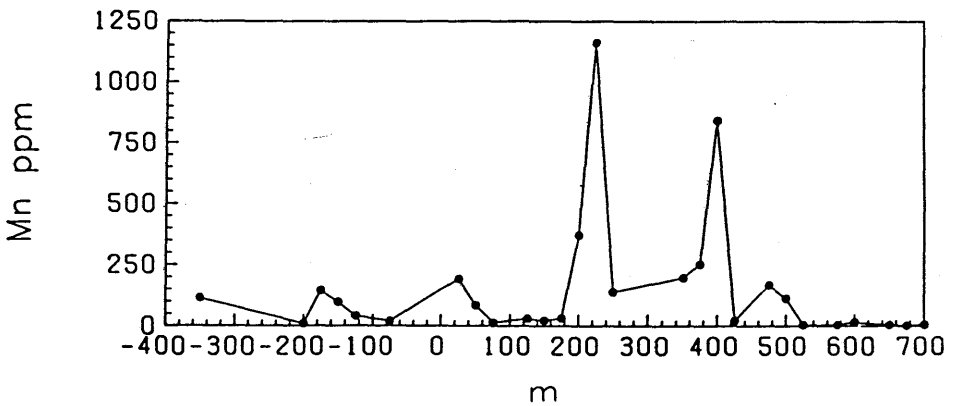


Fig 6.20 Meall Mor: till traverse MM02
Geological symbols as for Fig 6.15









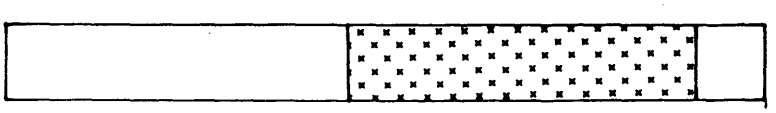


Fig 6.21 Meall Mor: till traverse MM03
Geological symbols as for Fig 6.15

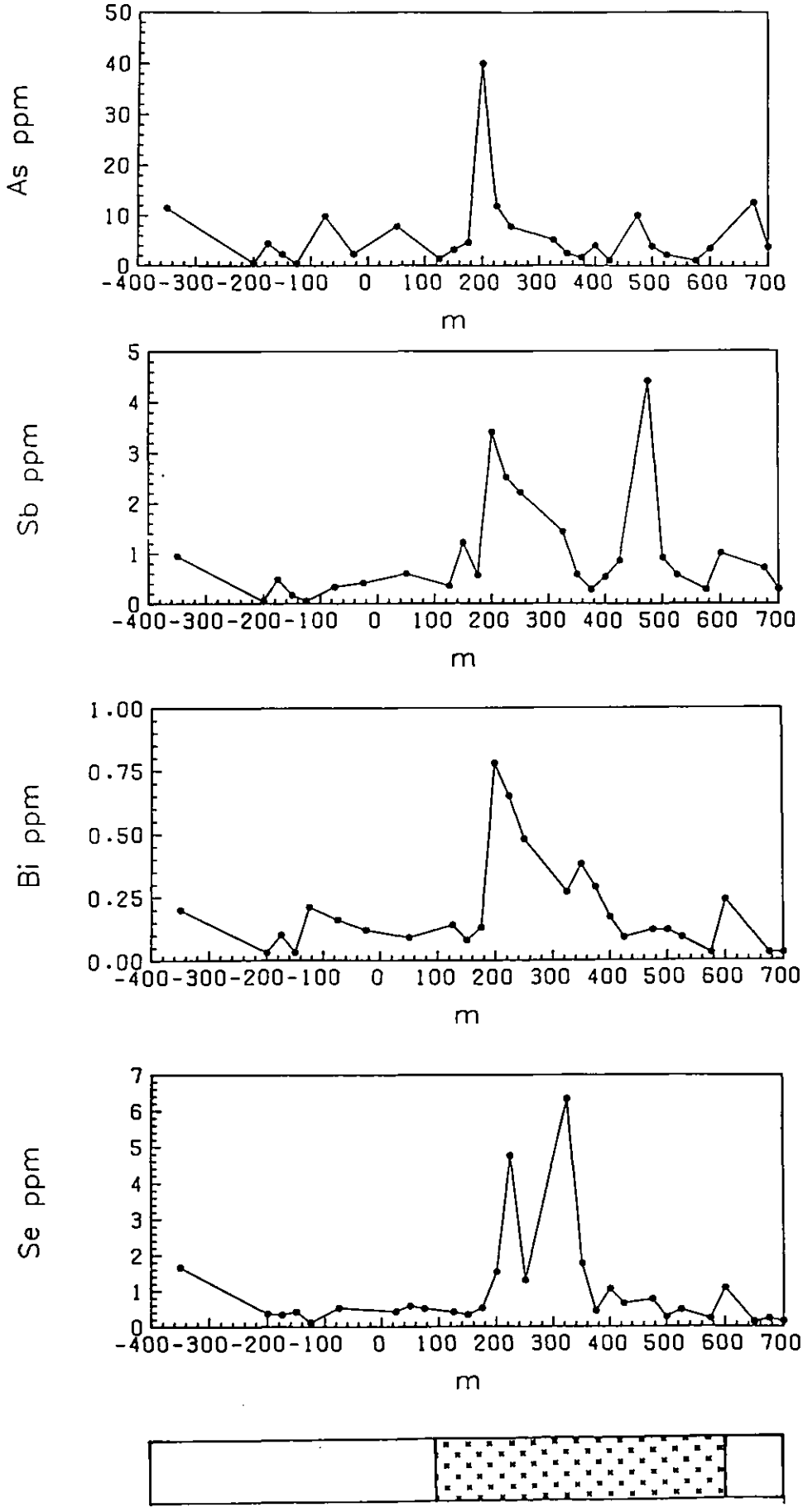


Fig 6.22 Meall Mor: till traverse MM03
Geological symbols as for Fig 6.15

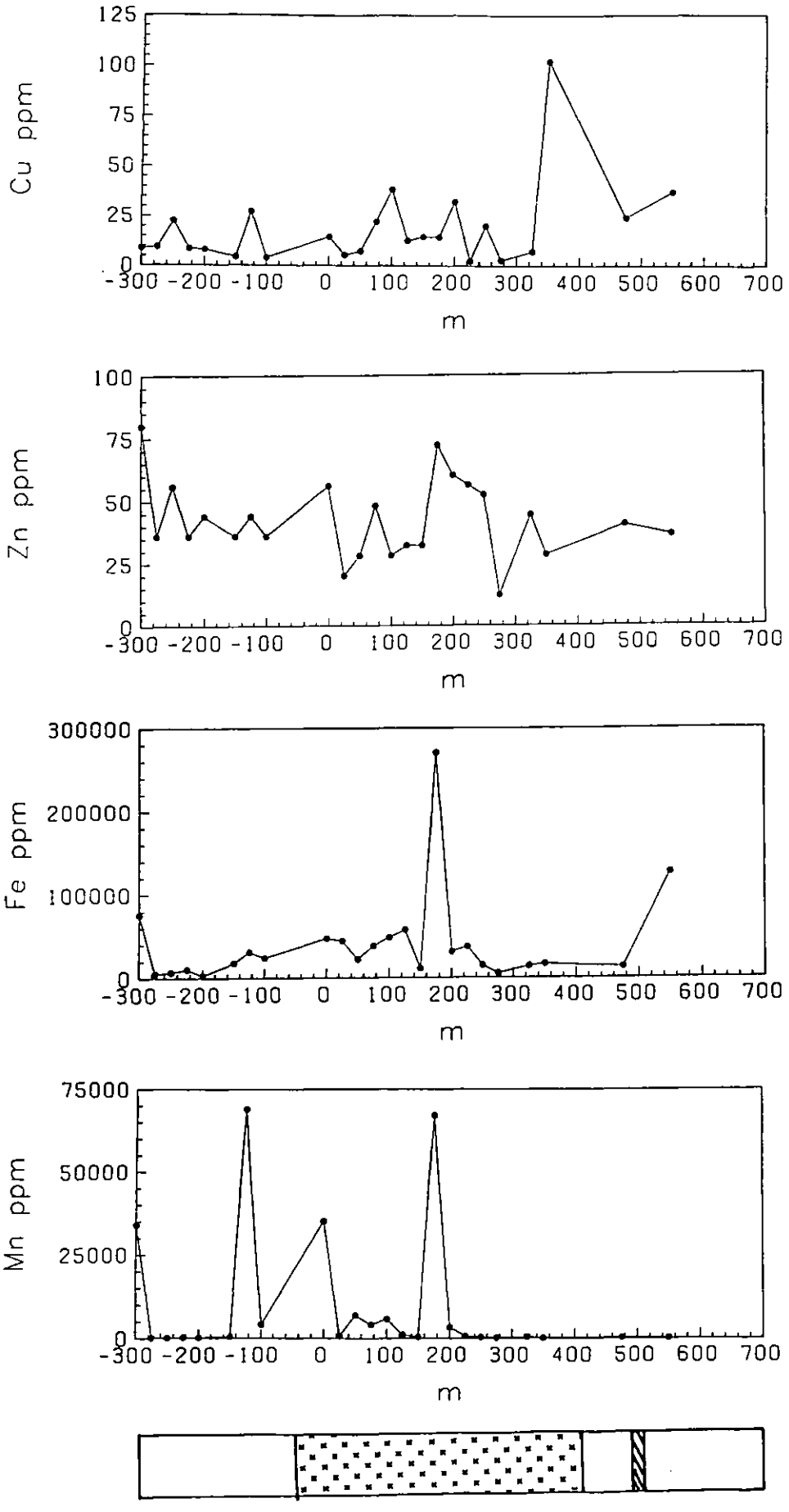


Fig 6.23 Meall Mor: peat traverse MM02
Geological symbols as for Fig 6.15

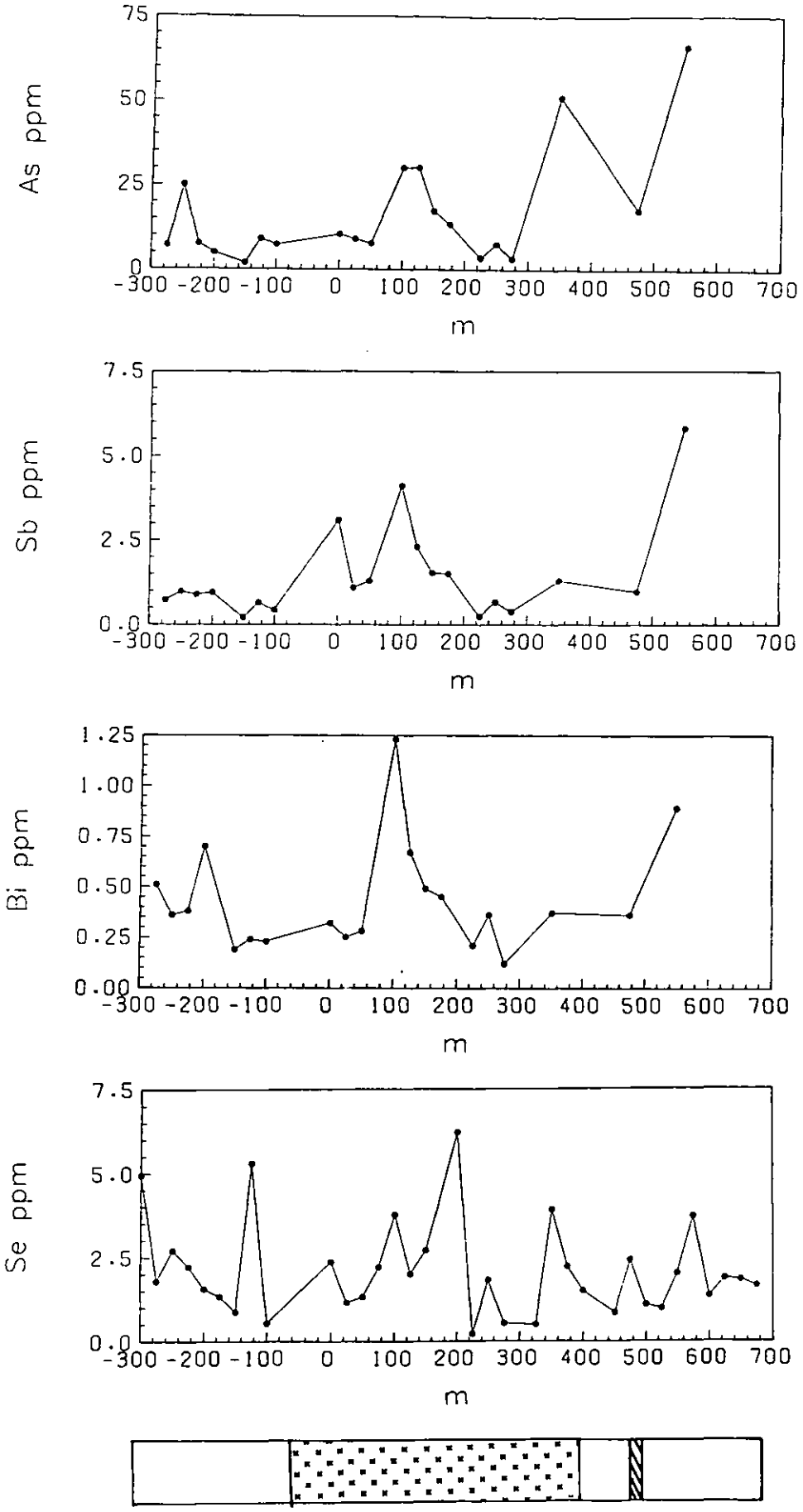


Fig 6.24 Meall Mor: peat traverse MM02
Geological symbols as for Fig 6.15

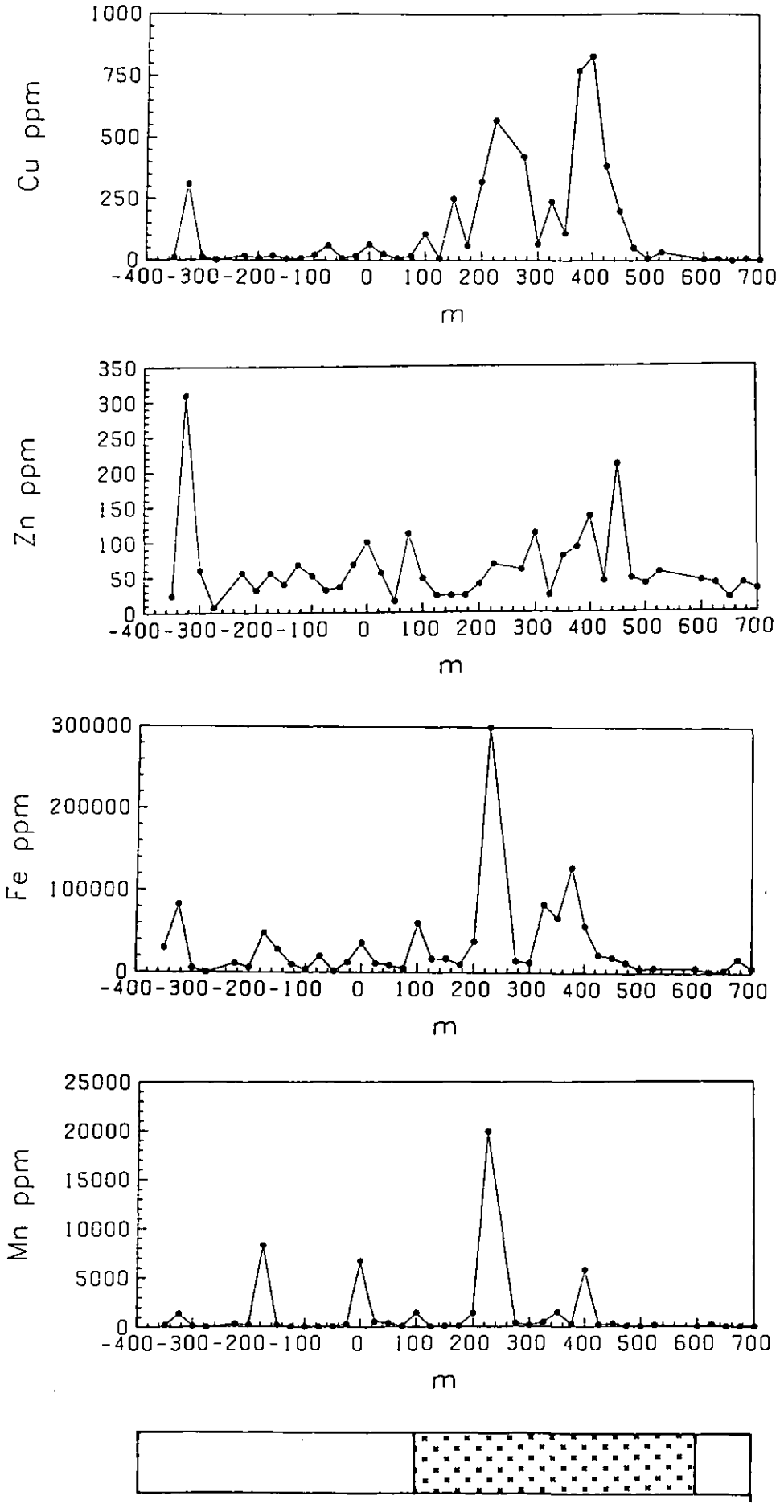


Fig 6.25 Meall Mor: peat traverse MM03
Geological symbols as for Fig 6.15

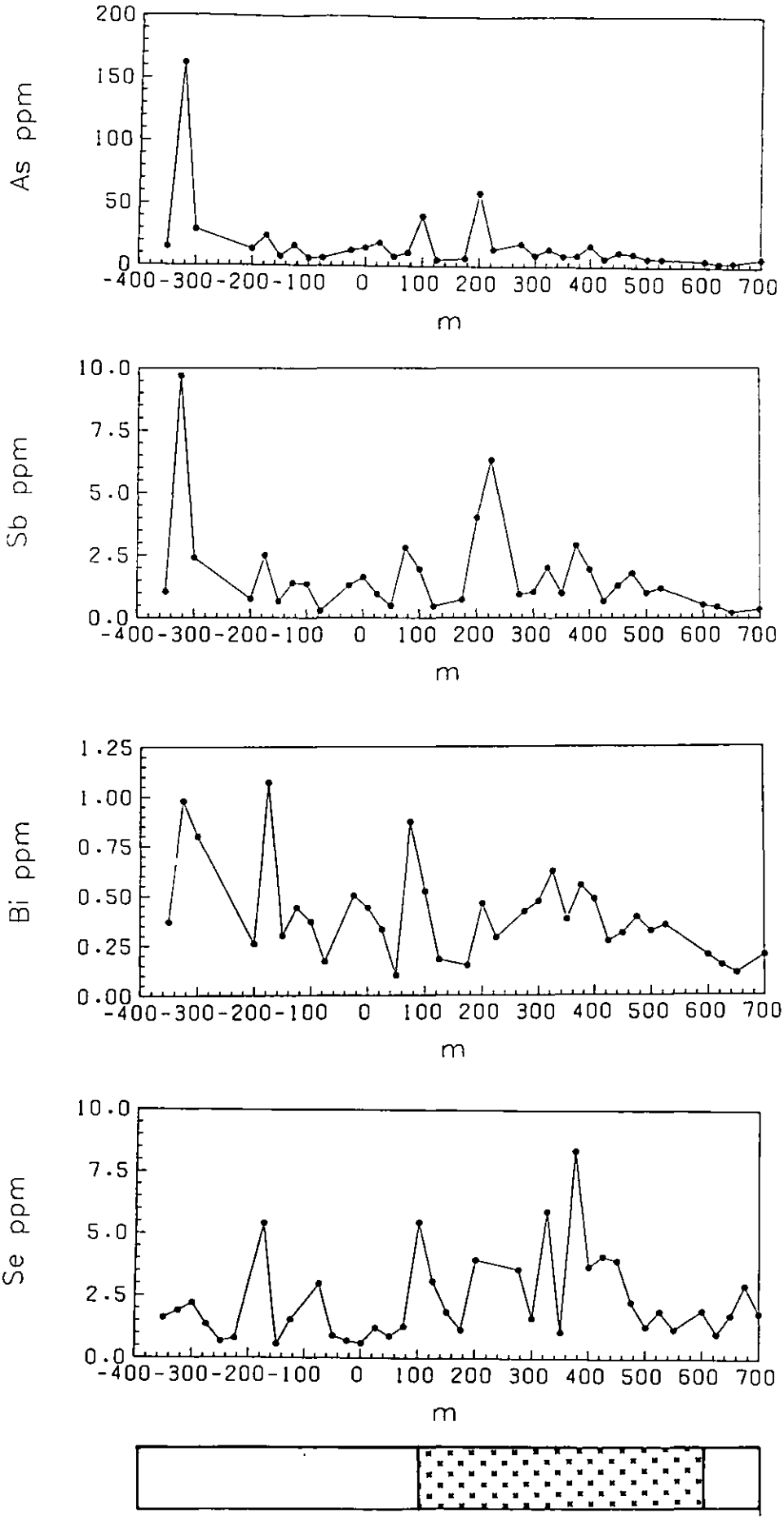


Fig 6.26 Meall Mor: peat traverse MM03
Geological symbols as for Fig 6.15

copper in MM03 (reaching 6.5 ppm relative to 0.5 ppm background) while it is erratic in MM02. In contrast, antimony is enriched over much of the pyritiferous zone on MM03, particularly near its western edge, but is associated (as is arsenic) with a single point lead anomaly on MM02. On MM03 arsenic is much more erratic with only single point anomalies, again mainly at the edge of the pyritiferous zone. Bismuth is also enriched over the pyrite zone on MM03 and very erratic on MM02.

Pathfinders are generally higher in peats than the till with selenium particularly enriched (Fig. 6.23 - 6.26). The more consistent till anomalies of MM03 are reflected in the antimony and selenium anomalies over the pyritiferous zone while the single point high (Cu, Zn, As, Sb) is associated with a peaty area draining anomalous bedrock. Pathfinder patterns along MM02 are more erratic and in general show little correlation with known mineralization. Copper is the only useful indicator element in peats, where it mirrors anomalies in till. Iron and manganese in peat are much more erratic than in the underlying till.

c) Stream Sediments and Waters (MM01)

In the regional survey arsenic and antimony give coherent though differing anomalies. The major arsenic high (Fig. 6.27) is upstream from the pyrite zone and reflects input from two tributaries draining south across the lower part of the Upper Erins Quartzite. Anomalous antimony values are found downstream from both a lead zinc show (83057385) and, more importantly, from the copper occurrences within the pyritiferous zone. Selenium values are erratic, and highs are associated with peat accumulation (87607400 and 82507410). Minor selenium enrichments also occur downstream from the pyrite zone. Bismuth has a

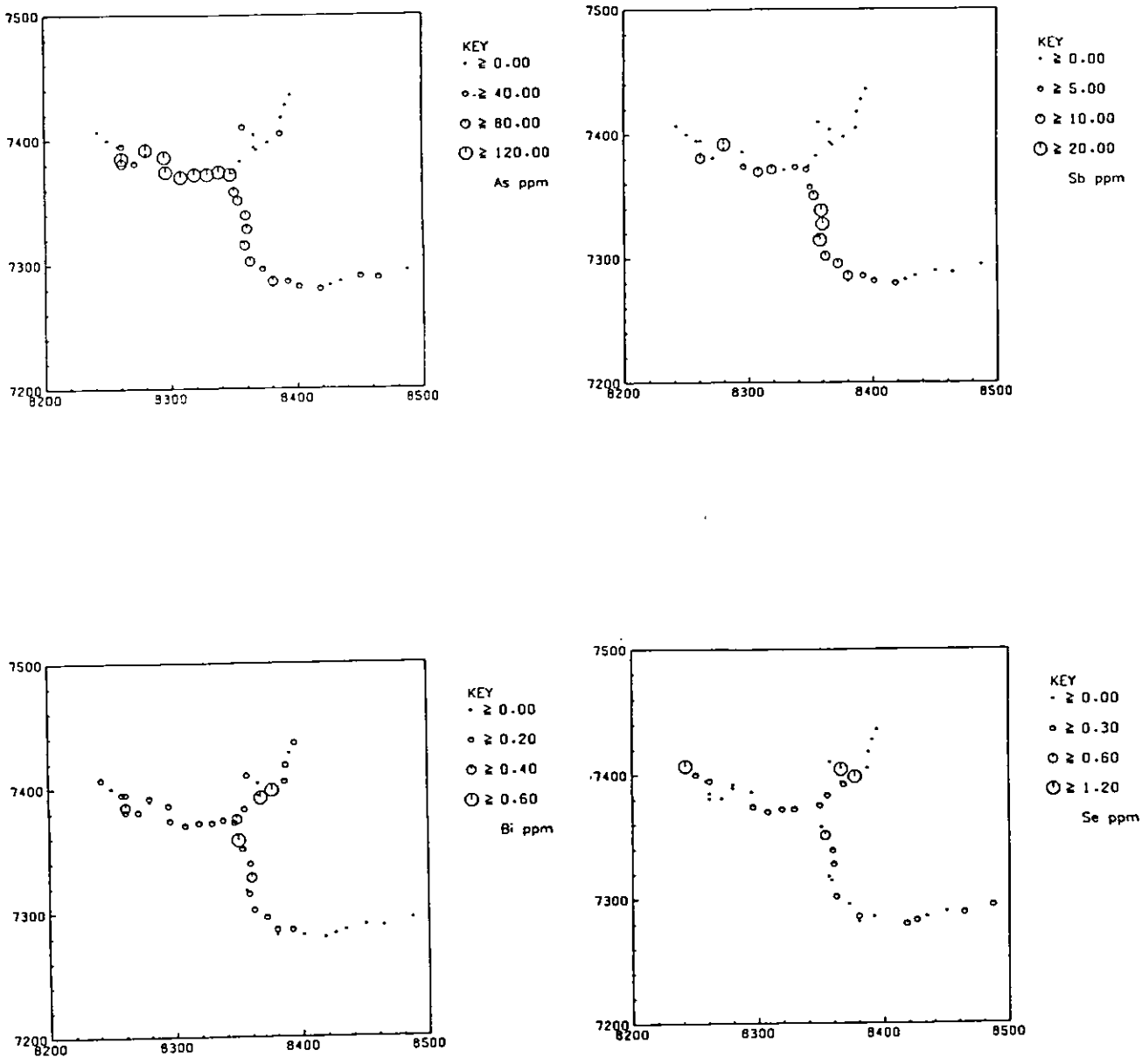


Fig 6.27 Meall Mor: stream sediments

background distribution.

The detailed sediment fractionation (Fig. 6.28 - 6.29) shows considerable contrast between arsenic and antimony. Arsenic is strongly anomalous near the origin of the traverse, reflecting the mineralized inputs noted above. The coarser fractions are enriched for 500 m downstream but arsenic is relatively enriched in the finest fractions. Antimony is anomalous in all fractions with relatively slow downstream dispersion (300 m) from the main input at 900 m while there is a lesser source coincident with the main arsenic anomaly. The limited selenium data show that selenium is enriched in the finest fraction, as to a lesser degree is bismuth.

Limited water samples were collected along the same stretch of the river. The main sediment arsenic input is reflected in the particulates but not in the dissolved phase (Figs. 6.30, 6.31). Antimony concentrations are near the analytical detection limit for the dissolved phase with all values below it (.03 μg/l) for particulates, except for a distinct enrichment in the soluble antimony downstream from the upper input. There seems little pattern in the bismuth concentration in soluble or particulate phases but soluble selenium is high downstream from the main occurrences.

6.2.3 Discussion

Primary antimony and selenium anomalies occur in the pyritiferous quartzite. Their distribution differs in detail from that of copper and zinc possibly as a consequence of metamorphic remobilisation. Regional stream sediments indicate that the main arsenic concentration is found in the lower part of the Upper Erins Quartzite distant

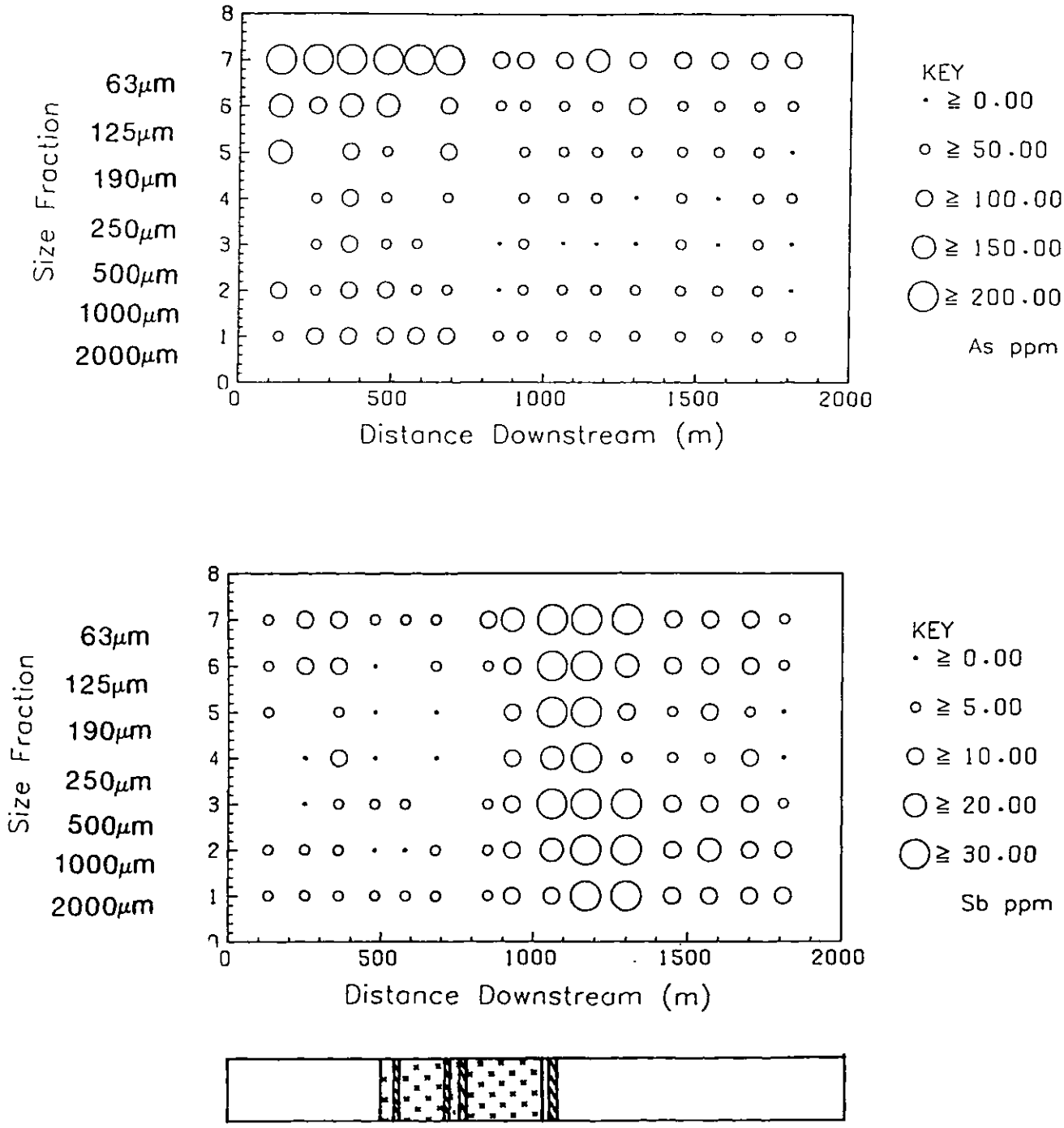


Fig 6.28 Meall Mor: fractional separation of stream sediments
Location and geological symbols shown in Fig 6.15

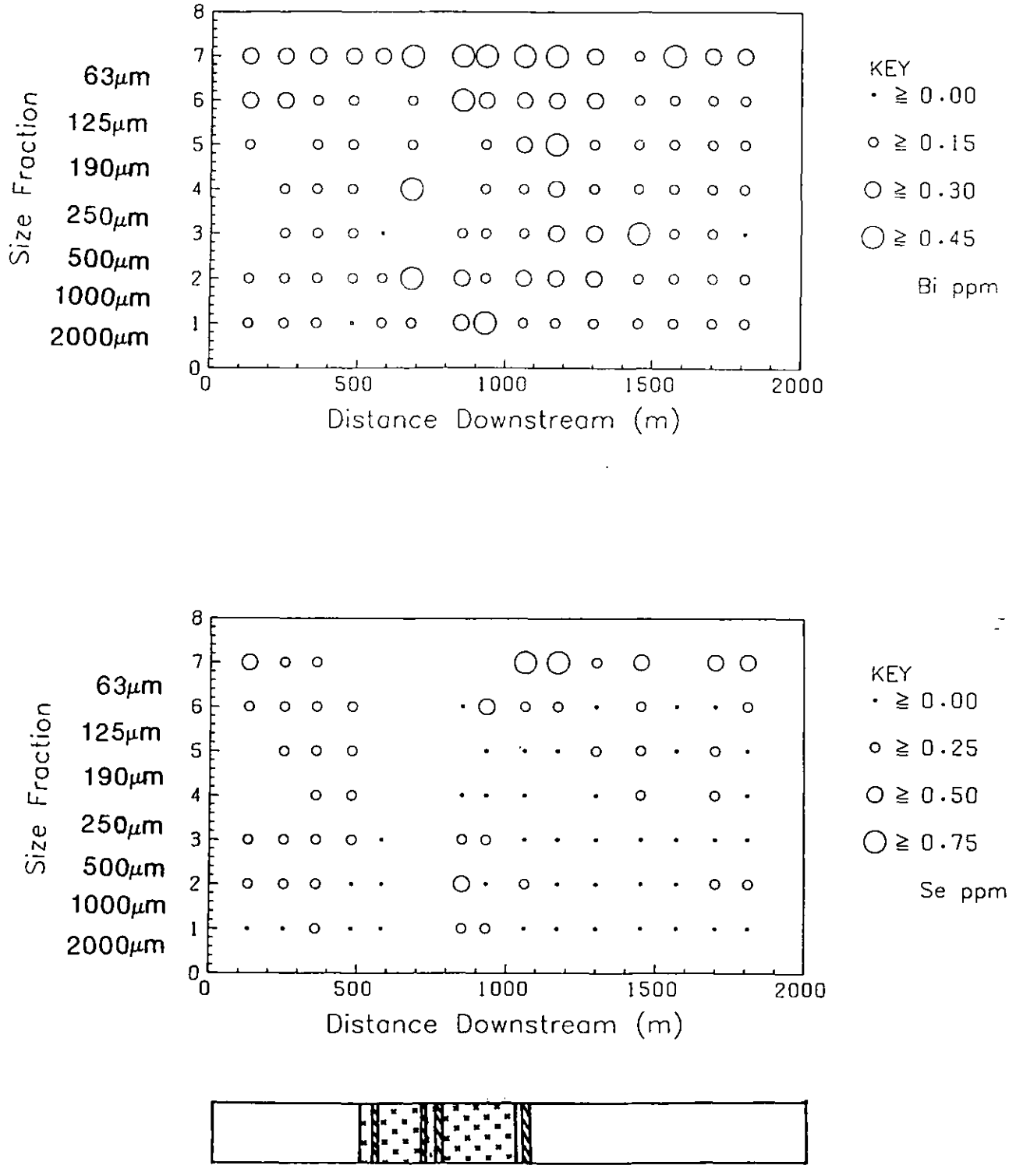


Fig 6.29 Meall Mor: fractional separation of stream sediments
Location and geological symbols shown in Fig 6.15

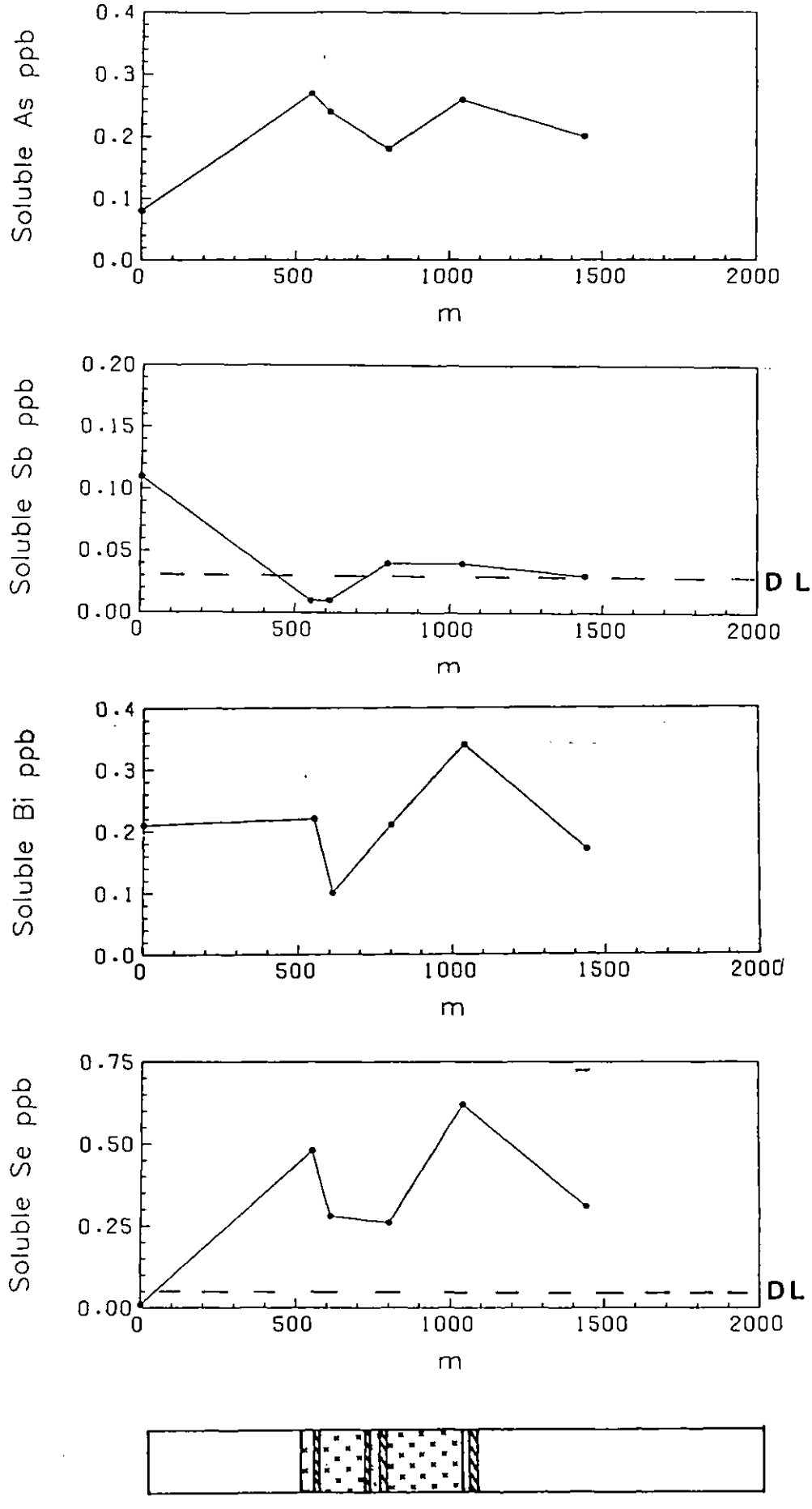
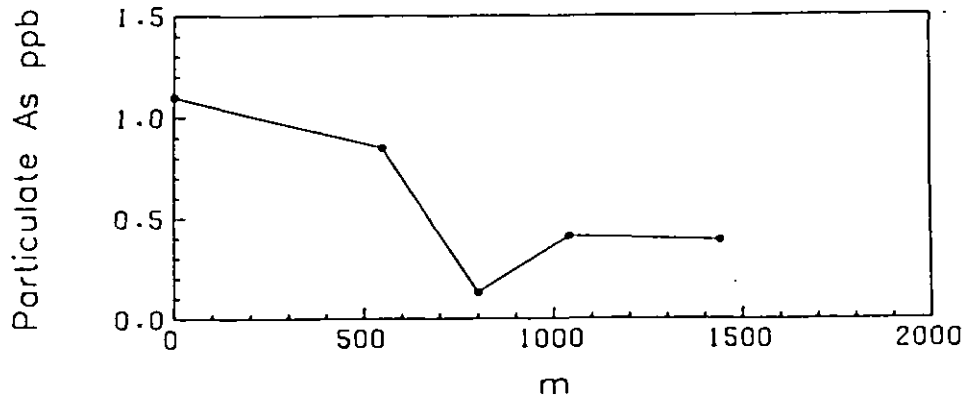
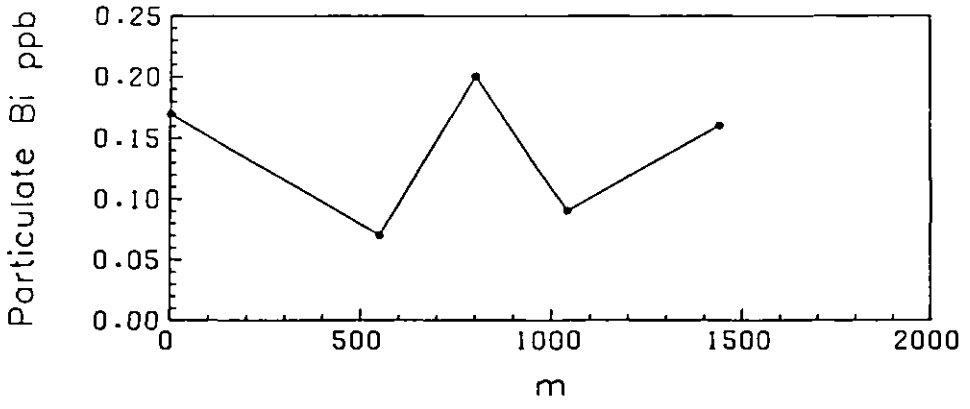
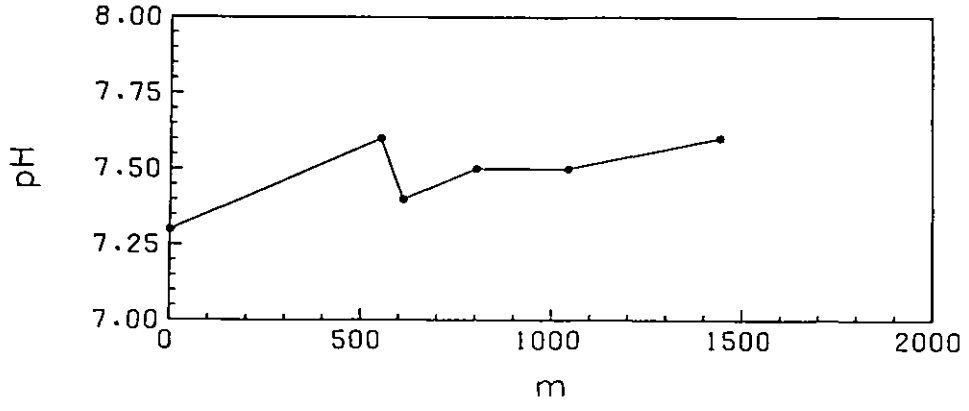


Fig 6.30 Meall Mor: stream waters
Location and geological symbols shown in Fig 6.15







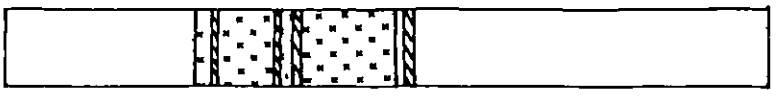


Fig 6.31 Meall Mor: stream waters
Location and geological symbols shown in Fig 6.15

from the pyritiferous quartzite, although minor concentrations occur at its edge and together with antimony, in lead-rich veins.

