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TRACE ELEMENT GEOCHEMISTRY OF WALLROCK ALTERATION IN THE PENNINE OREFIELDS AND CUMBERLAND IRONFIELD

by

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ABSTRACT

The variations in the trace elements Rb, F, Pb, Sr, Mn, Zr, Zn, Cu, Ni and Fe have been studied in limestone wallrocks next to lead - zinc - fluorite - barite mineralization in the Northern Pennine Orefield and Derbyshire Orefield; and next to haematite orebodies in the Cumberland Ironfield. Trace element aureoles have also been investigated in sandstones and shales.

An analytical technique for the determination of fluorine in limestones was developed using the optical emission spectrograph, and found to give satisfactory results. Standard X-ray fluorescence techniques were employed for the determination of the other trace elements. The petrology, mineralogy and chemistry of certain aureoles have been examined in detail.

The heavy metal content of the limestone wallrocks in the majority of cases, illustrates widespread and irregular dispersion patterns. It is suggested that migration of the metals has taken place through fractures developed prior to, or contemporaneously with, the mineralization. Diffusion of the heavy metals has occurred into massive country rocks at certain localities and results in a logarithmic decrease in concentration away from the ore and more restricted aureoles.

The width of the dispersion patterns varies next to the veins, but in general a wider aureole is developed in Derbyshire than in the Alston Block.

It is concluded that, at the time of emplacement, the Derbyshire veins were at a higher pressure than the veins in the Alston Block, but that variation in the temperature of the ore solutions was not an important parameter controlling the migration of the heavy metals.

The alteration of the limestone wallrocks is discussed and suggestions are put forward to explain the possible origin of some of the replacement minerals.

Adjacent to the veins, a depletion in strontium is recorded. This is related to the recrystallisation of the calcite which has liberated strontium from the crystal lattice. The strontium content of the Great Limestone and the D_2 Limestone, the respective sampling horizons in the Alston Block and the Derbyshire area, are considerably different and it is concluded that this reflects either the original aragonite content of the limestones, or differing conditions of deposition in the two areas.

Migration by diffusion into massive country rocks has occurred in the Cumberland Ironfield to far greater distances than in the Pennine Orefields; the depletion of strontium is also more extensive. It is suggested that the ore solutions were emplaced at higher temperatures than in the Pennine Orefields.

The trace element aureoles in sandstone and shale wallrocks indicate that the heavy metals have been migrated through fractures, as irregular and widespread patterns are observed.

A comparative study was conducted on the trace element variations which occur next to the veins which intersect the Whin Sill (quartz-dolerite) in the Alston Block. Contrary to previously reported widespread dispersion aureoles in igneous rocks, a narrow aureole is formed where diffusion has taken place into the wallrocks. A profound chemical change between the unaltered and altered quartz-dolerite has occurred where CO_2, K_2O and H_2O are enriched, while Na_2O, MgO, total iron and CaO are depleted. The quartz-dolerite has been converted into a carbonate and clay-rich rock called the White Whin. The chemical and mineralogical variations are related to the variations in the trace elements where Rb, Ba, Pb and Zn are concentrated while Cu, Ni, Zr, Sr, V and Cr are depleted next to the veins.

A geological and geophysical survey over altered and mineralised quartz-dolerite dykes at Closehouse mine, Lunedale near Middleton-in-Teesdale has produced results, which, it is hoped, will elucidate the complexities of the area.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

Major advances in the fields of pure and applied geochemistry have been made since the pioneering days of Sandberger (1882), Pošepny (1902), and Curtis (1884) and by now the dispersion patterns of the elements in some geological environments have been adequately summarised. Over the past 30 years applied geochemical studies have largely been directed at secondary dispersion patterns, concerned mainly with anomalies in drainage water, sediments and soils (see Ginzberg, 1960 and Hawkes and Webb, 1962). Primary geochemical dispersion patterns have however received scant attention, in the words of Hawkes and Webb (1962), 'the application of primary dispersion patterns to mineral exploration is still strictly in the experimental stage'. Few studies have been made of the distribution of heavy metals in the wallrocks of ore deposits in relation to these deposits or to concealed mineralization.

The aim of the present study was not primarily to locate new areas of mineralization, but to collect further basic data concerning the variation of trace element contents adjacent to mineralization in calcareous environments, with subsidiary investigation of wallrock aureoles in sandstones, shales and quartz-dolerite host rocks, and if possible, to determine the probable methods of introduction of the elements, and the implications that the dispersion patterns may have as to the genesis and composition of the ore fluids. Some of the information it is hoped will make a significant contribution to the use of primary dispersion patterns in unexplored regions, and hence bring the search for ore on to a more scientific and reliable basis.

Wallrock Anomalies

General Considerations

The classification by Hawkes and Webb (op.cit. table 1-1) of the primary dispersion patterns distinguishes syngenetic and epigenetic types, each with further sub-divisions. This present study is concerned with what are believed to be hydrothermal dispersion patterns of the epigenetic type, especially wallrock anomalies but with subsidiary reference to leakage anomalies. Throughout this thesis, the term 'hydrothermal' is used in its broadest sense, that is, to indicate hot aqueous fluids, whatever their source or direction of movement, which transport the economic elements. Before considering previous research into wallrock anomalies, reference must be made to certain empirical parameters which are helpful in identifying and interpreting geochemical anomalies, where the abundance of an element is greater than in the surrounding areas.

Geochemical Parameters

These include:-

(1) the range of nonsignificant variation in background.

(2) the threshold between nonsignificant and anomalous values.

(3) the contrast between anomalous and background values.

(4) the homogeneity of the anomalous pattern.

Table 1-1

Classification and general characteristics of the principal types of primary dispersion patterns (after Hawkes and Webb, 1962 p.46)

Genetic Classification			Origin	Emplacement	Matrix	Form of Dispersion Pattern
Epigenetic Patterns	Hydrothermal Dispersion Patterns	Wallrock Anomalies	Precipitation from solutions related to ore-forming fluids.	Movement of solutions, diffusion of solutes	Rocks adjoining ore deposits	Aureoles
		Leakage Anomalies	Precipitated from ore-forming fluids	Movement of solutions	Rocks in and adjoining solution channelways leading upwards from ore	Haloes
		Compositional Zoning	Differential depletion of certain constituents of ore fluids with distance from source	Movement of solutions	Minerals deposited from hydrothermal solutions	Systematic variation with distance from source

Background Range

Normally, the concentration of elements in areas where the equilibrium has not been upset by the presence of a mineral deposit lies statistically within a well defined range. Patterns of non-significant variations however, all of which fall within the background range, also appear in geochemical surveys, and can readily be misinterpreted as geochemical anomalies if their true significance is not recognised.

Threshold

This is the value below which the variations represent only normal background effects and above which they have significance in terms of possible ore.

Contrast

The significance of an anomaly is the geochemical relief or contrast between anomalous values and background values.

Homogeneity

This is defined as a measure of the smoothness of, or absence of local variations, in the distribution of the indicator element. It is of importance in considering the optimum spacing of samples for a survey.

Previous Research

General Works

Classic investigations into wallrock alteration, which have greatly influenced subsequent studies were carried out by Lovering (1949) and Sales and Meyer (1948). Two general reviews, containing extensive bibliographies are by Kerr (1955), who summarised the field and laboratory data on hydrothermal alteration, and Schwartz (1955) who discussed altered rocks as guides to ore. Within the last decade, the amount of investigation into hydrothermal alteration is voluminous and it is not considered pertinent to precis all the works which deal with major chemical and mineralogical changes adjacent to mineralization, but reference will be made to them where appropriate.

Trace Elements in Altered Wallrocks

As this work covers variation in trace elements in several different environments, the following review is sub-divided accordingly.

Trace Element Aureoles in Limestone

Previous studies have been undertaken by several investigators, especially between the years 1880 and 1910 and 1950 and 1965. One of the earliest was conducted by Sandberger (1882, 1885) on the heavy metal content of ore shoots in the mining districts of central Europe. The discovery of traces of the heavy metals in the wallrocks led him to formulate his famous hypothesis of lateral secretion. Shortly afterwards this idea was challenged by Pošepny (1902) who collected evidence, refuting Sandberger's theories and stating:- 'the minute metallic admixtures detected in the country rock by Sandberger's method are really derived from the ore deposit, i.e. are not idiogenous but xenogenous'.

Running concurrently with the interest in Europe, Curtis (1884), working on the Eureka mining district of Nevada, discovered assayable amounts of silver in the shattered and altered limestone wallrocks, adjoining high-grade silver replacement bodies. The silver-content decayed from 17 ppm in the walls of the ore bodies through 8ppm 30 feet from the vein, to a background value of approximately 5ppm in unaltered limestone 100 feet from the ore.

A study similar to the present one but using less sophisticated analytical methods was made by Finlayson (1910) at the Vieille Montagne Co's mine at Nenthead (see table 1-2). The walls of a cross-cut normal to a lead-zinc vein were sampled at regular intervals in the Great Limestone. The result of his analyses (conventional wet analytical technique) are presented below:-

Table 1-2

Heavy Metal Dispersion pattern in the Great Limestone,
Nenthead, Northern Pennine Orefield.
(after Finlayson, 1910)

Distance from vein	%Pb.	%Zn.
Limestone in vein	.012	.040
Limestone on vein wall	.025	.015
Limestone at 10 feet	.015	.030
Limestone at 20 feet	.001	.004
Limestone at 40 feet	.002	.001
Limestone at 70 feet	.0005	.001

Between the years 1910 and 1950, interest in the subject declined, and it was not until Graf and Kerr (1950) published their results from Santa Rica, New Mexico that possible industrial applications were recognised. Working in fractured limestones adjoining lead-zinc deposits, they found zinc aureoles extending between 60 feet and 250 feet from ore and lead aureoles 20 feet to 30 feet wide, concluding that the metals were introduced through a system of small fractures in the limestone, since gradients extend only a few feet away from fractures in massive country rock. The lead aureoles are widest where the ground is silicified; zinc had been leached and redistributed to give clear logarithmic decay patterns. Schwartz (1950) reports limestones adjacent to lead-zinc deposits at Bisbee and Leadville to have been bleached, and their content of manganese and iron increased by as much as 12%(Mn) near to the ore. The Tintic district of Utah has been under careful investigation by several workers, and the papers by Lovering and Morris (1952) and Almond and Morris (1951) are of special interest. The latter paper, which concentrates primarily on the leakage anomaly of lead and zinc above a horizontal pipe-like ore body, found the elements enriched above the background for at least 350 to 500 feet above the ore, concluding that zinc was far more mobile than lead. In the former paper, bedrock dispersion patterns in dolomites and quartz monzonites were recorded, the conclusions being that diffusion was mainly responsible for the movement of the ore-minerals into the wallrock. They were able to predict accurately the location of a blind ore body. A striking example is quoted of a cross-cut ending in limestone where the metal content was well above the background value, which was later extended to prove a new ore body within 10 feet. The metal content of the wallrock fell off logarithmically from the ore, except where cracks permitted greater travel than normal. Along these cracks the metal content generally was found to decay linearly from the deposit. The width of the anomaly appeared to decrease with the chemical reactivity of the wallrock. In limestones the transportation distance was found to be very low, sometimes as little as 5 feet. This very limited aureole has been reported by other people as characteristic of limestones; e.g. Engel and Engel (1956) and Austin and Sackowski (1958), the latter authors reporting from the Darwin Mines, California, where lead-zinc-silver deposits occur in limestone. Here as the ore was approached the lead content increased logarithmically, the dispersion distance in massive wallrocks being 8 to 20 feet, with anomalous extensions to 30 and 60 feet. Webb (1959) reports similar primary dispersion aureoles in limestones from Derbyshire, as Finlayson did from the Northern Pennines. Webb's analyses were by 'rapid' chemical methods, his results being:-

Table 1-3

<u>Primary Dispersion Aureoles of Lead and Zinc in Limestone Wallrock enclosing Base Metal Veins in Derbyshire.</u>

(after Webb 1959, p.420)

Distance from vein (feet)	Metal content of limestone wallrock (ppm)			
	Fall Quarry, Ashover.		Great Rake, Matlock.	
	Zn	Pb	Zn	Pb
0	1900	1600	34000	600
5	850	600	500	1,700
10	180	230	800	1,600
15	220	220	900	1,300
20	260	120	900	1,300
25	80	60	1700	3,500

	Zn	Pb	Zn	Pb
30			400	1,200
40			850	1,250
50			60	130
60			170	440
70			600	1,440
80			1250	750
90	140	30	70	250
150			1000	1,200

At Fall Quarry, near Ashover, Derbyshire, the anomaly extends over a distance of about 20 feet from the vein, which occurs in massive limestone, unfractured and not visibly altered. The Great Rake locality gave extremely erratic values for a distance of at least 150 feet from the lode, the limestone here being extensively veined by stringers of calcite and fluorite. Webb remarks that the differences in the geochemical aureoles is almost certainly due to the extent of premineralization fracturing, that being far greater at Great Rake than at Fall Quarry, where the metals could only migrate outwards from the vein by diffusion through pore-spaces and microfractures. In the same paper, Webb reports on leakage anomalies over concealed ore bodies in Derbyshire, especially over Great Rake and Gregory/Branch Veins, but notes that no anomalies were found over Hucklow Lode (to be discussed in detail later) and over a replacement 'flat' at Alston in Cumberland. Another example of a leakage halo was reported by Kennedy (1956) from the Shullsberg district of south-western Wisconsin. He interpreted the erratic variations observed over the ore as evidence that the halo was accounted for , more by small veinlets, than by homogeneous diffusion of metals. Finally Wehrenberg and Silverman (1965), from the Leadville district, Colorado, studying the diffusion of zinc in limestones adjacent to ore bodies, concluded that an ideal diffusion pattern is destroyed as a result of reactions between the diffusing metals and the host rocks, and that the important factors controlling the dispersion of metals were the permeability and reactivity of the host rocks.

The above mentioned papers deal specifically with dispersion patterns (trace element aureoles). There is also a wealth of information on the background concentration in limestones and the trace element content of ores. The following (to mention only a few) will be considered:- Schwartz (1955), Lamar and Thomson (1956), Davis (1958), Rose (1959), Hawkes (1959) and Saukov (1960).

Trace Element Aureoles in Sandstones and Shales

Compared with studies in limestones, those into primary dispersion and leakage aureoles in sandstones and shales are very limited. Mention must be made of Cooper and Huff (1951) who described from Johnson Camp near Willcox, Arizona, a leakage halo in fractured silicated calcareous rock situated 600 feet above the Moore orebody, concluding that the presence of fractures does not necessarily bring about the concentration of metals. Between ore zones, high values were found for copper and zinc, which they believed to be due to minute fractures, while results from highly fractured areas gave only background values. Popov (1961) reports a lead aureole in sandstones in the Uck-Ochak area (U.S.S.R.) having an average width of 16½ feet and a maximum width of 60 feet.

Carpenter (1963) working on copper haloes in sandstones at the White Pine Mine, Michigan, correlates the width of the aureole with the concentration in the vein.

No results have been found which give data on trace element aureoles in shales, though Shaw (1954) gives some good background values for shales and pelitic rocks.

Trace Element Aureoles in Igneous Rocks

In environments less reactive than limestones, such as silicate and igneous rocks, Morris and Lovering (1952) reported aureoles up to thousands of feet wide. Stoll (1945) working on the beryllium pegmatites of New England found diffusion of the beryllium from the pegmatite into mica-schist, and mica-gneiss country-rocks. A very similar report also comes from Hornung (1962) on beryllium pegmatites in Africa. James (1957), discovered a logarithmic decay of the arsenic content away from ore deposits in Southern Rhodesia, recording an aureole width of 25 feet for sandstone wallrocks. The Front Range mineral Belt, Colorado, mainly in Precambrian metamorphic and igneous rocks, especially quartz-diorites showed according to Tooker (1963), that adjacent to mineralization, most of the trace elements were removed or at least displaced veinwards, concluding that there was no close correlation between width of the altered rock and the width of the vein. Finally Rao (1952) working on wallrock alteration in the Cornish granites reports that variation in the trace elements of the wallrocks is related to mineralogical and chemical changes produced during alteration. The trace elements are divisible into mobile and immobile, depending upon whether they show significant variation away from mineralization.

Conclusions

It appears from the available literature that very few wallrock aureoles have led directly to the discovery of new mineralization, the striking exception being Morris in the Tintic district. However, if certain shortcomings could be overcome they might be useful in underground exploration, where it would be advantageous to know whether or not the end of a crosscut or drill hole is within a short distance of ore.

Considering the variable width of wallrock anomalies Hawkes and Webb concluded that, 'either the chemical activity or the permeability of the rock types, together with the duration of the period of hydrothermal activity, is responsible for the large difference in aureole width'. Other authors attribute the variation in width either to direct diffusion through the massive rock or percolation through minute fractures. There are numerous other controlling factors, some of which have been no more than briefly mentioned so far, it is hoped to consider these in detail when discussing the present results and their implications.

Another effect which may considerably affect the aureole, is the alteration due to rock weathering, either at surface or by near-surface waters. One or two authors for example note the leaching of zinc. Throughout the study this effect has been borne in mind and specific samples have been collected from surface, near-surface, and as deep as possible to investigate this relationship.

CHAPTER II

SAMPLING AND ANALYTICAL PROCEDURE

Sampling Procedure

Sampling Areas

The present study was confined to three specific areas in the British Isles, the Northern Pennine Orefield (Alston Block subarea), the Derbyshire Orefield and the West Cumberland Ironfield, the approximate boundaries of which are shown in fig. 2-1. In the time available it was not found possible to sample the other major occurrences of lead and zinc in limestones, for example, in the southern part of the Northern Pennines (the Askrigg Block), the Mendips or North Wales. The majority of the samples came from disused or working limestone quarries which expose veins. In these it was found that the old quarrymen knew when the composition of a limestone was altering, by its effect on the efficiency of their limekilns, with the result that in numerous localities a bluff was left standing in the quarry. This indicated the position of the vein and facilitated the collection of samples along one horizon horizontally outwards from the mineralization (e.g. Newlandside Quarry, Heights Quarry, Harehope and Lanehead Quarries in Weardale). Second in importance came underground haulage ways or cross-cuts in accessible mines. Specific reference to these will be made when considering the mines in question; these gave excellent collecting traverses, but restricted ones, in the sense that the width of the traverse was governed by the distance the crosscut had been driven, or the inclination and direction of the haulage

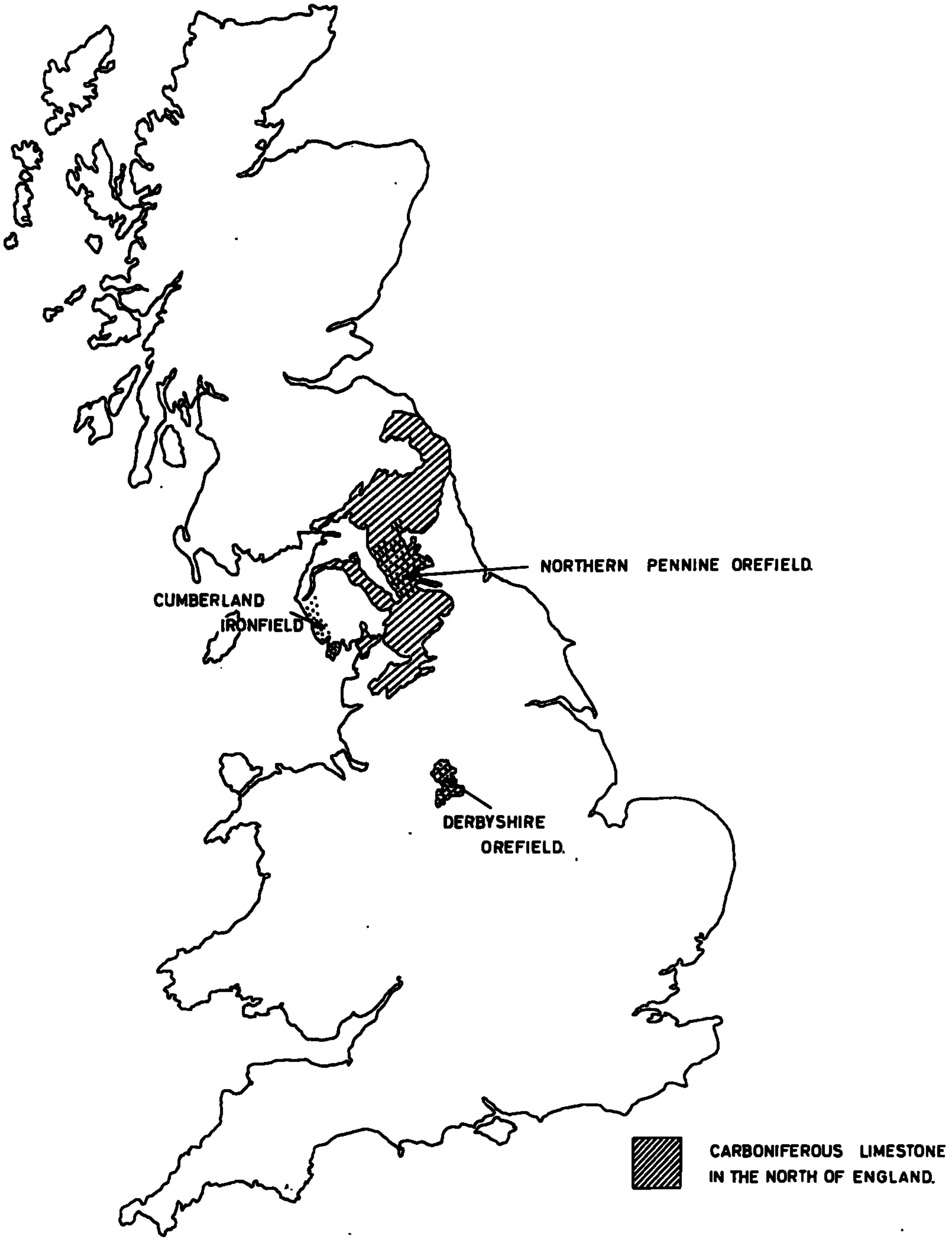


FIG. 2-1. OUTLINE MAP OF GREAT BRITAIN SHOWING THE OREFIELDS SAMPLED.

way. Finally a large number of samples were obtained from surface and underground exploratory boreholes; in a few specific cases boreholes were drilled by the mining companies specifically for the purpose of this investigation.

The Northern Pennine Orefield

The Orefield covers an area of 550 square miles and is delimited by major faults to the northwest and south with displacements of up to 3,000 feet, along which the main movements took place in Tertiary times. The block as a whole, is considered to have been initiated during Carboniferous movements. The ore deposits occur mainly in fissure veins that cut the rhythmic sequence of the Carboniferous sediments (alternations of limestone - sandstone - shale). Into this succession has been intruded the Whin Sill, an extensive system of quartz-dolerite sheets. Underlying the above is the Weardale Granite, recently proved by the Rookhope borehole (Dunham et.al., 1965). The doming of the Alston block in Permian times is believed to have resulted in the formation of an E.N.E., N.N.W. and W.N.W. fracture pattern in the Carboniferous rocks, in which the minerals were deposited.

The coincidence of the mineral zoning and the gravity anomaly associated with the Weardale Granite (Bott and Masson-Smith, 1957) suggests that, although the granite is of a pre-Carboniferous age, it must have exercised a strong structural control on the emplacement of the orefield, perhaps comparable with that of the Pre-Cambrian granite knobs on the Missouri lead - zinc deposits.

Consultation of the 'Geology of the Northern Pennine Orefield' by K.C. Dunham (1948) led to an organised sampling programme adjacent to the numerous veins in the area. It was decided to concentrate primarily on veins intersecting the Great Limestone, for two reasons : the great aerial extent of this lithological unit, which has little variation in thickness and composition, and the proven fact that most of the economic deposits worked in the past lay within this one horizon (op. cit. p.81).

The principal quarrying area, an important source of ironworks flux and tarmacadam, lies between Frosterly, where the limestone rises from the bed of the River Wear, and Stanhope. The bulk of the samples were collected from the following quarries in this region:- Harehope, Newlandside, East Ashes, Lanehead and Heights. An additional locality was at Garrigill, which gave an excellent section in the Tyne Bottom Limestone, for comparison with the Great Limestone.

With the kind permission of the Weardale Lead Company, underground samples from crosscuts and boreholes were collected from Redburn Mine, near Rookhope. The Owners of Settlingstones Mine Ltd., allowed access to Swinhope Mine, enabling the Great Limestone to be sampled adjacent to Williams Vein and subsidiary veins. Fig. 2-2 gives a plan of part of Swinhope Mine and marks the sampling localities.

The United Steel Company, who own West Blackdene Mine, near Ireshopeburn, gave permission to sample sandstone and quartz - dolerite wallrocks adjacent to fluorite mineralization (see fig. 2-3.)

SWINHOPE MINE.

No.1. INCLINE SHAFT DISTRICT.

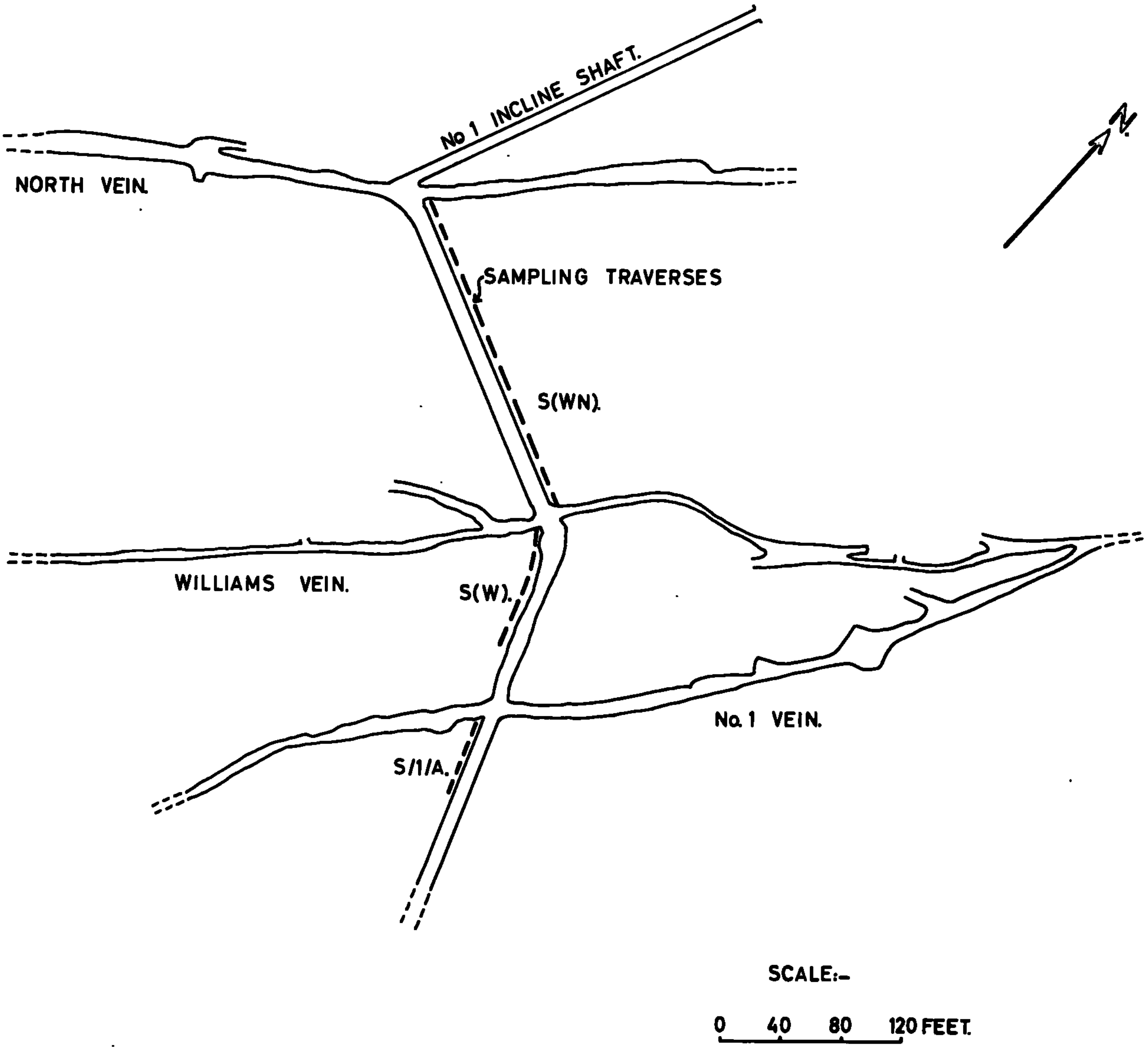


FIG. 2-2. UNDERGROUND SAMPLING OF THE GREAT LIMESTONE.

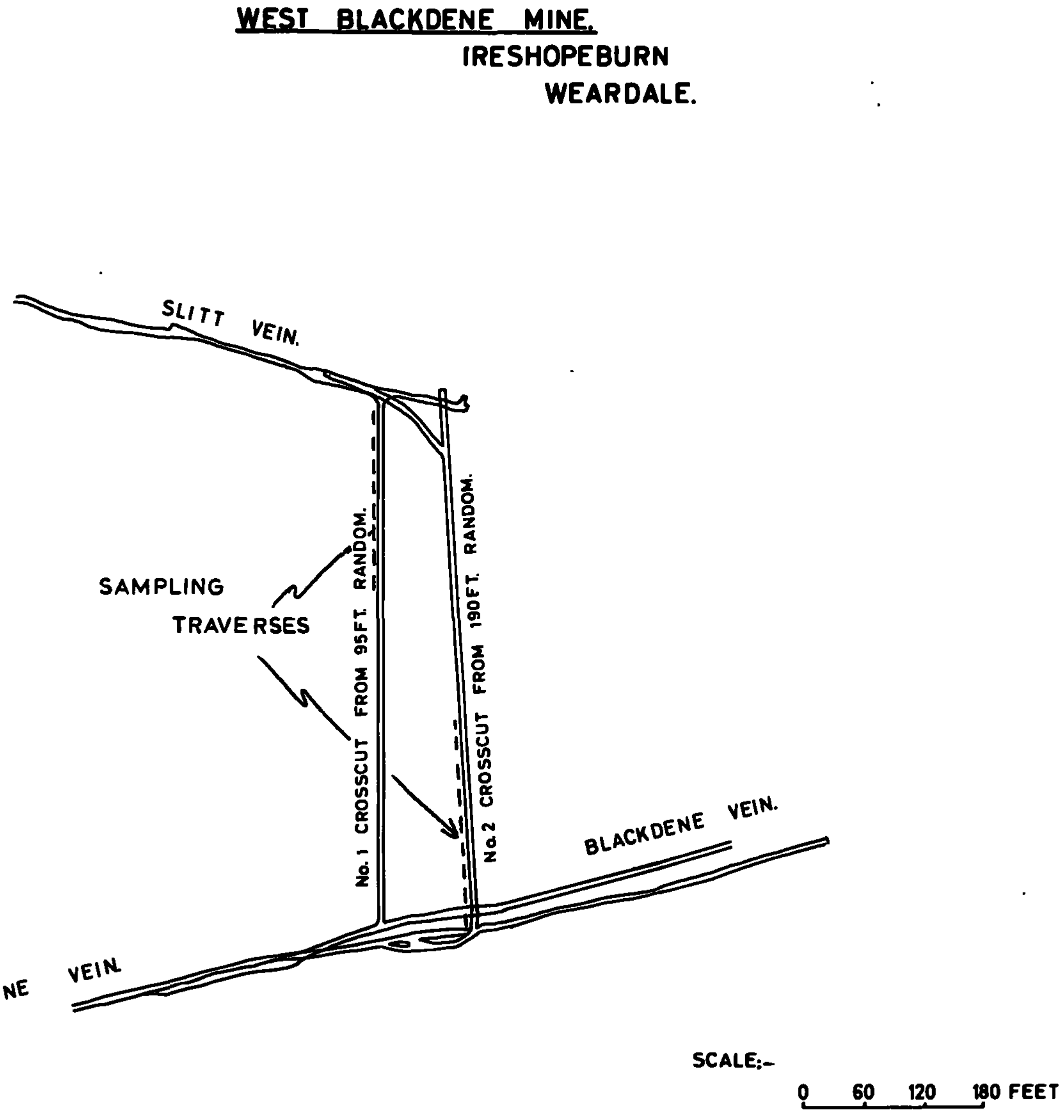


FIG. 2-3. SAMPLING LOCALITIES IN THE ALTERNATING BEDS AND SLATY HAZEL.

Within the Carboniferous sediments of the Northern Pennine Orefield occurs the well known system of quartz - dolerite sheets, which like the sediments have been affected by mineralization. Wager (1929), Smythe (1930) and Dunham (1948), note that adjacent to the veins an alteration from the dark, dense quartz - dolerite to a white, lighter rock, the 'White Whin', has occurred, with zones of alteration varying with distance from mineralization. 'White Whin' also occurs at contacts with carbonaceous strata. A.C. Dunham and Kaye (1965) reported trace element differences between this kind of 'White Whin' and 'normal' Whin Sill. However, no work has been done to study the minor elements involved in the systematic change which authors had noted resulting from hydrothermal alteration of the quartz - dolerite. The present study therefore, aimed at filling this gap in the geochemical knowledge of the alteration effects.

Samples were collected at surface where the Whin Sill was intersected by mineralization, i.e. Wynch Bridge (Wager, 1929) and Force Burn (Smythe, 1930) and also at depth where the mining activities had reached the Whin Sill. Here, excellent opportunities were afforded by Athole G. Allen, (Stockton) Ltd., at Closehouse Mine (see fig. 2-4, for the sampling localities adjacent to a Whin dyke), the owners of Settlingstones Mine Ltd., and by a small drill core from Cowgreen Mine (provided by Prof. K.C. Dunham). Fig. 2-5, shows the location of the underground drill holes at Settlingstones Mine. As noted previously, samples adjacent to a fluorite vein which cut the Whin Sill at West Blackdene Mine, were also collected.

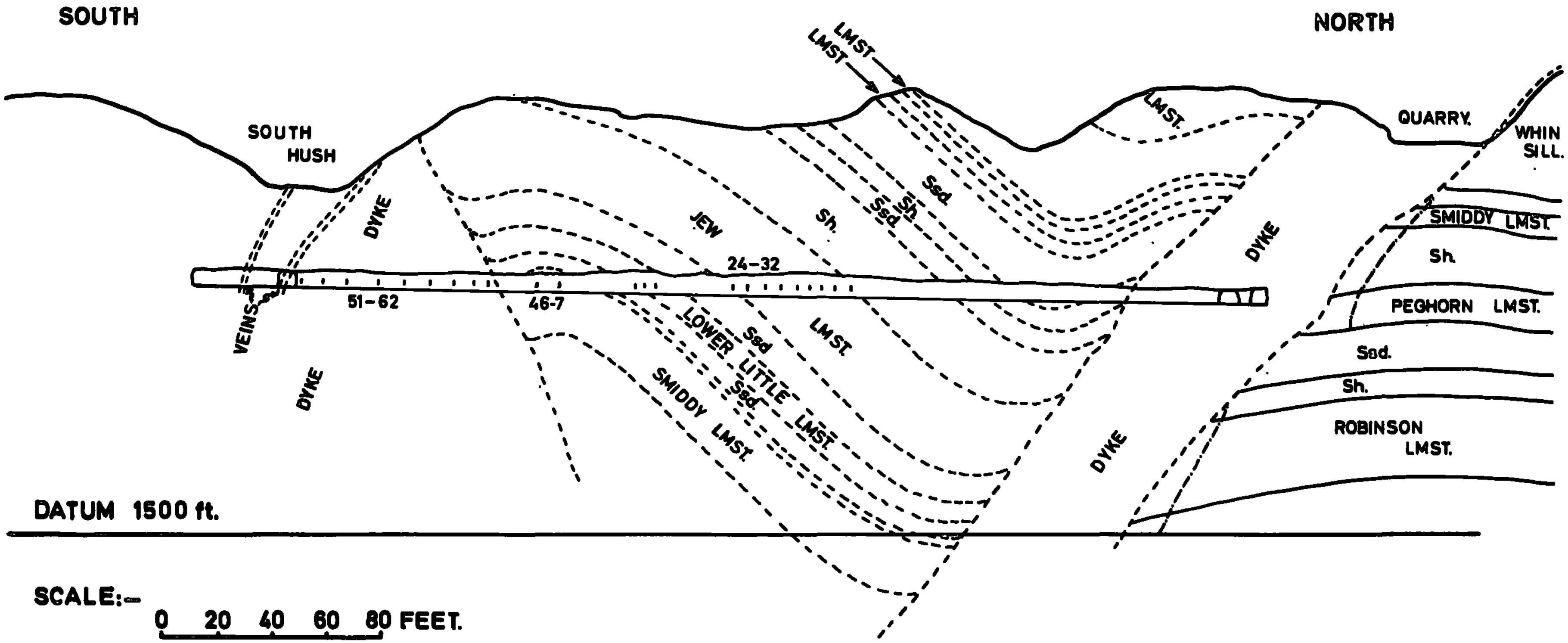


FIG. 2-4. SAMPLING LOCALITIES —— CLOSEHOUSE MINE.
(5 FATHOM CROSSCUT SOUTH)

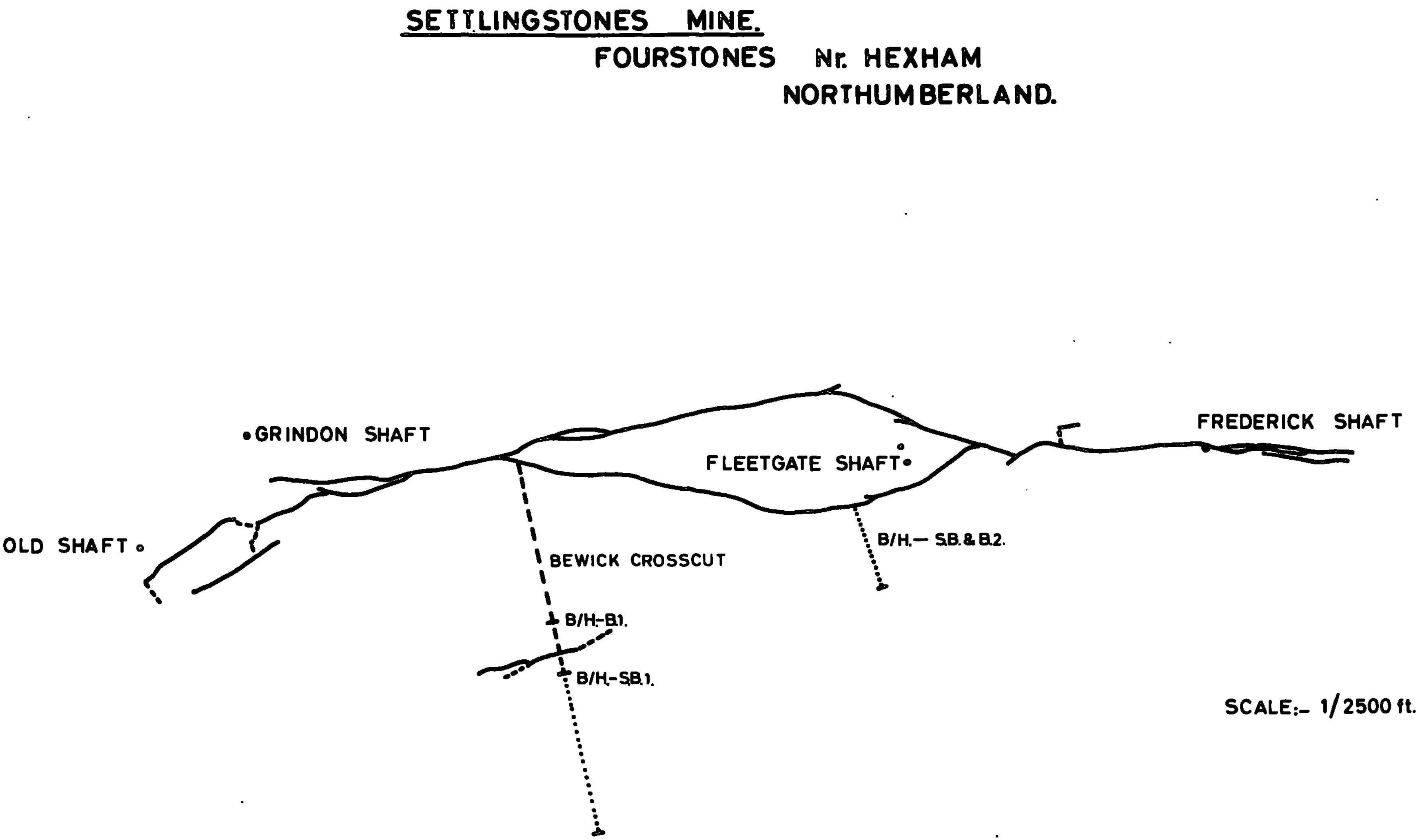


FIG. 2-5. UNDERGROUND BOREHOLES IN THE WHIN SILL.

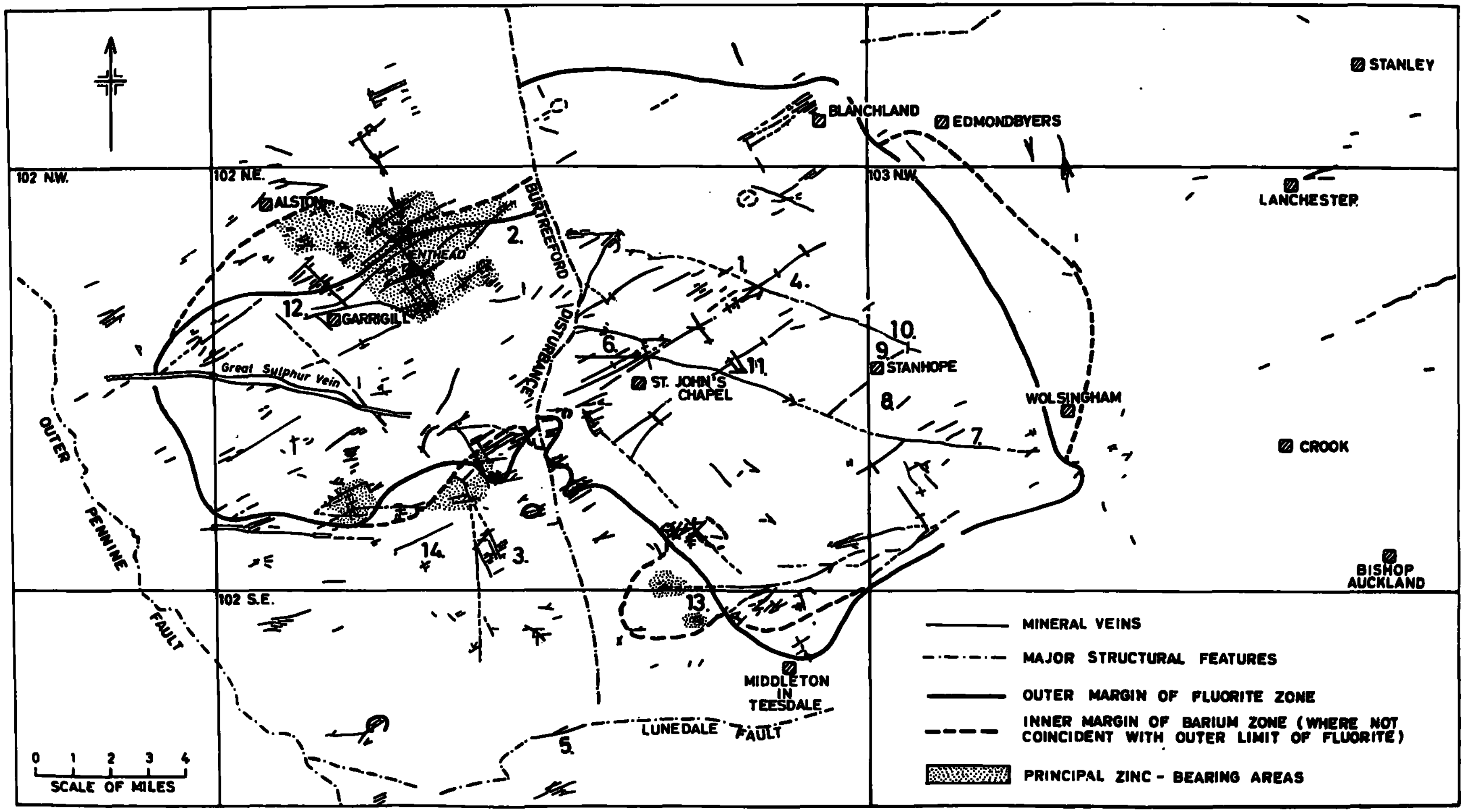


FIG. 2-6. SAMPLING LOCALITIES IN THE NORTHERN PENNINE OREFIELD.

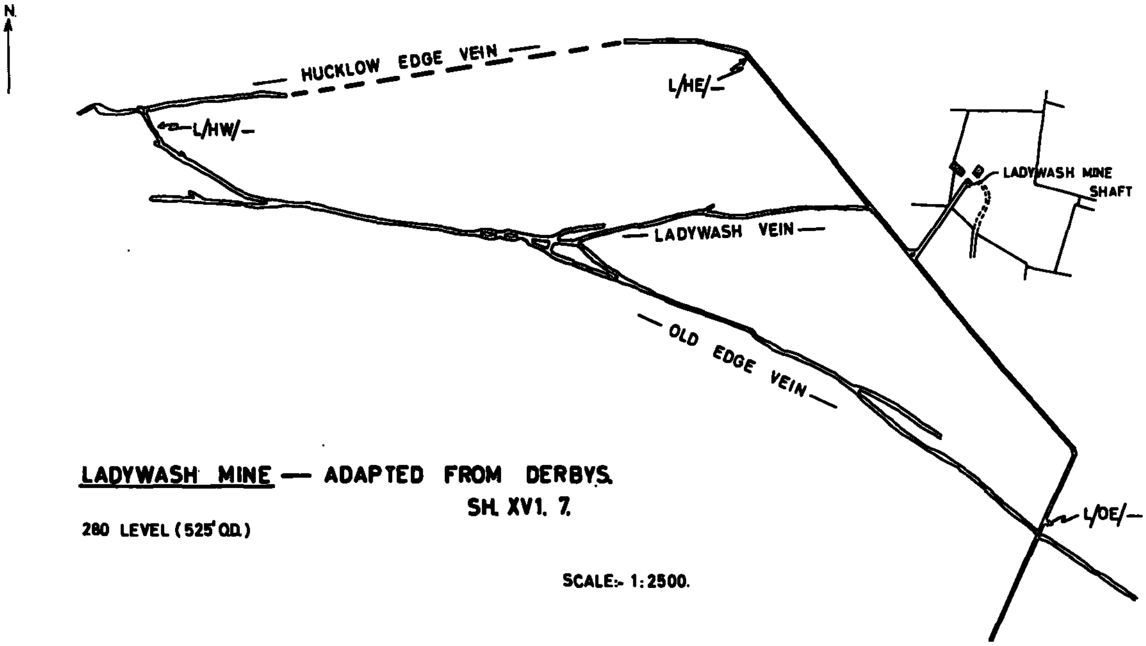
(AFTER DUNHAM 1948 PLATE II)

Fig. 2-6, reproduced from Dunham (1948), plate II), with slight modifications, illustrates the sampling localities from the northern Pennines.

The Derbyshire Orefield

The Derbyshire Orefield extends from Castleton in the north to Wirksworth in the south, with a subsidiary occurrence at Ashover and Crich to the east. The geological framework is a series of massive limestones, totalling not less than 1,500 feet in thickness, which contain interbedded basic lavas and tuffs with intrusive sheets and necks of dolerite. The stratigraphy of the Derbyshire Orefield is not as well documented as that of the Alston Block (see Dunham, 1952), but here prominent mineralization occurs in the limestones of the Upper Dibunophyllum subzone (D_2) in the form of fissure veins, bedded replacement deposits and irregular horizontal and vertical pipe-like replacement bodies. Analogous with the northern Pennines, a fluorite zone is discernable, but the orefield does not possess the zonal closure exhibited by the Alston Block. Structurally, the area may be regarded either as a broad dome, or an uplifted block of limestone with flanking limestone 'reefs'. Shirley and Horsfield (1944), indicate that the major veins, of the northern area, lie along the crests of subsidiary anticlines, within the major domal feature. It may be that this structural background has produced the system of NE-SW, and ENE - WSW veins.

To provide material for comparison with that from the Northern Pennine Orefield sampling was undertaken adjacent to a number of veins, at approximately the same stratigraphical horizon (D_2). Surface localities

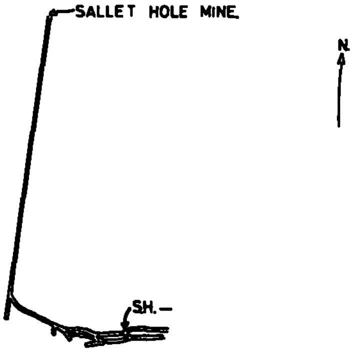


LADYWASH MINE — ADAPTED FROM DERBYS. SH. XV1. 7.

280 LEVEL (525' O.D.)

SCALE:- 1:2500.

FIG. 2-7. SAMPLING LOCALITIES GLEBE MINES, EYAM DERBYSHIRE.



SALLET HOLE MINE — ADAPTED FROM HUNTINGS SURVEYS SH. 2.

LEVEL 1 (738' O.D.)

SCALE:- 1:2500.

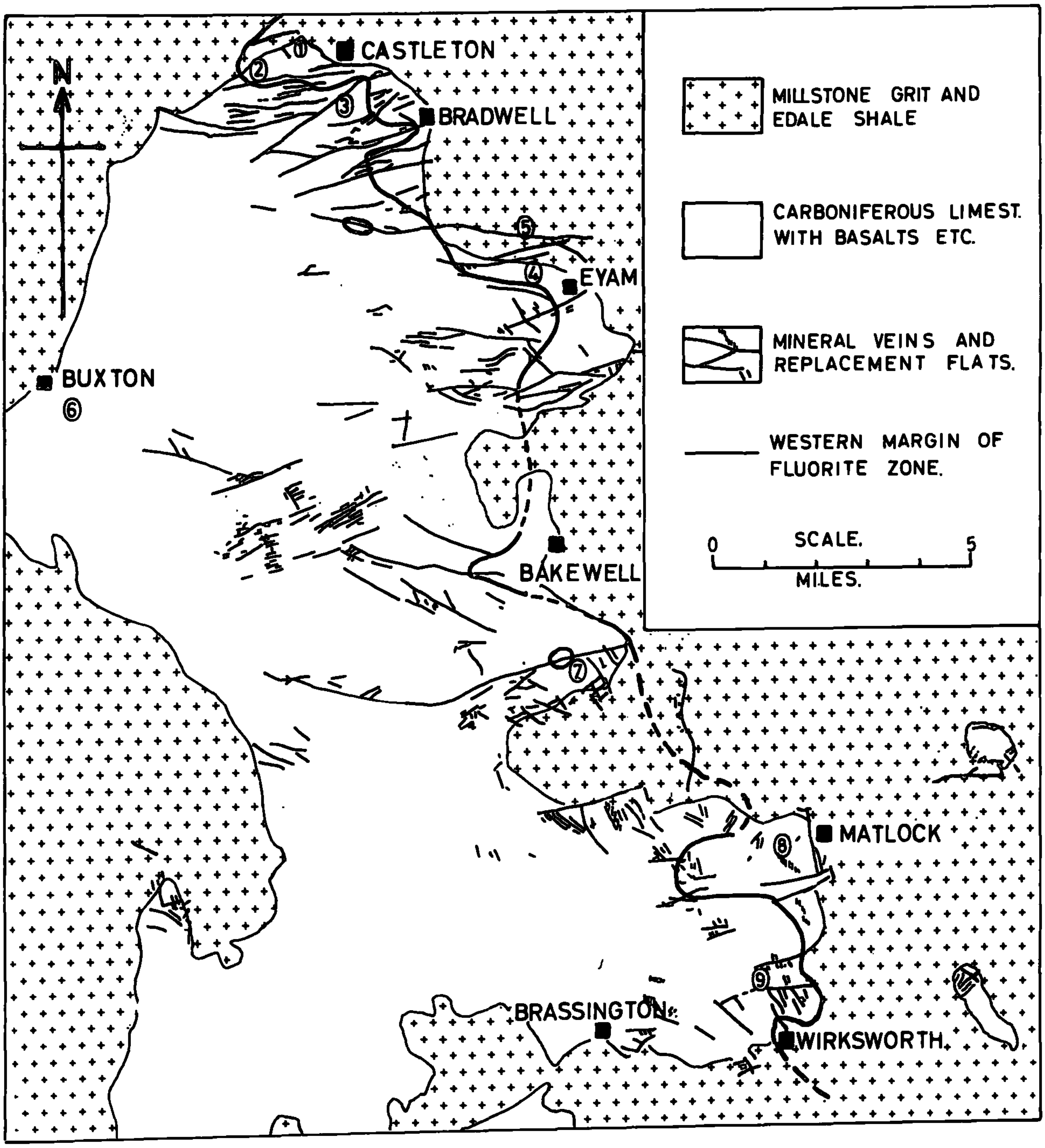


FIG. 2-8. SAMPLING LOCALITIES IN THE DERBYSHIRE OREFIELD (AFTER DUNHAM 1952. PLATE IV)

sampled were adjacent to fluorite ± lead - zinc deposits at Masson Hill Quarry, Odin Mine and Dirtlow Rake. G.E. Bacon and Sons of Youlgreave, gave permission for the sampling of Long Rake, and here it was possible to collect a traverse in shale adjacent to mineralization (see Raper Prospect). At their Middleton Mine, Derbyshire Stone Co. allowed sampling adjacent to two small barite veins, while sampling was carried out also at the famous 'Blue John' deposits near Castleton (Treak Cliff Mine - Mr. P. Thompson). Imperial Chemical Industries Ltd., allowed access to their quarry near Buxton, which intersects a barite vein.

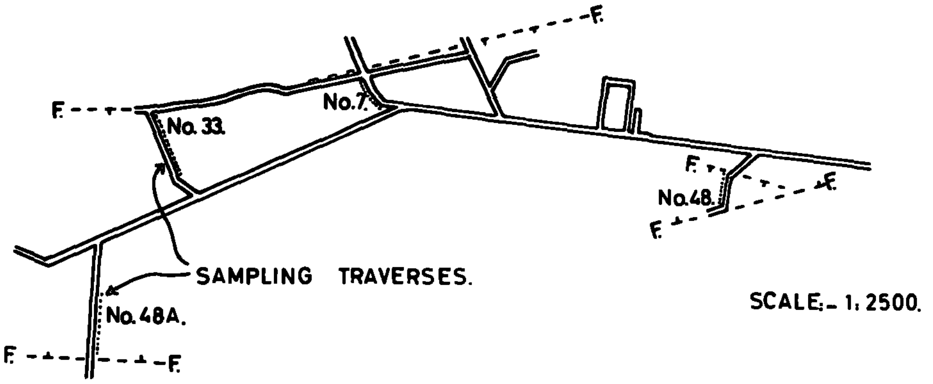
The largest number of samples from Derbyshire were made available through Laporte Industries Ltd. (Glèbe Mines). Ladywash and Sallet Hole Mines provided excellent traverses in the same lithological unit away from strong fluorite mineralization, while a surface borehole was provided for sampling the limestone vertically above Sallet Hole Mine, (see fig. 2-7 for the sampling localities).

The above mentioned localities are illustrated on the adjoining diagram (fig. 2-8,)modified after Dunham (1952, plate IV).

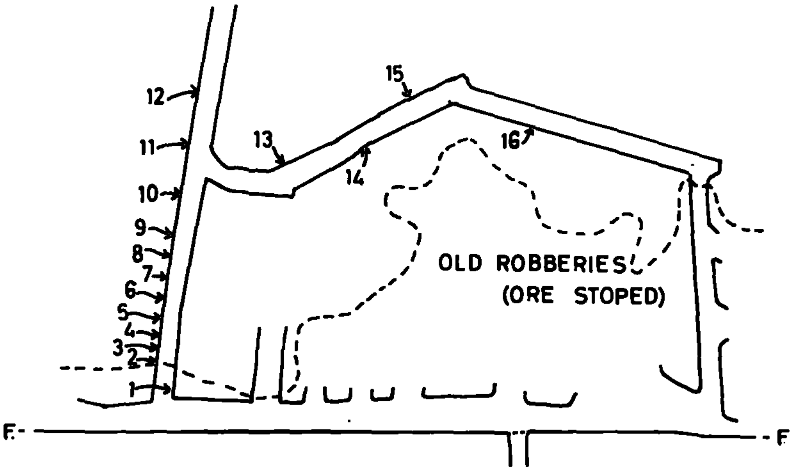
The Cumberland Ironfield

While the major part of this study is confined to dispersion patterns adjacent to lead - zinc - fluorite - barite mineralization in limestone, results obtained adjacent to haematite ore bodies in the Carboniferous Limestone of West Cumberland make an interesting comparison.

BECKERMET MINE.
CUMBERLAND.



101. BOREHOLE AREA
NEW SOUTH DIP.



68 AREA (upthrow).

FIG. 2-9. UNDERGROUND SAMPLING — HAEMATITE ORE.

Fig. 2-9 shows the underground sampling localities at Beckermet Mine near Egremont, owned by the United Steel Company Ltd.

Sampling Methods

As noted by Hawkes (1957, p.324), the 'elements occurring in rocks as primary dispersion patterns may be either evenly disseminated throughout the rock mass or segregated as clots or swarms of minute fracture fillings'. This inconsistency was recognised from the beginning of the work, with the result that two different methods of sampling, whenever possible, were adopted; (a) if examination of the strata indicated that it was relatively homogenous when single specimens were taken, or (b) if the rock mass appeared spotty or erratic, then channel or chip samples were taken (see Cooper and Huff, 1951).

However, with diamond drill cores, the above methods were impracticable, and it was found that splitting the core in 3 to 6 inch sections, at required intervals, gave satisfactory results.

The size of the sample taken was governed by the homogeneity of the rock type, and after preliminary experiments it was found that for limestone, whenever possible 2 kg. was sufficient. The same was true for the Whin Sill. With sandstones and shales, the quantity was increased twofold as far as possible. Diamond-drill cores however, only provided between 0.25 and 0.50 kg., depending upon their diameter, for, with a larger amount the length covered by a single sample became too large.

Surface Exposures

Most of the samples were taken from operating or disused quarries, and very few from natural outcrops. The amount of surface weathering appeared to be very small to the naked eye (5-10 mm., to non-existent). Nevertheless in none of the samples was the external surface collected, for contamination due to dust, organic matter and blasting were all possible.

Underground and Borehole Samples

Contamination here was very apparent by the thick coating of dust, whitewash etc. to be found on the walls of the crosscuts. In all cases extreme care was taken to remove thoroughly, not only surface coatings, but the outermost few inches of rock, prior to collection of any material.

The drilling mud used for lubrication of the diamond bits, was often encountered on the cores supplied, and without fail, this was washed off prior to splitting the core.

Tungsten carbide tipped hammers and chisels were used throughout; all samples were immediately placed in a polythene bag, sealed and finally enclosed in a numbered paper bag, with the object of keeping adventitious foreign material to a minimum.

Preparation

For the initial part of this study, the primary splitting of the material was done on a hydraulic press reducing the size to one inch pieces, with further reduction to about ⅛" using a piston and plunger arrangement on the same press. At a later period, the introduction of a Sturtevant Roll Jaw Crusher (type - 'Baeropen' - 2" x 6", with manganese steel jaws) eliminated the second stage as well as substantially reducing the initial crushing period.

A fraction of approximately 250gm; produced by cone quartering of the initial material was then pulverised in a Tema Laboratory Disc Mill (Type T - 100), for approximately five minutes, or longer if necessary, until the resultant powder was estimated to be approximately 20 microns in diameter. This process was repeated until cone and quartering of the powder gave a sample weighing around 100 gm., which was then stored in a screw topped plastic bottle.

Analytical Techniques

Choise of Elements under Investigation

Host Rocks

Prior to the main analytical study it was necessary to determine the background values in the respective host rocks under consideration. Thirty samples of each lithological unit were chosen, as far from mineralization as possible, and analysed by the same procedure as was to be followed for the mineralised samples, producing what was considered a mean value for the background concentrations of trace elements in respective suites. The results are given in the respective chapters. The following table summarises the elements chosen for study in the respective rock types:-

Table 2-1

Elements investigated in the respective rock types

Limestone:-	Rb, Pb, Sr, Mn, Zr, Cu, Zn, Ni, Fe, and F
Sandstone:-	Rb, Pb, Sr, Mn, Zr, Cu, Zn, Ni and F
Shale:-	Rb, Pb, Sr, Mn, Zr, Cu, Zn, and Ni
Quartz-dolerite:-	Rb, Ba, Pb, Sr, Mn, Zr, Cu, Zn, Ni, Cr, V & F

Ore Veins

Not uncommonly the ore metals fail to form a dispersion pattern around a mineral deposit. In this event, consideration must be given to the distribution of associated non - economic elements, or 'pathfinders', as described by Warren and Delavault (1953). Pathfinders are elements which may be present in the ore in major or minor amounts, but not of commercial value. Under favourable conditions these may migrate as far as, if not farther than, the main economic elements.