The lack of data on primary distribution means that conclusions on pathfinder dispersion are tentative. Augering by the I.G.S. demonstrates the till is thin (mainly less than 1 m) and till anomalies in copper directly overlie bedrock highs. The only feature which provides some clue as to the mechanism of dispersion is the correlation of anomalies in peat with those in the underlying till. Bismuth, antimony and selenium are dispersed from the more coherent anomaly on MM03 but the selenium high is indistinguishable from 'noise' over background rocks. The arsenic distribution in peats is enigmatic and bears little relation to till anomalies or to iron.

The stream sediments are much more useful with arsenic, antimony and selenium giving distinctive anomalies. Arsenic is concentrated in the finest fraction of the sediments and dispersion in the fine (-190μm) fraction sampled probably develops by transport of the arsenic enriched particulate phase as there is little arsenic in solution and it shows no correlation with the sediment highs. In contrast antimony is anomalous in all fractions downstream from the main copper occurrences, with a larger anomalous dispersion train in the course fractions. This, coupled with low concentrations in water, suggests that the mechanism of dispersion is predominantly clastic. Selenium is concentrated strongly in localised organic accumulations and in background samples in the finest fractions. This probably reflects adsorption from waters enriched in selenium.

Although antimony and selenium are anomalous in copper-rich pyritiferous quartzite they show little

correlation in detail with copper or zinc. Thus they are of little use in detailed exploration at Meall Mor although they may be useful in similar deposits where indicator elements are leached.

6.3 Glendinning, Borders, Scotland

The Glendinning antimony deposit, which was mined in the early part of this century, was selected for further investigation as generally high pathfinder values were reported by I.G.S. in surficial material (Gallagher et al, 1982). Such values make environmental effects easier to measure, although they may quantitatively differ from those at lower concentrations.

6.3.1 Geology (Gallagher et al, 1982)

The deposit has a similar association to Clontibret, but is essentially isolated. It is mainly stratiform but has later vein mineralization superimposed.

The host sediments are Silurian turbidites (Fig. 6.32) comprising interlaminated fine sandstone and siltstones. They generally strike NE with a steep SE dip and show tight folding and shearing in NNE zones.

The stratiform mineralization is predominantly pyrite and stibniferous arsenopyrite (100 ppm Sb) and this is concentrated in fine grained sandstones and intraformational breccias. The mineralization probably occurs over a few tens of metres of stratigraphical thickness.

The later stage mineralization consists of dolomite with pyrite, arsenpyrite, galena, bournonite, sphalerite and chalcopyrite with still later stibnite and dolomite. This last phase is tentatatively correlated with the previously worked mineralization, which is thought to occur in a vein.

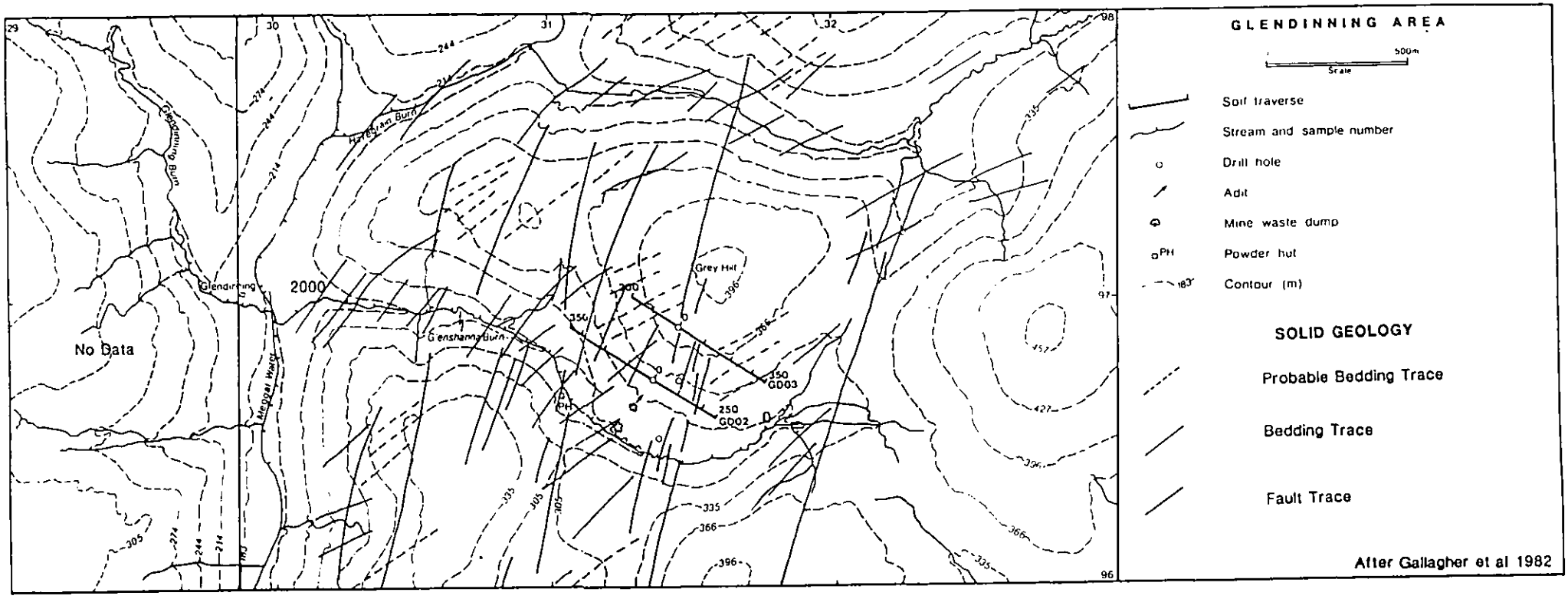


Fig 6.32 Glendinning: solid geology

a) Surficial Geology

The area has been extensively glaciated but the only remnants are paleo valley fill. This reaches tens of metres near the old mine where it is slightly to the north of but approximately parallel to the present day river. Thin peats cover much of the area.

6.3.2 Programme

Two parallel soil traverses (GD02 and GD03) were sampled to establish the distribution of arsenic and antimony upslope from the old mine.

Stream sediments were taken both in the stream draining the known mineralization (Glenshanna Burn) and background rivers. This was followed up by detailed water sampling in Glenshanna Burn.

a) Soil Traverses GD02 and GD03

The arsenic and antimony of both traverses is similar to the regional distribution established by the I.G.S. Both elements form linear anomalies striking NNE with some arsenic enrichment in the valley floor (Fig. 6. 33) 6.34). The highest anomalies (Figs. 6.36 - 6.40) (maximum 3000 ppm As relative to 15 ppm background, 90 ppm Sb relative to 5 ppm) correlate with the projections at the surface of mineralization intersected by diamond drilling (Fig. 6.35). There seems little overall correlation with iron and manganese except at the eastern anomaly (GD02, 125 m).

Minor base metal anomalies (nitric acid attack) correlate with arsenic and antimony highs but the patterns are much less definitive than those found by the I.G.S. They only reach twice background and values are also

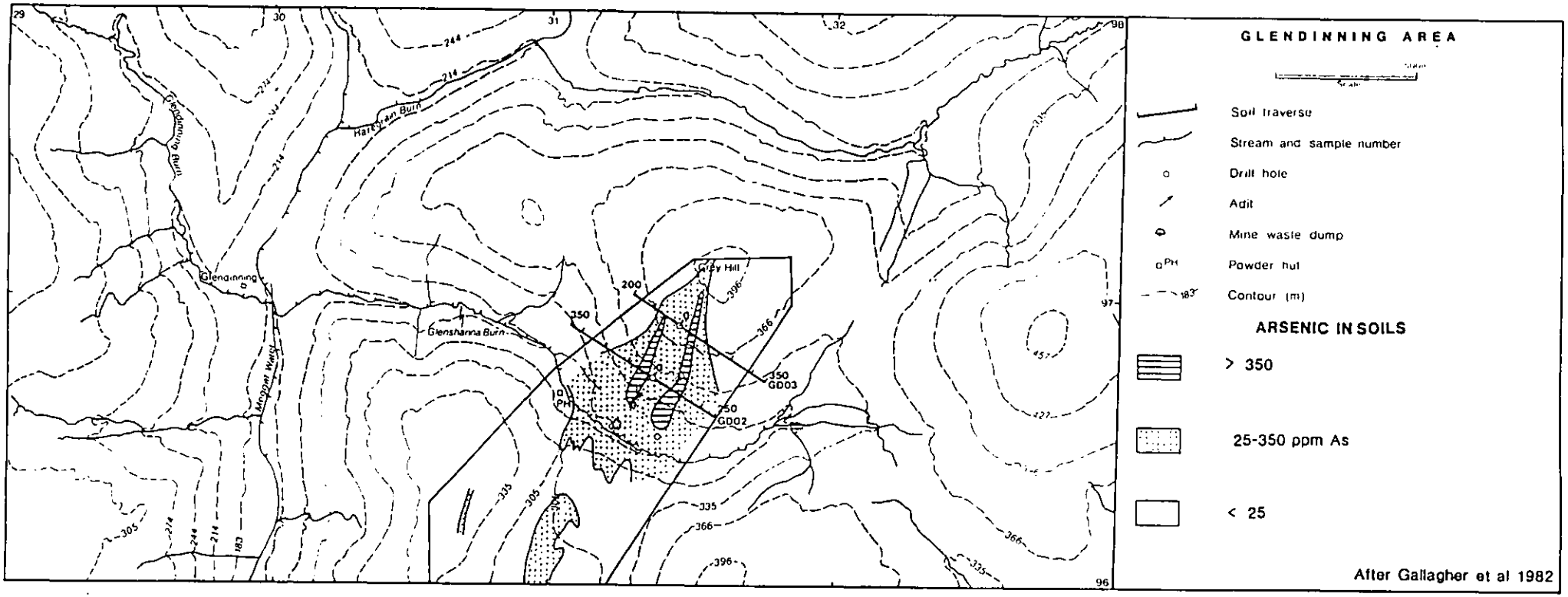


Fig 6.33 Glendinning: regional arsenic soil geochemistry

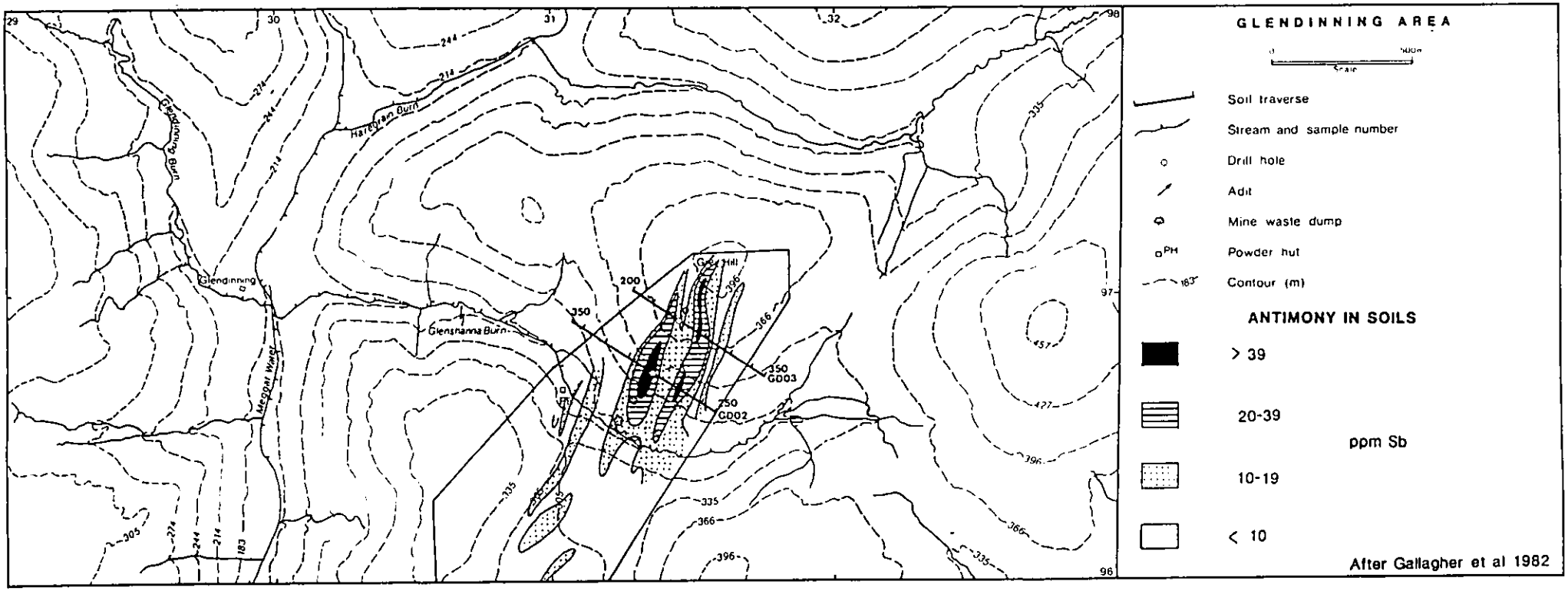


Fig 6.34 Glendinning: regional antimony soil geochemistry

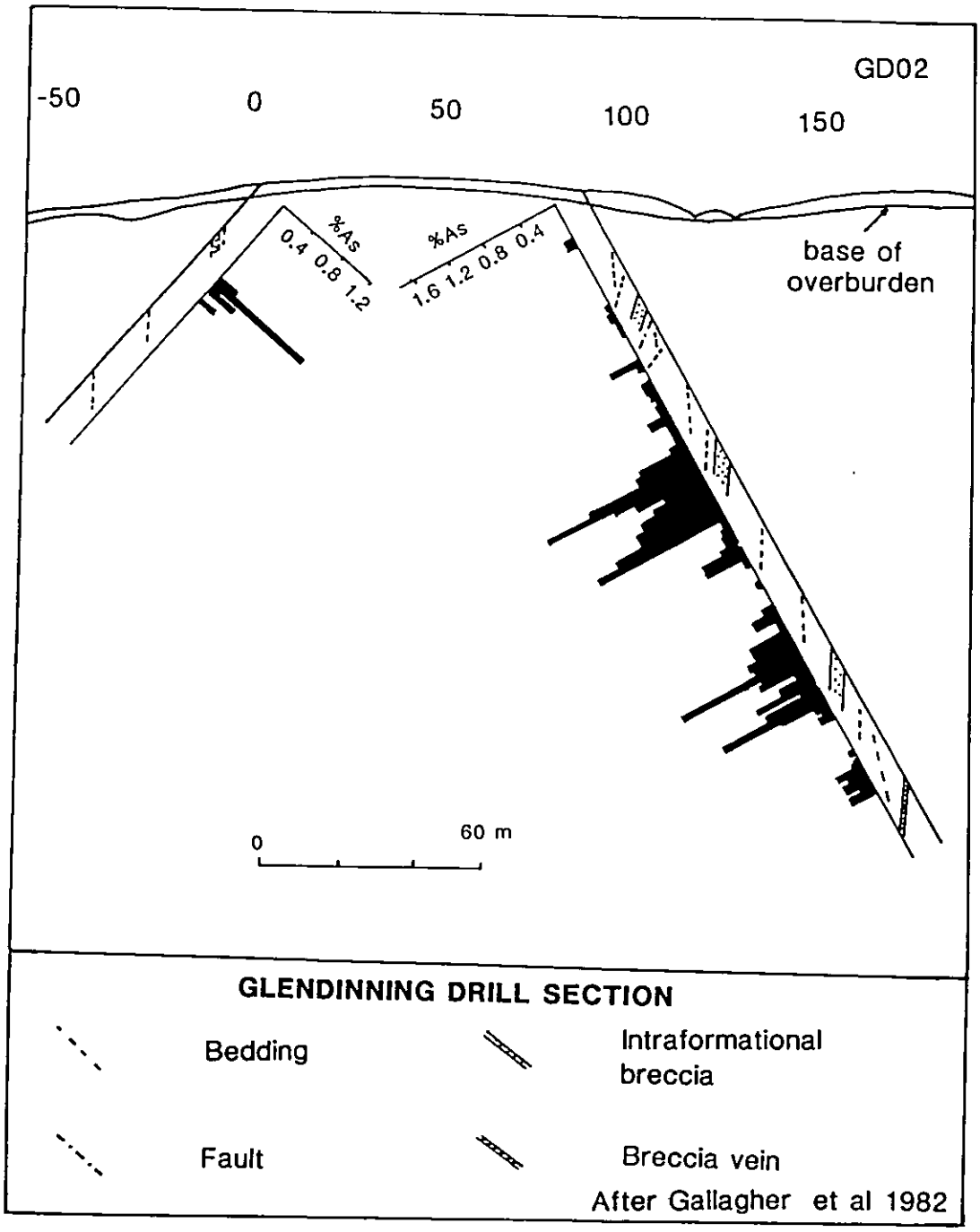


Fig 6.35 Glendinning: drill section under traverse GD02

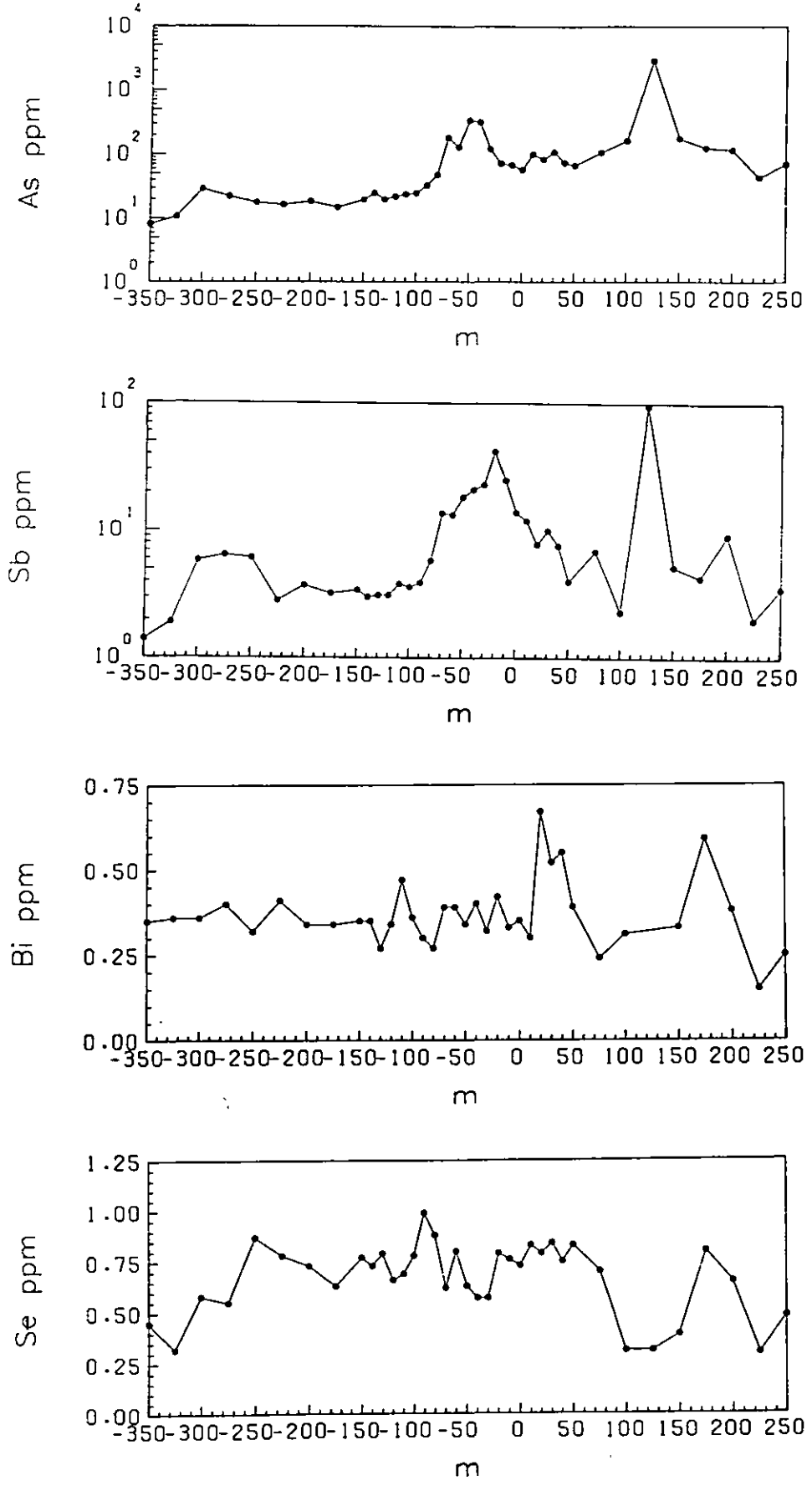


Fig 6.36 Glendinning: soil traverse GD02

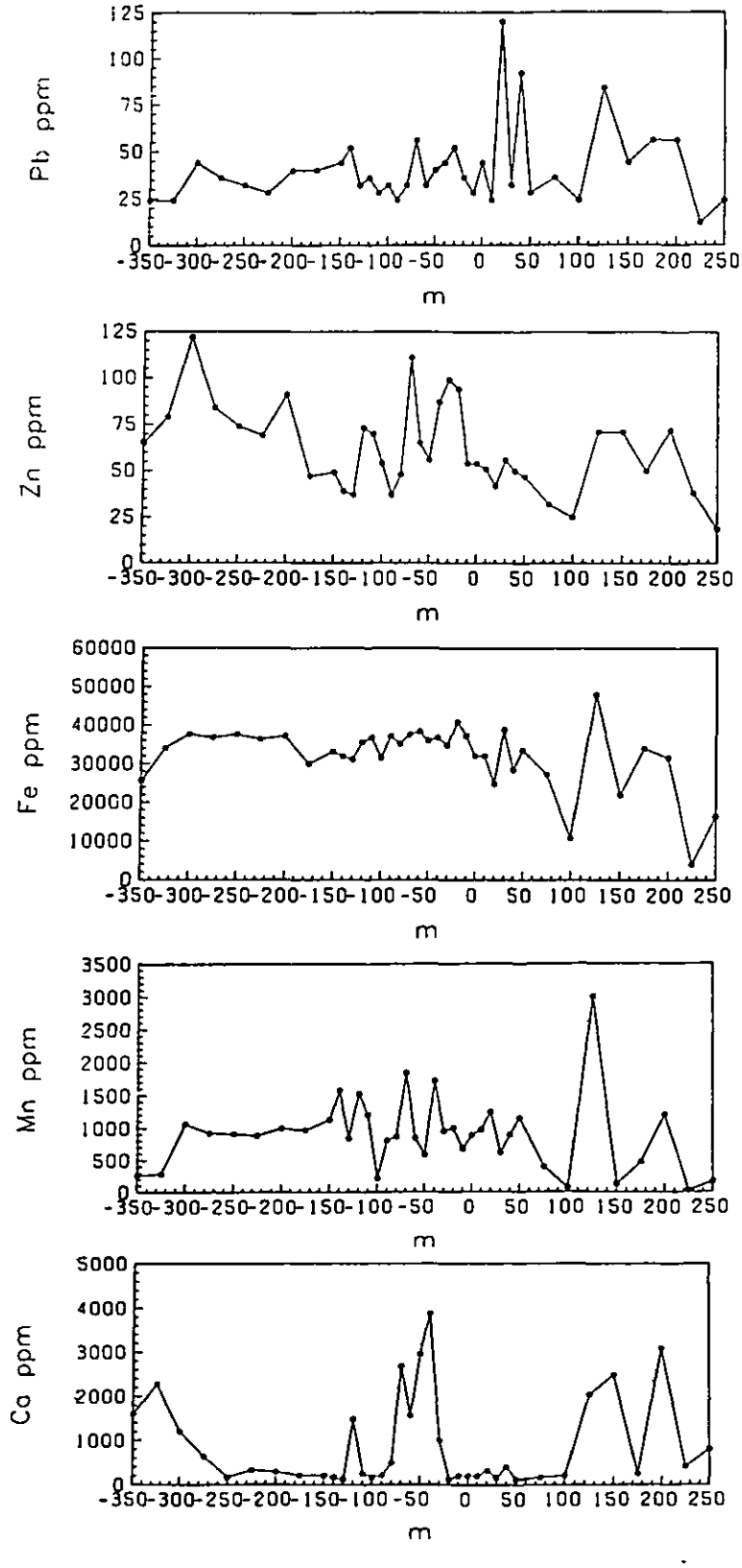


Fig 6.37 Glendinning: soil traverse GD02

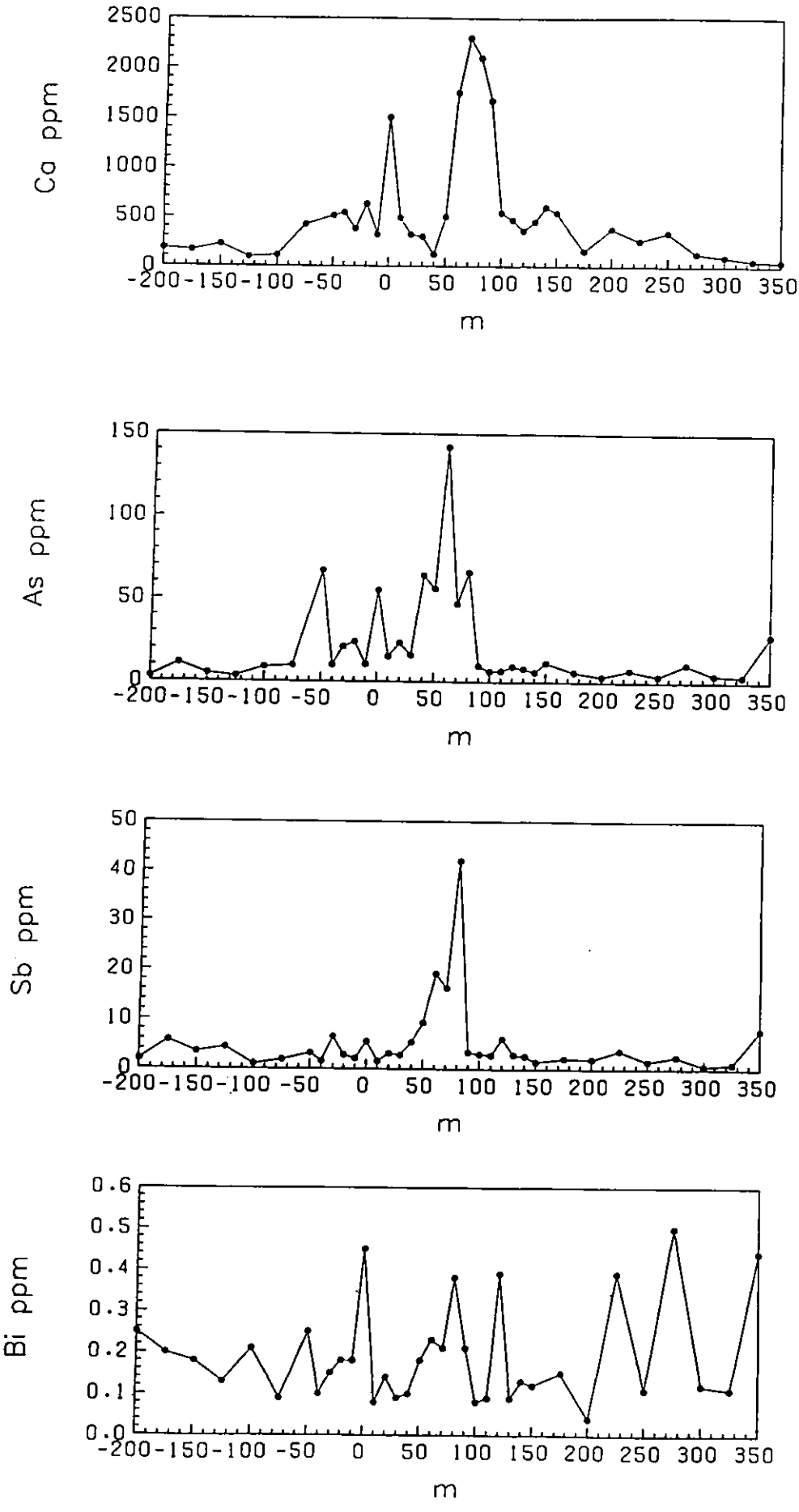


Fig 6.38 Glendinning: soil traverse GD03

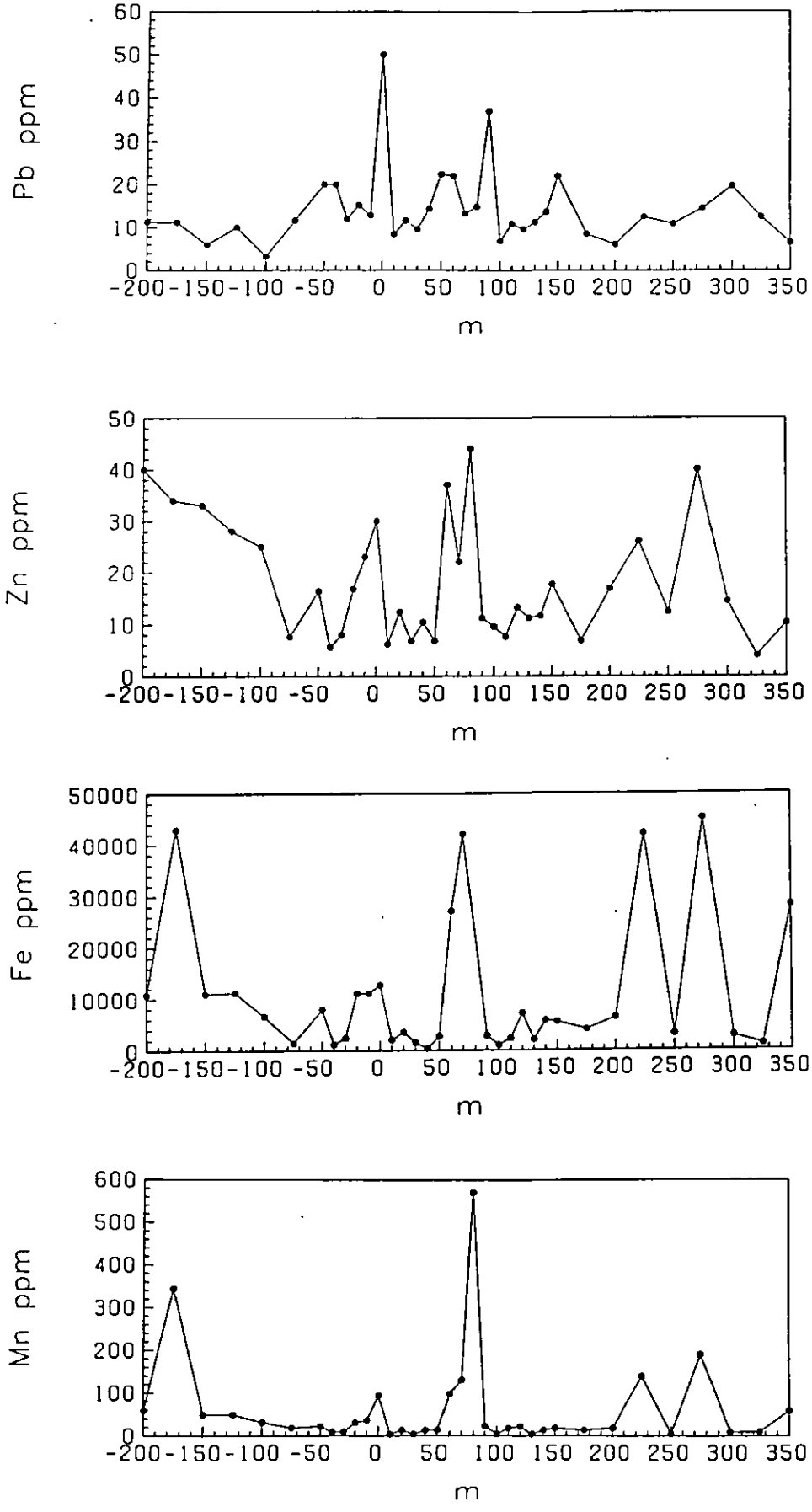


Fig 6.39 Glendinning: soil traverse GD03

high at a distance from the mineralization. Calcium is more convincing with anomalies reaching 4000 ppm Ca relative to 200 ppm background.

Bismuth and selenium show background distribution.

b) Stream Sediments GD01

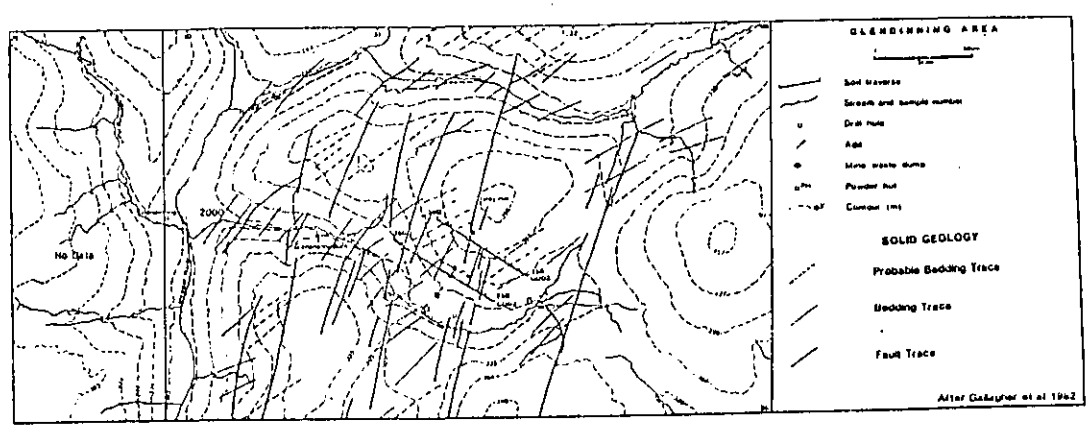
Both arsenic and antimony (Fig. 6.40) are strongly anomalous in the Glenshanna Burn. Typical values are 200 ppm As relative to 12 ppm in sediments and 30 ppm Sb relative to 3 ppm background. The distribution of these environments is described in section (c). The elements are also enriched in Meggat Water south of its confluence with Glenshanna Burn but these enrichments may be related to smelting contamination near Glendinning Farm. Bismuth and selenium shows little variation except perhaps that selenium is slightly higher in Glenshanna Burn.

No comparable data is available for the transition metals.

c) Detailed Investigation of Glenshanna Burn

Water and stream sediments were collected at approximately 100 m distances along the rivers and examined in detail.

Comparison of the arsenic and antimony content of the dissolved and particulate water phases and stream sediment (arsenic, Fig. 6.41) demonstrate that there are several inputs of mineralized material. Three inputs can immediately be identified: the area south of the adit mouth, consisting of mine spoil;a minor tributary north of the powder hut; and a tributary west of the western end of GD02. The The first and second mentioned inputs are probably more important than the third. In addition they may be some


GLENDINNING AREA
Soil traverse
Streams and sample number
Drill Hole
Adit
Mine waste dump
Powder hut
Contour (m)
SOLID GEOLOGY
Probable Bedding Trace
Bedding Trace
Fault Trace
After Gallagher et al 1962
No Data
2000

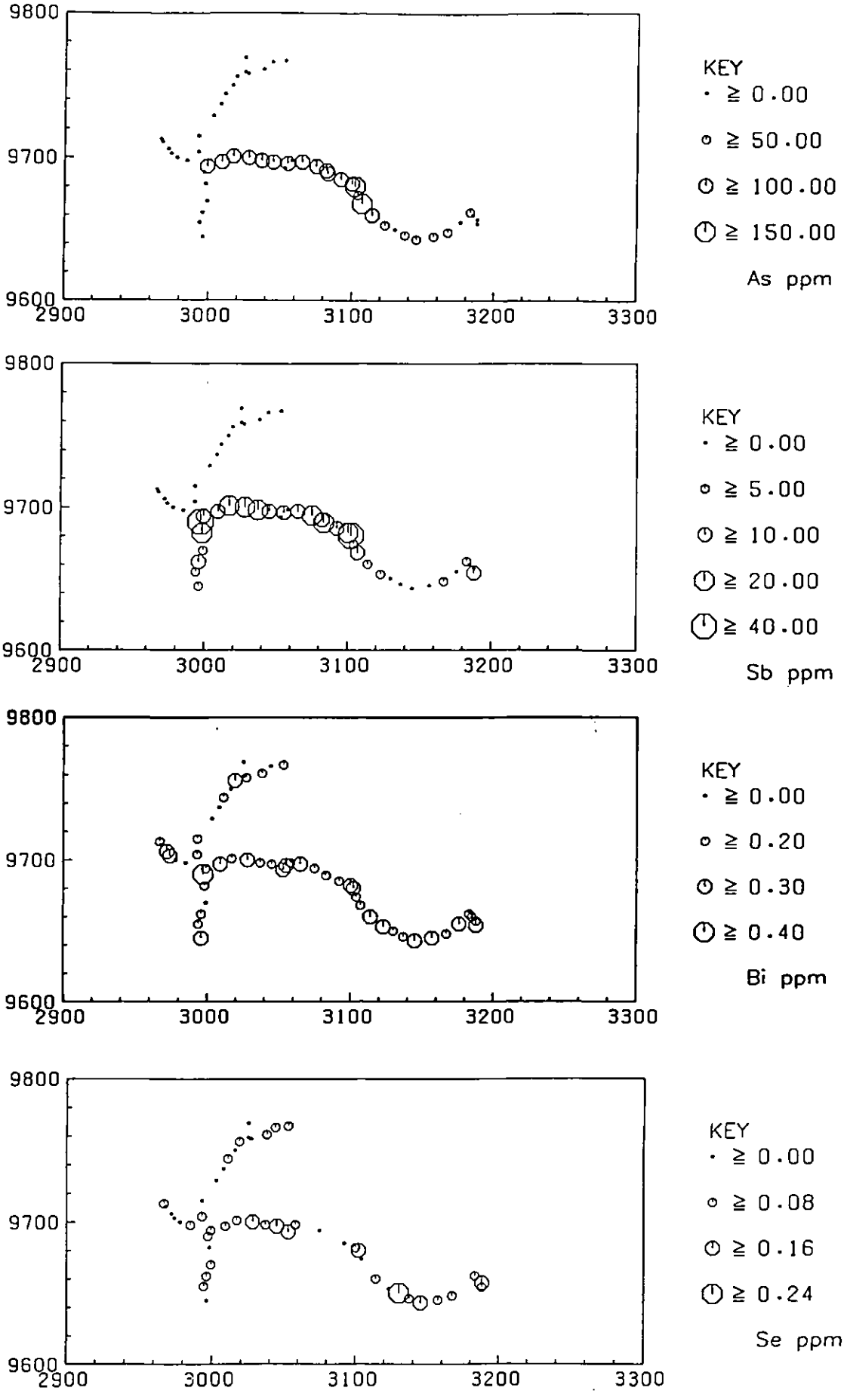


Fig 6.40 Glendinning: stream sediments
Overlay of geology opposite

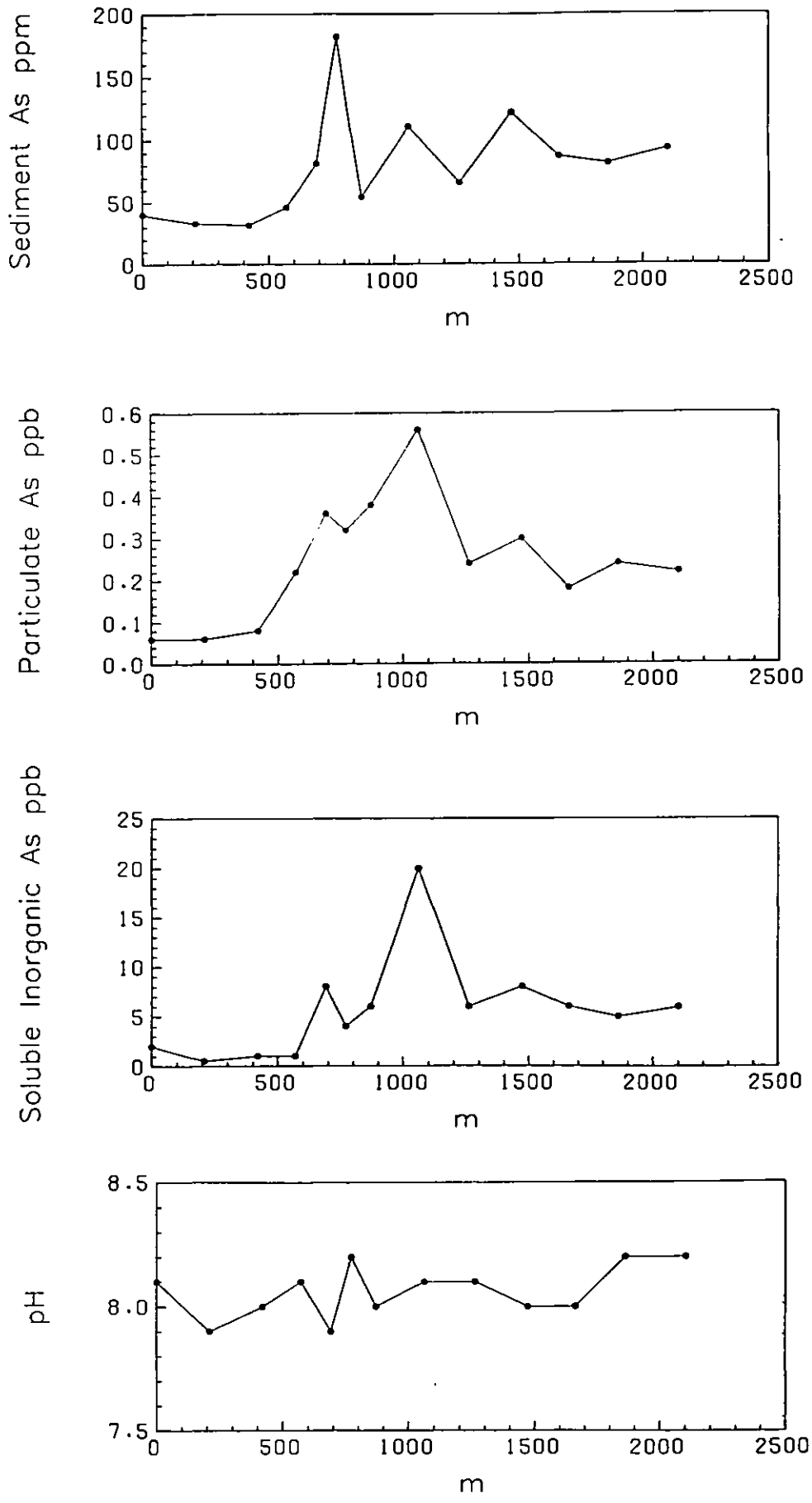


Fig 6.41 Glendinning: arsenic in various media along Glenshanna Burn
Location in Fig 6.32

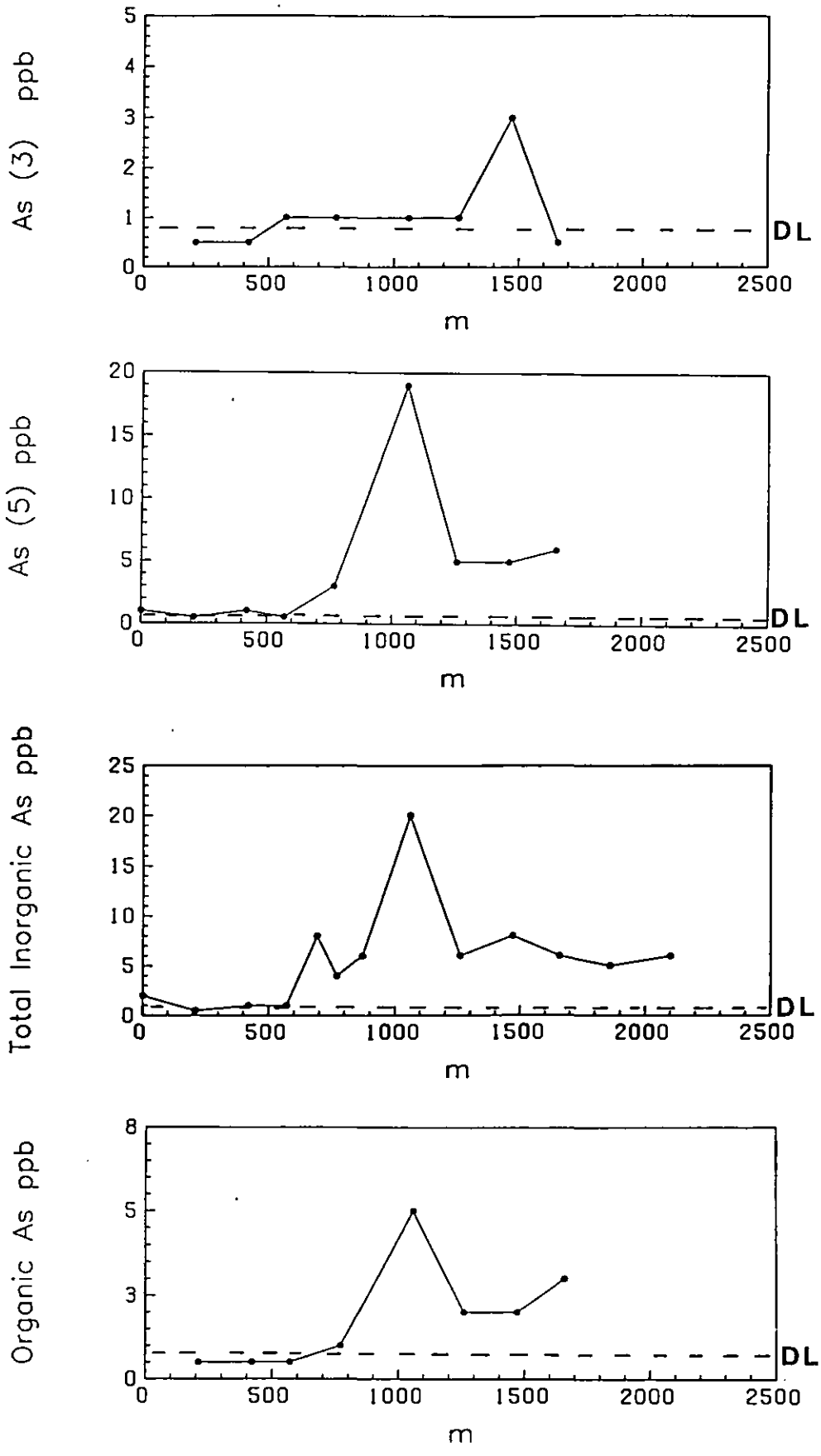
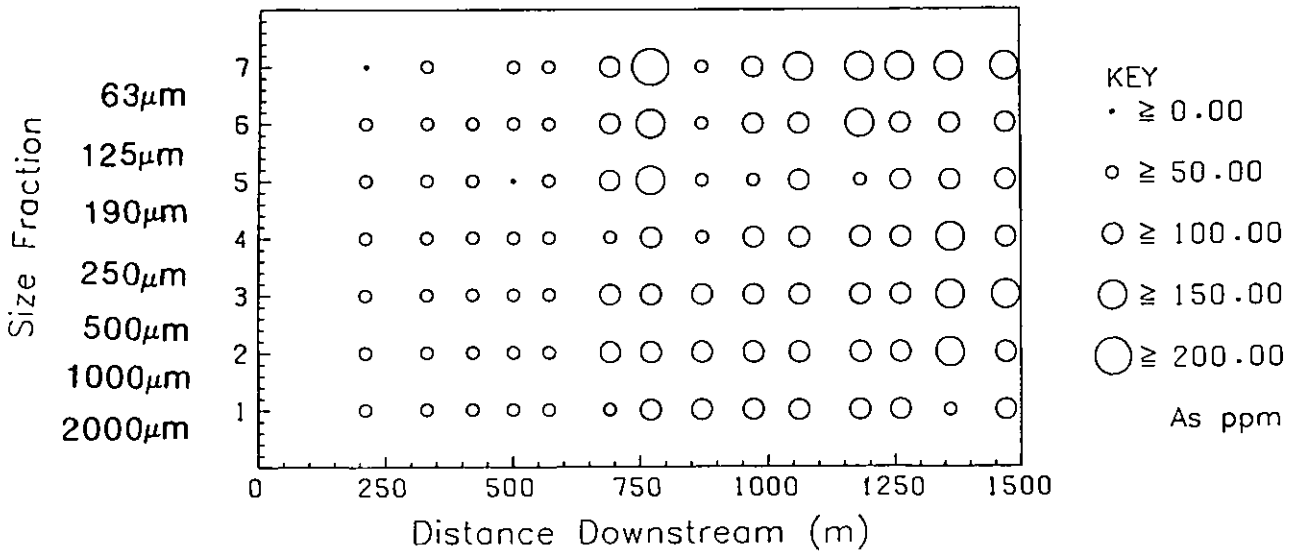


Fig 6.42 Glendinning: arsenic speciation along Glenshanna Burn
Location shown in Fig 6.32



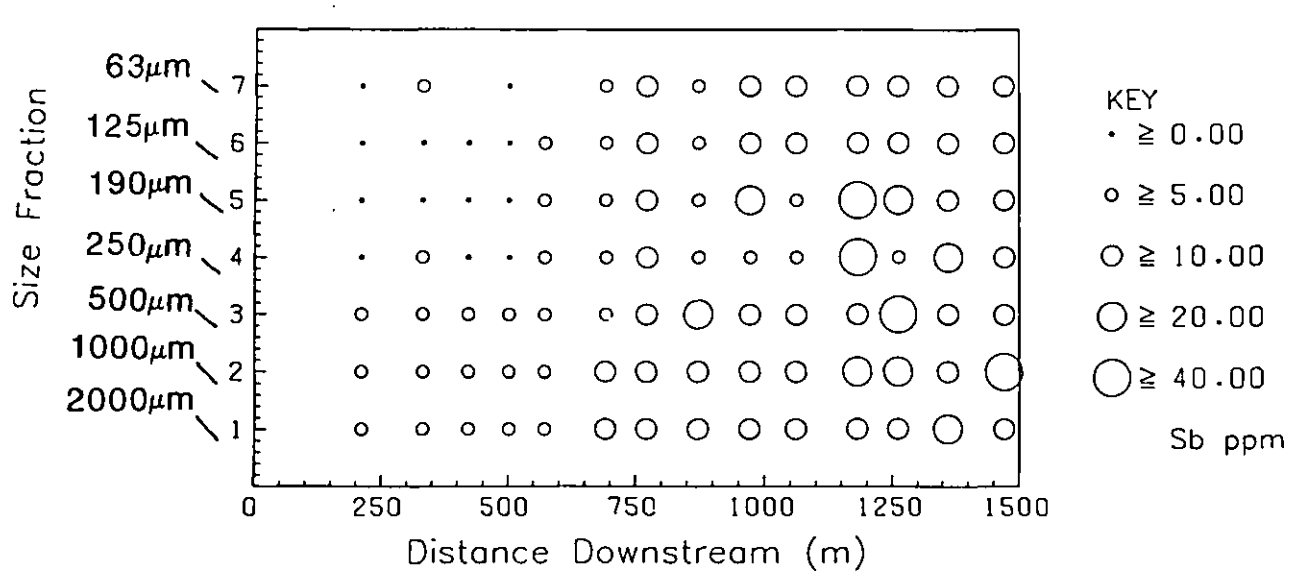


Fig 6.43 Glendinning: fractional separation of stream sediments along Glenshanna Burn. Location shown in Fig 6.32

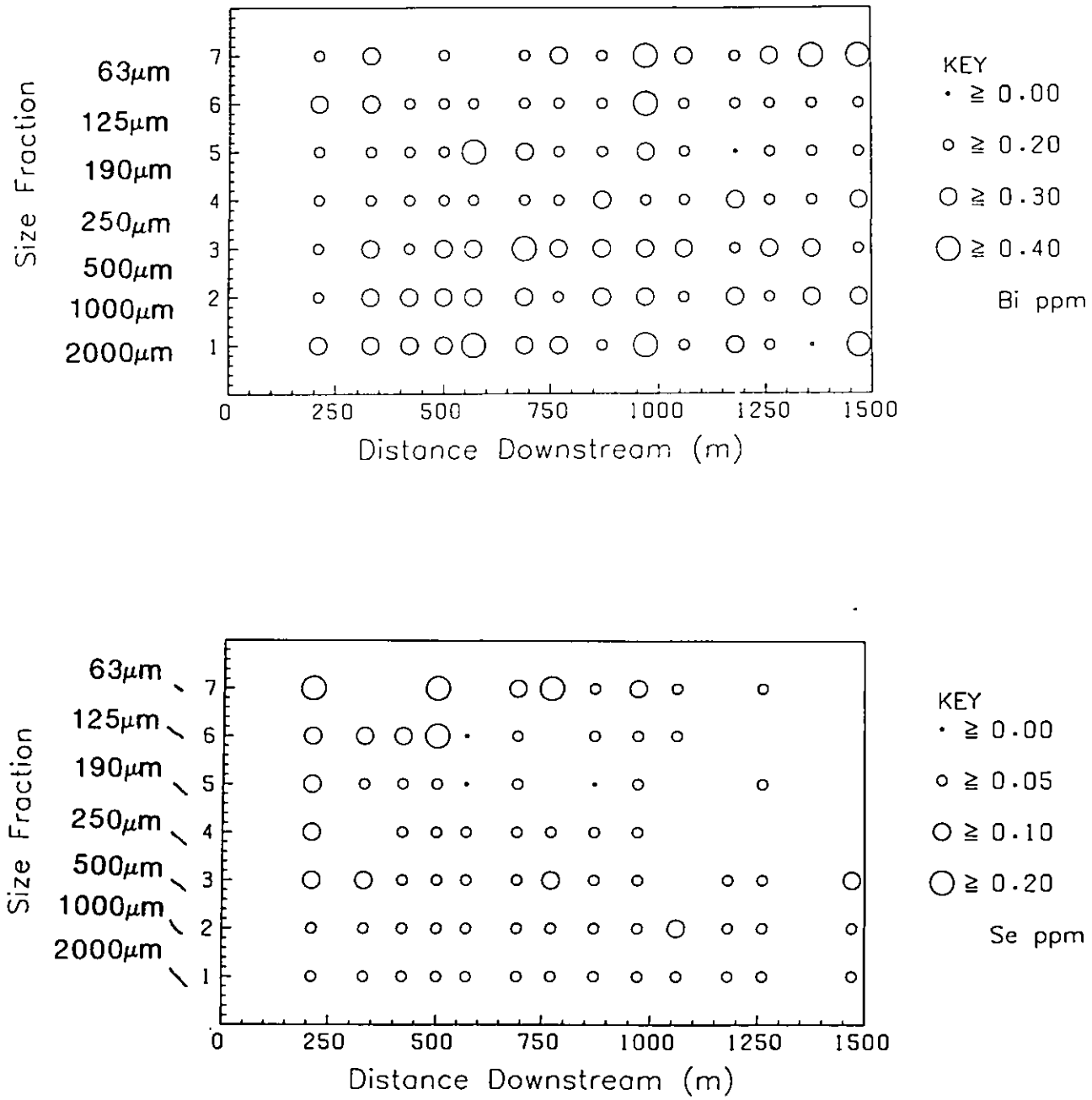


Fig 6.44 Glendinning: fractional separation of stream sediments along Glenshanna Burn. Location shown in Fig 6.32

input from the regional soil anomaly around the powder hut.

The most immediate response to the mineralized input from the mine spoil contamination (at 650 m) is in the particulate phase of the waters but this is followed immediately downstream by sharp increases in dissolved and stream sediment arsenic. The main particulate and dissolved arsenic anomalies occur (at 1060 m) immediately downstream from the second mineralized input (arsenic values of 480 ppm in tributary stream sediments). Arsenic anomalies persist down Glenshanna Burn in all phases with those in the dissolved phase particularly enriched. Speciation studies (Fig. 6.42) of the dissolved phase (using the method of Pahlavanpour and Thompson, 1981) demonstrate that arsenic is transported almost exclusively in the arsenic (5^+) valency state with very localised and lesser concentrations of organic species downstream from the lower inputs (Fig. 6.42). Physical separation of the stream sediment into size fractions (Figs. 6.43 - 6.44) demonstrates that arsenic occurs predominantly in the finest grained fractions of the sediment although all fractions are enriched to at least twice background downstream from the mineralization. The limited iron data does not show a strong correlation with arsenic.

Antimony concentrations are much lower than those of arsenic and are near the analytical detection limit in particulate phase and in solution. Anomalous values (Table 6.4) in both particulates and solution are present downstream from the lower mineralized inputs. The more sensitive co-precipitation method gave determinations of 0.1 ppb Sb in background waters and in a reconnaissance sample from Megatt Water, compared to up to 14 ppb in Glenshanna Burn, suggesting that these waters are strongly anomalous in antimony. The behaviour of antimony in

Table 6.4 Antimony Values in Glenshanna Burn

Sample No.	m	Dissolved Sb (ppb)	Particulate Sb (ppb)	-190 μm Stream Sediment Sb (ppm)
5	0	< 5	<.04	4.9
7	210	<5	<.04	4.7
9	420	<5	<.04	4.2
11	570	<5	<.04	5.4
12	690	<5	<.04	7.4
13	770	<5	<.04	13.3
14	870	<5	<.04	8.2
17	1060	14	.06	10.8
20	1260	5	<.04	25.3
23	1470	6	<.04	16.0
26	1650	5	<.04	24.0
28	1870	<5	<.04	28.0
30	2100	<5	<.04	14.6

stream sediment is very different from arsenic with enrichment only in the coarser fractions downstream from 1150 m, but all fractions reflect the mineralized input of spoil at 600 m. Unfractionated stream sediments also show strong enrichment further down Glenshanna Burn (Fig. 6.40).

Bismuth is also enriched mainly in the coarser fractions but with occasional high values in the finest sediments.

6.3.3 Discussion

The enigma at Glendinning is the location of the previously worked antimony vein, which was not intersected during the I.G.S. drilling investigation, and it is thus difficult to discuss the soil geochemistry with total confidence. The two linear soil anomalies seem, on extrapolation from subsurface data (Fig. 6.35) to represent the surface expressions of stratiform and fracture hosted arsenic and antimony mineralization. Although both anomalies occur in minor stream beds scavenging (or at least correlation with iron and manganese) is only associated with the highly anomalous eastern area. Arsenic and antimony are the most effective elements to locate the mineralization where soil is thin. In the glacial paleovalley broad arsenic anomalies are observed from the I.G.S. data and probably represent hydromorphic dispersion.

Regional stream sediments show that Glenshanna Burn is strongly anomalous in arsenic and antimony. The anomalies in Meggat Water downstream from its confluence with Glenshanna Burn are probably partly due to contamination from ore smelting at Glendinning Farm. Contamination is also a problem in Glenshanna Burn and it is difficult to decide what contribution it makes to metal input. The spoil heap (at 700 m) is certainly one of the main inputs

into the river and Gallagher et al (1982) report that fresh sulphides can be panned from the river near the powder hut. Data presented here, however, suggest that the most important input (at 1000 m) is derived from a minor tributary which drains anomalous till and carries pathfinders in solution. Thus a high proportion of metal in the drainage originates from the soil anomaly.

Arsenic is transported both in the particulate and more abundant dissolved phases. The interaction between these phases and sediments is difficult to establish but particulate and sediments show a high correlation. The enrichment in the finest fraction suggests that arsenic is co-precipitated with or adsorbed onto fine particles. Speciation studies demonstrate that $As(5^+)$ is dominant in solution with only minor proportions of $As(3^+)$ and organic arsenic species in peaty areas.

Antimony is strongly anomalous in sediments and waters, but differs from arsenic in that anomalous values occur in all fractions downstream from the bedrock anomaly but especially in coarser fractions further downstream. This distribution is compatible with placer development (for theory see Gladwell, 1981) and suggests that dispersion is exclusively clastic. Interpretation of dissolved and particulate data is hampered by the number of samples near or below the analytical detection limit. Anomalous concentrations in water are almost exclusively confined to the soluble phase and derived from the natural soil anomaly.

CHAPTER 7 CARBONATE HOSTED DEPOSITS IN GLACIATED TERRAIN

The carbonate hosted zinc-lead and copper silver deposits of the central Irish plain exemplify the problems of using exploration geochemistry in glaciated terrain. All of the major discoveries, to date, are credited to geochemistry in some degree and the most important discovery, Navan, was a direct result of soil geochemical methods. The prospective area with shallow till cover has been now explored and the current problem is to recognise geochemical signatures through thicker deposits (Cazalet, 1982). This has led to the routine use of deep sampling techniques to collect samples of basal (lodgement) till and to detailed mapping of the Quaternary deposits (Cohen and Stanley, 1982).

In this research, two reconnaissance surveys (at Keel and Mallow) were designed to assess the mobility of pathfinder elements and compare them with the indicator elements (Pb, Zn, Cu) normally used in Ireland.

The mineral deposits of the Irish Midlands show considerable variation in character ranging from vein like deposits to the recently discovered prospects in Co. Kildare, which are comparable to the brecciaform ores of East Tennessee. Calcareous shoreline to marginal marine sediments of Carboniferous age are the host rocks.

The expoited Zn-Pb-Cu deposits are stratabound and probably deposited as a result of paleo-seafloor exhalative activity during the deposition of carbonate sediment. In contrast the copper-silver deposits (occuring in the sourthern part of the Irish plain) are associated with sediments transitional between clastic and carbonate deposition and are more obviously epigenetic in character. They are, however, probably of similar origin to the zinc rich type. (Little is known of the Karstiform (Zn-Pb)

deposits of the upper (Chadian) part of the sequence.) Mallow is a good example of the epigenetic copper silver type while the Keel zinc deposit does not fit into either end member type but has an epigenetic character.

7.1 Keel, Co. Longford, Ireland

The original geochemical surveys by Riofinex, (which led to the subsurface exploration of the prospect), and subsequent research (Evans 1971) discovered complex lead zinc soil anomalies. The anomalies are broad and the location of the relatively narrow mineralization is not obvious.

The prospect is located 10 km south of Longford City and resources are estimated at 1.8 m tons of 7% Zn. The topography is gently rolling with hills of approximately 100 m in height.

7.1.1 Geology (Patterson, 1970)

a) Solid Geology (Fig. 6.1)

The host sediments to the deposit are a mixture of Lower Carboniferous clastic and carbonate sediments. They were deposited unconformably on a basement of deformed Silurian coarse sandstones and shales, which are thought to form partial horst blocks (Smith, 1980).

The host sediments reflect a gradual marine transgression from the south. The basal clastic unit consists of alternations of arenaceous conglomerate and sandstone and is overlain by the Mixed Beds, which comprise a basal impure sandstone, followed by bioclastic dolomite and finally interbedded dolomitized sandstones and mudstones. The succeeding Bioclastic Limestone is made up of interbedded fossiliferous limestone and sandstone, and it

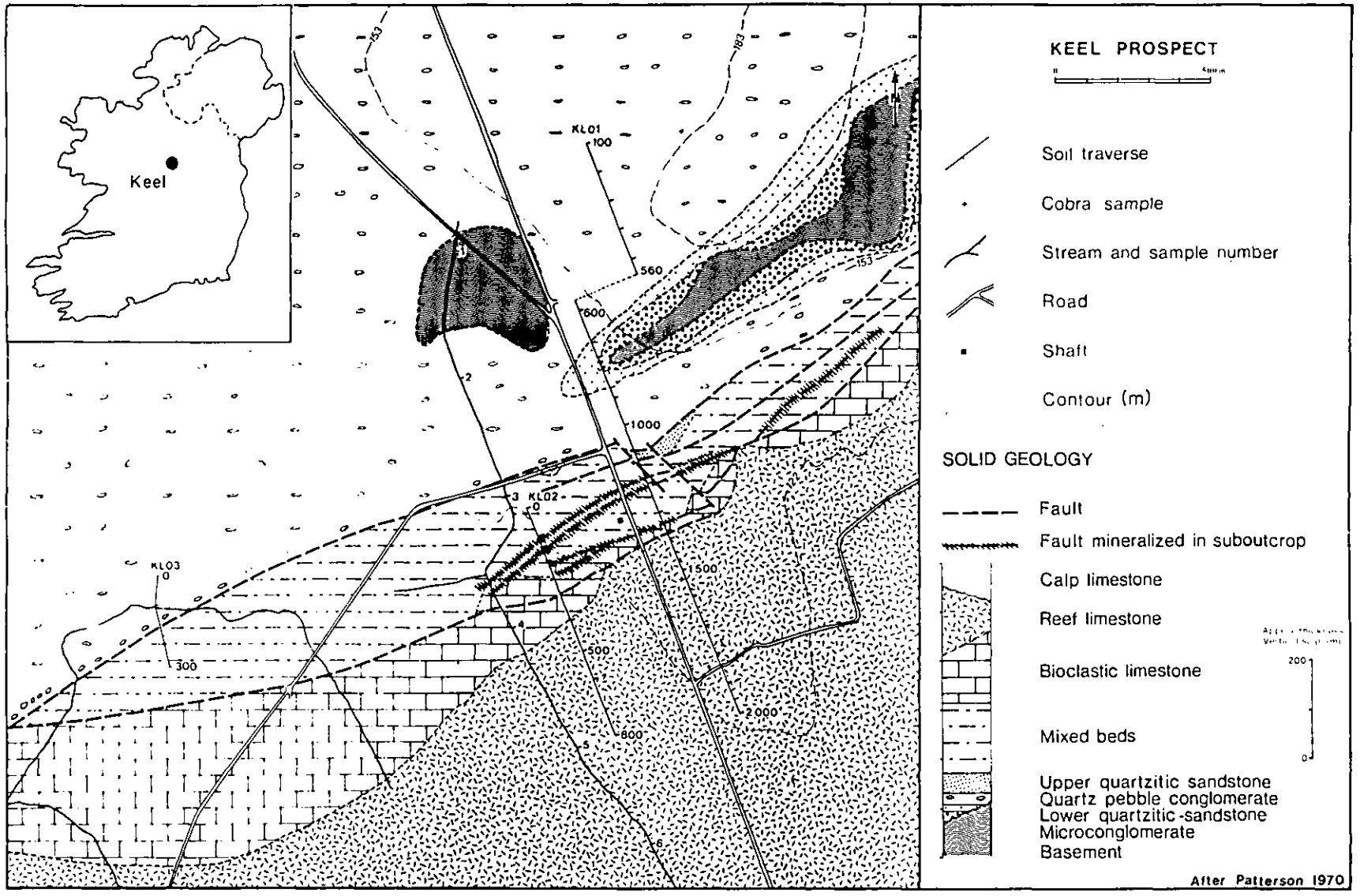


Fig 7.1 Keel: solid geology

interdigitates with the overlying massive Reef (or, more accurately, bank) Limestone, the base of which is patchily pyritic.

Hercynian tectonism folded the Lower Carboniferous beds, tilted the sequence to the south, and produced north dipping low angle normal faulting and south dipping high angle faulting. There are also later (?Tertiary) faults throwing both east and west.

Massive sulphides are structurally controlled and occupy some of the Hercynian high angle faults. The mineralization is restricted to the Mixed Beds and Lower Clastic units and is sharply truncated at the overlying Bioclastic Limestone and underlying Silurian basement.

Typically the mineralization grades 2 - 15% Zn over 3 - 15 m. The main ore mineral is cadmium-rich sphalerite with minor galena, argentian tetrahedrite, pyrite, marcasite and traces of sulphosalts. The gangue is carbonate and quartz.

Minor disseminated stratabound sphalerite is known from the Mixed Beds and Upper Quartzitic sandstone. Significant massive pyrite, with minor galena and sphalerite, occurs in the 'Reef' limestone.

b) Lithogeochemistry (Watling, 1973)

Watling's investigations show there is no indicator element halo surrounding the mineralization, although the Upper Mixed Beds are enriched in iron and manganese. Concentrations of cadmium, mercury and silver correlate with zinc as, to a lesser extent, does copper. There is some suggestion that the Zn/Pb ratio of the mineralization decreases with the depth and northwards. Emission spectrograph determinations show that silver is preferentially

enriched in galena (approx. 3% of ore minerals), as is antimony. Typical concentrations in galena are 1000 ppm Ag and 5000 ppm Sb while the sphalerite has 150 ppm Ag, 1000 ppm Sb and 15000 ppm Cd.

c) Surficial Geology (Evans, 1971)

An important feature of Keel geology is the development of a sub-till gossanous zone in the Mixed Beds. This lies to the north of, and is not contiguous with the mineralized faults. The gossanous area is known as the Decomposed Zone and probably represents the weathered remains of disseminated sulphides. The age of the zone is unknown but is probably a composite of pre-, inter- and post-glacial weathering and is comparable to the secondary orebody at Tynagh. The Decomposed Zone is considerably enriched in several elements: notably manganese (2 - 9%), iron (1 - 30 %), mercury (2 - 160 ppm) and barium (1000 - 17000 ppm); with localised enrichments in antimony (mean 16 ppm) and arsenic (mean 95 ppm).

During the Pleistocene glacial till was deposited over the Keel area from the north and west. The till is typically 2 - 7 m thick, but locally reaches 18 m. At surface, poorly drained podzols have developed, although their A and B horizons have been admixed by ploughing. Basin peats are locally developed, notably west of the Keel shaft.

7.1.2 Programme

The three soil traverses were designed to investigate specific aspects of Keel geochemistry. A long regional traverse (KL01) crosses the Decomposed Zone, mineralized faults and the main part of the complex lead-zinc anomalies. Deep overburden Cobra drill sampling was used to follow up

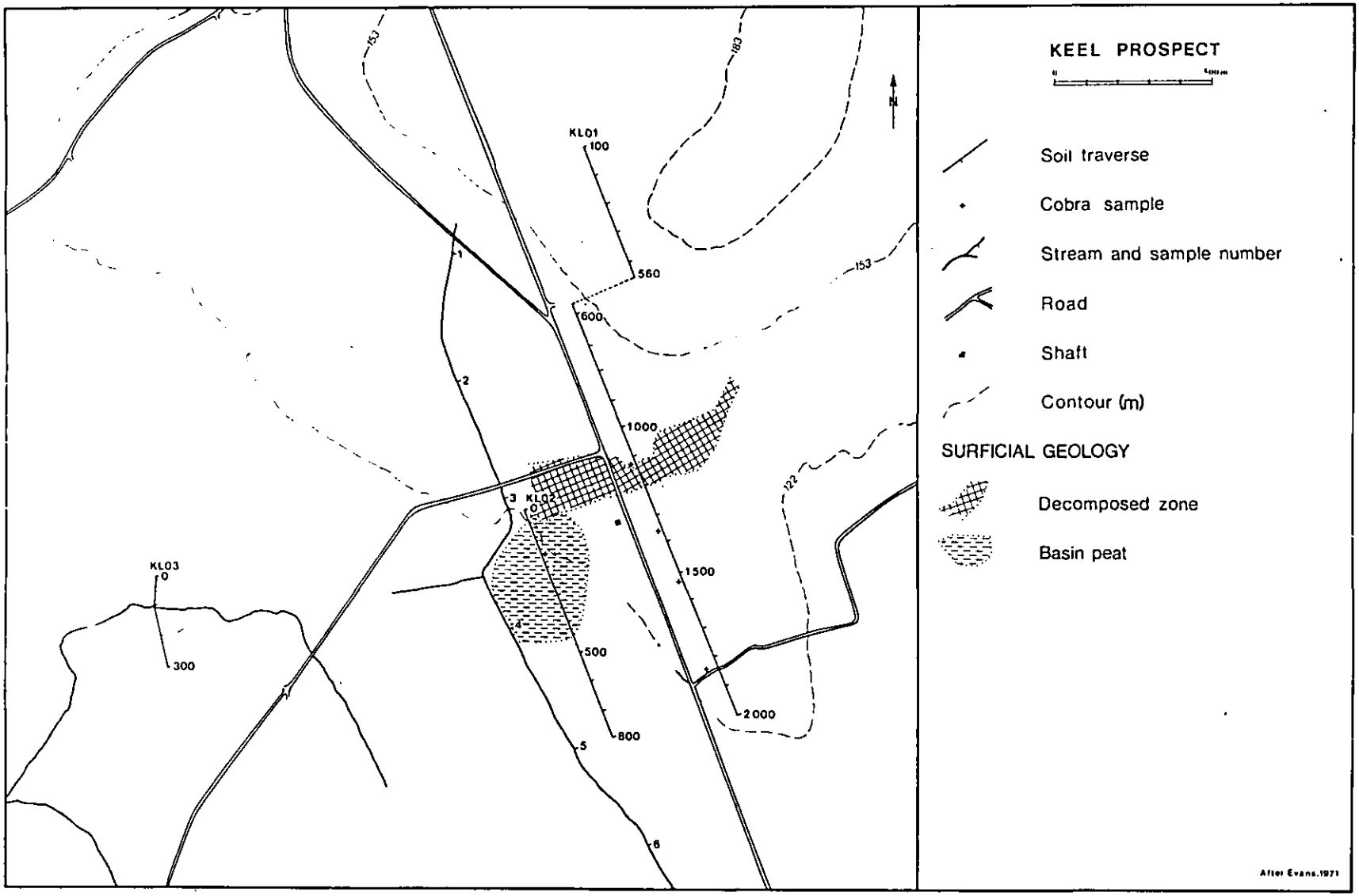


Fig 7.2 Keel: surficial geology

this traverse. Two other traverses were used to study element enrichment in the basin peat (KL02) and hydromorphic anomalies associated with the banks of drainages (KL03). In addition, six stream sediment and water samples represent a limited investigation of dispersion in surface drainage.

a) Regional Traverse KL01

The lead and zinc concentrations (Fig. 7.5) are comparable to those of the regional studies (Figs. 7.3, 7.4). The lead maximum is 800 ppm relative to 20 ppm background on the Silurian, while comparable zinc values are 1200 ppm relative to 50 ppm. The twin peaked lead pattern is more consistent than zinc which is very ragged. The indicator elements are high over the subcrop of the Decomposed Zone but lower over that of mineralized faults (1200 m and 1350 m respectively). A lead peak and high zinc values north of the Decomposed Zone (950 m) are thus developed upslope and upice from the known mineralization. Anomalous zinc values at 1800 m occur on the banks of a minor drainage channel. Copper has a background distribution with only single point highs

Iron and manganese have very different distributions. Manganese shows a distinct anomalous population with the highest values over the subcrop of the Decomposed Zone at 1120. Factor analysis shows that manganese, arsenic, antimony and to a lesser extent lead and zinc have highs loading on one factor (factor 1, Table 7.1) and that high factor scores occur over the subcrop of the Decomposed Zone and to a lesser degree over the Silurian inlier (at 800 m). Calcium is low over the suboutcrop of the lowest Carboniferous units (700 -850 m) and Mixed Beds (1000 - 1400 m), while organic carbon shows little variation

	FACT 1	FACT 2	FACT 3	FACT 4	FACT 5
CU	-.4899	-.0286	.5550	-.1767	-.1508
PB	-.6523	-.6781	-.0115	-.0194	.0706
ZN	-.7382	-.5232	.1076	-.0165	-.0213
FE	-.3672	.6012	.0556	.4846	-.1123
MN	-.6689	.4860	.1386	.0720	.1071
CA	.2284	-.2141	.3274	.6696	-.4876
NI	-.1303	.1727	-.1989	-.5025	-.7823
AS	-.8491	-.1290	-.2227	.1793	-.0085
SB	-.8719	-.1766	-.0925	.0220	-.0635
BI	-.4450	.5795	-.0736	-.0197	-.0460
SE	-.3990	.4471	.4792	-.2381	.1967
C	.2943	-.1785	.8321	-.1224	-.0279