Hence the veins were sampled prior to the main analysis to determine which, if any, trace elements the ores carry with them and which might therefore produce a detectable wallrock aureole.

The results obtained are summarised below :-

Main Vein Material	Associated trace elements
Pb/Zn	Rb, Mn, Cu, Ni and Fe
Ba	Pb, Cu, Zn, Ni and Fe
Fluorine	Ba, Pb, Mn, Zr, Cu, Zn, Fe and Ni.

The following survey was therefore directed to the analysis of the following elements:-

Rb, Ba, Pb, Sr, Mn, Zr, Cu, Zn, Fe, Ni, Cr, V and F

The Choice of Instrumental Techniques

The aim was to obtain the maximum number of accurate analytical results and the following considerations were borne in mind in selecting the methods.

(1) The chosen method should produce, in as short a time as possible, the maximum number of trace elements results.

(2) While considering the speed of the analytical technique, the method should have reasonable precision and accuracy.

On this basis the following methods were found to be the most suitable for the analysis of the material collected :

(1) X - ray fluorescence for the determination of Rb, Pb, Sr, Mn, Zr, Cu, Zn, Ni and Fe in solid rock samples.

(2) Emission spectroscopy for the determination of Ba, V, Cr and F in solid rock samples.

X - ray Fluorescence Analysis

The prepared powders were analysed using a Phillips X-ray spectrograph with a universal vacuum attachment (PW. 1540) and electronic timer (PW.4062).

Sources of Error

The major sources of error in X-ray fluorescence analysis can be traced to three principal causes of deviation from proportionality, classified by Liebhafsky and Winslow (1958) as:-

(1) Instability of the instrument.

(2) Effects derived from heterogeneity in the samples, i.e. surface effects and segregation.

(3) Absorption and enhancement effects related to the chemical nature of the sample.

The first of these is by far the easiest to eliminate. As recommended by Davies (1958), the instrument was housed in a relatively small room, the temperature of which was controlled by a G.E.C. air conditioner, reducing the fluctuations in temperature and the resulting variations in the lattice spacing of the analysing crystal, which minimised deviations in the peak position, as well as loss in counts produced by instability of the electronic circuitry.

The effect arising from heterogeneity in the sample has been investigated by numerous authors, however the work by Bernstein (1962), summarises the causes and possible rectifications. It has been shown that the intensity of radiation increases with decrease in particle size, until a certain degree of 'fineness' is achieved, when further reduction in size produces relatively small intensity changes. With the present grinding techniques this source of error cannot be eliminated, but it can be reduced to a reasonably low level by grinding the sample to a very fine powder. The crushing procedure, previously described, was considered sufficient to reduce this deviation to an acceptable level.

To detect and counteract any instrumental drift, as well as deviations which might be produced by the packing of the powders, one sample was reloaded and counted at regular intervals throughout the analytical work.

The absorption and emission of X-rays is a function of the entire chemistry of the sample, controlling, as Liebhafsky et al (1960) have shown, the extent to which any element in the material affects the fluorescent radiation. It is therefore necessary to allow for effects due to the entire chemistry of any sample. Methods have recently been introduced to eliminate or predict intersample differences. None of these methods provide a universal solution to the problem, and it must be emphasised that when this study was undertaken, very few of the methods had been perfected. It was considered sufficient, at the time, to correct for this effect in the following ways :-

(1) By the preparation of standards from the material being analysed i.e. the use of 'addition standards' (see Ahrens and Taylor, 1961, p.158).

(2) By comparison with standards of a similar chemical composition. The International Standard Diabase W - 1 was employed when analysing Whin Sill samples; and the National Bureau of Standards, sample No. 1A. (Argillaceous Limestone) was taken to be of similar chemical composition to a number of the limestones under investigation.

Practical Methods - Trace Element Analysis

Standards were prepared by the addition method (as noted above), using unmineralised limestone, sandstone, shale and Whin Sill as the bases for the 'master Mixes'. These were made up to contain 2,500ppm of Rb, Pb, Sr, Mn, Zr, Cu, Zn, Ni and Fe, and each 'master mix' was shaken for 8 hours on a Spex Mixer Mill, and then diluted with its own base material to obtain the desired concentrations of:- 2,500; 1,000; 750; 500; 300; 200; 100; and 50ppm of each element.

Previous analyses have recorded contamination from two distinct sources:-

(1) The crushing and grinding apparatus

(2) The X-ray anode and tube filament

Considering the possible causes of contamination, the hydraulic jack has a splitting and not a grinding action, and if addition of material occurs at this stage, it may be taken to be of such a low magnitude as to be negligible.

The barrel and rings of the Tema Swing Mill are lined with tungsten carbide, which is bonded with cobalt and consequently will give cobalt and tungsten contamination, but these elements were of no interest in the present study.

In order to neutralise the contamination from the X-ray anode and tube filament, the intensity of the peak for each element was counted using 'spec. pure' $Si\ O_2$ and recorded as a fraction of the tungsten L1 line intensity. Only nickel, copper and lead were found to be contaminants, and, in all cases the intensity of the W L1 peak was measured, and a simple correction applied for contamination by use of this ratio.

Table 2-2

Operating Conditions for trace element determinations carried out by X - ray fluorescence

Tube and voltage :-	Tungsten target operated at 48 kV and 20 mA.
Crystal	Topaz
Collimator	480μ
Path	Vacuum
Counter	Scintillation
Fixed time	2 x 90 seconds
Holder	Rotating circular metal holder, with mylar window
Sample state	Powder

The intensity of the peak position was determined by subtraction of the mean background intensity on either side of the peak.

Element	Rb	Pb	Sr	Mn	Zr	Cu	Zn	Ni	Fe	W
Line analysed	Kα	Lβ	Kα	Kα	Kβ	Kα	Kα	Kα	Kα	L1
Low background (°2θ)	38.80	41.20	36.60	100.00	28.54	68.30	62.90	74.29	89.97	-
Peak Position (°2θ)	39.89	42.37	37.56	101.70	29.84	69.32	63.89	75.29	91.17	76.45
High background (°2θ)	41.20	43.50	38.80	-	31.14	70.40	64.90	-	-	78.00

The standard and relative deviations for the four types of material analysed are shown in Table 2-3. The samples chosen had often very low concentrations of certain elements (bordering on, if not below the detectability limit of the instrument - in such a case it was not considered justifiable to calculate the two deviations). The detectability limit was taken (as recommended by Campbell et. al. 1959) as the concentration that results in a line intensity equal to three times the standard deviation of the background counts. The detectability limit for each element is shown in table 2-4.

Table 2-3

Standard and Relative Deviations of X-ray analysis for nine replicate determinations of a limestone, sandstone, shale and quartz-dolerite.

Element	Mean ($\bar{x}$) (ppm)	Standard Deviation (ppm)	Relative Deviation (%
		Limestones	
Rb	< 5	-	-
Pb	61	± 1.9	3.1
Sr	385	± 5.5	1.4
Mn	378	± 23.3	6.2
Zr	< 10	-	-
Cu	< 15	-	-
Zn	62	± 2.8	4.4
Ni	20	± 2.8	12.0
Fe	378	± 23.8	6.2
		Sandstones	
Rb	165	± 15.7	9.5
Pb	24	± 7.0	27.0
Sr	189	± 12.0	6.3
Mn	1100	± 10.6	0.9
Zr	149	± 11.3	7.4
Cu	24	± 6.0	19.2
Zn	410	± 9.7	2.4
Ni	62	± 2.5	3.7
		Shales	
Rb	150	± 14.6	8.4
Pb	97	± 15.6	16.0
Sr	114	± 3.7	3.3
Mn	< 10	-	-
Zr	87	± 3.1	2.9
Cu	58	± 2.7	4.7
Zn	370	± 21.0	5.6
Ni	43	± 2.8	4.6

Whin Sill

Element	Mean ($\bar{x}$) (ppm)	Standard Deviation (ppm)	Relative Deviation (
Rb	35	± 2.5	4.1
Pb	31	± 8.1	23.1
Sr	426	± 7.8	1.7
Mn	1280	±16.1	1.2
Zr	138	±14.0	7.2
Cu	68	± 2.7	4.5
Zn	129	± 3.7	3.2
Ni	47	± 2.0	3.8

$$\text{Standard Deviation} = \pm \sqrt{\frac{\Sigma (x - \bar{x})^2}{N - 1}}$$

$$\text{Relative deviation} = \frac{\text{Standard deviation x 100}}{\bar{x}}$$

where x = value obtained in ppm

$\bar{x}$ = average

n = number of times the sample has been run

Table 2-4

Detectability limit of each element (ppm)

Element	Limestone	Sandstone	Shale	Quartz-dolerite
Rb	5	5	5	10
Ba	-	-	-	(200)
F	(250)	(250)	-	-
Pb	20	10	10	10
Sr	10	5	5	5
Mn	10	10	10	10
Zr	10	5	15	20
Zn	5	5	5	5
Cu	15	5	5	10
Ni	5	10	5	5
Fe	5	-	-	-
Cr	-	-	-	(20)
V	-	-	-	(100)

( ) for the optical spectrograph.

Table 2-5 presents analyses of two standard samples, Diabase W-1 and N.B.S. Argillaceous Limestone No.1A. With the exception of zirconium for W-1 and strontium, nickel and possibly manganese for sample No.1A, the results indicate the accuracy is satisfactory. With regard to calcareous limestones, sandstones and shales, no comparable samples were available to check the accuracy of the method.

Table 2-5

Analysis of Standard sample W - 1 and National Bureau of Standards Sample No 1A.

	Rb ppm	Pb ppm	Sr ppm	Mn ppm	Zr ppm	Zn ppm	Cu ppm	Ni ppm
Diabase (W - 1)								
recommended value:	22	8	220/175	1320	100	82	110	80/82
present study :	22	<10	217	1440	74	90	125	73

(reference Fleischer, 1965)

	Rb ppm	Pb ppm	Sr ppm	Mn ppm	Zr ppm	Zn ppm	Cu ppm	Ni ppm
Argillaceous limestone (1a)								
present study :	15	18	1025	260	50	20	<15	17
other analysts								
(a)	-	20	2-3000	500	60	-	~3	10
(b)						17/23		
(c)			1940					
(d)			1000	295				
(e)			2000					
(f)			1800					

(references :- (a) Clark and Swain, 1963
(b) Ball and Filby, 1965
(c) Grabowski and Unice, 1958
(d) Chemical analyses
(e) Turekian and Carr, 1961
(f) Wade and Seim, 1961).

Table 2-6

Operating Conditions - Major Element Analyses

Element	Si	Al	Fe	Mg	Ca	Na	K	Ti	Mn
Peak $^{\circ}2\theta$	78.00	112.56	57.41	106.78	82.92	73.35	106.52	55.90	62.89
Tube	Cr	Cr	W	Cr	Cr	Cr	Cr	Cr	W
Generator (kV.mA)	46,20	46,20	40,20	48,20	30,10	30,30	46,20	40,20	40,20
Crystal	EDDT	EDDT	LiF	ADP	LiF	Gypsum	LiF	LiF	LiF
Path	vacuum	vacuum	air	vacuum	vacuum	vacuum	vacuum	vacuum	air
Collimator	coarse	coarse	fine	coarse	coarse	coarse	coarse	coarse	fine
Counter	flow	flow	flow	flow	flow	flow	flow	flow	flow
Counter voltage (v)	1625	1625	1625	1650	1625	1660	1625	1625	1575
Discriminator	no	no	no	yes	no	yes	no	no	no
attenuation				27.0v		26.0v			
amplitude				2		2			
channel width				16		8			

Major Element Analyses

One hundred samples were analysed representing 11 sampling traverses. The samples were bricquetted using a standardised technique (Holland and Brindle, 1966, p.2090). The Phillips X - ray spectrograph (PW 1540) was operated using the conditions given in table 2-6. The standard used was the National Bureau of Standards sample number 1A (Argillaceous Limestone).

Intensity data from the spectrograph were converted directly, by computer, into total major element analyses, using the programme described by Holland and Brindle (1966). In the construction of the matrix block (op.cit. p.2089) to this programme, it was assumed that the three major elements, iron, magnesium and calcium were bonded as carbonates and that the remaining major elements were in the form of oxides.

The accuracy of the results only matches that of the standards, but the precision, statistically, was better than 0.5% of the analysed oxide or carbonate. However, because these results are undergoing internal comparison only, it is the precision which measures their reliability.

Emission Spectroscopic Analysis

As two separate and totally different determinations were employed, this section will be subdivided into :-

PART I The determination of barium, vanadium and chromium in the Whin Sill.

PART II The determination of fluorine in limestones and sandstones.

The Determination of Ba, V and Cr in the Whin Sill

The optical spectrograph was chosen for the determination of Ba, V and Cr content of the Whin Sill because all three elements were detectable on one plate covering the wavelength range of 3800 - 5300 Å, while use of the X - ray fluorescence apparatus for the determination of the elements would have entailed a separate analysis for each element.

Ahrens and Taylor (1961, p.189) discuss the analysis of the involatile group of elements, within which the above three are to be found. It is not deemed necessary to consider further here the theoretical aspects, or the analytical shortcomings of the method. The procedure given in Table 2-7 is a slight modification of the technique used by Taylor (1962).

The opacity of the lines was read on a Hilger and Watts non-recording microphotometer (L.450). The self - calibrating method as described by Ahrens and Taylor (1961, p.159 - 161) was employed, using a 7 step, step - sector (ratio 2:1) and using the first 3 steps.

The working curve was prepared from the international standards, Granite G - 1 and Diabase W - 1, using the values given below, (Fleischer 1965). Additional standards included Tonalite T - 1 (Thomas and Kemp, 1963); Syenite S - 1 (Webber, 1965) and Granite G - R (Govindaraju, 1963).

	Ba (ppm)	V (ppm)	Cr (ppm)
W - 1	200	240	120
G - 1	1200	-	22
T - 1	680	96	24
S - 1	300	88	-
G - R	-	90	112

In general, these standards bracketed the composition of the Whin Sill under investigation.

Table 2-7

Operating Conditions for the determination of Barium, Vanadium and Chromium

Instrument

Hilger and Watts Automatic Large Spectrograph E.742 with Glass Optical system E.744.

Charge preparation

Internal standard :- Johnson Matthey 'Specpure' Ammonium chloropalladite $(NH_4)_2PdCl_4$

Buffer :- National Carbon Company - Graphite (S.P.2)

Total sample mix :- 1 part sample and 3 parts Internal standard/buffer mixed in a plastic vial on a Spex Mixer Mill (No.8000).

Electrode Type

Anode :- National Carbon Co. - Carbon rods, special grade (L.3806) Diameter 0.180".

Dimensions of crater :- 2.5 mm. depth
⅛" diameter

Cathode :- National Carbon Co. - Carbon rods, special grade (L.3863). Diameter p.120".

Optical System

G lass Prism

Wavelength range :- 3800 Å - 5300 Å

Lens System :- A double lens optical system (using lenses F958 F 1025 & screen) with a 7 step sector, using the first 3 steps.

Slit :- height 3cm. width 10μ.

Camera diaphragm :- 4 mm.

Plate :- Ilford N 30

Analytical gap :- 4 mm.

Exposure

Current :- 6.8 A d.c. short circuit

Burn :- 5.6 A d.c.

Timing :- Preburn :- 10 seconds
Exposure:- 30 seconds

Photographic

Developer :- Kodak DX.80 for 3 minutes at 18°C.

Fixer :- Kodak AM 33 + H for 3 minutes

Washing :- 30 minutes

Finishing :- Plates rinsed in distilled water containing Kodak Photo - flo solution to ensure drying free from spots

Drying :- On an Applied Research Labs. Inc. dryer for 5 minutes

Lines

Analysis :- Ba 4934.086 Å
V 4379.238 Å
Cr 4254.346 Å

Internal standard :- Pd 4473.590 Å

The precision of the method was checked as with the X - ray fluorescence method of analysis. One sample was arced 10 times at random on the plates. Table 2-8 gives the precision data, which is considered satisfactory for the use to which the data ~~is~~are applied in this study.

Table 2-8

Analytical precision for Ba, V and Cr.

Element	Mean (ppm)	Standard deviation (ppm)	Relative deviation (%)
Ba	325	± 36.7	11.3
V	292	± 20.7	7.1
Cr	62	± 8.6	13.8

The Determination of Fluorine in Limestones

A large number of the wallrocks investigated in this study lie adjacent to fluorite veins or lead - zinc veins with subsidiary fluorite. It was therefore deemed imperative to investigate the wallrocks to determine whether or not an aureole of fluorine was present.

Seraphim (1951) indicates that the precision attainable by spectrochemical methods (in the region of 15 - 20%) is similar to that achieved chemically by Koritnig (1950). It was therefore decided to investigate the fluorine content spectrochemically rather than by 'wet' chemical methods.

Spectrochemical methods of detecting and determining fluorine have been used since Ryde and Yates (1926) discussed the intense and sensitive emission of CaF 5291 from a d-c arc. In 1930, Papish, Hoag and Shee were the first to use CaF 5291 in the analysis of minerals. Unfortunately no published work has been located in which the fluorine content of limestones was determined, it was therefore necessary to develop an analytical technique of reasonable accuracy and precision. The CaF bandheads are in the region of fairly intense background and it was necessary to keep this background to a minimum while not reducing the intensity of the CaF bandhead. To achieve this the following methods were available :-

(1) Careful choice of plate
(2) Use of a 'Stallwood' type gas jet to reduce the CN emission

Of the plates available covering the wavelength range 4600 - 9600 Å, Ilford R40 was found to give the best line to background intensity, in comparison with Ilford HP3 and FP4 plates.

Closely following the method, described by Curtis (1962), a modified Stallwood jet was made in the University workshop of stainless steel with a 'vitreoseal' internal collar, through which a gas mixture of the ratio (80% argon : 20% oxygen) was passed at a flow rate of 4 litres/minute. This reduced the background adjacent to the CaF bandhead considerably. Plate 2-1 shows the jet assembly on the optical spectrograph.

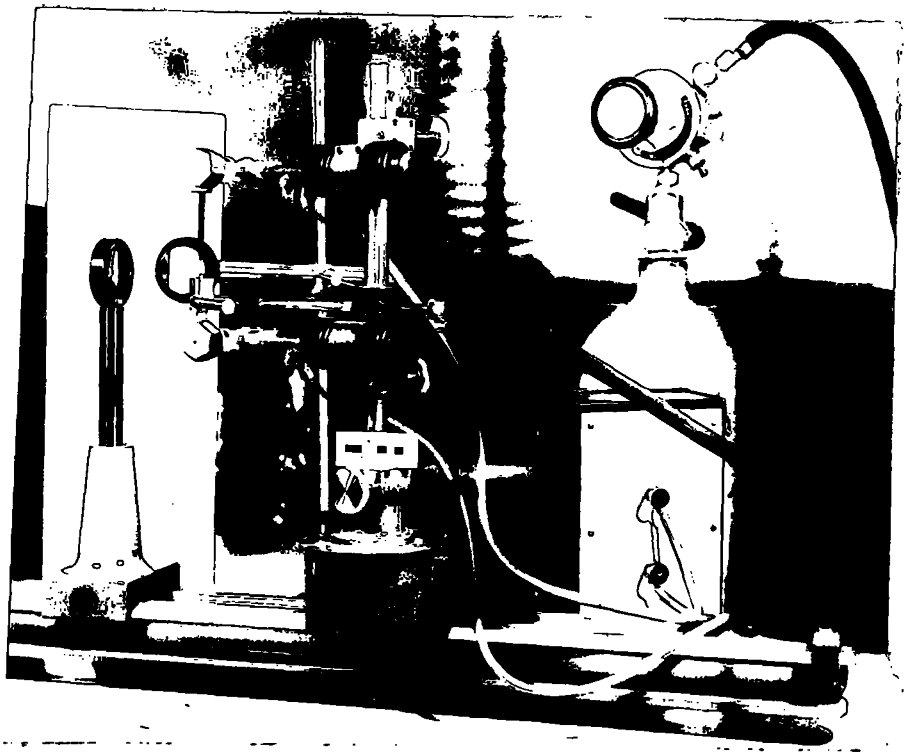


Plate 2-1.

The Stallwood jet assembly on the Hilger and Watts Automatic Large Spectrograph. (E. 742)

The reported reproducibilities for fluorine determinations are not very good (see Seraphim, 1951), but were found to be improved by the use of an internal standard, CaO (5488 Å), a component of the CaO orange band had been used previously as an internal standard for CaF 5291, where the rock type had a low calcium content. The intensity of CaO 5488 was found to be too great in the limestones.

Copper was chosen as an internal standard for this determination, as suggested by Gillis, Eeckhout and Kemp (1952) who determined fluorine in slags. Of the copper lines available (5105, 5153, 5220 and 5292) Cu 5105 was found to be satisfactory. Without an internal standard the reproducibility level was 25 - 35%, while with the addition of copper, as the internal standard, a reduction to the 15 - 20% level was attained

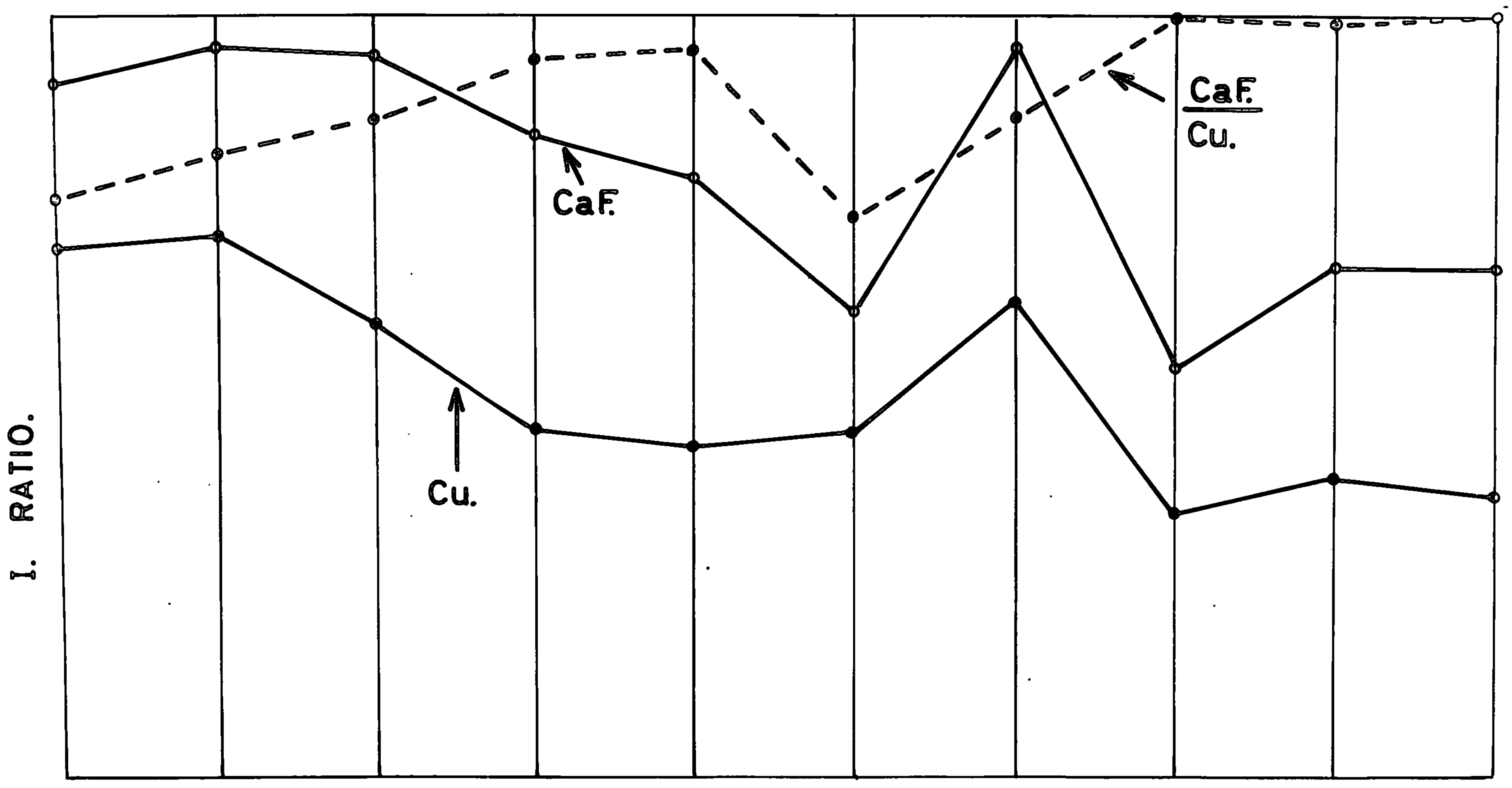


FIG. 2-10 REPLICATE DETERMINATIONS OF CaF 5921 & Cu 5105.

(see table 2-10). Fig. 2-10 illustrates the reproducibility of the method.

The effect due to the variation of the matrix of the samples, is counteracted by the addition of a suitable buffer (see Ahrens and Taylor 1961, p.128). In this study a preliminary test was made of carbon, and this element was found to give satisfactory results. Within the time available it was not possible to experiment with other types of material.

The calibration method was essentially similar to that used for the determination of Ba, V and Cr, except that the intensity readings from the microphotometer were fed into a computer programme (kindly supplied by Dr. M. Barrett of Keele University) which calculated the ratio :- Intensity CaF/Intensity Cu.

As no natural standards were available, a working curve was produced by the use of addition standards as previously described. The operating cohditions used throughout the analysis are shown in table 2-9.

Table 2-9

Operating conditions for the determination of Fluorine in Limestone

Instrument

A Hilger and Watts Automatic Large Spectrograph E 742 with glass optical system (E 744)

Charge preparation

Internal Standard :- Johnson Matthey 'Specpure' Cupric Oxide (CuO) J.M. 40.

Buffer :- National Carbon Co. - Graphite (SP2)

Ratio, sample to Internal Standard/Buffer :- 1 part sample to 2 parts Internal Standard/Buffer mixed in a plastic vial using Spex Mixer Mill No. 8000.

Electrode type

Anode :- National Carbon Co. Carbon rods (Cat.No. L.4306) Diameter 3/16"

Dimensions of crater :- ⅛" x 2.5 mm.

Cathode :- Johnson Matthey Carbon Rods (Cat.No.J.M. 1205) Diameter :- 5mm.

Optical System

Glass Prism

Wavelength range :- 4600 - 9600 Å

Lens system :- Hilger E 958 focussed on slit - 7 step sector using first 4 steps (2:1 ratio).

Slit :- height :- 6 mm. width :- 10μ.

Camera diaphragm :- 7mm.

Plate :- Ilford R40

Analytical gap :- 5 mm

Exposure

Special conditions :- arc in an atmosphere of Argon : Oxygen (ratio 80 : 20) - at a flow rate of 5 Litres/min. - through a modified Stallwood jet.

Current :- 6.8 A d.c. short circuit

Burn :- 6 A. d.c.

Timing :- preburn :- none; Exposure :- 30 secs.

Photographic

Developer :- Ilford PQ Universal for 4 minutes at 20°C.

Fixer :- Kodak AM 33 + H for 3 minutes

Washing :- 25 minutes

Finishing :- Plates rinsed in distilled water containing Kodak Photo - flo solution to ensure drying free from spots

Drying :- On an Applied Research Labs. Inc. dryer at mark 2 for 3 minutes.

Lines

Analysis :- CaF 5291.0 bandhead

Internal standard :- Cu 5105.541

As a check on precision, two samples were both arced six times (L/OE/3 and L/HW/4).

Table 2-10

Analytical Precision for Fluorine

Sample	Mean	Standard deviation	Relative deviation
L/OE/3	3.7%	± .372%	10%
L/HW/4	7250 ppm	± 864.3ppm	12%

As there was no limestone 'standard' samples with known fluorine content it is very difficult to assess the accuracy of the method. The two limestones used for the precision determination, were kindly analysed by Dr.P.G.Jeffery of Warren Springs Laboratory; using neutron activation and pyrohydrolysis techniques; the following table summarises the results obtained:-

Table 2-11

Comparative Fluorine Analyses of Two Limestones

Sample	Emission Spectrographic (D)	Neutron Activation (W.S)	Pyrohydrolysis (W.S.)
L/OE/3	3.70%	5.50%	5.21%
L/HW/4	0.72%	0.70%	0.44%

D - Durham University

W.S - Warren Springs Laboratory

The Determination of Fluorine in Sandstones

The fluorine content of twenty three sandstones was determined by Mrs. M.Kaye using an essentially similar technique as previously described, however, no internal standard was used and the calibration was done on a single characteristic curve. As a measure of the precision of the method, sample BL.4 (mean content of fluorine 500 ppm.) was arced 15 times giving a standard deviation of ± 74 ppm and a relative deviation of 15%.

Table 2-12

Comparative results of the fluorine content of two sandstones (ppm)

Sample	Emission Spectroscopy	Neutron Activation	Pyrohydrolysis
B.S. 12	750	4600	800
B.L. 4	500	3600	360

X - Ray Diffraction Analysis

The Clays in the White Whin

To effectively separate the clay minerals, the White Whin was disaggragated under distilled water in an agate mortar and pestle. After a minimum amount of grinding the contents of the mortar were transferred to a large diameter (12 mm.) bottle, shaken vigorously and allowed to settle for 90 minutes. The top 12 cms. of suspension were withdrawn after this period and evaporated to dryness at a temperature of less than 100°C. This fraction is composed essentially of clay minerals and a small proportion of quartz impurity. Flocculating agents added to the suspension did not improve the separation and introduced the possibility of contamination.

The identification of the clay minerals was undertaken using a Phillips X - ray diffractometer (P.W. 1050) with the operating conditions as specified in the following table :-

Table 2-13

Operating conditions of the X - ray diffractometer

Tube and voltage :- Copper target operated at 40 kV and 20 mA.

Filter :- Nickel

Slits :- Divergence 1°, receiving 0.1°, scatter 1°.

Scan speed :- 1° (2θ) per minute

Chart speed :- x20 or 800 millimetres/hour giving 10 chart divisions for 1° (2θ)

Rate meter :- 2

Time constant :- 8

Multiplier :- 1

Counter :- proportional counter at 1730 volts

Discriminator :- amplitude :- 20.0 volts
channel width :- 4.0 volts
attenuation :- 4.0 volts

The normal cavity mount produced preferred orientation of the sample, to overcome this effect an 'end-on' loading cavity mount was employed. Subsequent analyses indicated that although not completely eliminated, the preferred basal orientation had been reduced to an acceptable level.

The scheme for the identification of the layered silicates was identical to that described by Warshaw and Roy (1961). The sample is treated as follows:

(i) X - ray an unorientated sample

(ii) X - ray the orientated sample after treatment with ethylene glycol.

(iii) Heat the sample to 250°C and 500°C, X-raying at each temperature.

Changes in lattice parameters and crystal structure induced by stages (ii) and (iii) limit the identification of clay minerals to narrow fields of composition.

The Quantitative Mineralogy of the Limestones

The quantitative mineralogy of the limestones was determined on orientated powder samples using a Phillips X - ray Diffractometer (P.W. 1050). The method was similar to that described by Schultz (1964) and Tennant and Berger (1957).

Standards were prepared by making up various combinations of mixes of finely ground pure minerals, that is, quartz, dolomite, siderite, calcite and clay. A total of 10 standards was prepared by finally grinding and mixing on a Spex mixer Mill (No.8000) and finally by hand with an agate pestle and mortar.

The standards covered the following ranges :-

Quartz	5% - 40%
Dolomite	5% - 40%
Siderite	0% - 15%
Calcite	30% - 90%
Clay (Kaolinite)	0% - 15%

Working curves were constructed for each mineral and found to be satisfactory with the exception of clay and samples containing a large percentage of iron.

The samples were the same as those employed for the trace element analysis. Four separately prepared cavity mounts of each sample were run on the diffractometer. The instrument conditions are shown in table 2-14.

Table 2-14

Operating Conditions for the Quantitative Mineralogy of Limestones

Tube and voltage :- Copper target operated at 40 kV and 20 mA
Filter :- Nickel
Slits :- Divergence 1°, receiving 0.1°, scatter 1°
Scan speed :- $\frac{1}{4}^{\circ}$ (2θ) per minute
Chart speed :- x20, or 800 millimetres/hour
Ratemeter :- 32 for calcite, 16 for quartz and dolomite,
8 for siderite and clays.
Time constant :- 4
Multiplier :- 1
Counter :- proportional counter at 1730 volts
Discriminator :- amplitude - 31.0 volts
channel width - 8.0 volts
attenuation - 4.0 volts

To attain maximum stability of the diffractometer the X - ray generator (low tension), the counter, discriminator and associated electronics were left on for the duration of the analysis. To ensure better stability a wider channel width (8) than normal was used.

The following peaks were used :-

Quartz :- 3.34 Å
Dolomite :- 2.88 Å
Siderite :- 2.79 Å
Calcite :- 3.03 Å
Clay :- 4.50 Å

Background was subtracted from the lines used and a plot of peak - background against concentration (in per cent) was used.

The accuracy of the method was checked against the major element analyses, where the chemically determined CO_2 was converted to the respective carbonates. Satisfactory agreement was obtained for the majority of the determinations.

The precision of the method was found by reloading separately prepared cavity mounts. For quartz and calcite the relative deviation was less than 10%, for dolomite and siderite less than 15%. At low concentrations these elements gave a poor precision which improved with increasing concentration, so that in excess of 5% the relative deviation was under 10%.

Additional Analytical Techniques

Total Chemical Analysis

To assist in the petrological examination of the alteration of the quartz-dolerite dykes at Closehouse Mine, total chemical analyses were carried out on altered and unaltered samples. The analytical procedure was similar to that described by Shapiro and Brannock (1962). All the analyses were done in duplicate.

CHAPTER III

TRACE ELEMENT WALLROCK AUREOLES IN SEDIMENTS

The mineralogical alteration of the wallrocks adjacent to the lead-zinc-fluorite-barite veins of the Pennine orefields has been described by Dunham (1948 and 1952). The present study was primarily concerned with the minor element variations which accompany the major chemical and mineralogical changes in the wallrocks.

The prerequisite assumption in the investigation of dispersion patterns adjacent to orebodies, is that the abundance of an element is relatively constant in an area which has not been affected by the presence of a mineral deposit. This factor is called the background concentration of the element. The initial sampling programme was therefore directed towards an estimation of the average concentration of the trace elements in unmineralised areas. Samples from the Alston Block and the Derbyshire orefield were collected as far as possible from the mineralization. Table 3-1 gives the trace element content of thirty samples from each area. The variation is seen to be small for most of the elements.

Table 3-1

The Background Concentration of the Trace Elements in the Pennine Limestones (in ppm)

	Alston Block		Derbyshire	
	(Great Limestone)		(D_2 Limestone)	
Element	Average	Range	Average	Range
Rb	< 5	-	< 5	-
Pb	~ 22	20-30	86	20-95
Sr	1750	1680-1900	550	500-620
Mn	350	330-370	200	170-245
Zr	< 10	-	< 10	-
Zn	< 6	5-10	< 5	-
Cu	~ 15	15-20	~ 15	15-25
Ni	20	15-25	8	5-12
Fe	200	100-320	-	-
F	< 250	-	< 250	-

The results give an average trace element concentration for the two limestones. However, work carried out by Lamar and Thomson (1956) indicates that within a given limestone the trace element content may vary in both a horizontal and vertical traverse. The dispersion anomalies revealed by this investigation were not, therefore, considered to have attained a background concentration when the above figures had been obtained. In this work, if after a zone in which the elements showed radical variations, they approached a reasonably constant value, the background value was considered to have been attained (see figs. 3-1 to 3-22, in illustration of this practice).

Trace Element Variations in Limestones

Trace element variations in limestone host rocks are described under the same headings as those adopted for the description of the sampling areas.

The Northern Pennine Orefield

The Great Limestone at Surface

Six traverses through limestone adjacent to veins were taken across outcrops of the Great Limestone in Weardale. The resultant variations in trace elements are illustrated in figures 3-1 to 3-6 and 3-8.

Heights Quarry, situated between Eastgate and Westgate, is intersected by four veins. During this investigation two of the veins, the South vein and the West Cross vein, were studied, since recent quarrying operations had made wallrocks easily available. The West Cross Vein where exposed in the quarry is approximately 5 feet wide, and is composed of fluorite, limonite and some galena; the limestone wallrocks show intermittant limonitization. The sampling traverse, was chosen so that this limonitic zone was avoided. Fig. 3-2 illustrates the trace element aureole adjacent to the vein. Significant variation is seen to extend for approximately 9 feet into the wallrocks.

The points of interest are the small, but significant aureole of zirconium (5 feet wide); beyond 5 feet the element was not detected, while at 3, 1 and 0 feet, the concentrations of 17, 20 and 30 ppm. were recorded; a very narrow zone (2 feet), in which strontium decreased from a value of 1640 ppm. to one of 40 ppm.; while beyond 2 feet the content varied between 1900 and 1340 ppm. The similar aureole widths of zinc and lead are noted, which beyond 9 feet were uniform in value; lead increased from 35 ppm. to 945 ppm, and then decreased to 515 ppm as the vein was approached; while zinc at 15 ppm. increased to 2000 ppm. again to decrease to 505 ppm. adjacent to the vein. Values of 20 and 38 ppm. respectively for copper and nickel on the vein wall, were found to be below the detection limit of the analytical technique; for the other samples, except for anomalous results from 3 feet where values of 65 ppm. (copper) and 12 ppm. (nickel), were recorded. The expected aureole of fluorine was not found, the only sample which contained a detectable amount was that from the vein wall which gave a value of 4000 ppm. fluorine. The background value, of 300 ppm. for manganese, increased logarithmically towards the mineralization where it attained a value of 7500 ppm. Iron values recorded from the six samples gave very erratic values (5900 to 1220 ppm.) and iron was seen to be the only element which did not, in excess of 9 feet, produce a uniform pattern with respect to the other elements. It is concluded that the trace element aureole adjacent to the West Cross Vein has a width of 9 feet, beyond 9 feet the trace element content of the limestone has reached a relatively constant value, which is here taken as the background value.

Heights South Vein (fig.3-1) trends N80°E and consists of coarse fluorite and quartz with no visible contamination due to lead or iron; where sampled it had a width of 3 feet. A different dispersion pattern is shown to that of the West Cross Vein. All the principal element variations occur within 3 feet of the vein. In this distance lead and zinc decrease to an undetectable level, strontium decreases to 40 ppm. and no zirconium is evident. At distances in excess of 3 feet, apart from an increase in lead at 9 feet, the trace element content of the limestone assumes a constant background level.

Comparison of the two aureoles indicates that the aureole width adjacent to the West Cross Vein is three times as great as that against the South Vein. This is consistent with the visual strength of mineralization in the two veins.

Coves, or Park Vein, exposed in Ashes Quarry north of Stanhope, carries fluorite, quartz and siderite as the vein constituents. The sampling traverse was restricted to a single horizon which appeared

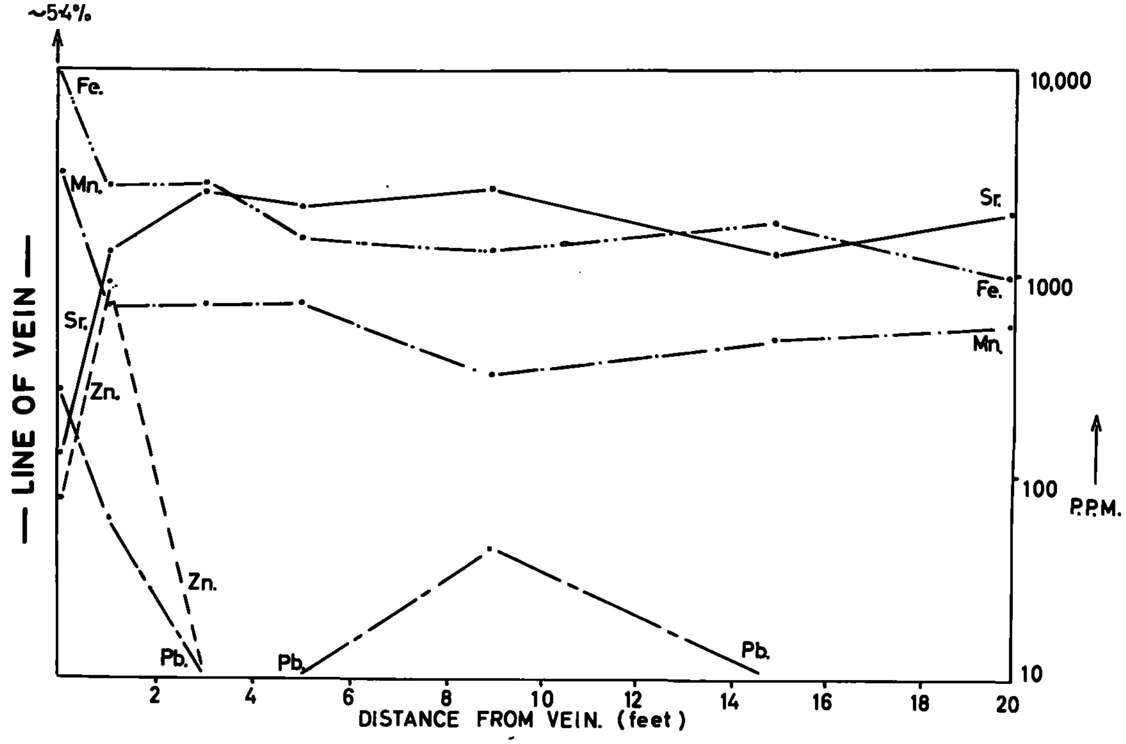


FIG. 3-1 DISPERSION PATTERN — HEIGHTS QUARRY.

SOUTH VEIN

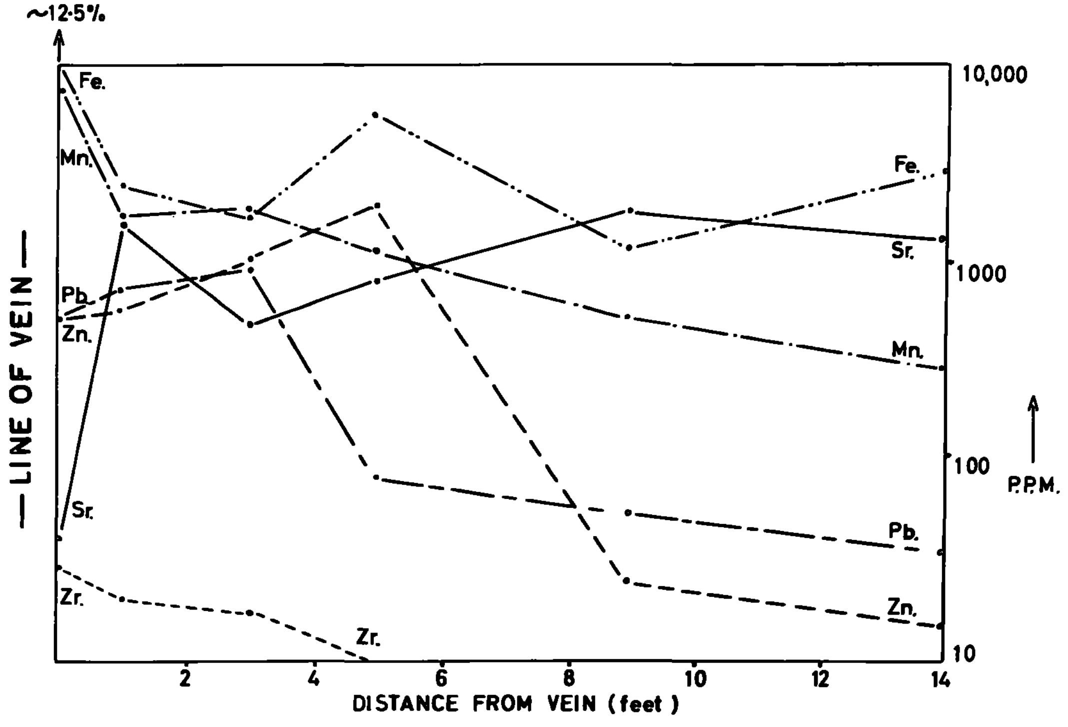


FIG. 3-2 DISPERSION PATTERN — HEIGHTS QUARRY.

WEST CROSS VEIN

to be a fresh, unaltered limestone. Small and irregular fluorite flats were, however, exposed approximately 20 feet above the sampling traverse. Fig.3-3 illustrates the trace element variations. Copper and nickel, respectively 32 ppm. and 30 ppm., were detected in the vein, the concentration decaying to 15 and 23 ppm. within 2 feet and becoming undetectable at greater distances. Fig.3-3 illustrates the decrease in strontium and the increase in iron, manganese, zinc and zirconium towards the vein. Lead gives erratic values along the traverse, while fluorine, undetectable in this part of the traverse, increases with horizontal distance from the vein, although it is not visibly present as fluorite. Summarising the results, variations in the trace elements are restricted to a zone of approximately 5 feet wide on either side of the vein, with abnormalities introduced by fluorine, lead and zirconium to distances of 20 feet.

What is described locally as a 'vein rider', intersects Harehope Quarry, and consisting mainly of limonitic material, was studied for comparison with the known veins of the orefield. Fig.3-4 illustrates the major variations in the trace elements. The high iron content in wallrocks to a distance of 4 feet was not surprising, but the depletion of strontium to a distance of 8 feet is considerable in relation to the size and mineral content of the vein. A very restricted aureole of zinc is indicated (maximum extent of 1 foot), nickel and zirconium likewise give a restricted aureole. The evidence suggests that the 'rider' carried appreciable amounts of ore.

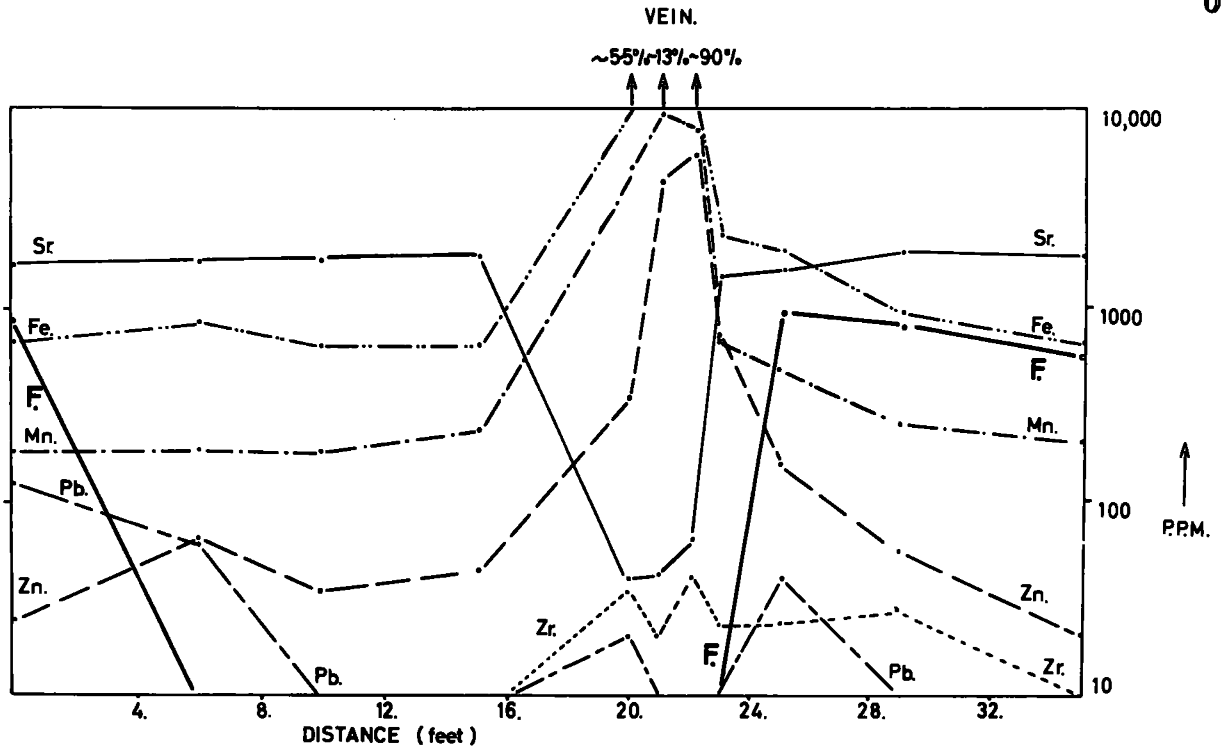


FIG. 3-3 DISPERSION PATTERN — ASHES QUARRY.

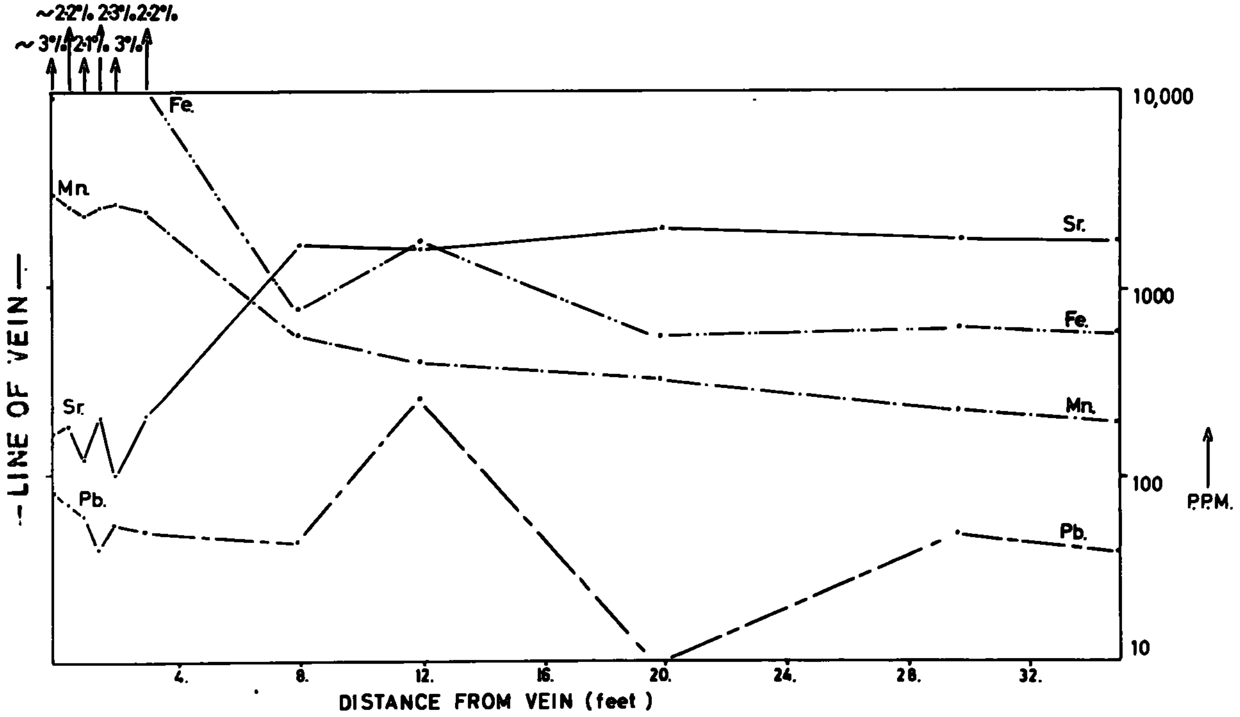


FIG. 3-4 DISPERSION PATTERN — HAREHOPE QUARRY.

Newlandside Quarry, south of Stanhope, is intersected by two unnamed veins; they are prominently displayed in the large bluffs left standing in the quarry face. The largest of these veins has extensive fluorite flats visible, but unattainable, from the quarry floor. Sampling of one stratigraphic horizon through which two very small fractures (1-3" in width) passed was undertaken, to determine if one or other could have been a possible feeder to the mineralization. Fig. 3-5 shows the results obtained from the ten samples collected. Both the fractures have wide aureoles in relation to their size. The easterly aureole has a width of 5 feet while the westerly one gives an extensive zone (13 feet) of trace element divergence from the background values. A curious feature is the absence of detectable fluorine, although large cubes of yellow fluorite were situated at a higher level.

Figs. 3-6 and 3-8 illustrate the trace element aureoles produced adjacent to a small, unnamed vein less than 2 feet wide, trending NW-SE which intersects Lanehead Quarry, north of Stanhope. A little fluorite and galena with quartz comprise the vein's constituents. Diagrams A and B are traverses to the south of this vein. A suitable horizon to the north was unobtainable, as scree material from the quarrying operations obscured in situ material. Although all the samples collected were free from visible mineralization, at a distance of between 15 and 35 feet and a height of 30 feet, a small flat was discovered in the limestone. The erratic values of lead and zinc shown on the diagrams indicate the proximity of the flat.

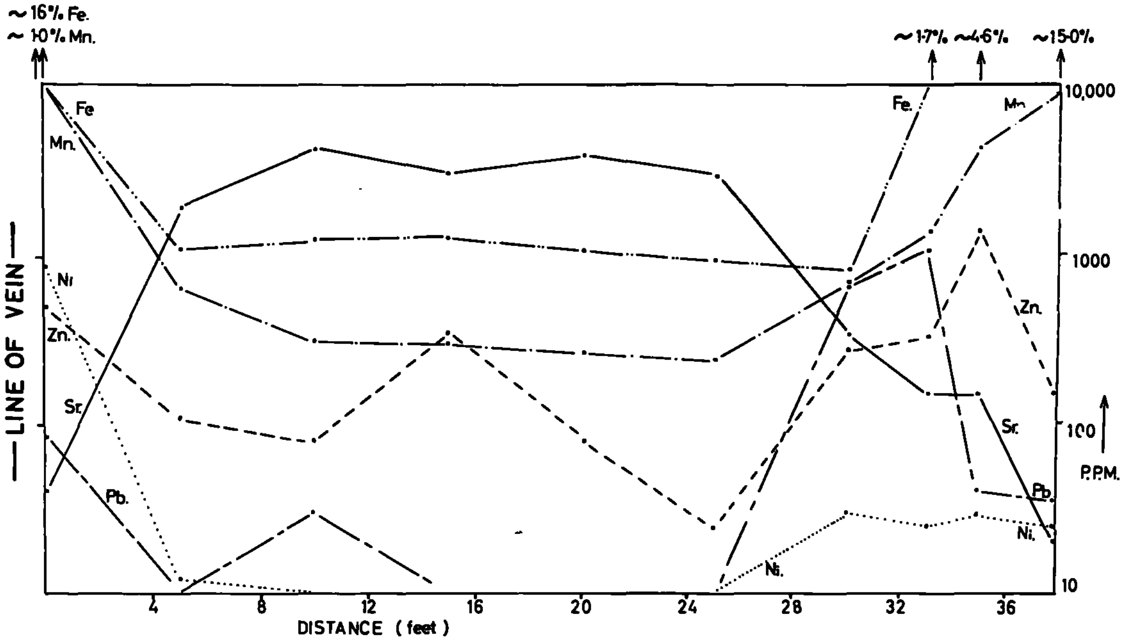


FIG. 3–5 DISPERSION PATTERN — NEWLANDSIDE QUARRY.

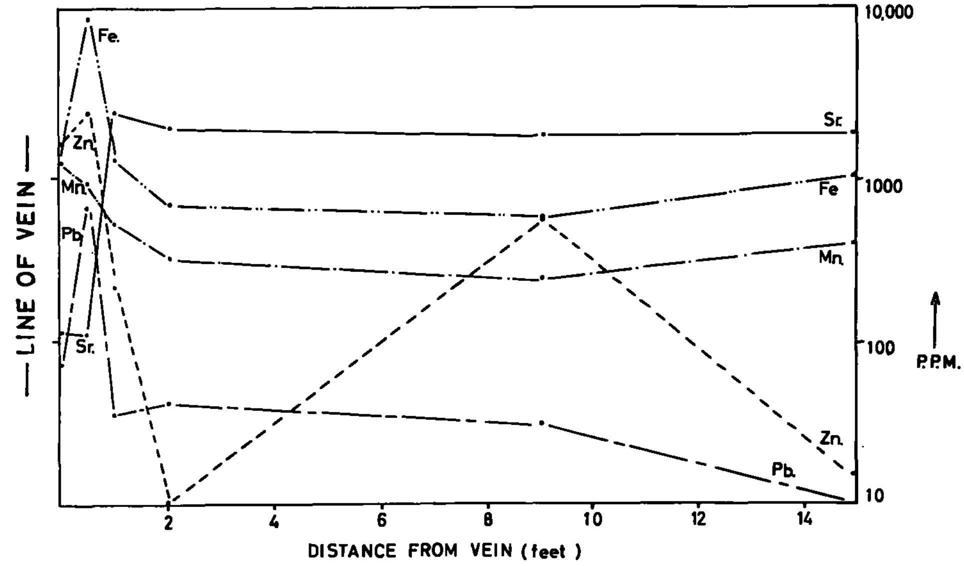


FIG. 3–6 DISPERSION PATTERN — LANEHEAD QUARRY. (A).

While discussing the aureoles from surface localities in the Northern Pennine Orefield, it is considered pertinent to include here the dispersion pattern of the trace elements adjacent to a vein which intersects the argillaceous Tyne Bottom Limestone, for comparison with aureoles in the clearer Great Limestone.

The wallrocks of Browngill Vein, exposed in the stream to the north of the village of Garrigill, were sampled to a distance of 40 feet from the vein. The vein is composed of a small number of irregular stringers which carry galena and limonite with quartz-filled vugs. A distinct vein margin was undefinable under these conditions, and the sampling commenced at an arbitrary point in the wallrocks north of the vein and extended in a southerly direction. Fig.3-7 illustrates the trace element variations. It might be argued that the background level has been attained at approximately 24 feet, but it is more likely that the traverse at 35 feet had not reached the background level. If this conclusion is correct, the width of the aureoles is substantial in comparison to the vein strength, composition and character. The migration of the elements studied, is of a far greater magnitude than in any other calcareous environment investigated; with extensive aureoles of copper, zirconium, zinc and fluorine. It may be noted that near Garrigill, at the old Tynebottom and Rotherhope Fell mines, very extensive replacement deposits extending as much as 100 feet from the vein, were formerly worked (Dunham, 1948, p.177).

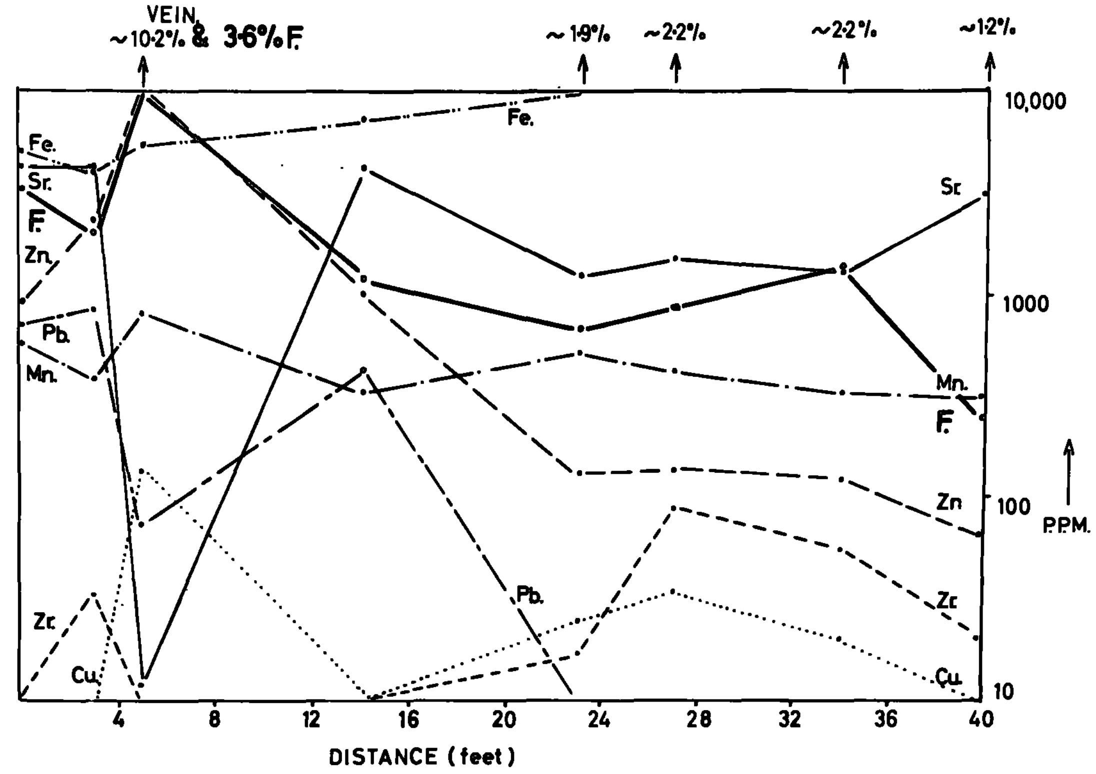


FIG. 3-7 DISPERSION PATTERN — GARRIGILL.