Table 7.1 Factor loadings unrotated 5 factor model : Keel soils

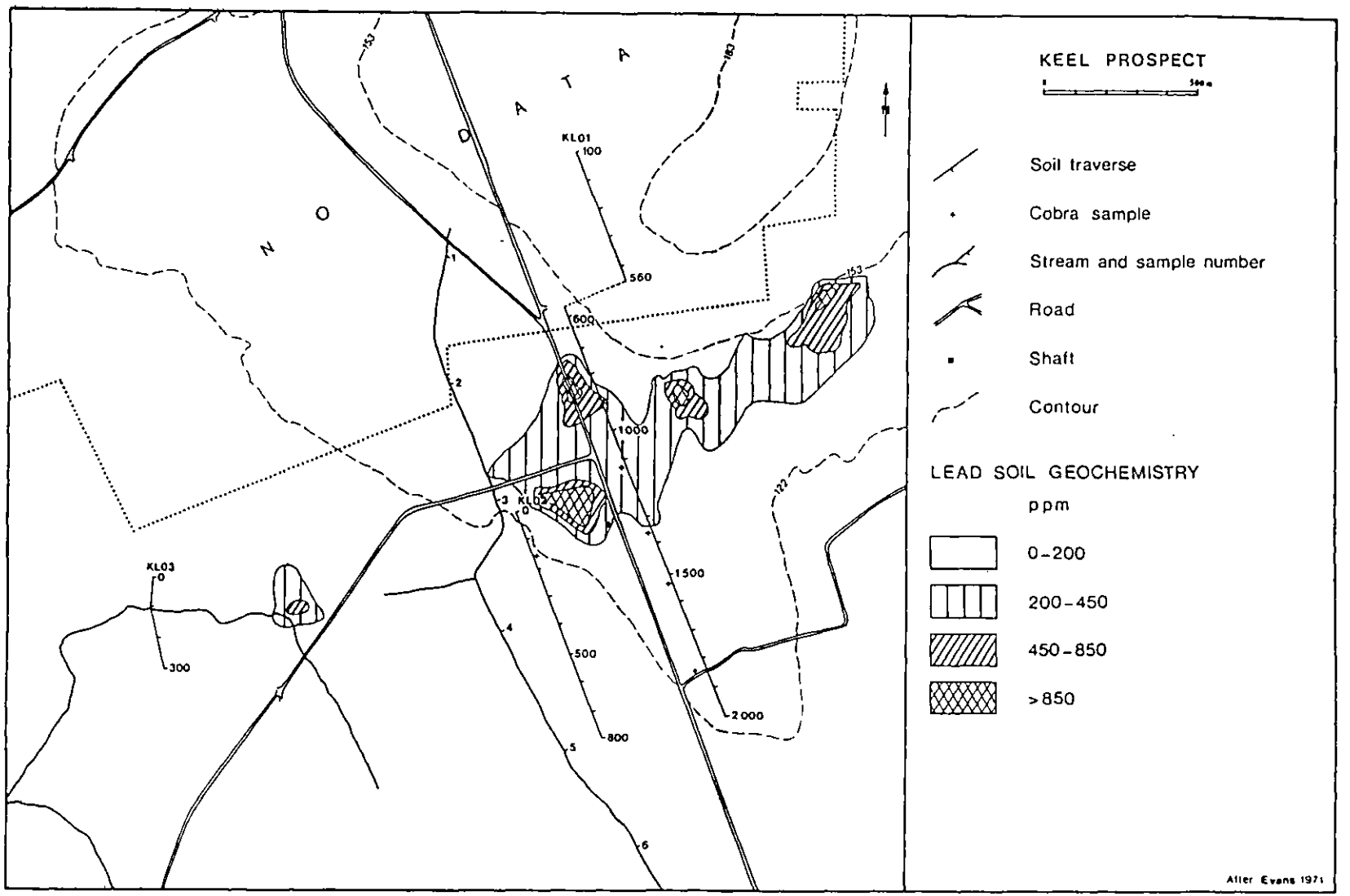


Fig 7.3 Keel: regional lead soil geochemistry

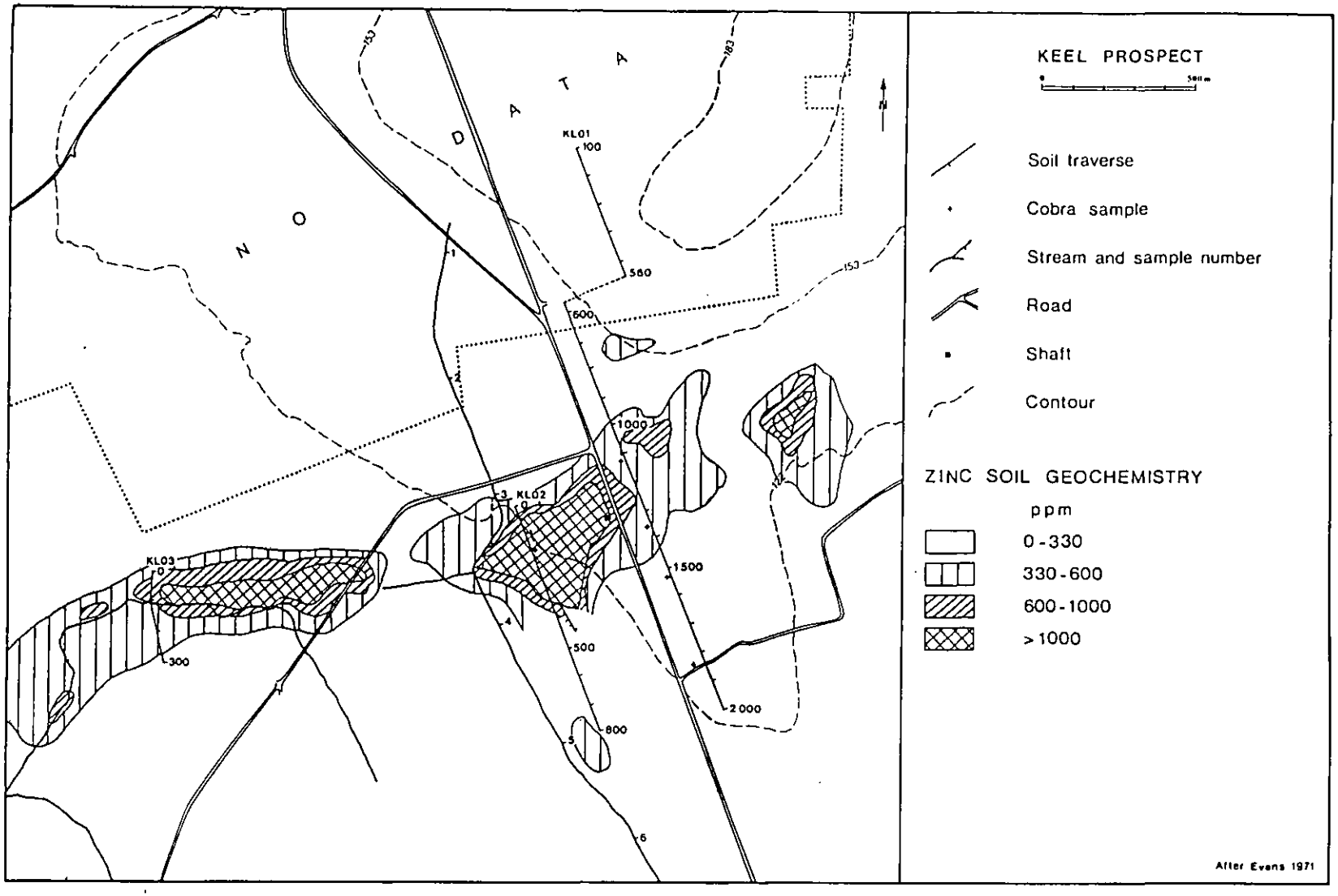


Fig 7.4 Keel: regional zinc soil geochemistry

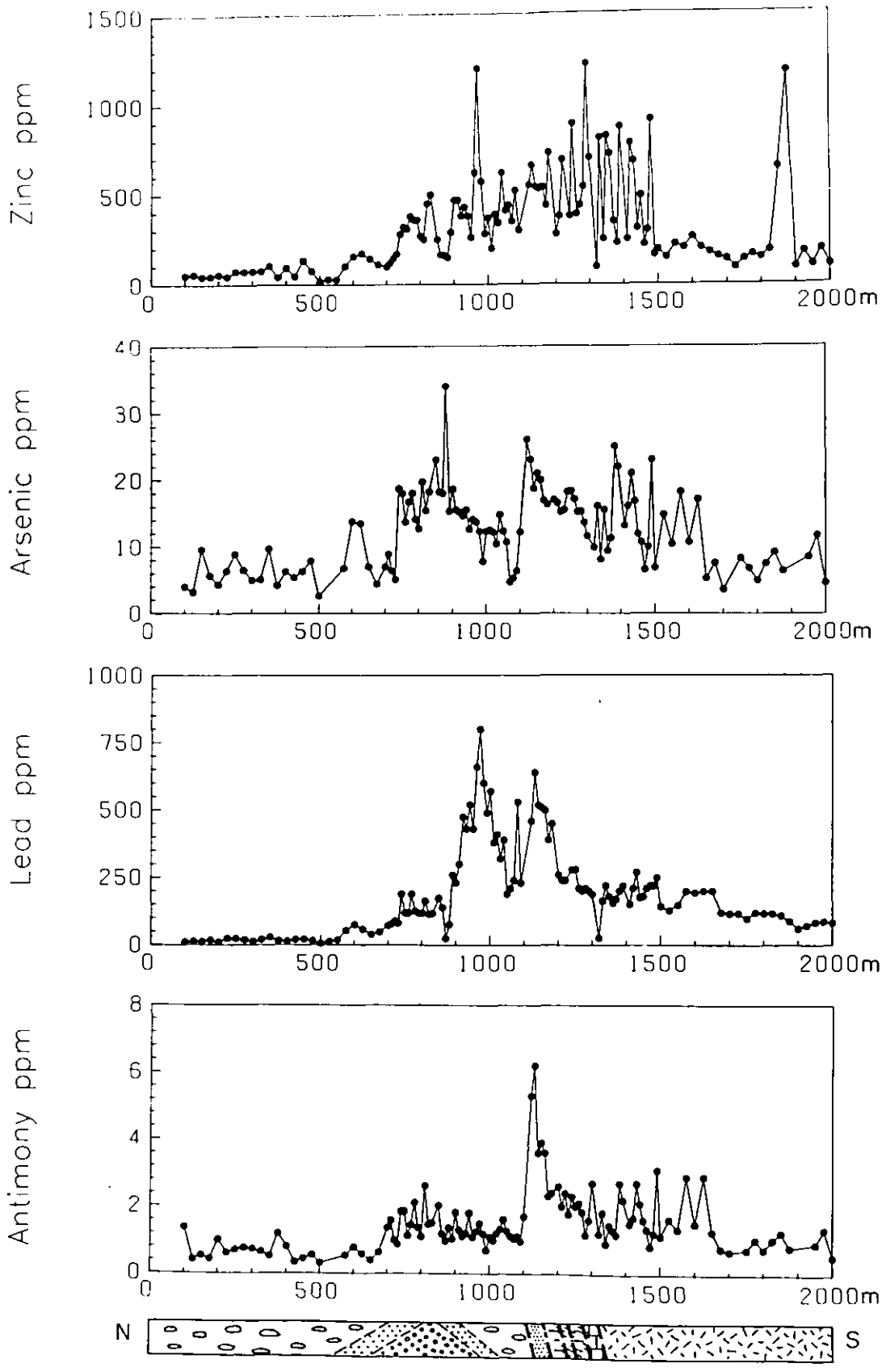


Fig 7.5 Keel: soil traverse KL01
Geological symbols as for Fig 7.1

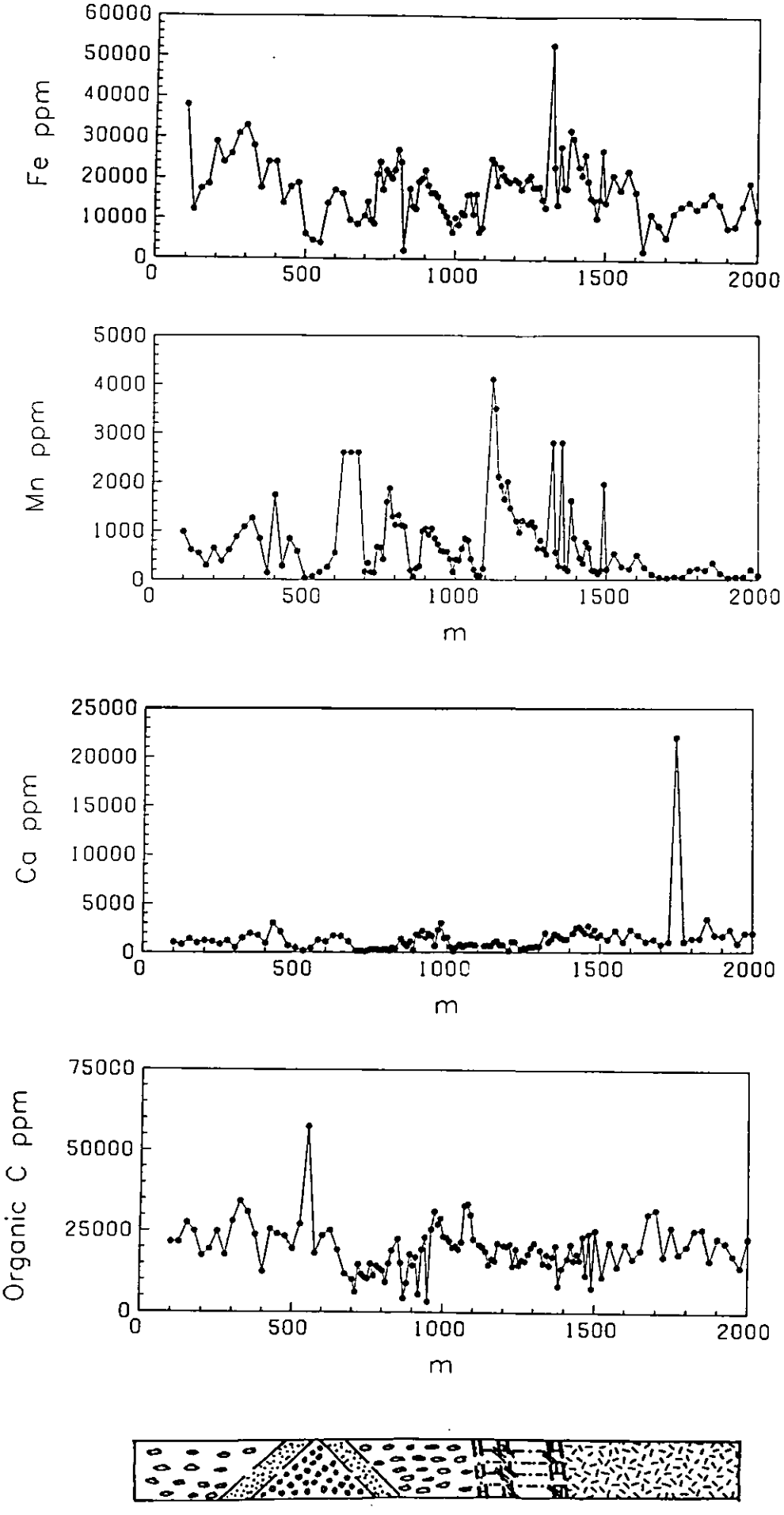


Fig 7.6 Keel: soil traverse KL01
Geological symbols as for Fig 7.1

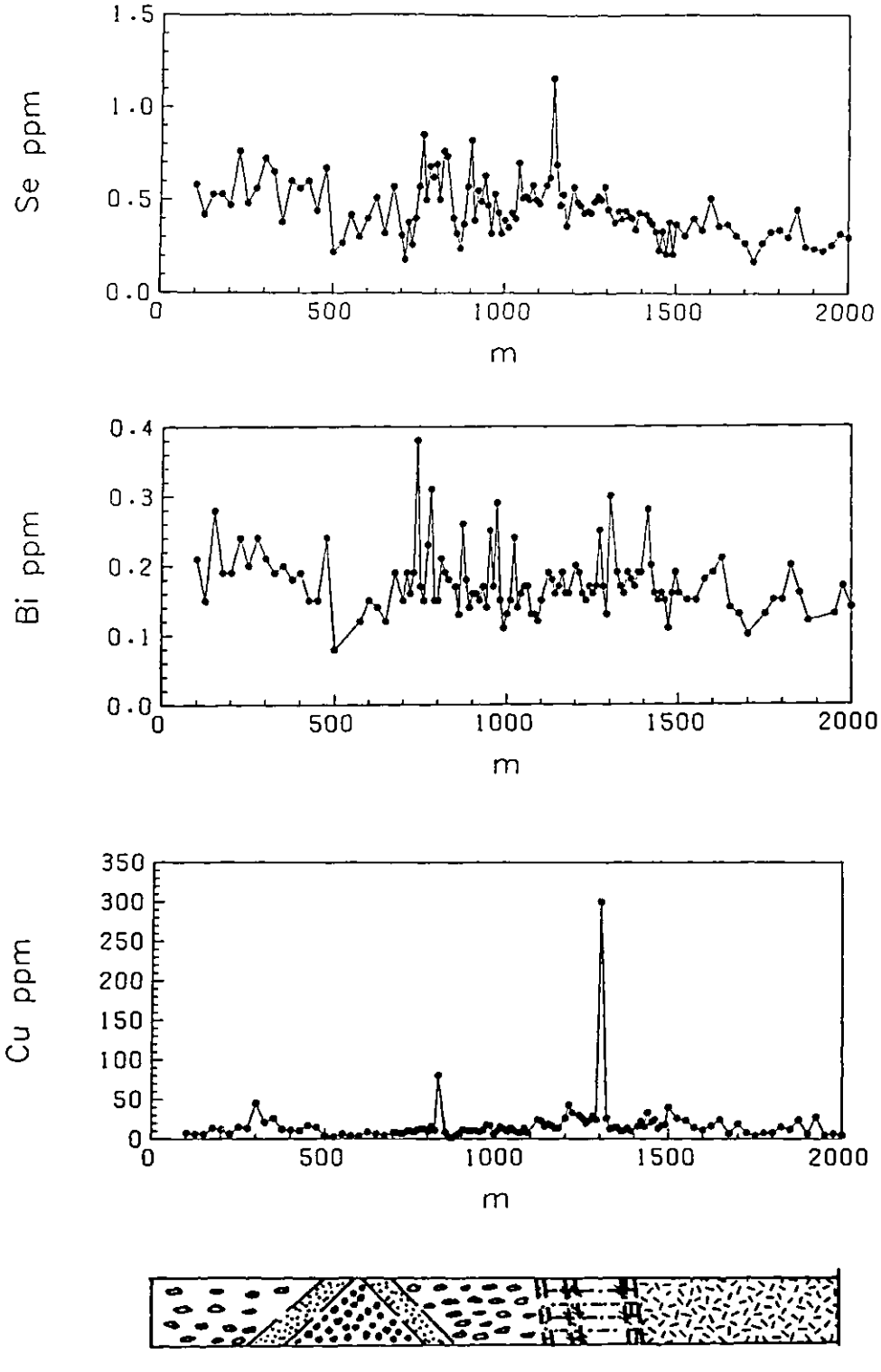


Fig 7.7 Keel: soil traverse KL01
Geological symbols as for Fig 7.1

except for a peak over a bog at 550 m.

Antimony has a distinct peak over the subcrop of the Decomposed Zone (Fig. 7.5) reaching 6.5 ppm relative to background of 1 ppm. There are lesser highs to its south and over the Silurian inlier. Arsenic has a somewhat similar distribution to antimony with the high at 850 more pronounced, reaching 35 ppm relative to background of 10 ppm As, and that over the Decomposed Zone less obvious. Bismuth has a background distribution,as has selenium (apart from a single point high over the suboutcrop of the Decomposed Zone).

b) Till Profile (KL01)

Four Cobra drill holes were sunk through the till: at 1130 m over the main antimony anomaly; at 1350 m over the suboutcrop of a mineralized fault; and two background sites at 1530 and 1850 m.

Zinc, lead and cadmium (Fig. 7.8) show very similar distribution with enrichment throughout the profile at 1130 m and at the surface on 1350 m, where zinc and cadmium are strongly anomalous.

Silver, antimony, manganese (Fig. 7.8, 7.9) and to a lesser degree barium are also enriched in the profile over the Decomposed Zone. Antimony and silver are also enriched at 1 m depth, antimony at 1530 m and silver at 1350 m.

Iron shows a very different distribution with enrichment mainly at the surface and intermediate depth. It has strong correlation with arsenic, so that arsenic is enriched at the surface at 1130 and 1350 m and at 1 m in profiles 1530 and 1850 m. The distribution of calcium at depth correlates strongly with geology, as high values occur over the subcrop of the limestones. However, there is leaching of both calcium and magnesium from the surface.

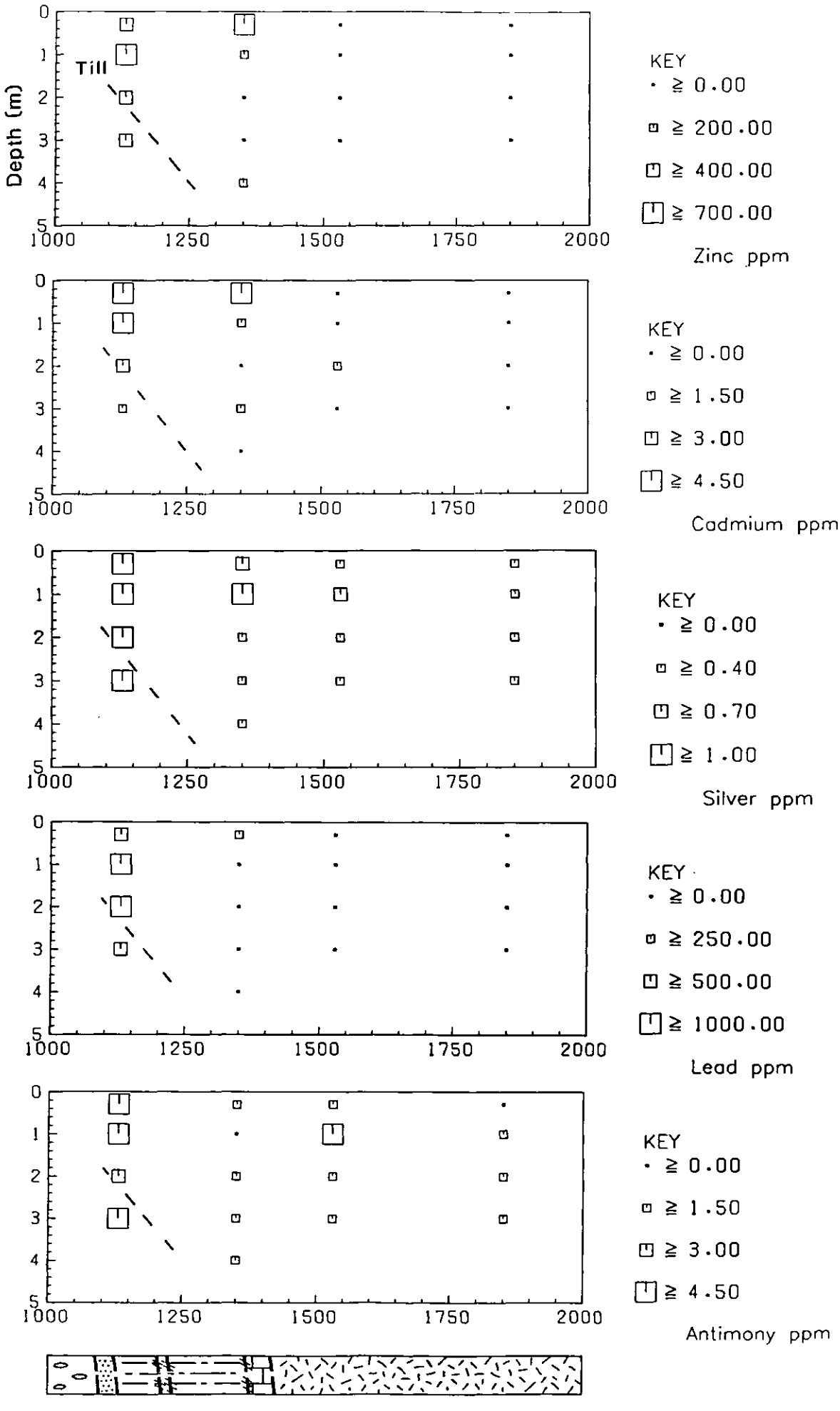


Fig 7.8 Keel: till profile KL01
Geological symbols as for Fig 7.1

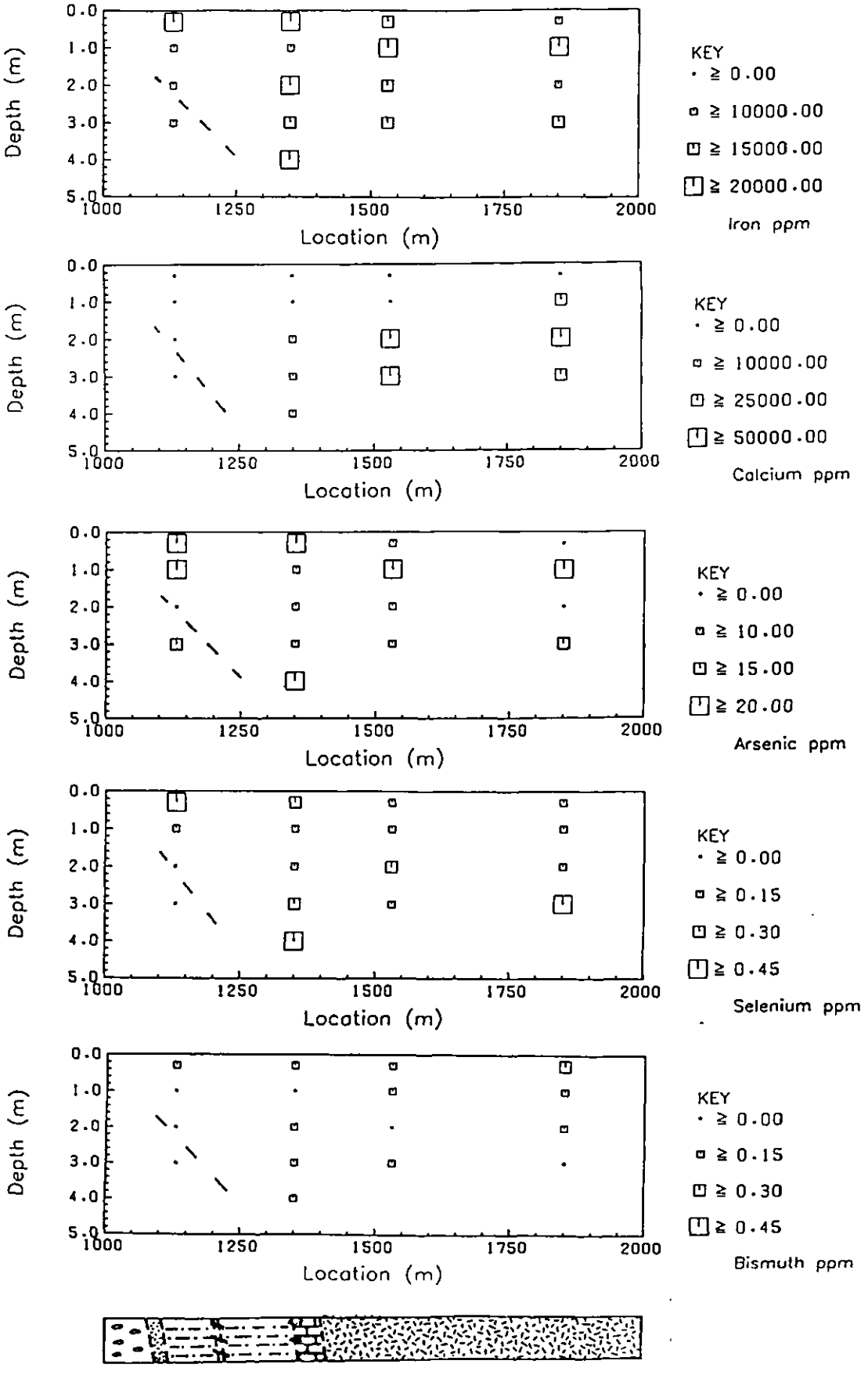


Fig 7.9 Keel: till profile KL01
Geological symbols as for Fig 7.1

Bismuth values are low and there is no obvious pattern except a marked concentration in the coarse ($^+$ 190μm) fraction. Selenium is enriched at the surface over the Decomposed Zone and at depth on profiles 1350 and 1830 m.

c) Soil Traverse KL02

High lead and zinc concentrations correlate with the location of the basin peat (Fig. 7.10) with high lead values also occurring over the subcrop of the Decomposed Zone. Maximum zinc values (in peat) are extremely high, reaching 16%, and they overlie the inferred subcrop of the mineralized fault beneath the peatbog. There is also a small copper anomaly in this area although the element is generally low over the bog.

Iron and manganese are low over the bog and concentrate at the southern edge (500 - 600 m). In contrast calcium is high over the bog.

Arsenic and antimony have very different patterns: antimony is high over the bog (14 ppm relative to 1 ppm background) while arsenic correlates with iron and is high at the edge of the bog. Bismuth has little contrast but it is generally lower over the bog.

d) Soil Traverse KL03

Zinc (Fig. 7.12) confirms the previous work with the centre of the zinc anomaly correlating with the river. There are no comparable anomalies in any other element.

e) Stream Sediments and Waters KL04

The limited drainage survey shows significant sediment anomalies in zinc and cadmium (Fig. 7.13) with zinc reaching 490 ppm relative to background of 100 ppm

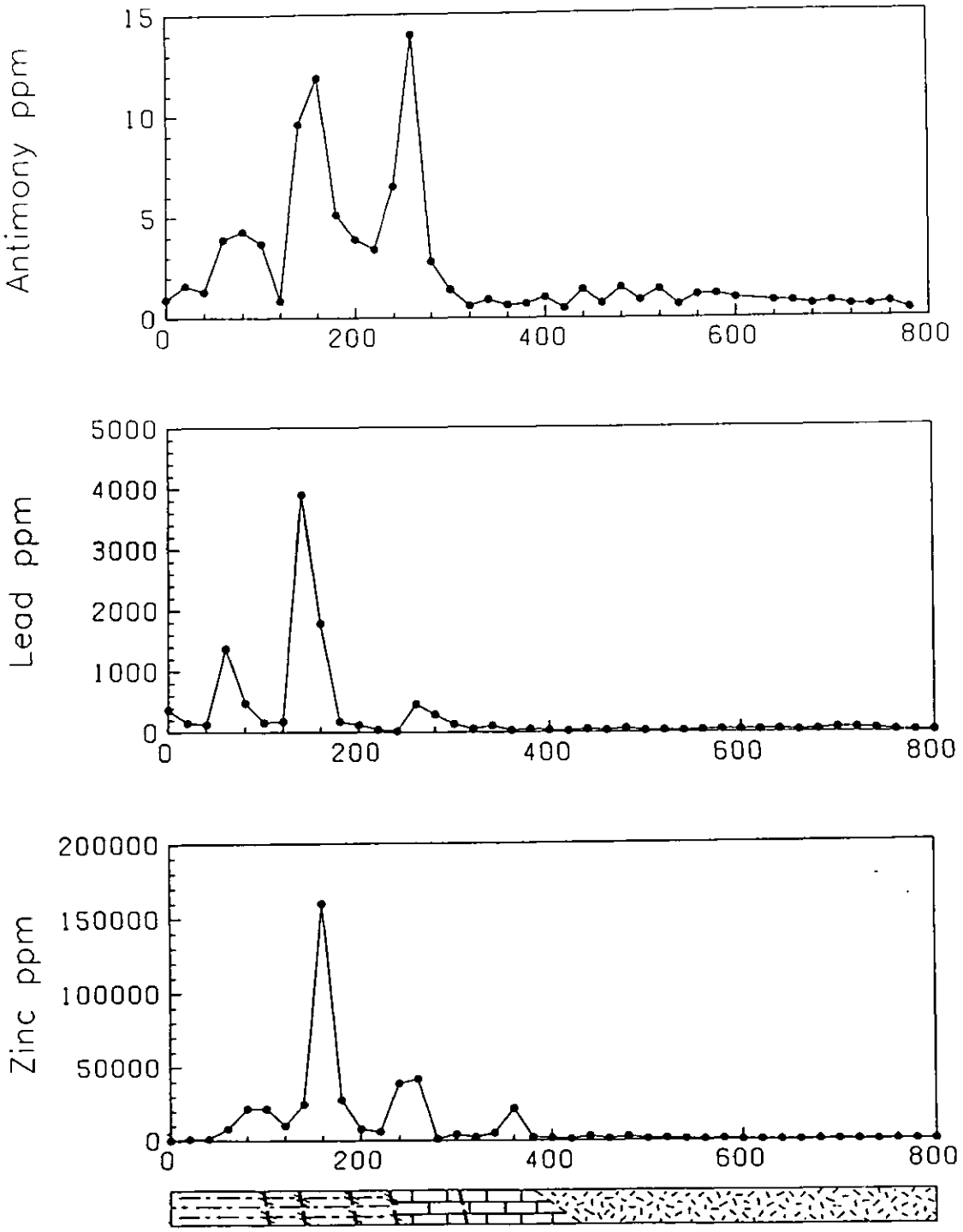


Fig 7.10 Keel: soil traverse KL02
Geological symbols as for Fig 7.1

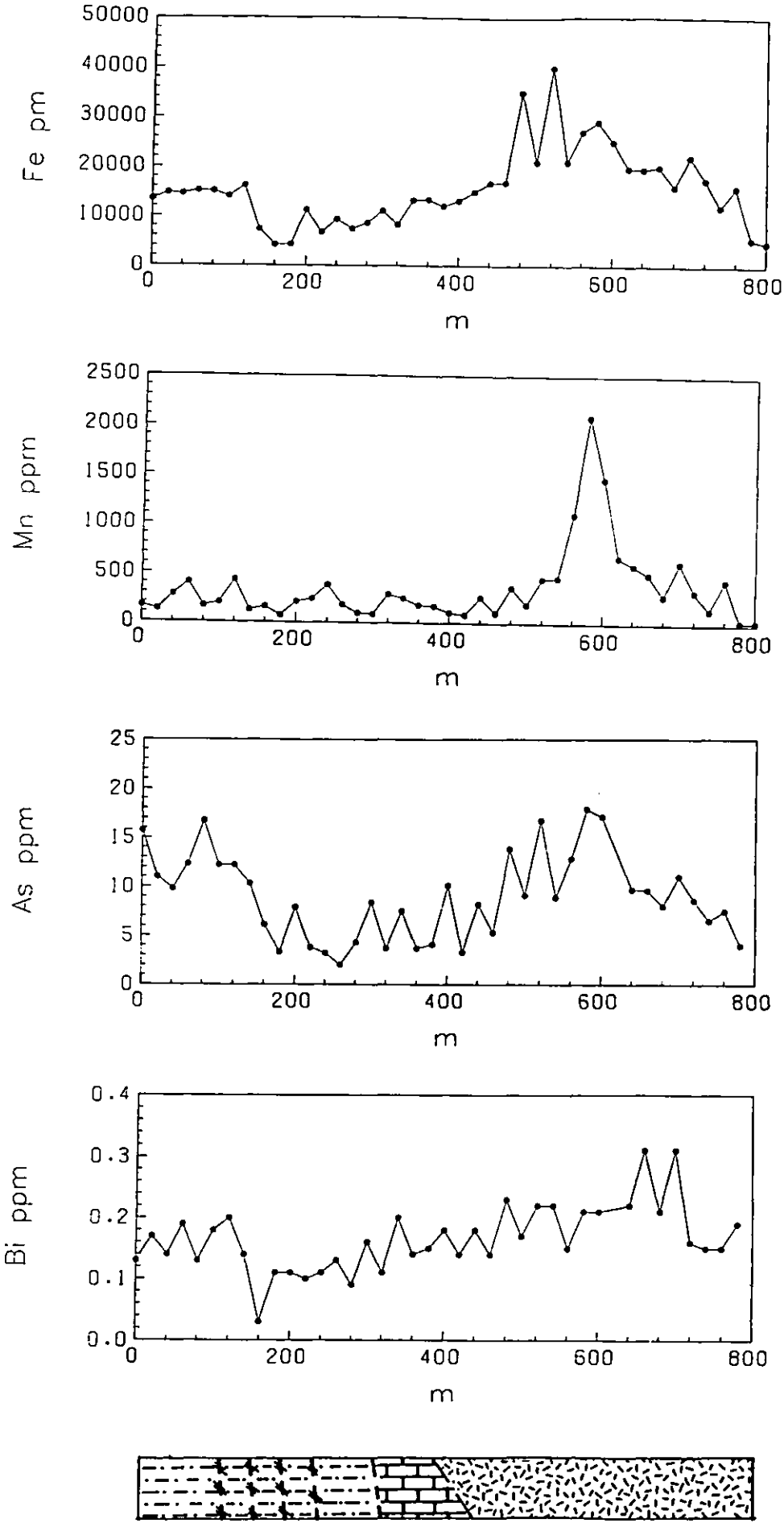


Fig 7.11 Keel: soil traverse KL02
Geological symbols as for Fig 7.1

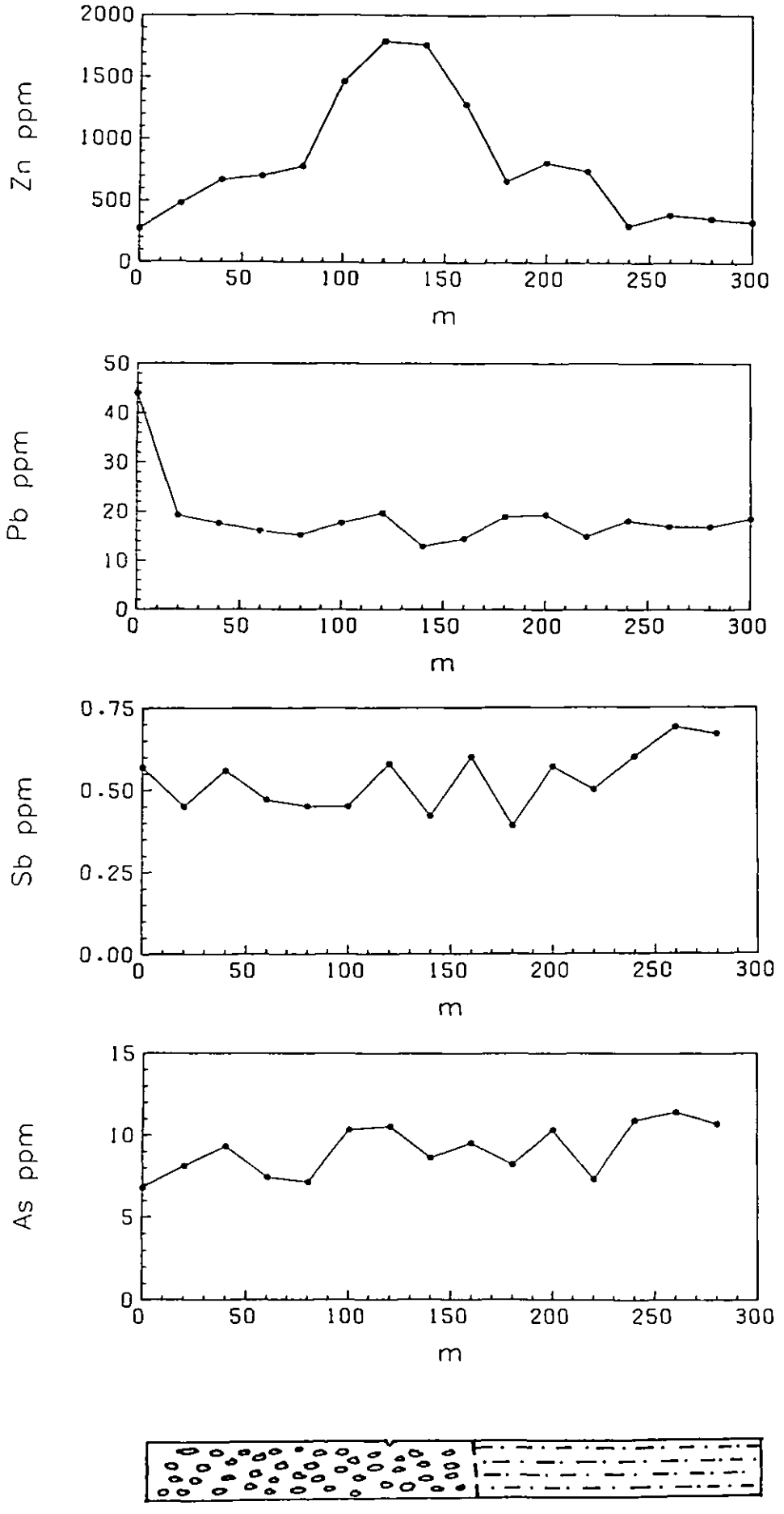


Fig 7.12 Keel: soil traverse KL03
Geological symbols as for Fig 7.1

and cadmium 24 ppm relative to 1 ppm Cd background. Calcium shows a very similar pattern but other elements including arsenic and antimony have little contrast.

Zinc in solution shows a similar distribution to that in the sediments reaching 140 ppb relative to background of 5 ppb. Arsenic shows a strong correlation with sodium and potassium and is not enriched downstream from the mineralization. Other pathfinders are at or near the analytical detection limit for the elements. There is little variation in pH except for the southernmost sample. There a pH increase correlates with a rise in dissolved calcium, as the stream flows onto till which overlies limestone (Fig. 7.14)

7.1.3 Discussion

Regional lead and zinc anomalies make the recognition of mineralization in the Keel area relatively easy but they do little to pinpoint drill targets. Antimony in well drained soils does however locate the Decomposed Zone and can be recommended in a detailed exploration programme. Complementary studies on vapour geochemistry demonstrate that COS is the only known geochemical guide to the mineralized faults although ΔO_2 and CO_2 locate the southernmost mineralized fault and mercury is particularly high over both the northern mineralized faults and the Decomposed Zone (Lovell et al, 1979; Hale and Moon, 1982).

The broad lead and zinc soil anomalies are not fully explicable from available data. Till profiles, with metals smeared on the surface to the south of the Decomposed Zone, demonstrate the hydromorphic nature of transport of metal southwards. The lack of surficial geochemical expression of the faults can be explained as a result of the inhibiting effect of the thicker till

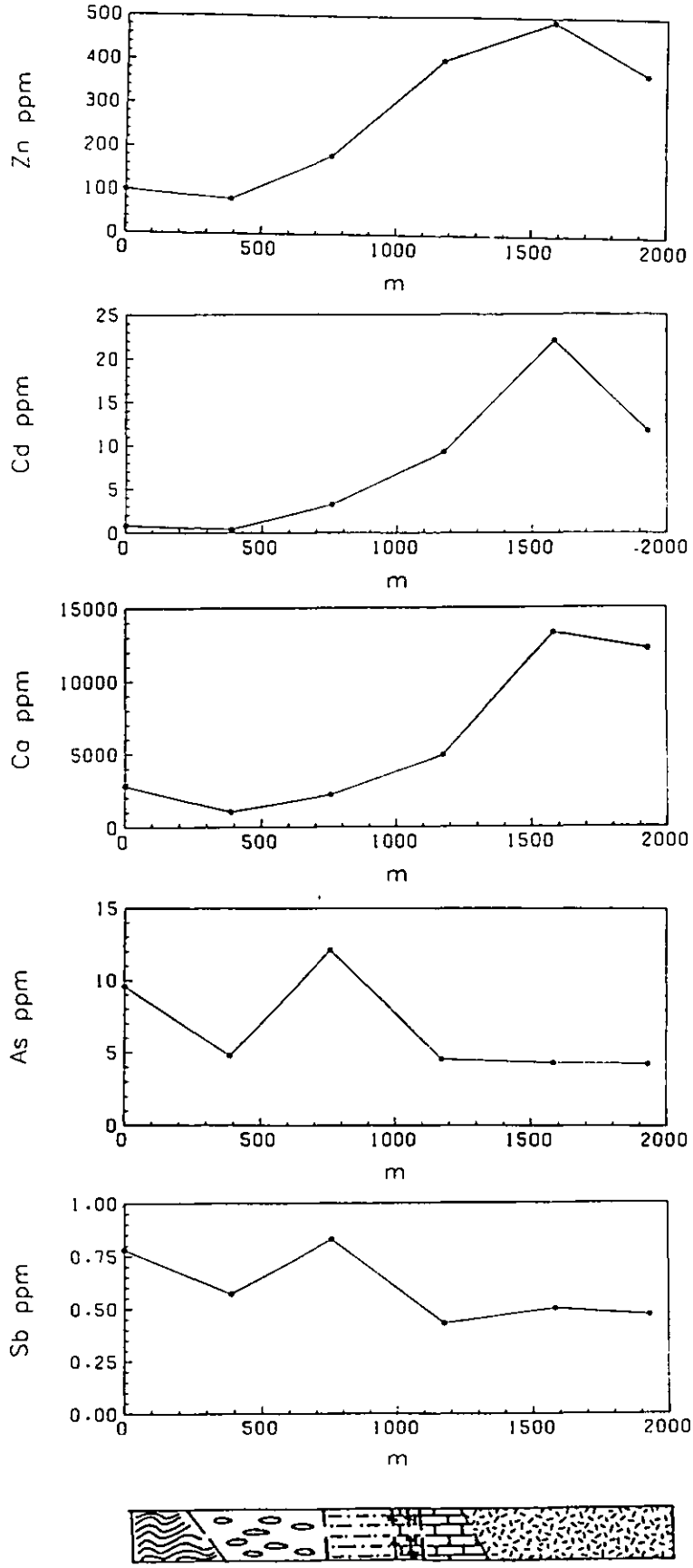


Fig 7.13 Keel: stream sediments KL04
Geological symbols as for Fig 7.1

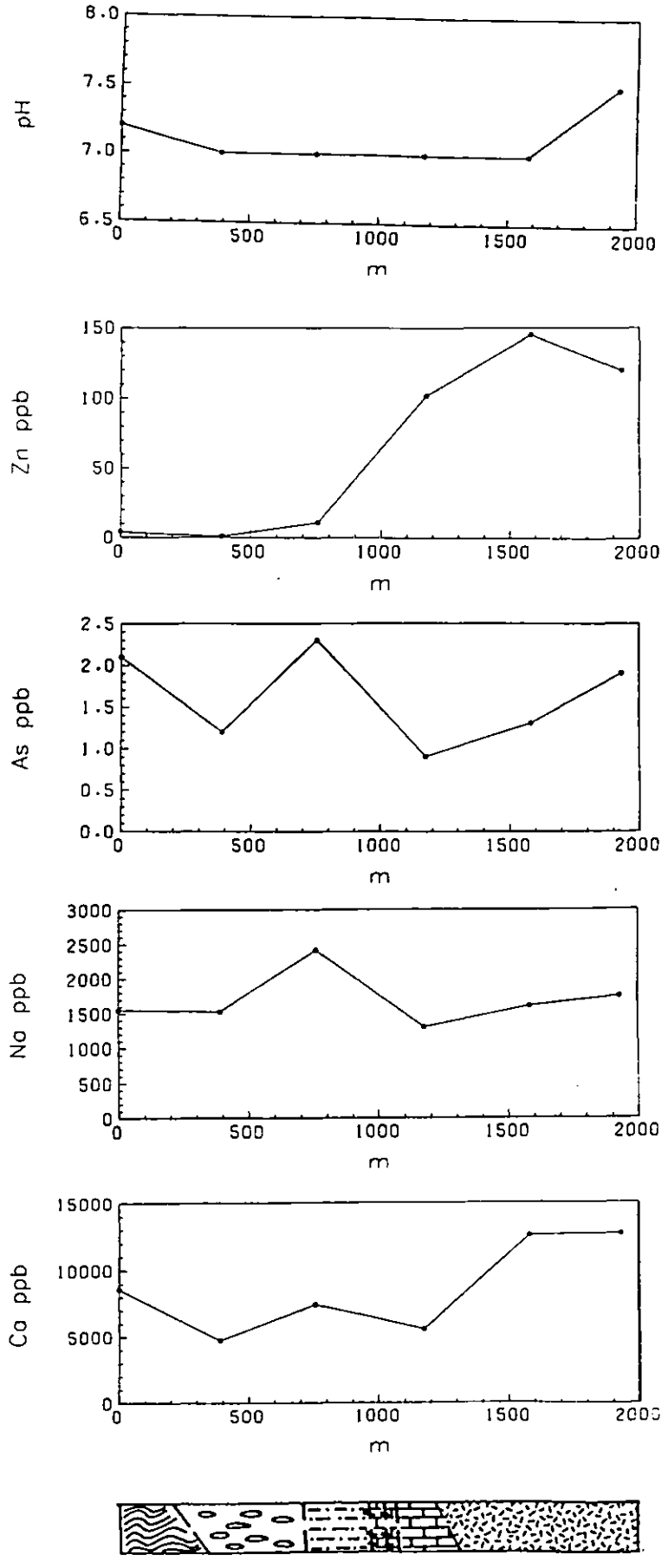


Fig 7.14 Keel: stream waters KL04
Geological symbols as for Fig 7.1

on element dispersion. Anomalous lead and zinc values occur north, and thus up-ice and upslope from the Decomposed Zone and require a different explanation. The metals in the anomaly north of the Decomposed Zone are possibly also more loosely bound than that south of it. (This suggestion is based on stepwise thermal volatilisation studies by A. Bourne which give highly anomalous values over this northern soil anomaly). Two obvious alternative explanations are: (i) that the gentle hydrostatic gradient and very shallow water table mean that upslope dispersion is possible or (ii) the anomalies represent dispersion southward from and undiscovered metal enrichment to the north of the Decomposed Zone, possibly related to the Silurian inlier (between 700 and 300 m on KL01). I favour the latter alternative as the metal in the northern anomalies is lead rather than the potentially more mobile zinc. Zinc is also strongly concentrated in the peat bog and along the banks of rivers, which transport the metal in solution (q.v.). It is not obvious whether the zinc and other metals in the bogare derived from the underlying mineralized faults or from infiltration of anomalous soil waters.

Antimony is anomalous over the subcrop of the Decomposed Zone and is strongly enriched in the basin peat bog. Dispersion in till is very limited, reflecting the relative insolubility of antimony. The association of antimony with the peat bog indicates that it is either fixed as reduced sulphide or by complexation with organic matter. The known affinity of zinc for organic matter (Cannon, 1955) and the zinc-antimony association suggest the latter possibility is more likely. Complexation of antimony with organic acids has been shown to occur experimentally (Bowen et al, 1979).

Arsenic is enriched over both base metal anomalies on KL01 but profiles indicate that it is relatively mobile

and fixed by iron oxides. This situation also applies to the peat bog in which arsenic is fixed by iron oxides precipitated around its margins.

Only zinc and cadmium disperse into stream sediments and waters. Arsenic and antimony values are background, presumably because the elements are fixed in soils or bogs. Hydromorphic infiltration anomalies along the banks of the rivers only occur for zinc and cadmium.

Lead, zinc, antimony, cadmium and, from literature evidence, mercury, are recommended in the analysis of soil samples. Basal till sampling is undoubtedly superior and this is the optimum medium. Stream sediment sampling for zinc, although initially effective in the Riofinex exploration programme, is of limited value as the rivers have limited erosive power and most of the area is covered with thicker till than the Keel area.

7.2 Mallow, Co. Cork, Ireland

The Mallow deposit is a resource of 4 million tons of 0.7% copper and 25 g/t silver and occurs 6 km north of the town of the same name (Wilbur and Royall, 1975).

The geochemical problem at Mallow is that the copper response in soils over the sub-outcrop of the mineralization is weak and not definitive. Pathfinder elements and volatiles are known to be associated with the similar Gortdrum deposit, which is 50 km to the northeast (Williams and McArdle, 1978; Steed and Tyler, 1979).

7.2.1 Geology and Regional Geochemistry

a) Solid Geology (Wilbur and Royall, 1975)

Mineralization occurs within a marginal marine carbonate sequence, which is laterally equivalent to

the host rocks at Keel, some 180 km to the northeast.

The basal unit at Mallow is Old Red Sandstone of mainly fluviatile origin. This is overlain by a 100 m thick section with interbedded calcarenites and shales ('Lowest Carboniferous Formation') followed by 60 m of crinoidal bedded limestone (Tullacondra Limestone) and a thick Waulsortian Reef complex.

Deformation in the Mallow area is more intense than at Keel and the area is immediately north of a major thrust belt. The mineralized section has been folded and thrust into a dome (Fig. 7.15), which is cut by later, approximately north-south trending dip-slip faults.

Mineralization is both stratabound, primarily in shales, and crosscutting in near vertical calcitic veins. The ore minerals, with chalcopyrite, bornite , chalcocite and tennantite dominant, occur as disseminations and fine veinlets. Other less common primary minerals are native copper, native silver, galena, sphalerite, pyrite and marcasite with calcite, dolomite, barite and quartz as gangue.

b) Surficial Geology

Till cover is ubiquitous and is of the earlier Munsterian age with the younger (Midlandian) deposition absent. Isopachs of drift (Fig. 7.16) demonstrate that till over the Old Red Sandstone is relatively thin (usually less than 5 m) but it is considerably thicker over the limestone, reaching maximum thickness north of the quarry. The soil cover is generally well drained except for boggy areas over the maximum till development.

c) Regional Geochemistry

A regional soil survey, carried out by Munster Base

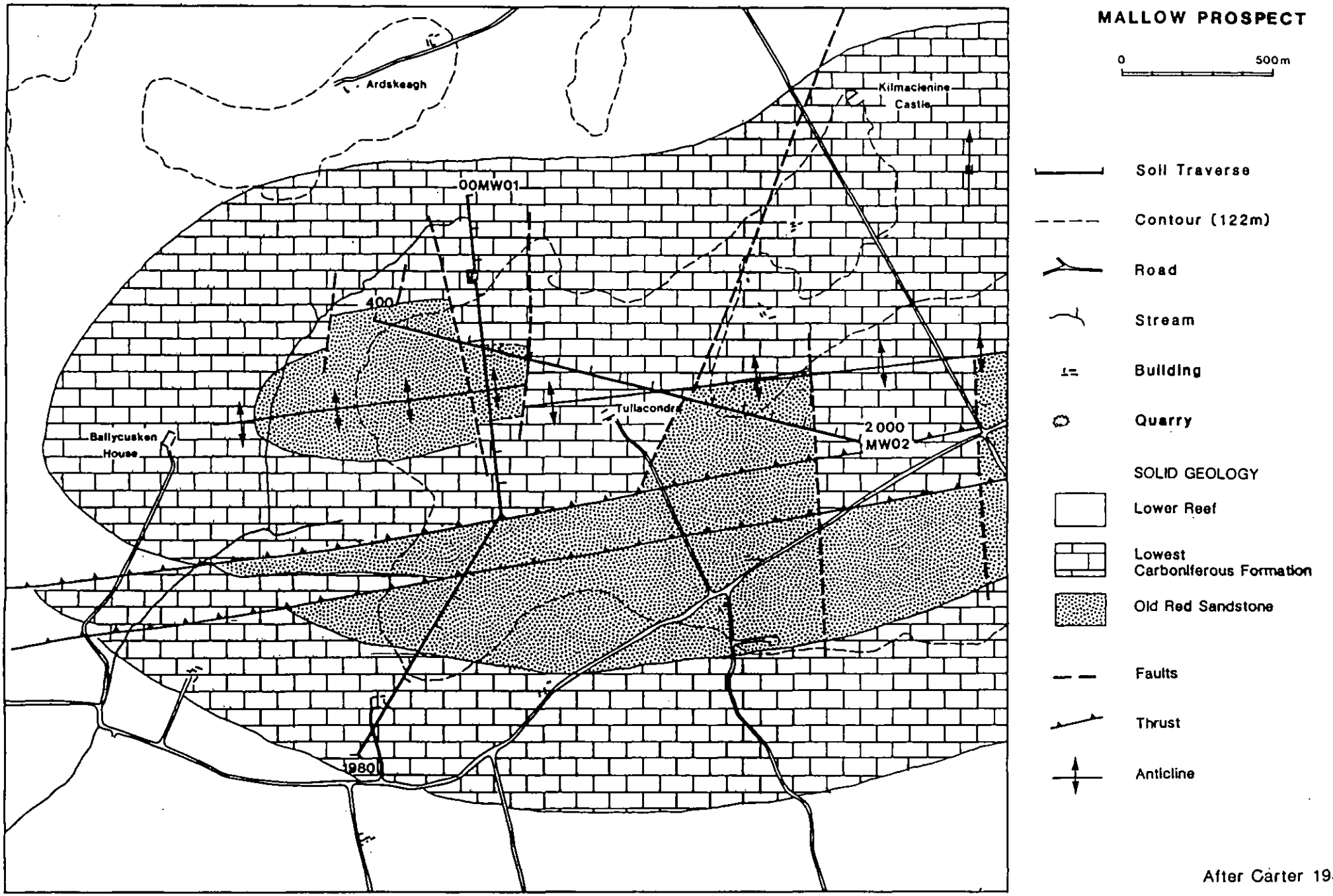


Fig 7.15 Mallow: solid geology

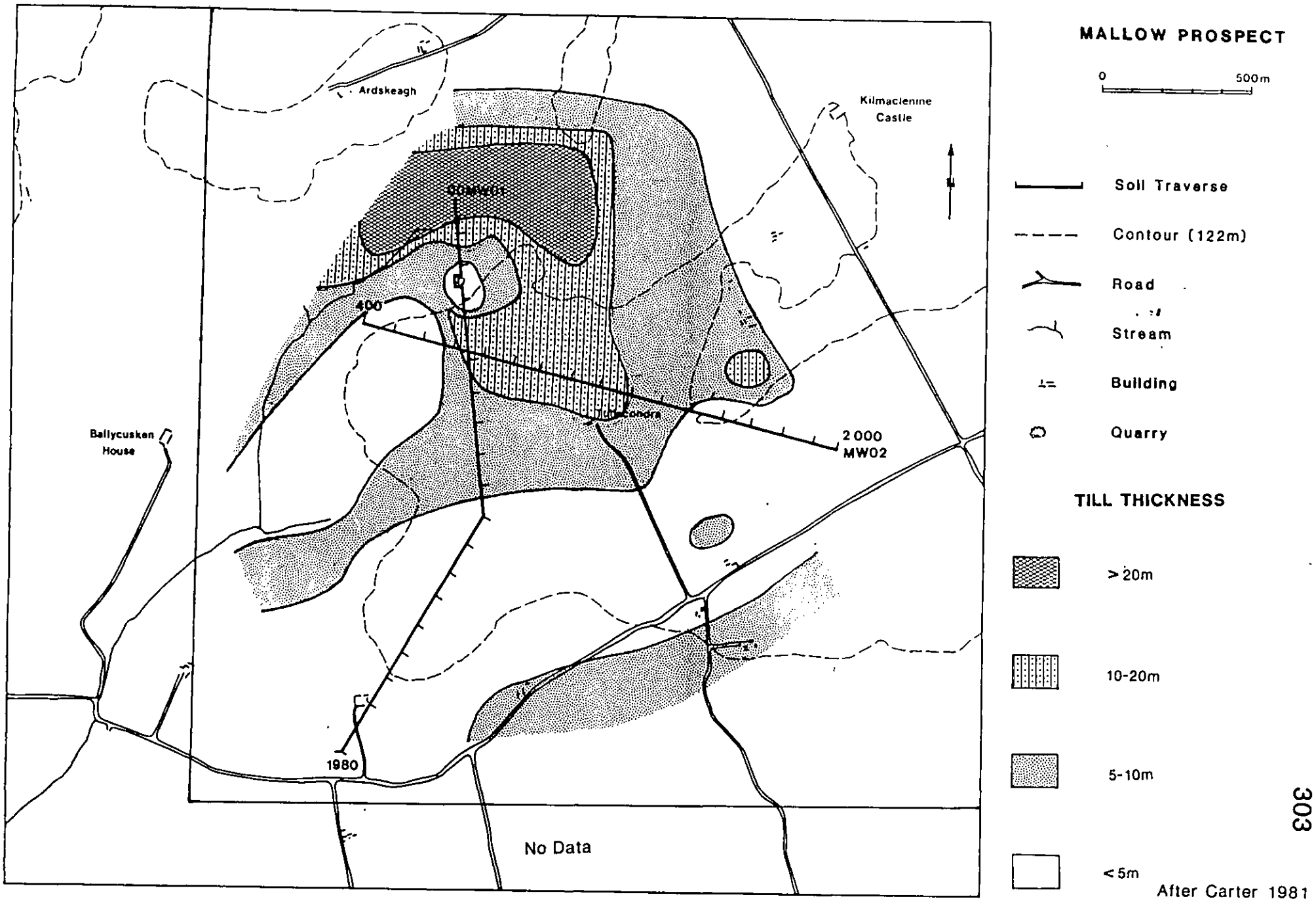


Fig 7.16 Mallow: till thickness

Metals Ltd. using a 150 m grid, shows anomalies of up to 80 ppm Cu relative to background of 40 ppm (colorimetric analysis, Wilbur and Royall, 1975). Follow up sampling (0.6 m depth) revealed a complex anomaly with a general north-south trend. More detailed investigation of till profiles highlighted the influence of till thickness, with an absence of surface anomalies in areas of greater than 4 m cover on mineralized limestones.

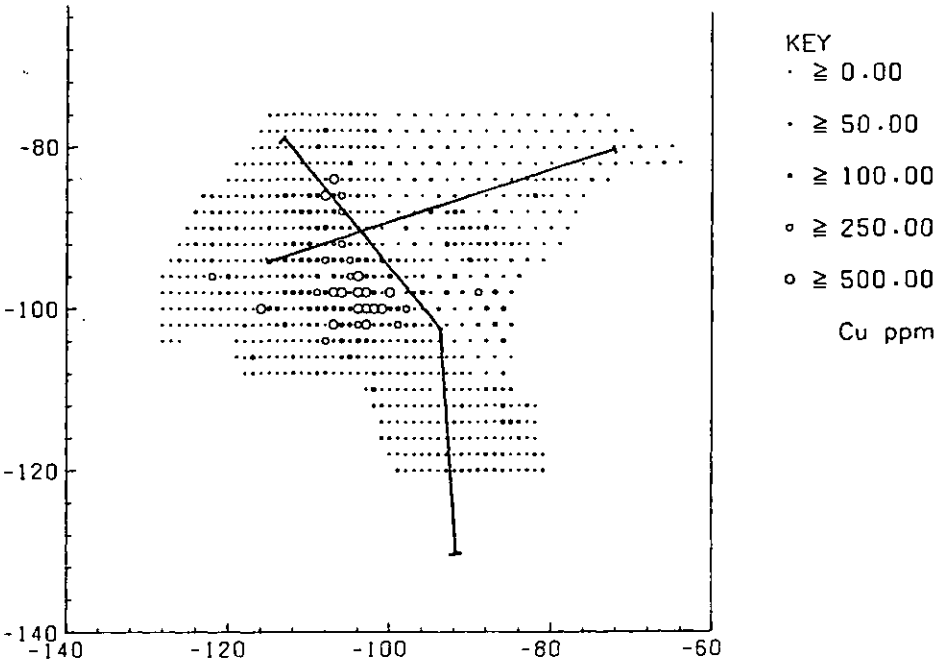
Regional till sampling data (at 2 m depth), kindly made available by Munster Base Metals, demonstrates the complex nature of the copper, lead and zinc anomalies. Copper shows a general SSW trend with high values mainly occurring over sandstone bedrock. The anomaly near the known mineralization is at the far north of the trend. Lead is high, with a north-south trend approximately 600 m to the south and slightly to the east of the copper anomaly. High zinc values are more restricted, occurring at the southern end of the lead anomaly (Fig. 7.17).

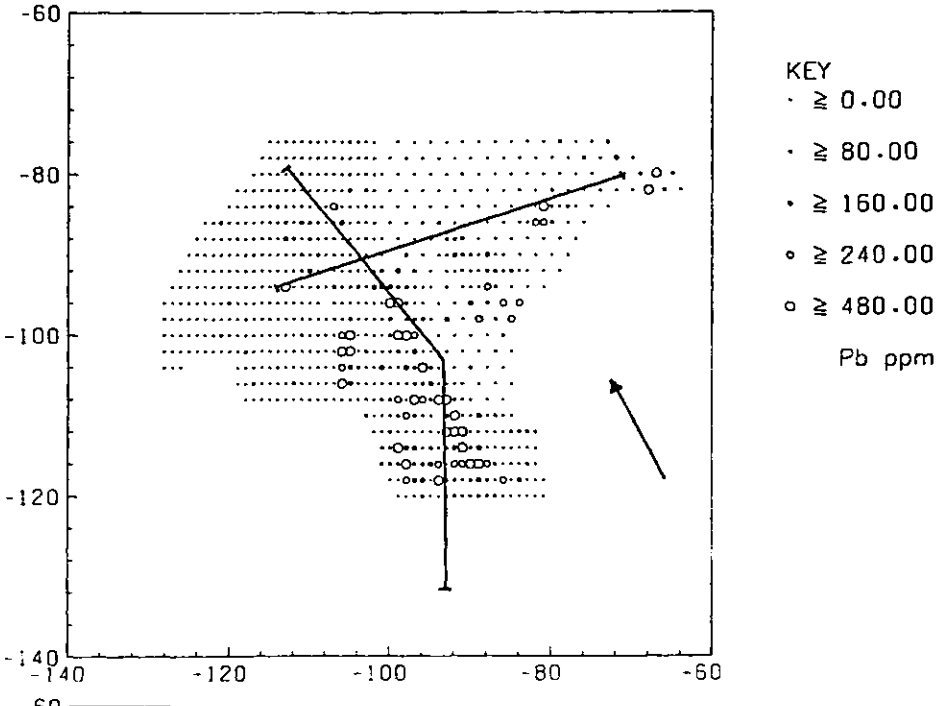
7.2.2 Programme

Two, roughly perpendicular, soil traverses were designed to cross the copper mineralization and also transect some of the untested lead and zinc deep overburden anomalies. Transition metals were determined by atomic absorption and pathfinders via the coprecipitation method (and MW02 samples using the lanthanum nitrate method).

a) Soil Traverse MW01

The suboutcrop of the mineralization is reflected in the prominent copper anomaly from 200 to 800 m (Fig. 7.18), which has a maximum of 300 ppm relative to 30 ppm Cu background. The twice background anomaly between 650 and 800 m overlies sandstone suboutcrop. Lead and zinc show very





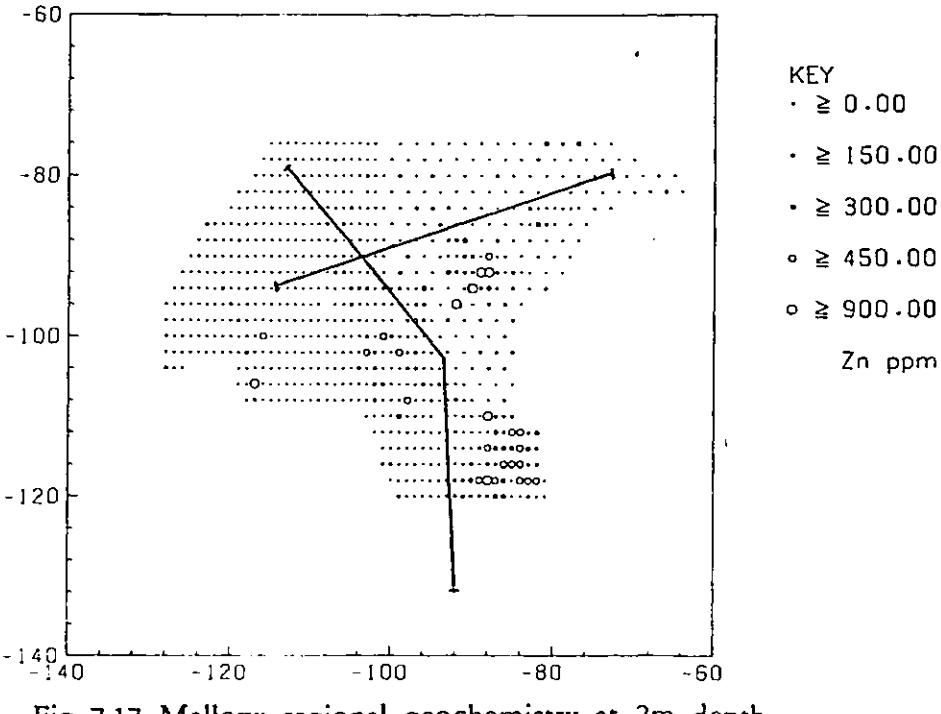


Fig 7.17 Mallow: regional geochemistry at 2m depth
Data from Munster Base Metals Ltd. Note that this grid is not oriented N-S and is in feet

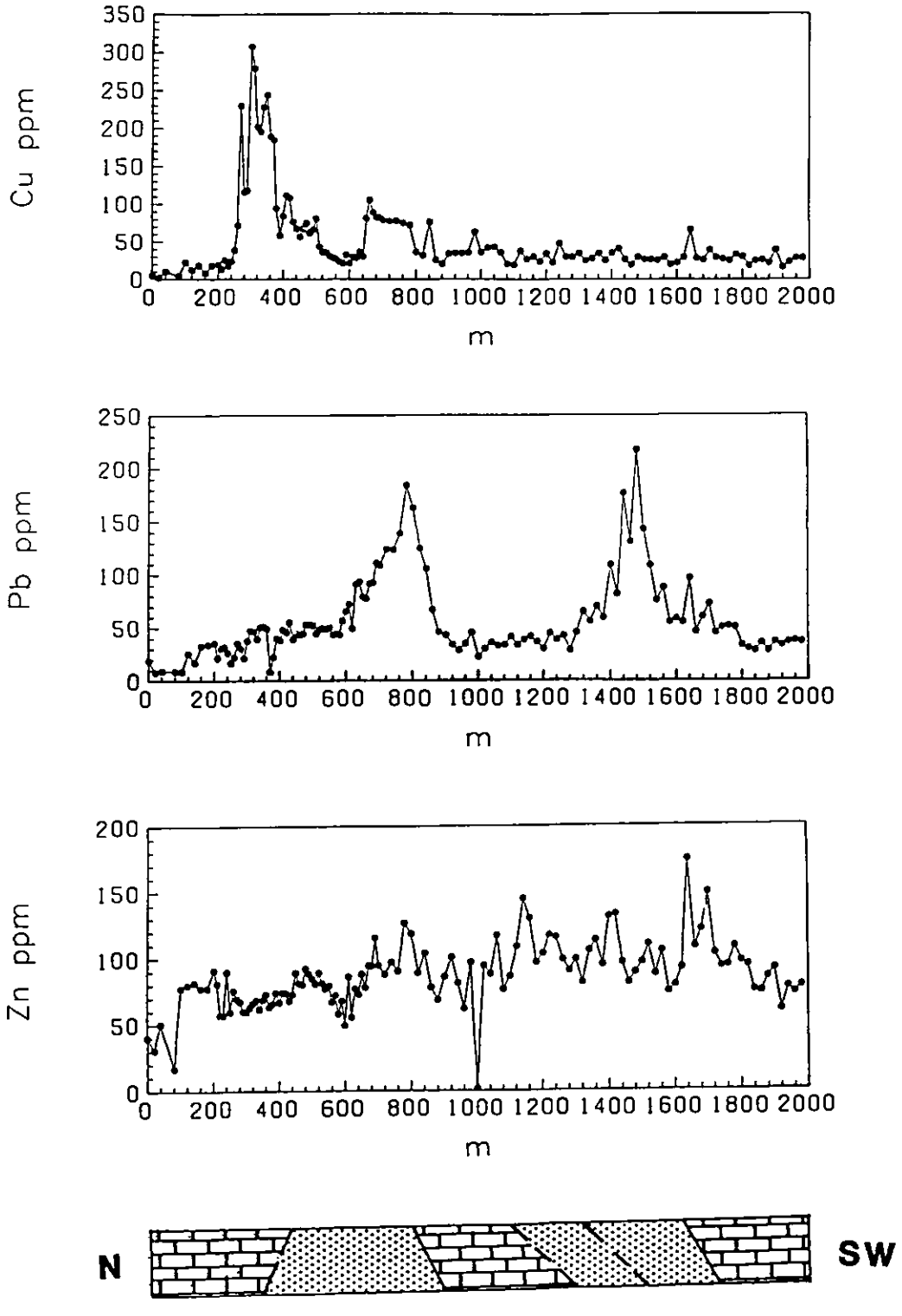


Fig 7.18 Mallow: soil traverse MW01
Geological symbols as for Fig 7.15

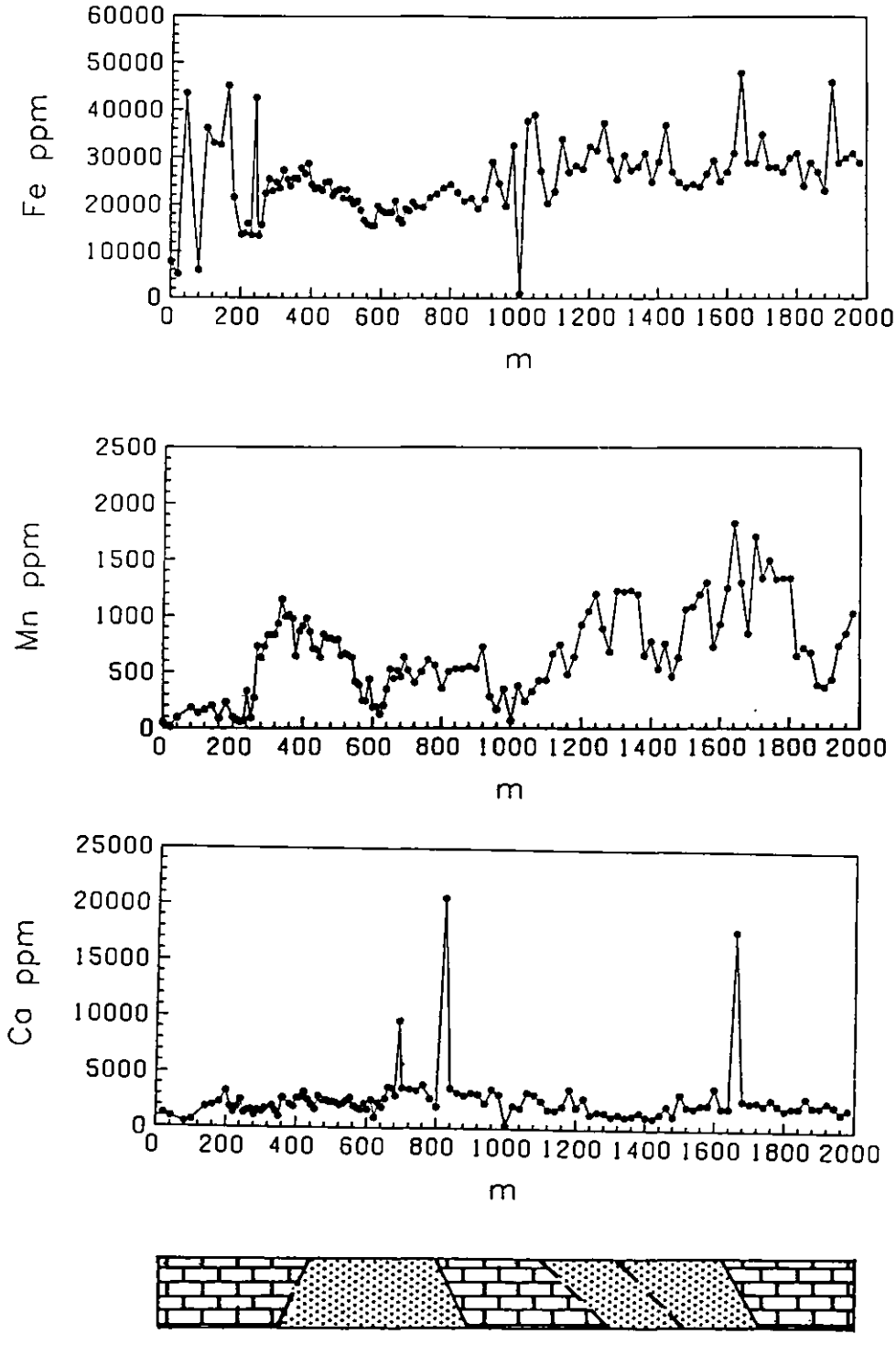


Fig 7.19 Mallow: soil traverse MW01
Geological symbols as for Fig 7.15

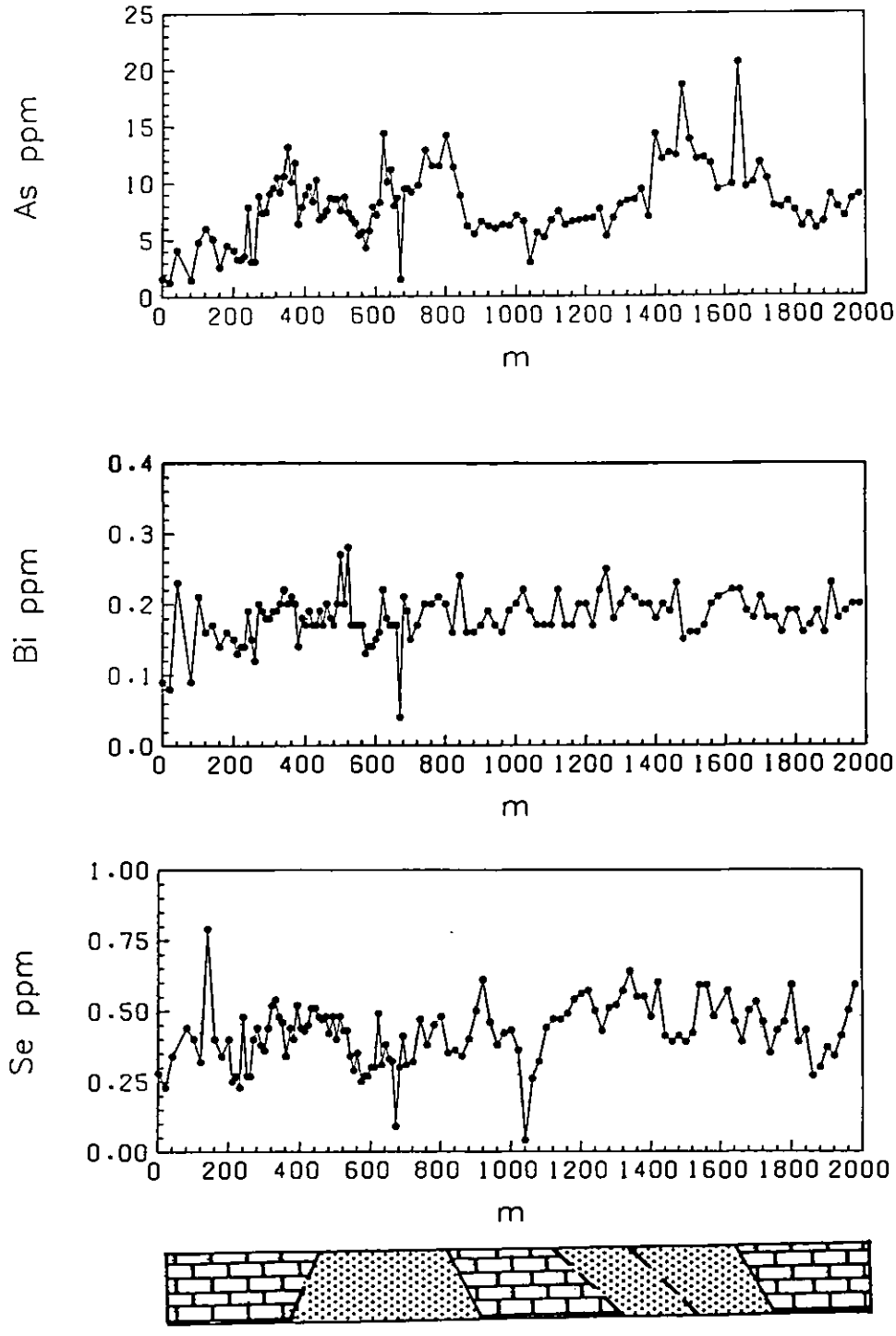


Fig 7.20 Mallow: soil traverse MW01
Geological symbols as for Fig 7.15

different distributions: lead is anomalous over much of the sandstone subcrop, reaching 230 ppm relative to 40 ppm background while zinc only reaches 150 ppm relative to 100 ppm background over the mixed lithologies (1600-1700 m). A very minor silver anomaly occurs over the mineralization with 3.5 ppm relative to 2 ppm background.

Iron shows little variation except at the northern end over a boggy area (0 - 250 m). In contrast manganese correlates with copper in the northern part of the traverse and in general it is high over the sandstone suboutcrop. Calcium gives some indication of the lithology of the bedrock but this pattern is subdued relative to the single point anomalies, presumably related to sampling limestone boulders (Fig. 7.19).

Of the pathfinders only arsenic shows much variation. Like manganese it is high over the sandstone suboutcrop but is correlated with anomalous copper values in the north of the traverse and lead in the south (reaching a maximum of 20 ppm relative to background of 7 ppm.

b) Soil Traverse MW02 (Figs. 7.21 - 7.23)

The distribution of the elements is similar to that of MW01 with a distinct copper anomaly from 500 - 650 m reaching to 180 ppm relative to 30 ppm background. There is a distinct diminution in the background £ of 1400 m. Lead anomalies are lower (90 ppm than MW01 but restricted to the eastern end of the traverse. Zinc, in contrast, has a background distribution with a low between 900 - 100 m.

Manganese shows considerable variation with a low from 700 - 1000 m but the highest values at the eastern end of the traverse. Calcium has a distinct change in background values at 1400 m.

Arsenic correlates with lead and there is a distinct change in background at 1600 m with a discrete anomaly

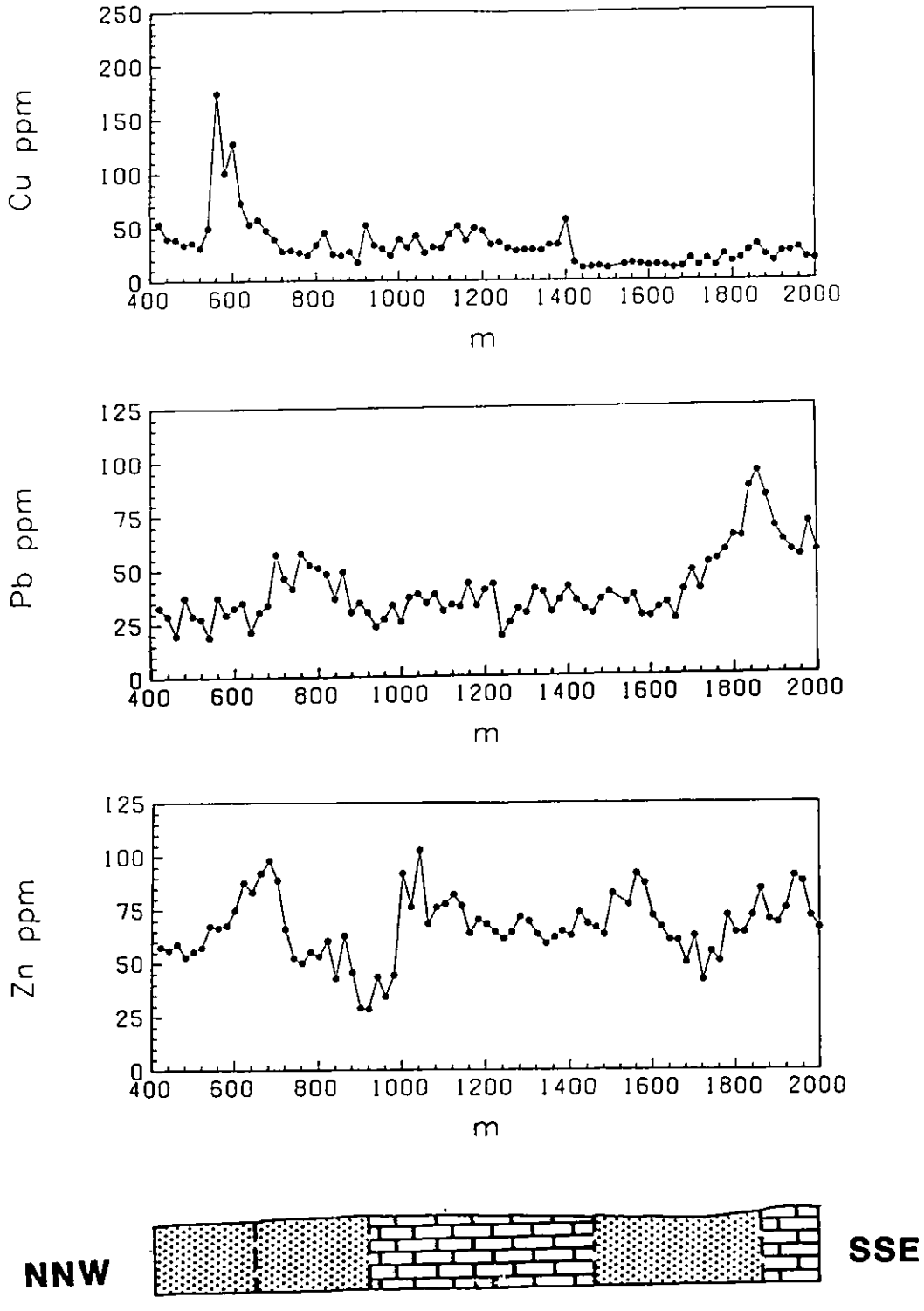


Fig 7.21 Mallow: soil traverse MW02
Geological symbols as for Fig 7.15

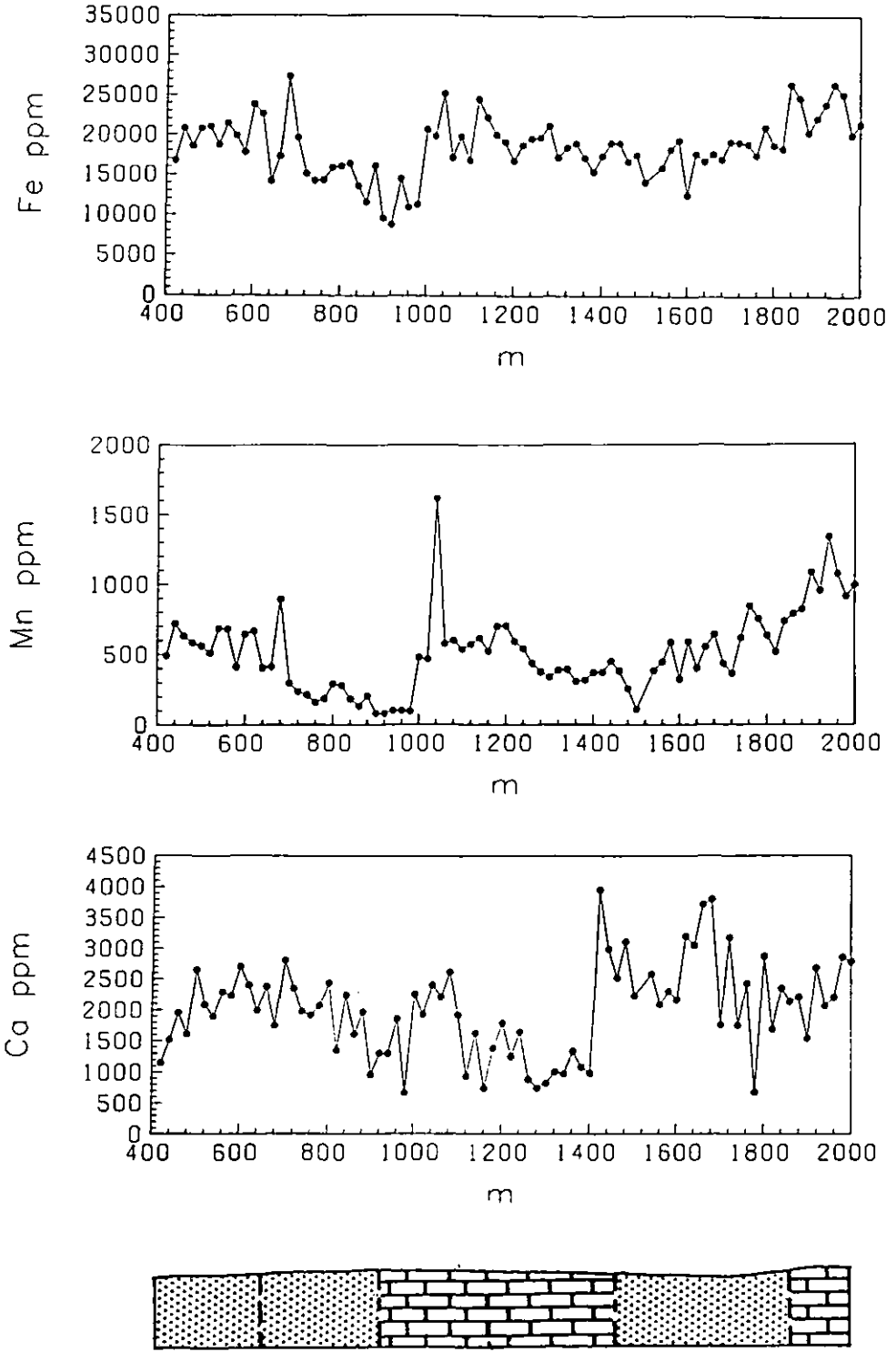


Fig 7.22 Mallow: soil traverse MW02
Geological symbols as for Fig 7.15

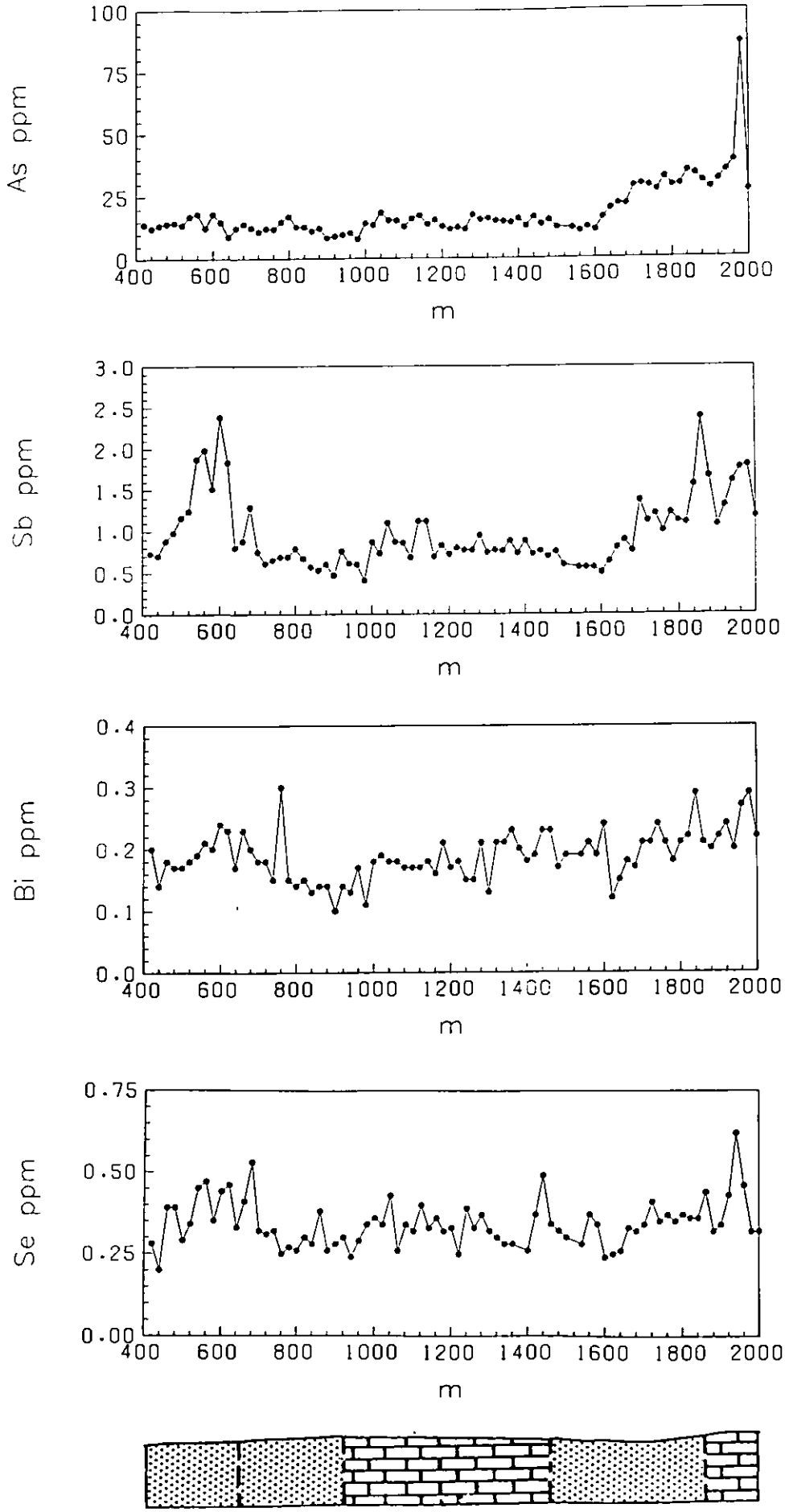


Fig 7.23 Mallow: soil traverse MW02
Geological symbols as for Fig 7.15

reaching 80 ppm As (relative to 30 ppm background east of 1600 m and 15 ppm west of 1600 m). Antimony has a distinct anomaly (2.5 ppm Sb relative to 0.8 ppm background) associated with the copper high but is also high at the eastern end of the traverse. Bismuth and selenium have background distributions.