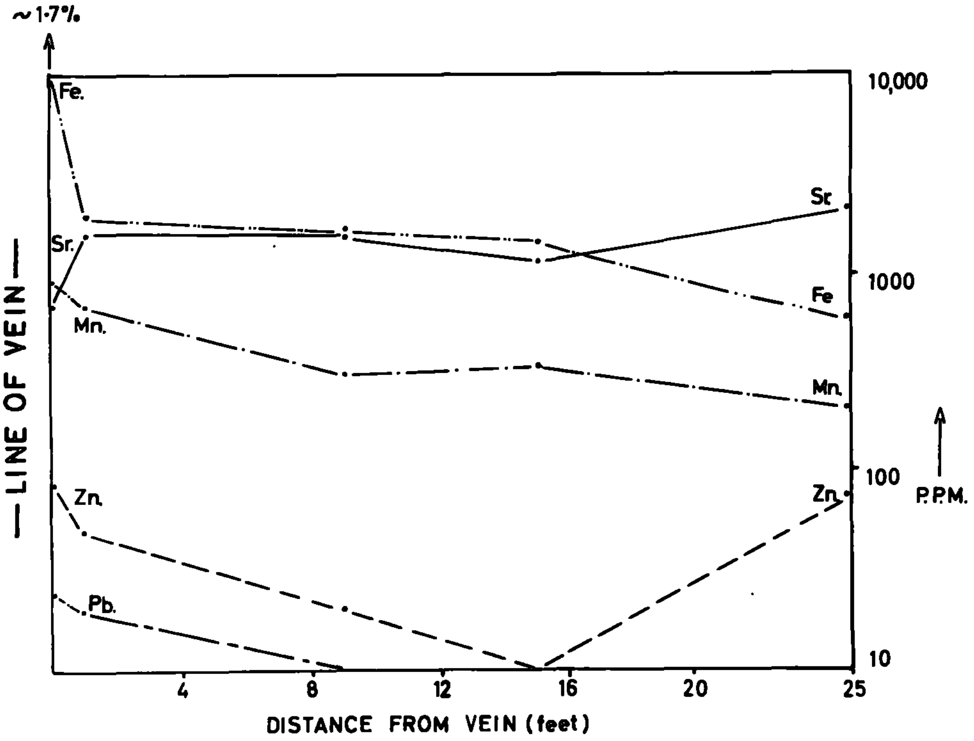


FIG. 3-8 DISPERSION PATTERN — LANEHEAD QUARRY. (B).

The Great Limestone at Depth

The secondary mobilisation of certain elements due to near-surface leaching by groundwaters, has been reported (Hawkes, 1957). In order to ascertain whether any of the previously described dispersion patterns had been affected by groundwaters circulating in the oxidation zone, a sampling programme was undertaken at depth adjacent to similar mineralization and in similar wallrocks. The comparison of the width and concentration of the respective dispersion patterns from surface and underground localities, would, it was hoped, indicate if this possibility was real.

The two underground sampling programmes in the Great Limestone were adjacent to veins of different mineral composition. Swinhope Mine is transected by four veins thought to be interconnected, but which carry predominantly zinc; while Redburn Mine at the same stratigraphical horizon is working the Red Vein, the major producer of fluorite.

An exploratory crosscut at Swinhope Mine, previously indicated in fig. 2-2, enabled the wallrocks adjacent to Williams Vein, the North Vein and the Number One Vein to be sampled. Fig. 3-9 illustrates the results obtained from the analytical work on the samples. Williams Vein is the continuation, in the Swinhope Valley, of the Barneycraig Vein of the West Allen Area, and perhaps of the St. Peter's Vein beyond the Burtreeford Disturbance. Where intersected in the mine, the vein varies in width from 1½ feet to 5 feet, with some small flats developed on either side of the main leader.

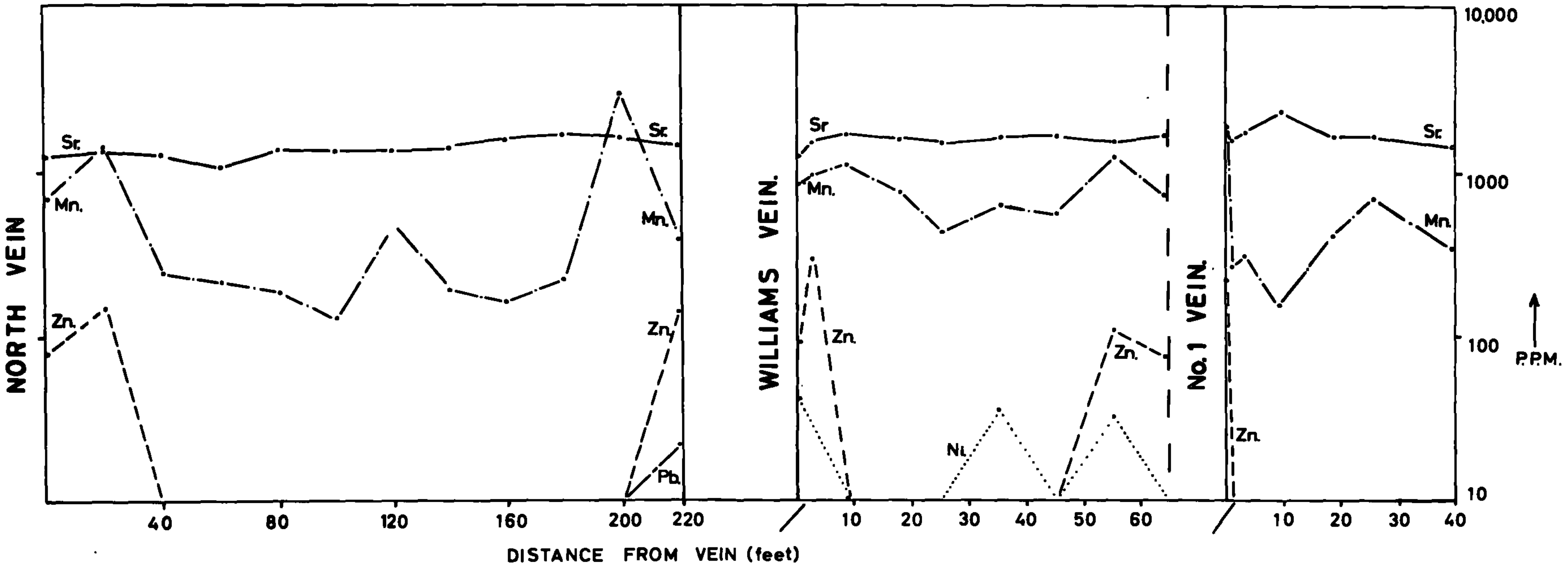


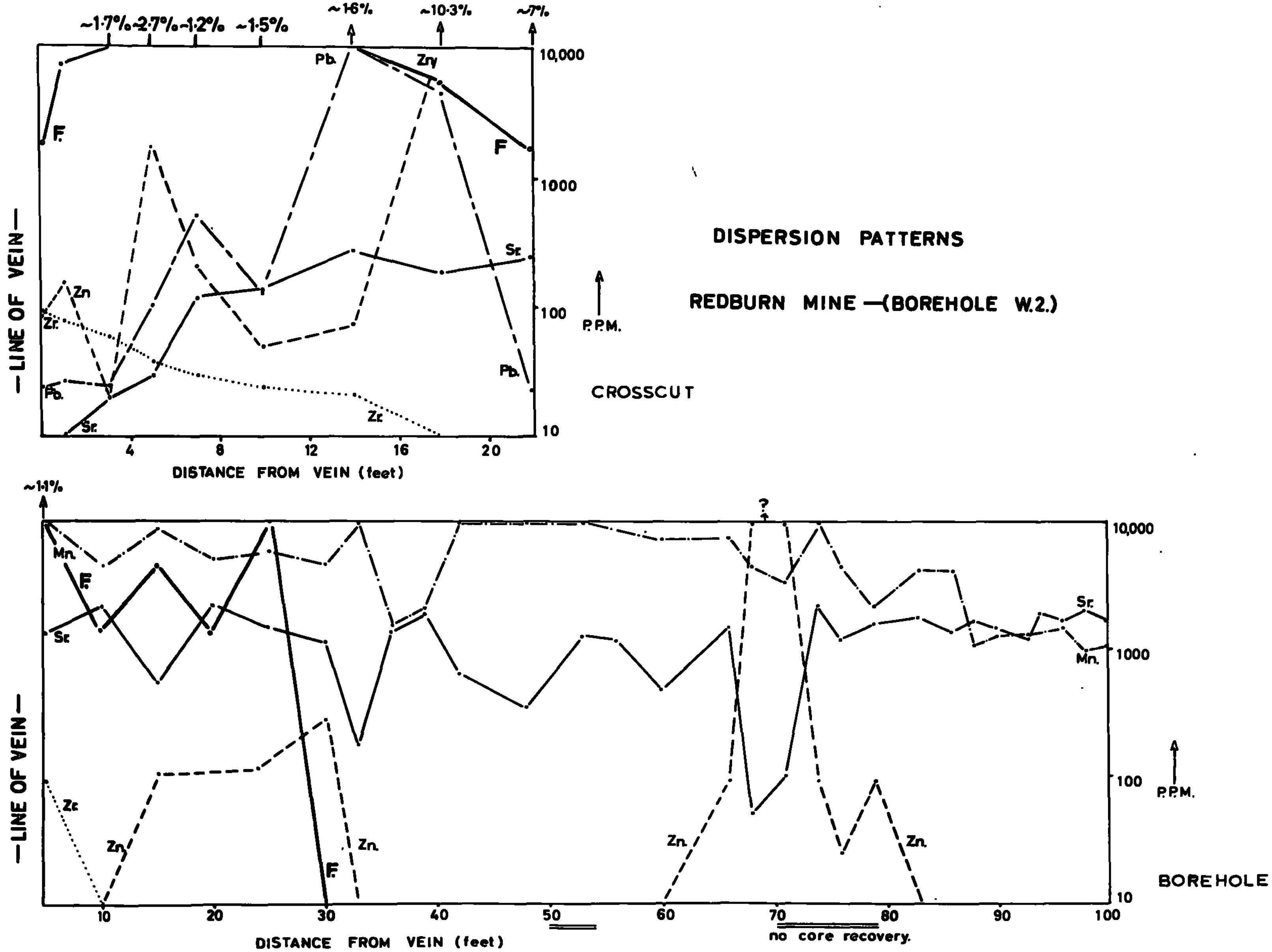
FIG. 3-9 DISPERSION PATTERNS — SWINHOPE MINE.

Sphalerite, galena, pyrite, quartz and siderite are present, but no fluorite was observed. The mineralogical composition of the North and Number One Veins are similar, North Vein is reported to have a greater amount of sphalerite with only minor galena (personal communication Mr. J. Lee). The trace element variations adjacent to these veins substantiate the above remarks, for the widest zinc aureole was located adjacent to North Vein, while Williams and Number One Veins have restricted zinc aureoles. Lead was only detected in the wallrocks adjacent to the Williams Vein. The expected decrease of strontium occurred near the ore, but was limited in width and magnitude (i.e. 5 feet wide with a drop of 120 ppm.) The traverse between the Williams and the Number One Vein produced anomalous values of nickel, while along the three traverses manganese showed erratic variations.

Two horizontal, exploratory diamond drill holes, out from the Red Vein at Redburn Mine, enabled the dispersion patterns adjacent to this major vein to be studied. The possible existence of another vein was also investigated, this vein occurring in a region where core recovery had been impossible (see fig.3-10).

Red Vein is the northernmost of the three great 'Quarter-point' veins of Weardale (Dunham, 1948, p.243), the other two are the Sedling - Longsike Vein and the Slitt Vein. All three have common characteristics, the oreshoots are spread over a considerable vertical range of strata and they support wide orebodies in which fluorite is the principal mineral, the lead values are generally of a low amount. Red Vein, where sampled, was no exception, the vein width was between 12 and 15 feet wide, composed predominantly of fluorite with an appreciable amount of intermixed silica, ankerite and a little galena. Figs.3-10 and 3-11 show the results obtained from the two diamond drill holes. The uppermost diagrams in fig.3-10 gives the dispersion pattern in a small crosscut driven prior to extending the main W - 2 borehole. As both boreholes were driven out from the same vein, comparable dispersion patterns were expected, but this was not found to be the case for certain elements. Borehole W - 2 (fig.3-10) in which no core was recovered in two sections, has a typical dispersion pattern. The strontium value decreases from a distance of 14 feet as the ore is approached. The aureole of lead is large, 22 feet in width, while the zinc aureole is of a greater width and of a more erratic nature. Compared to other fluorite veins, zirconium presents a substantial aureole (18 feet in width). Fluorine was not detected in the limestones at a distance greater than 30 feet from the vein. The rapid decrease of strontium with a concurrent increase in the zinc content near the area of zero core recovery, suggested that a vein of some magnitude might be present between 72 and 75 feet from the major orebody.

Fig.3-11 illustrates the dispersion pattern obtained from borehole N - 2 this aureole shows a comparable decrease of strontium adjacent to, and for a distance of 30 feet from mineralization, with erratic values of zinc and nickel along the total length of the hole. The absence of lead in the aureole might be attributed to the fact that at this locality



DISPERSION PATTERNS

REDBURN MINE —(BOREHOLE W.2.)

FIG. 3-10

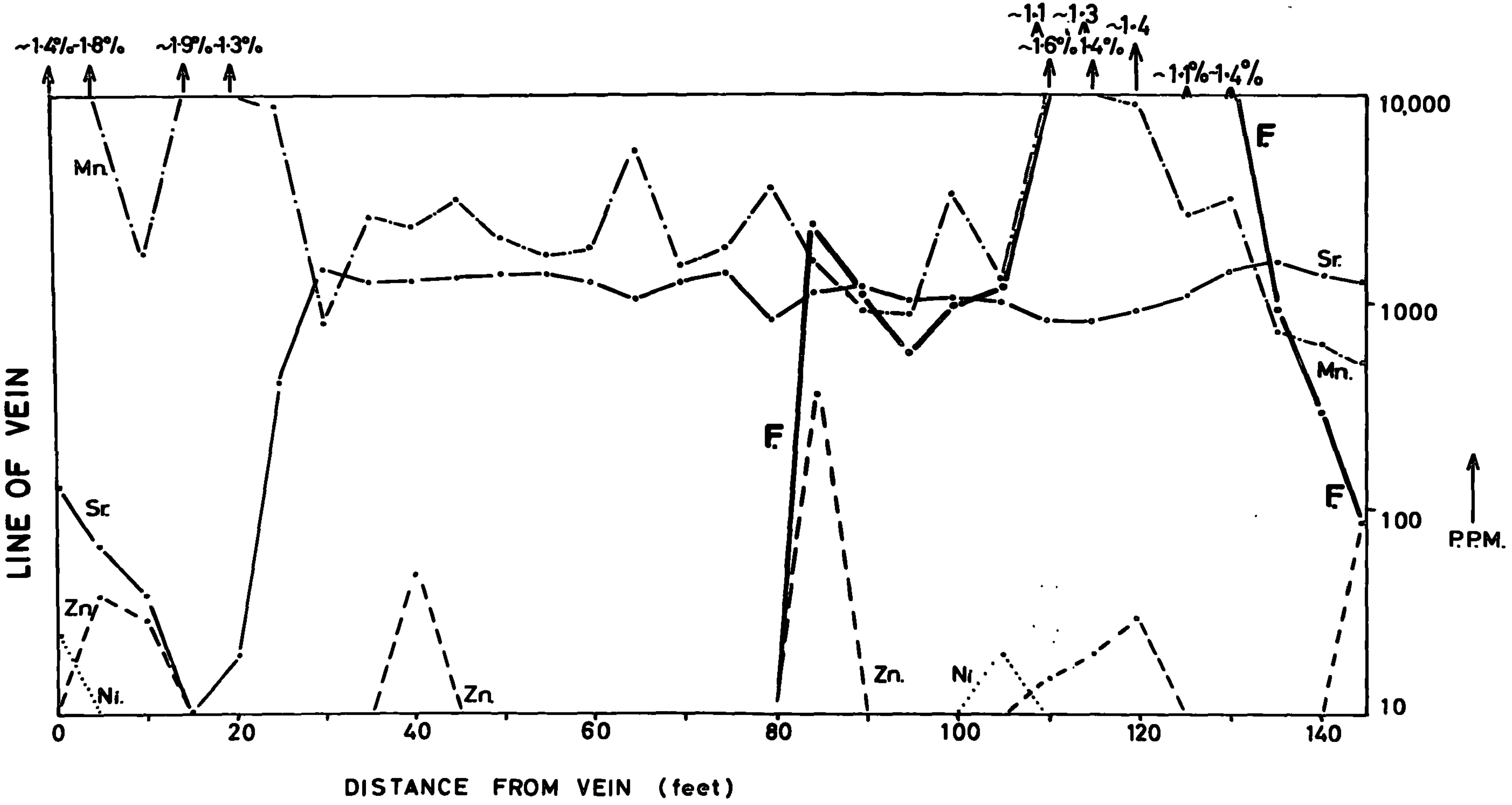


FIG. 3-11 DISPERSION PATTERN — REDBURN MINE (BOREHOLE N.2.)

the major vein carried little or no lead. The erratic nature of manganese is again evident, with a substantial increase towards the main orebody. The notable feature of this pattern is the incoming of fluorine at a distance greater than 80 feet from the Red Vein, which continued as far as the borehole was extended, although no detectable fluorine was found adjacent to this vein. Within the 60 feet of core which showed anomalous fluorine values, the zinc, nickel and manganese contents increase while strontium, although depleted, is not decreased to the same extent, as is the case adjacent to the known mineralisation. No visible leader or vein was detected in the core, which had a high recovery.

The Derbyshire Orefield

Trace element dispersion patterns adjacent to the fluorite veins of the Derbyshire Orefield were studied for comparison with the aureoles from the Northern Pennine Orefield. It has already been shown that the Carboniferous D_2 Limestones of Derbyshire (see table 3-1) are purer than the Great Limestone; for example, the average strontium contentwas 250 ppm. compared to 1400 ppm. for the Great Limestone. It was expected that the basic differences in the limestone would be reflected in the type of dispersion pattern, its width and magnitude.

The majority of the sampling traverses adjacent to mineralization in the Derbyshire Orefield, were in the Upper Dibunophyllum subzone (D_2) of the Carboniferous Limestone, in strata for the most part, probably older than the strata sampled in the Alston Block area.

The Laporte Concessions Area

The mineralization of the Eyam district of Derbyshire is substantial and includes three major veins, together with numerous subsidiary orebodies. Hucklow Edge, Old Edge and Longstone Edge vein systems are the predominant fissure veins of the district. These veins were sampled in the Ladywash and Sallet Hole mines. The northernmost of the three veins, Hucklow Edge vein, has been investigated at the present extremity of the eastward and westward workings in Ladywash Mine (see fig.2-7). The results obtained are presented in figures 3-12 and 3-13.

A cursory glance at the two diagrams indicates a remarkable similarity, especially in the width of the fluorine aureole (35 feet), and the constant background values of strontium and manganese. The erratic variation of lead and zinc is also a common feature. In detail the two diagrams reveal substantial divergence. The Hucklow Edge (West) sampling traverse has higher background values for lead, a very wide aureole of zirconium, and a zone of approximately 10 feet within which element variations are considerable. The reason for this is evident, when it is realised that a basaltic lava flow underlies the limestone sampled, at a depth not greater than 15 feet. This flow is known to rise westwards, for it is encountered in the continuation of the mining operations. Predominantly composed of fluorite with galena, calcite and some limonite to the east, the vein also changes composition westwards, its limonitic content decreasing with a concommitent increase in barite.

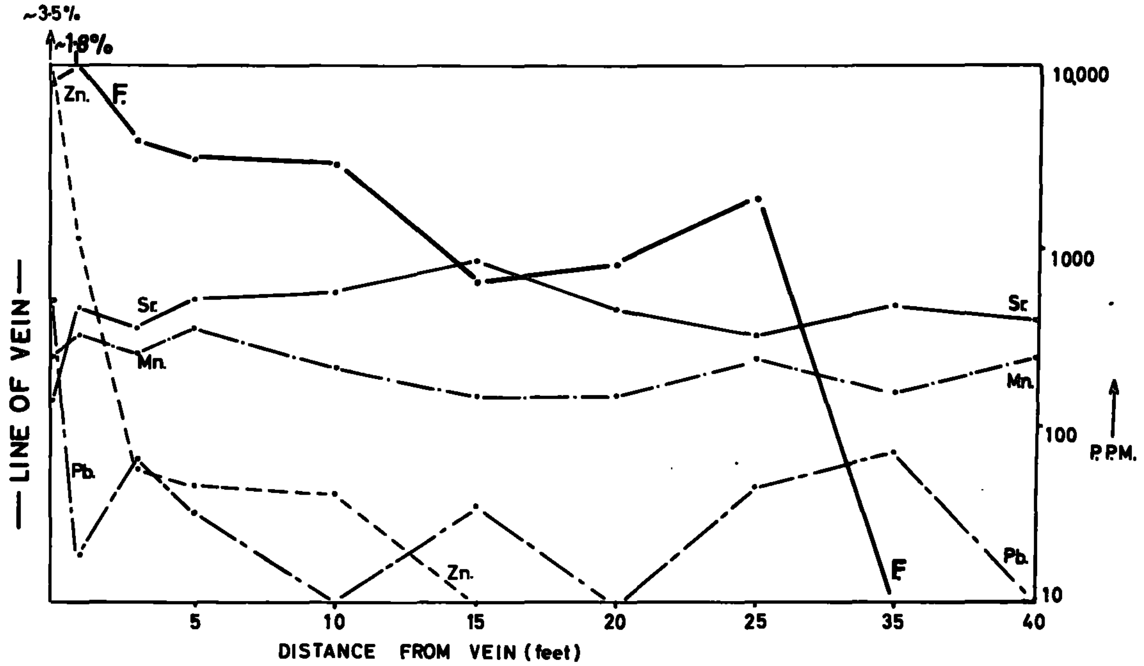


FIG 3-12 DISPERSION PATTERN — LADYWASH MINE.
(HUCKLOW EDGE VEIN — EAST)

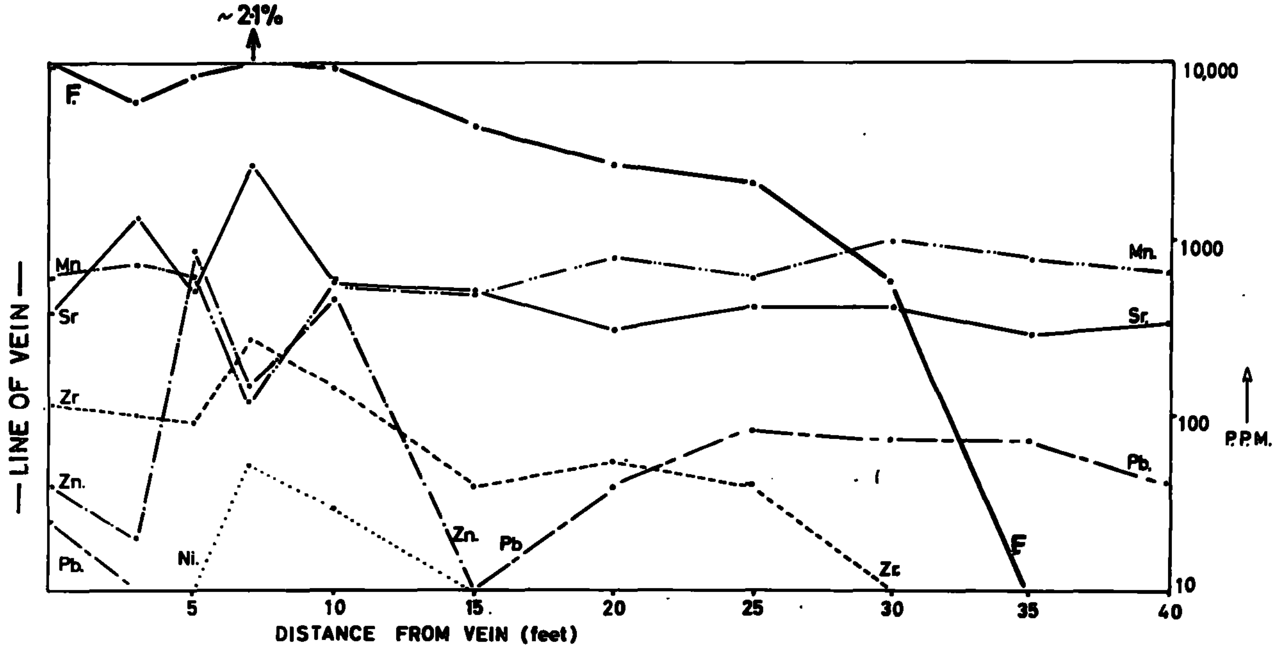


FIG 3-13 DISPERSION PATTERN — LADYWASH MINE.
(HUCKLOW EDGE VEIN — WEST)

Considering the 'strength' of the mineralization, (average vein width of at least 5 feet, with a strike length of 2 to 3 thousand feet), the width of the aureole adjacent to Hucklow Edge Vein (East) is large in comparison to the northern Pennine deposits, and the fluorine anomaly is more noticeable. General comparisons with the Hucklow Edge Vein (West) are not possible due to the presumed effect of the underlying lava.

Old Edge Vein (fig.3-14), also worked at Ladywash Mine, provided a comparative study of another major fissure vein. Fluorite is the major vein constituent together with calcite, galena and barite, copper staining was also apparent. The sampling traverse, at right angles to the strike of the 5' 6" wide vein, was taken along a crosscut used as the main haulage way. The aureole is 30 feet wide, beyond which the lead and zinc contents fall below the detection limit. The lead and zinc contents are fairly uniform, although lead is depleted adjacent to the footwall. Strontium and manganese, with very constant background values, increase in the proximity of the vein; the expected decrease of strontium was not encountered. Fluorine has a remarkably wide aureole similar to that of the Hucklow Edge Vein, and in contrast to other fluorite orebodies studied.

The southernmost of the great fissure veins of the Eyam district, the system of veins on Longstone Edge, was accessible in Sallet Hole Mine, where a crosscut at right angles to the mineralization provided an excellent sampling traverse. The analytical results are represented on fig.3-15.

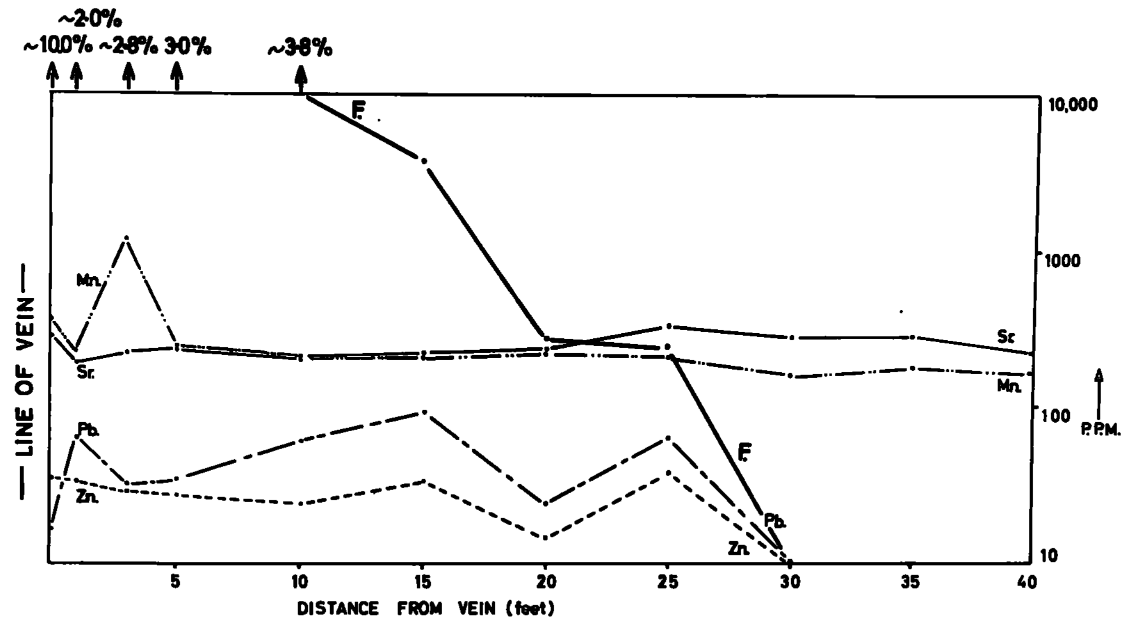


FIG. 3-14 DISPERSION PATTERN — LADYWASH MINE
(OLD EDGE VEIN)

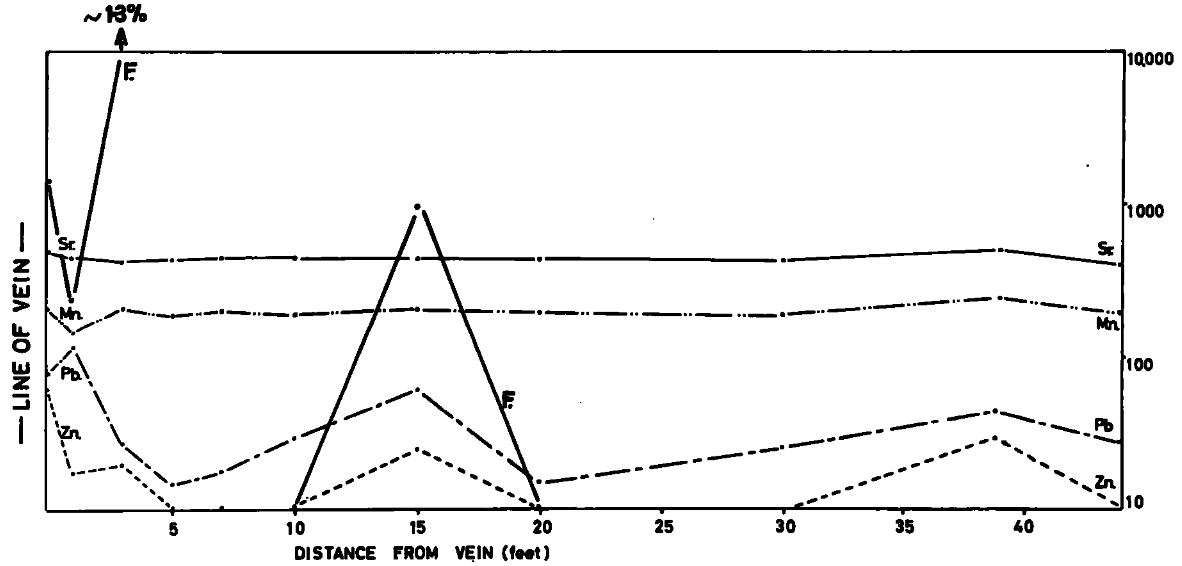


FIG. 3-15 DISPERSION PATTERN — SALLET HOLE MINE
(LONGSTONE EDGE VEIN)

In comparison to the aureoles illustrated in figures 3-12 and 3-14 there is a marked difference in the dispersion pattern. Strontium and manganese, again with a very constant background value, do not show any variation until 1 foot distant from the ore, where an increase is noted. Lead and zinc are both concentrated adjacent to the ore, but anomalous values extend to the farthest point sampled in the traverse. Zinc values fluctuate slightly more than the lead values. Copper (35 ppm., in the vein) has no detectable dispersion pattern nor has zirconium with a vein content of 200 ppm. Fluorine, previously predictable, has no dispersion aureole, but erratic values at 2 and 15 feet are thought to be due to impregnation along minor fractures.

Fig. 3-16 illustrates the dispersion pattern in samples provided by Glebe Mines from a borehole situated on Longstone Edge. This borehole descended through the Carboniferous Limestone and intersected two tuffaceous horizons prior to encountering mineralization at a depth of 345 feet. In considering the trace element variations, the trace element contents of the two igneous horizons must not be compared with those of the limestone. Fig. 3-16 represents a leakage anomaly above a bedded deposit and is therefore not strictly comparable with previously described wallrock aureoles.

The background trace element content of the limestone varies, but within narrow limits. This ∧ especially true for strontium. Only lead and zinc show marked variation from the mean in near surface samples, where

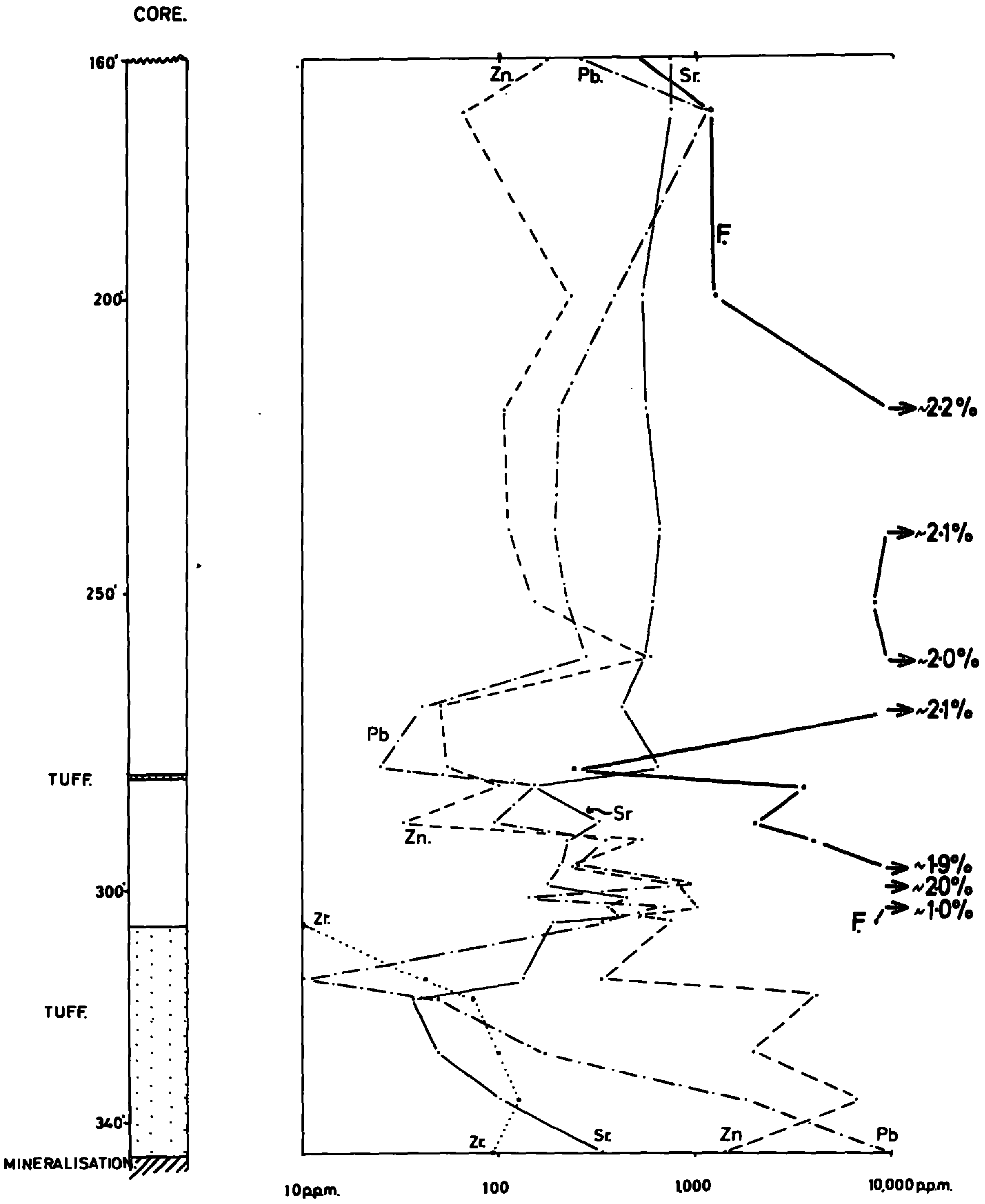


FIG. 3-16 DISPERSION PATTERN.
LONGSTONE EDGE—BOREHOLE 19.

secondary mobilisation could possibly have occurred. The fluorine content is high in most samples, reducing to a reasonable background level at 140 feet above the deposit. This level may, however, be greater than the average background for the area. Additional features of interest are the erratic variation of all elements between the two igneous horizons; the aureole of zirconium found in the lowermost of the tuffs and the rapid increase in lead and zinc as the ore is approached.

The Castleton and Masson Hill Areas

These areas may be considered together since they both display mineralization of an irregular nature in the form of replacement deposits.

In the Castleton area a promontory of limestone in the region of Treak Cliff occurs, projecting into the shale outcrop of Mam Tor, at the extreme northern end of the Derbyshire orefield. This limestone contains the distinctive deep purplish-blue and yellowish-white concentric banded variety of fluorite known as 'Blue John'. The mineralization occurs in highly irregular replacements of the crinoidal reef limestone, not obviously related to any main vein or feeder. Within the surrounding district there are however, two large veins. Odin Mine has previously worked one of these, the other is the fissure vein known as Dirtlow Rake. Sampling was undertaken adjacent to all three types of deposit.

The mining of the Blue John deposit has never been undertaken on a large scale, with the result that exploratory cross-cuts have not been driven. The maximum possible sampling distance was only 5 feet. Fig.3-17 illustrates two traverses collected adjacent to apparently uncontaminated purple fluorite. In both cases the aureoles are restricted to a zone of 1 to 2 feet in width. In the first diagram there is little variation in the strontium content and likewise in the lead and zinc content, the only abnormality occurs where a minor fracture was encountered at 1 foot. Fluorine has very erratic values adjacent to the ore. The second of the two diagrams shows a slight aureole with a decrease in strontium and a logarithmic decrease of fluorine, lead, zirconium, copper and nickel away from the mineralization.

The trace element variations in the wallrocks adjacent to the fluorite vein; interbanded with galena, barite and sphalerite at Odin Mine are shown in fig.3-18. The proximity of this vein to the Treak Cliff Mine may explain some of the abnormalities. A striking similarity with the results from the Hucklow Edge Vein is seen; the principal element changes are restricted to a zone of 5 feet wide. Strontium decreases, while manganese, lead and zinc all increase in this zone. A small but significant amount of zirconium is found, comparable with other fluorite deposits. The aureole of fluorine, with an extent of 35 feet, is very similar to the previously described results from the Eyam district. The marked increase in the majority of the elements at a distance of 55 feet from the vein is taken as

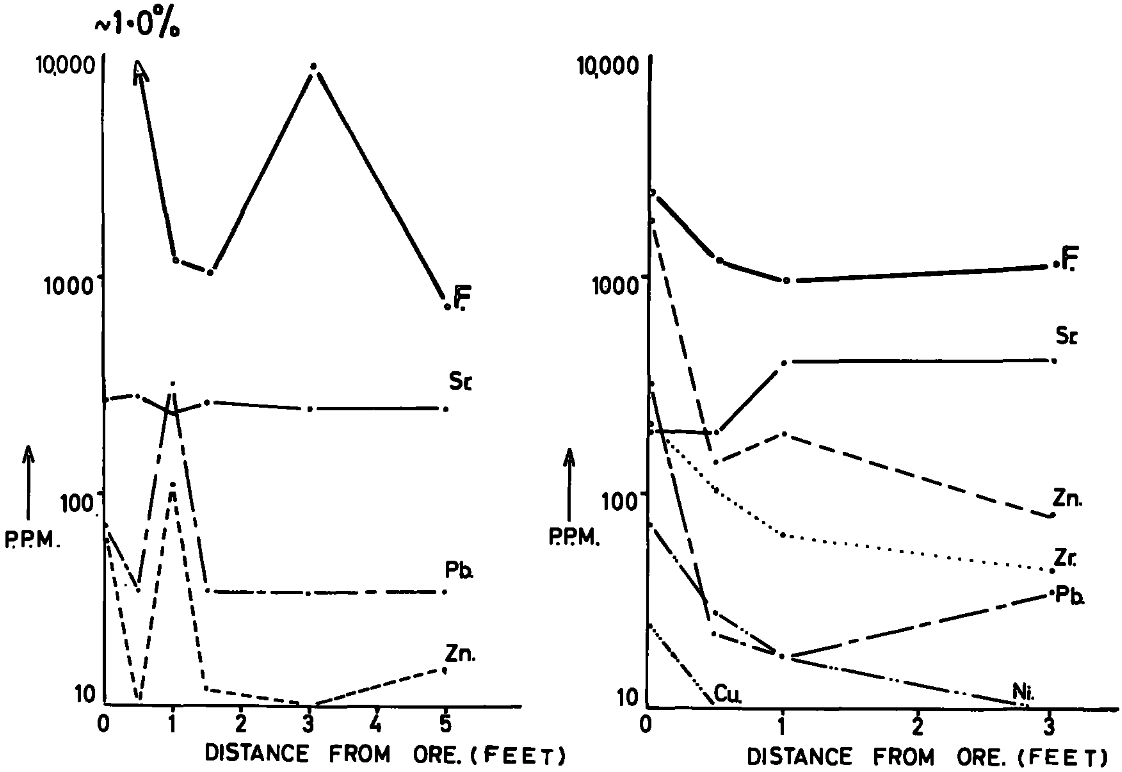


FIG. 3-17 DISPERSION PATTERN — TREAK CLIFF MINE.

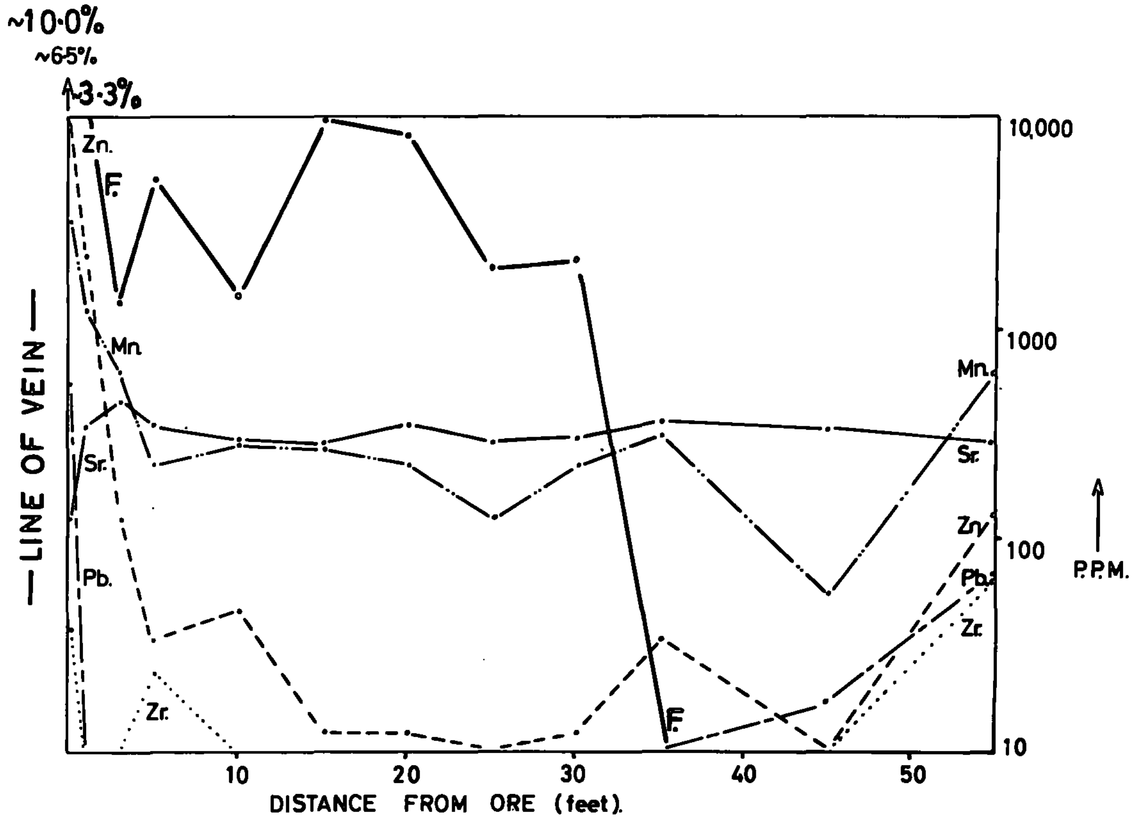


FIG. 3-18 DISPERSION PATTERN — ODIN MINE.

evidence that another vein is in the vicinity. This however cannot be confirmed, as scree material obscures the in situ limestone.

The prominent opencast workings along Dirtlow Rake lie to the south west of Castleton. The analytical results from this area are shown in fig.3-19. The vein contains massive calcite with barite and galena, adjacent to it the aureole has a width of 2 feet. The zirconium content of the vein and the erratic nature of the lead are noteworthy. Zinc shows an logarithmic decrease outwards from the mineralization to a distance of 7 feet.

At Masson Hill a fluorite replacement flat is situated between two Toadstones, resting on the lower one and replacing the limestone between this, the lower Toadstone, and a stratigraphically higher one, the Little Toadstone. The mineralization of the 18 feet of limestone between these two basaltic horizons appears to have developed from a series of joints or 'scrins' and to have resulted in a complete replacement of the limestone (Dunham, 1952). Above the Little Toadstone the ore is mainly restricted to joints in the sediments.

Intersecting the quarry at Masson Hill are numerous small veinlets, one of which was sampled. Visual logging of the hand samples indicated that from 6 to 25 feet the limestone had been extensively altered. It is believed that the results obtained (fig.3-20) illustrate the observed alteration of the limestone. Substantial

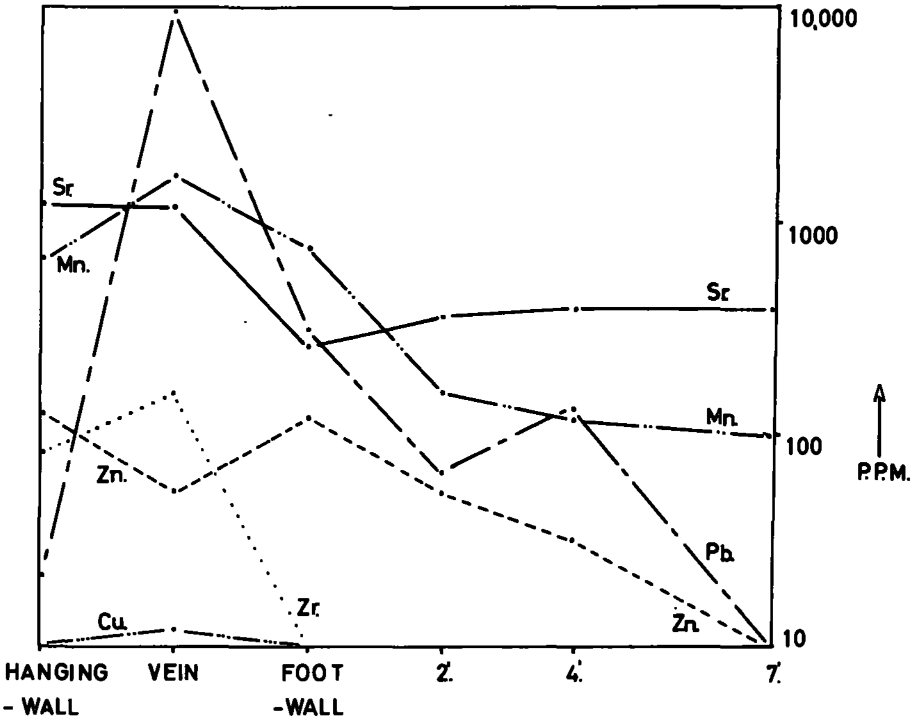


FIG 3-19 DISPERSION PATTERN — DIRTLOW RAKE.

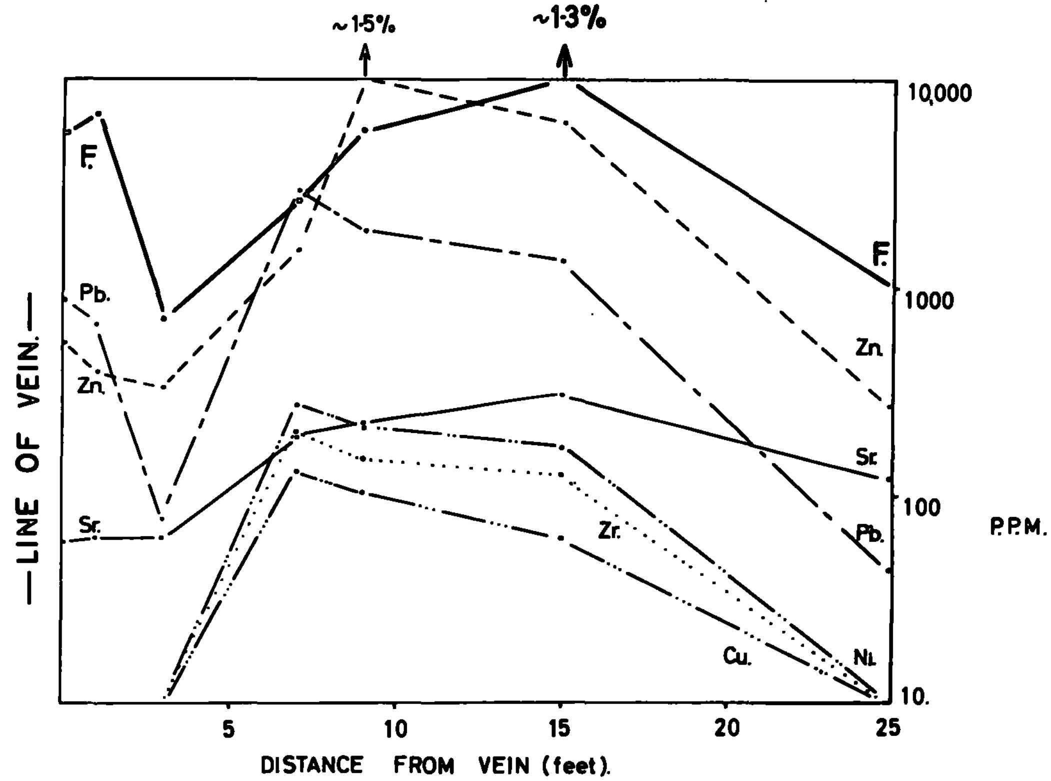


FIG 3-20 DISPERSION PATTERN — MASSON HILL QUARRY.

increases in all the elements occur in the altered zone, with the detectable presence of copper, nickel and zirconium. A comparable effect is to be found in the results from the Tyne Bottom Limestone at Garrigill.

Additional Localities

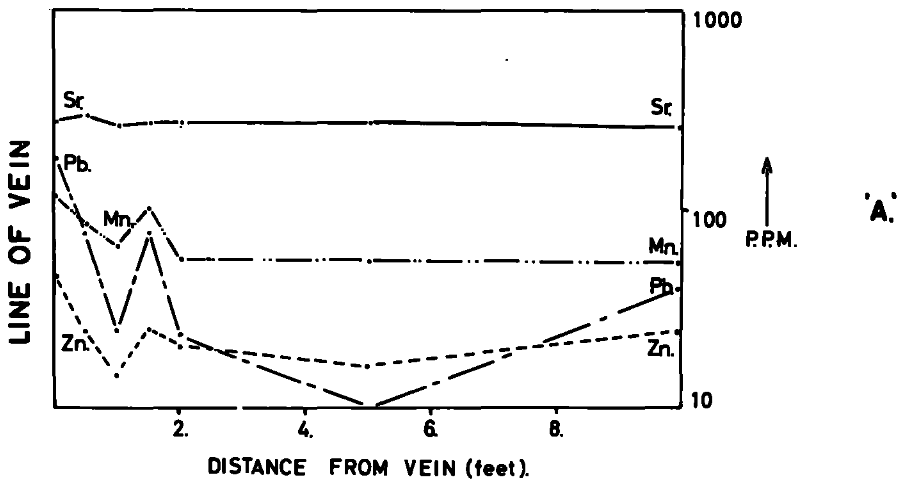
Included in this section are the sampling localities at Middleton Mine near Wirksworth, Imperial Chemical Industries' Limestone Quarry at Buxton and the Raper Prospect near Youlgreave.

Intersecting the limestone mine of the Derbyshire Stone Company at Middleton-by-Wirksworth, there are two veins, 1'6" in width with barite and galena as their constituents. Figs.3-21/22 illustrate the dispersion patterns adjacent to these veins. In the uppermost diagram the aureole width of 2 feet is comparable with the size of the vein, the unusual features are the high background values for lead and zinc, together with a low manganese content of the limestone. The lower of the two diagrams has similar points of importance; the degrease of strontium is negligible in both cases. The high background values for lead and zinc and the low manganese level possibly reflect the composition of the limestone rather than the primary dispersion pattern adjacent to these veins.

Raper Prospect, with opencast and underground workings, has exposed an excellent section of the Long Rake fissure vein. An estimated total movement of 80 - 100 feet (with a throw to the south), has resulted in the juxtaposition of a dark cherty limestone with a thick shale. The deposit of fluorite with barite and traces of galena is believed to be a replacement deposit in the limestone, in which numerous chert nodules have been left unreplaced. It was possible to sample to distances of 25 feet in the limestone, and 20 feet in the shale adjacent to the main leader. In this section consideration will be restricted to fig.3-24, which illustrates the trace element variations in the limestone. Fig.3-23 will be discussed later.

Concentrations in the wallrocks are high, the fluorine content of all samples was in excess of 10% while the lead content averaged approximately 0.9%. In contrast to previously described aureoles, strontium increases adjacent to the vein, as does zirconium. Copper and zinc show erratic values, while manganese drops to very low levels beyond 3 feet.

Finally at the westerh extremity of mineralization in the Derbyshire Orefield, the dispersion pattern of a small (2 feet wide) barite, galena and calcite vein, in a limestone quarry near Buxton, was studied. Fig. 3-25 shows normal patterns for strontium and lead which extend to distances of 5 and 30 feet respectively. Manganese with erratic values in the country rock, suddenly decreases logarithmically towards the vein.



DISPERSION PATTERNS — MIDDLETON MINE.

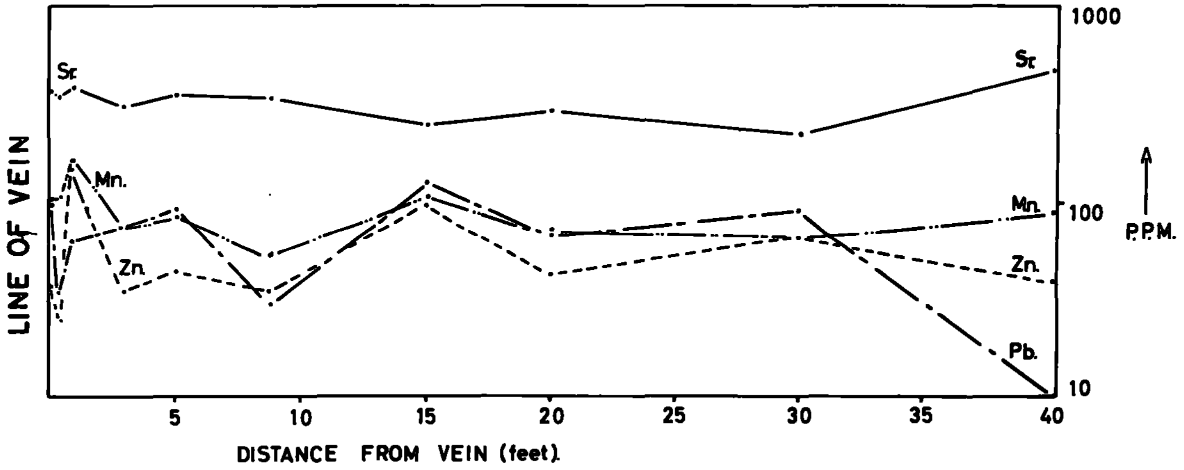


FIG. 3-21/22

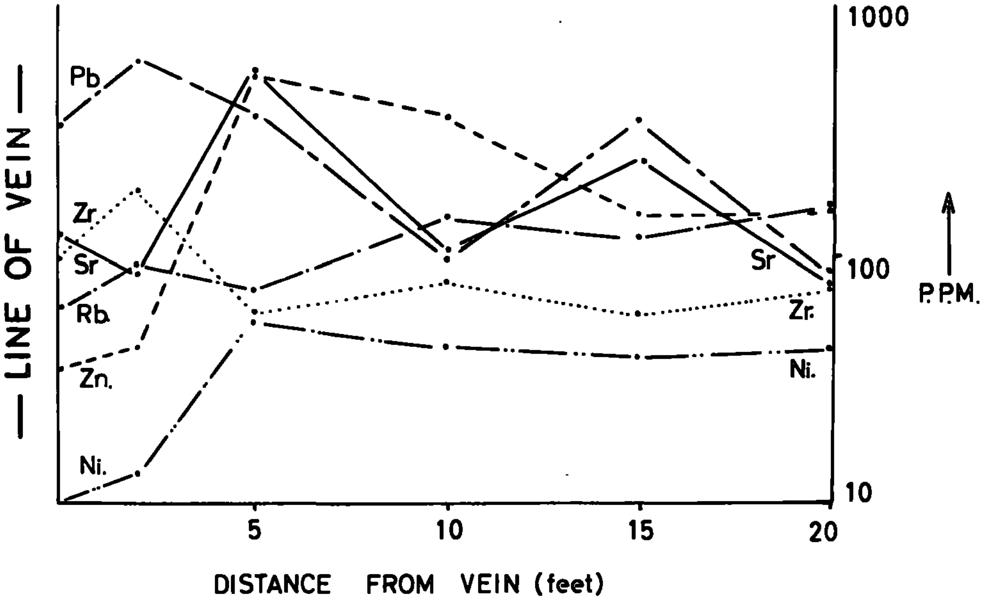


FIG. 3-23 DISPERSION PATTERN — RAPER PROSPECT.

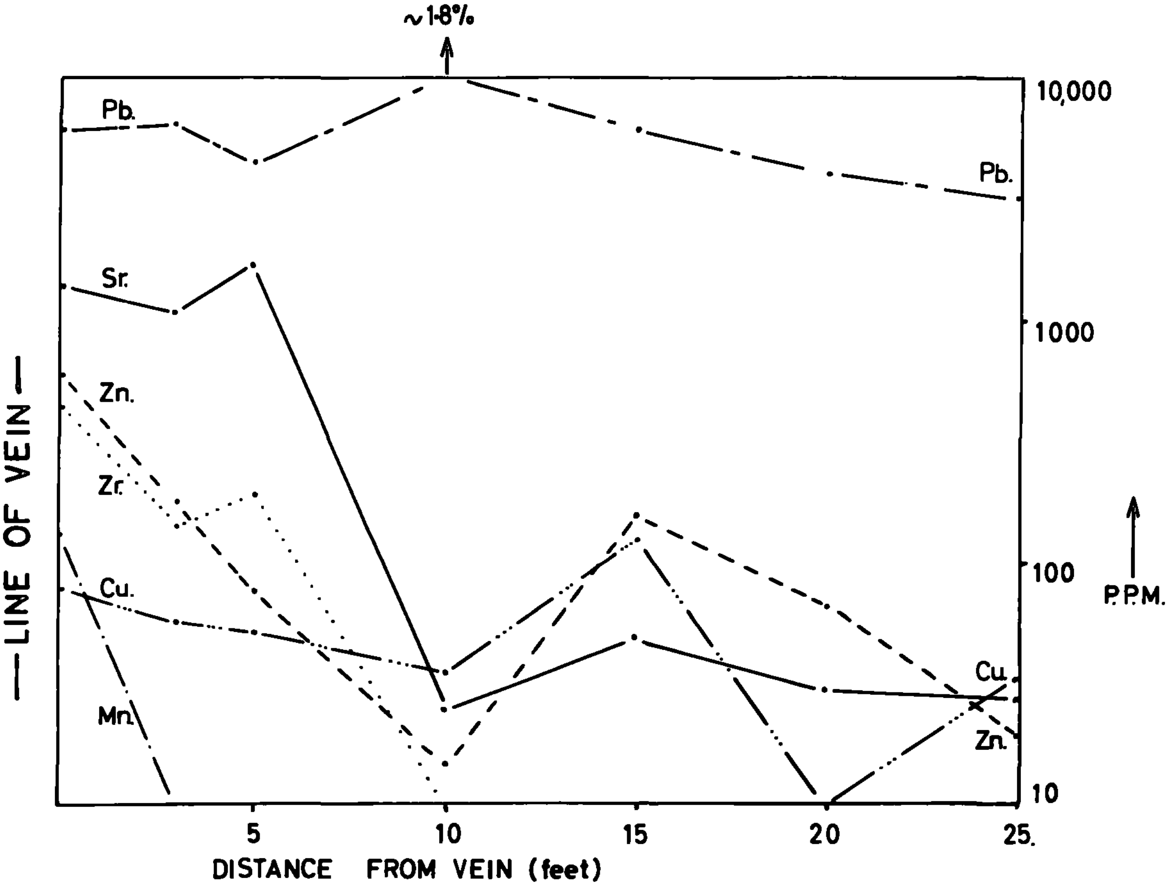


FIG. 3-24 DISPERSION PATTERN — RAPER PROSPECT.

Additional Areas

Sierra de Gador - Spain

Replacement deposits of fluorite in ?Triassic limestones are situated in the province of Almeria in southern Spain. A sampling traverse was obtained from the area, adjacent to a fluorite vein (with a width of 6 feet). Fig.3-26 illustrates the dispersion pattern of the trace elements.

The aureole is seen to be 10 feet in width with erratic values of fluorine, zinc, manganése, iron, strontium and lead. Beyond this point a steady, though high background concentration is achieved. A tentative explanation of this feature is the suggestion that the whole area has been 'soaked' by mineralising fluids with local concentration into economic deposits.

The Cumberland Ironfield

An investigation of the trace element dispersion patterns adjacent to haematite orebodies, was undertaken in the Cumberland Ironfield, the United Steel Company kindly allowed access to, and sampling of Beckermet Mine.

Beckermet Mine

Irregular flats and vein - like bodies near faults, occur

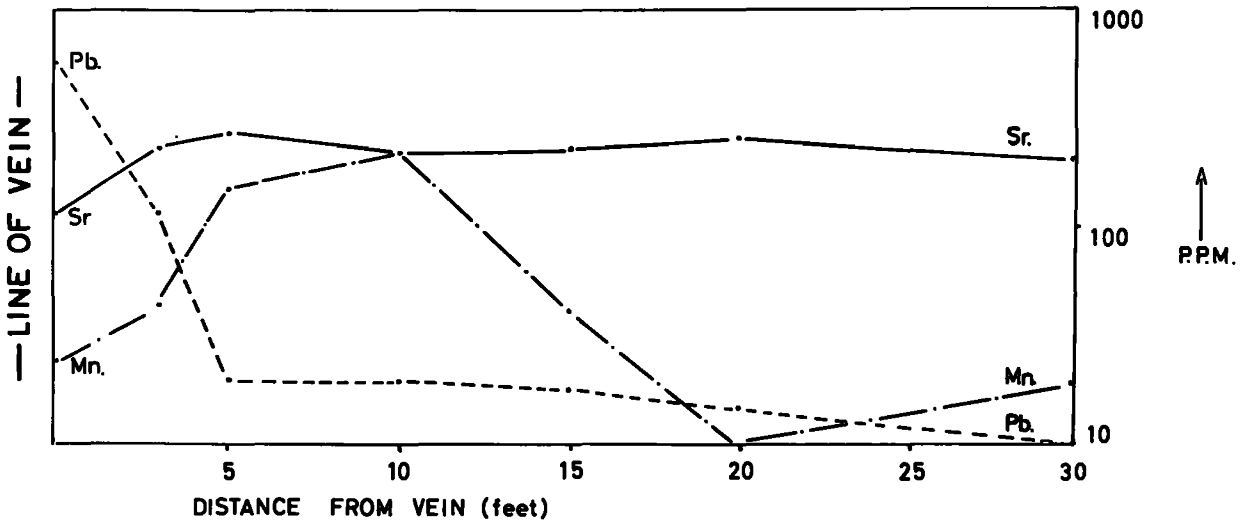


FIG. 3–25 DISPERSION PATTERN — I.C.I. QUARRY (BUXTON.)

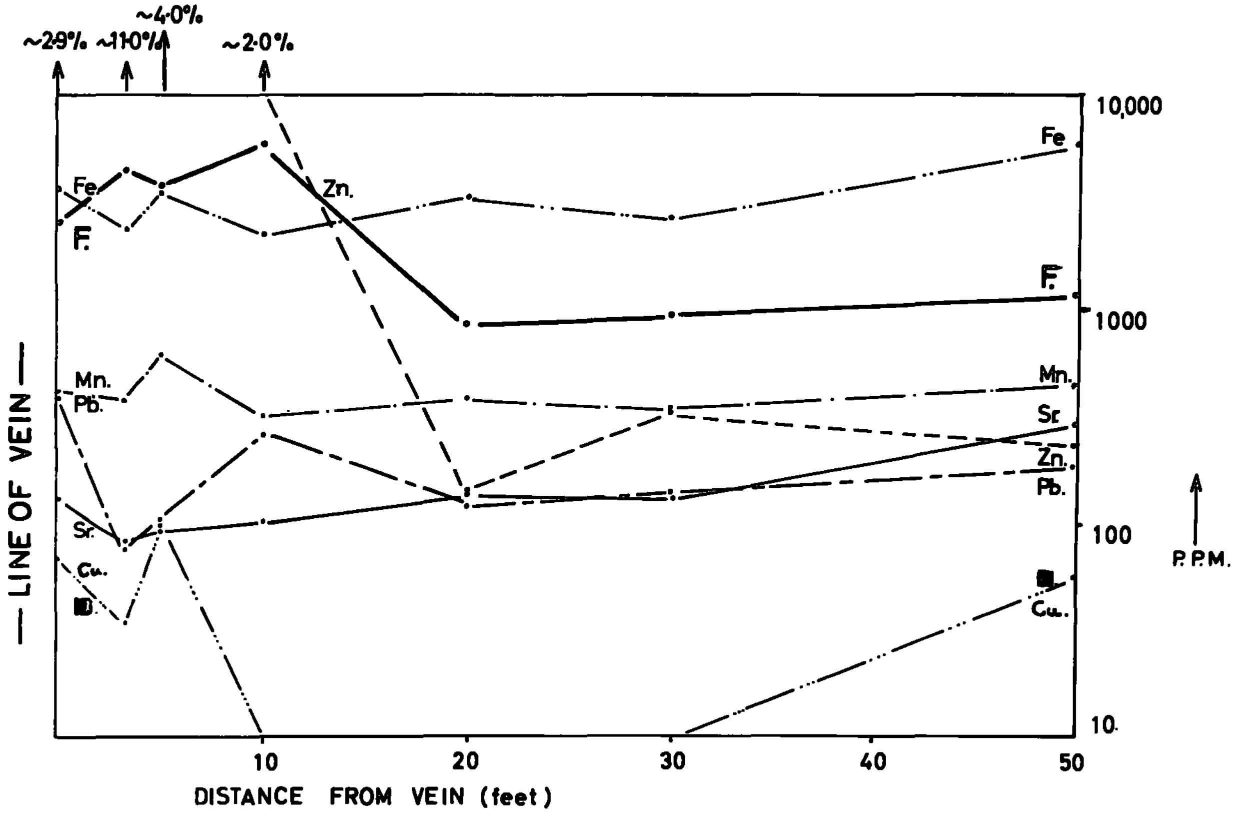


FIG. 3–26 DISPERSION PATTERN — SIERRA DE GADOR (SPAIN)

in the Carboniferous Limestone and have been worked for over fifty years. They comprise the southernmost of the workable haematite deposits in the Whitehaven Ironfield, and lie in an area where the limestone is buried to depths up to 1,150 feet under the New Red Sandstones.

The sampling was restricted to one location in the mine, as shown on fig. 2-9, and care was taken throughout to avoid contamination due to haematite dust. Figures 3-27 and 3-28 illustrate the trace element variations in the limestone adjacent to the orebodies, and the background values for the trace elements are taken when their variation does not exceed ± 10%.

The ore was found to be reasonably free of trace elements, an average of 17 ppm. nickel and 5 ppm. copper was detected. Anomalous values were obtained from the ore at location B/48 where zinc (115 ppm.) and rubidium (275 ppm.) were detected in the haematite.

Considering the diagrams in general, an aureole of 'excess' iron (that is greater than 1%) out to 50 feet was a regular feature adjacent to most of the orebodies. Manganese also shows background values in excess of 50 feet with slight but detectable variations at less than 50 feet. Strontium from localities 68, B/48 and B/48A was depleted within 5 feet of the ore. Traverses B/7 and B/33 gave element variation widths of approximately 50 feet for iron, manganese and strontium.

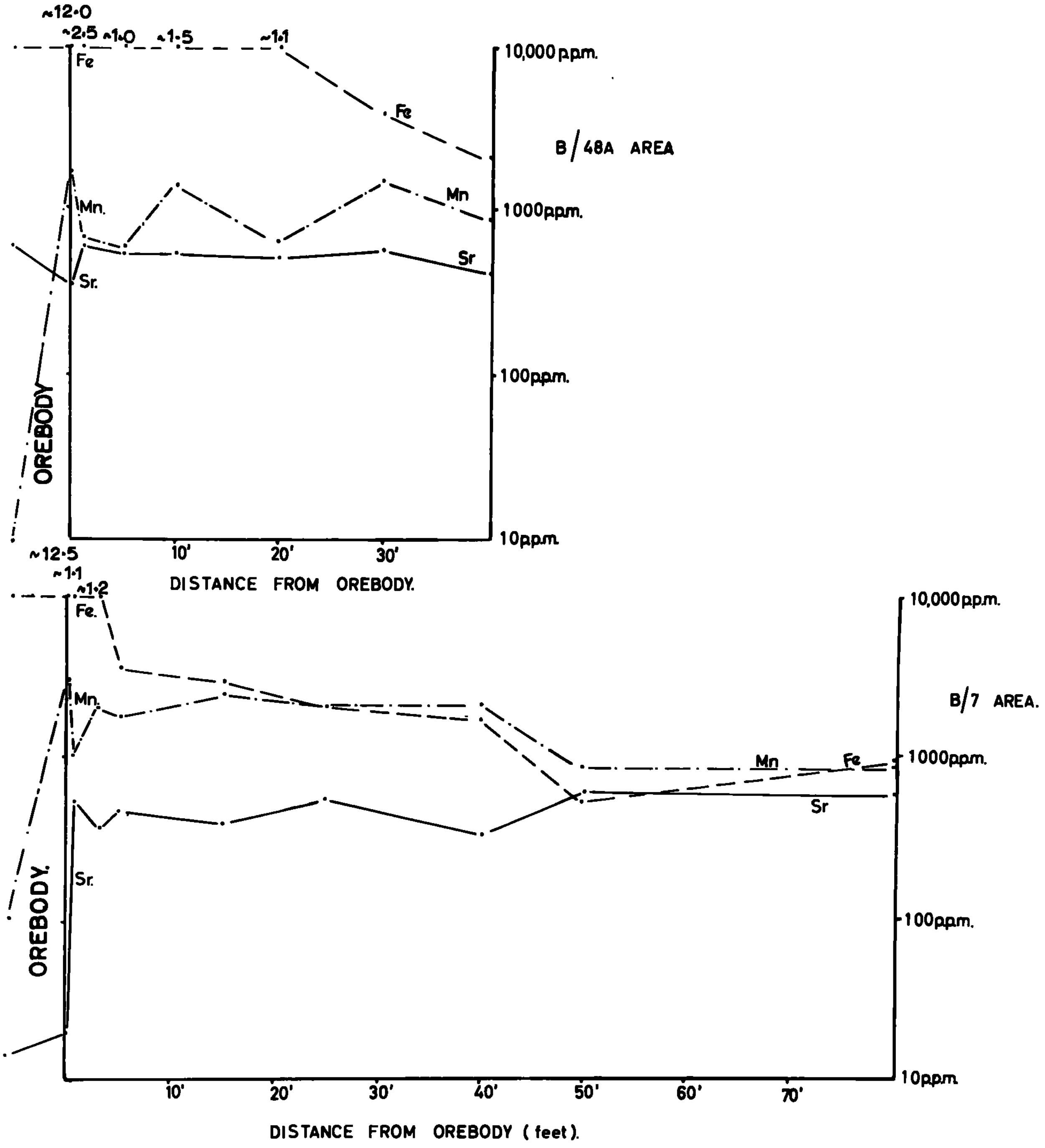


FIG. 3-27 DISPERSION PATTERNS — BECKERMET MINE.

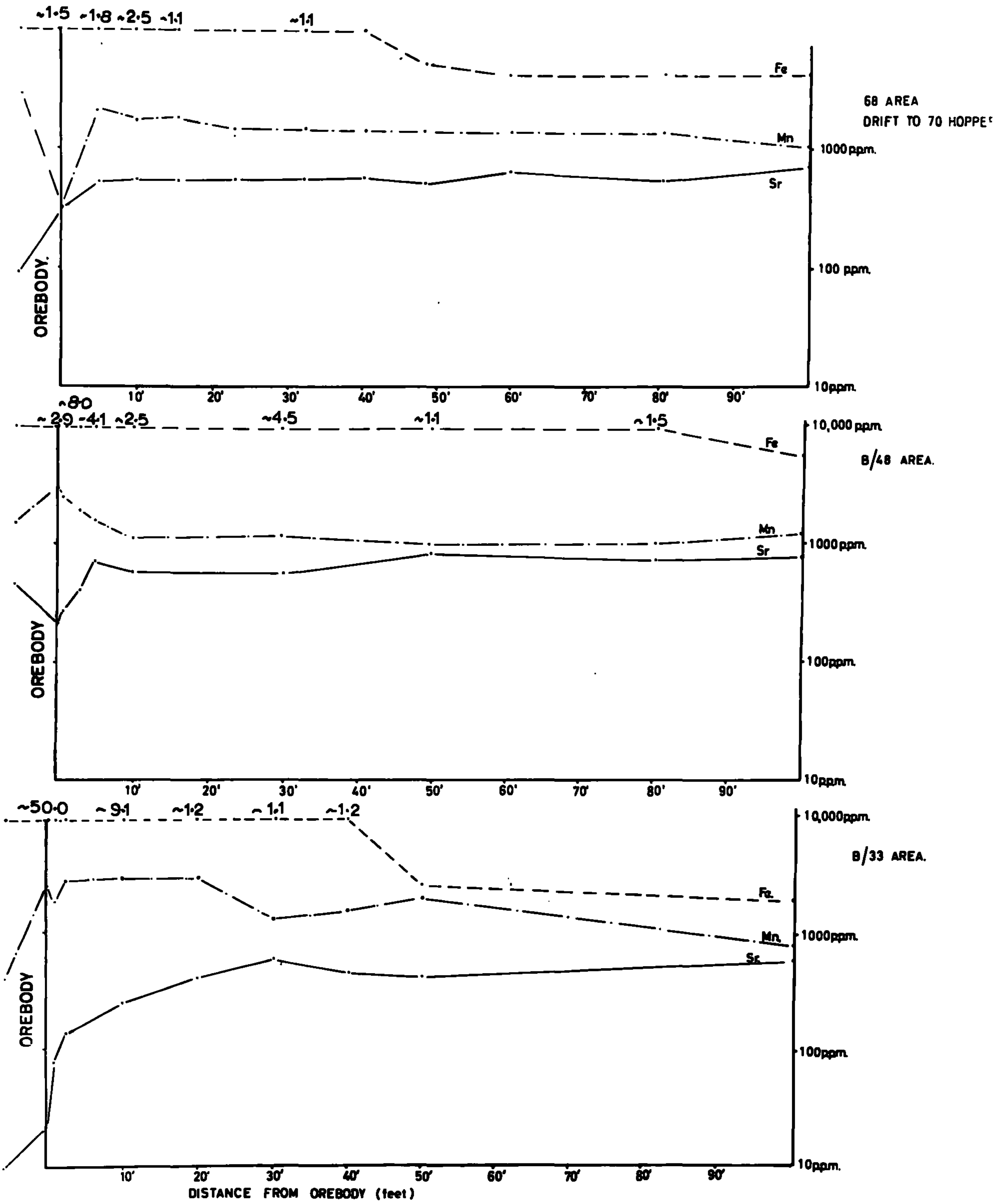


FIG. 3-28 DISPERSION PATTERNS — BECKERMET MINE.

It is noteworthy that both these localities were adjacent to the same orebody at different positions along strike. The haematite was generally very low in strontium, while manganese, although depleted at the margins of the deposit, was enhanced in the ore. The limestone wallrocks indicated that lead, zinc and nickel were the only elements to be detected at spasmodic occurrences.

Trace Element Variations in Sandstones and Shales

The Northern Pennine Orefield

Dunham (1948, p.79) conducted a statistical analysis of the horizons of the vein oreshoots in the orefield, and showed that workable deposits in sandstones are restricted in comparison to those in the limestones. The size and features of aureoles in sandstones were studied for comparison with those developed in limestone wallrocks.

West Blackdene Mine

Of the working mines in the orefield, West Blackdene Mine, near Ireshopeburn, has economic deposits of fluorite in sandstones; Slitt and Blackdene Veins are the ore bearing fissures. Underground crosscuts between the two veins provided sampling traverses (see fig.2-3). Adjacent to Slitt Vein the Number 1 crosscut enabled sampling in the Slaty Hazel; while Blackdene Vein intersected by Number 2 crosscut provided samples from the Alternating Beds.

Slitt Vein, the longest single vein of the orefield (13½ miles), where interesected in the mine, varies in width from 25 feet to a few inches. The predominent filling is fluorite, with minor galena, quartz and iron carbonates. Blackdene Vein, in contrast maintains a reasonably constant width of about 5 feet, and composition (fluorite, quartz with some galena).

The dispersion patterns adjacent to these two veins are shown in the lower of the three diagrams in fig. 3-29. The width of the aureole adjacent to Blackdene Vein is approximately 40 feet. In this region strontium and rubidium are substantially depleted, while fluorine and zirconium only show marked changes within 1 foot of the ore. In comparison, Slitt Vein has an initial aureole of 5 feet where fluorine and zirconium are erratic, strontium and rubidium values are irregular along the whole traverse. Although not shown, the lead and zinc contents of the wallrocks are below the detection limits apart from an isolated sample with high values, this is associated with the presence of minute fractures.

The dispersion pattern labelled 'Number 3 incline' is in the Whin Sill and will therefore be considered in Chapter 6.

The Derbyshire Orefield

Raper Prospect

As previously mentioned, the only traverse in shale wallrocks was that sampled at Raper Prospect, the results are shown in fig. 3-23.

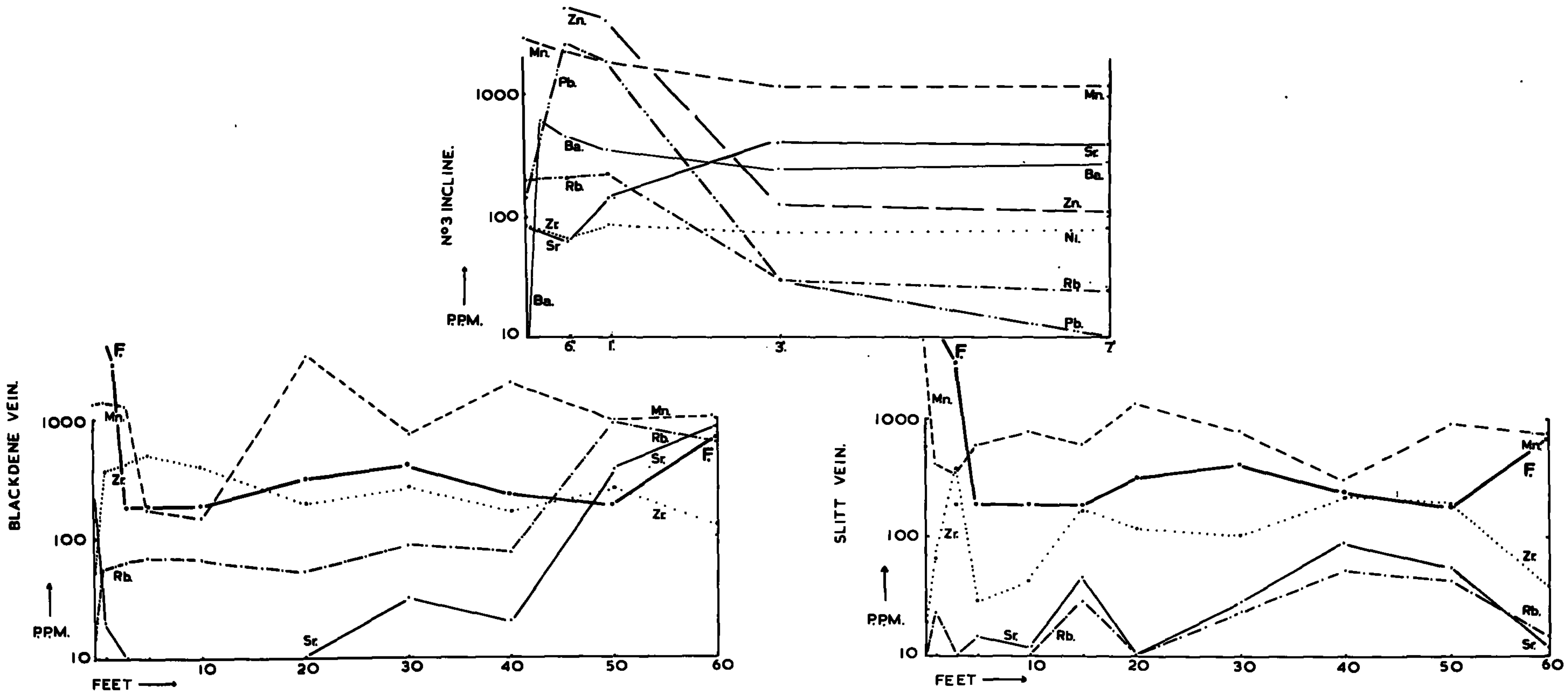


FIG. 3-29 DISPERSION PATTERNS — WEST BLACKDENE MINE.

An aureole width of 5 feet is apparent, where nickel, zinc rubidium, zirconium and strontium decrease towards the vein. Background values of nickel, zirconium and rubidium are maintained beyond this distance. Adjacent to the vein, zinc is depleted but moving away from the vein rapidly reaches a value of 543 ppm., thereafter the zinc content decreases from the vein to a background level of 160 ppm.

Summary of the Results

The minor element dispersion patterns studied reveal certain features which require explanation.

General Features

The wallrocks of Hucklow Edge Vein have similar dispersion aureoles (figs. 3-12 and 3-13), extending 35 feet from the vein. The traverses next to Red Vein (figs. 3-10 and 3-11) a crosscut and two borehole cores, all give different dispersion patterns. The results from Beckermet Mine show that next to the orebodies, the trace element patterns are similar. Variations occur from a distance of 5 or 50 feet, where strontium decreases and manganese and iron increase towards the orebodies.

Examining the traverses from the northern Pennines and Derbyshire, it is evident that either the aureoles are narrow, between 1 and 5 feet, or wider, between 20 and 35 feet.

Specific Features

The dispersion patterns in the limestones wallrocks, illustrated in figs. 3-1 to 3-28, show specific features which appertain to individual elements, these are as follows.

Strontium

The strontium content of the wallrocks decreases as the orebody is approached. The lateral extent and depletion in strontium is not proportional to the size of the vein. Anomalous patterns are shown from the Eyam district of Derbyshire. At Sallet Hole Mine and Ladywash Mine (Old Edge Vein), the strontium concentration of the wallrocks is constant to within inches, rather than feet, of the vein (see figs. 3-14 and 3-15).

Fluorine

A fluorine aureole was detected adjacent to fluorite mineralization in Derbyshire, in contrast, the wallrocks of fluorite veins in the northern Pennines did not invariably show a fluorine aureole.

Zirconium

The presence of zirconium aureoles in the wallrocks of fluorite veins and the absence of zirconium adjacent to lead, lead-zinc and barite veins was a characteristic feature. This is illustrated in figs. 3 - 2, 3, 7, 10, 11, 12, 13, 14, 15, 16, 17, 18, 20, 24 and 26.

Lead and Zinc

In most aureoles the dispersion pattern produced by lead is erratic, for example, figs. 3-1 and 3-12. Lead was often detected in samples beyond the general aureole indicated by other trace elements.

Similarly erratic, but often more widespread patterns are shown by zinc illustrated for example in figs. 3-6, 3-13 and 3-15.

Copper and Nickel

These elements present in the vein were not always detected in the dispersion aureole. Typical aureoles containing these elements are illustrated by figs. 3-9, 3-13, 3-16 and 3-20.

Rubidium

Often below the detection limit of the analytical technique (i.e. 5 ppm.) rubidium was found however at Garrigill (fig.3-7) and from boreholes at Longstone Edge (fig. 3-16), and Redburn Mine (figs.3-10 and 3-11).

Manganese

This element increased adjacent to all but one of the veins, where it decreased in value towards a barite vein, (fig. 3-25).

Igneous Horizons

The presence of an igneous horizon resulted in erratic concentrations for most of the trace elements. Copper and nickel were usually enhanced while strontium was depleted. The aureoles at Ladywash Mine and Longstone Edge (figs. 3-13 and 3-16), illustrate the variations in the trace element concentrations.

Sandstones and Shales

The traverses in sandstone wallrocks (fig.3-29) showed that strontium and zirconium decreased towards the vein. Rubidium from a background value of 170 ppm. decreased towards the vein, while manganese gave erratic results. The width of the dispersion patterns at West Blackdene Mine were 40 feet and 5 feet respectively.

The trace element variations in shale wallrocks were erratic. General conclusions cannot be drawn from one traverse.

CHAPTER IV

THE MINERALOGICAL AND MAJOR ELEMENT VARIATIONS ADJACENT TO MINERALIZATION

Introduction

An interpretation of the trace element patterns in the limestone wallrocks cannot be made without a knowledge of the major chemical, mineralogical and petrological nature of the samples (see Hawkes and Webb, 1962, p.69).

The trace element studies indicated a series of different minor element patterns in the wallrocks. It was not practical to undertake a complete petrological, mineralogical and major chemical analysis on all the samples, consequently traverses were chosen, for a detailed examination which were either typical of a large number of traverses, or which were unusual in their trace element content.

The following traverses were chosen for mineralogical and major element analysis.

Locality	Trace Element Patterns	Comments for choice
Redburn Mine	Figs.3-10 and 3-11	Unusual patterns from three traverses next to the same vein

Locality	Trace Element Patterns	Comments for choice
Heights Quarry	Figs.3-1 and 3-2	Typical patterns (N. Pennines)
Garrigill	Fig.3-7	Argillaceous limestone, unusual dispersion pattern
Ladywash mine	Figs.3-12 and 3-13	Typical patterns (Derbyshire)
Middleton mine	Figs. 3-21 and 3-22	Narrow strontium aureole, high background values for lead
Masson Hill Quarry	Fig. 3-20	Altered limestone and a limonite zone
Odin mine	Fig. 3-18	Patches of fluorite along the traverse

Petrography

Hagni and Saadallah (1965) working on limestone wallrocks adjacent to lead-zinc orebodies in the Tri-State district of the United States, demonstrated the following changes as the orebody was approached :-

(a) The fossiliferous content of the limestones decreased towards the orebodies.

(b) The proportion of secondary calcite increased towards the mineralization.

(c) Gradual changes in the limestone wallrocks commenced at distances of between 40 and 80 feet from the ore.

They concluded that the presence of limestone alteration haloes indicated the epigenetic origin of the ore deposits.

Dunham (1948 and 1952) observed that ankeritization, dolomitization and silicification of the wallrocks occurred in the Pennine orefields, the northern part of the Pennines, the Alston Block being remarkable for the abundance of iron, magnesium and calcium carbonates. Dunham suggested that ankerite was an important mineral in the wallrocks, and not dolomite, as had been previously suggested. He also indicated that there was strong evidence to suggest that the earliest effect of the mineralising solutions, on the limestone wallrocks, was the conversion of the limestone to an ankerite rock with subordinate siderite and chalcedony. This type of alteration, he postulated, provided an environment unfavourable to the replacement of the limestones by the later phases of the mineralization and caused the ore fluids to break through the ankeritised belt with the result that the ores were deposited beyond this altered zone. In explaining the occurrence of ankerite and siderite, which are confined to the Alston Block, Dunham, (1948, p.107) suggested that they may owe their origin to Mg and Fe leached from the Whin Sill.

The Northern Pennines

The unaltered limestones are uniform in composition and texture, light to medium grey in colour and consist of macrofossils and fossil fragments in a fine grained groundmass. Towards the orebodies the limestones are altered. A coarse grained, fractured, and light brown rock in characteristic. Occasionally small 'clots' or patches of the vein material are seen in the wallrocks.

The unaltered limestones are composed of between 50% and 70% of fossils and fossil fragments, which include crinoids, brachiopods, bryozoans and foraminifera. The central cavity of the crinoids and the tests of the brachiopods are often filled by secondary calcite. The groundmass is an admixture of fossil fragments and microcrystalline calcite. The limestones are predominantly calcite (95%) with subordinate quartz and siderite.

Towards the veins the samples illustrate the following changes :-

(a) The development of fractures, increasing in width from 0.1 mm to 3mm near the vein. Often, but not invariably they are lined with quartz and fluorite together with galena and sphalerite.

(b) Recrystallization of the groundmass

(c) Recrystallization of the fossils resulting in their destruction

(d) Calcite is joined by ankerite, siderite and chalcedony.

(e) The fractured zone corresponds to the width of the trace element aureole.

The presence of ankerite and siderite in the wallrocks, was confirmed by refractive index measurements and X-ray diffraction analyses.

The respective traverses show the above mentioned general alteration trends. In detail, each traverse illustrates some abnormal features. Ankerite is more abundant in the crosscut than in the borehole (W2) at Redburn Mine, while siderite is dominant in borehole N2. Ankerite and siderite were not detected next to the West Cross Vein and South Vein at Heights Quarry.

The Tynebottom limestone at Garrigill has been altered more than the Great Limestone. The calcite is replaced by quartz and clay minerals.

Plates 4-1 and 4-2 illustrate the unaltered and altered limestone adjacent to a fluorite vein at Heights Quarry.

The Derbyshire Pennines

The unaltered limestones have a 40% to 50% fossil content in a fine grained calcite groundmass. They are light grey in colour and are composed of about 98% calcite with subordinate quartz and dolomite.

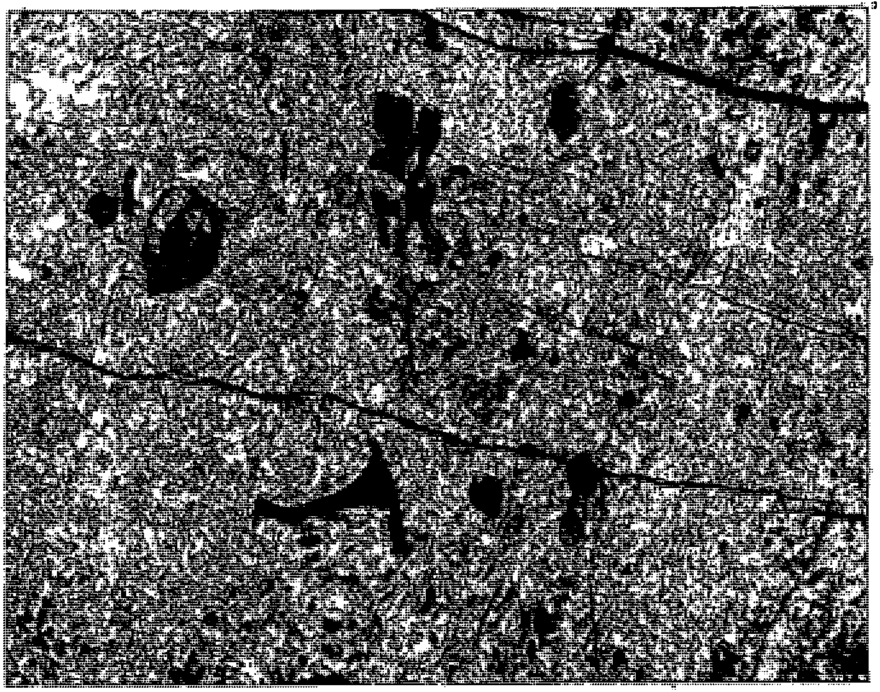


Plate 4-1

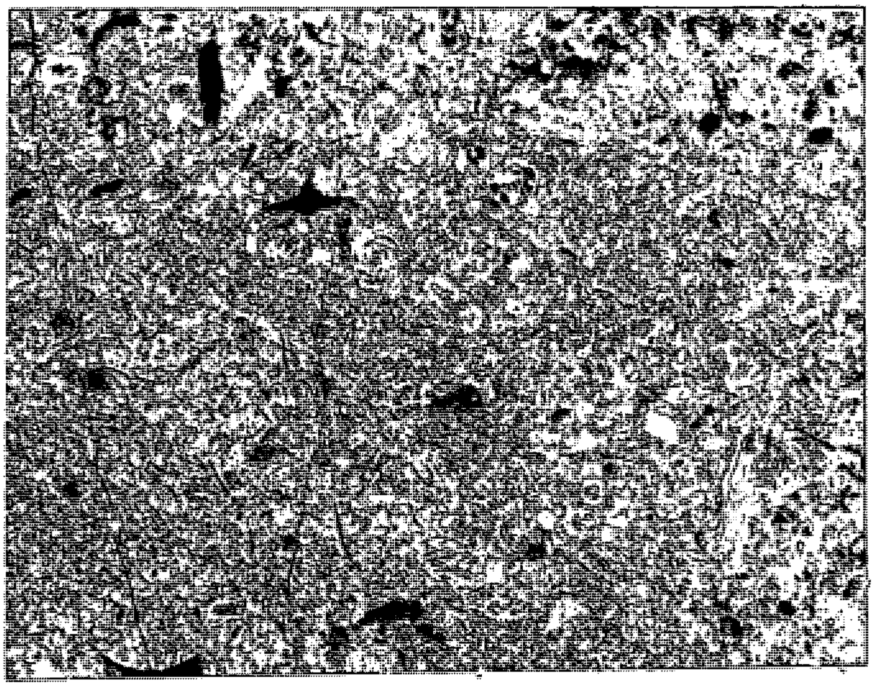


Plate 4-2

Towards the mineralization the following alteration effects are visible :-

(a) Fracturing of the wallrocks increases towards the vein. Initially a 'thread-like' pattern is visible, while transgressing the vein wall are fractures 1 to 3 mm in width coated with quartz and infilled with fluorite and calcite.

(b) Recrystallisation of the groundmass and the fossils occur producing secondary calcite which exhibits polysynthetic twinning.

(c) An average of 5% dolomite is present in the limestones. Ankerite and siderite were not detected in the wallrocks.

(d) The width of the trace element aureole is related to the extent of the fractured wallrocks.

Altered wallrocks were not encountered at Middleton mine. At Masson Hill Quarry the limestone is highly altered, adjacent to the vein the limestone contains 20% dolomite and quartz, while between 7 and 15 ft. from the vein, the limestone has been replaced by quartz, micaceous minerals and iron carbonates. Limestone wallrocks at Odin mine are characterised by discrete fluorite crystals in joints and cavities, the wallrocks are composed of approximately 95% calcite with subordinate dolomite and quartz.

Plates 4-3 and 4-4 illustrate the unaltered and altered wallrocks next to Hucklow Edge Vein.

Plate 4-3

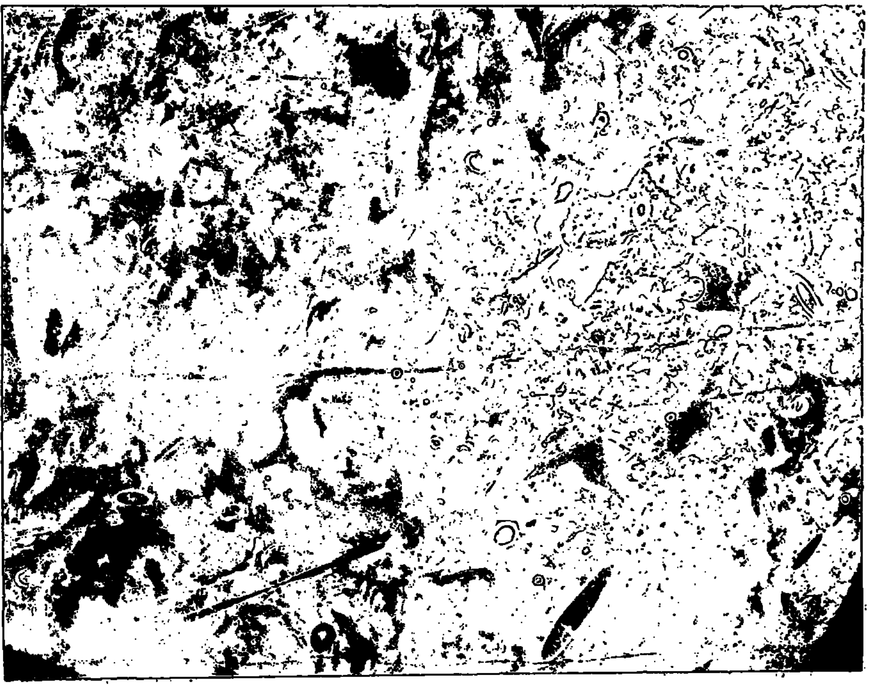


Plate 4-4

Conclusions

The petrology of the limestone wallrocks indicates that the fracturing of the sediments coincides with the trace element aureoles and that recrystallised calcite is invariably developed. Fractures are possibly the consequence of the injection of the orefields, while their width and extent are not proportional to the size of the vein. Ankerite, siderite and quartz are developed in the wallrocks of the northern Pennines, while dolomite and quartz are the dominant accessory minerals in Derbyshire.

These conclusions are similar to the previous investigations. The suggestion that ankerite is the predominant wallrock mineral in the Alston Block (Dunham 1948) is not supported by this investigation. It may be fortunate that Dunham examined localities at which the mineral was abundant (e.g. Boltsburn mine and Stosfield Burn mine) and it is noteworthy that the majority of these localities were adjacent to massive replacement bodies, whereas the present investigation was restricted to well defined veins.

Major Chemical and Mineralogical Variations

The following data was derived by X-ray fluorescence and X-ray diffraction techniques as described in Chapter 2. The mineralogical composition of the limestones was determined by the method developed and described by Schultz (1964), while the chemical analyses were obtained by a modification of the method of Holland and Brindle (1966). The chemical analyses for calcium, magnesium and iron were recast as $CaCO_3$, $MgCO_3$ and $FeCO_3$.

The Northern Pennine Orefield

The chemical and mineralogical variations from Redburn mine, Heights Quarry and Garrigill are illustrated on figs. 4-1 to 4-6.

Redburn Mine

The major chemical and mineralogical composition of the crosscut to borehole W2 and a portion of borehole W2, together with the first 45 feet of borehole N2, are shown on 4-1 to 4-3.

Fig. 4-1 illustrates the increase in TiO_2, K_2O, MnO, Na_2O and Al_2O_3 and the decrease in $CaCO_3$ towards the vein. SiO_2, $FeCO_3$ and $MgCO_3$ contents are erratic throughout the aureoles. Mineralogical analyses supported the deductions based on chemical analyses for the constituents ankerite, siderite, calcite and quartz. The alteration zone is 18 feet wide.

Borehole W2 (fig. 4-2) illustrates increases in Na_2O, K_2O, MnO, $MgCO_3$ and Al_2O_3 and decreases in $FeCO_3$ and $CaCO_3$ between 60 and 78 feet.

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS.

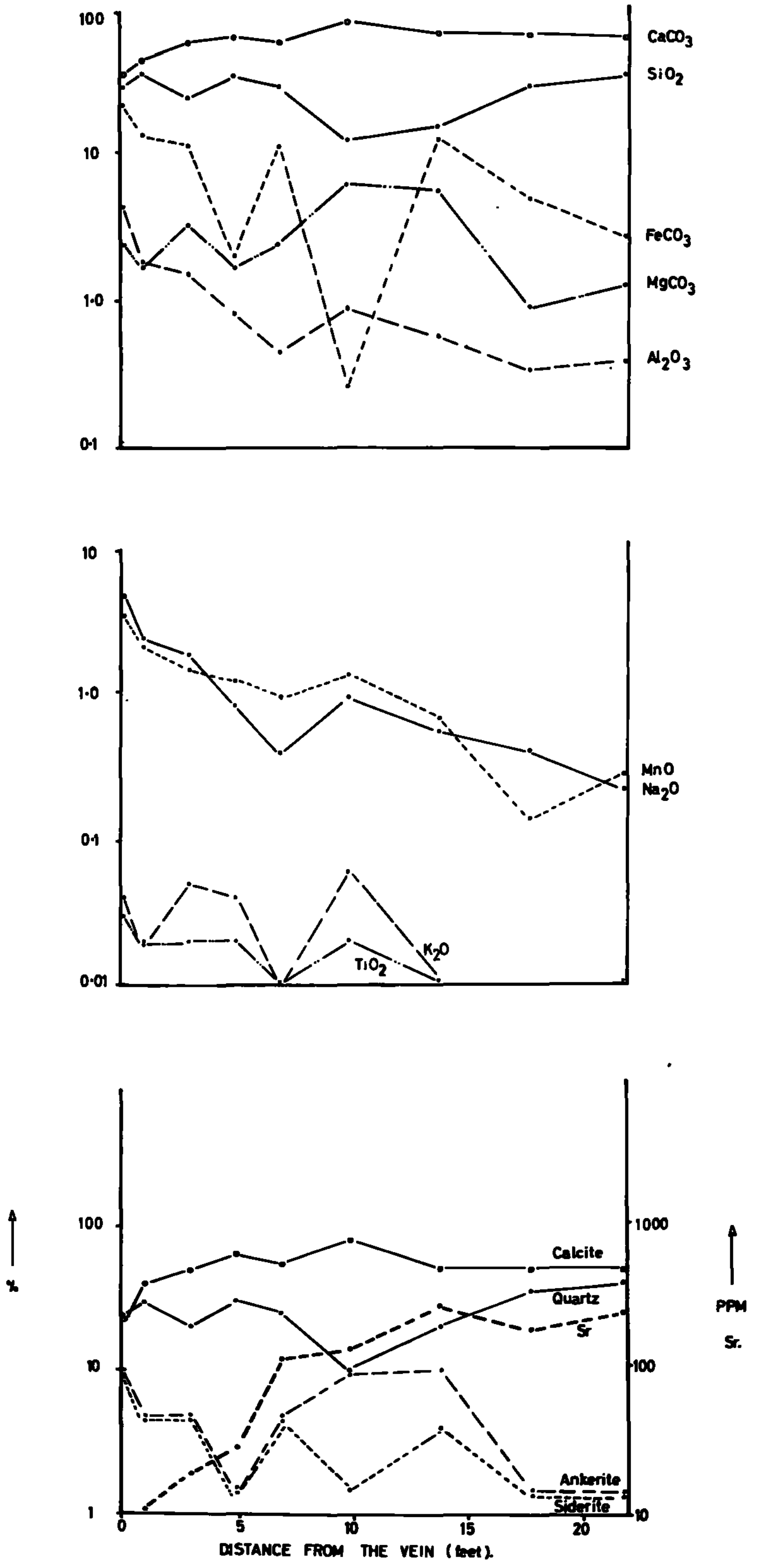


FIG 4-1 REDBURN MINE.
(CROSSCUT TO BOREHOLE - W.2.)

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

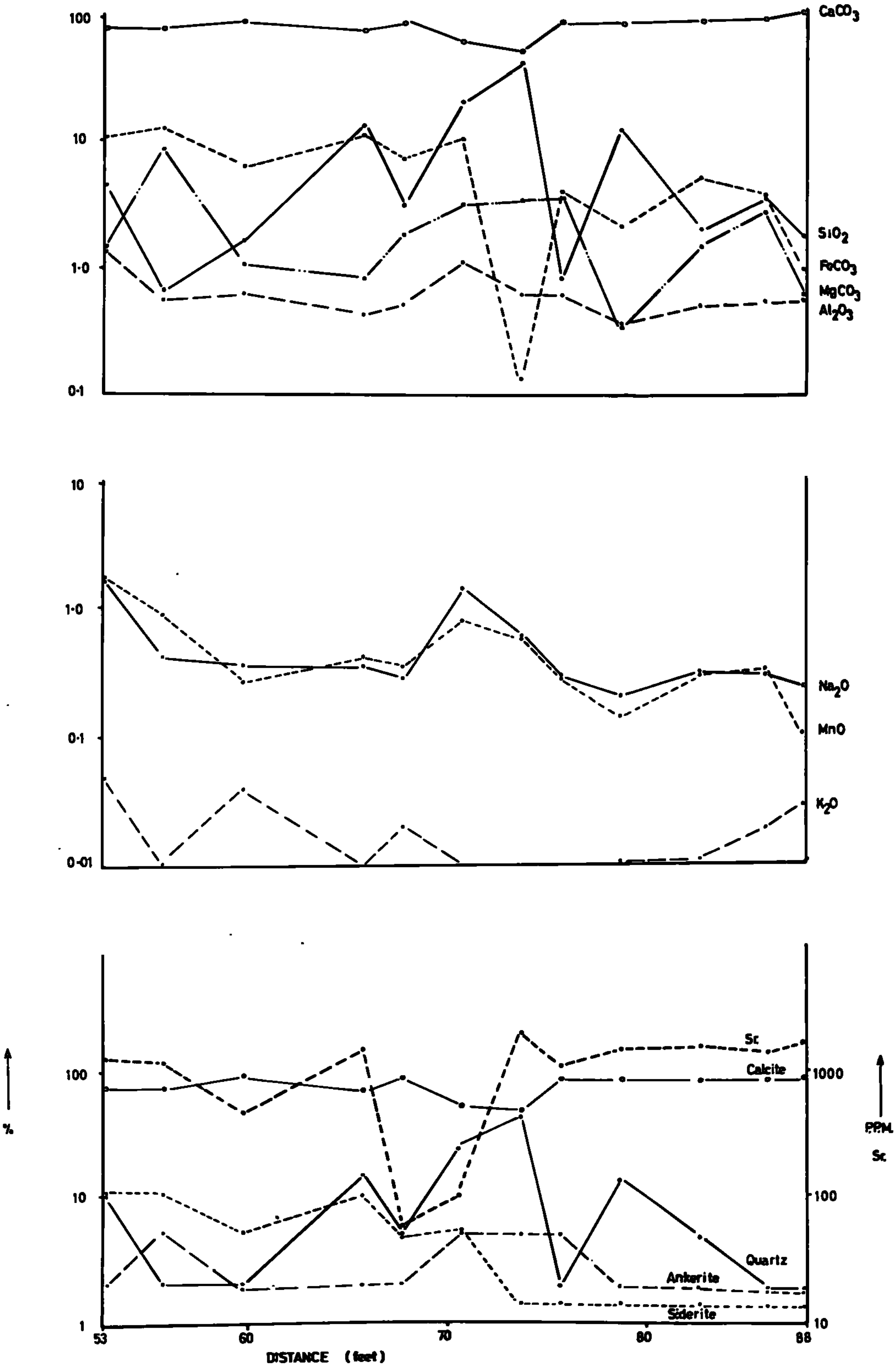


FIG. 4-2 REDBURN MINE.
(BOREHOLE - W. 2)

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

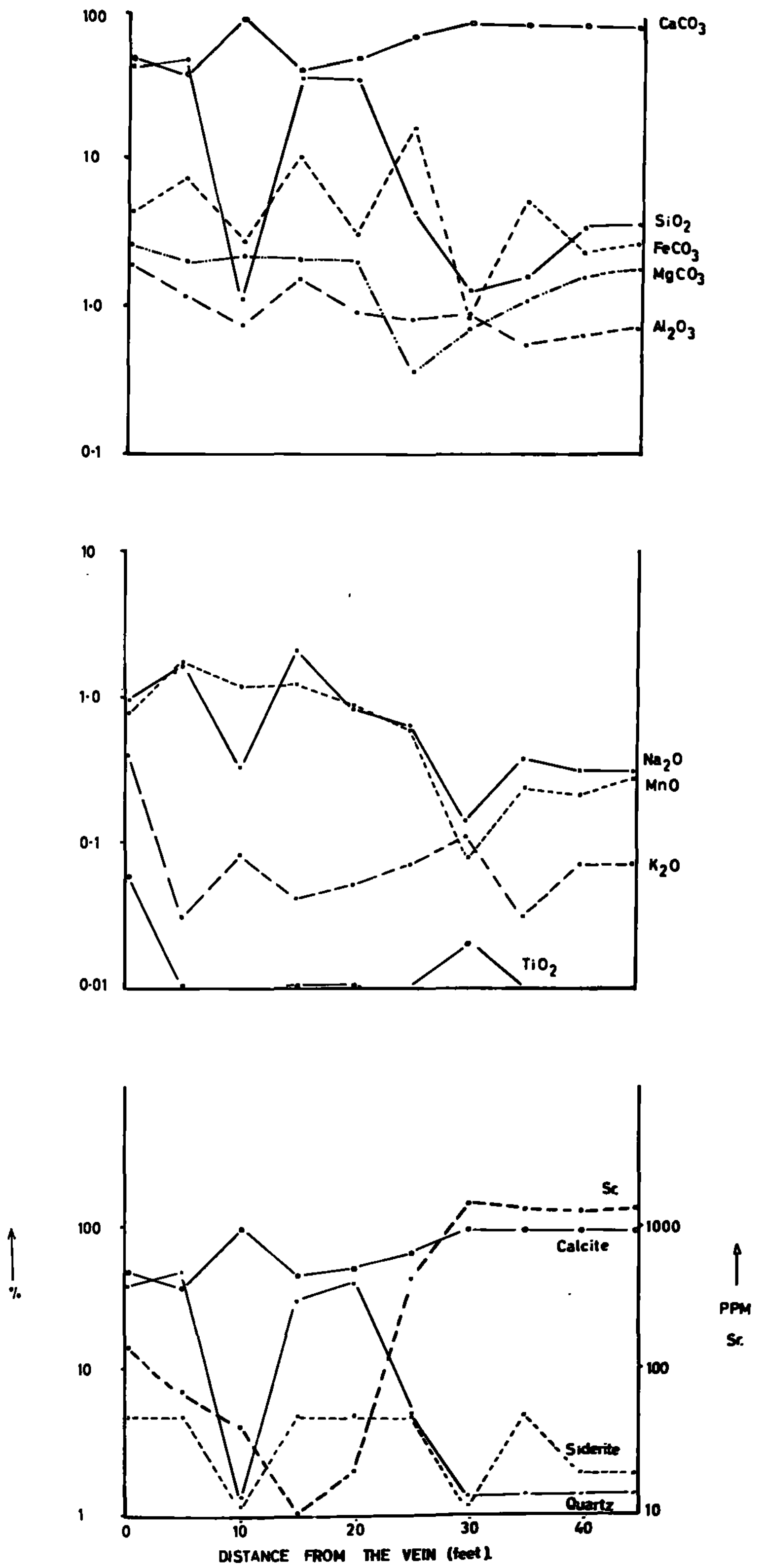


FIG. 4-3 REDBURN MINE.
(BOREHOLE - N 2)

The SiO_2 content is variable throughout the aureole. Mineralogical analyses indicate a decrease in calcite and an increase in quartz, siderite and ankerite between 60 and 78 feet.

Increases in Na_2O, MnO, Al_2O_3, $MgCO_3$, SiO_2, K_2O and TiO_2, a decrease in $CaCO_3$ towards the vein are illustrated in fig.4-3 (borehole N2). $FeCO_3$ results are erratic. Mineralogically, quartz and siderite increase towards the vein. The alteration zone is 30 feet wide.

Heights Quarry

The variation in the major chemical and mineralogical composition of the wallrocks of the West Cross Vein and the South Vein are illustrated on figs. 4-4 and 4-5 respectively.

Fig. 4-4 illustrates the increase in $FeCO_3$, SiO_2, Al_2O_3, Na_2O, MnO and K_2O and the decreases in $CaCO_3$ towards the vein. The $MgCO_3$ content is erratic throughout the aureole. Mineralogical analyses indicate the increase in quartz and the decrease in calcite within the aureole. Ankerite and siderite were not detected in the traverse.

Chemical and mineralogical analyses indicate the insignificant variation of the constituents to within 1 foot of the South Vein (fig.4-5). SiO_2, $FeCO_3$, Na_2O and MnO increased, while Al_2O_3, K_2O, $MgCO_3$ and TiO_2 decreased within this narrow aureole. Mineralogical

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

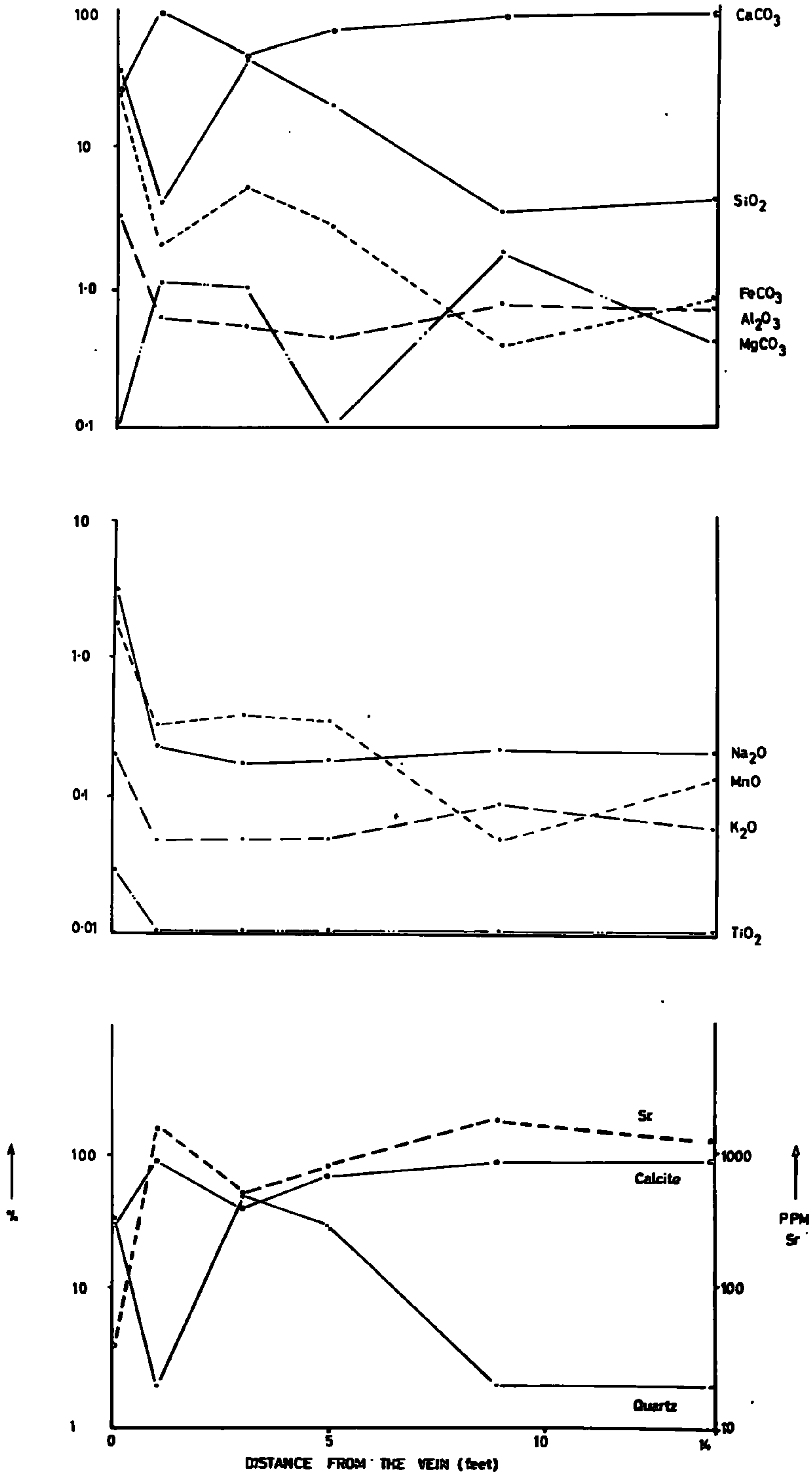


FIG. 4-4 HEIGHTS QUARRY.
(WEST CROSS VEIN)

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

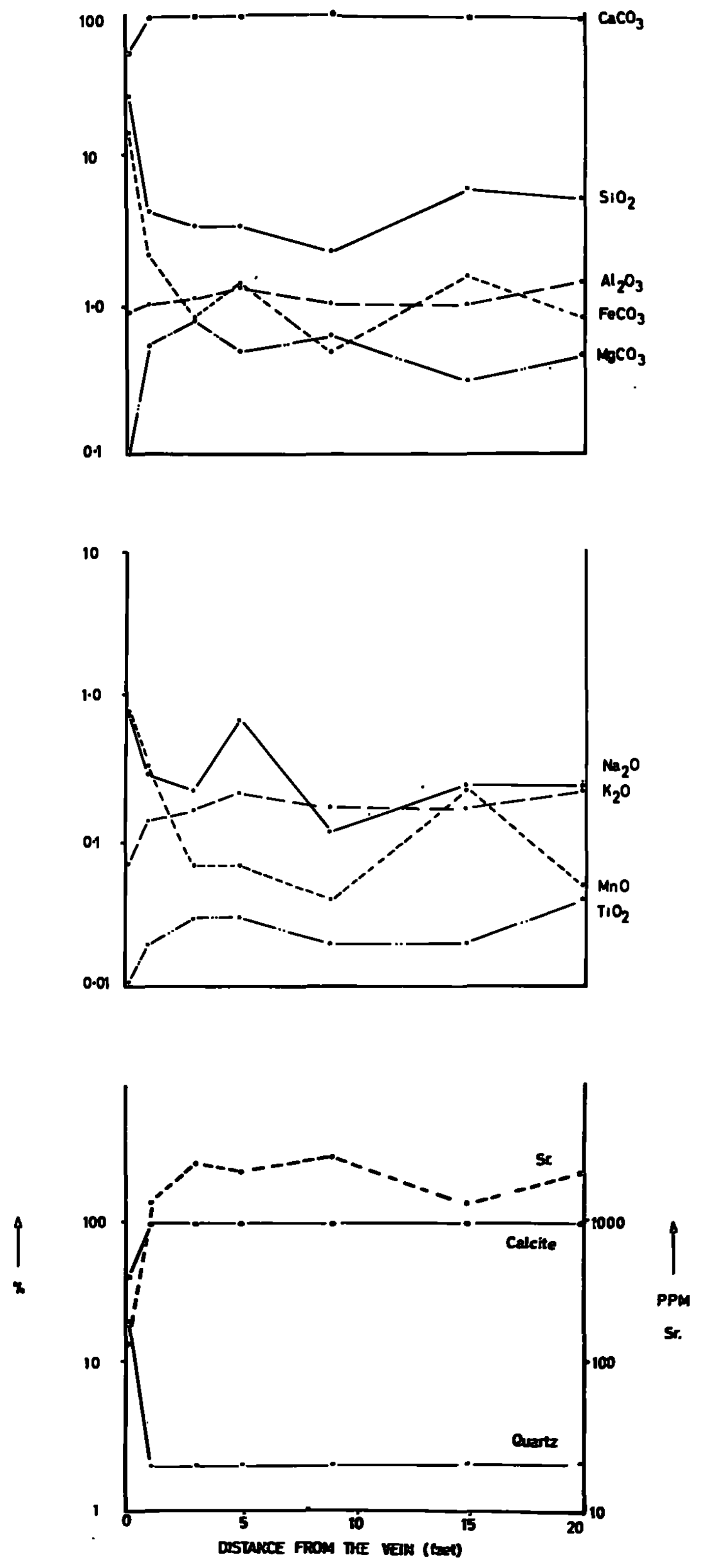


FIG. 4-5 HEIGHTS QUARRY.
(SOUTH VEIN)

analyses [illegible] support the deducations based on chemical analyses. Small amounts of pyrite and fluorite are present in this restricted aureole.

Garrigill

The chemical and mineralogical fluctuations next to Browngill Vein are illustrated in fig. 4-6. Near the vein SiO_2, Na_2O, Al_2O_3 and K_2O increase, while $CaCO_3$, $MgCO_3$, Fe_2O_3 and TiO_2 decrease. Between 12 and 35 feet, $CaCO_3$ and MnO decrease while the remaining seven constituents increase in concentration. Mineralogical analyses indicate the decrease in calcite near the vein and the subsequent enrichment with distance from the vein. A background composition of the Tynebottom Limestone is 73% $CaCO_3$, 10% SiO_2, 6% $FeCO_3$, with subordinate Al_2O_3, Na_2O and K_2O.

The Derbyshire Orefield

The variations in the major chemical and mineralogical composition of the limestone wallrocks are illustrated in figs. 4-7 to 4-11.