7.2.3 Discussion

Interpretation of pathfinder dispersion is complicated by two problems: (i) lack of knowledge of primary indicator and pathfinder dispersion; and (ii) lack of profiles through the till. Arsenic soil anomalies are associated with lead highs while antimony is enriched in both lead and copper anomalies.

Bedrock copper anomalies are developed within the Lowest Carboniferous formation and the sandstones, about 500 m to the south (Wilbur, pers. comm., 1982). Thus the deep till copper anomalies probably reflect the primary distribution rather than the glacial dispersion. The source of the lead and zinc till anomalies is unknown although till geochemistry suggests that the sandstones may be locally high in lead with zinc concentrated in the lowest Carboniferous formation. Considerable further research is required into the relation between primary concentrations of various metals.

Detailed evaluation of the till profiles by Wilbur and Royall (1975) suggests that copper dispersion through the till is largely hydromorphic and inhibited by large (>5 m) thicknesses of drift. There is probably local copper contamination of soils, as slaked copper rich limestone has been used as a fertilizer (Wilbur, 1982 pers. comm.)

The conclusions from this study are that the association of antimony with copper suggests that it is probably a

useful pathfinder for copper-silver deposits in the Irish Central Plain although high values will be encountered over bedrock lead enrichments. This zonation is similar to that described from the Gortdrum deposit (Steed and Tyler, 1979). Lithogeochemical studies there demonstrate an outer zone of galena, sphalerite and arsenopyrite three to four kilometres distant from the nucleus of the copper-silver deposit. There is also lithological control with copper concentrated in Old Red Sandstone and mixed clastic/limestone unit while lead and zinc are associated with the upper limestone. Arsenic is said to be concentrated in an impure limestone unit (not present at Mallow) but the case for this seems unproven, given the sampling pattern.

The lack of dispersion through till, and the association of thick till with the prospective mixed pelitic/carbonate host formation means that basal till sampling is the recommended technique. Soil copper (and antimony) anomalies will be greatly enhanced over areas of the sandstone outcrop relative to those derived from similar grade mineralization in the Lowest Carboniferous formation.

Part III :
Comparison of Detailed Studies with Published Descriptions of Pathfinder Surficial Dispersion; Exploration Implications; and Conclusions

CHAPTER 8 BEHAVIOUR OF PATHFINDERS IN THE SURFICIAL ENVIRONMENT AND APPLICABILITY IN PROSPECTING

This chapter is intended to draw together the pathfinder data from the areas of detailed study (described in Chapters 3 - 7), compare them with theoretical and other observational evidence available, reach conclusions about the relative importance of the mechanisms that control dispersion and suggest how these might apply in other climatic/pedological environments. The available case histories of pathfinder geochemistry are then reviewed and compared with results obtained here.

8.1 Surficial Dispersion - Theory and Evidence: A Review

Dispersion of pathfinder elements from rock involves the removal of elements from rock into soils and solution, and further into circulating groundwaters, sediments, plants and the atmosphere (Fig. 8.1). The main dispersion mechanisms are aqueous solution and clastic transport although there are other mechanisms, such as electrochemical dispersion. Gaseous dispersion, which is not normally applicable to transport of transition metals, is of importance for the pathfinders.

Practical considerations mean that exploration geochemists are interested in local dispersion (usually less than ten kilometres) but global considerations can be of a priori importance for the atmophile elements (particularly selenium).

The geochemical literature on the four pathfinders is variable in quantity with little data available for bismuth or antimony but with a voluminous literature for the toxic pathfinders arsenic and selenium.

8.1.1 Arsenic

Arsenic sulphides are soluble in oxidising environments

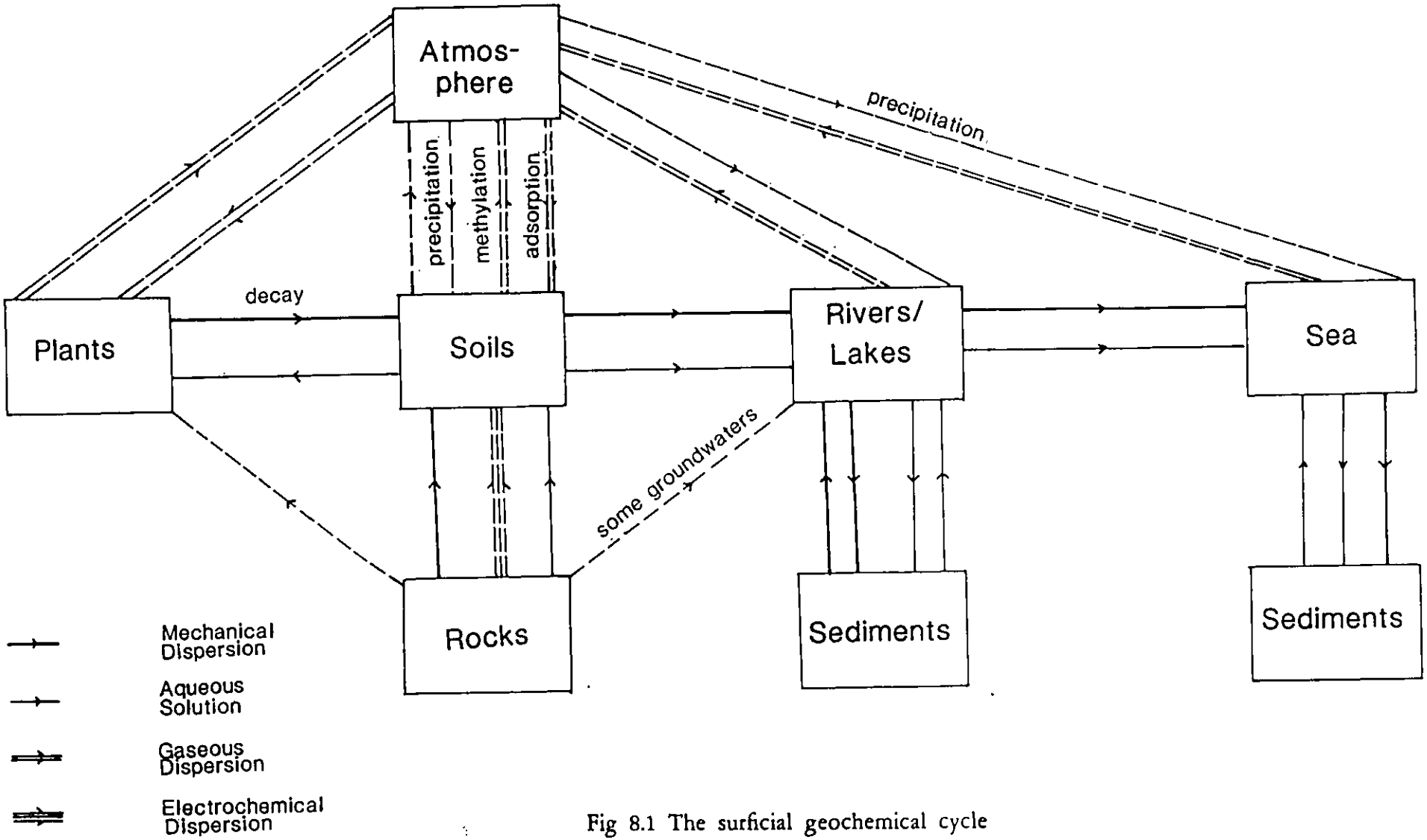


Fig 8.1 The surficial geochemical cycle

giving rise to arsenite ($^{+3}$) and arsenate ($^{+5}$) complex anions. Past consideration of these reactions has been largely limited to inorganic chemistry but organic chemistry is extensive and important. This particularly applies to oxidation reactions where bacteria such as Thiobacillus ferooxidans, can catalyze the oxidations of arsenopyrite to arsenite and arsenate causing an increase of seven times in the rate of reaction (Ehrlich, 1981).

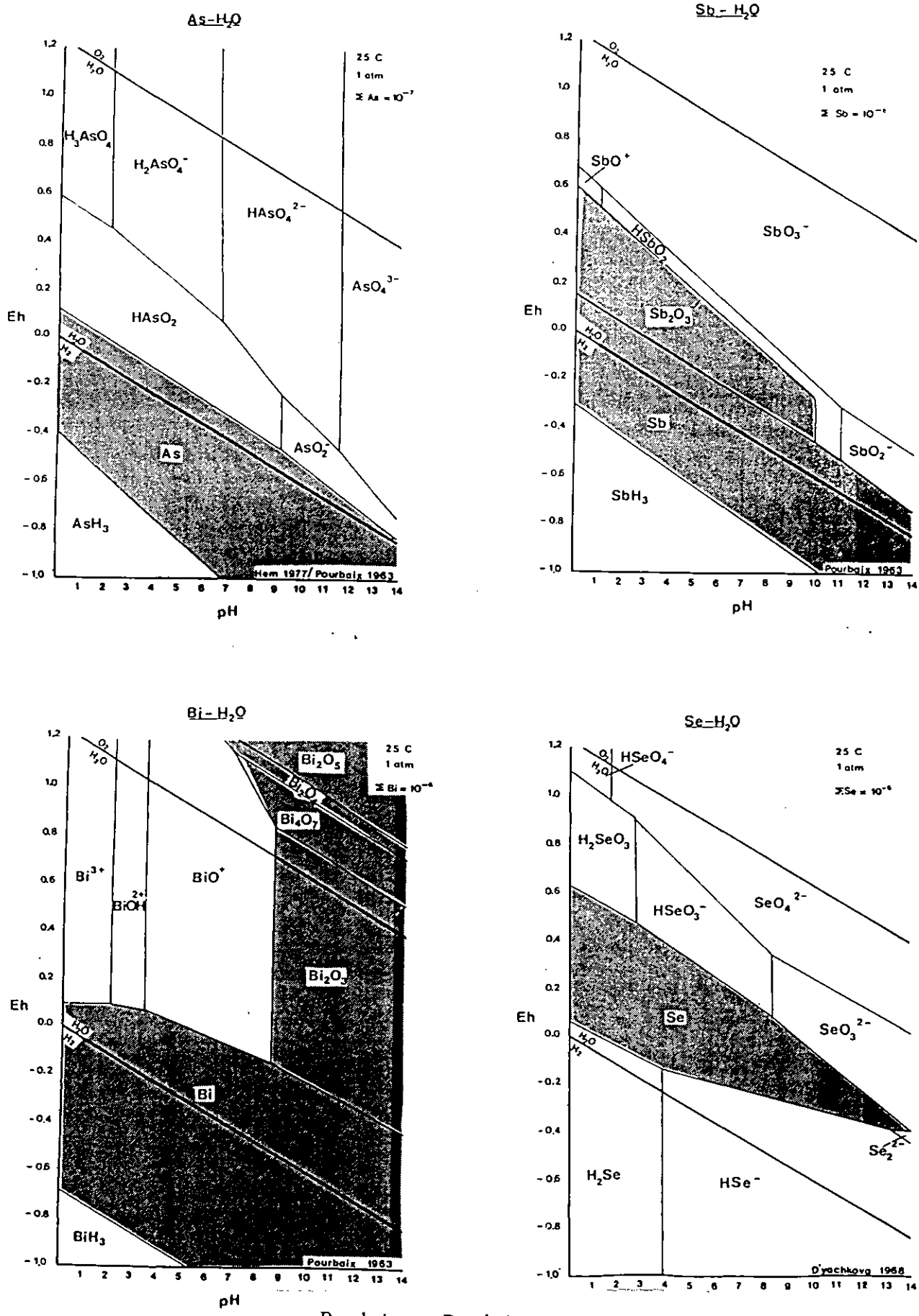
An Eh-pH diagram for the very simplistic As-O_2-H_2O system (Fig. 8.2) suggests that arsenate is the dominant complex in oxidising environments while arsenite is stable in more reducing conditions. Arsenic forms a number of organic compounds, both in solution and as gaseous phases, of which the most important are summarised in Table 8.1.

Analytical difficulties mean that speciation of arsenic in background soil is unreported and information is dependent on fractionation using sequential extraction. Most arsenic is bound to reactive iron where this is high but binding to reactive calcium or aluminium will predominate where iron is low (Woolson et al, 1971). Information on the relative proportion of organic/inorganic species is lacking, but the correlation of arsenic with iron coupled with the observations that adsorption of arsenate and MMAA (Table 8.1) follows a Langmuir isotherm (Holm et al, 1979) suggests that the latter species dominate soil arsenic systems. Arsenite complexes are adsorbed by iron but adsorption shows a correlation with arsenic concentration (Holm et al, 1979). Further research is, however, required.

The picture for waters and stream sediments is much clearer and speciation techniques are now routine (Braman et al, 1977; Andrae, 1977; Yamamoto et al, 1981; Pahlavanpour and Thompson, 1981). Arsenate is the predominant ion in surface waters with methylated compounds forming about 10% of species (Waslenchuck and Windom, 1978)

Table 8.1 Summary of Major Environmental Arsenic Species (from Holm et al, 1979)

Formula	Name	Valency	
AsO_4^{3-}	Arsenate	+5	
AsO_3^{3-}	Arsenite	+3	
$CH_3AsO(OH)_2$	Metharsonic Acid (MMAA)	+3	
$(CH_3)_2AsOOH$	Hydroxydimethyl Arsenic Oxide (DMAA)	+3	
AsH_3	Arsine	-3	Gaseous
$(CH_3)_2AsH$	Dimethyl Arsine	-3	Gaseous
$(CH_3)_3As$	Trimethyl Arsine	-3	Gaseous



Pourbaix = Pourbaix et al
D'yachkova = D'yachkova and Khadakovsky

Fig 8.2 Eh / pH diagrams for the pathfinders

Shaded areas are solid phases

Typical values in rivers from the eastern U.S. are 0.4 - 0.7 ppb (μg/l) of dissolved arsenate (Waslenchuck, 1978). The particulate arsenic content of one river was 0.03 - 0.16 μg/l relative to dissolved contents of 0.08 - 0.45 μg/l (Table 8.2). Transported particulate arsenic is deposited at the freshwater/seawater interface while dissolved arsenic mixes conservatively with seawater (Waslenchuck, 1978). In spite of its predominance the behaviour of dissolved arsenate is apparently not ideal as a result of the complexation with low molecular weight organic matter (Waslenchuck, 1979). When arsenate ions are reactive it appears that adsorption is the most important reaction, while co-precipitation (which is favoured thermodynamically but not kinetically) is unimportant (Holm et al, 1979; Wagemann, 1978). Particulate arsenic in river water, once produced, is apparently not labile (Waslenchuk :, 1978). Speciation of pore waters from sediments indicates that arsenate is the dominant anion near the surface, partly as a result of microbially mediated demethylation, but organic arsenic species are important at depth (Holm et al, 1979). The implication of this observation is that arsenic is fixed at the stream bottom but mobility is possible at depth.

Investigation of ground water demonstrates that arsenic is transportable in the As(3) valency state (Hawkins et al, 1980; Gulens et al, 1979). It also seems possible that $As(3^+)$ can form a soluble complex with iron in the 3^+ valency state (Gulens et al, 1979).

These observations are consistent with the reported behaviour of As from oxidising sulphide deposits. Arsenic is strongly concentrated in gossans as summarised in Fig. 8.4 (presumably by adsorption followed by compound formation) but data from Chuquicamata indicate that significant amounts of arsenic are concentrated in the

Table 8.2 Typical Pathfinder Content of Waters (ng/l)

		As	Sb	Bi	Se
Rivers	Dissolved	80 - 4500	25 - 4900	-	1100 - 350
	Particulate	30 - 160	-	-	-
Seawater		740 - 1600	120 - 1100	.13 - 2	95 - 140
Rainwater		200	16 - 160	3	-

- no data

Data from: Waslenchuk 1978, 1979 for As

Andrae et al, 1981 and Schutz and Turekian, 1965 for Sb

Lee, 1982 for Bi

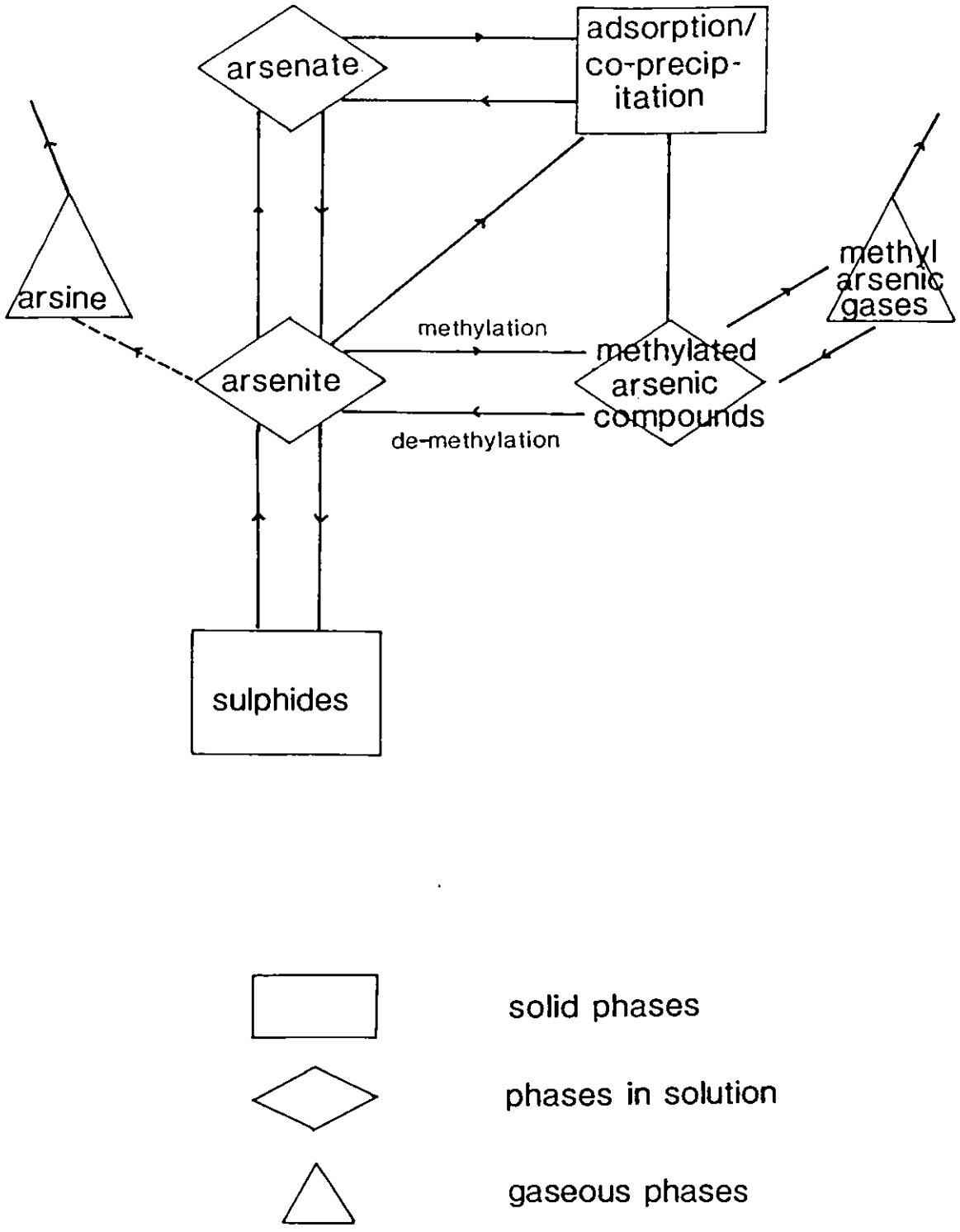


Fig 8.3 The surficial arsenic cycle

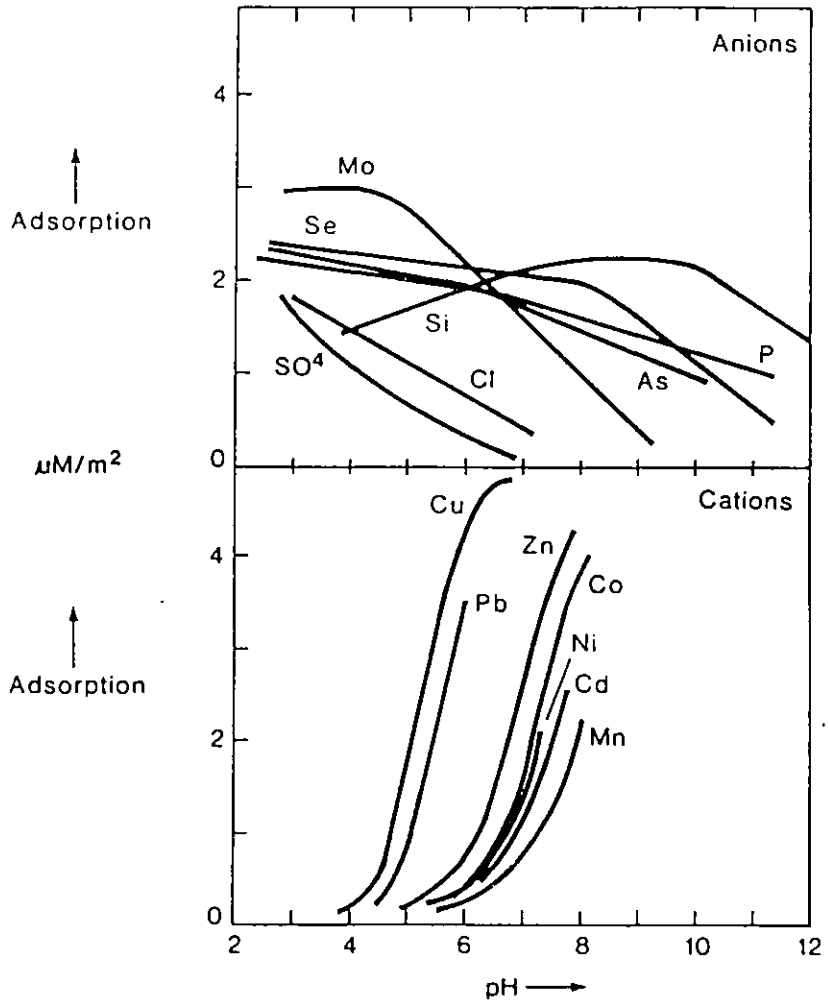


Fig 8.4 Compilation of adsorption data for anions and cations onto goethite as a function of pH.

(from Smith 1982)

secondary Exotica deposit, some 7 km distant (Smith, 1982; Wraith, 1982).

Methylated compounds form in solution from reduced arsenite anions and can give rise to methylated gases (Fig. 8.3). Recent experiments, however, show that relatively little arsenic is transformed into gaseous methyl arsenic compounds, (Baker et al, 1981); a maximum of 0.7% transformation was formed in two weeks with the reaction enhanced below pH5.5 although reaction occurs over a range of 3.5 - 7.5 pH.

8.1.2 Antimony

Much less data are available for antimony but its key geochemical characteristics seem to be: the very low solubility of antimony sulphide and sulphosalts; the almost total lack of an organic chemistry in aqueous solutions; and its lower volatility relative to arsenic as evidenced by lesser volcanic input and probable absence of volatile methylated compounds.

Consideration of a simplistic Eh-pH diagram (Fig. 8.2) shows that native antimony is a good deal more stable than its arsenic counterpart. Antimony is usually present as sulphides or sulphosalts and laboratory studies indicate that they are virtually insoluble in inorganic aqueous solution (Boyle, 1975). This picture changes if organic species are considered and Russian studies quoted by Ehrlich (1981) demonstrate that microbially mediated oxidation does occur and may be important. The dominant complex formed in solution is the antimonate, SbO_3^- (or more correctly, the hydrolyzed species $Sb(OH)_6^-$) with the antimonite field much more restricted (Baes and Mesmer, 1976). Adsorption or co-precipitation of antimonate ions with ferric hydroxides is probably qualitatively similar to that of arsenate anions, although co-precipitation is possibly relatively

more important in the case of antimony.

Antimony also forms complex anions of the ($Sb(SO_4)_2^-$) type, which are soluble except in the presence of lead, and may be of importance in oxidising sulphide deposits (Boyle, 1975). Complexation with humic and fulvic acids occurs at neutral to alkaline pHs with dissociation under more acid conditions (Bowen et al, 1979; Valente, 1978). The search for methylated antimony compounds, analagous to those of arsenic, continued unsuccessfully for several decades but culminated in the recent discovery of minor concentrations in water (Challenger, 1978; Andrae et al, 1981).

Few data are available on the form of antimony in soils. In Alaska dispersion is thought to be almost entirely clastic with minor amounts taken up by organic matter while antimony is associated with B horizon iron oxide concentrations in New Brunswick (Sainsbury, 1957; Presant, 1971). Research on antimony uptake in plants shows that the element is taken up mainly in roots but values in the stalk can reach those of extractable antimony in soil (Pearce, 1979).

Recent analytical developments allow the speciation of antimony in solution and initial results confirm the predominance of Sb(5+) complexes (Andrae et al, 1981). Total dissolved antimony concentration is of the order of 25 - 320 ng/l (Table 8.2) with only very minor amounts (<10%) of Sb(3+), and lesser concentrations of methylstibnic acid ($CH_3SbO(OH)_2$) or dimethylstibnic acid ($(CH_3)_2SbO(OH)$). The only reports of the transport of antimony in surface waters are derived from the mineralogical studies of Boyle(1975) in the Yukon. He observed that finely comminuted grains of antimony sulphides and sulphosalts were present in the stream sediments and concluded that the main mechanism of transport is as clastic

grains with minor transport as co-precipitated coatings. Mineralized groundwaters in the Carpathians contain antimony in the form of SbO_3^{2-}, $HSbO_2^{o}$ and $Sb(OH)_3^{o}$ (Krainov et al, 1979).

8.1.3 Bismuth

Data on bismuth, particularly at background concentrations are very scarce. Native bismuth oxidises slowly and bismuthinite is slightly soluble (Boyle, 1979; Wedepohl, 1969). In contrast to the other pathfinders, bismuth is present in solution only as the (3+) valency state and almost exclusively as a cationic complex. The simplistic Eh-pH diagram (Fig. 8.2) suggests that the bismuthyl ion (BiO^{+}) is stable in neutral to acid solutions (also observed by Naumev et al, 1979). More sophisticated studies show that the ion is hydrolysed in natural solution with $Bi_9(OH)_{22}^{5+}$ and to a lesser extent $Bi(OH)_3^{o}$ the stable ions. The anionic complex $Bi(OH)_4^{-}$ is much less stable than the cationic complexes (Turner et al, 1981).

These differences in chemistry would, one expect cause differences in surficial geochemistry relative to other pathfinders. The overall behaviour, however, seems similar to that of arsenic with concentrations in ferric oxides, especially gossans (Boyle and Dass, 1971; Smith et al, 1982; Schiefler, 1966) These similarities can be explained by specific adsorption or the formation of insoluble bismuth oxides/salts as the result of acid-base reactions (Stumm and Morgan, 1970; Boyle, 1979). These salts are known to form rapidly and are frequently described from the oxide zone of bismuth rich deposits (Chukhrov et al, 1979). SEM scans of a bismuth enriched gossan (Whim Creek) from Western Australia have not, however, revealed any discrete minerals. This contrasts with the easy identification of silver as halides (silver is

present in similar concentrations to bismuth)(Nickel, pers. comm., 1983). Data from Chuquicamata porphyry demonstrate that bismuth is concentrated in both the gossan and supergene zones suggesting adsorption /co-precipitation and sulphide development (Wraith, 1982). Typical concentrations of mineralized ground waters range from 0.1 - 1 ppb Bi (Boyle, 1979).

The low temperature organic geochemistry is unknown, but by extrapolation from the behaviour of antimony is probably limited. Systematic data on the concentration of bismuth in waters is lacking and it is only recently that any information has become available; it is summarised in Table 8.2 (Lee, 1982).

8.1.4 Selenium

Controls on selenium dispersion are qualitatively quite similar to those of arsenic, with the formation of mobile oxy-anionic complexes and a wide-ranging organic chemistry.

Consideration of a simplistic Eh-pH diagram (Fig. 8.2) suggests that native selenium is stable under reducing conditions and selenite (Se^{4+}) is the dominant soluble phase. The occurrence of the selenate ion has been the subject of considerable controversy with recent work (Peterson et al, 1981) taking the view that the ion does exist in natural conditions but is confined to extremely alkaline oxidising conditions. The form of selenium has great significance, as selenite is strongly adsorbed by ferric oxides in contrast to selenate which is not fixed at iron oxide geochemical barriers (Howard, 1977).

Iron oxides are undoubtedly the main control in inorganic conditions but the influence of organic geochemistry is unclear from the literature. Experimental studies

(Nye and Peterson, 1975) concluded that much of the selenium is complexed by organic matter and it can form a complex with organic matter and iron (Levesque, 1974). Micro-organisms probably play an important role in the transformation of selenium species in soils and the known reactions are summarized in Fig. 8.5. The quantitative implications of these are generally unknown except for volatilisation. This process is less important than for arsenic (Baker et al, 1981) and is directly correlatable with the availability of water soluble selenium (Zeive

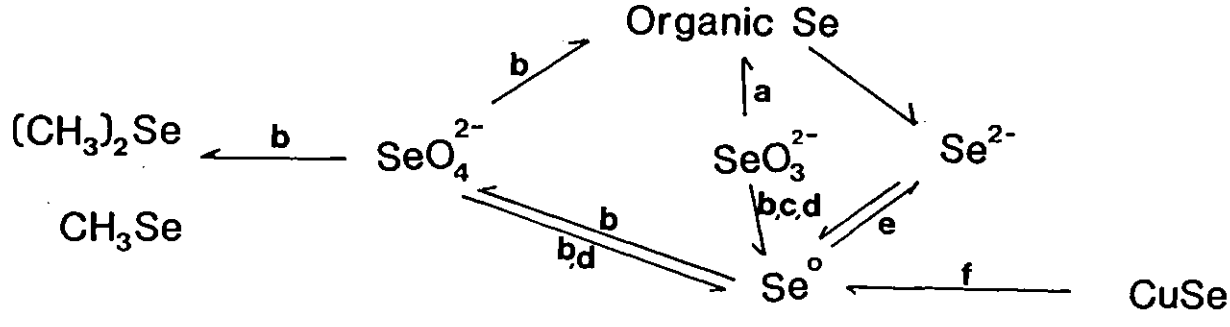


Fig. 8.5 Selenium cycle: a - E. coli; b - bacteria; c - actinomycetes; d - fungi; e - M. lactelyticus; f - Thiobacillus ferooxidans

(After Ehrlich, 1981)

and Peterson, 1981). There is probably also a chemical mechanism by which these volatile selenium compounds are re-adsorbed by soils from the atmosphere (Peterson et

al, 1981) and it has been argued that there is a correlation between the selenium content of soil and rainfall in Norway (Lag and Steinnes, 1978). It should be noted that anthropogenic emissions are responsible for substantial, though minority, percentage of the atmospheric selenium content (Lantsky and Mackensie, 1979).

Selenium is taken up by plants into all parts of their structures, and concentrations may exceed those of soils. Selenate is taken up actively while the role of selenite is passive. Seleno-amino-acids are generated as a result of these uptakes but the mechanism is unclear (Shamberger, 1981).

Detailed research on Canadian soil profiles shows that selenium is enriched in near surface organic layers and in the B horizon (Levesque, 1974b). The element correlates strongly with organic carbon, and less with parent material and Levesque suggests that enrichment of the B horizon may be the result of downward migration of organo-selenium-(iron) complexes. Recent research at Imperial College extends these observations and found selenium accumulated in the organic rich A and iron rich B horizon in podzols (Smith, 1983). In brown earths selenium concentrations decreases downward with decreasing iron oxides and organic carbon while some gleyed soils are significantly enriched at depth suggesting reduction to elemental selenium. There is, however, overall correlation between the concentrations of selenium parent material and content in soil.

Speciation studies of selenium in river water from Southern England indicate that the dominant species is selenate (Measures and Burton, 1978). These data are in conflict with the thermodynamic calculations of Howard (1976) but further work on seawater seems to confirm the predominance of Se(6) (Wrench and Measures, 1982) as does that of Peintre on mineral springs (Peintre, 1963). Russian

work has detailed the subsurface dispersion of selenium in acid oxidising ground waters away from a mineral deposit and deposition in more alkaline conditions (Goleva and Lushnikov, 1967).

Selenium is strongly enriched in gossans. This is brought out by research at Chuquicamata, which also demonstrates concentration in the zone of secondary sulphide enrichment (Wraith, 1982).

8.2 Comparison of Pathfinder Surficial Distribution Mechanisms Evidenced in Detailed Studies with Those from the Literature

The areas studied in detail provide evidence on pathfinder distribution over both enriched and background bedrock. The main line of reasoning throughout has been statistical inference and comparison with the mobility of well understood elements. Although the controls on soils, stream sediments and stream waters are qualitatively similar they differ quantitatively and are considered separately.

8.2.1 Arsenic

a) Soils and Overburden

The strong correlation between iron and arsenic in many of the detailed study areas (Kilmelford, Keel, Avoca, Meall Mor) and in many literature studies suggests that iron oxide distribution is the main control on that of arsenic in near surface soils. This is in accord with theoretical studies, quoted in the previous section, which indicate that arsenic minerals are soluble, forming arsenate anions which are then adsorbed by iron hydroxide (following a Langmuir isotherm).Convincing evidence of the hydromorphic nature of much arsenic dispersion is afforded by measurements at Arthrath. The distinct arsenic high in

soil waters near the soil anomaly constrasts with low arsenic concentrations in gossanous fragments. There is in general little evidence (in localities of low iron content) of arsenic concentration by other mechanisms, as suggested by some observers. The exceptional area is Ballinglen, where there is an overall lack of correlation between iron and arsenic and the most obvious explanation, given the well drained nature of the area and its ruggedness, is that clastic dispersion is important. The broader dispersion of arsenic relative to the exclusively clastic dispersion of tungsten, however, demonstrates that hydromorphic dispersion is also important and it is suggested that dispersion is by a combination of these two mechanisms (Fig. 8.6).

Organic matter seems to play a limited role in the geochemistry of arsenic. There is little correlation between organic carbon and arsenic in areas of detailed studies, particularly the peat bog at Keel and the peats at Meall Mor and Kilmelford. Gaseous arsenic compounds, probably, (given the limited stability of arsine) of the methylated arsenic type are generated directly over both a primary anomaly and over a seepage zone at Ballinglen. The generation of reduced organic arsenic volatiles in this seepage area suggests that arsenic is more likely to be transported in the (3^+) valency in ground waters rather than in (5^+) form which requires re-reduction to form the volatiles: and this is in accord with the suggestions of Hawkins et al, 1980.

Background values of arsenic in soil (Table 8.3) vary from 2 - 15 ppm but the causes of these variations are not particularly obvious.

b) Stream Waters and Sediments

Physical separation of waters from suspended sediment

Table 8.3 Background Concentration of Pathfinders in Non-Organic Soil Samples (ppm)

	As	Sb	Bi	Se
Arthrath	3*	-	0.2*	0.4
Avoca	15	1.0	0.5	0.8
Ballinglen	10	0.3	0.4	0.9
Clontibret	10	4.0	-	-
Dalbeattie	10	1.0	2.0	0.5
Glendinning	5	3.0	0.4	0.7
Keel	10	0.5	0.2	0.8
Kilmelford	5*	-	0.5*	0.8
Mallow	10	0.8	0.2	0.5
Marl Slate	4*	-	0.3*	0.5
Meall Mor	2	0.3	0.2	0.4

* Partial Extraction - Co-Precipitation Method

\- Not Determined

Table 8.4 Background Concentrations of Pathfinders in Waters (μg/l)

		As	Sb	Bi	Se
	Dissolved	1.0	2.0	1.8	2.0
Ballinglen	Particulate	0.1	0.08	0.08	-
	Total	1.1			
	Dissolved	0.3	0.1 ?	0.1	-
Glendinning	Particulate	0.08	0.04	0.04	-
	Total	0.38			
	Dissolved	1.0	1.0	2.0	-
Keel	Particulate	0.1	0.15	0.15	-
	Total	1.1			
	Dissolved	0.1	0.05	0.1	0.1
Kilmelford	Particulate	0.04	0.03	0.03	-
	Total	0.14			
	Dissolved	0.2	0.1	0.2	0.3
Meall Mor	Particulate	0.1	0.03	0.1	-
	Total	0.3			

- Not determined

Table 8.5 Background Concentration of Pathfinders in Stream Sediments (ppm)

	As	Sb	Bi	Se
Arthrath	5*	-	0.08	0.15
Ballinglen	20	0.7	0.2	0.2
Clontibret	10	3.0	-	-
Glendinning	3	2.0	0.2	0.1
Keel	8	0.7	0.15	0.15
Kilmelford	15*	-	0.3*	0.4
Meall Mor	20(?)	1.2	0.2	0.2
South West Background	6	-	0.2	0.2

* Partial Extraction - Co-precipitation Method

\- Not Determined

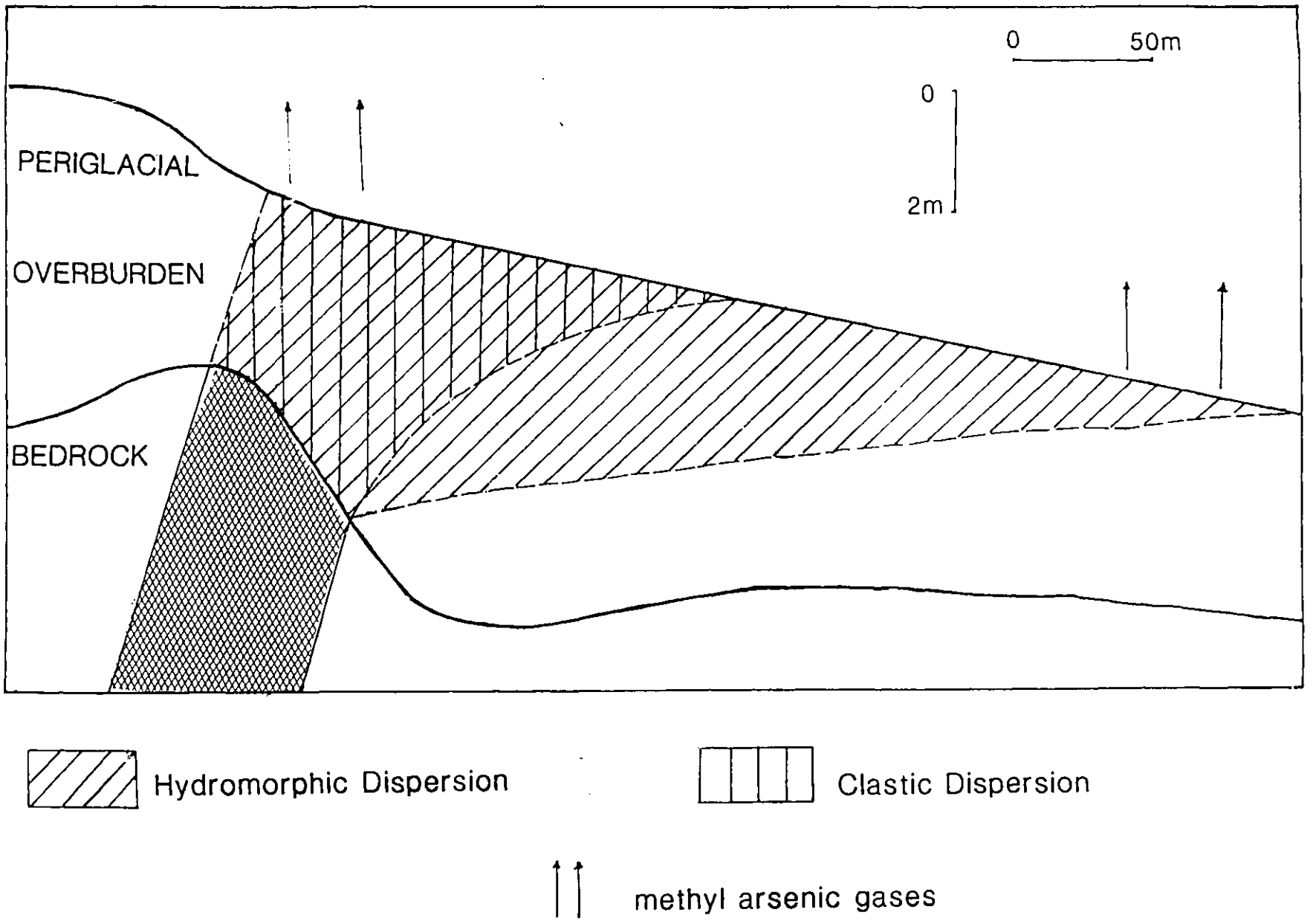


Fig 8.6 Schematic summary of dispersion at Ballinglen

at Ballinglen and Glendinning shows that most arsenic is transported in solution. Speciation of the soluble phase at Glendinning demonstrates that arsenic is transported in surface waters in the As (+5) state with only very minor As(3+) or organic arsenic compounds and this observation agrees with theoretical studies. The strong correlation of arsenic with iron in stream sediments (particularly at Kilmelford and Ballinglen) is compatible with laboratory studies indicating the adsorption of As(+5) or iron hydroxides following a Langmuir isotherm. There is no evidence of the formation of insoluble arsenates by co-precipitation.