Ladywash Mine

The variations next to Hucklow Edge Vein (West) are shown on fig. 4-7. Increases in Al_2O_3, $FeCO_3$, Na_2O and K_2O, while decreases in

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

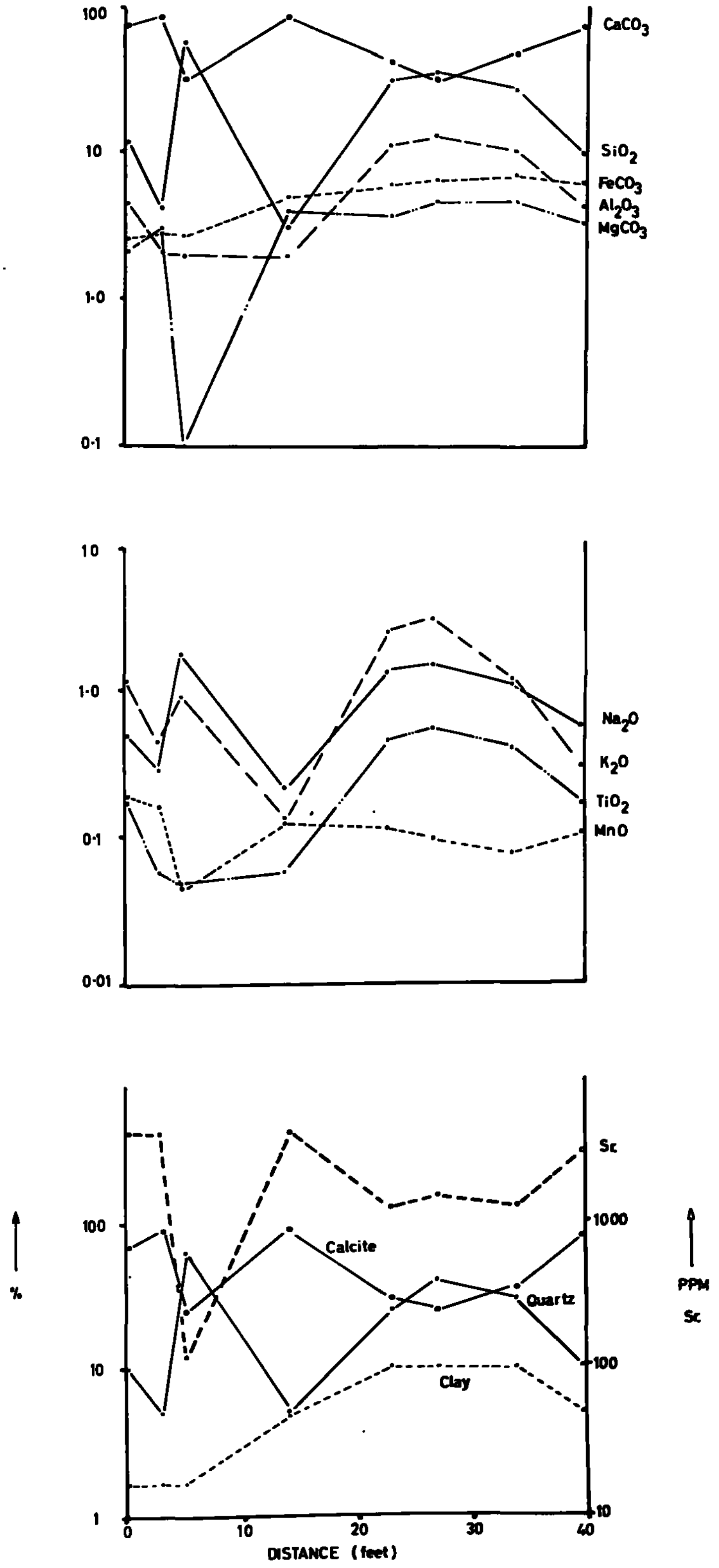


FIG. 4–6 GARRIGILL.

$MgCO_3$, TiO_2, $CaCO_3$, and MnO are noted near to the vein. The SiO_2 content is erratic throughout the aureole. Abnormally high values for Na_2O, TiO_2, and Al_2O_3 are present at 7 feet from the vein. Mineralogical analyses supported the deductions based on chemical analyses for the constituents quartz and calcite.

Fig. 4-8 illustrates the aureole next to Hucklow Edge Vein (East). A sample at 20 feet from the vein has high SiO_2 and very low Na_2O and Al_2O_3 values, otherwise the following variations are valid. A decrease in $CaCO_3$, $MgCO_3$, and K_2O towards the vein and an increase in SiO_2, Al_2O_3, $FeCO_3$, Na_2O and MnO are indicated. Mineralogical analyses confirm the proportions of quartz and calcite as well as indicating the presence of fluorite, pyrite and sphalerite on the vein wall. The marked differences exhibited in the westerly traverse are, it is suggested, related to the underlying tuff, which is not present directly below the sampling traverse at the eastern extremity.

Odin Mine

Increases in SiO_2, Al_2O_3, $FeCO_3$, MnO and K_2O with concommitant decreases in $CaCO_3$, $MgCO_3$ and Na_2O towards the vein are illustrated on fig. 4-9. Mineralogical analysis supports the chemical analyses for quartz and calcite and indicates the presence of dolomite in the limestone wallrocks.

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

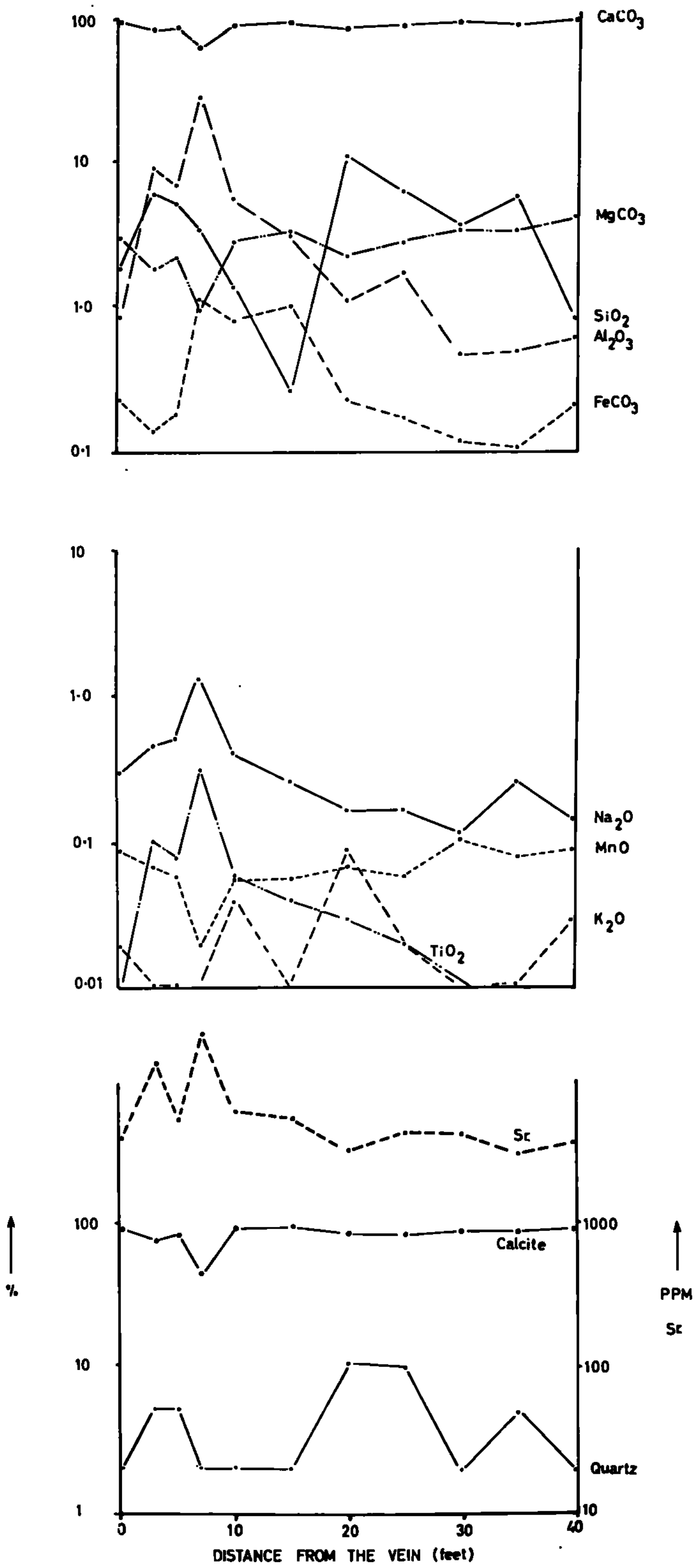


FIG. 4-7 LADYWASH MINE.
(HUCKLOW EDGE VEIN - WEST)

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

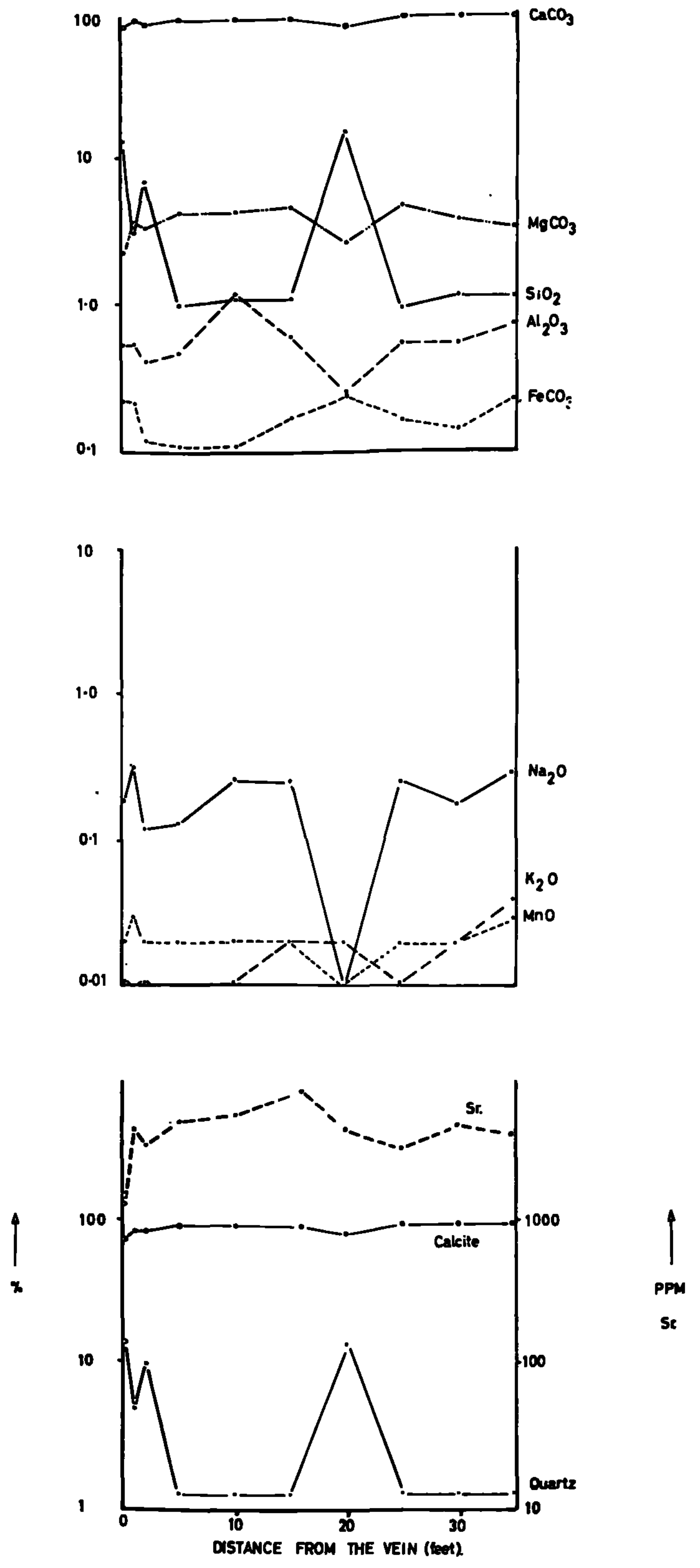


FIG. 4-8 LADYWASH MINE.
(HUCKLOW EDGE VEIN - EAST)

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

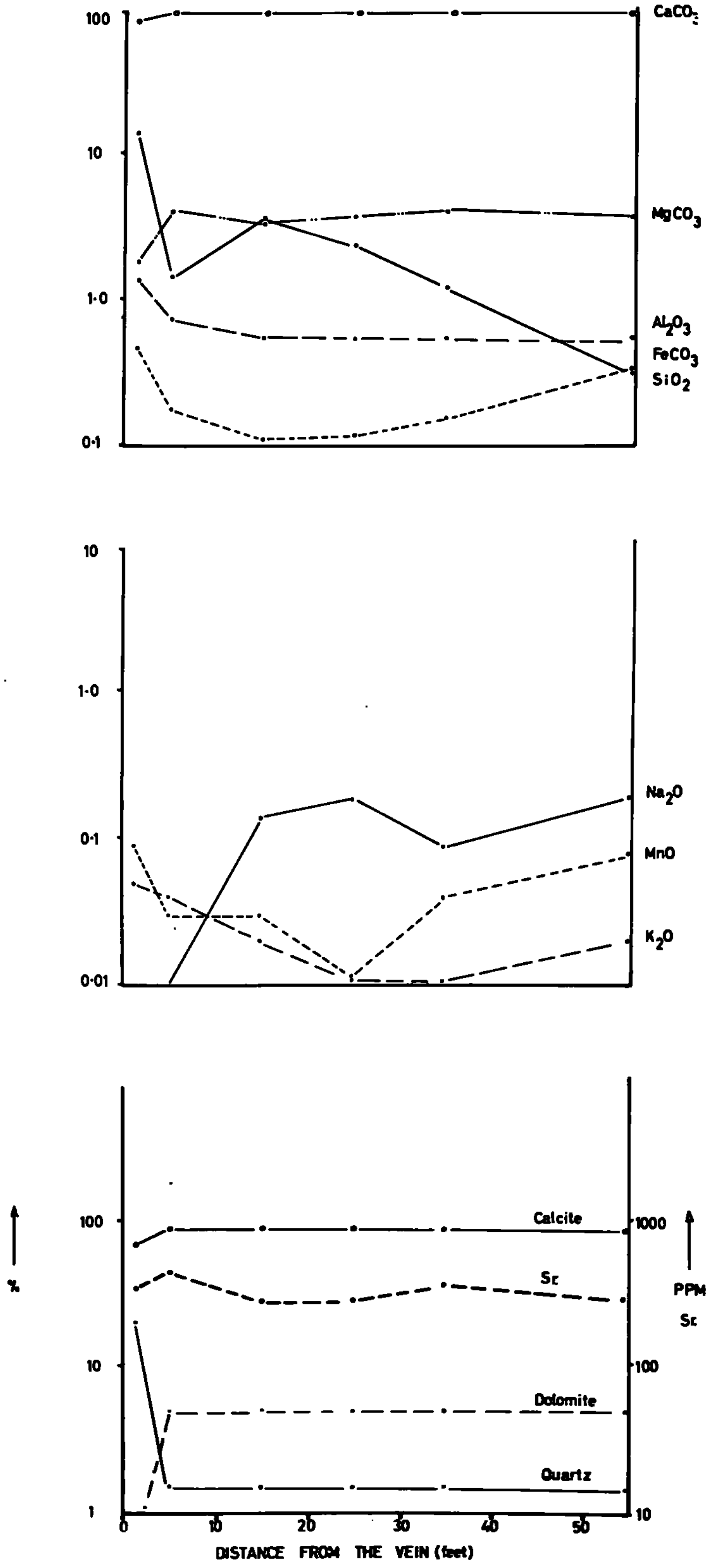


FIG. 4-9 ODIN MINE

Masson Hill Quarry

The chemical and mineralogical analyses illustrated in fig. 4-10 show a decrease in SiO_2, $FeCO_3$, Al_2O_3, $CaCO_3$, Na_2O, K_2O and TiO_2 and an increase in $MgCO_3$ and MnO next to the fluorite vein. Between 5 and 10 feet from the vein, SiO_2, $FeCO_3$, Al_2O_3, Na_2O, K_2O and TiO_2 increase and $CaCO_3$, $MgCO_3$ and MnO decrease. Mineralogical analyses supported the deductions based on chemical analyses for the constituents quartz, calcite and dolomite, as well as indicating small amounts of galena, sphalerite, fluorite and limonite in this region.

Middleton Mine

Fig.4-11 illustrates the variations next to the barite/galena vein at Middleton Mine. SiO_2, $MgCO_3$, and Na_2O decrease, while Al_2O_3, TiO_2 and MnO increase next to the vein. Chemical and mineralogical analyses confirm the constant composition of the wallrocks beyond 5 feet.

Summary of the Results

The main chemical and mineralogical properties and variations of the sediments next to the veins may be summarised as follows:-

SiO_2

An increase in SiO_2 occurs next to all but two of the veins.

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

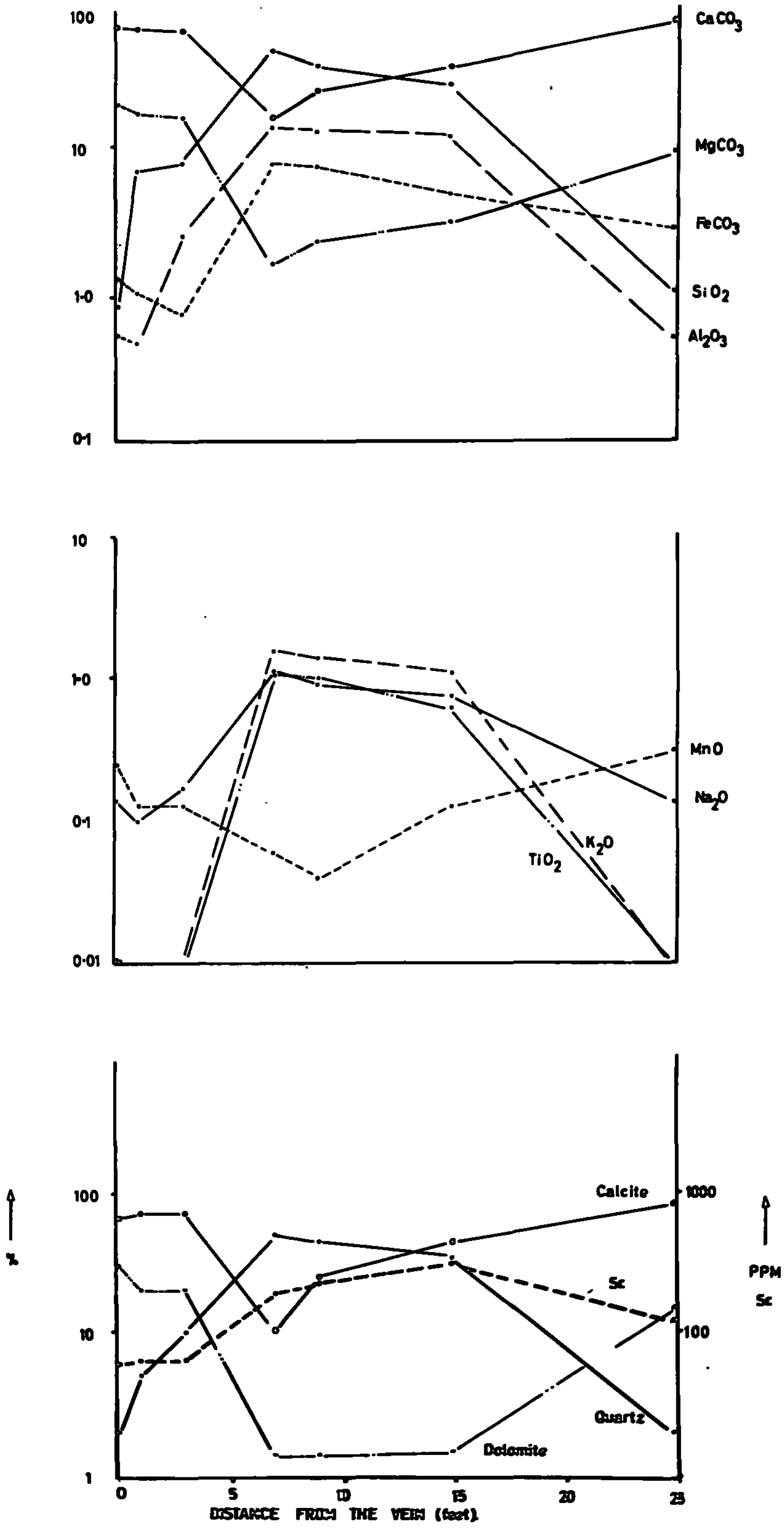


FIG. 4-10 MASSON HILL QUARRY.

MAJOR CHEMICAL AND MINERALOGICAL VARIATIONS

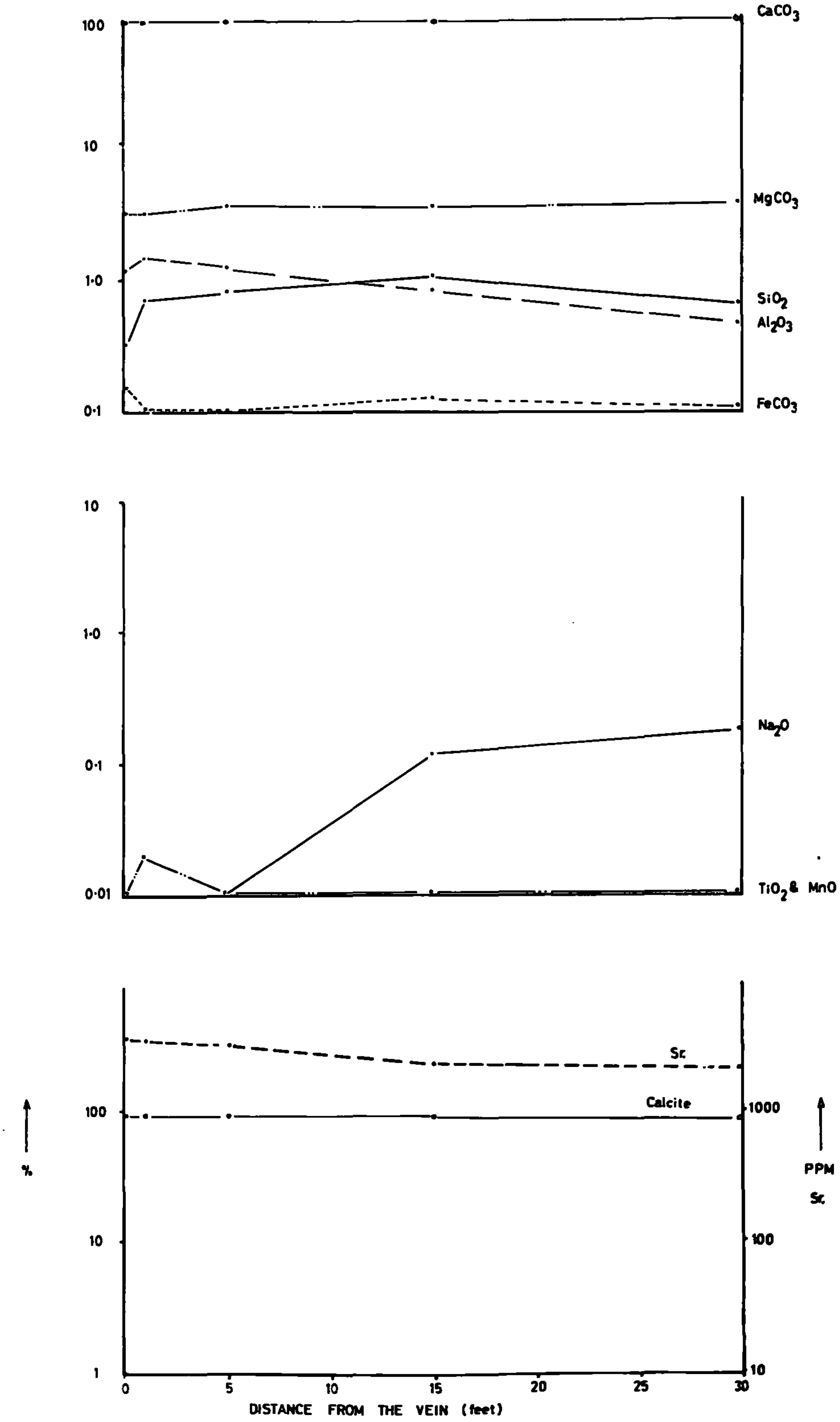


FIG. 4-11 MIDDLETON MINE

SiO_2 decreases at Masson Hill and Middleton Mine

Al_2O_3

The Al_2O_3 content increases adjacent to most veins. A decrease is noted at Garrigill, Heights Quarry (South Vein) and at Masson Hill.

$FeCO_3$

Decreases in $FeCO_3$ occur at Redburn Mine (borehole U2) and Masson Hill, elsewhere the carbonate increases next to the vein.

$MgCO_3$

Six of the traverses illustrate an increase in $MgCO_3$ (see figs. 4-1, 2, 3, 6, 8 and 10) while a decrease is noted next to five of the veins.

$CaCO_3$

A decrease in $CaCO_3$ was found next to all the veins.

Na_2O

Odin Mine, Masson Hill and Middleton Mine illustrated a decrease in Na_2O in the wallrocks. The other localities show an increase next to mineralization.

K_2O

Six of the traverses illustrate an increase in K_2O, four show a decrease and the wallrocks at Middleton Mine do not contain greater than 0.01% K_2O

TiO_2

TiO_2 was not detected at Redburn Mine (borehole W2), Hucklow Edge Vein (East) and Odin Mine. Decreases in TiO_2 occur at Heights Quarry (South Vein), Masson Hill Quarry and Hucklow Edge Vein (West). Other localities illustrated an increase in TiO_2 next to the vein.

MnO

An increase in MnO next to the mineralization is recorded from all but one locality. At Garrigill, MnO decreases in concentration adjacent to the vein.

Calcite

A decrease in calcite is found next to all the veins, in agreement with the calcium analyses which were recast as $CaCO_3$.

Dolomite

Dolomite is not present in the wallrocks of the northern Pennines. It was detected in Derbyshire, where at Odin Mine a decrease, and at Masson Hill an increase was recorded.

Quartz

An increase in quartz next to most of the veins was observed. Erratic results were recorded next to Hucklow Edge Vein and quartz was not detected in the limestone wallrocks at Middleton Mine. These results are in reasonable agreement with the analyses for SiO_2.

Ankerite

Ankerite was detected in samples from the Alston Block. Less than 5% ankerite was invariably present in the limestones, although it is concentrated next to the Red Vein at Redburn Mine. It was not detected in Derbyshire limestones.

Siderite

The mineral was not detected next to veins in Derbyshire. Apart from the boreholes at Redburn Mine, it was not found in the samples from the Alston Block.

Clay Minerals

Kaolinite and illite are present in the Tynebottom limestone at Garrigill. These minerals were not detected in any other samples.

Abnormal Results

The mineralogical analyses do not invariably confirm the chemical analyses. The explanation is that the data for iron, calcium and magnesium was converted, during processing by the computer, to $FeCO_3$, $CaCO_3$ and $MgCO_3$, in which form the analyses were expressed. The programme did not allocate calcium, magnesium and iron to the actual minerals, dolomite, $CaMg(CO_3)_2$ or ankerite $(Fe,Ca,Mg)(CO_3)_2$. Furthermore, expression of iron as $FeCO_3$, siderite must be considered only a first approximation particularly if other iron bearing minerals are present, such as pyrite. These results appertain to a small number of samples and do not invalidate the majority of the results.

CHAPTER V

THE GEOCHEMISTRY OF THE DISPERSION PATTERNS

Trace element aureoles, major chemical and mineralogical variations together with the petrology of the limestone wallrocks indicate that certain conclusions are possible regarding the alteration of the limestone wallrocks, the migration of the trace elements and the prospect of using primary cycle geochemical prospecting in locating mineralization.

Correlation Coefficients

Correlation coefficients between trace elements and major chemical constituents indicate the degree of association between these variables. This is particularly pertinent for associations between trace elements and mineralogical constituents. The correlation coefficients are illustrated in tables 5-1 to 5-9. Very strong positive correlation between calcite and Ca expressed as $CaCO_3$, quartz and Si expressed as SiO_2 confirm that the X-ray fluorescence analysis and X-ray diffractometry give these constituents comparable results. SiO_2 and $CaCO_3$ are therefore omitted in the correlation tables. Total Fe expressed as $FeCO_3$ and Mg as $MgCO_3$ are also omitted where ankerite and siderite are present. However, as the Fe : Mg ratio of ankerites may vary, the $FeCO_3$ and $MgCO_3$ results are included where ankerite is present and siderite is not detected.

Table 5-1

Correlation Coefficients - Redburn Mine - (borehole W2)

	Dist.	Al_2O_3	Na_2O	K_2O	Qtz.	Calc.	Ank.	Sid.	Rb.	Pb.	Sr.	Mn.	Zr.	Zn.	Cu.
Al_2O_3	.32														
Na_2O	.24	.97													
K_2O	-.40	-.01	.05												
Qtz.	-.54	.19	.35	.81											
Calc.	.15	-.48	-.62	-.59	-.81										
Ank.	-.40	.19	.22	.40	.43	-.61									
Sid.	.51	.37	.45	.01	.12	.53	.07								
Rb	-.33	.09	.24	.34	.03	-.59	.55	-.04							
Pb	.06	.09	.11	.29	.19	-.14	.35	.12	.10						
Sr	-.01	-.53	-.68	-.45	-.77	.87	-.21	-.53	-.43	.04					
Mn	.27	.32	.38	.46	.36	-.64	.36	.77	.17	.46	-.45				
Zr	.57	.78	.74	-.01	.03	-.21	v.19	.45	-20	.32	-.36	.48			
Zn	-.56	.34	.45	.66	.86	-.81	.63	.01	.66	.01	-.68	.18	-.10		
Cu	.13	.91	.96	-.09	.31	-.55	.21	.31	.30	-.05	-.64	.17	.59	.47	
Ni	.11	-.23	-.14	-.07	.05	-.17	-.20	.51	-.27	-.25	-.23	.32	-.06	-.18	-.14

Significance Levels

99%	.71
95%	.66

Qtz. = Quartz; Calc. = Calcite; Dol. = Dolomite; ank. = ankerite; sid. = siderite

Table 5-2

Correlation Coefficients. Redburn Mine (borehole N-2)

	Dist.	Al_2O_3	$FeCO_3$	$MgCO_3$	Na_2O	K_2O	TiO_2	Qtz.	Calc.	Rb	F	Pb	Sr	Mn	Zr	Zn	Cu
Al_2O_3	-.75																
$FeCO_3$	-.17	.16															
$MgCO_3$	-.56	.53	-.37														
Na_2O	-.59	.69	.46	.41													
K_2O	-.45	.68	-.19	.38	-.03												
TiO_2	.63	-.63	-.09	-.28	-.52	-.25											
Qtz.	-.73	.74	.11	.57	.76	.26	-.65										
Calc.	.72	-.78	-.40	-.43	-.84	-.25	.61	-.95									
Rb	.86	-.57	-.37	-.57	-.67	-.15	.55	-.72	.75								
F	-.66	.75	.47	.42	.93	.12	-.61	.89	-.97	.76							
Pb	-.66	.69	-.28	.61	.07	.90	-.43	.39	-.31	-.42	.21						
Sr	-.25	.06	.89	-.42	.18	-.05	-.12	.02	-.27	-.39	.27	-.08					
Mn	-.64	.81	.01	.49	.38	.80	-.35	.64	-.63	-.38	.52	.76	.04				
Zr	-.13	-.15	-.61	.46	-.48	.28	.09	-.23	.40	-.11	-.45	.49	-.35	-.12			
Zn	-.39	.38	.84	-.13	.73	-.18	-.20	.35	-.57	-.44	.64	-.24	.63	.15	-.65		
Cu	-.09	-.18	-.22	.18	-.05	-.19	.39	.04	.03	-.06	-.08	-.17	-.25	-.19	.31	.04	
Ni	-.18	.62	.32	.29	.52	.40	-.19	.22	-.35	-.17	.45	.31	.12	.54	-.36	.36	-.58

Significance Levels

99%	> .76
95%	> .71

Table 5-3

Correlation Coefficients - Redburn mine (Crosscut to borehole W2)

	Dist.	Al_2O_3	Na_2O	K_2O	TiO_2	Qtz.	Calc.	Ank.	Sid.	Rb	F	Pb	Sr	Mn	Zr	Zn	Cu
Al_2O_3	-.69																
Na_2O	-.73	.99															
K_2O	-.52	.42	.43														
TiO_2	-.66	.77	.78	.81													
Qtz.	-.39	-.15	-.63	-.63	-.34												
Calc.	.28	-.68	-.68	.29	-.22	-.41											
Ank.	-.39	.48	.46	.39	.43	-.80	-.08										
Sid.	-.57	.57	.56	-.13	.12	-.20	-.59	.47									
Rb	.91	-.17	-.19	-.31	-.41	-.03	.09	-.33	.55								
F	.08	-.42	-.43	.30	-.08	-.70	.83	.39	-.29	.03							
Pb	.37	.28	-.29	-.39	-.33	-.15	-.04	-.33	.01	-.31	.29						
Sr	-.15	-.65	-.69	-.54	-.66	.14	.26	-.03	-.36	-.08	.26	.65					
Mn	-.89	.88	.90	.34	.66	-.12	-.57	.32	.65	.09	-.35	-.41	-.86				
Zr	-.90	.89	.92	.43	.75	-.18	-.61	.38	.60	-.05	-.39	-.34	-.84	.95			
Zn	.77	-.38	-.39	-.53	-.57	.68	-.06	-.62	-.50	-.24	-.34	.03	.51	.53	-.57		
Cu	-.13	.01	.06	-.49	-.18	.59	-.35	-.41	.13	.30	-.44	-.34	-.23	.26	.22	.16	
Ni	-.65	.58	.58	.44	.53	.09	-.21	-.14	.32	.30	-.38	-.89	-.84	.73	-.63	-.29	.28

Significance Levels

99%	> .79
95%	> .75

Table 5-4

Correlation Coefficients. Heights Quarry (West Cross Vein)

	Dist.	Al_2O_3	$FeCO_3$	$MgCO_3$	Na_2O	K_2O	TiO_2	Qtz.	Calc.	Ank.	F	Pb	Sr	Mn	Zr	Zn	Cu
Al_2O_3	-.44																
$FeCO_3$	-.58	.96															
$MgCO_3$	-.08	.13	.01														
Na_2O	.49	.99	.98	.06													
K_2O	-.37	.98	.92	.23	.97												
TiO_2	-.49	.99	.98	.05	.98	.97											
Qtz.	-.53	.27	.49	-.26	.32	.21	.34										
Calc.	.66	-.62	-.80	.13	-.67	-.57	-.68	-.91									
Ank.	-.62	.97	.88	.09	.97	.92	.98	.40	-.74								
F	-.49	.99	.98	.05	.99	.97	.98	.33	-.68	.98							
Pb	-.73	.11	.29	.17	.15	.02	.15	.55	-.57	.35	.15						
Sr	.52	-.62	-.79	.39	-.67	-.55	-.69	-.87	.95	-.72	-.69	-.40					
Mn	-.67	.95	.99	.04	.97	.90	.97	.46	-.78	.99	.97	.36	-.76				
Zr	-.81	.69	.77	.17	.71	.60	.71	.43	-.69	.84	.71	.77	-.59	.83			
Zn	-.41	-.23	-.01	-.62	-.14	-.27	-.13	.59	-.37	-.10	-.12	.15	-.42	.01	-.05		
Cu	-.38	.07	.26	.08	.09	.02	.11	.82	-.72	.23	.11	.76	-.59	.25	.45	.21	
Ni	-.57	.93	.98	.05	.95	.89	.95	.56	-.85	.97	.95	.37	-.82	.97	.79	-.04	.40

Significance Levels

99%	> .92
95%	> .88

Table 5-5

Correlation Coefficients - Heights Quarry (South Vein)

	Dist.	Al_2O_3	$FeCO_3$	$MgCO_3$	Na_2O	K_2O	TiO_2	Qtz.	Calc.	Ank.	Rb	F	Pb	Sr	Mn	Zr	Zn	Cu
Al_2O_3	.64																	
$FeCO_3$	.47	-.54																
$MgCO_3$	-.67	-.37	.64															
Na_2O	-.47	-.19	.72	.35														
K_2O	.68	.91	-.81	-.65	-.38													
TiO_2	.57	.93	-.67	-.37	-.32	.92												
Qtz.	-.44	-.50	.97	.68	.70	-.79	-.64											
Calc.	.44	.50	-.98	-.67	-.70	.79	.64	-.98										
Ank.	-.44	-.51	.90	.68	.70	-.79	-.64	.97	-.90									
Rb	-.39	-.45	.98	.68	.70	-.75	-.60	.98	-.98	.97								
F	-.41	-.46	.90	.67	.69	-.76	-.62	.97	-.98	.98	.97							
Pb	-.35	-.46	.75	.64	.36	-.71	-.70	.79	-.79	.79	.80	.78						
Sr	.26	.57	-.84	-.19	-.59	.69	.64	-.78	.87	-.79	-.79	-.75	-.42					
Mn	-.44	-.42	.95	.71	.76	-.72	-.55	.97	-.96	.95	.94	.97	.72	-.73				
Zr	-.24	-.39	-.12	-.33	-.20	-.17	-.26	-.22	-.22	-.22	-.32	-.23	-.33	-.27	-.32			
Zn	-.42	-.35	.01	-.08	-.08	-.23	-.25	-.08	.08	-.08	.94	-.09	-.18	-.27	-.19	.94		
Cu	-.44	-.50	.97	.67	.70	-.79	-.64	.97	-.98	.97	-.22	.96	.79	-.79	.98	-.22	-.08	
Ni	-.09	-.12	.87	.53	.59	-.48	-.29	.89	-.89	.89	-.31	.91	.63	-.71	.88	-.31	-.16	.89

Significance Levels

99%	>.87
95%	>.83

Table 5-6

Correlation Coefficients - Garrigill

	Dist	Al_2O_3	$FeCO_3$	$MgCO_3$	Na_2O	K_2O	TiO_2	Qtz.	Calc.	Rb	F	Pb	Sr	Mn	Zr	Zn	Cu
Al_2O_3	.56																
$FeCO_3$	.93	.74															
$MgCO_3$	.64	.63	.81														
Na_2O	.16	.51	.18	-.24													
K_2O	.22	.88	.42	.33	.66												
TiO_2	.57	.99	.75	.64	.49	.88											
Qtz.	.01	.25	-.01	-.43	.94	.43	.23										
Calc.	-.23	-.68	-.31	.05	.96	-.77	-.66	-.86									
Rb	.34	.94	.55	.51	.49	.96	.95	.22	-.64								
F	-.42	-.39	-.54	-.87	.58	-.13	-.41	.77	-.39	-.36							
Pb	-.77	-.58	-.72	-.21	-.71	.96	-.59	-.59	.71	-.44	-.15						
Sr	-.32	-.47	-.30	.19	-.96	-.53	-.46	-.91	.92	-.38	-.55	-.38					
Mn	-.58	-.17	-.60	-.84	.64	.19	-.18	.71	-.51	-.01	.86	-.04	-.50				
Zr	.49	.73	.58	.64	.29	.59	.71	.19	-.40	.58	-.36	-.33	-.28	-.38			
Zn	-.37	-.38	-.50	-.85	.59	-.12	-.40	.78	-.40	-.36	.99	-.19	-.58	.83	-.35		
Cu	-.22	-.09	-.29	-.69	.81	.16	-.11	.93	-.66	-.08	.94	-.50	-.78	.83	-.12	.95	
Ni	.15	.46	.17	-.24	.99	.60	.45	.95	-.95	.41	-.61	-.68	.97	.60	.29	.63	.83

Significance Levels

99% > .84

95% > .79

Table 5-7

Correlation Coefficients - Hucklow Edge Vein (West)

	Dist.	Al_2O_3	$FeCO_3$	$MgCO_3$	Na_2O	K_2O	TiO_2	Qtz.	Calc.	Rb	F	Pb	Sr	Mn	Zr	Zn	Cu
Al_2O_3	-.47																
$FeCO_3$	-.34	.81															
$MgCO_3$	.70	-.81	-.57														
Na_2O	-.51	.98	.82	-.79													
K_2O	.09	-.31	-.01	.01	-.32												
TiO_2	-.57	.13	.16	-.19	.23	-.09											
Qtz.	.11	-.23	-.29	-.23	-.27	.68	-.27										
Calc.	.44	-.95	-.71	.88	-.93	.22	-.15	.01									
Rb	.74	-.38	-.34	.63	-.37	-.24	-.25	-.25	.35								
F	-.73	.87	.84	-.77	.92	-.21	.48	-.32	-.79	-.56							
Pb	.75	-.54	-.45	.51	-.55	.06	-.19	.33	.36	.66	-.67						
Sr	-.42	.97	.76	-.77	.94	-.34	.14	-.25	.94	-.32	.81	-.47					
Mn	.47	-.82	-.79	.58	-.84	.23	-.28	.30	.69	.57	-.86	.58	-.76				
Zr	-.71	.88	.87	-.82	.91	-.11	.43	-.22	-.83	-.59	.98	-.83	.83	-.84			
Zn	-.43	.20	.24	-.28	.27	-.03	-.07	-.09	-.14	-.33	.36	-.49	.02	-.18	.31		
Cu	-.22	.51	.48	-.67	.49	.10	-.29	.35	-.61	-.22	.37	-.07	.44	-.20	.47	.43	
Ni	-.35	.88	.95	-.71	.86	.04	.01	-.11	-.83	-.40	.81	-.45	.82	-.74	.86	.27	.64

Significance Levels

99% > .73

95% > .68

Table 5-8

Correlation Coefficients - Hucklow Edge Vein (East)

	Dist.	Al_2O_3	$FeCO_3$	$MgCO_3$	Na_2O	K_2O	Qtz.	Calc.	Rb	F	Pb	Sr	Mn	Zn	Cu
Al_2O_3	.04														
$FeCO_3$	.18	-.37													
$MgCO_3$	.11	.38	-.64												
Na_2O	.09	.63	-.06	.41											
K_2O	.79	.06	.39	-.23	.07										
Qtz.	-.41	-.51	.54	-.83	-.62	-.10									
Calc½	.67	.34	-.46	.70	.45	.32	-.92								
Rb	.72	-.21	.14	-.20	-.05	.72	.08	.44							
F	-.66	-.03	.23	-.18	.34	-.60	.23	-.44	-.47						
Pb	-.39	-.12	.25	-.59	-.06	-.16	.56	-.63	-.22	.24					
Sr	.15	.23	-.27	.66	.15	.12	-.54	.41	-.32	-.26	-.63				
Mn	-.47	-.04	-.19	.08	.22	-.52	-.12	-.02	-.09	.56	.02	-.32			
Zn	-.41	-.06	.34	-.62	-.03	-.13	.58	-.68	-.26	.29	.98	-.63	.04		
Cu	-.42	.05	.36	-.57	-.10	-.15	.58	-.71	-.37	.22	.94	-.53	.02	.97	
Ni	-.35	.01	.30	-.55	.01	-.09	.51	-.61	-.27	.20	.98	-.56	-.03	.99	.97

Significance Levels

99% > .76

95% > .71

Table 5-9

Correlation Coefficients - Masson Hill Quarry

	Dist	Al_2O_3	$FeCO_3$	Na_2O	K_2O	TiO_2	Qtz.	Calc.	Dol.	F	Rb	Sr	Mn	Zr	Zn	Cu
Al_2O_3	.14															
$FeCO_3$	.30	.93														
Na_2O	.12	.98	.96													
K_2O	.12	.98	.97	.99												
TiO_2	-.19	.69	.70	.74	.74											
Qtz.	.07	.99	.94	.98	.99	.69										
Calc.	.14	-.93	-.89	-.96	-.96	-.81	-.96									
Dol.	.07	.97	.95	.99	.99	.77	.98	-.97								
F	-.04	.34	.17	.22	.29	.28	-.58	-.21	.26							
Pb	-.13	.86	.86	.93	.91	.84	.88	-.96	.95	.23						
Sr	-.29	-.32	-.49	-.38	-.41	-.49	-.29	.34	-.42	-.49	-.51					
Mn	.54	-.48	-.40	-.47	-.50	-.27	-.58	.62	-.48	.05	-.50	-.19				
Zr	.48	.86	.79	.78	.81	.48	.79	-.63	.77	.59	.58	-.45	-.07			
Zn	.14	.67	.67	.57	.66	.48	.65	-.56	.57	.39	.42	-.25	-.48	.66		
Cu	.06	.95	.96	.99	.98	.77	.97	-.98	.99	.15	.95	-.40	-.53	.70	.58	
Ni	.11	.98	.96	.99	.99	.96	.76	-.96	.99	.27	.93	-.42	-.48	.79	.61	.99

Significance Levels

99% > .87

95% > .83

The significance at each locality varies according to the number of samples analysed, while a reduction in the strength of an association may be due to the low quality of the analytical data when an element is near the detection limit of the method. These factors result in variations in the strength of an association, however the following conclusions are considered valid.

Major Chemical Components

Al_2O_3

A very strong positive correlation is noted between Al_2O_3, Na_2O, K_2O and TiO_2. These components are associated principally with the clay minerals in limestones. Strong positive correlation exists with rubidium and moderate correlation is noted with zirconium, copper, lead, zinc and nickel.

$FeCO_3$

A distinct positive association between ankerite and $FeCO_3$ reflects the high iron content of the ankerites. This result agrees with the chemical analyses of Smythe and Dunham (1947), who showed that the ankerites were rich in iron with an average value of 20.2% FeO. Some of the iron, recast as $FeCO_3$ will be associated with the pyrite recorded in the mineralogical analyses.

$MgCO_3$

Very strong correlation is shown between $MgCO_3$ and dolomite at

Masson Hill Quarry, the only locality where extensive dolomitization of the limestone wallrocks has occurred. $MgCO_3$ shows negative correlation with quartz and a noteworthy absence of correlation with strontium. The latter result is in agreement with Kulp (1952) who found an insignificant correlation between strontium and magnesium.

Na_2O, K_2O and TiO_2

Very strong positive correlation between Na_2O, K_2O, TiO_2 and Al_2O_3 noted above, indicate their association with the clay fraction. The correlations suggest that these components are almost exclusively present in the clay minerals.

Mineralogical Components

Quartz

Very strong negative correlation is recorded with calcite and strontium, while positive correlation exists with lead, copper and nickel at certain localities.

Calcite

Excellent positive correlation with strontium shows the close association of calcite and strontium.

Ankerite

Ankerite shows strong positive correlation with $FeCO_3$ and moderate positive correlation with $MgCO_3$, quartz and the clay fraction. Moderate negative correlation with calcite is noted.

Siderite

A positive correlation with manganese is found and clearly a large proportion of the manganese is associated with siderite.

Trace Elements

Apart from strong positive associations between rubidium and the elements which favour the clay fraction, strontium and calcite and manganese and siderite, no other positive correlations are found which apply at all the localities.

Lead and Zinc

Moderately strong positive correlations with the components which favour the clay fraction (Al_2O_3, K_2O, Na_2O and TiO_2) and quartz are evident at certain localities, elsewhere they show no correlation with any major components.

Copper and Nickel

Very strong positive correlation between the two elements reflects their close relationship. They are sometimes associated with the clay fraction and quartz, but generally have no correlation with the other components, and possibly occur as discrete minerals.

Zirconium and fluorine

At certain localities a moderate positive correlation of both zirconium and fluorine with Al_2O_3, Na_2O and K_2O may possibly reflect an association with the clay fraction of the limestone. At Hucklow Edge (West) a very strong positive correlation between zirconium and fluorine may reflect an association.

Manganese

A moderate positive correlation between manganese and siderite suggests that siderite contains manganese. In the absence of siderite, manganese shows no correlation with the other components and may be present as a discrete mineral phase, possibly psilomelane or pyrolusite.

Summary and Conclusions

Positive correlations are evident between the majority of the chemical constituents. Al_2O_3, Na_2O, K_2O and TiO_2 are all closely associated and it is suggested that they are present in the clay minerals. As rubidium shows a good correlation with these constituents, it is inferred that it is held in the clay minerals. Occasionally lead, zinc, copper and nickel correlate with the clay components, suggesting their absorption by the clay minerals.

Strontium has a strong positive correlation with calcite, and each have a strong negative correlation with the clay and quartz fraction of the limestones. This indicates that strontium is held in calcite and suggests that calcite has been replaced by the clay minerals and quartz.

Occasionally certain constituents show positive correlation, for example quartz and lead, zinc and nickel. At these localities, therefore, positive correlation merely implies a sympathetic relationship. One possibility is that quartz and the trace elements emanated from the vein at the same time and both have a normal diffusion gradient. An alternative possibility is that the parallel distribution is purely coincidental. Under these circumstances correlation coefficients should be used with caution and related to known mineralogical conditions.

Similarly the absence of a correlation between certain constituents does not necessarily mean that a particular trace element occurs in a discrete mineral phase. Correlation coefficients will not illustrate an association between an exponential decrease of a trace element from a vein and a component which does not decrease in a similar manner. For example, lead, zinc, copper and nickel do not always show an association with clay minerals. In these circumstances the correlation coefficients merely indicate that there is an antipathetic relationship between the trace element and a constituent of the clay fraction. Mineralogical relationships must therefore be considered in these circumstances.

Non-significant correlation coefficients are recorded between components of the limestones and the distance from the vein. This would imply that there was a random distribution of the components away from the vein. However, a logarithmic decrease will not be evident from the correlation coefficients. In these circumstances the correlation coefficients cannot be considered to be infallable and due caution must be exercised in interpreting the results.

Wallrock Alteration

Northern Pennine Orefield

Quartz, clay minerals and $FeCO_3$ are concentrated next to the veins, while $MgCO_3$ and calcite are depleted. Ankerite and siderite have been detected next to some of the veins, however, it is possible that small amounts, below the detection limit, are present in the limestones.

It is suggested that the ore fluids, due to either the leaching of the basement rocks or wallrock reactions at depth, were concentrated in certain elements. The Alston Block is remarkable for the presence of ankerite and siderite in the limestone wallrocks. The origin of these minerals may have been from the metasomatic alteration of the Whin Sill. Alteration of the quartz - dolerite has resulted in the loss in iron and magnesium, while alteration of the overlying limestones has resulted in the deposition of minerals containing these elements. The Derbyshire limestones are not replaced by ankerite and siderite, and are not, as far as is known, underlain by a possible source of these minerals.

The enrichment of K_2O, Na_2O and TiO_2 next to the veins in the Alston Block may also indicate a possible source of these elements from the ore fluids. Sawkins (1966) suggests that, as the sodium content of fluid inclusions exceeds the potassium content, a large proportion of the potassium 'is constantly being fixed in the reconstitution of degraded clay minerals'. He therefore provided a possible explanation for the origin of the potassium. The loss in Na_2O by metasomatism of the Whin Sill may account for the enrichment in Na_2O in the wallrocks at higher stratigraphic levels. The origin of the TiO_2 in the limestone wallrocks is not documented by analytical results. There is no marked decrease in TiO_2 on metasomatism of the Whin Sill, and the veins do not contain detectable amounts of titanium. It must however be concluded that when the orefluids were transgressing the limestones they contained titanium which was not deposited in the wallrocks.

The Derbyshire Orefield

The alteration of the limestone wallrocks in Derbyshire has resulted in the replacement of calcite by quartz and dolomite. A decrease in Na_2O, Al_2O_3, K_2O and TiO_2 next to the veins would suggest that the clay minerals were decomposed by the ore fluids.

The absence of ankerite and siderite in the wallrocks indicates that the orefluids did not contain these elements. The large replacement orebody at Masson Hill indicates a difference in the alteration of the limestones of the two orefields. The dominant alteration process in Derbyshire is the replacement of the limestone by dolomite while in the northern Pennines, the limestones are replaced by ankerite and siderite. This fundamental difference indicates that the composition of the orefluids which gave rise to the two orefields were not identical, although they resulted in the deposition of similar ore mineral suites.

Situation of the Trace Elements

The correlation coefficients have indicated that for certain trace elements very strong correlation is present with a major constituent of the limestones, and together with additional data, firm conclusions are possible regarding these constituents. In certain cases, however, it is not possible to state positively the situation of a trace element, they may be present in discrete minerals or absorbed by certain minerals.

Petrology of the limestone wallrocks shows that sphalerite, galena, barite, pyrite and fluorite are present in the fractures next to the vein. The concentration of other elements, for example copper and nickel, rarely exceed 100 ppm next to the vein. It cannot therefore be assumed that a mineral containing copper or nickel is not present, but that the mineral being in submicroscopic amounts, is not detectable.

It is possible that the minerals are not only present in fractures, but are also located along grain boundaries. Brown (1953) postulates such a position for trace elements, as the leaching of rocks liberated the trace elements but did not modify the major mineral phase.

The analysis, by X-ray fluorescence, of a crystal of calcite from Masson Hill, indicates that the trace elements may be present on cleavage surfaces. An artificially cut surface and a cleavage surface were examined. A five fold increase in manganese was found on the cleavage surface with respect to the cut surface.

Strontium, rubidium, and manganese to a limited extent, are exceptions to the above statements. Strontium shows a close association to calcite, rubidium to the clay fraction and manganese to siderite. These trace elements are present in the crystal lattice, in which they substitute for the appropriate major element.

Deer, Howie and Zussman (1962, vol.5) state that 'small amounts of strontium commonly substitute for calcium in calcite though strontium is less abundant in calcites than aragonites, the larger strontium ion being more acceptable in the aragonite structure'. The experimental co-precipitation of strontium with calcite and aragonite, has been studied by Oxburgh et. al. (1959) and Holland et. al. (1964). The results indicate that strontium is present in calcite and aragonite, although strontium is less readily incorporated in calcite than in aragonite. It may be inferred from these results, and the good correlation of strontium and calcite that the strontium is held in the calcite lattice. Prior to the recrystallisation of aragonite to calcite, the majority of the strontium may have been held in the aragonite lattice, for Kulp (1952) reports that the recrystallisation of aragonite liberates the strontium.

Rubidium has a close association with Al_2O_3, K_2O, Na_2O and TiO_2, which reflect the clay fraction of the limestones. The geochemistry of rubidium is closely related to that of potassium with a result that rubidium may replace potassium in crystal lattices. The present results indicate that such a replacement has occurred.

Graf and Kerr (1950) suggests that the association of trace elements and altered rocks which contain layer-lattice minerals will be strong, due to the high absorption and base exchange properties of the minerals. The clay minerals have a layer-lattice structure and the correlation of some of the trace elements with the clay fraction would suggest the sorption of the trace elements by the clay minerals. Goldschmidt (1958) maintains that nickel, copper, lead and zinc may be absorbed by clay minerals. This study has shown these elements are often associated with the clay fraction reflecting either a limited amount of sorption, or the incorporation of the trace elements directly into the newly formed clay minerals.

The moderate correlation of manganese and siderite suggests the substitution of manganese for Fe^{2+}. The pure end-member ($FeCO_3$) of the solid solution series (siderite - rhodochrosite) has an inferred refractive index of 1.875 (w), which diminishes with substitution of Mn for Fe^{2+}. The refractive index (w) of the northern Pennine siderites ranges from 1.838 to 1.843 (Dunham, 1948. p.93), and suggests that a limited amount of manganese has substituted for the Fe^{2+} in the lattice. Strong positive correlation between manganese and siderite is not found, suggesting the limited presence of a discrete manganese mineral, possibly psilomelane or pyrolusite.

Width of the Dispersion Aureoles

Hawkes and Webb (1962) note that the metal content of aureoles developed in massive rocks commonly decays logarithmically with distance from the ore contact. This logarithmic pattern, they suggest, would be expected if the mechanism for the transfer of material was diffusion through a static medium. While fracturing, even on the micro-scale, permits a certain amount of flow of the invading solutions and results in an irregular and more extensive distribution of metal in the aureole, than where diffusion is the only process.

Petrological examination of the wallrocks indicates a strong association between the trace element aureole and the width of the fractured limestone. The trace element aureoles show that, in the majority of cases, the distribution of the metals in the wallrocks is irregular. Additional confirmation is obtained from the variability of the aureoles next to the same vein. Next to Red Vein at Redburn mine, the three traverses show trace element aureoles of different width and type in which irregular concentration of the elements is recorded. Similarly at Sallet Hole mine, in Derbyshire, irregular concentrations of fluorite were detected in the wallrocks. Next to Hucklow Edge Vein, the two aureoles showed irregularities away from the ore contact. It is therefore concluded that the metal content of the limestones is related to the fractured nature of the wallrocks.

Certain localities, however, indicate a logarithmic decay in the concentration of a trace element with distance from the ore contact. Migration of the trace elements, by diffusion, into the wallrocks is considered possible at these localities. For example, Ashes Quarry, Newlandside Quarry, Treak Cliff and Masson Hill Quarry have logarithmic decay patterns. It is therefore suggested that the mineralization occurred in massive country rocks at these localities.

Considering the dispersion aureole at Masson Hill Quarry where the wallrock is composed of limestone and dolomite; it is possible that the following explanation may account for the dispersion pattern. Rove (1947) concluded that limestones 'flow' (twinning and recrystallisation) while dolomites 'fracture and flow' during deformation. Open spaces are not developed when flowage occurs, thus permeation by the ore fluids into the wallrocks would be minimal. In contrast, the relatively permeable character of a fractured dolomite is more suitable for the migration of the ore fluids. Wehrenberg and Silverman (1965) considered that the permeability of a limestone was the controlling factor in the dispersion of the ore fluids, and it is possible that at certain localities, such as Masson Hill, alteration of the limestone has increased the permeability.

The large replacement orebodies in the Pennines, of which Masson Hill was the only one investigated, may have originated by the initial alteration of the limestone to a more permeable rock which was subsequently invaded by the ore minerals. Ames (1961) considered this hypothesis valid for the large replacement orebodies, of fluorite in limestone, in the United States. The width of the trace element aureoles are related to the amount by which, and the extent to which, the wallrocks have been fractured. An extensive pattern will not only permit migration to greater distances from the orebody, but will contain larger amounts of metals, in comparison to a relatively unfractured wallrock. The marked differences, recorded for the trace element aureoles are almost certainly due in a large part to the extent of pre-mineralization fracturing, although the subsequent fracturing, of the wallrocks due to the injection of the solutions cannot be overlooked. It is suggested that the initial fluids infilled the existing fractures, while a second phase may either infill the channelway but not migrate into the wallrocks, or, if the pressure was sufficient to fracture the wallrocks, produce a second phase where migration occurred. The presence of one series of fractures containing a specific mineral assemblage and cut by a latter phase containing a distinct mineral assemblage has not been found. These possibilities are envisaged, since Dunham (1948, p.100) suggests that several minor phases of reopening of the veins are evident, but no general 'order of deposition of minerals can be postulated'.

The processes controlling the fracturing of the wallrocks are therefore envisaged to have occurred prior to, or contemporaneously with, the injection of the ore fluids and it is these processes which have indirectly influenced the migration of the trace elements into the wallrocks. The following suggestions which may explain the differing trace element aureoles, are tentative and are based partly on the general geological framework of the area. It is suggested that the earth movements which formed the Pennine uplift resulted in the formation of the fissures through which the ore solutions traversed, but that continuing eustatic uplift of the Weardale Granite resulted in wider fissures in the Alston Block than in Derbyshire. Wider aureoles of most of the trace elements, and especially fluorine, are present in Derbyshire than in the Alston Block. This may reflect a difference in the pressure of the ore fluids at the time of formation of the veins. It is suggested that the pressures operative in the Alston Block were not as great as those in Derbyshire, due to the more open fracture system. The work of Trotter and Hollingworth (1928), and Eastwood (1963), has shown that the maximum stratigraphical thickness that existed above the level of the Great Limestone could not have exceeded 1,100m while the maximum cover above the D_2 limestone in Derbyshire is estimated at 3,000m. (T.D. Ford personal communication). This difference in the overlying sediment cover may have been sufficient to produce a difference in the confining pressure between the two orefields.

The time factor and the temperature of the ore solutions may also influence the width of the dispersion aureole. It is possible that the period over which the mineral deposits were formed in Derbyshire was greater than in the Alston Block, and consequently the prolonged mineralization episode resulted in the continuing migration of the metals into the wallrocks, in Derbyshire. A higher depositional temperature may result in an increased temperature gradient between the ore solutions and the wallrocks and facilitate extended migration away from the ore solutions. If this parameter is important in controlling the width of an aureole, it may be concluded that the temperature of some of the Derbyshire veins was in excess of the majority of the Northern Pennine veins. A.J. Stoyel (personal communication) indicates that the temperature of the late stage deposition of fluorite in Derbyshire is between 85°C and 95°C. In comparison with the more extensive results of Sawkins (1966) the temperature of the late stage deposition of the fluorite in the northern Pennines ranged between 120° and 170°C. These results do not substantiate the hypothesis that the width of the aureole is related to the temperature of the ore solutions, since wider aureoles would be expected in the Alston Block than in Derbyshire.

Specific Trace Element Variations

Strontium

Strontium depletion has been recorded in limestones. It has not however, previously been indicated in limestone wallrocks next to mineralization.

Kulp et. al (1952) report that strontium is more abundant in fossils than in the carbonate matrix of limestones. Also the finer matrix material of some limestones is more readily replaced or recrystallised, and it is this alteration which liberates the strontium. They noted a poor correlation between strontium and magnesium and concluded that the recrystallisation of a limestone always lowers the Sr : Ca ratio in varying amounts. Sternberg et. al. (1959) came to a similar conclusion after studying the Triassic Steinplatte reef complex limestones of Austria. Recrystallisation of the limestones, they conclude decreases the strontium content of the limestones.

Strontium is depleted next to the veins, the amount and the extent to which it is depleted varying from vein to vein. The correlation coefficients show a good positive correlation between strontium and calcite and indicates that the two are closely related. The petrological examination of the wallrocks shows that recrystallisation of the calcite has taken place. It is therefore concluded that recrystallisation of calcite has been liberated strontium, which was incorporated in the ore solutions and transported to higher stratigraphic levels. The occurrence of strontianite at Greenlaws mine, Weardale may indicate a locality where sufficient strontium has been incorporated in a vein to form a major constituent.

Considering the two orefields in general, strontium is depleted to a greater extent in the Alston Block than ~~in~~ the Derbyshire Orefield. It is suggested therefore that the higher temperatures in the Alston area resulted in more extensive recrystallisation of the limestones, and greater depletion of strontium than in Derbyshire.

The Great Limestone of the Alston Block contains approximately three times as much strontium as the D_2 limestones of Derbyshire. This difference may be attributed to either the fossil content of the two limestones or the differing conditions of deposition of the limestones.

The Great Limestone contains, in relation to the D_2 limestones of Derbyshire a larger proportion of fossils. Kulp (1952) reports that strontium is more abundant in fossils than in the carbonate matrix of the limestones. This difference in the fossiliferous content of the limestones, which may in part have been aragonite and hence helping to enhance the strontium content, may explain the difference in the strontium content, although it is also possible that the difference is related to conditions of deposition. Kulp (1952) suggests that the Sr : Ca ratio is related to the Sr : Ca ratio of the water from which the limestones were deposited; while Sternberg (1959) relates the strontium content of limestones to the different areas of deposition and subsequent recrystallisation. Considering these two suggestions, it is concluded that the former explanation is more probable, being based on facts, rather than the latter which presupposes unknown parameters.

Zirconium

The background values of zirconium are less than 10ppm, while values of 200 ppm are recorded next to fluorite mineralization. A threshold value of zirconium cannot be calculated and the contrast must be approximately 20 : 1. This ratio indicates the significance of the anomaly and the relationship of zirconium to the ore deposits.

It is possible that the zirconium has been leached from lower stratigraphical horizons, incorporated in the ore solutions and together with the other heavy metals deposited at higher stratigraphical levels. The depletion of zirconium from the wallrocks next to the veins which traverse the Whin Sill (see Chapter 6) may account for a proportion of the zirconium detected in the overlying limestones. Likewise the limestones overlying the 'toadstones' in Derbyshire have a zirconium aureole next to the vein, for example, the traverse at Hucklow Edge Vein (West) overlies the toadstone which contains 215ppm of zirconium.

However, it is also possible that the zirconium associated with the ore deposits indicates that the ore fluids originated from a deep seated magmatic source, and that due to processes operative at depth the zirconium remained in solution until the late stage emanations gave rise to the ore deposits.

Ringwood (1955, p.251) states that 'the principal factor determining the crystallisation sequence of accessory minerals is the degree of polymerisation of the magma'. In acidic rocks magmas there is a high degree of polymerisation where the complex forming ions e.g. Zr^{4+}, form complexes which share oxygen anions with neighbouring SiO_4^{-4} tetrahedra. In such a position the 'solution energy' of Zr^{4+} ions is considerbly lower than when the Zr^{4+} is able to form separate ZrO_4^{-4} and $Zr(OH)_6^{-2}$ complexes. In the former case, where anion-sharing occurs the higher charged central cations are brought nearer together, than in the latter case, and as a result the replusion of one cation and another lowers the solution energy.

Ringwood relates the solution energy, which is 'the energy evolved when one mole of the constituent ions of the crystal separated by an infinite distance are dissolved in the liquid', to the solubility of a mineral in a magma, and states that 'the greater the solution energy of the crystals, the greater the solubility'. When therefore, there is a high degree of polymerisation in a magma, the solubility of the complex forming ions is reduced in relation to a magma possessing a low degree of polymerisation, and the mineral will crystallise out at an early phase.

A volatile rich magma, contains a preponderance of $(OH)^-$, Cl^- and F^- ions which occupy similar structural positions in the magma to oxygen. The complex forming ions are not therefore as easily attached to the SiO_4^{-4} tetrahedra and exist as separate complexes with an increased solubility. These conditions will therefore prevent the early crystallisation of the zirconium and explain its enrichment in the late stage fractions.

If the Pennine ore fluids originated from a magma, it must have been relatively rich in volatiles, especially F^- and Cl^- ions for it to have provided fluorite for the veins and chlorides for the fluid inclusions (Sawkins, 1966). The degree of polymerisation would therefore be low, the zirconium remaining in solution until the late stage fraction, which in these areas, are manifested by the deposition of the mineral veins.

Copper and Nickel

Next to Longstone Edge Vein (borehole 19), Hucklow Edge Vein (West) and at Masson Hill Quarry, copper and nickel are present in unusually large proportions. The limestone at these localities overlies an altered lava. Analysis of the toadstone at Ladywash mine, by X-ray fluorescence, indicated the presence of 41ppm copper and 108ppm nickel. It is suggested that the enhanced values of copper and nickel at the above localities result from the leaching of the elements from the lava and their redeposition in the overlying sediments.

The majority of the dispersion aureoles in the Northern Pennines contain significant amounts of copper and nickel. The Great Limestone contains 15 and 20ppm of copper and nickel respectively, while the Whin Sill contains 64 and 56 ppm of copper and nickel. It is suggested that metasomatism of the Whin Sill has resulted in the liberation of these elements, which have been incorporated in the ore fluids, carried to higher stratigraphical levels and subsequently migrated into the wallrocks.

Lead and Zinc

The wide aureoles of lead and zinc show that these elements are capable of more extensive migration than is normal for other elements. This fact has been indicated by previous workers (Hawkes and Webb, Ginzberg etc.) and is substantiated in this study. Secondary mobilisation of these elements may have occurred near the surface. Borehole 19 (Longstone Edge) shows that erratic results for lead and zinc are present above 200 feet; while below 200 feet a constant background value is attained. This does not suggest that the lead and zinc must have been redistributed near the surface.

Rubidium

Fixation of rubidium in the clay fraction of the limestones has been indicated, this is substantiated by the high rubidium values shown by clay partings at Redburn mine and borehole 19 (Longstone Edge).

Fluorine

Migration of fluorine into the wallrocks is more extensive in Derbyshire than in the northern Pennines. Next to Hucklow Edge Vein the dispersion zone is 35 feet wide, while at Sallet Hole mine (Longstone Edge Vein) the spasmodic occurrences of fluorine in the wallrocks suggests migration through fractures. Distinct fluorine aureoles are only developed next to the Red Vein at Redburn mine and the Slitt Vein at Blackdene mine on the Alston Block.

It is suggested that the migration of fluorine is related to the fracturing of the wallrocks and the pressure of the ore fluids at the time of injection into the sediments, as discussed earlier.

The Derbyshire 'Toadstones'

The effect of the toadstones has been not only the enhancement of copper and nickel in the overlying aureoles, but the concentration of the clay fraction in the limestone. This is not surprising as the toadstones are composed of 'a sticky clay-substance' which Dunham (1952) suggests may be beidellite. The alteration of the lavas and tuffs has not given rise to ankerite and siderite in the overlying limestones, as in the northern Pennines, and it is suggested therefore that large amounts of iron were not incorporated in the ore fluids due to the metasomatism of these horizons.

Conclusions

The Pennine Orefields

The following conclusions are possible from the present study of wallrock alteration and trace element aureoles in the Pennine Orefields.

The manifestation of limestone wallrock alteration in Derbyshire is recrystallisation of calcite and impregnation by quartz. At certain localities dolomitisation of the limestone has occurred, this is related to replacement deposits rather than the fissure veins. In the northern Pennines, recrystallisation of the wallrocks has taken place with limited amounts of ankerite, siderite, quartz and clay minerals replacing the limestones. Ankerite and siderite are predominant in large replacement orebodies rather than next to the fissure veins. It is suggested that, although the solutions in the two districts gave rise to similar economic mineralization, the composition of the solutions was different, the northern Pennines solutions containing more iron than those of Derbyshire. The large replacement orebodies may have resulted from the increased permeability at certain localities, due to premineralization alteration of the wallrock limestones.

The majority of the dispersion aureoles show a widespread and irregular concentration of the metals, and it is concluded that fracturing of the limestones has permitted the migration of the solutions into the wallrocks. The fractures may have been developed prior to the mineralization or contemporaneously with the injection of the ore fluids under pressure. Certain localities have restricted aureoles where a logarithmic decrease occurs away from the ore contact. It is suggested that diffusion of the metals has taken place into unfractured country rocks at these localities.

The elevated temperature of the ore solutions has caused the recrystallisation of calcite and release of strontium. The pressure of the solutions has governed the extent of migration of the metals into the wallrocks. The strontium content of the respective limestones suggests that the depositional environment in the northern Pennines was different to that in Derbyshire. A temperature varient is not considered to be of prime importance, although the Sr : Ca ratio of the waters may be a controlling factor together with the mode of deposition.

A proportion of the zirconium which has migrated into the limestone wallrocks may have originated from the metasomatic alteration of the Whin Sill in the Alston Block and the alteration of the lavas in the Derbyshire orefield. However, a substantial amount may also have originated as emanations from a deep seated magmatic source.

Primary cycle geochemical prospecting would seem to be of limited use in locating economic mineralization, where migration through fractures can result in very irregular dispersion aureoles. For example, analysis of core samples from a horizontal drill hole at Redburn mine indicated a local decrease in strontium and an increase in the metal content of the limestone. These results when compared with other dispersion aureoles suggested the presence of mineralization. Subsequent cross-cutting has intersected a vein and proved economic mineralization. The local decrease in strontium may be thus an important prospecting tool.

The Cumberland Ironfield

Although exhaustive investigation of the dispersion aureoles next to the haematite orebodies was not undertaken, certain conclusions are possible from the results obtained.

Strontium, manganese and iron are the only trace elements (of the group investigated) present in the limestone wallrocks. Strontium is depleted, while manganese and iron are concentrated next to the haematite. The aureoles are approximately 50 feet wide and illustrate the gradual depletion or concentration next to the ore. Temperature measurements on late stage quartz and fluorite give values of 102° to 108°C and 112° to 144°C respectively (A.J.Stoyel, personal communication) while sulphur isotope measurements give values of δS^{34} of 33.1, 29.2, 34.3, 35.4 and 35.7 an average value being 33.5 (M.Soloman, personal communication, analyst T.A.Rafter). The former results indicate that the late stage deposition of the gangue minerals was at temperatures comparable with the primary mineralization of the Pennines. The sulphur isotope results compare favourably with similar results quoted by Jensen (1959) as 'groundwater hydrothermal deposits'. A magmatic origin for the ore deposits cannot be suggested as a marked divergence from the accepted δS^{34} value for magmatic sulphur (22.220) is present. The late stage mineralization may however, have originated from a comparable source to that which gave rise to the Pennine deposits.

Recrystallisation of the limestones and the depletion of strontium has occurred to a greater extent than in the Pennines and hence, if similar conclusions are possible regarding the extent and nature of the dispersion patterns in the Cumberland Ironfield as in the Pennine Orefields, the main wave of ore solutions were, at the time of emplacement, at higher temperatures than the Pennine solutions even though those depositing the later gangue minerals were cooler than the fluorine-zone mineralization around Alston. However, temperatures in excess of 400°C cannot be envisaged, for lime silicates are not developed in the wallrocks nor are skarn minerals.

The uniformity of the dispersion patterns indicates that diffusion of iron and manganese has occurred into unfractured country rocks.

The width of the dispersion patterns suggests that primary cycle geochemical prospecting could be of assistance in locating mineralization. As yet, however, there are no instances of the technique being used to locate orebodies.

Sandstones and Shales

Irregular dispersion patterns are present next to mineralization in sandstones and shales, and indicate that the metals have migrated through fractures into the wallrocks. Adjacent to Blackdene Vein, a gradual decrease occurs in strontium and rubidium. It is suggested that the unaltered sandstones contain a small proportion of calcite and clay minerals. The calcite may have been recrystallised and the strontium liberated, from the calcite lattice and incorporated in the vein. The decrease in rubidium would suggest the decomposition of the clay minerals next to the vein.

CHAPTER VI

WALLROCK AUREOLES IN THE WHIN SILL

A comparative study was made of the trace element variations and the major chemical changes which have taken place due to the action of the metasomatic processes and mineralising fluids on the Whin Sill in the Northern Pennine Orefield.

Closehouse Mine, near Middleton-in-Teesdale, afforded a previously undescribed locality at which these alteration processes have occurred. A detailed petrological and total chemical analytical investigation was undertaken, together with a re-examination of the micaceous content of the altered quartz-dolerite. Trace element analyses were conducted, not only on these specimens, but on specimens provided by extensive subsurface exploration and surface exposures throughout the orefield.

Mineralogical and Major Chemical Variations

Previous Research

Mineralogical Variations

The classic petrographic description of the Whin Sill by Teall (1884), was followed by several important contributions, which have included Finlayson (1910), Holmes and Harwood (1928), Tomkieff (1929), Smythe (1930, p.118) and Dunham (1948, p.57). An estimate of the mineral composition of the quartz-dolerite, given by Dunham (1948, p.56) is quoted here:- pyroxene 34%, plagioclase feldspars 46%, hornblende, biotite, chlorite 4½%, iron-titanium oxides 8%, quartz, orthoclase and micropegmatite 5½% and calcite, pyrite, apatite 2%.

Alteration of the dark, dense quartz-dolerite to a white lighter rock, termed the 'White Whin' has taken place adjacent to the mineral veins. The alteration processes have been discussed by previous workers which include Wager (1929 a, p.106) and Dunham (1948, p.103); however a brief summary is considered necessary for a fuller understanding of the major chemical and minor elemental variations which have occurred as a result of the metasomatic processes.

The alteration has resulted in radical mineral changes, and produced a rock of the 'white trap' type, composed of secondary carbonates, kaolinite, mica, anatase or leucoxene with residual quartz and apatite. Wager (1929 a, p.106), summarises the successive stages of alteration, as demonstrated by the following sequence of mineral changes:-

(a) The outer margin of the alteration is characterised by the conversion of the ferromagnesian minerals into carbonates with minute anatase inclusions.

(b) Approaching the vein, the calcic cores of the plagioclase are initially attacked, followed, at a further stage by the alteration of the sodic margins and the orthoclase.

(c) The most advanced stages of alteration of the quartz-dolerite are believed, by Wager, to be the replacement of the feldspars by kaolinite together with an unidentified micaceous mineral.

Additional localities substantiate the alteration assemblage described above. Dunham (1948, p.105) noted that from Force Burn in Teesdale, the alteration had not proceeded to the most advanced state, in that the feldspars remained unaltered, although the pyroxenes had been converted into carbonates. Material investigated from Cowgreen and Settlingstones mines was regarded as being in an intermediate stage between the Wynch Bridge and the Force Burn rocks. White Whin from Rotherhope Fell, initially investigated by Finlayson, and re-investigated by Dunham, has a substantial amount of quartz and pyrite together with fluorite; this the authors attributed to the unusual low carbonate content of what is considered a highly altered dolerite.

Chemical Variations

Finlayson, Wager, Smythe, Dunham (op.cit.supra) and A.C.Dunham and Kaye (1965) have reported major chemical analyses of the altered and unaltered quartz-dolerite, the last-mentioned working on marginal alteration related to carbonaceous sediment, not to mineralization. The results of a selected number of these analyses are presented in table 6-2.

These analyses indicate that the following chemical changes have occurred. Consistent gains in carbon dioxide, potash and combined water occur, while marked losses in CaO, magnesia, soda and iron are general. Anomalous results occur where the 'White Whin' itself has been replaced by introduced minerals, such as quartz and pyrite, e.g. at Rotherhope Fell where the analyses indicate a high silica and iron content. It may therefore be concluded that the 'White Whin' was itself susceptible to metasomatism during the later stages of mineralization.

New Data

Situated on the Lunedale Fault, at the southern extremity of the Alston Block subarea of the Northern Pennine Orefield, the surface and underground workings of Closehouse mine expose an important example of the intrusion of quartz-dolerite into a major fault, of which there are few other locations, as indicated by Clough (1880). A detailed geological description of the area is presented in an Appendix together with a magnetic survey over the mineralised dyke.

Petrological studies were undertaken along with major element chemical analyses of the altered dolerite from the North Fault dyke. The bulk of the specimens examined came from the 5 and 17 fathom levels.

Petrographic Examination

Thirty samples from the North Fault dyke were studied and showed a graduation from unaltered dolerite to the 'White trap' type of rock.

The initial stages of the alteration was the 'clouding' of the pyroxenes, while progressive alteration resulted in the formation of carbonate pseudomorphs after the pyroxenes. Further decomposition of the dolerite resulted in the alteration of the plagioclase. Initially the central calcic cores were replaced, while at a more advanced stage the alkaline margins were pseudomorphed by a mixture of clay and carbonate minerals.

The greater part of the dolerite dyke has undergone complete alteration and this is chosen for a detailed description. No fresh plagioclase or pyroxene remain, but the original shapes of the grains are discernable. The plagioclase has been converted to a fine grained micaceous and calcareous aggregate. The micaceous minerals, occurring as minute crystals, are irregularly arranged within the lath-shaped pseudomorphs. The individual crystals of the micaceous material have a length and breadth of approximately 0.005 mm. Under crossed nicols these areas have a speckled appearance, and illustrate the first order interference colours; the evidence suggests that they are hydromicas (illite).

Large areas show grey interference colours, with crystals of 0.01 to 0.07 mm. in length and breadth, almost straight extinction, length slow and low relief. These areas are identified as kaolinite.

The carbonate occurs in two distinct forms. The largest areas form 'cloudy patches' (with minute inclusions having the form and colour of anatase clusters), and have the shape of the original pyroxene crystals. Carbonate is also visible as clear isolated masses with no pseudomorphic character. These are believed to represent the aggregation of calcite, the calcium of which has been liberated by the decomposition of the plagioclase. The presence of iron carbonates, as illustrated by the X-ray diffraction analyses, suggests that subsidiary amounts of these minerals occur but they have not been identified optically.

Isolated groups of anatase crystals are thought to represent original ilmenite, while the remaining constituents are represented by quartz and apatite, which have not been decomposed but are frequently obscured by a layer of micaceous material.

A.C. Dunham and M.Kaye (1965), report the occurrence of olivine and euhedral pseudomorphs after olivine from the Little Whin Sill, while the only recorded olivine in the Great Whin Sill was made by Allport (1874) from Ward's Hill, Northumberland. A pseudomorph after olivine has been located in the present examination, the sample was obtained from a small sill developed adjacent to the North Fault dyke. Alteration is at an advanced stage, however the euhedral outline may be seen.

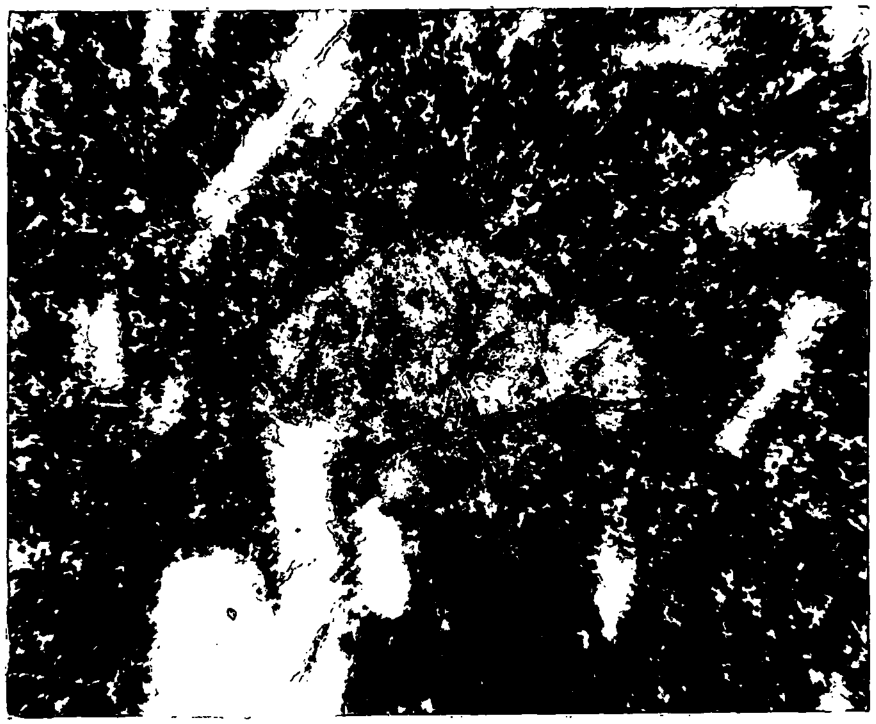


Plate 6-1

Euhedral olivine pseudomorph. The grain has been entirely replaced by serpentinous material. DN 1, crossed nicols x 175.

Composition of the Clay Fraction

The identification of the clay minerals in the white whin was reattempted. The inference that kaolinite and a muscovite (possibly a paragonite mica) were present had been made by Wager (1929, p.99), while Dunham (1948, p.105) noted that the clay mica had a higher silica/alumina ratio than muscovite and suggested a clay of the illite type. A.C. Dunham and Kaye (1965) reported the possible presence of illite, but noted that the basal 10 Å peak was weak, while the peaks at 4.98 Å and 2.98 Å were absent.

The White Whin contains approximately 30% to 35% of clay minerals together with Ca-Mg-Fe carbonates (35%), quartz (15%) and pyrite, anatase etc. (15%). These estimates were made by a technique devised by Schultz (1964). Separation of the $< 2\mu$ fraction of the clay minerals was achieved by flocculation in distilled water and drying at less than 90°c.

The systematic analysis of the material was conducted according to the procedure outlined by Warshaw and Roy (1961). The results indicate that illite and kaolinite are present. Additional confirmation was obtained by a comparison of the observed diffraction pattern with accepted values (A.S.T.M.) for the peak positions (Å) and the intensity ratios. Table 6-1 compares these values and it is suggested that agreement between the two confirms the presence of illite and kaolinite.

Table 6-1

Comparison between the A.S.T.M. and observed 'd' spacings and intensity ratios for Illite and kaolinite

Illite				Kaolinite			
Å		Intensity Ratio		Å		Intensity Ratio	
ASTM	Observed	ASTM	Observed	ASTM	Observed	ASTM	Observed
9.9	9.92	80	55	7.15	7.12	50	100
4.9	4.97	60	50	4.46	4.45	75	45
4.46	4.47	100	100	3.56	3.57	50	80
3.36	3.32	100	75	2.55	2.55	85	50
3.10	3.08	50 B	40	2.52	2.50	50	40
2.57	2.55	100	40	2.48	2.48	85	45
2.39	2.37	60	35	2.33	2.33	95	55
1.992	1.990	60	35	1.483	1.487	100	50
1.500	1.497	80	40				

Sample	C 1	C 2	A	B	C	D
	%	%	%	%	%	%
SiO_2	52.00	49.75	49.14	35.10	47.73	50.32
Al_2O_3	11.60	13.25	15.90	18.09	15.73	15.41
Fe_2O_3	2.51	3.00	1.24	trace	3.36	3.09
FeO	7.20	8.15	6.02	3.74	v9.87	8.92
CaO	11.75	10.57	6.98	11.89	9.15	8.86
MgO	3.14	3.95	1.81	5.79	5.05	4.89
Na_2O	2.49	2.60	0.23	1.03	2.55	2.03
K_2O	0.85	0.99	2.45	1.60	0.62	1.06
H_2O+	2.62	1.90	2.34	4.18	1.00	1.30
H_2O-	0.60	0.70	0.60		0.14	0.75
TiO_2	1.97	2.10	2.98	2.31	2.57	2.48
P_2O_5	0.29	0.25	0.36	-	0.28	0.22
CO_2	4.14	3.50	9.41	16.12	2.84	0.46
Total	101.16	100.71	99.46	99.84	100.09	99.82
	ppm	ppm	ppm	-	ppm	-
Rb	65	73	165		20	
Ba	750	810	nd		nd	
Pb	10	15	75		33	
Sr	475	493	180		449	
Mn	1525	1468	nd		1538	
Zr	207	225	266		203	
Zn	127	133	142		109	
Cu	68	71	38		59	
Ni	53	66	56		54	
Cr	75	79	nd		nd	
V	295	303	nd		nd	

Summary of the Results

The main chemical and mineralogical variations of the Whin Sill which occur adjacent to the veins may be summarised as:-

Chemical Variations

A striking similarity is noted between the present results and previous analyses (see table 6-2) of the altered and unaltered quartz-dolerite. These variations are consistent gains in carbon dioxide, potash and combined water and marked losses in CaO, magnesia, soda and iron. The major chemical variations which occur, due to metasomatism, are the same at Closehouse as elsewhere in the Northern Pennines.

Mineralogical Variations

This study has confirmed the previously reported mineralogical alteration (see page 171) of the quartz-dolerite and proved the presence of illite and kaolinite in the White Whin.

The following table gives the mineralogical composition of the Whin Sill, prior to and after alteration.

Table 6-3

The Mineralogy of the Unaltered and Altered Whin Sill

Unaltered dolerite:- Pyroxenes, plagioclase feldspars, hornblende, biotite, chlorite, iron-titanium oxides, quartz, orthoclase, calcite, pyrite and apatite.

Altered dolerite:- Ankerite, siderite, muscovite, illite, kaolinite, anatase, quartz, calcite and pyrite.

Minor Element Variations

In the Northern Pennines, mining operations within the Whin Sill are at the present in progress in mines which exploit witherite/barite, barite and fluorite, respectively at Settlingstones, Closehouse and West Blackdene. These localities provided material, the analytical results of which are shown in figs. 6-1 to 6-10. Additional sampling traverses adjacent to mineralization in the Whin Sill, were collected from Wynch Bridge and Force Burn in Teesdale. A core, from the abandoned Cowgreen Mine, supplied by Professor K.C. Dunham was also investigated (see figs.6-11 to 6-13).

Prior to the investigation of the trace element variations adjacent to mineralization, the background trace element concentration of the Great Whin Sill was determined, 30 samples from 10 localities were used to determine the average background and range.

Table 6-4

The Background Trace Element Content of the Great Whin Sill

Element	Concentration (ppm)	
	Average	Range
Rb	200	178-234
Ba	737	530-880
Pb	<10	-
Sr	478	434-520
Mn	1522	1320-1710
Zr	200	178-234
Zn	131	125-140
Cu	64	62-70
Ni	56	51-315
V	297	255-315
Cr	76	68-89

The dispersion patterns obtained from the Whin Sill attain a background concentration which showed less than a 10% deviation from the above figures, clearly the Whin Sill is remarkably constant in composition over the whole of its lateral and vertical extent.

Alteration Adjacent to Barium Mineralization

Closehouse Mine

Samples were taken from the 5 fathom crosscut south, which permitted the collection of material between the two mineralised dolerite dykes (see fig. 2-4) and from two localities along the 17 fathom level. The first, illustrated in fig.6-3 was from a crosscut driven from the North Fault dyke, which cut a limestone with irregular barite and galena replacement horizons. Fig.6-4 shows the trace element variations from a small sill injected into a quartzite on the footwall of the North Fault dyke.

The trace element variations, adjacent to a barite vein, 2 feet in width, which cuts the Closehouse - Standards dyke are illustrated in fig.6-1. The dolerite dyke, which is partially decomposed, displays a zone of 'White Whin' approximately 9 feet in width adjacent to the vein. In excess of 10 feet, the strontium and zirconium content of the dolerite maintains a very constant background level (475 and 210 ppm. respectively), while adjacent to the barite vein the strontium content decreases to 120 ppm. and zirconium to 135 ppm.

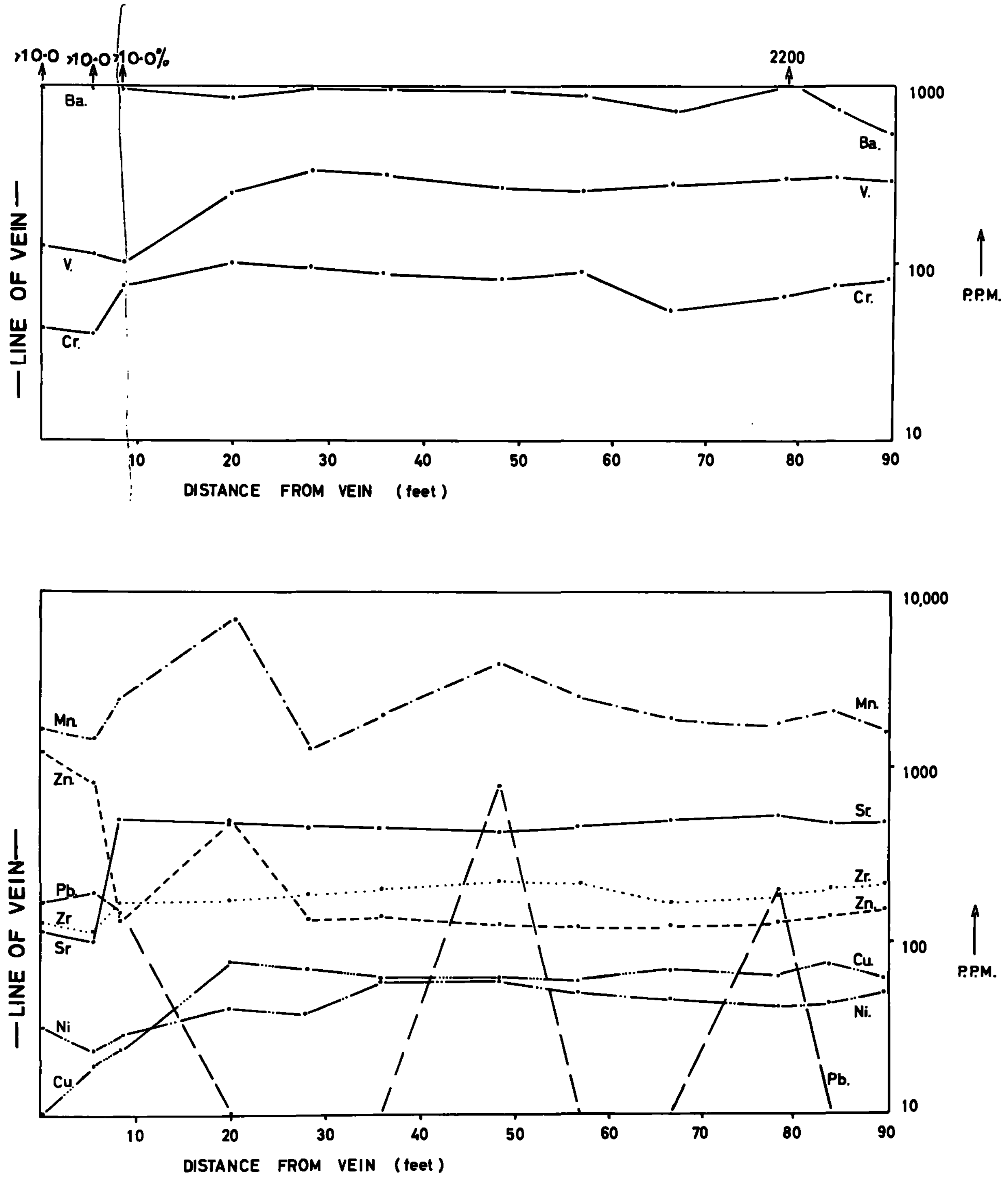


FIG. 6-1 TRACE ELEMENT VARIATIONS —— CLOSEHOUSE MINE
(5 FATHOM CROSSCUT SOUTH)

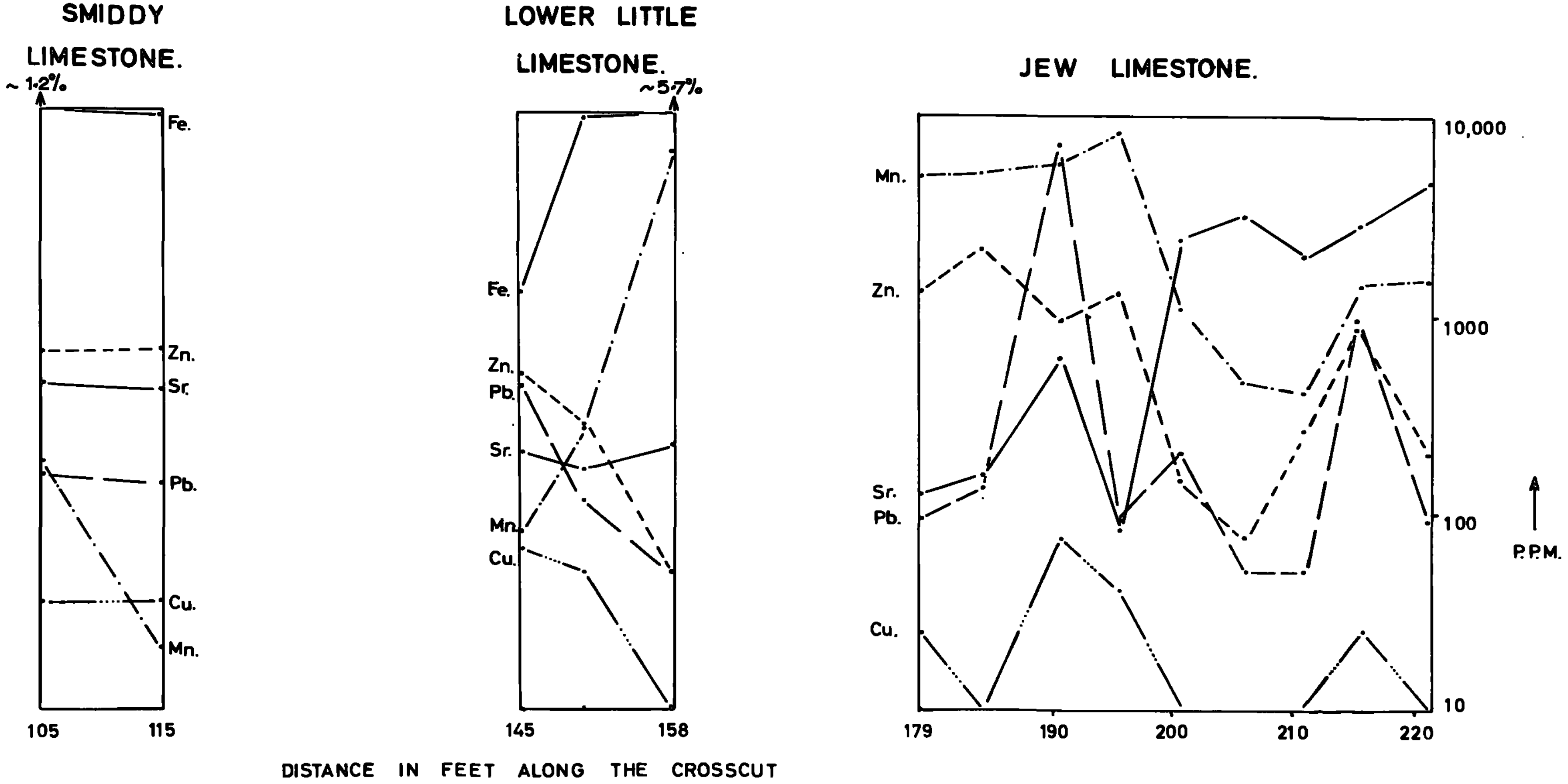


FIG. 6-2 TRACE ELEMENT VARIATIONS —— CLOSEHOUSE MINE
(5 FATHOM CROSSCUT SOUTH)

Copper and nickel with background concentrations of 68 and 56 ppm. respectively, diverge from these values at a distance of 20 feet from the vein; copper diminishing to 10 ppm. and nickel to 33 ppm. Apart from an erratic value at 20 feet (500 ppm), zinc, with a background value of 130 ppm, increases to a value of 1220 ppm. adjacent to the vein. The lead and manganese contents of the dolerite wallrocks are very erratic. Barium, vanadium and chromium decrease from background levels of 850, 300 and 80 ppm respectively. Over a distance of 10 feet, chromium decreases to a value of 43 ppm., while vanadium is depleted veinwards by 178 ppm. from a distance of 30 feet. The wallrocks are enhanced in barium out to a distance of 10 feet.

As shown in fig. 2-4, a series of folded and fractured limestones, sandstones and shales occur between the Closehouse - Standards dyke and the North Fault dyke. The limestones were analysed, to determine the trace element content between the two zones of mineralization and, as can be seen in fig. 6-2 the variations are highly erratic. This is believed to be due to the minute fracturing of the sediments, and in part to the fact that sampling was not restricted to a single lithological horizon.

Samples collected from the south crosscut on the 17 fathom level, fig.6-3, have anomalous values for lead and zinc in the dolerite and in the limestone. As noted previously this zone had undergone considerable fracturing, and although samples were not visibly mineralized, it is believed that the whole area is intersected by minute fractures which carry lead and zinc sulphides. The alteration zone adjacent to the barite vein in the

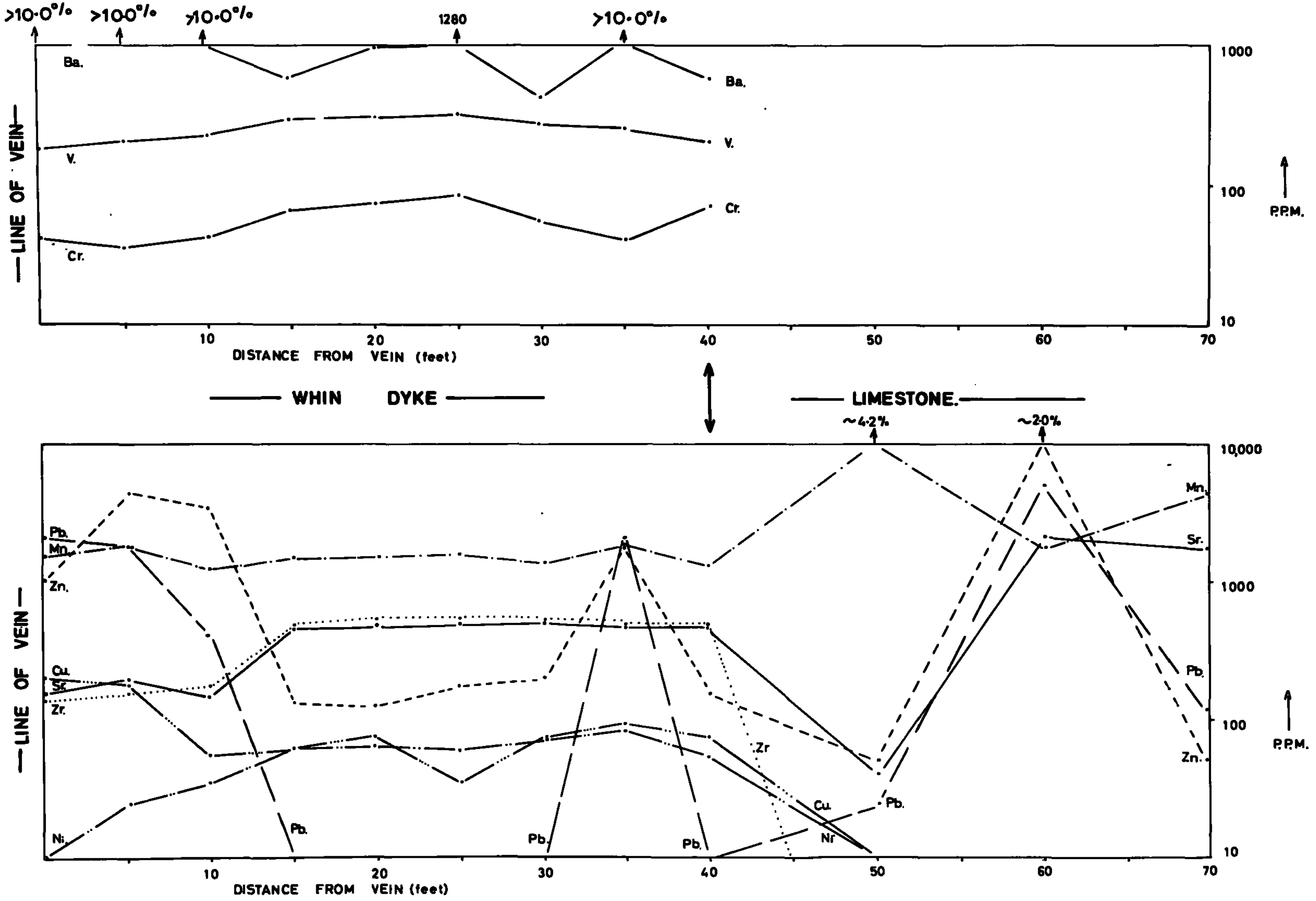


FIG. 6-3 TRACE ELEMENT VARIATIONS — CLOSEHOUSE MINE.

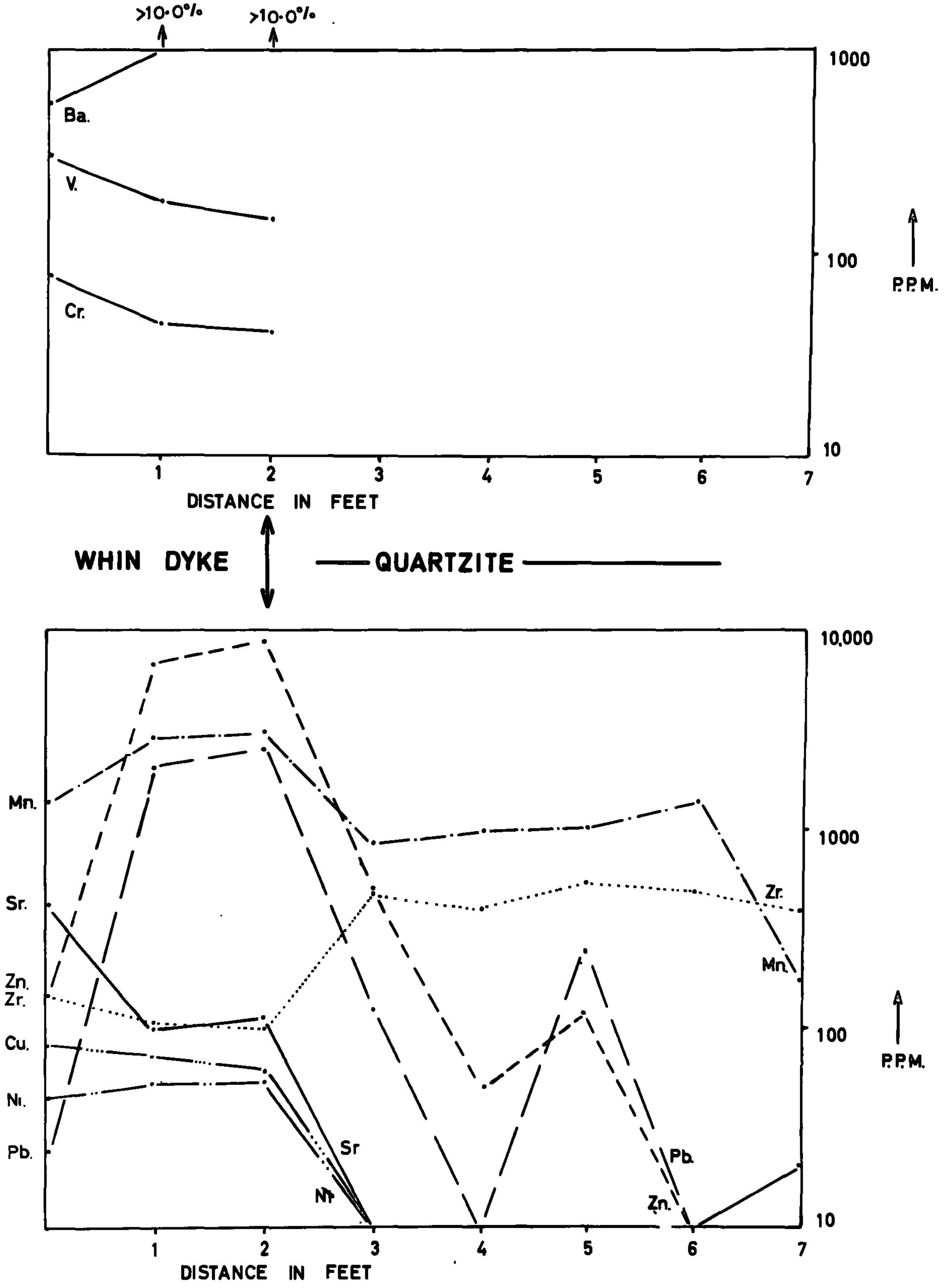


FIG. 6-4 TRACE ELEMENT VARIATIONS — CLOSEHOUSE MINE.

dyke is approximately 15 feet wide. Similar trends are evident; as previously indicated, zirconium, copper and strontium decrease, while lead and zinc increase, manganese shows no radical change in concentration as the vein is approached. The decrease in vanadium and chromium values, are not of the same magnitude as previously reported.

The small sill of unaltered dolerite injected into a quartzite (fig.6-4) again revealed a decrease in vanadium and chromium with an increase in the barium content as the quartzite was approached. Losses in nickel, copper, strontium and manganese were noted. Erratic values in lead and zinc were seen, while a substantial increase in the zirconium contents occurred, and resulted in a constant background value in the quartzite.

Settlingstones Mine

The majority of the samples, provided by the Owners of Settlingstones Mine, came from underground diamond drill holes, (see fig.2-5). As a comparative study a zone of alteration in the 120 fathom level was investigated, the analytical results are displayed in fig.6-5. The sampling traverse was situated within the vein complex along the south branch vein (Settlingstones Vein). An analysis of this material, reproduced from Dunham (1948, p. 324), is given below:-

Table 6-5

Analysis of an average run - of - mine ore sample,

Settlingstones Mine

	%
$BaCO_3$	77.74
$BaSO_4$	4.51
$CaCO_3$	5.58
$MgCO_3$	0.79
SiO_2	6.72
Fe_2O_3	0.77
Al_2O_3	1.56
FeS_2	0.19
ZnS	0.56
PbS	0.01
Total	98.43

The vein is subject to the development of 'loops' both on the small and the large scale, and two such loops, the north and south branches are respectively 600 and 1000 feet long. Both loops rejoin the main vein and carry workable witherite/barite (see fig.2-5). The diamond drill holes and the underground sampling traverse were all restricted to the south branch of the main vein, which has been reported to contain minor amounts of niccolite, ullmanite and harmotone (Russell, 1927).

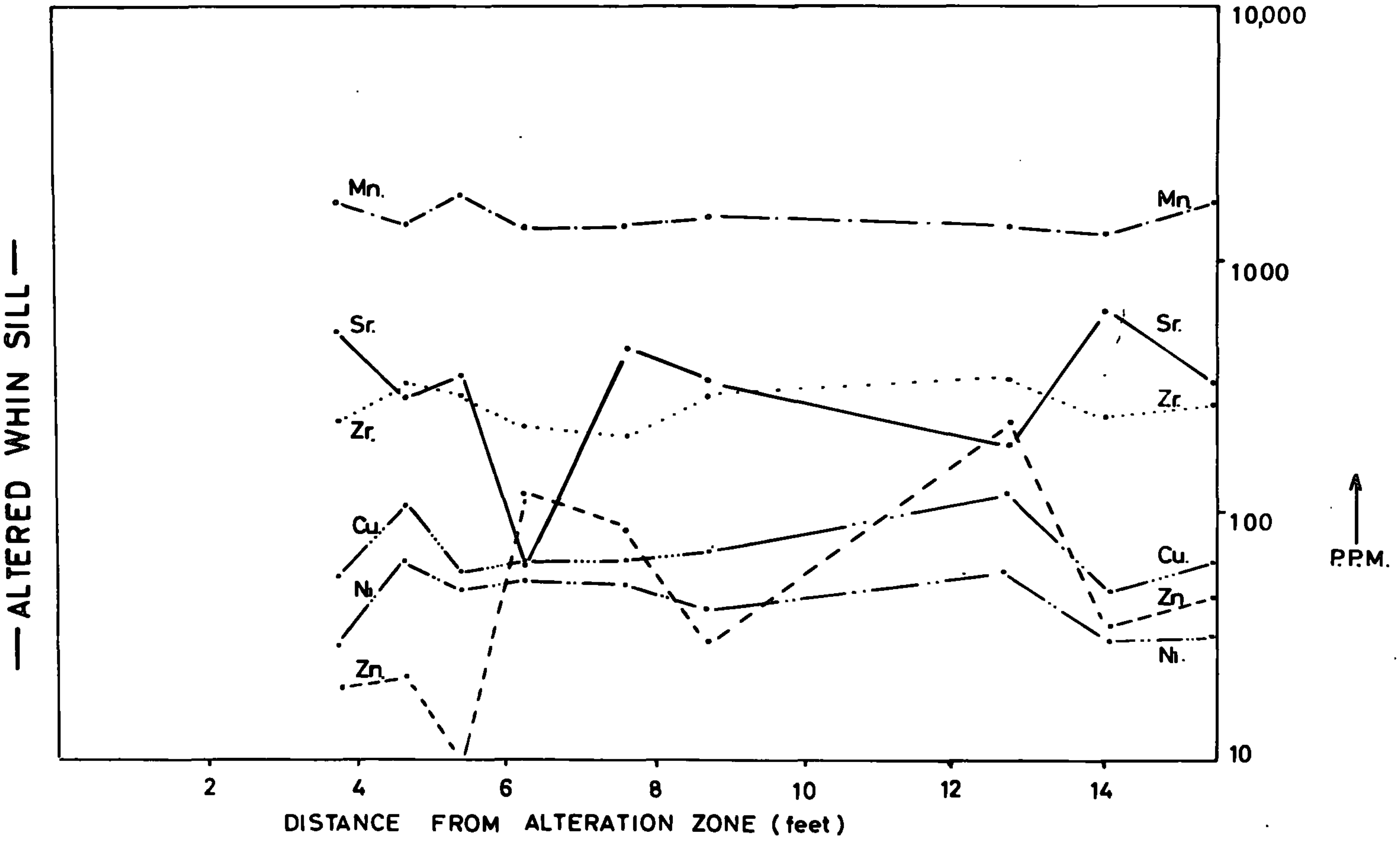


FIG. 6-5 TRACE ELEMENT VARIATIONS — SETTLINGSTONES MINE.

Fig. 6-5 illustrates the trace element variations from the underground samples. Zinc and strontium both show erratic values, while copper, nickel and zirconium are depleted, as the altered zone was approached. Manganese shows only slight divergence from background. In comparison to the subsequent results from diamond drill holes, the background variations of certain elements was excessive, possibly due to contamination by subsequent migration of the elements within the vein.

Figures 6-6 to 6-10 illustrate the trace element variations adjacent to Settlingstones south branch vein (boreholes SB and B2) and the Bewick Vein (or Dixon-Brown Vein) located to the south of the main vein (boreholes B1 and SB1).

Borehole SB was drilled horizontally from the south branch vein to a distance of 15 feet, while borehole B2, parallel to the former, was 300 feet in length. The analyses from these two boreholes are combined in fig.6-6 and 6-7 together with a sketch of the core.

The striking feature of the results from the Whin Sill, is that within a short distance, from the margin of the alteration, particular trace elements reach a uniform background value; this is reached at a distance equivalent to the visual alteration zone. Nickel, strontium and manganese all show a decrease, while copper and zirconium although erratic in places, illustrate an increased concentration adjacent to the vein,

SETTLINGSTONES MINE —
BOREHOLES SB & B2.

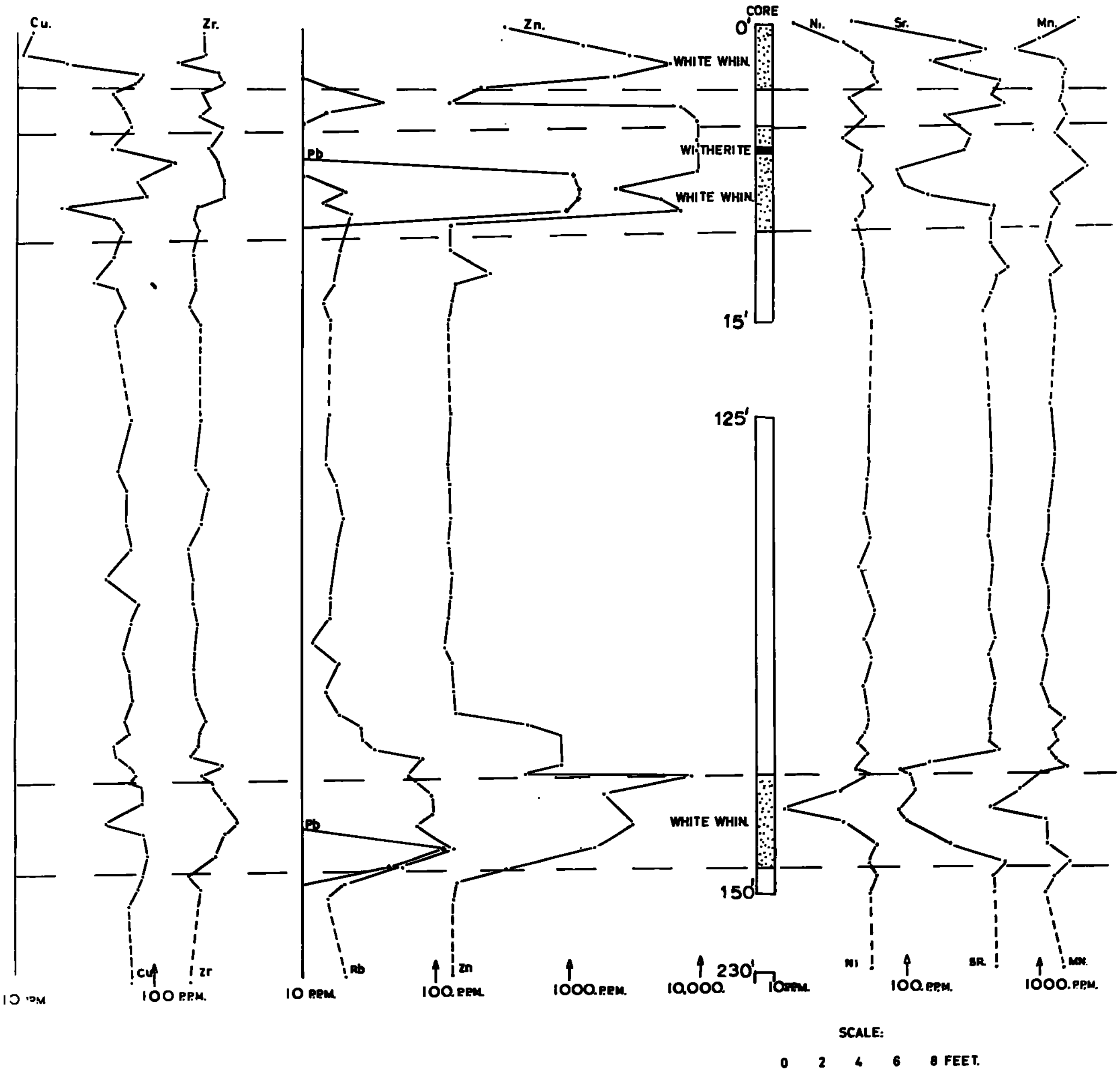


FIG. 6-6 TRACE ELEMENT VARIATIONS IN THE WHIN SILL.

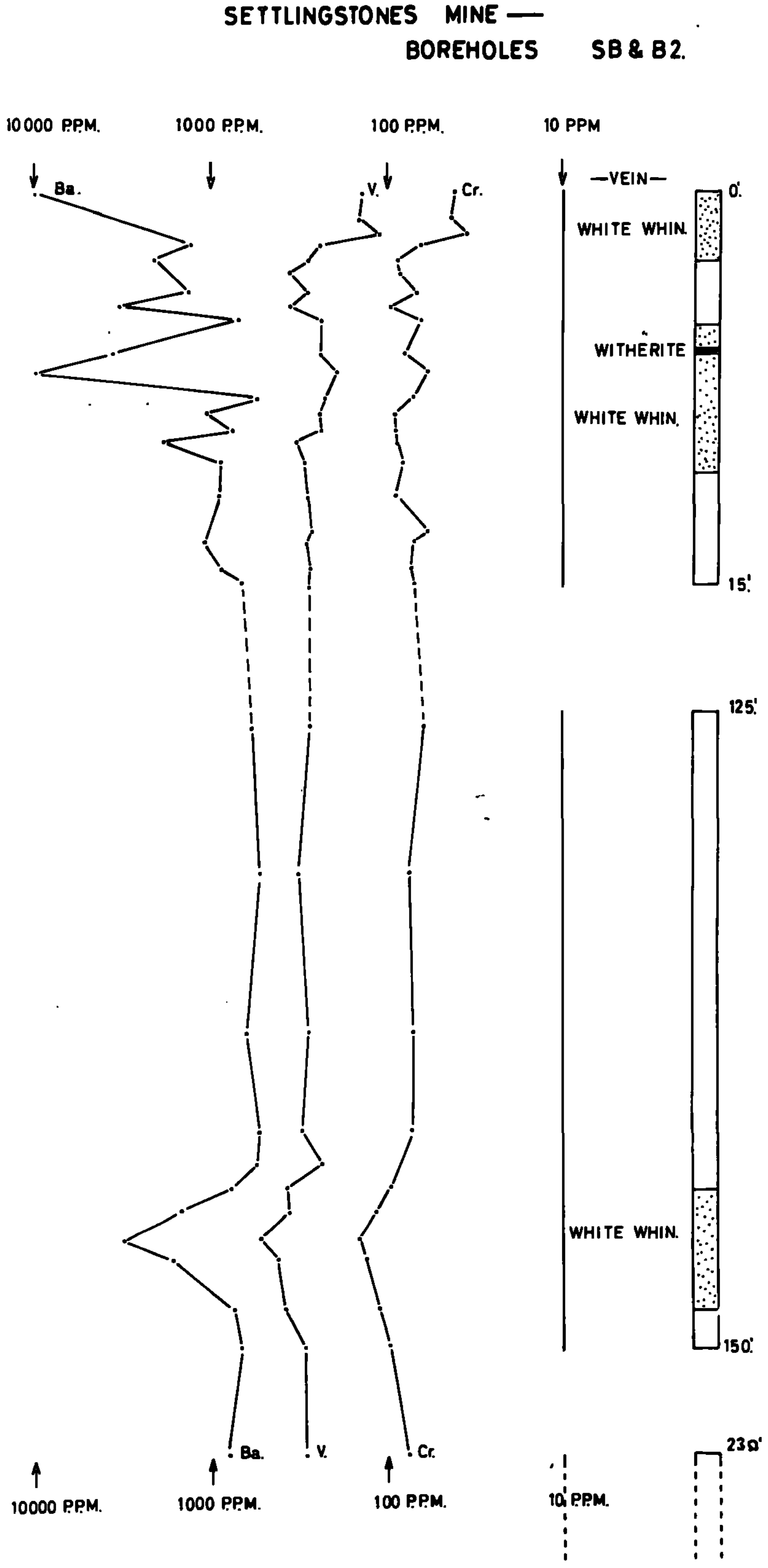


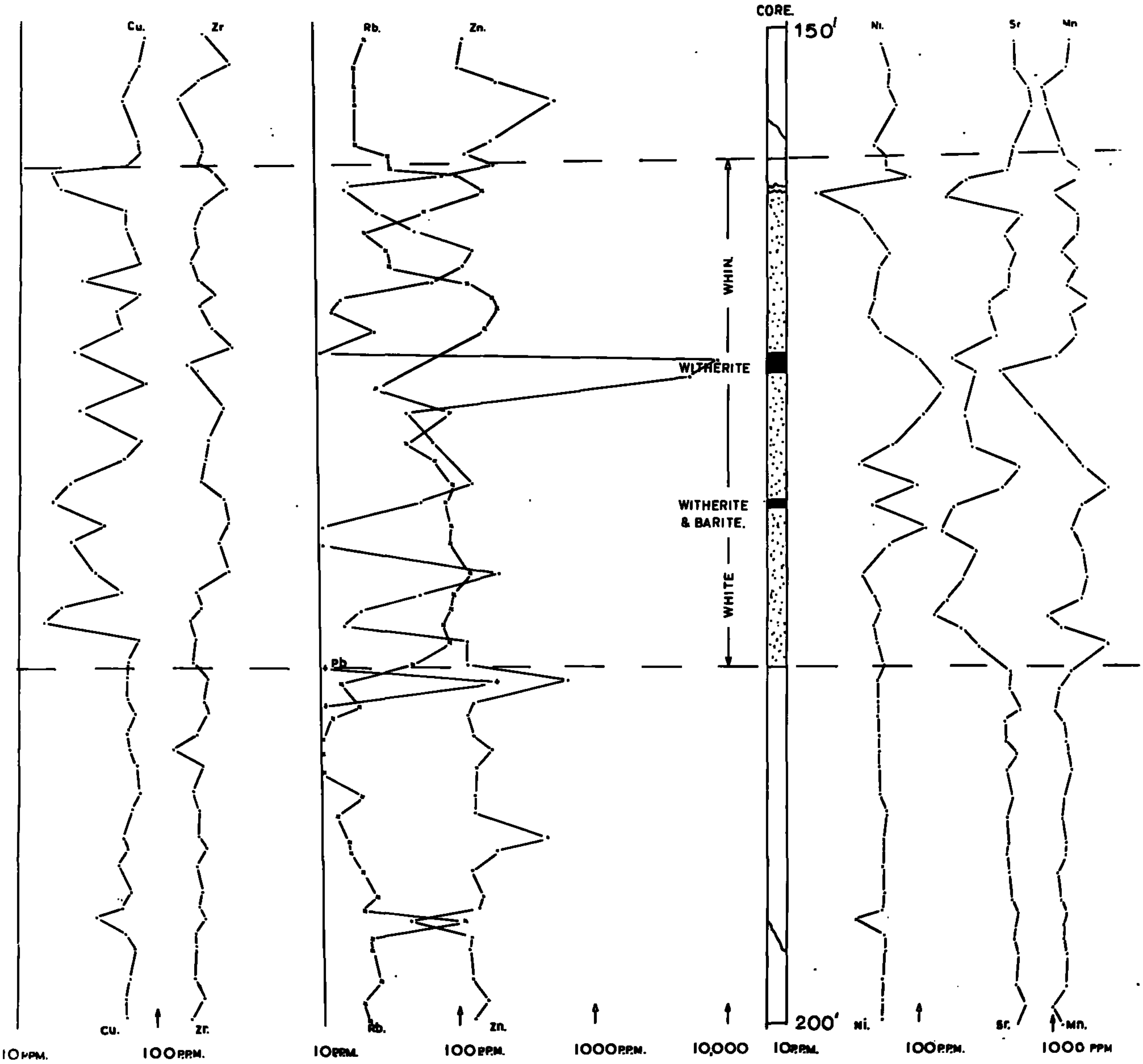
FIG. 6-7 TRACE ELEMENT VARIATIONS IN THE WHIN SILL.

as well as in the unmineralised white whin. The substantial increase in the zinc, lead and rubidium content of the alteration zone is seen in fig. 6-6, where the dispersion aureole extends 8 feet beyond the alteration zone.