The mode of stream sediment anomaly formation is unclear. Physical separation of sediment at Meall Mor and Glendinning into different grain sizes demonstrates that arsenic is concentrated in the finest grain size and enrichment in this finest fraction is reflected in the distribution of arsenic in the particulate phase rather than the dissolved phase at Ballinglen and Meall Mor. This suggests that fine fraction dispersion trains (of the type routinely sampled) are the result of the transport of particulates which presumably form by adsorption of arsenic near the subcrop of the mineralization/groundwater seepage. Most arsenic in sediments is transported in the coarser fractions, probably in iron oxide coatings.

8.2.2 Antimony

a) Soils and Overburden

The detailed studies at Keel, Arthrath, Ballinglen and Clontibret demonstrate that the key feature of antimony geochemistry is its immobility. At Keel it is distinctly less mobile than the transition metals on traverse KL01 and increases with depth to bedrock at Arthrath. The data from Ballinglen are less clear

as primary enrichment is low and limited, but antimony dispersion is restricted to basal till. The mobility through till at Clontibret seems more limited than arsenic, although it may have an erratic primary enrichment. Evidence of limited antimony mobility is also provided by the investigations at Avoca and Keel. Profiling at the former location suggests that the limited soluble antimony is co-precipitated with iron oxides. This is compatible with transport in the (+5) state as anionic complex. At Keel antimony is concentrated in the peat bogs and in peats overlying till at Meall Mor. This is explicable by complexation and fixation of antimony by humic/fulvic acids or fixation as sulphides, as evidenced by Valente (1978).

Comparison of background values of the different areas show considerable contrast between those in the areas with antimony deposits (Glendinning and Clontibret) and the others. This could be explained by clastic dispersion from bedrock, which shows regional enrichment.

b) Stream Sediments and Waters

The key feature of antimony geochemistry in stream sediments is, as in soils, its low solubility. This is well demonstrated at Glendinning and Meall Mor where the element is enriched in all fractions downstream from the mineralization. Comparison with the base metal and arsenic patterns suggests that antimony is almost exclusively introduced and transported as clastic grains. This also seems to be the case at Clontibret but the evidence is less conclusive with much antimony derived from result of contamination.

Anomalous levels of soluble antimony are present in

stream waters at Glendinning but they are restricted to an area around the soil anomaly. Concentrations in the particulate phase are invariably below the analytical detection limit suggesting that the particulate phase does not have an important role in anomaly formation. In contrast to soils there is little correlation with iron or organic matter.

8.2.3 Bismuth

a) Soils and Overburden

Dispersion of bismuth through overburden is well displayed at Avoca and Ballinglen. The element is intermediate in mobility between clastically dispersed tungsten and widely dispersed arsenic at the latter location, suggesting limited hydromorphic dispersion. Overburden profiles in both areas give some evidence of bismuth concentration in near surface soils implying complexation with organic matter or possibly precipitation. Profiles over mineralization low in bismuth at Keel and Arthrath, however, give no indication of near surface concentration. The other soil traverses which are relevant are those at Kilmelford and Meall Mor. There, minor peaks occur in both till and peats over mineralized bedrock with some evidence of down slope leaching and base of slope concentration, confirming limited hydromorphic dispersion. All the data, thus, indicate limited hydromorphic dispersion but the mechanism of concentration is enigmatic. The low correlation of bismuth with iron and organic matter but its concentration in gossans indicate that the precipitation of insoluble salts (co-precipitation in gossans), as suggested by Chukhrov et al, 1979, is important. This theory needs to be tested by determination of the bismuth content of soil/groundwaters and detailed mineralogical investigation.

Background concentrations in soils vary little between the areas with the exception of high values over the granite at Dalbeattie (Table 8.3).

b) Stream Sediments and Water

Evidence of mechanisms controlling bismuth distribution in stream water and sediments is less convincing than for soils, particularly as background levels of the element in water are of the order of X ppt.

The two areas in which bismuth anomalies were encountered are Ballinglen and Kilmelford. At Ballinglen the anomaly is minor and rapidly dissipated downstream while at Kilmelford similarity with lead dispersion suggests a clastic mode of bismuth dispersion. This latter observation may be caused by the presence of bismuth in isomorphous solution for lead.

Perhaps a more revealing approach is to consider the behaviour of bismuth in background areas. At Meall Mor the fractional separation of sediments shows enrichment in the finest fraction while the evidence at Glendinning is less clear, with enrichment in the coarser fractions. Overall these patterns suggest that bismuth is hydromorphically dispersed. This observation is in accord with the close relationship between granite outcrop and stream sediment concentrations which contrasts with the obviously clastic dispersion of tin.

8.2.4 Selenium

a) Soils and Overburden

Selenium shows very different patterns to the other pathfinders and concentrations in surface soils often do not reflect bedrock anomalies. Examples of these at Ballinglen and Avoca demonstrate that the

processes which concentrate selenium in the near surface are not simply the upward movement of clastic grains or solutions. There is also strong evidence of absolute concentration of selenium in the near surface (Avoca, Ballinglen) and in peats (Kilmelford, Meall Mor). Selenium shows a close association with organic carbon at Keel (statistically) and organic accumulations at Kilmelford and Meall Mor (observationally). Thus it seems that organic carbon is often a stronger control on near surface selenium concentration than the selenium content of the parent material. This agrees with the conclusions of Levesque(1974b, 1974a) who showed that selenium is concentrated by organic carbon/iron oxide complexes, (which are prevalent in the soil B horizon). The role of iron in this process in not well demonstrated, with little correlation between selenium and total iron in areas studied in this research

The mode of transport of selenium is less clear. At Arthrath the surficial anomaly reflects clastic dispersion of the selenium enriched gossan. This appears to be an exception and the accumulation of selenium in peats downslope from bedrock anomalies at Meall Mor and Kilmelford suggests that most selenium is transported in solution as indicated by the Eh/pH diagram. The lack of surface anomalies over bedrock anomalies could then be explained as the result of saturation of organic matter in selenium with anomalous concentrations of selenium merely dispersed in solution. An alternative or complementary explanation invokes the atmophilic nature of selenium. Weathering of sulphides provides a supply of inorganic selenium which is known to be more amenable to methylation than organically bound selenium and thus anomalous selenium could be removed into the atmosphere (Zeive and Peterson, 1981). The high background concentrations of

selenium in surface soils may be related to input from atmospheric sources as well as from weathering. Adsorption or rainout from the atmosphere are viable, if unquantified, mechanisms.

The picture which emerges from the areas of detailed study is very different from that available from published sources. The role of organic matter is more important than previously thought and the -190μm fraction of surface soils may not reflect local bedrock highs.

b) Stream Sediments and Waters

The strong affinity of organic matter for selenium is shown in all the areas examined. Invariably this means concentration at the heads of streams and in peaty areas.

The most complete example of selenium dispersion from this study is at Kilmelford. Water analyses show that anomalous selenium is present in solution downstream from bedrock selenium anomalies and reflected in stream sediments. These sediment anomalies, however, have a much lower contrast than those sediments in organic areas, formed by concentration of solutions derived from areas of bedrock showing anomalous or background selenium concentrations. Similar patterns occur at Meall Mor. Size fractionation of sediment at Meall Mor and Glendinning demonstrates that selenium is strongly concentrated in the finest fractions, also indicating concentration by organic matter or iron oxides. On a broader scale the data from South West England indicates that selenium concentrations in stream sediments generally reflect bedrock concentrations with relatively few organic related highs.

The overall behaviour of selenium is transport in solution (in unknown valency state),and concentration in sediments by organic matter or possibly (to a much lesser

degree) iron oxides.

8.3 Exploration Implications of the Studies: Compilation of the Detailed Studies and Comparison with Published Accounts

Arsenic has been, and is, extensively and successfully applied in geochemical prospecting while antimony and bismuth have had limited application. There are only a very few reports (mainly Russian) of the use of bismuth and it is only recently that all four pathfinders have been used in consort, and then only for the specialised problem of gossan discrimination in lateritised areas, particularly Western Australia (Smith, 1982).

The successful applications from the present study (summarised in Tables 8.6 and 8.7) are arsenic, antimony and bismuth at Avoca; arsenic, antimony and selenium in the delineation of sulphides at Arthrath; arsenic and bismuth at Dalbeattie; arsenic and antimony at Clontibret and antimony at Keel and Mallow. Their usefulness in surficial prospecting (with the possible exception of arsenic) is in detailing drill targets and this depends on their low mobility in the secondary environment.

8.3.1 Arsenic

Most of the published case histories are concerned with its application in the search for precious metals with less data on igneous related deposits and base metals(well summarised in Boyle and Jonasson, 1973).

Arsenic shows a wide range of anomalies in the primary environment reflecting the diversity of modes of leaching and transport.

Data from Arthrath confirm that arsenic is often enriched in nickel-copper sulphides, although there is

Table 8.6 Usefulness of Pathfinder Geochemistry in Soil/ Overburden Samples

Area		As	Sb	Bi	Se	Suggested Elemental Suite
Arthrath (Ni - Cu)	Soil	*	-	0	*	Ni Cu As Sb Se
	Overburden	*	*	0	*	
Avoca (Cu - pyrite)	Soil	*	*	*	0	Cu Pb Zn
	Overburden	*	*	*	1	As Sb Bi
Ballinglen (W - Sn)	Soil	*	0	*	1	W As Bi
	Overburden	*	1	*	1	Cu
Clontibret (Au)	Soil	*	2	-	-	As
	Overburden	*	*	-	-	As Sb Au
Dalbeattie (U)	Soil	*	2	*	0	As Bi Pb Cu Ca
Glendinning (Sb)	Soil	*	*	0	0	As Sb
Keel (Zn - Cd)	Soil	1	*	0	0	Pb Zn Cd Hg Sb
	Overburden	1	*	0	0	
Kilmelford (Cu)	Peat	0	-	1	1	Cu Pb Mo
	Till	0	-	.2	1	
Mallow (Cu - Ag)	Soil	2	*	0	0	Cu Pb Zn Mo
Meall Mor (Cu)	Peat	0	1	0	0	Cu Pb Zn
	Till	2	2	0	2	

Key
- * As Good or Better than Indicator Elements
- 2 Significant Additional Information
- 1 Minor Additional Information
- 0 No Use
- - Not Determined

Table 8.7 Usefulness of Pathfinder Geochemistry in Stream Sediments/Waters

Area		As	Sb	Bi	Se	Recommended Elemental Suite in in Sediments
Arthrath (Ni - Cu)	Sediments	Does Not Intersect Mineralization				
Ballinglen (Sn - W)	Sediments	*	0	1	0	W As
	Waters	2	-	-	-	
Clontibret (Au - Sb)	Sediments	*	*			(As Sb) of Doubtful Value
Glendinning (Sb)	Sediments	*	*	0	0	As Sb
	Waters	2	2	-	-	
Keel (Zn - Cd)	Sediments	0	0	0		Zn Cd
	Waters	0	0	0	-	
Kilmelford (Cu)	Sediments	0	-	1	1	Cu Pb Mo
	Waters	0	0	0	0	
Meall Mor (Cu)	Sediments	2	*	0	0	Cu Zn
	Waters	1	0	0	0	
South West England	Sediments	*	-	*	1	Varies with Deposit Type

KEY

Stream Sediments		Water
Better or as good as Indicator Elements	*	
Significant Additional Information	2	Detectable Anomalies
Minor Additional Information	1	Minor Anomalies
Of No Use	0	No Anomalies
Not Determined	-	Not Determined

no anomaly at Munali, Zambia. The detailed controls on primary arsenic disptribution in this type of deposit are not clear at present.

One major association evidenced by the detailed studies is with granitic rocks. Arsenic is anomalous in most, if not all, tin-tungsten bearing structures/disseminations although detailed studies suggest that arsenic is an equivocal guide to deposits in South West England. Here a broad halo of disseminated arsenic occurs around the Dartmoor Granite, in addition to high concentrations in copper and tin bearing structures. The presence of arsenic accumulations in the intruded sediments suggests that remobilisation of these concentrations is a more plausible explanation for this distribution than diffusion from the intrusive. The patterns around the Leinster Granite are different, with arsenic highs mainly restricted to greisen dykes and no halo around the granite and low concentrations in the intruded sediments. Its absence tends to confirm the importance of sedimentary concentration as a source of arsenic in granite-hosted mineralization. Arsenic anomalies also occur in the sub-economic sulphosalt rich veins around the South West England granites. These deposits form at a lower temperature than those containing tin with an assemblage very similar to that at Dalbeattie. Here arsenic gives well defined primary anomalies with little wallrock alteration. The metal assemblages suggest that mineralization may well result from reduction of relatively low temperature solutions.

All three base metal deposits studied in Ireland are enriched in arsenic but its position in the paragenetic sequence relative to the indicator elements differs. At the Kuroko-style Avoca deposits the element is enriched throughout the mineralized sequence and may have a broad supra-ore halo similar to that described from Canadian and Spanish deposits. Arsenic at Keel is probably mainly

concentrated in the veins, while at Mallow it occurs both with the copper-silver mineralization and the surrounding disseminated lead-zinc zone.

The other major association of arsenic is with gold. Data from Clontibret are not conclusive on the how the two elements are associated in the primary environment but recent evidence suggests that gold may be transported as arsenic-sulphur complexes implying a very strong correlation (Boyle, 1979; Grigor'yeva and Sukneva , 1982). Arsenic is the most universal pathfinder for hypogene gold and discoveries include the Cortez deposit, Nevada (with antimony) and the Mururtan deposit, U.S.S.R. (Boyle, 1979a).

Soils are the most favoured prospecting medium in areas of residual soil and lateritisation. Surveys in temperate climates generally use the B horizon and fine fractions. This study confirms that this is generally the fraction leading to maximum anomaly contrast. In lateritised areas, however, it seems that sampling of the coarse fraction is often more effective as arsenic is scavenged by the very iron-enriched soils and then subject to very limited clastic dispersion (Mazzucchelli and James, 1966; Webb, 1958). This scavenging causes considerable problems in some areas, particularly Keel and Avoca, where it is responsible for smearing and thus poor definition of the arsenic anomalies. Considerable care should therefore be taken in areas where the anomalies sought may be of limited size, areas of podzolation noted and/or iron determined.

Sampling of A horizons may be effective in forested areas although there is no evidence in the present study. Its utility depends on trees tapping bedrock anomalies covered by exotic /impermeable overburden. Arsenic is taken up into leaves which then decay to form forest litter enriched in arsenic (Talipov et al, 1976 ; Boyle and

Dass, 1971). Direct sampling of Douglas Firs has shown them to contain anomalous concentrations (up to 10000 ppm As) overlying gold mineralization in British Columbia (Warren et al, 1964).

Successful stream sediment surveys are numerous with the constraint of spurious anomalies generated by concentration at iron oxide barriers. The extent of this problem can be gauged from the detailed studies. In these it is most acute where very peaty waters are present giving rise to much secondary iron hydroxides, e.g. at Kilmelford, and arsenic distribution seem almost exclusively related to scavenging by these hydroxides. This is, however, not the case in lowland areas where it seems likely that the most intense iron anomalies are related to weathering of primary sulphide concentrations. Thus correlation of iron with arsenic does not necessarily imply scavenging, although iron should routinely be determined and anomalies carefully ground-checked.

Arsenic is the only one of the pathfinders with a high enough concentration in waters to be used in exploration at present. The detailed studies confirm that anomalous concentrations are present in stream waters downstream from mineral deposits but any practical application of hydrogeochemistry lies in the realm of subsurface waters.

The determination of arsenic in soil gases by Ruan (1981) is, as far as the author is aware, the first to be reported. This study demonstrates that they are generated at seepage zones, i.e. as a result of hydromorphic dispersion, as well as directly over primary enrichments.

8.3.2 Antimony

Antimony has had application mainly in the search for gold, lead-zinc and antimony mineralization. The

detailed studies confirm the associations and add that of antimony with nickel-copper sulphides.

The evidence from Arthrath suggests that antimony is concentrated in residual fluids of basic magmas but the data quoted in Chapter 2.2 suggest that not all nickel sulphides are enriched. Antimony shows very limited concentration in granitic hosted tin-tungsten deposits and is associated with minor sulphosalt development. It forms a distinct halo around silver bearing mineral belts at Coeur d'Alene, Idaho (Gott and Cathrall, 1980) In contrast it is strongly enriched in sediment hosted base metal deposits exemplified by Avoca, Keel and Mallow in Ireland and there is particularly strong correlation with lead/zinc. At Avoca antimony is concentrated in the upper, lead-zinc rich, part of the mineralized sequence. This is a more restricted stratigraphical position than arsenic but antimony may also have a broad lateral halo. At Keel and Mallow antimony is closely related to the main ore minerals and evidence of this study suggests limited primary dispersion. Data from Meall Mor shows concentration of antimony in the pyritiferous zone.

Antimony, like arsenic, is closely associated with many gold deposits and may be associated with sulphur in the transport of gold. The data from Clontibret suggests that it is more erratically enriched than arsenic although still a useful guide. Primary antimony dispersion at Glendinning seems limited but this may not apply to other hypogene antimony deposits.

Soils are by far the most commonly used medium. Over antimony deposits in Alaska the element is concentrated at the bedrock/overburden interface and the base of the humus layer (Sainsbury, 1957). Results from an antimony prospect in Burma show only limited clastic dispersion (Chakrabarti and Solomon, 1970). Iron rich soils in

Zimbabwe give narrower antimony anomalies than those of arsenic but anomalies are broader in iron poor soils (James, 1957). The detailed profiles at Keel, Avoca and Arthrath confirm that the key control on antimony mobility is its insolubility, giving rise to limited dispersion through overburden. The limited amounts of antimony dispersed hydromorphically are probably adsorbed/co-precipitated by iron oxides or organic matter. Thus overburden sampling will be much more effective than conventional soil sampling in locating primary antimony anomalies where the overburden is more than about 2 m thick. The affinity of antimony for organic matter implies that the A horizon or peat sampling may be a useful technique. Background soil values at Glendinning and Clontibret are significantly higher that other areas suggesting that wide spaced sampling may indicate prospective districts.

Detailed description of antimony dispersion in stream sediments is almost entirely lacking. The only investigation encountered during a literature search suggests that antimony is dispersed clastically in finely comminuted grains with short dispersion trains (Boyle, 1975). The detailed studies at Meall Mor and Glendinning provide convincing evidence of the almost exclusive introduction and transport of antimony as clastic grains. This mode of dispersion has considerable implications as panned concentrate samples are likely to be more effective in detecting localised enrichments. Regional stream sediment sampling of the fine fraction may however be effective in outlining regional enrichments as background values at Glendinning and Clontibret are significantly enriched on a regional scale.

Application of the element in hydrogeochemical prospecting has been almost entirely restricted to the U.S.S.R. There it is only recommended for deep seated

orebodies with anomalous concentrations reaching 80 ppb Sb (Adilov et al, 1971). The data from this study suggest that routine application of this method will be difficult, not least because background levels are near analytical detection limits.

8.3.3 Bismuth

Very few detailed case histories are available outside the U.S.S.R. where the element seems to form a prominent part of multi-element prospecting (Beus and Grigorian, 1977).

Recent data from Cornwall suggests that bismuth is a useful pathfinder for tourmalinised granite cusps and vein structures (Ball et al, 1982). The data from studies at Ballinglen and South West England and literature studies quoted in Chaper 2.2 confirm its close association with tin-tungsten mineralization and it seems to have limited primary dispersion. There are however a number of unsolved problems. The first is that at Ballinglen bismuth is associated with sulphide development and the form of bismuth in other tin-tungsten deposits low in sulphides is not known. The second is that it is not clear how much, if at all, the bismuth anomalies are influenced by assimilation of bismuth enriched sediments by the granite. Bismuth is not enriched in the porphyry at Kilmelford but only in the later faulting/lead mineralization. This evidence is at variance with data from Chuquicamata which show some bismuth concentration,but consistent with data from Ely, Nevada showing a bismuth halo around copper mineralization (McCarthy and Gott, 1978). The granitic related polymetallic veins at Dalbeattie are consistently enriched, perhaps indicating low temperature leaching from granite and concentration by reduction.

Bismuth is anomalous at the Avoca massive sulphide deposit but not in the carbonate hosted deposits at Keel and

Mallow. Its concentration in lower zones of Avoca is compatible with the empirical zonation sequence of Beus and Grigorian (1977). Highs occur at Boudennec and Porte-aux-Moines, Brittany but their relation to geology is not obvious from the available data (Wraith, 1982). Bismuth is enriched in black shales in Somerset and erratically over the stratiform copper mineralization at Meall Mor. High concentrations occur in copper and precious metal deposits at Lubin, Poland and bismuth seems a useful pathfinder in this environment.

The only detailed investigations on bismuth in soils are in forest mull over gold deposits in Colorado (Curtin et al, 1974), dambo sediments in Zambia (Schiefler, 1967), with the recent addition of information from South West England showing limited dispersion (Ball et al, 1982). In Zambia bismuth seem hydromorphically dispersed from enriched veins into soil and dambos with concentration in iron oxide rich fraction of the soil. It shows clastic dispersion in lateritic pisolites at Golden Grove, Western Australia, where bismuth geochemistry has been successfully applied. Detailed profiling at Avoca and Ballinglen demonstrates limited hydromorphic dispersion with some concentration at the surface. This pattern also seems to hold for Kilmelford where bismuth is probably present in the primary environment in solid solution in galena as opposed to native bismuth/sulphide/sulphosalts at Avoca and Ballinglen. Thus bismuth can be successfully used in soils and fine fraction sampling methods are adequate.

Smith (1982)

No detailed description of bismuth dispersion in stream sediments is available in the literature although there is some evidence of hydromorphic dispersion of bismuth into Zambian dambos (Schiefler, 1967). The data from detailed studies, although not providing a convincing example of the effective use of bismuth, shows that fine

fraction grab sampling would detect primary enrichments. This technique will detect both bismuth hydromorphically dispersed from primary enrichments as sulphide/sulphosalts and at least in part clastically dispersed from lead rich deposits. Russian reports suggests anomalies in waters of up to 0.1 ppb relative to background of 0.05 ppb around gold deposits (Goleva, 1968). These concentrations are below the detection limit of the method used in this study and thus the routine application of hydrogeochemistry must be considered as being some time distant.

8.3.4 Selenium

Selenium has had very specific application in the search for shale hosted base metal deposits, selenide veins, sandstone uranium deposits and the discrimination of gossans over nickel deposits.

The element is strongly concentrated in nickel sulphides at Arthrath and Munali, Zambia (Wraith, 1982) and enriched in sulphides at the Kilmelford copper porphyry. This almost certainly reflects increased isomorphous substitution of selenium for sulphur at high temperatures. Minor selenium anomalies occur in bedrock at Avoca and Ballinglen; typical concentrations in hydrothermal ores can be anticipated to range from 1 - 20 ppm Se (based on S/Se ratios of 10000 -30000) Reduction and/or organic complexation are, however, the main mechanisms by which selenium is concentrated. Their effects are well demonstrated in the association of selenium with black shales, both Dinantian and Jurassic, in South West England. Selenium is strongly enriched in metalliferous sediments of the Kupferscheifer and the stratiform sulphides at Meall Mor. The element is also concentrated in polymetallic veins at Dalbeattie, which probably formed by reduction.

The most comprehensive account of the application

of selenium comes from East Germany, where soil selenium anomalies occur over seleniferous veins in the Ezgebirge and metalliferous sediments in the Kupferscheifer (Leutwein and Starke, 1957). Anomalous concentrations reach 2 ppm Se relative to 0.3 ppm background. Research in Finland shows that anomalous concentrations of selenium occur around Outokumpu-type sulphides at Luikonlahti, with concentrations reaching 13 ppm in gossans (Kõljonnen, 1976). The present study casts much doubt on the effectiveness of selenium in humid terrains. Although anomalous concentrations were found (e.g. Arthrath) they are often of lower contrast than spurious anomalies formed by scavenging by organic matter in background localities. In addition bedrock anomalies at Ballinglen and Avoca are not reflected in surface soils. Thus, selenium can only be recommended for use in the search for nickel sulphides or copper porphyries, and heavy mineral concentrates will probably be more effective than total soil samples. Deep sampling is a more useful technique than surface soils. Selenium will almost certainly be more effective in lateritised terrains where selenium will be largely retained in iron oxides.

Selenium accumulator plants, such as Austragalus Pattersoni, have been used in the search for uranium deposits in the Colorado Plateau, U.S.A. but more recent research indicates that their distribution is more dependent on the presence of uranium (Cannon, 1979).

Although minor selenium anomalies occur downstream from anomalous bedrock (Kilmelford, Meall Mor) they have, like soil anomalies, much lower contrast than spurious highs formed by scavenging by organic matter. Selenium is, thus, not recommended for use in temperate terrains.

Anomalies in groundwaters have only been reported on a research basis from the U.S.S.R. (Goleva and Lushnikov, 1967). The method may be of some potential in arid areas in the long term but analytical methods need to be refined.

CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

9.1 Conclusions

The factors which control the surficial distribution of pathfinders are a combination of their primary distribution, solubility and mobility in the secondary environment.

9.1.1 Conclusions: Primary Distribution

All the pathfinders are strongly chalcophile with crustal abundances ranging from 0.05 - 1.8 ppm (Se<Bi<Sb<As). Selenium, however, has a very strong affinity for organic carbon at low temperature and is atmophilic. They are all very low in tenor in silicates from basic rocks (Se<Bi<As<Sb) and are concentrated in shales (particularly those enriched in organic matter), with bismuth also enriched in granitic rocks.

All the pathfinders are concentrated in mineral deposits formed by residual fluids from basic magmas and stable native elements (with the exception of arsenic) can form as a result of low temperature reduction. Arsenic, antimony and bismuth are enriched in a variety of mineral deposits precipitated at intermediate temperatures and their distribution probably reflect the stability of transporting complexes. Their zonation is described by the empirical sequence of Beus and Gregorian (1977):-

Ba-Sb-As-Ag-Pb-Zn-Au-Cu-Bi-Ni-Co-Mo-U-Sn-Be-W

Selenium is different from the other pathfinders as it substitutes isomorphously for sulphur. This process is dominantly temperature dependent although other factors, notably element availability, are important.

An important constraint of this study is that it has been concerned with a small area of the globe and a short span of time, almost exclusively in the Phanerozoic. In older rocks, an important consideration could be the effect

of the postulated low-oxygen atmosphere in the Archean: this would have a considerable impact on the low temperature transport of pathfinders as anionic complexes. In the author's opinion environmental factors are a more important control than evolutionary trends on the distribution of the pathfinders, and the conclusions arrived at here can be extended to other areas and to older rock.

a) Arsenic

Arsenic is enriched in a wide range of mineral deposits and occurs as several different mineral types: arsenides; arsenopyrite; sulphosalts; and arsenates.

Nickel-copper sulphides in basic rock at Arthrath have associated arsenic concentrations. The element has wide dispersion forming a halo around the Dartmoor Granite, which is mineralized in tin and tungsten, and shows higher arsenic concentrations in the tin mineralized structures. The halo may form as a result of remobilisation of pre-intrusive sedimentary arsenic concentrations in the Dinantian. This situation is further complicated by late stage sulphosalt-bearing structures which form at lower temperatures. The pattern around the Dartmoor Granite contrasts with the limited primary arsenic dispersion associated with tin-tungsten bearing microgranite dykes at Ballinglen, Ireland. Here the main granite body is unmineralized and has no arsenic halo. A different type of mineralization at Dalbeattie, in which the granite-related polymetallic assemblages is probably precipitated from low temperature solutions, shows limited primary arsenic dispersion. Data from the Kilmelford porphyry copper show that arsenic is not enriched in the porphyry, and there is little evidence of a halo around it.

Arsenic is enriched in all three hydrothermal base metal deposits examined in Ireland. At Avoca it is

concentrated in, underneath and over the massive sulphide with some evidence of a broad supra-ore halo. The pattern at Keel is different with enrichment in veins while arsenic has wider concentration in both copper-silver and lead-zinc zones at Mallow.

The relation between arsenic and gold is often close, partly as a result of the transport of gold in arsenic-sulphur complexes. The data from the limited study at Clontibret is not conclusive about the nature of the arsenic-gold relationship although arsenic is concentrated both in particular stratigraphical units and in veins. At the geologically similar but non-auriferous Glendinning deposit, arsenic seems enriched in sedimentary units rather than in the later veins.

In sediments which show no obvious hydrothermal alteration arsenic is concentrated in both sulphide rich and iron oxide facies (e.g. Dinantian and the Inferior Oolite in South West England). It is enriched in the quartzites at Meall Mor but distant from the cupriferous iron pyrite zone. Arsenic anomalies in sediments should, however, be carefully examined as they may represent the distal effects of hydrothermal solution rather than sedimentary concentration

b) Antimony

Antimony is concentrated in a range of mineral deposit less diverse than arsenic with particular enrichment in sediment hosted mineral deposits.

An exception is at Arthrath where antimony is enriched in nickel-copper sulphides. Data from this Ballinglen show that it has very restricted enrichment in granitic environment . Antimony is however high at Dalbeattie where there is erratic, limited primary dispersion, probably reflecting reduction from relatively low temperature solutions.

The three base metal deposits studied in Ireland all show antimony concentration. At Avoca it is closely correlated with lead/zinc and mainly enriched in the lead-zinc zone above the cupriferous zones. In the carbonate hosted deposits antimony is closely associated with the main mineralized zones at Keel (zinc veins) and both the copper-silver and lead-zinc zones at Mallow.

Antimony, like arsenic, often shows correlation with gold, probably partially as a result of their transport in gold-antimony-sulphur complexes. The evidence from Clontibret is limited and equivocal, probably with limited antimony enrichment around the vein. At Glendinning antimony is concentrated both in sediments and in the fracture hosted mineralization.

There is considerably less evidence on the nature of antimony in sediments. It is however closely associated with stratiform copper enrichments at Meall Mor.

c) Bismuth

Bismuth is particularly enriched in granitic hosted deposits and high temperature hydrothermal deposits.

This element is only slightly enriched in nickel-copper sulphides at Arthrath. This contrasts with the strong concentration in the tin-tungsten mineralized Dartmoor Granite and microgranite dykes at Ballinglen, Ireland. Both these areas show more limited primary bismuth concentration than arsenic with high bismuth values associated with sulphide development at Ballinglen. The polymetallic veins at Dalbeattie are consistently enriched in the element, which is probably concentrated by reduction. In contrast the Kilmelford porphyry is not enriched but peripheral lead/zinc veins/skarns show bismuth concentrations.

Bismuth is strongly enriched in the lower (copper

rich) zone of the Avoca deposit but only shows background concentrations in the carbonate hosted Keel and Mallow deposts.

The element is concentrated in Jurassic shales in Somerset but gives erratic anomalies in the pyritiferous zone at Meall Mor. There is also minor enrichment in iron rich sediments e.g. the Inferior Oolite.

d) Selenium

Selenium is strongly concentrated in nickel sulphides, as a result of high temperature substitution of selenium for sulphur, and in organic rich reducing shales. Significant enrichments were encountered in two types of igneous hosted deposits studied: nickel sulphides at Arthrath (and at Munali, Zambia) and the copper porphyry at Kilmelford. Minor bedrock anomalies occur at Avoca and to a lesser extent at Ballinglen. In general only minor anomalies can be anticipated from hydrothermal sulphides.

The major selenium anomalies are associated with organic rich shales and coals, as exemplified by Jurassic and Dinantian black shales in South West England. The element is also enriched in sediments hosting copper deposits at Meall Mor.

9.1.2 Conclusions: Secondary Mobility

The pathfinders show variable valency in the surficial environment and this governs their behaviour to a considerable extent. Arsenic, antimony and selenium in their inorganic forms are transported in solution as anionic complexes (arsenic, antimony +3, +5 and selenium +4, +6). Bismuth is exclusively present in the +3 state and predominantly as a cationic complex. Their behaviour in the natural environment is modified by interaction with

organic matter: arsenic and selenium readily form methylated compounds. Similar compounds are known, although not widely distributed, for antimony, but are unknown for bismuth. Both arsenic and selenium can also form gaseous methylated compounds. Selenium and arsenic minerals are generally soluble in oxidising environments, bismuth minerals less so, and antimony minerals virtually insoluble.

a) Arsenic

This study is in accord with much of the well documented surficial chemistry of arsenic. Theoretical and laboratory work shows that arsenic is transported in oxygenated waters as the arsenate complex or in ground waters as arsenite. These are adsorbed by amorphous ferric oxides (arsenate more strongly than arsenite) and this is the key control on surficial arsenic distribution. This is particularly evident in peaty areas where rapid Eh/pH changes cause precipitation of iron oxides (Meall Mor and Kilmelford).

Studies of stream water at Glendinning confirm that arsenic is transported in the +5 oxidation state with only minor concentrations in the 3^+ state and as organic arsenic. The mode of arsenic stream sediment anomaly formation is less clear and may be grain size dependent. The element is concentrated in the finest sediment (-63 μm) fraction and the particulate (>0.45 μm) arsenic anomalies in stream water are developed downstream from the peak sediment anomalies. Thus it seems likely that fine (<190 μm) fraction sediment anomalies downstream from mineralization are generated by transport of arsenic in suspension, (possibly adsorbed onto iron). The bulk of arsenic is, however, transported in the coarse fraction in iron oxide coatings or as arsenic rich grains. The arsenic content of these coatings may be due to adsorption from waters enriched in

arsenic (if erratically).

The behaviour of arsenic in overburden is less clearly established in this study. Its close association with iron enriched horizons suggest that dispersion is hydromorphic (Avoca, Keel). Direct evidence of the hydromorphic nature of dispersion is provided by anomalous contents of arsenic in soil pore waters over the Arthrath soil anomaly. In the more rugged and arsenic enriched area of Ballinglen, clastic dispersion is probably also important. Arsenic gases (probably methylated) are generated over the subcrop of the mineralized microgranite and over seepage zones, presumably resulting from the transport of arsenic in ground waters.

b) Antimony

The key feature of its behaviour in the surficial environment is its very limited solubility.

Antimony is almost exclusively introduced and transported in stream sediments as clastic grains (Meall Mor, Glendinning). Determination of antimony present in stream water gives only very localised anomalous values in solution at Glendinning and no evidence of anomalous concentration in particulates. There is no evidence of concentration by either iron oxides or organic matter in these areas.

Overburden profiling demonstrates the limited solubility of antimony with concentrations invariably increasing with depth. At Avoca there is some evidence of its correlation with iron oxides, which might be anticipated from theoretical predictions of antimony transport as an (+5) anionic complex. Another facet of antimony geochemistry is its complexation and local enrichment in organic matter as evidenced by its concentration in peats at Keel and Meall Mor.

c) Bismuth

Bismuth shows limited hydromorphic dispersion in profiles at Avoca and Ballinglen. There is evidence of its concentration in the near surface and this is best explained by precipitation of insoluble salts. The element shows some enrichment in peats (Kilmelford and Meall Mor) but it is not as pronounced as for antimony.

Physical fractionation of stream sediment suggests that bismuth is dispersed hydromorphically, although the evidence of the detailed studies is not convincing. The data from Kilmelford indicate that dispersion may be dependent on primary mineralogy and clastic where bismuth is contained in lead minerals.

d) Selenium

The key control on surficial selenium distribution is complexation by organic matter.

Selenium in soils does not always reflect deep overburden anomalies and there is some evidence of absolute selenium concentration in the near surface (Avoca, Ballinglen). The element is readily soluble but anomalous selenium in waters is not always adsorbed, perhaps because of saturation of organic matter in selenium or preferential volatilisation of inorganic selenium. The atmophilic nature of the element could also explain enrichment of selenium in near surface soils with atmospheric selenium supplied to them either by rainout or adsorption. At Arthrath there is evidence of clastic transport of selenium through the profile in gossanous fragments.

Selenium is transported in solution in stream waters from bedrock anomalies at Kilmelford, giving rise to sediment anomalies but these have lower contrast than spurious anomalies formed by concentration in organic

matter. Iron oxides may also be a control on selenium but are less important than organic matter.

9.1.3 Implications for Geochemical Prospecting

The pathfinders, arsenic, antimony and bismuth, have considerable although specific application in geochemical exploration, both in lithogeochemistry and surficial prospecting. Selenium is of very limited use in surficial prospecting in humid climates as scavenging by organic matter often produces higher contrast anomalies than those derived from primary concentrations. The hydride generation/ I.C.P. method, following the magnesium nitrate attack (for arsenic, antimony and bismuth) or co-precipitation method for selenium, is a precise and accurate method of determining background pathfinder concentrations; and a considerable advance on previous methods. Its cost in commercial usage will be intermediate between that of A.A. determination of transition metals and multi-element I.C.P. Thus determination of the pathfinders is a viable addition to the determination of indicator metals in geochemical prospecting.

Lithogeochemistry using arsenic, antimony and bismuth will be most effective in the search for sediment hosted or exhalative deposits, where zonation is well developed. A good example of this is at Avoca where the pathfinder and transition metals could be used to determine way-up of the deposit with bismuth at the base and antimony at the top. Other associations are discussed in the section on primary pathfinder distribution. Arsenic and bismuth can be used to locate tin-tungsten deposits, and districts with bismuth having more restricted distribution. Selenium is of little use as a lithogeochemical pathfinder with the possible exception of indicating reducing environments in sediments. It is, however, difficult to apply even

in this situation except for roll front uranium deposits, as controls on its distribution involve organic concentration as well as oxidation/reduction mechanisms.

The pathfinders (with the possible exception of arsenic) are most effectively employed in surficial exploration in temperate zones to detail areas for more expensive, drilling and trenching, following target selection, by geology, geophysics or geochemistry. They may have more regional uses in lateritised zones where transition metals are ineffective due to leaching and re-concentration. This study confirms the general applicability of using the -190μm fraction in temperate soils and stream sediments.

The major problems of applying arsenic are its relatively wide primary dispersion and concentration by ferric oxides during secondary processes. This causes smearing of soil arsenic anomalies at Keel and the development of spurious anomalies in the peaty areas of Kilmelford and Meall Mor. The partial remedy for this is to carefully note areas of podzolation and input of peaty waters and/or routinely determine iron. Not all iron-arsenic anomalies are spurious and iron concentrations may reflect weathering of iron sulphides. Prospecting using arsenic in soil gases is a viable technique although it has no advantage over soil sampling in temperate terrains, as it reflects seepage zones as well as subcropping mineralization.

Application of antimony should take account of the limited solubility. Dispersion through till is often poor, as evidenced by profiles at Avoca and Ballinglen, and deep sampling is the recommended technique in moderate to thick overburden. Scavenging by iron oxides and complexing with organic material may produce spurious anomalies in soils/overburden although the problems are much less important than for arsenic. The almost exclusively

clastic nature of antimony dispersion in surface drainage means that anomalies will represent a very limited part of the drainage basin and that panned concentrates will be more effective than fine fraction sampling.

Bismuth is much easier to apply and no special sampling techniques are required. Good contrast anomalies can be anticipated in soil samples possibly with some near surface concentration. Stream sediment sampling using fine fraction samples is generally successful in detecting primary anomalies but there may be clastic dispersion of bismuth in lead rich veins.

Selenium is not recommended for use in humid terrains as organic scavenging often gives higher contrast anomalies than those derived from primary anomalies. It may be a more useful discriminant in lateritised areas where selenium is retained by iron oxides.

9.2 Further Research

The data presented in this thesis represent some preliminary observations on the geochemistry of bismuth and antimony and some more advanced ones on arsenic and selenium. Much further work is required for a thorough understanding of the geochemistry of these elements.

9.2.1 Primary Geochemistry

Little is known of the fundamental controls on the distribution of pathfinders in hydrothermal fluids or magmas. Experimental investigations should concentrate on the leachability of pathfinders from various rock types and transport as different complexes, particularly of the chloride or sulphide type. The transport of gold as a complex with arsenic and antimony with/or without sulphur is worthy of thorough research: some work along these

lines is available in very recent Russian literature (Ovchinnikov et al, 1982; Grigor'yeva and Sukneva, 1982). The partition coefficients of pathfinders in magmas should be established.

Detailed investigation of other types of deposit, particularly Cyprus and Besshi types of massive sulphide deposit, and other examples of the deposit types which appear promising, will clarify the general applicability of pathfinder geochemistry.

9.2.2 Surficial Geochemistry

The scope for research on antimony and bismuth is wide. Little fundamental data on solubility of their sulphides and no up to date Eh-pH diagrams are available.

New techniques, notably combined gas chromatography-mass spectroscopy after modified hydride generation allow the identification of pathfinder in both inorganic and organic compounds at the ppt level (c.f. work on organo-tin compounds(Jackson et al, 1982)). These will undoubtedly provide breakthoughs in the understanding of pathfinder reactions at natural concentrations. Routine determination of identified species will then be carried out by combined chromotography-hydride generation - A.A./I.C.P. (c.f. Fish et al, 1982). Determination of total antimony and bismuth in solution will probably be routinely made by hydride generation-flameless A.A. methods (c.f. Lee, 1982).