Barium, vanadium and chromium are also enriched within the White Whin (see fig.6-7), where mineralization is not visible, while the presence of witherite, in the alteration zone has the effect of producing somewhat erratic values, not only for the three elements above mentioned but also those shown in fig.6-6. Approaching the economic mineralization, vanadium, chromium, copper and zinc decrease while barium and manganese increase.

Borehole B1, rising at an angle of 57° from the horizontal, intersected, between 156 and 181 feet, a large zone of White Whin, in which was situated two ore zones, one of witherite and the other an admixture of witherite and barite. Figs. 6-8 and 6-9 are the diagrammatic representation of the analytical results. A similarity with the previous borehole results is indicated, for within the altered zone, erratic variations in the majority of the elements was displayed. However the following conclusions are valid. An overall decrease in nickel, strontium, copper and manganese is noted, together with a marked increase in rubidium, lead, zinc, barium, vanadium and chromium.

SETTLINGSTONES MINE —
BOREHOLE B.1.



SCALE:-
0 2 4 6 8 FEET

FIG. 6-8 TRACE ELEMENT VARIATIONS IN THE WHIN SILL.

SETTLINGSTONES MINE—
BOREHOLE B.1.

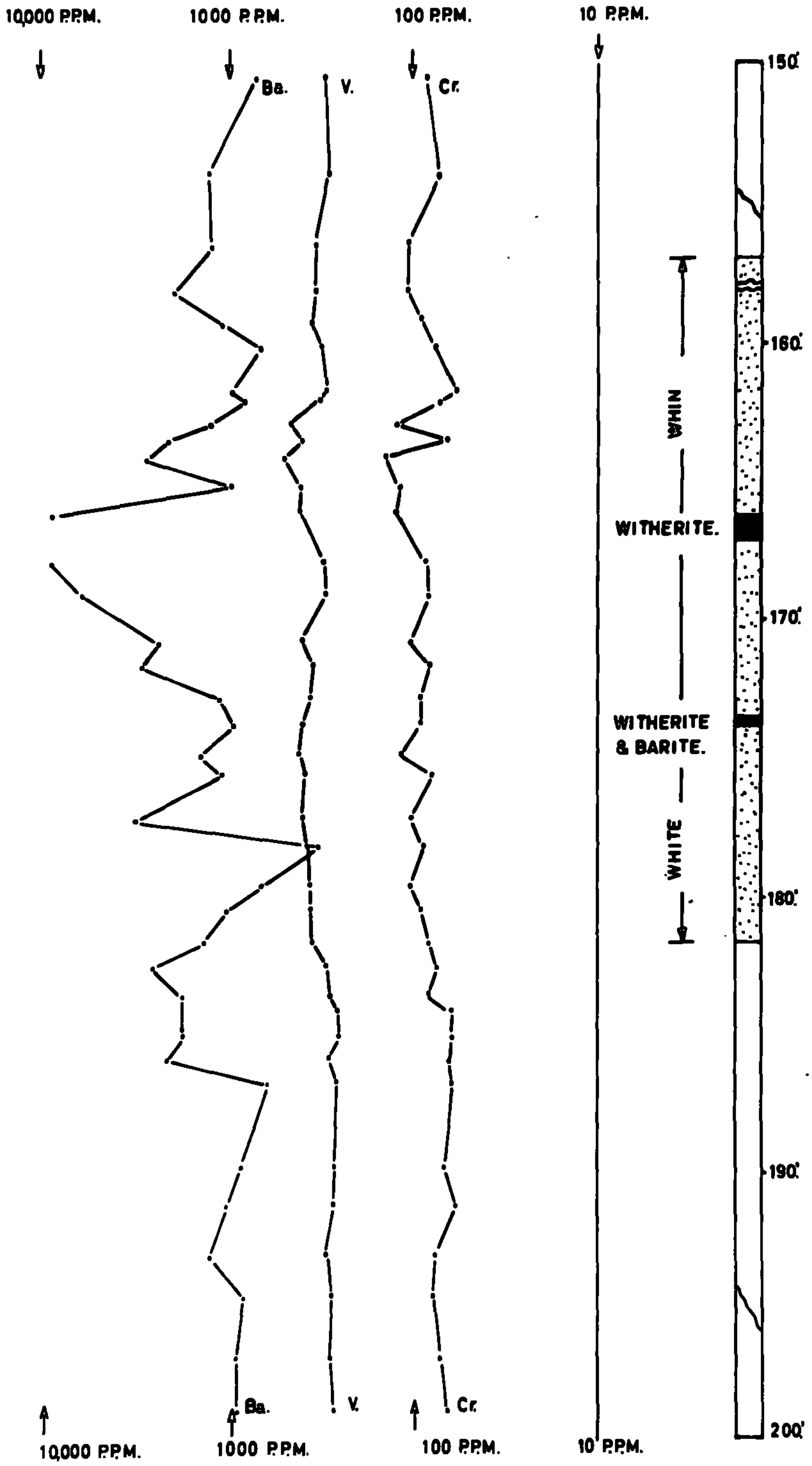


FIG. 6-9 TRACE ELEMENT VARIATIONS IN THE WHIN SILL.

A fracture at 195 feet, produced radical variations in some of the trace elements. Copper, zinc and nickel decrease from normal background values while rubidium shows a marked enrichment. The above results may suggest the percolation of mineralising fluids and the initial stages of the metasomatic alteration of the dolerite.

Fig. 6-10 illustrates the barium, vanadium and chromium content of samples collected from a borehole (SB1) which was located to the south of Bewick Vein, and driven to test the possibility of mineralised ground in that direction (see fig.2-4).

Vanadium and chromium are remarkably constant (respectively 112 and 72 ppm) although the overall concentration of vanadium is less than that normally indicated for the Whin Sill (see Table 6-3). Barium however shows very erratic values along the length of the core, which cannot be correlated with the spasmodic occurrences in the White Whin. The only marked variation in the vanadium and chromium content occurred at 500 feet where a decrease is indicated.

The remarkably consistent values for vanadium and chromium with erratic barium results would, it is suggested, indicate a zone of spasmodic alteration with no strong mineralization.

Additional Localities

Traverses adjacent to barium mineralization were collected from the Whin Sill at Cowgreen mine, Force Burn and Wynch Bridge in Teesdale.

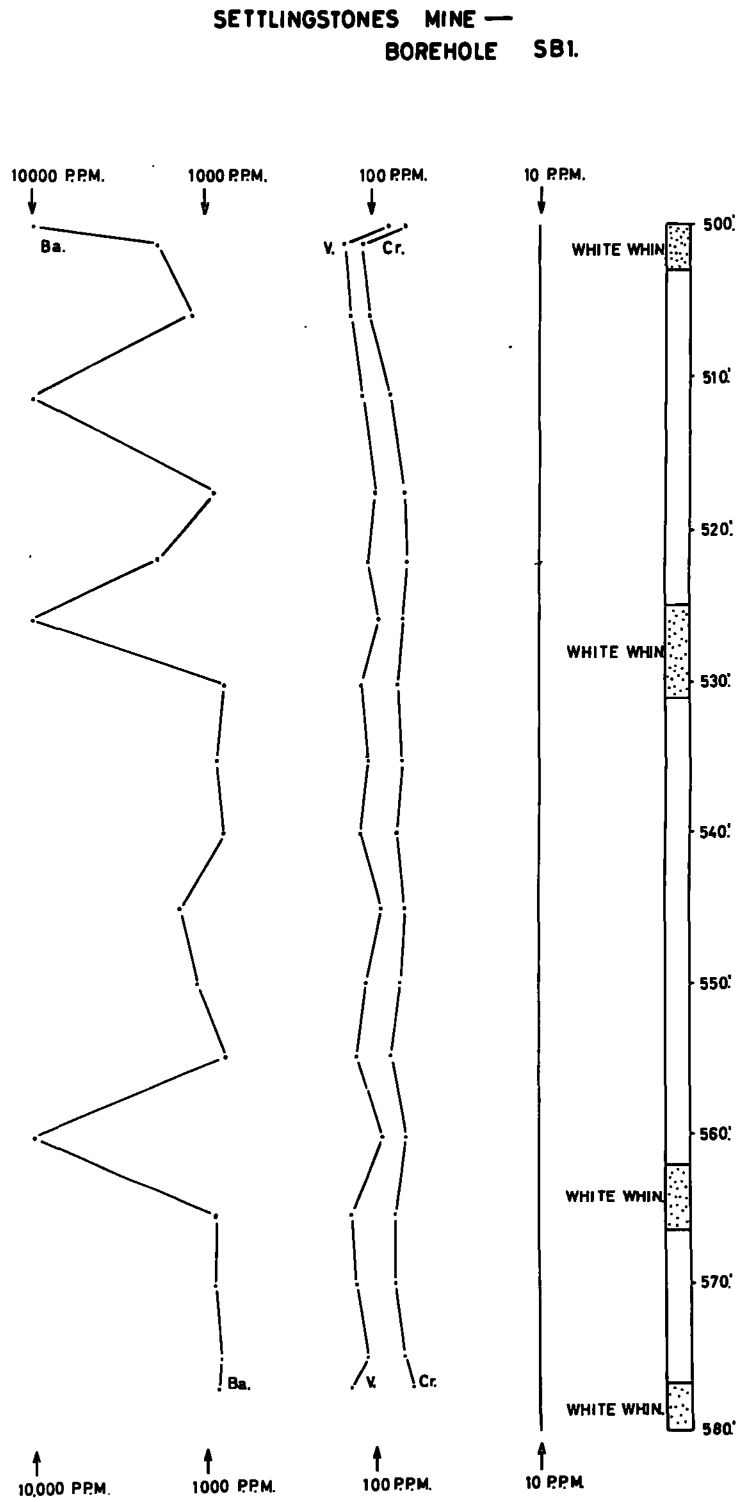


FIG. 6-10 TRACE ELEMENT VARIATIONS IN THE WHIN SILL.

The trace element variations are illustrated in figs. 6-11 to 6-13.

From Cowgreen mine, the core was from a hole drilled horizontally at right angles through Greenhush Vein on the 106 fathom level; the horizon was approximately 30 feet below the top of the Whin Sill. The section was practically complete and showed the transition from dark to light whin as the vein was approached and also some unusual pinkish barite towards the vein walls.

Fig. 6-11 subdivided to avoid confusion, illustrates the relative enrichment and depletion of the elements. The previously described element variation patterns were found to be substantially modified in this traverse and likewise from the samples collected at Force Burn, fig. 6-12.

Strontium which decreased between 1 and 8 inches, increased again adjacent to the vein to 3000 ppm. Nickel and copper had background values of 72 and 75 ppm, and from a distance of 1 foot decreased in value towards the vein, while the reverse was apparent for zinc. Lead and manganese showed no definite trend towards the mineralization, while zirconium, concentrated between 1 and 5 inches from the vein, decreased near the vein wall. The increase in barium is noted, from a distance of 8 inches, while the vanadium and chromium decreased within this zone (from 352 and 95 ppm. respectively they decreased to 287 and 75 ppm).

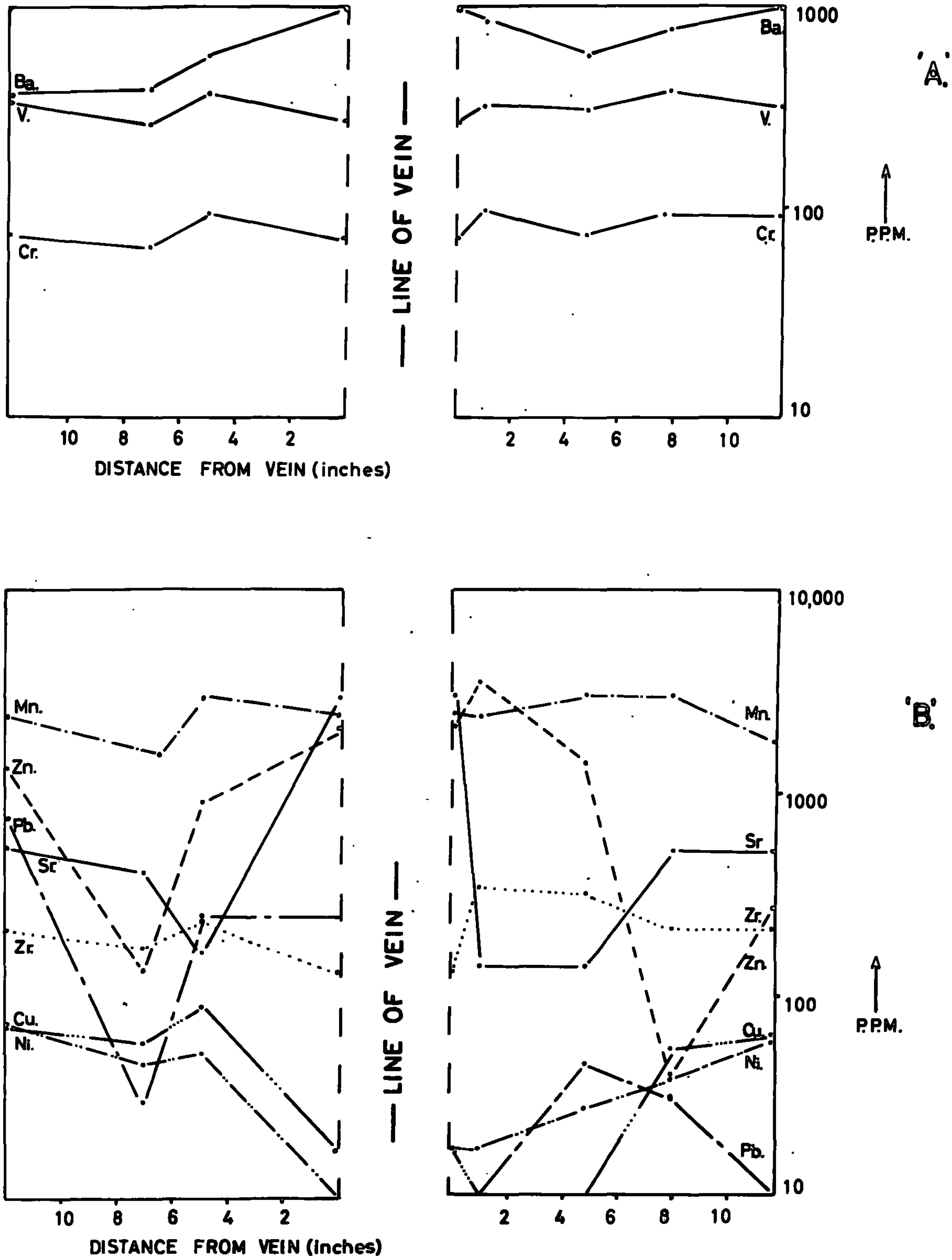


FIG. 6-11 TRACE ELEMENT VARIATIONS — COWGREEN MINE.

The presumed continuation of the Dubbysike vein in a westerly direction, was sampled at Force Burn on the Moor House National Nature Reserve. The vein, mineralised predominantly with barite, also contained galena and quartz, the width of which varied between 6 inches and 4 feet with an alteration zone of approximately 6 feet. Between 1 and 6 feet, strontium, nickel and copper are decreased; zinc, lead, rubidium and manganese increased, while the variations illustrated in the upper diagram do not show such a radical change within this zone. Vanadium and chromium depleted at distances of 2 to 5 feet are enriched between 1 and 3 feet to be finally depleted adjacent to the vein. Barium has erratic values throughout the traverse, and is unusual in the fact that it is not concentrated veinwards to such a marked degree as might be expected from the vein content of barite.

The classic locality at Wynch Bridge where the alteration processes were studied by Wager, provided a traverse between two chalybite - calcite - quartz stringers the analytical results are displayed in fig. 6-13. The background concentrations of the elements have a constant value, while variations are noted when the junction of altered to unaltered dolerite is encountered. Within the alteration zone the concentration of zirconium, barium, vanadium and chromium is recorded with a corresponding diminution in strontium and zinc, while copper and nickel values remain relatively constant. The decrease in manganese, recorded from other localities was not found adjacent to this vein.

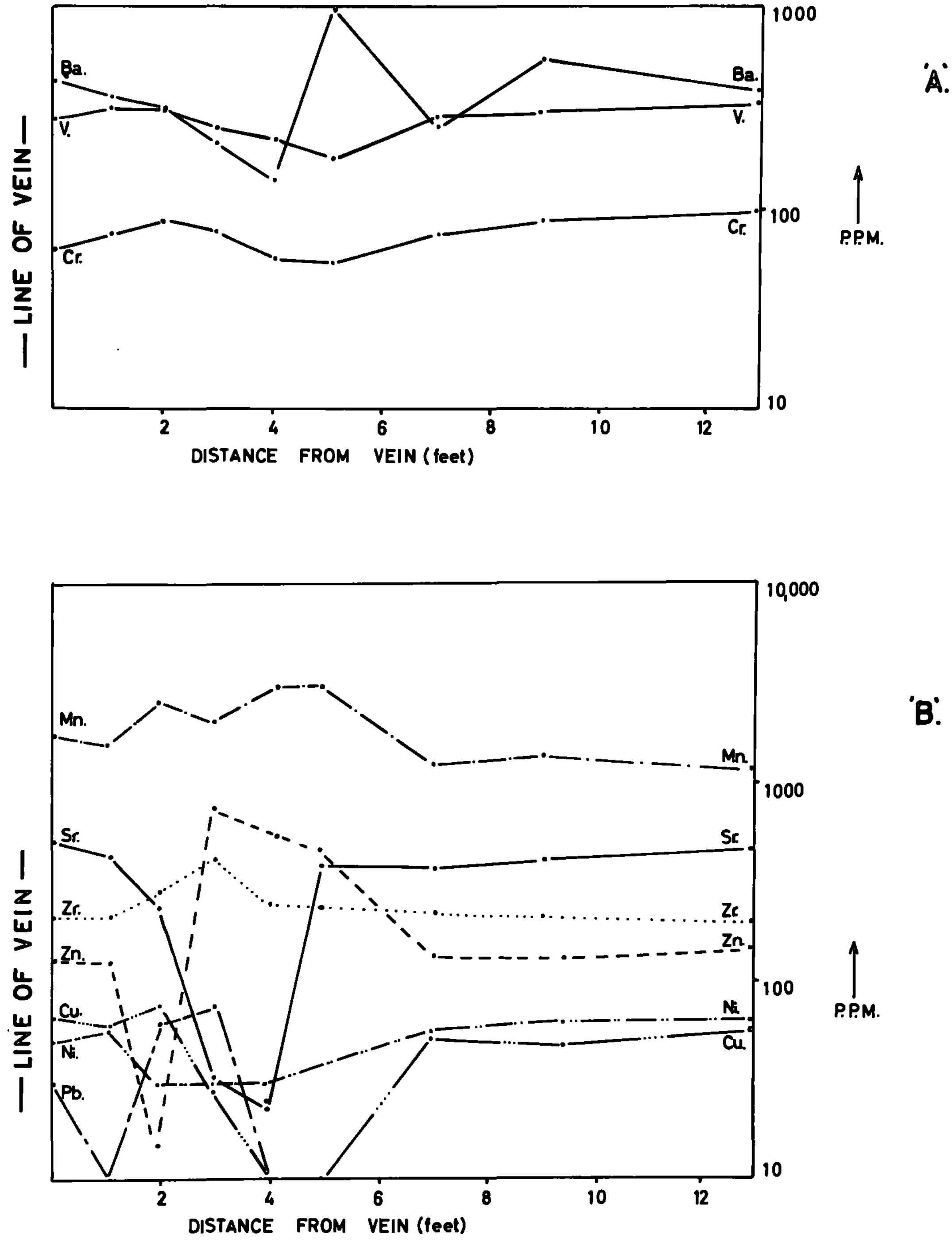
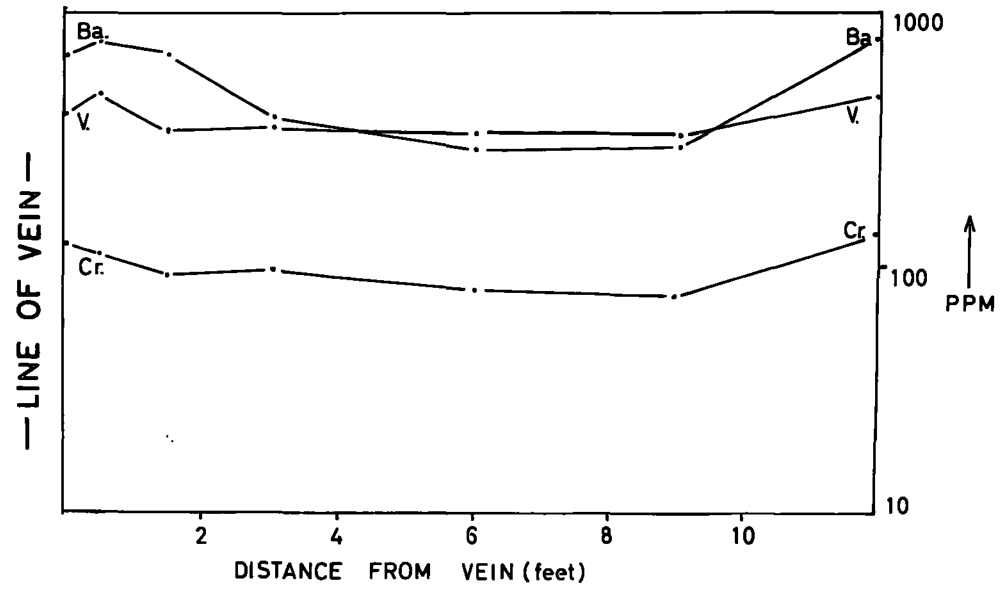


FIG. 6-12 TRACE ELEMENT VARIATIONS — FORCE BURN.



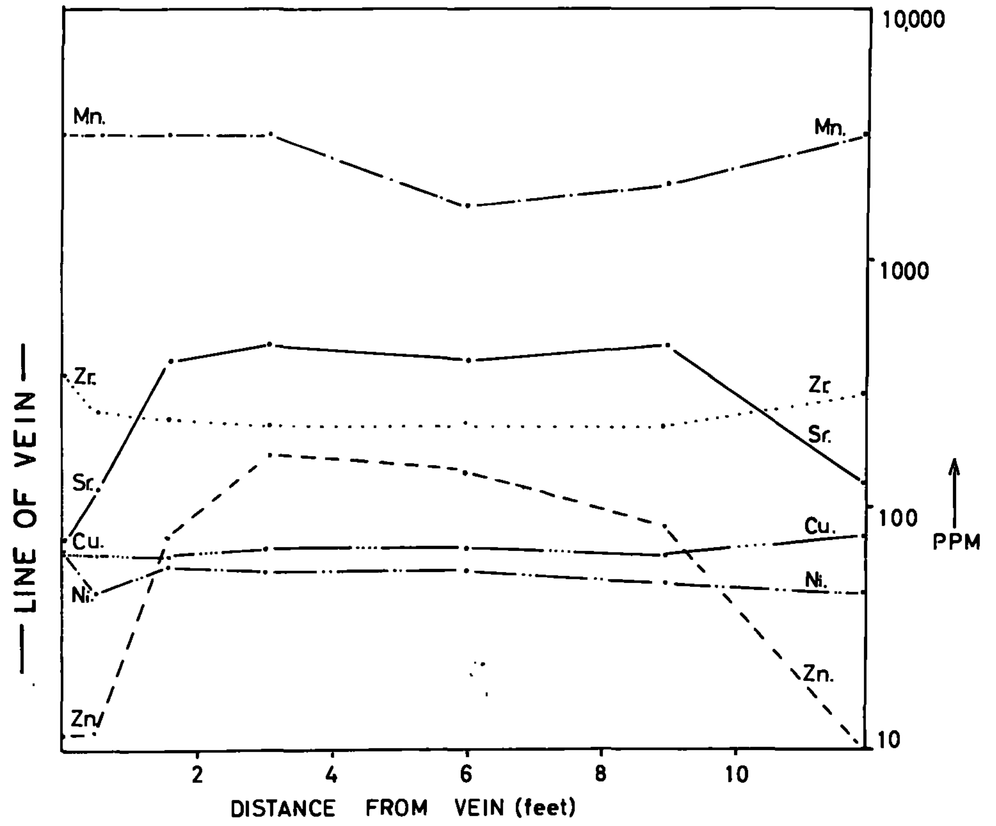


FIG. 6-13 TRACE ELEMENT VARIATIONS — WYNCH BRIDGE.

Alteration Adjacent to Fluorite Mineralization

The previous remarks on the element variations have been with respect to wallrock samples adjacent to barium mineralization, from West Blackdene Mine however, it was possible to collect samples in the Whin Sill adjacent to a fluorite vein (Blackdene Vein). The resultant analytical figures are shown on the uppermost of the three diagrams in fig. 3-29.

The alteration, visible over 3 feet, is seen to be the boundary at which the elements resume a normal constant background value. Towards the vein, increases in rubidium, lead, zinc, manganese, and barium are noted, while the strontium content decreases. The divergence from the background concentration, with reference to zirconium takes place, not at 3 feet, but is restricted to a zone within 12 inches of the mineralization.

The interesting feature, is the logarithmic decay or increase of all the elements from the vein into the country rocks, which would indicate the diffusion of all the elements out from the vein.

Summary of the Results

The minor element variation patterns studied reveal the following features:-

General Features

The boundary between the altered quartz-dolerite and the unaltered rock is a transitional junction. Major chemical mineralogical and trace element variations from the constant background results, occur at this boundary.

Specific Features

Individual trace elements illustrate certain general trends as a mineralised area is approached, these are as follows:-

Rubidium

Rubidium values increase in the altered dolerite, the concentration of the element increasing from the junction of the alteration towards the mineralization.

Barium

Most of the wallrocks sampled were adjacent to barite veins, barium invariably increased towards the vein. Fig.3-29 (labelled No.3 incline) shows that barium also decreases next to a fluorite vein at West Blackdene Mine, and similarly barium is enhanced in the wallrocks of the siderite vein at Wynch Bridge (fig. 6-13).

Lead

Lead does not show constant trends next to the veins.

Strontium

Traverses showed that strontium decreased next to the veins, except at Cowgreen Mine, where it was concentrated on the vein wall.

Manganese

Ten of the dispersion aureoles illustrated a decrease in manganese next to the vein, while traverses from Closehouse, Force Burn and Wynch Bridge (figs. 6-5, 6-12 and 6-13) showed that it was concentrated in the wallrocks.

Zirconium

The element was depleted towards the mineralization in all but two localities. At Settlingstones Mine (fig.6-6) and Wynch Bridge (fig.6-13) a concentration of zirconium in the wallrocks was recorded.

Zinc

An increase in the element adjacent to the vein is recorded from all but two localities. A decrease in zinc was found next to the siderite vein at Wynch Bridge (fig.6-13), and spasmodic occurrences in the quartzite next to the dolerite sill at Closehouse Mine (fig. 6-5).

Copper and Nickel

Both elements were depleted within the altered zones bordering the veins in the northern Pennines.

Chromium and Vanadium

In five of the traverses chromium and vanadium decreased towards the orebody, and in three localities they increased in concentration (figs. 6-7, 6-9 and 6-13 from Settlingstones Mine and Wynch Bridge respectively).

Interpretation

The chemical, mineralogical and trace element results have indicated certain features which require explanation. These are the boundary at which the variations cease, and the decrease or increase in the trace element content of the altered zones.

The Alteration Boundary

The junction between the unaltered and altered quartz-dolerite is a zone approximately 6 cm. wide. Progressive alteration processes are visible within this zone and samples from either side show profound differences in chemical, mineralogical and trace element composition. Wager (1929) showed that the metasomatic changes were the result of the action of the vein solutions, the present study confirms this suggestion.

The sharp boundary, the uniformity of the dispersion patterns, and the logarithmic decay in the concentration of an element with distance from the vein, suggest that diffusion in the capillary openings of the solid rock, rather than migration through open fractures, is responsible for the alteration of the quartz-dolerite. Capillary 'openings' may have been formed by the escape of gases and liquids at the time of cooling of the Whin Sill. James (1957) also noted that the logarithmic decay in concentration of an element with distance from the vein, was indicative of diffusion rather than migration through fractures.

Theoretical diffusion curves have been calculated for limestones (see Wehrenberg and Silverman, 1965); a similar study has not been made for igneous rocks. Morris and Lovering (1952) suggest that diffusion continued to operate as long as a concentration gradient existed between the ore solutions and the wallrocks. The ions in solution will move from a zone of high concentration to one of low concentration proportional to the diffusion coefficients of the ions. Diffusion coefficients are related to the composition and temperature of the transporting medium. Sawkins (1966), from fluid inclusion studies, indicates that the Pennine ores were deposited over temperatures ranging from less than 50°C to greater than 200°C. Quartz was deposited at temperatures ranging between 300°C and 120°C, fluorite between 200°C and 100°C, and barite from 130°C down to less than 50°C. He also suggested that the temperature data indicated that the hydrothermal solutions must have been considerably hotter than the wallrocks. The composition of the ore fluids however, is an unknown factor. With only one parameter, partly confirmed, the diffusion coefficients cannot be calculated.

Bundy (1958) suggests that wallrock alteration and elemental variation is a function of the time and pH conditions, rather than changes in temperature and the pressure of the veins. Hemley and Jones (1964) refute Bundy's ideas and attribute the alteration of silicate host rocks to the temperature and pressure of the solutions. The large number of possible parameters, none of which, at present, have been proved to be fundamental in the alteration of silicate rocks, leaves the controlling factors open to doubt. The mineralogical and chemical variations which occur at the boundary of the unaltered and altered dolerite indicates the extent to which diffusion, and hence alteration of the wallrocks took place.

The boundary of the alteration zone indicates the depth of penetration of the ore fluids. Wager (1929) considered that a change in the composition of the invading solutions and especially the carbon dioxide concentration has limited the extent of alteration. He assumed that the temperature and pressure of the system was, during metasomatism, approximately constant. There is no evidence for this, and Sawkins work would suggest that a temperature gradient existed between the ore fluids and the wallrocks, and that the ore fluids changed temperature with time.

The boundary between the unaltered and altered quartz-dolerite is in fact a transitional zone, in which the pyroxenes are the first minerals to be altered, followed by the alteration of hornblende, plagioclase, biotite and finally orthoclase. Although these changes occur within 6 cm, it does indicate that changes occurred at the dispersion 'front' and suggests that the reactivity between the invading fluids and the wallrocks was being diminished rapidly. It is tentatively suggested that a decrease in the temperature of the differing solutions resulted in the preferential alteration of the minerals at the diffusion boundary, and that pyroxenes are altered at lower temperatures than hornblende and plagioclase, while orthoclase was resistant to decomposition until a certain temperature had been attained.

Trace Elements

The trace elements may be present in three environments in the host rock, these are:-

(1) In discrete minerals of which they are the major constituents.

(2) In submicroscopic material dispersed along fractures and grain boundaries. Brown (1953) studied the leaching of rocks and illustrated that trace elements can be removed from minerals without modifying the crystal lattice.

(3) Situated in the lattice of major rock forming minerals.

Petrographic examination of the dolerite revealed that fractures in the altered and unaltered rock contain small amounts of quartz, barite and galena.

A crystal of calcite, from Masson Hill Quarry, was examined by X-ray fluorescence on a cleavage surface and on an artificially cut surface. A five fold increase in manganese was found on the cleavage surface with respect to the cut face. This would indicate that either a discrete, but submicroscopic mineral phase of manganese is present, or that the manganese has been 'sorbed' onto the calcite along the cleavage surface.

The third, and most probable, position for the trace elements is in the crystal lattice. Goldschmidt and others state that an element may be either camouflaged, admitted or captured in a crystal lattice, depending on the ionic size and charge of the element in relation to the host minerals. Ringwood (1955) modified these rules, and indicated that considerations of the electronegativity and ionic potential are necessary. Taylor (1966) summarises the enrichment of specific elements in certain minerals in relation to the above considerations and shows, for example, the presence of rubidium in potassium minerals, nickel in biotites and manganese in ferromagnesian minerals.

Two conclusions are possible for the variation in the trace elements. Firstly, that the erratic results are due to discrete mineral assemblages occurring in visible or submicroscopic fractures, and secondly, that the regular trace element variations are related to chemical and mineralogical changes.

Trace element variations are clearly closely related to variation in the host rock mineralogy. Decreases in CaO, MgO, Na_2O and total iron are associated with decreases in strontium, zirconium, vanadium, chromium, nickel and copper. An increase in rubidium is associated with an increase in K_2O and the clay minerals, while barium, manganese, lead and zinc have been introduced into the wallrocks from the ore fluids. A decrease in trace elements and major chemical components in the wallrocks suggests that they have been 'leached' by the ore fluids. If it is envisaged that the trace element is situated in a crystal lattice, the decomposition of the lattice, due to metasomatism, will consequently 'liberate' the trace element. The present study has shown that certain elements are depleted and others are concentrated in the altered zone. This evidence suggests that the removal of certain elements has taken place, while other elements have been introduced from the ore fluids into the wallrocks.

A total rock trace element analysis was undertaken rather than a mineralogical analysis. The amount of material available from most localities was restricted to diamond drill cores. It was found that to separate enough material for a mineralogical analysis, at least one foot of 'Ax' core was required. The alteration zones vary in width, but an average width is approximately 5 feet, this would have enabled five samples to be analysed for the whole of the alteration zone. The results from five samples would not have indicated the regular variations which have been found. The result of a whole rock analysis is to indicate the overall concentration of a trace element in a rock, but does not indicate the position of the trace element in the rock.

Previous studies on the relationship between the major and trace element contents of igneous rocks has been undertaken by numerous people. Nockolds and Mitchell (1948), and Wager and Mitchell (1951) report the variable trace element content in specific minerals. Plagioclase feldspars contain the majority of strontium in an igneous rock, an average value of 1000 ppm. is reported by Wager and Mitchell. Nickel is held preferentially in biotite, although pyroxenes may contain 150 ppm. of nickel. Vanadium and chromium are reported as being present in pyroxenes, hornblende, biotite and magnetite. It may therefore be tentatively suggested that the alteration of biotite is related to the decrease in nickel, MgO, and iron content of the rock. Decomposition of the plagioclase has liberated the majority of the strontium and is related to the decrease in Na_2O, while alteration of the pyroxenes has decreased the chromium, vanadium, MgO and iron content of the rock.

The increase in rubidium, K_2O and the clay minerals in the altered zone suggests the introduction of these constituents from the ore fluids. Sawkins (1966) from fluid inclusion studies reports the enrichment of sodium in relation to potassium and suggests that the potassium 'is constantly being fixed in the reconstitution of degraded clay minerals'. These results suggest that potassium is derived from the ore fluids and fixed in the clay minerals. The decrease in Na_2O would indicate that sodium is not absorbed by the clay minerals and had been incorporated in the ore fluids. Rubidium is similar in size and chemical characteristics to potassium, with which element it shows a close association. It is able to replace potassium, and is absorbed by the potassium rich clay minerals. Rubidium is not present in the veins, however the results indicate that at the time of alteration of the dolerite, the ore fluids contained appreciable amounts of rubidium.

Chromium, vanadium and zirconium are concentrated next to the veins at Settlingstones Mine and Wynch Bridge, while strontium is enriched in the wallrocks next to the barite vein at Cowgreen Mine. A decrease in zinc occurs in the white whin at Wynch Bridge, and these localities are therefore considered to show anomalous results. Confirmation of some of these results is given by Dunham (1948, p.104) who quotes analyses from Cowgreen and Settlingstones Mines. These localities have appreciably more chromium, barium and strontium in the altered dolerite, than elsewhere in the orefield.

These results, it is suggested, imply that processes operative at these localities were different from elsewhere in the northern Pennines. There is no evidence to indicate either an additional source of these elements, nor the presence of mineral phases next to the vein, in which the elements may be held. It is concluded that the ore fluids were enriched in these elements. It is possible that chromium, vanadium and strontium were leached at lower levels to be deposited in the wallrocks at higher levels in the Whin Sill.

A barium aureole next to a fluorite vein (West Blackdene Mine) supports Solomon (1966) who suggested that the ore fluids carried barium in solution. Barium is not present in the vein, and this may reflect the difference in the solubilities of $BaSO_4$ and CaF_2. Solomon notes that the solubility of $BaSO_4$ is greater than that of CaF_2 under similar conditions. The barium aureole would indicate that the solubility of $BaSO_4$ was equal to, or exceeded that, of CaF_2 in the wallrocks at the time of formation of the aureole, but that the solubility product of $BaSO_4$ was not exceeded in the vein, and hence barite was not deposited.

The results have shown that the trace element variations are related to mineralogical and chemical changes occurring as a result of the metasomatism of the quartz-dolerite. The origin of the economic deposits has always been, and still is, very much in dispute. The origin of the dispersion patterns, is however, related to the composition of the ore fluids when the aureole was formed. It is possible that, as the composition of the ore fluids varied, additional elements were introduced or removed from the wallrocks. The result being that the present aureole may reflect numerous phases of the ore fluids. It is, however, generally possible to tell at least the direction of movement of the ore forming fluids with respect to the wallrocks. This question has been discussed by Reitan (1959) whose diagrams are illustrated in fig. 6-14.

There can be little doubt that the emplacement of the ore material resulted in the diffusion of the ore metals into the wallrocks, for the recurring pattern of the ore metals is of Reitan's type A. It is evident that either before, during, or after the ore forming stage, the fluids were capable of dissolving and carrying limited amounts of additional material. Patterns similar to type B are

Wallrock dispersion patterns after Reitan (1959)

Diagram A. implies high concentration in the vein with movement of the element into the country rock.

Diagram B. implies low concentration in the vein with the apparent depletion in the country rock caused by movement of other elements into the wallrocks.

Diagram C. implies movement from the vein into the surrounding rocks, of surrounding rock material already low in the vein.

Diagram D. implies the apparent enrichment in the wallrocks caused by movement of other elements into the vein.

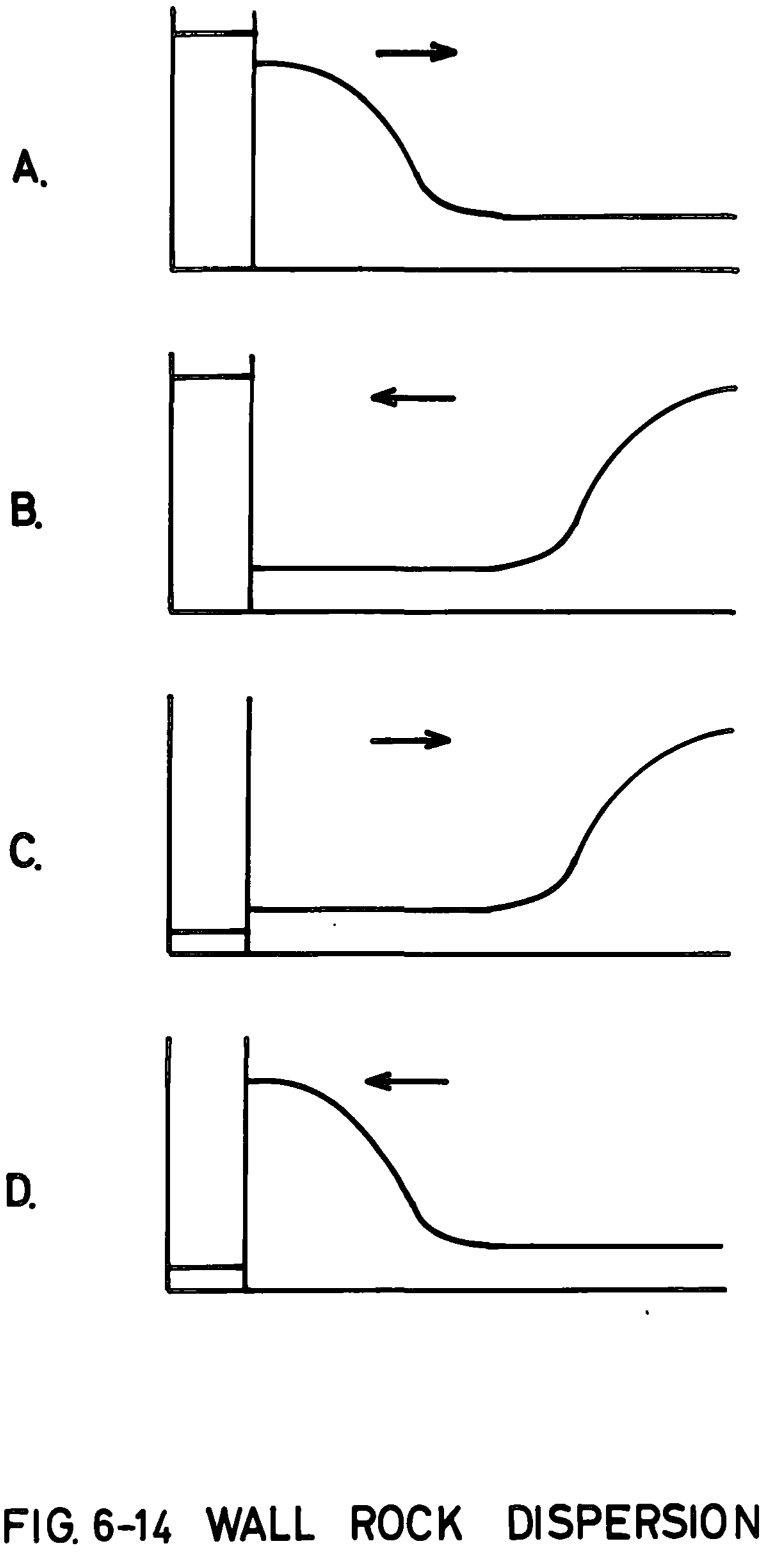


FIG. 6-14 WALL ROCK DISPERSION PATTERNS. (REITAN 1959)

common, however the enrichment in the vein is not present at the sampling locality and would indicate transportation to higher stratigraphical levels. This possibility is strengthened by the report of such minerals as niccolite (NiAs) and harmotome ($(K,Ba)(Al_2Si_5)O_{14}.5H_2O$) in the veins at Settlingstones Mine. They may have been formed by the concentration of material removed from the dolerite due to metasomatism. Likewise the occurrence of strontianite ($SrCO_3$) at Settlingstones and Greenlaws mines may indicate abnormal localities where sufficient strontium has been concentrated, after removal from the wallrocks, to form a separate mineral phase. If these processes are considered valid, then the enrichment of vanadium, chromium, and strontium, as noted previously, can be attributed to similar reactions, whereby material is leached out at one horizon to be deposited at another horizon. Dispersion patterns similar to types C and D have not been found next to the Pennine mineralization.

An observation from the results of this survey is that because of the restricted trace element aureoles, primary cycle geochemical prospecting will be of little use in locating new ore deposits in the Whin Sill. In many respects this is similar to the conclusions of Rao (1952) and Bradshaw (1965) who investigated wallrock aureoles next to cassiterite veins in the Cornish granites.

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Locality References

Derbyshire

Sample Ref. No.	Locality	Vein
L/HE/-	Ladywash Mine	Hucklow Edge (East)
L/HW/-	"	" " (West)
L/OE/-	"	Old Edge
SH/-	Sallet Hole	Longstone Edge
19/-	Longstone Edge	" "
MQ/-	Middleton Mine	not named
MQ/1/a	nr Wirksworth	
ICI/-	Masson Hill	Flat assoc. with Great Rake?
R/-	Raper Prospect	Long Rake
RA/-	Youlgreave	
TC/-	Treak Cliff Mine	Blue John Deposit
TC/1/a		
OM/-	Odin Mine, Castleton	Odin Vein
DR/-	Dirtlow, nr Castleton	Dirtlow Rake

Northern Pennine Orefield

A. Mines

R/W2/-	Redburn Mine, Rookhope	Red Vein
R/W2/1A		
R2N/-		
S/W/-	Swinhope Mine	Williams Vein
S/1/A		No.1. Vein
S/WN/-		Williams/North Veins.
B1/-	Settlingstones Mine	Bewick Vein
B2/SB		" "
SB1		Dixson-Brown Vein
B2-A-		none
OSM		Bewick Vein-South branch
5xC/-	Closehouse Mine	5 fathom crosscut south
DN3/-		12 fathom sub-drift
SC/-		17 fathom drift

Northern Pennine Orefield

Sample Ref. No.	Locality	Vein
C/-	Cowgreen mine	Greenhush Vein
BL/- BS/- BL/3/-	West Blackdene Mine	Blackdene Vein Slitt Vein Blackdene Vein

B. Additional Localities

Sample Ref. No.	Locality	Vein
FB/-	Force Burn	Force Burn = Dubbysike Vein
WB/-	Wynch Bridge	not named

C. Great Limestone Localities

Sample Ref. No.	Locality	Vein
S(W)1-	Heights Quarry	South Vein
H(W)-		West Cross Vein
LH/A/- LH/B/-	Lanehead Quarry Stanhope	not named
EA/-	East Ashes Quarry Stanhope	Coves or Park Vein
H/E/-	Harehope Quarry, Frosterley	no name
N/-	Newlandside Quarry Stanhope	East Newlandside Flat/Vein
G/-	Garrigill	Browngill Vein

Cumberland

Sample Ref. No.	Locality	Vein
Cumb/- B7/- B48/- B48A/- B33/-	Beckermet Mine	none named

Spain

Sample Ref. No.	Locality	Vein
Minersa	Sierra de Gados	not named

LIMESTONES

Derbyshire

Laporte Concession Area

Ladywash Mine

(Hucklow Edge Vein-East) Samples L/HE/1 to 11.

Distance from the Vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
Vein	<5	> 10%	>6%	<10	137	~10	~1.3%	<15	< 5
0	<5	8000	500	135	235	< 10	~3.5%	100	125
1	~5	~1.8%	~20	450	321	~10	1080	<15	~5
3	8	3850	62	350	258	<10	55	~15	~5
5	~5	3000	32	500	353	< 10	45	18	5
10	< 5	2980	<20	550	201	< 10	40	~15	8
15	< 5	620	34	810	143	< 10	5	15	15
20	5	800	20	450	144	< 10	5	18	~5
25	8	1950	46	320	232	< 10	5	<15	10
30	7	< 250	70	480	151	< 10	5	~15	10
35	13	< 250	20	400	253	< 10	5	< 15	5

(Hucklow Edge Vein-West) Samples L/HW/1 to 12.

Distance from the Vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
Vein	< 5	>10%	292	570	< 10	155	705	18	10
0	< 5	9900	27	400	651	120	40	~15	< 5
3	< 5	6150	< 20	1350	757	105	20	~15	12
5	< 5	7250	< 20	520	678	95	900	~15	12
7	< 5	~ 2.1%	< 20	2750	128	285	150	15	53
10	< 5	9950	< 20	600	571	150	490	15	30
15	< 5	4575	< 20	550	538	40	< 5	< 15	< 5
20	< 5	2710	40	320	828	57	20	< 15	15
25	< 5	2130	85	440	659	42	5	< 15	9
30	< 8	600	76	440	1016	<10	5	< 15	6
35	8	< 250	76	310	824	< 10	5	< 15	< 5
40	5	< 250	42	380	724	< 10	5	~15	7

(Old Edge Vein) Samples L/OE/1 to 12.

Distance from the Vein(feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
Vein	<5	>10%	<20	180	564	45	~2.7%	~15	18
0	<5	~ 2%	~20	300	399	<10	37	<15	<5
1	~5	~3.7%	67	200	235	<10	35	<15	<5
3	10	~3.0%	33	230	1285	<10	30	<15	8
5	9	~3.8%	36	240	243	<10	29	<15	5
10	9	3980	63	215	202	<10	24	~15	~5
15	~5	280	97	230	205	<10	35	<15	9
20	~5	<250	25	250	231	<10	15	<15	~5
25	9	<250	65	360	213	<10	39	~15	<5
30	9	<250	~20	280	162	<10	<5	~15	~5
35	9	<250	20	290	188	<10	<5	~15	<5
40	8	<250	22	235	179	<10	<5	<15	~5

Sallet Hole Mine

(Longstone Edge Vein) Samples SH/1 to 12

Vein	<5	>10%	~1.6%	1730	78	200	440	35	<5
0	<5	1500	77	500	214	20	60	~15	~5
1	~5	250	116	460	149	~20	17	~15	~5
3	<5	~1.3%	27	435	219	<10	19	~15	~5
5	~5	<250	~20	440	194	<10	5	<15	~5
7	~5	<250	<20	445	208	<10	5	<15	5
10	~5	<250	29	455	197	<10	5	<15	<5
15	~5	1000	61	450	215	<10	25	<15	<5
20	8	<250	~20	450	205	<10	<5	<15	<5
30	~5	<250	26	435	198	<10	<5	<15	<5
40	8	<250	46	520	253	<10	30	<15	<5
44	8	<250	27	415	200	<10	~5	<15	<5

Borehole 19 (Longstone Edge)

Samples 19/1 to 24

Distance from the mineralization	Rb (ppm)	Ba "	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
0	<5	>6000	-	~7.0%	350	<10	95	1420	15	<5
9	<5	>6000	-	1810	105	~10	128	6874	140	75
17	10	2800	-	175	50	~10	100	2002	47	41
26	40	217	-	50	37	~10	75	4389	75	105
30	15	1300	-	<10	137	480	43	345	17	18
35	10	>6000	-	<10	155	400	35	500	20	10
40	7	>6000	-	350	195	360	30	780	17	13
41	8	-	-	431	400	598	30	540	~15	10
42	16	-	9000	707	355	319	30	1030	25	28
44	20	-	~1.0%	153	440	287	28	950	25	32
46	16	-	~2.0%	939	175	292	22	860	34	21
49	10	-	~1.9%	267	200	487	<10	245	<15	~5
53	9	-	4120	359	220	447	25	543	16	10
57	8	-	2080	97	320	401	<10	33	~15	<5
63	~5	-	3750	229	150	5534	<10	100	<15	31
66	~5	-	240	25	640	1509	~10	55	<15	10
76	6	-	~2.1%	41	410	551	<10	51	15	<5
85	<5	-	~2.0%	284	550	432	29	600	<34	27
95	9	-	8600	166	600	450	~10	225	<15	~5
107	~5	-	~2.1%	195	650	329	<10	112	<15	~5
126	7	-	~2.2%	198	570	367	<10	108	<15	10
146	~5	-	1250	379	540	409	~10	230	<15	~5
177	7	-	1150	1103	790	224	<10	65	<15	~5
187	<5	-	500	276	785	216	<10	180	<16	~5

Castleton Area

Treak Cliff Mine

Samples TC/1 to 6

Distance from ore (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
0	~5	>1.0%	70	270	345	12	60	<15	11
6"	<5	>1.0%	35	273	285	<10	10	<15	~5

Distance from ore (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
1	~5	1200	327	235	250	134	110	<15	12
1'6"	~5	1040	35	260	245	<10	12	<15	~5
3	<5	9600	~20	253	215	<10	<5	~15	~5
5	~5	740	35	240	300	26	15	15	~5
Samples TC/1/a to d									
0	<5	2600	328	195	1950	212	1864	25	72
6"	~5	1210	22	192	585	102	140	<15	6
1	<5	1000	~20	405	275	67	190	~15	17
3'	~5	1200	35	193	440	44	80	~15	<5
Dirtlow Rake									
Sample Dr 1 to 6									
Vein	<5	-	9800	1200	1700	155	55	~15	<5
Hangingwall	<5	-	22	1210	700	84	130	~15	<5
Footwall	<5	-	320	270	765	<10	120	~15	<5
2	<5	-	68	375	160	<10	56	~15	8
4	~5	-	133	470	410	<10	23	<15	~5
7	<5	-	~20	400	100	<10	~5	<15	<5
Odin Mine									
Samples OM 1 to 12									
0	<5	>10%	550	125	3250	37	~6.5%	35	480
1	<5	~3.3%	<20	350	1250	<10	2240	~15	10
3	<5	1400	~20	450	650	<10	125	~15	6
5	~5	5200	<20	346	225	23	<5	<15	~5
10	~5	1500	<20	300	285	<10	33	<15	<5
15	~5	~1.0%	~20	290	275	<10	45	~15	~5
20	<5	8200	<20	365	225	<10	12	<15	<5
25	<5	2000	~20	295	125	<10	~5	~15	~5
30	~5	2170	~20	225	305	<10	12	~15	~5
35	30	<250	<20	370	310	<10	33	<15	<5
45	13	<250	~20	355	55	<10	~5	<15	~5
55	<5	<250	70	300	640	66	135	<15	~5

Additional Areas

Masson Hill Quarry

Samples MH 1 to 7

Distance from the vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
0	<5	6000	900	60	3150	<10	560	<15	11
1	~5	7300	700	63	1700	<10	410	~15	~5
3	12	760	17	63	1750	<10	340	<15	~5
7	<5	2840	3000	195	1500	204	1568	135	275
9	~5	6000	1900	225	800	153	~1.5%	103	220
15	<5	~1.3%	1400	315	3000	130	6609	62	175
25	~5	1000	45	125	3900	<10	280	<15	~5

Imperial Chemical Industries Quarry

(Buxton) Samples I.C.I. 1 to 6

Vein	<5	-	600	120	25	<10	<5	<15	<5
3	<5	-	120	240	45	<10	<5	<15	<5
5	<5	-	20	270	155	<10	<5	<15	~5
10	<5	-	20	230	240	<10	<5	<15	~5
15	<5	-	~20	243	43	<10	<5	<15	<5
20	<5	-	~20	260	~10	<10	<5	<15	<5
30	<5	-	~20	225	20	<10	<5	<15	<5

Raper Prospect

(Youlgreave) Samples R 1 to 7

0	<5	>10%	6500	1475	140	492	660	82	~5
3	<5	4500	6900	1115	<10	152	190	60	<5
5	<5	>10%	4800	1720	<10	202	80	55	<5
10	10	>10%	~1.8%	25	<10	<10	15	37	<5
15	<5	>10%	6400	50	<10	<10	170	137	<5
20	<5	>10%	4200	30	<10	~10	70	<15	<5
25	<5	>10%	3500	27	<10	<10	20	36	~5

Middleton Mine

(near Wirksworth) Samples MQ 1 to 10

Distance from the vein (feet)	Rb	Pb	Sr	Mn	Zr	Zn	Cu	Ni
0	<5	100	375	100	<10	38	<15	~5
6"	<5	35	355	110	<10	25	<15	<5
1	<5	65	380	165	<10	150	<15	<5
3	<5	75	305	75	<10	35	<15	~5
5	<5	92	358	85	<10	45	<15	<5
9	~5	30	350	55	<10	35	<15	<5
15	<5	130	265	110	<10	100	<15	~5
20	~5	70	300	85	<10	45	<15	<5
30	10	95	240	70	~10	70	<15	<5
40	<5	~20	500	100	15	43	<15	<5

Samples MQ/1 a to 9

Distance from the vein (feet)	Rb	Pb	Sr	Mn	Zr	Zn	Cu	Ni
0	~5	178	270	115	<10	45	<15	~5
6"	12	76	295	83	<10	25	<15	~5
1	~5	25	265	65	<10	15	<15	<5
1'6"	~5	76	270	100	<10	25	<15	<5
2	~5	23	260	55	<10	20	<15	<5

Northern Pennine Orefield

Weardale - Great Limestone

Heights Quarry

(South Vein) Samples S(W) 1 to 7

Distance from the vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Fe "
Vein	<5	>10%	280	45	310	<10	<5	15	~5	>10%
0	~10	~2.8%	65	135	3300	60	80	35	20	~5.4%
1	~10	<250	~20	1380	750	~10	970	<15	<5	2900
3	~10	<250	<20	2680	800	~10	<5	<15	<5	1980
5	~10	<250	~20	2280	770	<10	<5	<15	~5	1600
9	10	<250	45	2800	330	~10	<5	<15	~5	1400

Distance from the vein(feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Fe "
15	10	< 250	~20	1340	500	20	<5	~15	~ 5	1900
20	10	1350	~20	2040	580	<10	< 5	< 15	10	1000
(West Cross Vein)				Samples H(W) 1 to 6						
Vein	<10	>10%	~5.4%	<20	4500	<10	215	< 15	< 5	>10%
0	<10	4000	515	40	7500	30	505	20	38	> 10%
1	<10	< 250	720	1640	1730	20	585	~15	~ 5	2500
3	< 10	< 250	945	500	1900	17	1080	65	12	1700
5	<10	<250	82	830	1200	<10	2000	<15	~ 5	5900
9	<10	<250	55	1900	565	<10	25	<15	< 5	1220
14	<10	< 250	35	1340	300	<10	15	<15	~5	3060
Newlandside Quarry										
				Samples N 1 to 10						
0	<10	-	83	40	~1%	25	500	<15	885	>16%
5	<10	-	< 20	1960	630	<10	110	<15	12	1100
10	< 10	-	30	4400	305	40	80	< 15	~5	1260
15	< 10	-	< 20	3060	300	< 10	350	~15	< 5	1300
20	< 10	-	~20	4000	270	28	80	~15	~ 5	1100
25	< 10	-	< 20	3000	250	<10	25	<15	~5	980
30	< 10	-	680	340	700	45	280	25	30	820
33	< 10	-	1010	152	1400	~10	330	20	25	~1.7%
35	~10	-	40	150	4300	20	1500	20	28	~ 4.6%
38	~10	-	35	20	9000	25	155	<15	25	> 15%
Harehope Quarry				Samples H(E) 1 to 11						
Vein	<5	-	75	~10	9430	<10	1400	225	20	>10%
0	<5	-	80	165	3000	12	20	<15	~5	~ 3%
6"	< 5	-	80	180	1600	20	25	<15	12	~2.1%
1	<5	-	60	120	2400	85	< 5	<15	~5	~2.2%
1'6"	<5	-	40	200	2600	20	19	<15	17	~2.3%
2	<5	-	55	100	2700	<10	< 5	~15	~5	~3.0%