The immediate areas for further research are:-

Arsenic: Detailed investigation of organic - arsenic reactions in soils.

Antimony: Transport and complexation by organic matter. Quantification of its fixation by iron oxides in soils.

Bismuth: Identification of bismuth species in gossans and mechanism of concentration in near surface soils.
Solubility in surface and groundwaters.
Investigation of surficial organic chemistry (if any).

Selenium: Investigation of the importance of adsorption from the atmosphere relative to dispersion from bedrock.
Identification of selenium species in black shales.

9.2.3 Exploration Techniques

The major area for further research is in my opinion the application of lithogeochemistry. This has mainly advanced and will continue to advance in the immediate future by understanding the mechanisms of ore formation (notably by observation of present day processes e.g. the Red Sea and the East Pacific Rise). A more thorough appreciation of the theoretical basis of pathfinder distribution (outlined in 9.2.1) will probably not be immediately forthcoming but advances will probably come from sensible application of the empirical relations derived by Russian workers (Beus and Gregorian, 1977).

Further research on the application of arsenic vapour geochemistry using the methods suggested by Ruan (1981) is merited. This will be probably be limited to arid areas, as spurious anomalies generated by seepage will almost certainly nullify its usefulness in temperate terrains

Hydrogeochemistry may be useful in arid areas with a large number of water wells and in areas of detailed drilling. This is less prospective than the other areas of investigation and initial research should check the major ion dependency of the pathfinders.

Publications associated with this thesis

Hale,M and Moon,C.J. (1982) Expression at surface of mineralization concealed beneath till at Keel, Eire. pp223-239 in Davenport,P (ed) **Prospecting in Areas of Glacial Terrain 1982, C.I.M.**

Moon,C.J. and Hale,M. (in press) Dispersion of As,Sb,Bi,Se from sulphide mineralization at Avoca, Eire in **Journ. Geoch. Exploration Saskatoon Symposium Volume**

REFERENCES

Adilov, V.B., Shvartseva, N.M. and Lyan, D., (1971). Antimony in the subsurface waters of some gold-ore deposits of the Kuramisk Range. Chem. Abs. 81, 94129m

Aguilar, R.A.N., (1974). The Regional Distribution of Arsenic in South West England. Unpub. Ph.D. Thesis, Imperial College, London.

Andrae, M.O.,(1977). Determination of arsenic species in natural waters. Anal. Chem. 49, 820-828

Andrae, M.O., Asmodé, J-F, Foster, P. and Van't dack, L., (1981). Determination of antimony (III), antimony (V) and methylantimony species in natural waters by atomic absorption spectrometry with hydride generation. Anal. Chem. 53, 1766-1771

Armour-Brown, A. and Nichol, I., (1970). Regional geochemical reconnaissance and the location of metallogenic provinces. Econ. Geol. 65, 312-330

Aston, S.R., Thornton, I. and Webb, J.S., (1975). Arsenic in stream sediments and waters of south-west England. Science of the Total Environment 4, 347-358.

Avery, B.W., (1955). The Soils of the Glastonbury District of Somerset. Mem. Soil Surv. G.B., 296

Baes, C.F. and Mesmer, R.E., (1976). The Hydrolysis of Cations. John Wiley.

Baker, M.D., Wong, P.T.S., Chau, Y.K., Mayfield, C.I. and Inniss, W.E., (1981). Methylation of lead, mercury, arsenic and selenium in the acidic aquatic environment. In 'Heavy Metals in the Environment', Amsterdam, pp 645-648 C.E.P. Consultants

Ball, T.K., (1982). Vapour Geochemistry. Unpub. talk at E.E.C. Raw Material R and D Group, London.

Ball, T.K., Basham, I.R., Bland, D. and Smith, T.K., (1982) Aspects of the geochemistry of bismuth in south-west England. Proc. Ussher Soc. 5, 376-382

Barnes, H.L., (1979). Solubilities of ore minerals. pp 404-460 in Barnes, H.L. (ed). In 'Geochemistry of Hydrothermal Ore Deposits', Wiley

Barnes, H.L. and Czamanske, G.K., (1967). Solubilities and transport of ore minerals. In 'Geochemistry of Hydrothermal Ore Deposits', (H.L. Barnes ed). 334-381. Holt, Reinhart and Winston, New York.

Basham, I.R., (1974). Mineralogical changes associated with deep weathering of gabbro in Aberdeenshire. Clay Miner 10, 189-202

Bente, K., (1982). S-isotope investigations and geothermometric application of bismuthinites. Mineral. Deposita 17, 119-132

Beus, A.A. and Grigorian, S.V., (1977). Geochemical Exploration Methods For Mineral Deposits. Applied Publishing Ltd.

Bowen, H.J.M., Page, E., Valente, I. and Wade, R.J., (1979). Radio-tracer methods for studying speciation in natural waters. Journ. Radioanalyt. Chem. 48, 9-16

Boyle, R.W., (1974). Elemental associations in mineral deposits and indicator elements of interest in geochemical prospecting (revised). Geol. Surv. Canada. Paper 74-75

Boyle, R.W., (1975). The geochemistry of antimony, Keno Hill area, Yukon. In 'Recent Contributions to Geochemisty and Analytical Chemistry'. John Wiley (A.I. Tugarinov ed) p.354-370

Boyle, R.W., (1979). Geochemistry of Gold. G.S.C. Bull 280, Ottawa.

Boyle, R.W., (1979a). Geochemistry overview in Geophysics and Geochemistry in the Search for Metallic Ores, (ed. P.J. Hood). Geol. Surv. Canada, Econ. Geol. Report no. 31 p.25-32

Boyle, R.W. and Dass, A.S., (1971). The geochemistry of the supergene processes in the native silver veins of the Cobalt-South Lorraine area, Ontario. Canad. Mineral. 11, 358-390

Boyle, R.W. and Jonasson, I.R., (1973). The geochemistry of arsenic and its use as an indicator element in geochemical prospecting. J. Geochem. Expl. 2, 251-296

Braman, R.S., Johnson, D.L., Foreback, C.G., Amons, J.M. and Brucker, J.L., (1977) Separation and determination of nanogram amounts of inorganic arsenic and methylarsenic compounds. Anal. Chem. 49, 621-625

Cannon, H.L. (1955) Geochemical relations of zinc bearing peat to the Lockport Dolomite, Orleans Co. New York. U.S.G.S. Bull 1000-D 119-185

Cannon, H.L., (1979). Advances in botanical methods of prospecting for minerals, Part I. Advances in geobotanical methods of prospecting. p. 385-396 in Geochemistry in the Search for Metallic Ores (ed. P.J. Hood). Geol. Surv. Canada, Econ. Geol. Report no. 31

Carter, J., (1981). Mallow-Munster Base Metals Report. Unpublished.

Cazalet, P.M.D., (1982). A review of geochemical exploration techniques 1971-1981, pp 148-156 of Brown, A.G. ed. Mineral Exploration in Ireland. Wexford Meeting, 1981. Irish Association for Economic Geology.

Chaffree, M., (1981). A geochemical study of the Kalamazoo porphyry copper deposit, Pinal County, Arizona. In Titley, R.S. ed. Porphyry Copper Deposits. Advances in Geology of South Western North Americal. Univ. of Arizona Press.

Chakrabarti, A.K. and Solomon, P.J., (1970). A geochemical case history of the Rayburi antimony prospect, Thailand Econ. Geol. 65, 1006-1007

Challenger, F., (1978). Biosynthesis, Organo-metals and Organo-metalloid compounds. pp1-22 of Occurrence and Fate of Organometals and Organometalloids in the Environment. A.C.S. Symposium series.

Chukhrov, F.V., Senderov, V.M. and Ermilava, L.P., (1979). The mineralogy of bismuth in the zone of oxidation, pp 355-357 of Angino, A.A. and Long, D.T. eds. Geochemistry of Bismuth. Dowden Hutchinson Ross

Clapperton, C.M. and Sugden, D.E., (1977). The late Devensian glaciation of north-east Scotland in Studies in the Late Glacial Environment (ed. Gray, J.M. and Lowe, J.J.). Oxford.

Cohen, J.M. and Stanley, G.A., (1982). Geochemical prospecting in areas of thick glaciofluvial and glaciolacustrine sediments - an example from the Central Lowlands of Ireland. pp 336-387 of Davenport, P. (ed.) in 'Prospecting in Areas of Glacial Terrain', 1982, C.I.M.

Colbourn, P., Alloway, B.J. and Thornton, I., (1975). Arsenic and heavy metals in soils associated with regional geochemical anomalies in south west England. Science of Total Environment, 4, 359-363

Curtin, G.C., King, H.D. and Mosier, E.L., (1974). Movement of elements into the atmosphere from coniferous trees in subalpine forests of Colorado and Idaho. J. Geochem. Expl. 3, 245-263

Dines, H.G., (1956). The Metalliferous Mining Region of South West England. 2 vols. H.M.S.O.

D'yachkova, I.B. and Khadakovsky, I.L., (1968). Thermodynamic equilbria in the systems S-H_2O, Se-H_2O, Te-H_2O in the 25-300°C temperature range and their geochemical interpretations. Geochem. Int. 5, 1108-1125

Edmonds, E.A., Wright, J.E., Beer, K.E., Hawkes, J.R., Williams, M., Freshney, E.C. and Fenning, P.J., (1968) Geology of the Country around Okehampton. I.G.S. Mem. 324

Edwards, A.B. and Carlos, G.C., (1954). The selenium content of some Australian sulphide deposits. Austr. I.M.M. Proc. 1972, 31-64

Ehrlich, H.L. ed. (1981). Geomicrobiology. Marcel Dekker Inc.

Ellis, R.E. and others, (1977). Investigation of Disseminated Copper Mineralization near Kilmelford, Argyll, Scotland. J.G.S. Min. Reconn. No. 9

Esson, J., Stevans, R.H. and Vincent, E.A., (1963). Aspects of the geochemistry of arsenic and antimony, exemplified by the Skaergaard intrusion. Min. Mag. 35, 88-107

Evans, D.S., (1971). Secondary Dispersion of Mercury and Associated Elements at Keel, Eire, Unpub. PhD. Thesis, Imperial College, London.

Ferguson, J.F. and Garvis, J. (1972). A review of the arsenic cycle in natural waters. Water Research 6, 2159-2174

Finlow-Bates, T., (1980). The chemical and physical controls on the genesis of submarine exhalative orebodies and their implications for formulating exploration concepts. A review: Geol.Jahrb. D40, 131-168

Fish, R.H., Brinckman, F.E. and Jevett, K.L., (1982). Fingerprinting inorganic arsenic and organo-arsenic compounds in in-situ oil shale retort and process waters using a liquid chromatograph coupled

with an A.A. spectrometer detector. Environ. Sci. Technol. 16, 174-179

Flint, R.F., (1971). Glacial and Quaternary Geology. Wiley.

Franklin, J.M., Sangster, D.M. and Lydon, J.W., (1981). Volcanic-associated massive sulphide deposits. pp 485-627 in Skinner, B.J. (ed). Economic Geology Seventy-Fifth Anniversary Volume.

Gallagher, M.J., Michie, McL.U., Smith, R.T. and Haynes, L., (1971). New evidence of uranium and other mineralization. Trans. I.M.M. 80, B150-173

Gallagher, M.J. and others, (1982). Stratabound arsenic and vein antimony mineralization in Silurian greywackes at Glendinning, south Scotland. I.G.S. Min. Reconn. Report, no.59

Garrett, R.G. and Nichol, I., (1967). Regional Geochemical Reconnaissance in eastern Sierra Leone. Trans. I.M.M., 76, B97-B112

Gladwell, D.R., (1981). Research into Geochemical Exploration Techniques for Stanniferous Mineralization. Unpub. Ph.D. Thesis, Imperial College, London.

Glentworth, R. and Muir, J.W., (1963). The Soils of the Country around Aberdeen, Inverurie and Fraserburgh. Mem. Soil Surv. G.B. Sheets 77, 76 and 87/97. H.M.S.O.

Glover, J.E., Groves, D.I. and Smith, R.E. (eds.) (1979) Pathfinder and Multi-element Geochemistry in Mineral Exploration. Univ. Western Australia, Spec. Pub.

Goleva, G.A.,(1968). Hydrogeochemical Prospecting for Hidden Ore Deposits. Nedra Moscow (in Russian) cited by Boyle, R.W. (1979).

Goleva, G.A. and Lushnikov, V.V., (1967). Selenium distributions in the subsurface water of ore deposits and in certain types of mineralized waters. Geochem. Int. 4, 378-385

Goldschmidt, V.M., (1954). Geochemistry. Oxford Univ. Press

Gott, G.B., and Cathrall, J.B., (1980). Geochemical exploration studies in the Coeur d'Alene district, Idaho

and Montana: U.S.G.S. Prof. Paper 1116. 63 pp

Grant, J.N., Halls, C., Avila, W. and Avila, G., (1977). Igneous geology and the evolution of hydrothermal systems in some sub-volcanic tin deposits of Bolivia. pp 117-126 of Volcanic Processes in Ore Genesis. I.M.M./Geol. Soc.

Greenland, L.P. Gottfried, D. and Campbell, E.Y., (1973). Aspects of the magmatic geochemistry of bismuth. Geochim. Cosmochim. Acta. 37, 283-295

Gribble, C., (1967). The basic intrusive rock of Caledonian age of the Haddo House and Arnage districts, Aberdeenshire. Scot. J. Geol. 3, 25-36

Grigor'yeva, T.A. and Sukneva, L.C., (1982). Effect of Sulphur and of antimony and arsenic sulfides on the solubility of gold. Geochem.Int. 18, 153-158

Gulens, J., Champ, D.R. and Jackson, R.E., (1979). Influence of redox environments on the mobility of arsenic in ground water. pp 81-95 in Jenne, E.A. (ed.) Chemical Modeling in Aqueous Systems. A.C.S. Symposium Series 93

Gustafson, L.B. and Williams, N., (1981). Sediment hosted stratiform deposits of copper, lead and zinc. pp 139-178 in Skinner, B.J. (ed.) Economic Geology Seventy-Fifth Anniversary Volume

Hale, M. (1978). Geochemical Prospecting Techniques for Primary Nickel Ore in Central Africa. Unpub. Ph.D. thesis, Imperial College

Hale, M., (1981). Pathfinder applications of arsenic, antimony and bismuth in geochemical exploration. J. Geochem. Expl. 15, 307-323

Hale, M. and Moon, C.J., (1982). Geochemical expression at surface of mineralization concealed beneath till at Keel, Eire. pp 228-239 of Davenport, P. (ed.) Prospecting in Areas of Glacial Terrain, 1982, C.I.M.

Hawkins, D.B., Hok, C.I., Forbes, R.B. and Dinkel, D. (1980) Geology and geochemistry of arsenic in water, soil and rock, Fairbanks, Alaska area. G.S.A. Programmes with Abs. 12 (7) p.443

Heinrichs, H., Schutz-Dobrick, B. and Wedepohl, K.H., (1980). Terrestrial Geochemistry of Cd, Bi, Tl, Pb, Zn and Rb.

Geochim. Cosmochim. Acta. 44, 1519-1533

Hem, J.D., (1977) Reactions of metal ions at surfaces of hydrous iron oxide. Geochim. Cosmochim. Acta 41, 527-538

Holm, T.R., Anderson, M.A., Iverson, D.G. and Stanforth, R.S. (1979). Hetrogenous interactions of arsenic in aquatic systems. pp 711-736 of Chemical Modeling in Aqueous Systems (ed. E. Jenne). A.C.S. Symposium Series 93

Hosking, K.F.G., (1964). Permo-Carboniferous and later primary mineralization of Cornwall and South-West Devon pp 201-245. Hosking, K.F.G. and Shrimpton, G. (eds) in 'Present Views of Some Aspects of the Geology of Cornwall and Devon. Roy. Geol. Soc. Corn.

Howard, H.J., (1977). Geochemistry of Selenium: formation of ferroselite and selenium behaviour in the vicinity of oxidising sulphide and uranium deposits. Geochim. Cosmochim. Acta 41, 1665-1685

Howarth, R.J. and Martin, L., (1979). Computer-based techniques in the compilation, mapping and interpretation of exploration geochemical data. pp 545-547 in Hood, P.J. (ed) 'Geophysics and Geochemistry in the Search for Metallic Ores'. G.S.C. Econ. Geol. Report 31

Isaac, K.P., Turner, P.J. and Stewart, I.J., (1982). The Evolution of the Hercynides of central southwest England. Q.J. Geol. Soc. 139, 523-534

Jackson, J.A., Blair, W.R., Brinckman, F.E. and Iverson, W.P., (1982). Gas chromatographic speciation of methylstannanes in the Chesapeake Bay using purge and trap sampling with a tin selective detector. Envir. Sci. Technol. 16 110-119

Jackson, N.J., Halliday, A.N., Sheppard, S.M.F. and Mitchell, J.G. (1982). Hydrothermal activity in the St. Just Mining District, Cornwall. p 137 - 179 In Evans, A.M. (ed.) Metallization Associated with Acid Magmatism. Wiley

James, C.H., (1957). Applied Geochemical Studies in Southern Rhodesia and Great Britain. Unpub. Ph.D. Thesis. Imperial College, London

James, L.D., (1965). Regional Geochemical Reconnaissance in the Northern and Southern Section of the Sula Mountains Schist Belt, Sierra Leone. Unpub. Ph.D. Thesis. Imperial College, London

Jung, W., Knitzchke, G. and Gerlech, R., (1973). Zur selenführung des Kupferscheifers in SE-Harzvorland. Z. Agnew-Geol.19 57-67

Jung, W., Knitzchke, G. and Gerlack, R., (1974). Zu der Schadstaff-kamponenten arsen; antimon, wismut, tellur und quecksilber im Kupferscheifer des Sud est Harz-vorlands. Z. Agnew. Geol. 20, 205-211

Karker, D.P., Turekian, K.K. and Bertine, K.K., (1968). Stream sediment supply of dissolved Ag, Mo, Sb, Se, Co, Rb, Ce to the oceans. Geochim. Cosmoshim. Acta. 32, 285-298

Kennan, P.S., (1978). The origin of sulphide deposits in the Leinster Granite. J. Earth Sci. R. Dublin Soc. 1, 41-47

Knill, J.L., (1957). Pre-Tertiary Geology of the Craignesh-Kilmelford District, Argyllshire. Unpub. Ph.D. Thesis, Imperial College, London

Koljonnen, T., (1975). Selenium in certain metamorphic rocks. Bull. Geol. Soc. Finland, 45, 107-117

Koljonnen, T., (1976). Luikonlahti-selenium in the vicinity of Copper ore. J. Geochem. Expl. 5, 263-270

Kolonin, G.R., (1979). Native bismuth as a geological thermometer. IV. The existence of a stability field of metallic bismuth above its boiling point. pp 401-417 of Angino, E.E. and Long, D.T. (eds.) Geochemistry of Bismuth, vol. 49 Benchmark Papers in Geology, Dowden, Hutchinson, Ross

Krainov, S.R., Volkov, G.A. and Petrova, N.G., (1979). Antimony geochemistry in carbonate waters of the Carpathians in connection with low temperature ore formation. Geokhimya, 1979, 1488-1498

Lag, J. and Steinnes, E. (1978). Regional distribution of selenium and arsenic in humus layers of Norwegian forest soils. Geoderma 20, 3-14

Lantsky, R.J. and Mackensie, F.T., (1979). Atmospheric trace metals: global cycles and assessment of man's impact. Geochim. Cosmochim. Acta, 43, 511-525

Lee, D.S., (1982). Determination of bismuth in environmental samples by flameless atomic absorption spectrometry with hydride generation. Analytical Chem. 54, 1682-1685

Le Riche, M.M., (1959). The distribution of certain trace elements in the Lower Lias of Southern England. Geochim. Cosmochim. Acta. 14, 101-122

Leutwein, F. and Starke, R., (1957). Uber die moglichkeit der geochemischen propek tion auf selen, untersucht am berspiel des kupferscheifers und des tilkeroder Erzbezirks. Geologie 6, 349-378

Levesque, P. (1974a). Selenium distribution in Canadian soil profiles. Am. J. Soil Sci. 54, 63-75

Levesque, P., (1974b). Some aspects of selenium relationships in eastern Canadian soils and plants. Am. J. Soil Sc. 54 205-214

Lovell, J.S., (1979). Application of Vapour Geochemistry to Mineral Exploration. Unpub. Ph.D. Thesis, Imperial College, London

Lovell, J.S., Hale, M. and Webb, J.S., (1979). Soil air disequilibria as a guide to concealed mineralization at Keel, Eire. pp.45-50 of Prospecting in Areas of Glacial Terrain, 1979. I.M.M.

Mancey,S.J., (1980) Computer-based Interpretation of Large Regional Data Sets. Unpub. Ph.D. Thesis, Univ. of London

Mazzucchelli,R.H. (1965). Geochemical Dispersion Related to Gold Mineralization, Western Australia. Unpub. PhD. Thesis, Imperial College, London

Mazzucchelli,R.H. and James, C.H, (1966). Arsenic as a guide to gold mineralization in laterite-covered areas of Western Australia. Trans. I.M.M. 75, B286-B294

McCarthy, J.H. and Gott, G.B., (1978). Robinson (Ely) mining district near Ely, White River County, Nevada. J. Geochem. Expl. 9, 225-232

McGoldrick, P.J. and Keays, R.R., (1981). Precious and volatile metals in the Perserverance nickel deposit gossan: implications for exploration in weathered terrain. Econ. Geol. 76, 1752-1763

McKeown, M.C., Edmonds, E.A., Williams, M., Freshnay, E.C. and Masson-Smith, D.J., (1973). Geology of the Country around Boscastle and Holsworthy. Mem. I.G.S. 332

Measures, C.I. and Burton, J.D., (1978). Behaviour and speciation of dissolved selenium in estuarine waters. Nature 272, 293-295

Merritt, J.W., (1981). Sand and gravel resources of the country around Ellon, Grampian region. I.G.S. Mineral Assessment Report 76

Miller, J.M. and Taylor, K., (1966). Uranium Mineralization near Dalbeattie, Kircudbrightshire. Bull. Geol. Surv. Gt. Br. 25, 1-18

Mintser, E.F., (1979). The geochemical properties of the behaviour of bismuth in hypogenic processes. In The Geochemistry of Bismuth (Angino, E.E. and Long, D.T. eds). Benchmark Volume Dowden, Hutchinson and Ross Inc. pp 268-327

Möller, P., Germann, K. and Schneider, H.J., (1982). Geochemical proximity indicators for stratabound non-ferous massive sulphide ore deposit. E.E.C. Raw Material Contact Group, London.

Muff, R. and Saager, R. (1979). Metallogenic interpretations from a minerographic and geostatistical study of antimony ores of the Murchison Greenstone belt, South Africa. Geol Soc. S. Africa, Spec. vo. 5, 167-180

Naldrett, A.J., (1981). Nickel sulphide deposits: classification composition and genesis. pp 628-685 in Skinner, B.J. (ed.). Economic Geology Seventy-Fifth Anniversary Volume.

Nash, J.T., Granger, M.C., and Adams, S.S. (1981). Geology and concepts of genesis of important types of uranium deposits. pp 63-116 in Skinner, B.J. (ed.), Economic Geology Seventy-Fifth Anniversary Volume

Naumev, V.N., Pachadzhanov, D.N. and Buribenke, T.L., (1979) The behaviour of Bi, Ag, Pb and Zn in a process of secondary sulphide enrichment in The Geochemistry of Bismuth (Angino, E.E. and Lond, D.T. eds) pp 388-394

Nye, S.M. and Peterson, P.J., (1975). The content and distribution of selenium in soils and plants from seleniferous areas in Eire and England. Trace Subst. Environ. Hlth 9, 113-121

Onishi, H. and Sandell, E.B., (1955). The geochemistry of arsenic. Geochim. Cosmochim. Acta. 7, 1-33

Ovchinnikov, L.N. and Grigorian, S.V., (1971). Primary halos in prospecting for sulphide ore deposits. In 'Geochemical Exploration', C.I.M. Spec. Vol. 11, 375-380

Ovchinnikov, L.N., Kostov, E.D. and Rafalsky, C.P., (1982). Solubility of antimony in chloride solution under high temperatures. Geokhimya, 1290-1297

Pahlavanpour, B., Pullen, J.H. and Thompson, M., (1980a). The determination of trace amounts of selenium in soil and sediments by the introduction of hydrogen selenide into an inductively coupled plasma source for emission spectrometry. Analyst 105, 274-278

Pahlavanpour, B., Thompson, M. and Thorne, L., (1980b), The simultaneous analysis of trace concentrations of As, Sb, Bi in soils and sediments by volatile hydride generation and inductively coupled plasma spectrometry. Analyst 105, 756-761

Pahlavanpour, B. and Thompson, M.,(1981). The determination of arsenic species by selective reduction. Heavy Metals in the Environment. Amsterdam pp 661-664 C.E.P. Consultants

Patterson, J.M., (1970), Geology and Mineralization of the Keel Area, County Longford, Republic of Ireland. Unpub. Ph.D. Thesis, Imperial College, London

Pearce, J.A., (1979). The Effect of Antimony on Plants. Unpub. Ph.D. Thesis. Newcastle Univ.

Peintre, C., (1963). Valence du Selenium dans les eaux minérales de la Roche Posay. Compte. Rend. Aca. Colon. No.2

Perel'man, A.I., (1977). Geochemistry of Elements in the Supergene Zone. Israel Program for Scientific Translations, Jerusalem

Petersen, M.D. and Lambert, I.B., (1979). Mineralogical and chemical zonation around the Woodlawn Cu-Pb-Zn ore deposit, southeastern New South Wales. J. Geol. Soc. Australia 26, 169-186

Peterson, P.J., Benson, L.M. and Zieve, R., (1981). Metalloids. pp 279-342 in Lepp.N.W. (ed), Effect of Trace Metals on Plant Function Applied Science Publishers

Picot, P., (1979). Un exemple du contribution minéralogique à la métallogénie régionale: la distribution du bismuth dans les gites minéraux de la France continentale. Miner. Deposita 14, 153-160

Pierce, M.L. and Moore, C.B, (1982). Adsorption of arsenite and arsenate on amorphous iron hydroxide. Water Research 16, 1247-1253

Platt, J.W., (1977). Volcanogenic mineralization at Avoca, Co. Wicklow, Ireland and its regional implications in Volcanic Processes in Ore Genesis, I.M.M./Geol.Soc. 163-170

Pointon, C.R., (1980). Some environmental features of volcanogenic sulphide mineralization at Avoca, Eire and Parys Mountain, Anglesey, Wales. Norges Geol. Unders. 360, 259-268

Poubaix, M., Pitman, .A.L. and Zanbov,N., (1963). Atlas d'équilibres Electrochemique.Gauthier Villars, Paris

Presant, E.W., (1971). Geochemistry of Fe, Mn, Pb, Cu, Zn, As, Sb, Ag, Sn, Cd in the Soils of the Bathurst Area, New Brunswick. G.S.C. Bull, 174

Read, H.H. and Farquhar, O.C., (1951). The geology of the Arnage district, (Aberdeenshire): a Reinterpretation Q.J.G.S., 107, 423-440

Rice, R., (1975). Geochemical exploration in an area of glacial overburden at Arthrath, Aberdeenshire in 'Prospecting in Areas of Glacial Terrain'. 1975, I.M.M. p.82-86

Rich, R.A., Holland, M.D. and Peterson, V., (1977). Hydrothermal Uranium Deposits. Elsevier

Rickard, A.J.R., (1979). Geochemistry and Petrogenesis of Copper-bearing Diorites near Kilmelford, West Scotland. Ph.D. thesis Univ. Strathclyde

Rose, A.W., Hawkes, H.E. and Webb, J.S., (1979). Geochemistry in Mineral Exploration (2nd ed.). Academic Press

Ruan, T.J., (1981). Some New Approaches in Vapour Geochemistry. Unpublished Report, Imperial College, London.

Rugless, C.S., (1982). Lithogeochemistry of Wainaleka Cu-Zn volcanogenic deposit. Vitu Levu, Fiji and possible applications for exploration in tropical terrains. 9th Geoch.Expl. Symposium, Saskatoon Prog. with Abs. p.61-63

Rundquist, D.V., (1982). Zoning of metallization associated with magmatism. pp of 279-289 of Evans, A.M. (ed) Metallization Associated with Acid Magmatism. John Wiley

Rundquist, D.V. and Nezhensky, I.A. (1975). Zoning of Endogenous Ore Deposits Nedra Leningrad

Sainsbury, C.L., (1957). A geochemical exploration for antimony in southeastern Alaska. U.S.G.S. Bull. 1024-H

Schiefler, D., (1967) Some aspects of the Regional Geochemistry of the Lunga Basin Area, Zambia. Unpub. Ph.D. Thesis, Imperial College, London

Schutz, D.F. and Turekian, K.K., (1965). The investigation of the geographical and vertical distribution of several trace elements in seawater, using neutron activation analysis. Geochem. Cosmochim. Acta 29, 259-313

Scott, S.D., Kalogeropoulos, S.I., Shezelski, R.J. and Siriuras, J.M., (1982). Tuffaceous exhalites as exploration guides for volcanogenic massive sulphide deposits pp 55-57. 9th Int. Geochem. Expl. Symposium, Saskatoon Prog. with Abst.

Shamberger, R.J., (1981). Selenium in the environment. Sci. Tot. Environment, 17, 59-74

Sheppard, W.A., (1980). The Host Rock Geology and Geochemistry of the Avoca Mines, Co. Wicklow, Ireland. Unpub. Ph.D. Thesis, Trinity College, Dublin.

Sheppard, W.A., (1980a). The ores and host rock geology of the Avoca Mines, Co. Wicklow, Ireland. Norges. Geol. Unders. 360, 269-283

Shimazaki, Y. (1974). Ore minerals of the Kuroko-type deposits pp 311-322 in Geology of Kuroko Deposits. Mining Geology, Special Issue, No. 6

Sinclair, A.J., (1976). Applications of Probability Graphs in Mineral Exploration. Spec. vol.4 Assoc. of Expl. Geochemists

Smirnov, V.I., (1977). Ore Deposits of the U.S.S.R. 3 vols. Pitman

Smith, C.A., (1983). The Distribution of Selenium in Some Soils Developed on Silurian, Carboniferous and Cretaceous Systems in England and Wales. Unpub. Ph.D. Thesis, Imperial College, London

Smith C.G. et al, (1978). Investigation of stratiform sulphide mineralization at Meall Mor, South Knapdale, Argyll. I.G.S. Miner. Recon. Report No.15

Smith, D.C., (1980). Discussion and contributions to Prospecting in Areas of Glacial Terrain, 1979, Trans I.M.M. 89, B56

Smith, R.E. ed., (1982). Geochemical Exploration in Deeply Weathered Terrain. C.S.I.R.O., Perth Australia

Stanton, R.L., (1972). Ore Petrology, McGraw-Hill

Steed, G.M., (1978). Investigation of scheelite bearing specimens from Leinster, Ireland. Unpub. report, Irish Base Metals Ltd.

Steed, G.M. and Tyler, P., (1979). Lithogeochemical haloes about Gortdrum copper-mercury orebody. County Tipperary, Ireland. pp 30-39 of Prospecting in Areas of Glacial Terrain, 1979, I.M.M.

Steiger, R., (1977). Prospecting for Lithium and Tungsten in Ireland in Prospecting in Areas of Glacial Terrain, 1977 p.14-24

Steiger, R. and Bowden, A., (1982). Tungsten mineralization in Southeast Leinster, Ireland. pp 108-114 in Brown, A.G. ed. Mineral Exploration in Ireland. Wexford Meeting, 1981. Irish Association for Economic Geology

Stumm, W. and Morgan, J.J., (1970). Aquatic Chemistry, Wiley

Talipov, R.M., Gluschenko, V.M. and Tverskaya, K.L. and Nishanov, P. (1976). Some characteristics of the gold and antimony distribution of plants in ore deposits of the Chatkal-Kurama region. Chem. Abs. 85 119581K

Thompson, M., Phlavanpour, B. and Thorne, L. (1981). The simultaneous determination of arsenic, antimony, bismuth, selenium and tellurium in waters by an inductively-coupled plasma/volatile hydride method. Water Research 15, 411-416

Thomson, I., (1971). Regional Geochemical Studies of Black Shale Facies with Particular Reference to Trace Element Disorder in Animals. Unpub. Ph.D. Thesis, Imperial College, London

Thornton, I., Moon, R.N.B. and Webb, J.S. (1969) Geochemical reconnaissance of the Lower Lias. Nature 221, 457-459

Tono, N., (1974). Minor elements distribution around Kuroko deposits in northern Akita, Japan. pp399-420 in Geology of Kuroko Deposits. Mining Geology, Spec. Issue 6

Travis, G.A., Keays, R.R. and Davison, R.M., (1976). Palladium and iridium in the evaluation of nickel gossans in Western Australia. Econ. Geol. 71, 1229-1242

Turner, D.R., Whitfield, M. and Dickson, A.G., (1981). The equilibrium speciation of dissolved components in freshwater and seawater at 25°C and 1 atm. pressure. Ceochim. Cosmochim Acta 45,855-881

Valente, I.M.C.B.S., (1978). Aspects of the Environmental Chemistry of Antimony. Unpub. PhD. Thesis Univ. of Reading

Viljoen, M.J., (1979). The geology and geochemistry of the 'antimony line' in the United Jack complex, Murchison Range. Spec. Vol 5, Geol. Soc. S. Africa, p. 133-158

Wagemann, R., (1978). Some theoretical aspects of stability and solubility of inorganic arsenic in the freshwater environment. Water Research 12, 139-145

Warren, H.V., Delavault, R.E. and Barasko, J., (1964). The role of arsenic as a pathfinder in biogeochemical prospecting. Econ. Geol. 59, 1381-1389

Waslenchuk, D.G., (1978). The budget and geochemistry of arsenic in a continental-shelf environment. Mar. Chem. 7, 39-52

Waslenchuk, D.G., (1979). The geochemical controls on arsenic concentrations in south eastern United States rivers. 24, 315-325 Chem. Geol.

Waslenchuk, D.G. and Windom, H.L., (1978). Factors controlling the estuarine chemistry of arsenic. Estuar. Coast. Mar. Sci. 7 455-464

Watling, R.J., (1973). Mercury and Associated Trace Elements in the Primary Environment, County Longford, Ireland. Unpub. Ph.D. Thesis, Imperial College, London

Webb, J.S., (1958). Observations of geochemical exploration in tropical terrains. In Symposium de Exploracion Geoquimica, 20th I.G.C. Mexico City, 143-173

Webb, J.S., Nichol, I., Foster, R., Lowenstein, P.L. and Howarth, R.J., (1973). Provisional geochemical atlas of Northern Ireland. A.G.R.G., Imperial College, London.

Webb, J.S., Thornton, I. and Fletcher, K., (1966). Seleniferous soils in parts of England and Wales. Nature 211, 327

Webb, J.S., Thornton, I., Thompson, M., Howarth, R.J. and Lowenstein, P.L., (1978). The Wolfson Geochemical Atlas of England and Wales. Oxford Univ. Press

Wedepohl, K.H. ed., (1969). Handbook of Geochemistry. 6 vols. Springer-Verlag

Weissberg, B.G., Browne, P.R.L. and Seward, T.M., (1979). Ore metals in active geothermal systems. pp 738-786 in Barnes, H.L. (ed), Geochemistry of Hydrothermal Ore Deposits (2nd ed.), Wiley

Wheatley, C.J.V., (1971). Economic Geology of the Avoca Mineralized Belt, S.E. Ireland and Parys Mountain, Anglesey. Unpub. Ph.D. Thesis, Imperial College, London

Wilbur, D.G. and Royall, J.J., (1975). Discovery of the Mallow Copper-silver deposit, County Cork, Ireland. In Prospecting in Areas of Glacial Terrain, p.60-70 I.M.M.

Willan, R.C.R., (1980). Stratabound sulphide mineralisation in the Dalradian Supergroup of the Grampian Highlands, Scotland. Norges Geol Unders. 360 241-258

Williams, C. and McArdle, P., (1978). Ireland. pp319-345 of Mineral Deposits of Europe, vol.1 North West Europe. I.M.M. (Min. Soc. London)

Wojcichowska, J. and Serkies, J., (1972). The occurrence of traces of bismuth in the Fore-Sudetic copper deposit (regions of Lubin and Polowice). Bull. Acad. Polonaise des sciences. Sciences des Terre, 20, 217-220

Woolson, E.A., Axley, J.H. and Kearney, P.C., (1971). The Chemistry and phyto-toxicity of arsenic in soils. Soil Sci. Am. Proc. 35, 938-943

Wraith, D.E., (1982). The Natural Distribution of Some Group 5a and 6a Elements as Applied to Mineral Exploration. Unpub. Ph.D. Thesis, Imperial College, London

Wrench, J.J. and Measures, C.I., (1982). Temporal variations in dissolved selenium in a coastal ecosystem. Nature 299, 431-433

Yamaoka, K. and Asakura, E.(1974). Metallic ore minerals and associated clay minerals from the Kuroko deposits in the Nishi-Aizu district, Sukushama Prefecture, Japan. pp 363-370 in Geology of Kuroko Deposit. Mining Geol. Spec. Issue 6

Yamamoto, M., (1976). Relationship between Se/S and sulphur isotope ratios of hydrothermal sulphide minerals: Mineral Deposita 11, 197-209

Yamomoto, M., Urata, K., Murashiye, K. and Yamomoto, Y, (1981). Differential determination of arsenic (III) and arsenic (V), and antimony (III) and antimony (V) by hydride generation and its application to the determination of these species in sea water. Spectrochim. Acta 36B, 671-677

Yushko-Zakharova, O. Ye., Ivanov, V.V., Vorob'yeva, M.S. et al, (1978). Geochemistry of selenium, tellurium and bismuth in copper-zinc sulphide deposits in the Urals, and some problems of sulphide ore formation. Geochem. Int. 15, 59-68

Zainullin,C.G. and Korolev, N.V., (1964). New Data on the mode of occurrence of selenium and tellurium in the Noril'sk copper-nickel ores. Geochem. Int.1 897

Zainullin, C.G. and Pashinkin, A.S., (1964). Thermodynamic solution of some geochemical problems of selenium and tellurium in the copper-nickel sulfide of the Noril'sk region. Geochem Int. 1 874-881

Zeive, R. and Peterson, P.J. (1981). Factors influencing the volatilization of selenium from soil. Sci. Tot. Environment. 19, 277-284

Appendix- Details of Analytical Methods

Nitric acid-Perchloric acid attack for rock, soil, or stream sediment

Reagents

a) Perchloric acid (60%)

b) Nitric acid (70%)

c) Hydrochloric acid (6M). Dilute hydrochloric acid (534 ml, 36% acid) to 1 litre with water.

Equipment

a) Test tubes and racks

b) Liquid dispensers (4)

c) Deep heating block sited in a suitable fume cupboard

Procedure

a) Weigh each sample (0.250g, -80 mesh) into a clean, dry, numbered test tube.

b) Weigh standard and duplicate samples, and leave empty test tubes at random intervals for blank determinations.

c) Add nitric acid (4.0 ml) to each test tube.

d) Add perchloric acid (1.0 ml) to each test tube.

e) Place the test tubes in the cold block and raise the temperature to $150^{\circ}C \pm 5^{\circ}C$ over 2-3 hours. Leave at this temperature until copious evolution of fumes ceases.

f) Increase the temperature of the heating block to $185^{\circ}C \pm 5^{\circ}C$ and transfer the test tubes to wire racks when the residue is dry.

g) Allow the tubes to cool. Add hydrochloric acid (2.0 ml) to each test tube.

h) Place the tubes in a shallow heating block ($60^{\circ}C$) and leave for one hour. Transfer the tubes to wire racks and allow to cool.

i) Add water (8.0 ml) to each tube and mix thoroughly.

j) Allow the residue to settle (at least 4 hours) and aspirate the supernatant liquid directly from the test tube.

Remarks

a) This is a more powerful attack than nitric acid alone. In addition to the minerals completely attacked by the method 3.1, pyroxenes, biotite, limonite and some amphiboles are almost completely attacked. Trace element extraction from lateritic soil is almost complete. However, some common minerals containing important metals are attacked to a negligible extent (e.g. rutile, chromite, cassiterite, zircon, beryl), or a minor degree (barite).

b) Samples with a high organic matter content may react vigorously with nitric and perchloric acids. Such samples should be kept overnight in the heating block at $50^{\circ}C$ after the addition of the acids at stage (d). The normal procedure can be resumed at stage (e).

c) This method must not be attempted on samples containing oil or bitumen.

d) The dilution factor for this method is 40.

Co-precipitation Method for Selenium

1. 2:1 nitric-perchloric acid attack as for general elements except maximum temperature is 175 C and samples are removed when nearly dry.

2. Add few drops concentrated HCl

3. Mix thoroughly, and wash with about 5ml of D.I.W. into a 'centrifuge tube'.

4. Centrifuge for 2 minutes at 2000r.p.m.

5. Transfer supernatant into second 'centrifuge' tube containing 0.5ml of 5% lanthanum nitrate. Discard residue

6. Add 2ml ammonia

7. Mix thoroughly

8. Centrifuge for 2 minutes at 2000 r.p.m.

9. Discard supernatant carefully

10. Dissolve precipitate in about 5ml of 5M HCl containing 4% KBr

11. Make up to 10ml with HCl + KBr

12. Leave in a waterbath for 50 minutes at 50 C

Note: If supernatant is blue in step 9, redissolve the the precipitate in HCl and repeat steps 5-9 until blueness dissappears

Magnesium Nitrate Method for As,Sb and Bi

1. Weigh Ø.25g sample into a 5Øml pyrex beaker
2. Add 1ml saturated solution of magnesium nitrate
3. Mix carefully
4. Put into furnace and leave overnight at 1ØØ C
5. Increase temperature to 45Ø C for at least 4 hours
6. Cool, then add 5.Øml concentrated HCl
7. Shake gently overnight
8. Add 5.Øml Ø.2% KI, mix gently and transfer to a test-tube
9. Leave to settle overnight or centrifuge

Note: Any samples which remain yellow when settled should be discarded