Distance from the vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Fe "
3	<5	-	50	205	2500	33	<5	<15	~5	~2.2%
8	<5	-	45	1680	505	33	<5	~15	50	760
12	<5	-	260	1580	400	<10	<5	<15	~5	1720
20	<5	-	<20	2160	330	<10	<5	<15	<5	560
30	<5	-	50	1840	230	<10	<5	<15	<5	620
35	<5	-	40	1840	200	<10	<5	<15	<5	600

Lanehead Quarry

Samples LH/A/1 to 6

Vein	<5	>10%	~3.5%	<10	910	<10	95	<15	<5	>10%
0	10	1700	70	110	1200	<10	1580	40	~5	1200
6"	<5	5600	645	108	900	~10	2400	20	~5	8800
1	<5	<250	35	2400	515	<10	205	<15	<5	1220
2	<5	<250	40	1910	310	~10	10	<15	~5	680
9	<5	<250	30	1760	235	<10	545	<15	~5	660
15	<5	<250	~20	1768	390	<10	15	<15	<5	1020

Samples LH/B/1 to 5

0	25	<250	25	700	950	~10	87	~15	10	~1.7%
1	10	<250	20	1600	700	<10	50	~15	15	2000
9	5	<250	~20	1580	310	<10	20	~15	<5	1700
15	5	<250	20	1185	335	<10	<5	<15	~5	1480
25	5	<250	70	2120	205	12	75	~15	35	600

Additional Localities

Garrigill

(Browngill Vein - Tynebottom Limestone) Sample G 1 to 8

0	75	3420	740	4400	600	<10	975	~15	25	5200
3	<5	2070	895	4400	400	35	2500	<15	25	4200
5	<5	~3.6%	75	12	850	<10	~10.2%	135	105	5600
14	<5	1260	450	4400	350	<10	1030	~15	20	7600
23	175	700	~20	1300	540	17	135	25	75	~1.9%
27	190	900	~20	1580	450	140	90	35	80	~2.2%
34	80	1400	~20	1320	350	57	125	20	70	~2.2%

Distance from the vein(feet)	Rb (ppm)	F	Pb	Sr	Mn	Zr	Zn	Cu	Ni	Fe
40	20	250	~20	3100	320	20	65	~15	30	~1.2%

Underground Localities - Great Limestone

Swinhope Mine

(Williams - North Veins) Samples S(WN) 1 to 12

Distance from the vein (feet)	Rb (ppm)	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
0	<5	~20	1280	700	<10	80	<15	<5
20	<5	<20	1330	1420	<10	150	<15	<5
40	<5	~20	1280	245	<10	<5	<15	80
60	<5	~20	1080	215	<10	<5	<15	~5
80	<5	<20	1380	185	<10	<5	<15	<5
100	<5	<20	1340	130	<10	<5	<15	<5
120	<5	<20	1340	490	<10	15	<15	8
140	<5	<20	1400	190	<10	<5	<15	30
160	<5	<20	1570	160	<10	<5	<15	~5
180	<5	~20	1670	220	<10	<5	<15	<5
200	<5	<20	1620	3000	<10	<5	<15	~5
220	<5	<20	1450	385	<10	140	<15	<5
	(Williams Vein)			Samples S(W) 1 to 9				
0	<5	<20	1220	815	<10	90	<15	30
3	<5	~20	1490	945	<10	295	<15	<5
9	<5	<20	1670	1090	~10	10	<15	~5
18	<5	~20	1550	720	<10	~5	<15	~5
25	<5	~20	1500	425	<10	<5	<15	<5
35	<5	~20	1610	610	15	<5	<15	35
45	<5	<20	1660	560	<10	<5	<15	~5
55	<5	<20	1540	1285	12	110	<15	32
65	~5	~20	1700	735	<10	75	<15	~5

(Number 1 Vein) Samples S/1/A to G

Distance from the vein (feet)	Rb (ppm)	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
0	<5	20	1830	2000	<10	235	<15	31
1	<5	~20	1620	285	12	~5	<15	<5
3	<5	<20	1830	325	<10	<5	<15	<5
9	<5	<20	2500	160	<10	<5	<15	<5
18	<5	<20	1720	425	~10	<5	<15	<5
25	<5	<20	1720	705	~10	<5	<15	~5
40	<5	<20	1480	365	~10	<5	<15	~5

Redburn Mine

(Crosscut to borehole W2) Samples R/W2/1A to 1J

Distan6e from the vein (feet)	Rb "	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
Vein	<5	>10%	1744	25	2377	100	700	393	21
0	6	1700	25	~10	~3.4%	95	88	21	20
1	7	5600	27	10	~2.6%	80	158	91	15
3	6	5000	25	20	~1.9%	60	20	~15	15
5	6	~1.4%	108	30	~2.0%	38	1720	24	17
7	45	~1.23%	529	120	~1.9%	30	215	49	15
10	7	~2.7%	132	140	~1.4%	25	50	~15	12
14	<5	~1.75%	~1.6%	280	~1.1%	21	75	<15	<5
18	<5	7700	4594	190	~1.2%	10	~10.3%	36	8
22	10	1970	23	250	8058	5	~7.0%	41	12

(Borehole W2) Samples R(W2) 1 to 29

5	~5	<250	~20	1310	~1.1%	95	<5	~15	15
10	~5	1500	~20	2150	4500	<10	<5	<15	15
15	~5	4650	~20	550	8750	<10	105	~15	9
20	15	1320	<20	2185	5000	<10	110	<15	20
25	<5	~1.0%	<20	1450	5900	<10	115	~15	~5
30	~5	<250	~20	1110	4800	<10	275	<15	7
33	10	<250	<20	175	~1.0%	<10	<5	<15	15
36	<5	<250	<20	1350	1550	<10	<5	<15	<5
39	<5	<250	~20	1850	2100	<10	<5	<15	9

Distance from the vein(feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
42	11	<250	~20	625	~1.0%	<10	<5	~15	11
48	~5	<250	~20	350	~1.0%	21	<5	15	~5
53	11	<250	~20	1235	~1.0%	<10	~5	<15	~5
56	<5	<250	<20	1150	3200	<10	<5	<15	~5
60	~5	<250	<20	475	7600	<10	5	~15	9
66	~5	<250	<20	1550	4650	<10	90	<15	~5
68	15	<250	<20	50	3350	<10	~1%	18	<5
71	12	<250	<20	100	~1.0%	<10	~1%	~15	~5
74	<5	<250	~20	2150	4500	<10	90	<15	~5
76	10	<250	~20	1160	2150	<10	25	<15	<5
79	<5	<250	~20	1650	4100	<10	90	<15	~5
83	10	<250	<20	1725	4120	<10	<5	~15	~5
86	~5	<250	<20	1365	1025	<10	<5	<15	<5
88	10	<250	<20	1640	1250	<10	<5	~15	~5
90	~5	<250	<20	1430	1275	<10	<5	<15	~5
93	14	<250	~20	1185	5600	<10	<5	<15	~5
94	~5	<250	<23	1850	1500	<10	<5	<15	<5
96	<5	<250	~20	1625	965	<12	<5	<15	~5
98	~5	<250	<20	1950	1000	<10	<5	<15	~5
100	14	<250	~20	1665	1025	<10	<5	<15	10

(Borehole N2) Samples R(2N) 1 to 30

Distance from the vein(feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
0	20	<250	~20	140	~1.4%	<10	<5	15	26
5	7	<250	<20	70	~1.8%	<10	40	~15	~5
10	12	<250	~20	40	1850	<10	30	<15	~5
15	8	<250	<20	10	~1.9%	<10	<5	17	~5
20	10	<250	~20	20	~1.3%	<10	<5	65	20
25	6	<250	~20	430	9525	<10	<5	~15	~5
30	9	<250	<20	1550	850	<10	<5	~15	~5
35	6	<250	~20	1320	2800	<10	<5	~15	~5
40	6	<250	~20	1320	2575	<10	50	~15	<5
45	7	<250	~20	1400	3350	<10	<5	~15	<5
50	11	<250	<20	1430	2200	<10	<5	~15	~5
55	5	<250	~20	1430	1800	<10	<5	<15	~5
60	7	<250	<20	1310	1929	~10	<5	~15	~5

Distance from the vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
65	9	<250	<20	1100	5900	~10	<5	~15	~5
70	~5	<250	<20	1310	1600	<10	<5	<15	~5
75	9	<250	<20	1460	1925	<10	<5	<15	~5
80	~5	<250	<20	870	3750	<10	<5	~15	~5
85	9	1500	~20	1190	1675	<10	385	~15	~5
90	20	1150	<20	1230	960	<10	<5	<15	10
95	12	580	<20	1080	910	<10	<5	<15	~5
100	16	1000	~20	1100	3550	<10	<5	~15	~5
105	34	1210	<20	1050	1375	<10	~5	~15	20
110	8	~1.1%	~20	850	~1.6%	<10	15	~15	~5
115	6	~1.3%	~20	850	~1.4%	<10	20	<15	~5
120	8	~1.4%	<20	950	9250	~10	30	<15	~5
125	~5	~1.1%	~20	1160	2870	<10	<5	~15	~5
130	10	~1.4%	~20	1490	2280	<10	<5	~15	~5
135	10	920	~20	1680	780	<10	<5	~15	~5
140	~5	300	~20	1450	680	<10	<5	<15	<5
145	11	<250	~20	1370	565	<10	90	<15	~5

Cumberland

Beckermet mine

Samples Cumb. 1 to 16

Distance from the orebody (feet)	Rb (ppm)	Pb "	Sr "	Mn "	Zn "	Cu "	Ni "	Fe "
Vein	<5	<20	95	330	<5	~15	16	>47.0%
0	45	29	335	3000	<5	~15	9	~1.5%
5	47	~20	540	2030	<5	~15	10	~1.8%
10	75	22	570	2600	<5	<15	11	~2.5%
16	34	~20	560	1650	<5	<15	9	~1.1%
23	27	20	585	1750	<5	<15	~5	9000
32	36	~20	580	1860	<5	~15	~5	~1.1%
40	29	21	592	1520	<5	~15	9	~1.0%
48	13	~20	540	1550	<5	~15	~5	5200
61	10	27	660	1500	<5	~15	~5	4030

Distance from the orebody (feet)	Rb (ppm)	Pb "	Sr "	Mn "	Zn "	Cu "	Ni "	Fe "
80	10	40	550	1450	<5	~15	~5	4300
100	~5	<20	700	1090	<5	<15	<5	4420
(40)	35	37	590	2000	<5	<15	~5	~1.2%
(17)	33	33	470	2480	<5	~15	~5	~1.1%
(22)	~5	20	820	1330	<5	~15	<5	2480
(20)	17	35	680	1600	<5	<15	<5	2840
Samples B7/1 to 10								
Vein	~5	<20	15	105	<5	~15	15	>50%
0	~5	27	20	3000	<5	~15	~5	~12.5%
1	6	~20	510	1020	<5	<15	~5	~1.1%
3	~5	27	380	2080	<5	<15	~5	~1.2%
5	~5	~20	495	1880	<5	<15	~5	3690
15	6	27	400	2520	<5	<15	<5	3000
25	<5	~20	560	2140	<5	<15	~5	2090
40	5	23	350	2140	<5	<15	~5	1780
50	9	~20	630	900	<5	<15	<5	540
80	~5	~20	590	880	<5	<15	~5	990
Samples B 48A/ 1 to 8								
Vein	<5	<20	645	<10	<5	~15	17	>50%
0	<5	<20	380	1780	<5	~15	~5	~ 12%
1	<5	<20	630	700	<5	~15	<5	~2.5%
5	8	29	565	605	<5	~15	~5	~1.0%
10	<5	<20	570	1440	<5	<15	~5	~1.5%
20	8	~20	530	680	<5	<15	<5	~1.1%
30	8	23	595	1540	<5	<15	~5	3950
40	8	25	410	900	<5	<15	~5	2120
Samples B48/ 1 to 10								
Vein	275	<20	465	1580	115	~15	20	>50%
0	22	23	225	3000	40	~15	8	>50%
1	<5	<20	265	2660	<5	~15	~5	~21.9%
3	80	30	410	1960	30	~15	8	~8.0%
5	27	~20	730	1600	~5	~15	~5	~4.1%

Distance from the orebody (feet)	Rb (ppm)	Pb "	Sr "	Mn "	Zn "	Cu "	Ni "	Fe "
10	10	24	590	1120	<5	~15	<5	~2.5%
30	34	~20	580	1200	<5	<15	~5	~4.5%
50	27	~20	865	1030	<5	~15	~5	~1.1%
80	23	~20	750	1090	<5	~15	~5	~1.5%
100	20	~20	800	1200	<5	<15	~5	6020

Samples B33/1 to 10

Vein	~5	<20	10	440	<5	~15	16	>50%
0	<5	<20	22	2740	<5	~15	17	>50%
1	~5	~20	80	2000	<5	<15	9	>50%
3	5	38	145	3300	<5	~15	~5	>50%
10	~5	20	250	3000	<5	<15	10	~9.1%
20	~5	~20	430	3100	<5	~15	<5	~1.2%
30	8	20	610	1440	<5	<15	<5	~1.1%
40	10	40	465	1660	<5	~15	<5	~1.2%
50	<5	20	435	2100	<5	<15	~5	2700
100	13	37	570	820	<5	<15	~5	2000

Spain

Sierra de Gados

Samples:- Min 1 to 8

Distance from the vein(feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Fe "
Vein	<5	>10%	622	30	160	<10	~16.8%	70	<5	1780
0	<5	2750	400	135	430	<10	~2.9%	35	~5	3880
3	~5	4800	77	85	390	<10	~11.0%	105	~5	2550
5	~5	4000	110	95	630	<10	4000	<15	<5	3710
10	5	6300	268	105	330	<10	2000	<15	<5	2400
20	6	900	125	140	400	<10	140	~15	~5	3630
30	~5	1000	145	135	360	<10	350	~15	<5	2800
50	~5	1250	195	300	460	<10	240	57	~5	6100

SANDSTONES

Northern Pennine Orefield

West Blackdene Mine

(Blackdene Vein) Samples BL/1 to 11

Distance from the vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
Vein	<5	>10%	~10	22	150	<5	<5	~5	12
0	15	1600	35	221	1375	55	135	~5	~10
1	55	3300	<10	20	1450	390	<5	~5	10
3	65	500	~10	8	1320	460	<5	25	10
5	70	500	<10	15	175	525	<5	~5	~10
10	68	550	<10	<5	150	415	<5	~5	~10
20	52	8400	690	<5	3475	200	1438	40	25
30	87	800	<10	31	765	280	45	~5	11
40	75	850	~10	20	2100	175	<5	~5	27
50	195	2300	25	139	1225	275	25	~5	42
60	165	1500	25	188	1100	140	410	20	60

(Slitt Vein) Samples BS/1 to 12

Distance from the vein (feet)	Rb (ppm)	F "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
Vein	<5	>10%	4650	<5	610	<5	<5	<5	<10
0	~5	~1.5%	~10	9	5450	20	<5	~5	<10
1	24	~1.5%	~10	10	450	70	<5	<5	<10
3	~5	3100	~10	10	380	405	<5	12	<10
5	15	<250	<10	16	650	30	<5	<5	<10
10	~5	<250	<10	12	810	45	<5	~5	<10
15	30	<250	~10	48	650	175	<5	~5	18
20	~5	350	~10	9	1420	125	<5	<5	<10
30	25	450	~10	29	850	110	<5	12	<10
40	55	250	~10	94	325	230	<5	~5	~10
50	45	<250	<10	57	970	205	<5	~5	~10
60	15	750	<10	12	800	40	<5	~5	<10

SHALE

Derbyshire

Raper Prospect

Samples RA/1 to 6

Distance from the vein (feet)	Rb (ppm)	Pb (ppm)	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
0	63	343	125	<10	100	35	107	10

Distance from the vein (feet)	Rb (ppm)	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "
2	95	610	87	<10	190	43	257	13
5	75	375	580	<10	60	543	445	55
10	150	100	110	<10	80	378	50	45
15	125	370	263	<10	60	152	170	40
20	170	90	80	~10	78	168	65	45

QUARTZ-DOLERITE

Northern Pennine Orefield

Settlingstones mine

(Borehole B1) Samples B1/1 to 52.

Distance from the vein (feet)	Rb (ppm)	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
150'6"	24	730	<10	510	1300	216	120	80	50	85	305
152'8"	20	-	74	530	1260	354	230	71	57	-	-
153'	20	-	256	665	810	104	634	61	58	-	-
153'10"	20	1260	~10	695	880	144	210	55	64	71	287
155'8"	20	-	~10	506	1120	214	133	71	45	-	-
156'3"	35	1190	~10	484	1250	220	274	74	56	104	357
156'10"	36	-	~10	468	1580	204	87	60	55	-	-
157'3"	114	-	~10	224	1550	260	16	17	85	-	-
158	170	1950	<10	154	940	334	28	19	54	107	352
159	64	1060	<10	1550	212	212	55	59	37	93	352
161	23	680	102	442	1580	192	150	59	46	76	310
161'6"	33	980	~10	514	1160	206	125	67	59	60	282
161'10"	36	840	~10	478	1520	182	75	75	49	72	302
162'9"	135	1500	<10	478	1280	200	15	28	157	112	415
163'3"	207	2150	~10	335	1980	280	13	74	44	63	365
164	226	2750	<10	334	1580	214	22	50	40	131	480
165	182	1022	<10	334	1350	278	27	57	47	111	370
166	151	960	~10	380	1440	272	35	37	37	115	405
166'10"	111	>10%	~10	170	1090	372	~5	26	94	<20	<100
167'10"	<10	>10%	~10	268	400	170	~6.3%	315	~5	85	312
169	26	6000	<10	218	710	318	6020	81	147	75	260
170'8"	93	2400	<10	244	1250	242	45	27	100	97	408
171'5"	44	2945	~10	566	1730	230	70	75	60	78	340
172'8"	71	1100	74	406	2650	214	370	58	33	87	355
173'6"	96	950	<10	178	1620	320	136	23	94	92	387

Distance from the vein (feet)	Rb (ppm)	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
174'8"	86	1425	<10	144	1370	352	58	17	41	119	395
175'6"	94	1095	<10	266	1670	296	~5	40	103	80	365
177	91	3200	<10	200	1780	346	~5	23	56	93	382
178	130	325	<10	158	1680	200	203	35	35	88	367
178'9"	98	680	<10	128	900	222	55	54	43	97	348
179'6"	82	1045	~10	200	1160	182	20	68	47	91	335
180'4"	80	1350	<10	278	2720	202	15	68	43	71	350
181'5"	90	2625	~10	478	1110	250	122	75	51	81	310
182'4"	48	1800	~10	582	1020	234	124	62	46	89	295
183'4"	14	>10%	20	454	1230	260	694	60	48	65	250
184	19	1750	<10	466	1230	210	133	62	47	71	267
185	12	2170	<10	508	1230	132	125	71	48	74	315
185'9"	~10	635	<10	446	1320	230	145	65	48	64	278
186'6"	~10	-	~10	490	1160	190	186	72	49	-	-
187'9"	20	-	~10	446	1110	214	140	78	49	-	-
188'8"	13	-	~10	464	1230	212	135	66	56	-	-
190	16	870	274	508	1120	236	490	59	53	73	285
190'6"	16	-	~10	458	1200	240	200	63	53	-	-
191'5"	20	1050	~10	478	1030	206	130	56	50	70	312
192'9"	25	-	~10	494	1150	222	155	66	52	-	-
193'3"	20	1275	<10	544	1280	215	145	58	50	77	333
194	113	-	~10	520	1180	233	45	37	33	-	-
194'8"	23	850	10	520	1200	202	128	62	55	78	297
195'3"	23	-	<10	548	1260	202	122	74	56	-	-
197	27	937	<10	520	1260	200	130	67	53	80	312
198	20	-	~10	605	970	236	168	63	52	-	-
199	22	915	<10	544	1200	192	131	67	53	73	275
	(Borehole B2)				Samples B2/1 to 26						
125'6"	16	590	<10	450	1310	238	131	73	55	66	270
127	15	-	~10	462	1410	214	125	57	56	-	-
129	18	-	<10	460	1400	268	130	65	53	-	-
130'8"	20	525	~10	444	1280	238	130	66	48	76	312
132	20	-	~10	436	1270	188	125	70	54	-	-

Distance from the vein (feet)	Rb (ppm)	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
133'6"	12	-	<10	472	1100	202	134	46	45	-	-
134'8"	16	-	<10	443	1280	204	130	80	54	-	-
135'8"	16	-	<10	442	1280	222	125	70	59	-	-
137	12	630	~10	490	1120	208	115	61	48	97	278
138	19	-	~10	438	1240	202	132	68	56	-	-
139'6"	15	-	<10	494	1100	218	135	73	47	-	-
146'7"	19	537	<10	454	1250	250	140	63	50	70	310
141'2"	28	-	~10	442	1632	228	380	69	51	-	-
141'10"	28	550	204	448	1360	220	840	52	49	85	287
142'4"	35	-	170	442	1550	190	205	54	43	-	-
142'9"	80	793	~10	150	1240	332	15	67	50	96	380
143'4"	146	-	154	90	1550	230	860	76	64	-	-
143'8"	62	1472	<10	108	1700	282	460	67	42	117	372
144	70	-	~10	118	1070	282	8650	81	52	-	-
144'8"	93	3050	<10	88	730	340	1845	83	31	145	535
145'8"	91	-	<10	100	730	422	56	46	31	-	-
146'4"	70	1627	~10	218	1190	342	3050	85	33	131	423
147'6"	135	-	112	566	1190	296	1540	90	59	-	-
148'6"	56	760	44	460	1710	182	325	82	51	112	382
149'4"	20	-	<10	460	1320	228	140	75	58	-	-
150	15	675	<10	472	1190	220	130	66	51	96	295
		(Borehole SB)				Samples SB/1 to 21					
0	<10	>10%	<10	40	2200	240	335	10	14	43	140
1	<10	>10%	<10	262	1120	254	1360	13	79	43	148
1'6"	<10	>10%	<10	420	730	158	3050	11	36	35	111
2	23	1275	142	160	1530	312	6270	23	48	66	243
2'6"	95	2100	64	274	1780	342	2320	86	58	88	280
3	~10	~5%	~10	538	1630	232	225	79	57	85	352
3'8"	16	1290	~10	466	1630	272	126	52	63	68	270
4'2"	40	3200	2000	594	1535	228	7590	61	38	98	335
4'7"	15	700	<10	202	1830	336	~2.6%	70	52	65	270
5'9"	~10	3625	<10	328	1530	260	~1.8%	50	34	79	250
6'6"	~10	~5%	<10	298	1900	304	~2.1%	148	48	48	167
7'6"	~10	575	112	88	2630	342	~1.3%	77	45	69	225
8'2"	~10	1050	1250	100	1650	342	2360	92	58	81	245
8'8"	21	755	1200	154	1370	220	5250	21	47	62	230

Distance from the vein (feet)	Rb (ppm)	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
9'3"	15	1800	1000	490	1580	204	7500	52	50	85	320
10'	23	880	<10	460	1370	222	130	60	43	80	273
11'2"	19	920	~10	460	1210	202	120	52	48	88	282
12'5"	~10	385	<10	623	1710	210	260	37	49	67	260
13'	17	1133	<10	508	1320	210	140	55	48	82	292
13'10"	14	935	<10	466	1370	188	132	62	52	77	332
14'18	16	685	~10	396	1710	222	122	53	54	70	275

(Borehole B2 - continuation) Samples B2/A to H

Distance from the vein (feet)	Rb (ppm)	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
230'	20	810	<10	476	1550	190	130	70	55	78	300
240'	20	-	<10	520	1490	234	130	63	54	-	-
250'	15	1363	<10	514	1230	194	132	60	68	68	312
260'	15	-	<10	468	1500	204	125	63	54	-	-
270'	20	870	<10	492	1530	178	140	62	58	83	205
280'	12	-	<10	470	1710	204	132	65	51	-	-
290'	16	-	<10	454	1710	220	133	68	55	-	-
300'	20	530	~10	434	1370	126	63	54	74	-	280

(Crosscut on 120 fathom level) Samples OSM/ 1 to 9

Distance from the vein (feet)	Rb (ppm)	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
3'8"	128	-	~10	520	1670	228	20	55	29		
4'6"	70	-	<10	286	1370	310	22	102	62		
5'4"	72	-	<10	346	1780	294	~5	57	49		
6'2"	25	-	<10	60	1310	215	120	63	53		
7'6"	23	-	~10	440	1330	200	83	63	50		
8'6"	115	-	<10	326	1480	288	30	69	40		
12'8"	51	-	~10	186	1310	334	230	117	58		
14'	67	-	<10	620	1250	238	35	47	30		
15'6"	45	-	<10	328	1680	264	45	63	33		

(Borehole SB1) Samples SB1/ 1 to 22

Distance from the vein (feet)	Ba (ppm)	Cr (ppm)	V (ppm)
500'	>10%	64	80
501'	1850	112	146
506'	1150	102	136
511'	>10%	78	114
517'	880	63	95
522'	1820	61	105

Distance from vein (feet)	Ba (ppm)	Cr (ppm)	V (ppm)
526'	>10%	66	90
530'	760	67	117
535'	840	66	105
540'	780	70	117
545'	1360	64	88
550'	1080	69	113
555'	750	77	123
560'	>10%	63	87
565'	880	73	131
570'	890	74	123
575'	815	66	107
577'	825	58	132

Cowgreen Vein

(Greenhush Vein) Samples C/ 1 to 8

Distance from the vein(feet)	Rb (ppm)	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
1	75	375	800	570	2450	220	1390	72	75	78	352
7"	25	400	30	430	1600	180	140	60	48	69	270
5"	210	595	262	180	3000	250	950	90	53	100	395
0	<10	>10%	<10	3000	2520	135	2100	15	5	75	287
1"	140	880	~10	130	2400	345	3500	~10	17	101	330
5"	165	590	46	130	3000	320	1400	~10	28	78	315
8	107	785	30	526	3000	215	40	54	38	97	395
1	60	1030	<10	525	1780	215	275	63	59	95	325

Force Burn

(Dubbysike Vein) Samples FB/ 1 to 9

0	42	410	30	502	1760	130	215	69	50	60	270
1'	24	355	10	428	1600	215	125	61	39	72	302
2'	117	315	60	240	2500	278	15	78	30	82	300
3'	102	205	74	34	1950	405	745	28	30	74	245
4'	75	138	~10	23	3000	244	325	~10	30	55	215
5'	<10	3975	<10	376	3000	222	460	~10	31	53	172
7'	22	265	~10	400	1240	222	135	56	52	73	280
9'	33	350	~10	484	1310	210	130	63	48	86	297
13'	27	375	<10	454	1110	196	155	66	58	81	335

Wynch Bridge

(unnamed) Samples WB/ 1 to 9

Distance from vein (feet)	Rb	Ba	Pb	Sr	Mn	Zr	Zn	Cu	Ni	Cr	V
	ppm	"	"	"	"	"	"	"	"	"	"
Vein	24	>10%	<10	52	3000	40	~5	~10	~5	-	-
0	295	640	<10	74	3000	340	12	66	67	114	385
6"	340	730	<10	116	3000	248	12	63	45	106	450
1'6"	135	650	~10	390	3000	236	75	62	58	89	337
3	68	370	100	454	3000	215	160	69	56	91	347
6	27	285	~10	394	1580	220	135	68	55	77	320
9	40	290	~10	430	1930	210	80	63	49	72	318
12	290	760	~10	120	3000	272	~5	76	46	130	465

West Blackdene mine

(Blackdene Vein) Samples BL3/ 1 to

Distance from vein (feet)	Rb	Ba	Pb	Sr	Mn	Zr	Zn	Cu	Ni
	ppm	"	"	"	"	"	"	"	"
Vein	-	<200	-	-	-	-	-	-	-
0	205	630	150	87	3106	140	9205	87	54
6"	212	455	2890	63	1650	132	6167	69	41
1	235	360	1980	145	2000	145	4690	87	41
3	30	275	30	425	1285	130	130	75	48
7	25	340	~10	420	1320	100	115	81	48

Closehouse mine

(Crosscut north) Samples DN3/1 to 8

Distance from vein (feet)	Rb	Ba	Pb	Sr	Mn	Zr	Zn	Cu	Ni	Cr	V
	ppm	"	"	"	"	"	"	"	"	"	"
7	75	-	~10	20	175	390	<5	<5	15	-	-
6	80	-	<10	~5	1320	475	<5	~5	17	-	-
5	93	-	250	<5	1000	550	120	~5	<5	-	-
4	100	-	~10	<5	980	400	50	~5	~5	-	-
3	120	-	125	~5	745	473	500	<5	~5	-	-
2	220	>10%	2500	115	3000	100	8200	60	55	40	145
1	245	>10%	2000	100	2800	110	6500	75	54	45	175
0	35	530	25	425	1350	145	145	81	46	75	290

(Crosscut south) Samples SC/1 to 12

Distance from vein (feet)	Rb ppm	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
0	150	>10%	2000	150	1500	138	1000	200	10	40	175
5	127	>10%	1750	195	1700	142	4200	175	25	35	200
10	130	>10%	400	145	1200	173	3300	55	35	42	220
15	135	550	~10	447	1450	475	130	60	60	65	290
20	100	1000	<10	473	1480	520	125	75	63	72	300
25	97	1280	~10	482	1540	530	175	35	58	84	310
30	102	420	~10	490	1320	505	200	70	72	55	270
35	117	>10%	2000	470	1750	4750	1750	90	80	40	250
40	120	570	~10	1780	1780	470	155	75	55	70	200
50	<5	-	25	40	~42%	<10	50	<15	~5	-	-
60	<5	-	5000	2040	1700	<10	~2%	~15	<5	-	-
70	<5	-	120	1750	4200	<10	50	~15	~5	-	-

(5 fathom crosscut south) Samples 5 x c/ 1 to 26

Distance from vein (feet)	Rb ppm	Ba "	Pb "	Sr "	Mn "	Zr "	Zn "	Cu "	Ni "	Cr "	V "
0	85	>10%	175	120	1700	135	10	33	43	122	122
5	100	>10%	200	105	1500	120	850	20	25	40	111
8	95	>10%	155	510	2500	175	140	25	30	75	100
20	55	850	~10	490	7000	180	500	80	43	100	245
27	40	1000	<10	475	1300	195	140	72	40	94	328
36	35	1025	<10	472	2000	205	145	65	63	87	310
48	~10	950	800	430	3900	230	130	63	60	83	265
57	<10	890	<10	460	2500	220	125	60	52	90	255
67	~10	720	<10	500	1850	175	125	68	47	55	270
77	~10	2000	200	525	1700	185	130	63	43	65	300
84	25	750	<10	480	2000	200	140	75	45	75	300
89	20	550	<10	470	1550	220	150	60	50	80	270

Limestones

	Pb (ppm)	Sr "	Mn "	Zn "	Cu "	Fe "
106	150	425	175	605	34	~1.2%
115	135	400	20	625	35	9000
146	430	200	80	500	65	1275

Distance from vein (feet)	Pb (ppm)	Sr "	Mn "	Zn "	Cu "	Fe "
150	115	165	275	280	50	9600
158	50	220	6500	50	~15	~5.7%
179	95	125	4900	1300	25	~4.2%
184	135	155	5000	2100	~15	~4.1%
191	7000	600	5550	925	75	~5.5%
196	90	80	8000	1225	40	~5.4%
202	200	2320	1025	145	~15	3800
207	50	3000	460	75	<15	1300
211	50	1900	400	265	~15	4400
216	940	2700	1325	825	25	~1.6%
222	90	4500	1400	200	<15	~1.9%

MAJOR ELEMENT AND MINERALOGICAL ANALYSES

Redburn Mine (borehole 2N)

Samples Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Ank.	Sid.	Add Mins.
R2N/1	0'	41.51	1.97	4.34	2.72	47.19	0.98	0.40	0.06	0.80	40	40	5	5	F
R2N/2	5'	48.39	1.29	7.25	2.12	38.20	1.62	0.03	0.01	1.07	50	30	5	5	F
R2N/3	10'	1.11	0.74	2.87	2.46	91.19	0.33	0.08	nd	1.21	5	95	5	5	F
R2N/4	15'	38.22	1.54	10.70	2.20	43.88	2.14	0.04	0.01	1.26	30	45	5	5	F
R2N/5	20'	38.14	0.92	3.23	2.17	58.82	0.81	0.05	0.01	0.83	40	50	5	5	F
R2N/6	25'	4.69	0.85	17.46	0.37	75.29	0.67	0.06	nd	0.61	5	65	5	5	F
R2N/7	30'	1.31	0.91	0.93	0.74	95.73	0.15	0.11	0.02	0.08	5	95	5	5	
R2N/8	35'	1.69	0.58	5.62	1.12	90.31	0.39	0.03	nd	0.25	5	90	5	5	
R2N/9	40'	3.73	0.68	2.64	1.63	90.71	0.31	0.07	nd	0.22	5	90	5	5	
R2N/10	45'	3.99	0.74	2.92	1.90	89.75	0.31	0.07	nd	0.29	5	90	5	5	

B = barite; F = fluorite; G = galena; P = pyrite; S = sphalerite;

nd = below detection limit

Redburn Mine

Sample Number	Distance from Vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Ank.	Sid.	Add. Mins.
RB/W2/II	0'	29.32	4.34	20.21	2.43	35.24	4.83	0.04	0.03	3.65	25	25	10	10	P
RB/W2/HI	1'	35.12	1.85	13.28	1.84	43.31	2.45	0.02	0.02	2.10	30	40	5	5	P
RB/W2/IG	3'	23.98	1.53	11.48	3.23	55.83	1.90	0.05	0.02	1.59	20	50	5	5	P
RB/W2/IF	5'	34.09	0.80	2.00	1.72	59.22	0.82	0.04	0.02	1.28	30	65	5	5	F.G.P.
RB/W2/IE	7'	28.36	0.45	11.33	2.35	56.11	0.40	nd	nd	0.97	25	25	5	10	F.G.P.
RB/W2/ID	10'	12.05	0.88	0.26	5.47	78.95	0.95	0.06	0.02	1.35	10	80	10	5	F.G.P.
RB/W2/IC	14'	15.41	0.57	12.71	5.29	64.73	0.56	0.01	0.01	0.69	20	50	10	5	F.G.P.
RB/W2/IB	18'	29.66	0.34	4.91	0.89	63.35	0.40	nd	nd	0.14	35	50	5	5	S.P.
RB/W2/IA	22'	34.52	0.30	2.85	1.28	60.44	0.24	0.01	0.01	0.27	40	50	5	5	S.P.

Redburn Mine (borehole W2)

Sample Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Ank.	Sid.	Add Mins.
R/W2/II	48'	5.56	1.36	10.26	1.33	77.77	1.81	0.05	nd	1.82	10	70	5	10	F
R/W2/I2	53'	0.68	0.58	12.34	8.70	76.30	0.44	0.01	nd	0.94	5	70	5	10	F
R/W2/13	56'	1.63	0.63	6.53	1.19	89.30	0.39	0.04	nd	0.28	5	90	5	5	F
R/W2/14	60'	13.23	0.46	11.39	0.83	73.25	0.37	nd	nd	0.45	15	70	5	10	F
R/W2/15	66'	3.15	0.53	7.27	1.97	86.36	0.30	0.02	nd	0.37	5	90	5	5	F
R/W2/16	68'	20.09	1.04	10.44	3.23	62.70	1.53	nd	nd	0.81	25	55	5	5	F.S.
R/W2/17	71'	41.56	0.64	0.14	3.55	52.80	0.64	nd	nd	0.66	45	50	5	5	F.S.
R/W2/18	74'	0.88	0.64	4.05	3.89	89.80	0.31	0.01	nd	0.40	5	90	5	5	F
R/W2/19	76'	12.37	0.39	2.20	0.39	84.24	0.22	nd	nd	0.16	15	90	5	5	F
R/W2/20	79'	2.04	0.53	5.44	1.64	89.61	0.35	0.01	nd	0.36	5	90	5	5	F
R/W2/21	83'	3.76	0.55	3.50	2.84	88.67	0.31	0.02	nd	0.37	5	90	5	5	F
R/W2/22	86'	1.75	0.57	0.91	0.61	95.78	0.24	0.03	nd	0.11	5	90	5	5	F

Garrigill - Teesdale

Sample Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Clay	Add. Mins.
G 1	0'	12.72	4.78	2.79	2.30	75.33	0.53	1.15	0.18	0.20	10	70	5	
G 2	3'	4.31	2.24	2.99	3.06	86.37	0.30	0.48	0.06	0.17	5	90	5	S
G 3	5'	58.37	2.01	2.74	nd	33.93	1.88	0.96	0.05	0.05	65	25	5	P.S.
G 4	14'	3.04	2.00	5.19	4.13	85.05	0.23	0.15	0.16	0.14	5	90	5	
G 5	23'	31.99	11.71	6.36	3.89	41.35	1.40	2.68	0.49	0.12	25	30	10	P
G 6	27'	36.80	13.65	6.75	4.89	32.57	1.54	3.13	0.56	0.10	40	25	10	P
G 7	34'	26.93	10.57	6.23	4.77	47.61	1.13	1.25	0.42	0.08	30	35	10	P
G 8	40'	10.82	4.48	6.41	3.50	73.57	0.60	0.32	0.18	0.11	10	80	5	

Odin Mine (Castleton area)

Sample Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Dol.	Add. Mins.
OM 2	1'	14.99	1.45	0.48	1.95	80.97	nd	0.05	0.01	0.09	20	70	5	F
OM 4	5'	1.46	0.73	0.18	4.09	93.44	nd	0.04	0.01	0.03	5	90	5	
OM 6	15'	3.85	0.56	0.11	3.61	91.68	0.14	0.02	nd	0.03	5	90	5	F
OM 8	25'	2.44	0.55	0.12	3.98	92.70	0.19	0.01	nd	0.01	5	90	5	F
OM 10	35'	1.22	0.58	0.16	4.15	93.74	0.09	0.01	nd	0.04	5	90	5	
OM 12	55'	0.32	0.58	0.33	3.91	94.55	0.20	0.02	nd	0.08	5	90	5	

Heights Quarry - Weardale

Sample Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Ank.	Add.Mins.
H/W/1	0'	38.38	3.47	26.42	nd	26.30	3.25	0.21	0.03	1.95	35	30	25	P.F.
H/W/2	1'	4.01	0.62	2.13	1.12	91.47	0.24	0.05	0.01	0.35	10	90	5	
H/W/3	3'	46.45	0.55	5.66	1.01	45.71	0.18	0.05	0.01	0.40	50	40	5	
H/W/4	5'	22.30	0.45	2.94	nd	73.71	0.19	0.05	0.01	0.36	30	70	5	
H/W/5	9'	3.74	0.80	0. 40	1.98	92.70	0.23	0.09	0.01	0.05	10	95	5	
H/W/6	14'	4.58	0.71	0.89	0.43	92.96	0.22	0.06	0.01	0.15	10	95	5	
S/W/1	0'	27.85	0.93	15.71	nd	53.88	0.79	0.07	0.01	0.76	20	40	35	P.F.
S/W/2	1'	4.59	1.02	2.32	0.55	90.71	0.30	0.15	0.02	0.34	10	95	5	
S/W/3	3'	3.67	1.15	0.87	0.89	92.93	0.23	0.17	0.03	0.07	10	95	5	
S/W~~3~~4	5'	3.76	1.31	1.37	0.51	92.03	0.70	0.22	0.03	0.07	10	95	5	
S/W/5	9'	2.45	1.15	0.50	0.66	94.91	0.12	0.17	0.02	0.04	10	95	5	
S/W/6	15'	6.22	1.03	1.61	0.31	90.15	0.26	0.17	0.02	0.24	10	95	5	
S/W/7	20'	5.44	1.52	0.87	0.48	91.10	0.26	0.25	0.04	0.05	10	95	5	

Ladywash mine (Hucklow Edge Vein-West)

Sample Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Cal.	Add. Mins.
L/HW/2	0'	1.93	0.89	0.23	3.04	94.37	0.31	0.02	nd	0.09	5	90	
L/HW/3	3'	6.27	9.69	0.14	1.89	81.32	0.47	0.01	0.11	0.07	5	75	F
L/HW/4	5'	5.42	7.04	0.18	2.29	84.38	0.52	0.01	0.08	0.06	5	80	P
L/HW/5	7'	3.66	29.43	1.15	0.99	63.03	1.39	nd	0.32	0.02	5	45	F.P.
L/HW/6	10'	1.41	5.95	0.80	2.94	88.31	0.42	0.04	0.06	0.06	5	90	
L/HW/7	15'	0.26	3.27	0.11	3.39	92.58	0.27	nd	0.04	0.06	5	95	F
L/HW/8	20'	11.96	1.12	0.23	2.34	83.96	0.17	0.09	0.03	0.07	15	85	
L/HW/9	25'	6.56	1.79	0.17	2.90	88.29	0.17	0.02	0.02	0.06	10	85	
L/HW/10	30'	3.88	0.49	0.12	3.64	91.63	0.12	nd	nd	0.11	5	90	
L/HW/11	35'	6.04	0.50	0.10	3.51	89.46	0.27	0.01	nd	0.08	5	90	
L/HW/12	40'	0.75	0.61	0.21	4.38	93.77	0.15	0.03	nd	0.09	5	95	

Ladywash mine (Hucklow Edge Vein-East)

Sample Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Add. Mins.
L/HE/2	0'	14.57	0.55	0.22	2.31	82.10	0.19	0.01	nd	0.02	15	75	F.P.S.
L/HE/3	1'	3.21	0.56	0.21	3.88	91.75	0.32	nd	nd	0.03	5	85	F.P.
L/HE/4	3'	7.30	0.41	0.12	3.57	88.44	0.12	0.01	nd	0.02	10	85	
L/HE/5	5'	1.01	0.48	0.11	4.65	93.58	0.13	nd	nd	0.02	5	90	
L/HE/6	10'	1.12	1.22	0.11	4.62	92.60	0.27	0.01	nd	0.02	5	90	
L/HE/7	15'	1.11	0.61	0.17	4.98	92.79	0.27	0.02	nd	0.02	5	90	
L/HE/8	20'	15.79	0.26	0.25	2.85	80.81	nd	0.02	nd	nd	15	80	
L/HE/9	25'	0.96	0.55	0.16	4.87	93.14	0.26	0.01	nd	0.02	5	95	
L/HE/10	30'	1.19	0.55	0.14	3.78	84.12	0.18	0.02	nd	0.02	5	95	
L/HE/11	35'	1.14	0.72	0.22	3.46	94.07	0.30	0.04	nd	0.03	5	95	

Masson Hill Quarry and Middleton Mine

Sample Number	Distance from vein	SiO_2	Al_2O_3	$FeCO_3$	$MgCO_3$	$CaCO_3$	Na_2O	K_2O	TiO_2	MnO	Qtz.	Calc.	Dol.	Add.Mins.
MH 1	0'	0.86	0.54	1.34	21.27	75.57	0.14	0.01	nd	0.26	5	65	30	
MH 2	1'	7.13	0.48	1.07	18.25	72.84	0.10	nd	nd	0.13	5	70	20	F
MH 3	3'	8.22	2.77	0.77	17.67	70.26	0.17	nd	nd	0.13	10	70	20	
MH 4	7'	51.80	15.87	8.54	1.78	17.94	1.19	1.65	1.15	0.06	150	10	5	G.S.
MH 5	9'	42.20	14.47	8.37	2.69	28.83	0.91	1.46	1.02	0.04	45	25	5	S
MH 6	15'	32.85	13.68	5.62	3.56	41.58	0.77	1.11	0.68	0.13	35	45	5	F
MH 7	25'	1.18	0.54	3.19	10.70	83.88	0.15	nd	nd	0.34	5	85	15	F
MQ 1	0'	0.35	1.22	0.16	3.42	94.86	nd	nd	0.01	0.01	5	95	5	B.G.
MQ 3	1'	0.71	1.57	0.10	3.43	94.15	nd	nd	0.02	0.02	5	95	5	
MQ 5	5'	0.84	1.30	0.09	3.71	94.03	nd	nd	0.01	0.01	5	95	5	
MQ 7	15'	1.01	0.86	0.13	3.69	94.17	0.12	nd	0.01	0.01	5	95	5	
MQ 9	30'	0.67	0.48	0.11	3.95	94.59	0.18	nd	nd	0.01	5	95	5	

A Geological and Magnetic Survey at Closehouse Mine

The Cotherstone syncline which forms the southern boundary of the Alston Block sub-area of the Northern Pennine Orefield, has, along its northern side, a linked series of faults which include the Swindale Beck, Lunedale, Butterknowle and Wigglesworth faults. The Lunedale fault and the corresponding fold structure cuts the hills on the north side of the Lune Valley to the west of Middleton-in-Teesdale. Previous mining activities have partly exposed the fault zone in large hushes and indicated a large body of barite which is now exploited by Athole G. Allen Ltd. at Closehouse mine in the Arngill side valley.

Previous Research

The stratigraphy and structure of the area has been described by Dunham (1948 p.63 and 314-316). He described the quartz-dolerite dykes and the folding and faulting of the sediments, noting that the Lunedale fault was in existence before the intrusion of the Whin Sill, but that movement has occurred since that event. Dunham noted that the dolerite dykes had followed the line of the Lunedale fault, the irregular form of the orebody suggesting that it had originated, in part, by the replacement of the altered dolerite.

The geology of the ground to the north and south of the Lunedale fault has been mapped by the Geological Survey and published on the 6-inch scale (Yorks, 3 N.E.) No map of the detailed geology of the area to the east and west of the present mining operations had however been published. A modification of the 6-inch geological map was suggested as a result of a magnetic survey of the Closehouse area, carried out by Hallimond and Butler (1949). To the east of the Arngill valley they found a fault in the Whin Sill, with a displacement of 12 feet to the south, while to the west of the mine workings they postulated a throw of 150 feet for the North fault. They proved the continuation of the fault in a westerly direction, and concluded that if the mineralization in the North fault continued along the strike of the fault there was 'a favourable prospect as a source of barytes'.

The Present Investigation

The magnetic survey (Hallimond and Butler, 1949) had indicated certain structural deformities in this region. With the advent of more precise and faster magnetometers such as the proton precision instrument it was concluded that additional useful information could be obtained.

A geological map on the 2-chain scale had been built up through the years of operation of Closehouse Mine since 1943 by Mr.J.A.Hill, the mine superintendent, and Prof. K.C. Dunham. The writer, without being given access to this, undertook, at Prof. Dunhams suggestion, to remap the geology of the hushes and mine, and to extend the geophysical work by carrying out magnetometer traverses, especially in the Fish Lake valley. The results, although not necessarily interpreted here in the same way as the 'official' survey at the mine, serve to confirm and extend the geological picture available. This field work formed a valuable introduction to the problems of rock alteration at Closehouse, and the results are included as an appendix to the main study.

The General Structure and Stratigraphy

The Stratigraphy

On the south side of the fault zone are exposed the gently dipping beds of the northern limb of the Stainmore-Cotherstone syncline. The Great Limestone is seen in small quarries, and the Scar Limestone at the base of Closehouse Crags, dipping at 10° to 15° in a southerly direction. Intermittent exposures of sandstone and shale are seen in Arngill Beck and its tributaries, but a reconstruction of the stratigraphical sequence is not possible.

On the north side of the fault zone, the Arngill Valley exposes the lower beds of the Middle Limestone Group (the Smiddy Limestone to the Jew Limestone). The Smiddy Limestone, identified by the presence of the Girvanella band (Dunham, 1948, p.16) is exposed above the Fish Lake and below Arngill Force. Arngill Force and the crags to the east expose the Whin Sill, which is intruded into the sediments.

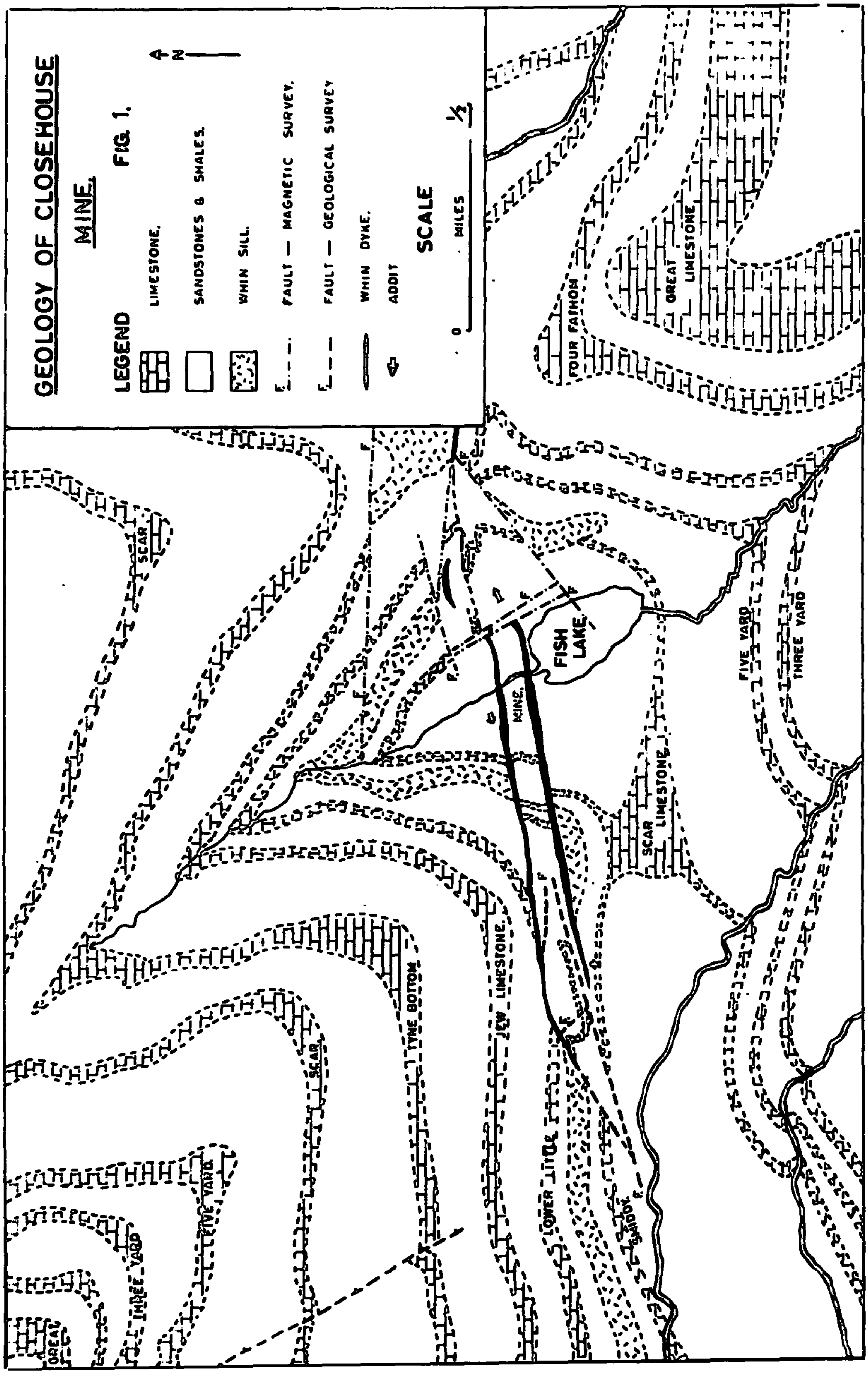
The Structure

The complex fault and fold structure (see Fig. I) is seen to extend from Closehouse Hush in the west to Standards Hush in the east. It consists of an asymmetric anticline, of which the south limb dips at 10° to 15° towards the Stainmore syncline, and the north limb at angles of between 45° and 80°. The crest of the structure is cut by the Closehouse-Standards fault (South fault), which has a throw of 400 feet to the south. On the north side of the steep limb is the North fault, with an approximate displacement of 100 feet, to the south. The North and South faults have been intruded by quartz-dolerite dykes.

Closehouse-Standards dyke (South dyke)

Deerfold Level (driven by the London Lead Company) cuts the south dyke under Closehouse Hush and proves the dyke to be 33 feet wide and vertical. Eastwards the dyke is seen in the main fault plane (West Hush) where it has been exposed by surface and underground workings. It contains a 4 feet wide vein of barite, has a fracture which hades 20° to the south, and a footwall fracture of 40° to the south. Old shafts, between Closehouse and West Hushes indicate that barite is present westwards, while Deerfold level shows only small quantities of barite in the fault.

A small dolerite sill has been intruded into the sediments and is exposed above the sandstone outcrop on Closehouse crags. The continuation of the South Fault dyke, in an easterly direction, is not seen beyond the Fish Lake.


GEOLOGY OF CLOSEHOUSE
MINE.
FIG. 1.
LEGEND
LIMESTONE.
SANDSTONES & SHALES.
WHIN SILL.
F — FAULT — MAGNETIC SURVEY.
F — FAULT — GEOLOGICAL SURVEY
WHIN DYKE.
ADDIT
N
SCALE
0
MILES
½
FOUR FATHOM
GREAT LIMESTONE
FISH LAKE
MINE.
SCAR LIMESTONE
FIVE YARD
THREE YARD
SCAR
TYNE BOTTOM
JEW LIMESTONE
LOWER LITTLE
SMIDDY
FIVE YARD
THREE YARD
SCAR
GREAT
F

The North Fault dyke

The dyke is seen in Closehouse hush where it is a breccia belt with barite stringers. The footwall is the Whin Sill which is overlain by a sandstone and the Lower Little Limestone. Deerfold Level (200 feet) beneath the hush shows the fault belt to be 20 feet wide and to consist of altered dolerite, shale gouge and silica.

The Whin Sill is the footwall in the West hush. The dyke has a width of 50 to 70 feet and a dip of 60° to the south. The dyke is not exposed in an easterly direction until Standards hush, where the north wall exposes unaltered Whin Sill with an adjacent breccia zone of altered dolerite, shale gouge, sandstone and barite stringers. Initially 30 feet wide, the breccia belt decreases in width to the east, where, in the vicinity of the presumed continuation of the Burtreeford Disturbance, the dyke is not exposed.

The Ore Deposit

The orebody situated in the North Fault dyke is exposed in the West hush and underground workings of Closehouse mine. The mineralization is predominantly barite with irregular occurrences of galena, which are confined to near vertical fissures in the southerly dipping dyke.

The footwall is the Whin Sill, underlain by the partly metasomatised Smiddy Limestone, a thick sandstone and shale, the Peghorn Limestone and the Robinson Limestone.

Mining operations indicate that although the predominant mineralization is in vertical fissures, an economic deposit lies on the footwall and is separated from the wallrocks by a thin shale gouge. The hangingwall of the dyke is a thick shale gouge (6" to 3 feet thick) which separates the dyke from a series of folded and fractured limestones, sandstones and shales (see fig.2-4, part I). Crosscuts driven into the footwall indicate that:-

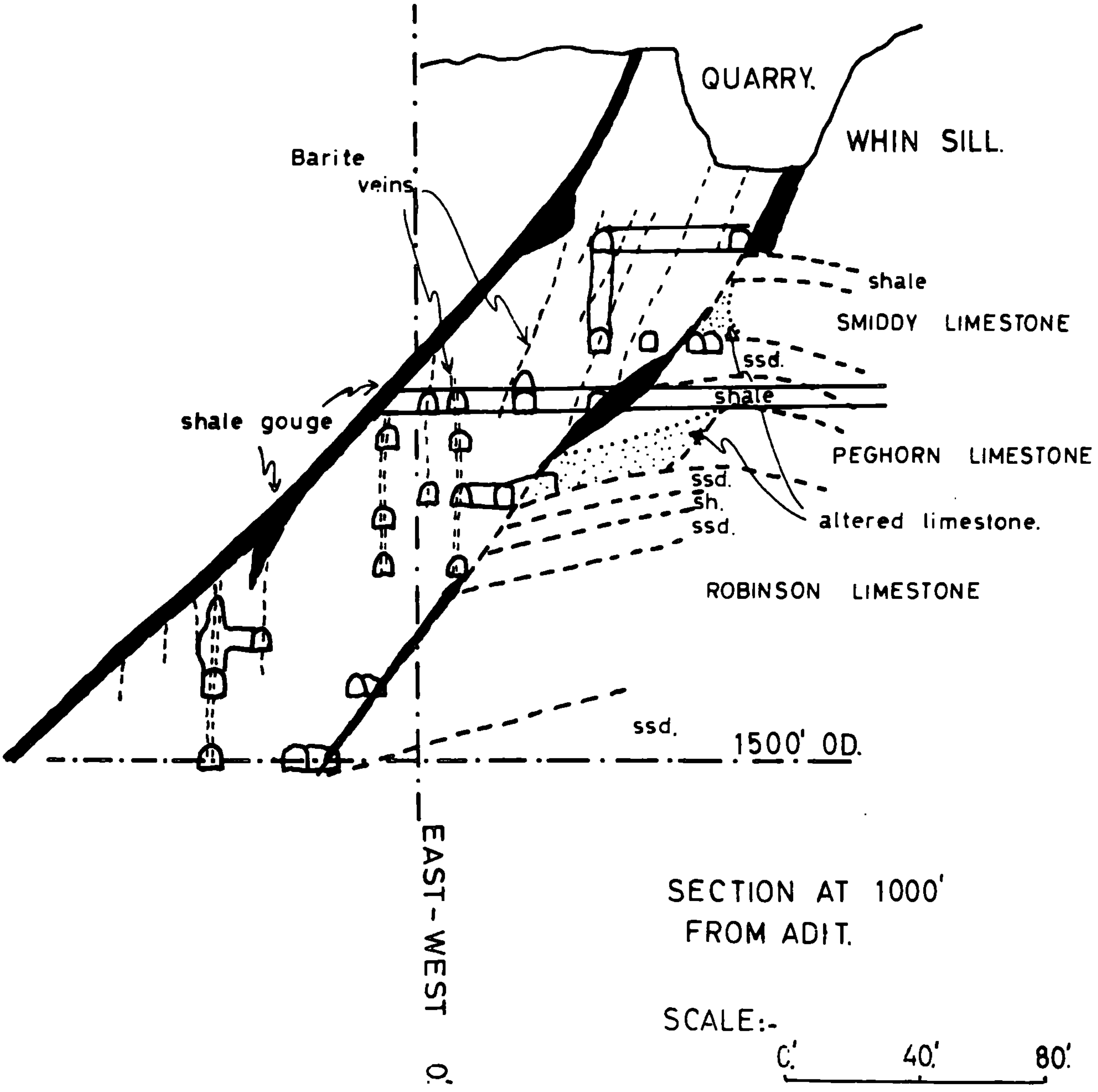
(a) a small unaltered dolerite sill has been injected into the sandstone between the Smiddy and Peghorn Limestones and

(b) irregularities of the footwall on the 5 fathom level may indicate disturbance of the Whin Sill by subseqnent movement.

The dolerite dyke has been completely metasomatised to 'white whin' (see chapter 6) although a few blocks of unaltered to partially altered dolerite have been recorded. These are regarded as fragments which have been torn from the footwall and incorporated in the dyke, after the initial metasomatism and during subsequent movement. The presence of altered and unaltered wallrocks would indicate that the wallrocks were sealed from the mineralizing fluids at certain localities. The shale gouge may have provided an impervious boundary.

Fig. 2, illustrates the nature of the mineralization and the stratigraphy of the footwall.

CROSS SECTION OF THE NORTH DYKE AND THE FOOTWALL STRATIGRAPHY.



SECTION AT 1000' FROM ADIT.

SCALE:-
0' 40' 80'

FIG. 2.

The Detailed Structure and Stratigraphy

The folding and faulting between the two major faults is too complex to describe in general terms, it is therefore subdivided into four sections.

Closehouse Hush

The most westerly of the four hushes shows the Whin Sill overlain by a sandstone and a thin dark 'blue' limestone. The hush exposes the North fault, which is a breccia belt of sandstone, altered dolerite and shale with irregular barite stringers. Near Closehouse, the Smiddy Limestone is exposed beneath the Whin Sill. The stratigraphically higher limestone - the Lower Little - therefore overlies the Whin Sill. The Smiddy Limestone can be traced eastwards round the south face of the escarpment to the north of Closehouse, where it is terminated against a NNW-SSE fault. To the east of the fault two thin limestones are exposed, they are separated by a sandstone and a shale, and folded and terminated against the South Fault. The scree face of the escarpment exposes the dolerite dyke with baked shale fragments. The South fault dyke is not exposed beyond Deerfold level, and it possibly terminates near Closehouse.

West Hush

Surface exposures between the North fault and south fault dykes show steeply dipping sediments including a sequence from the Tynebottom Limestone upwards, including the Cockleshell and Scar Limestones. The Scar Limestone is overlain by the Lower Brig Hazle.

This sequence may be seen in the 5-fathom crosscut (fig.2-4), where a series of limestones, sandstones and shales dip steeply to the north, with an anticline next to the South fault dyke and a syncline next to the North fault dyke.

East Hush

The continuation of the dolerite dykes is not seen in the East Hush. The exposed limestones, sandstones and shales are disturbed by a complex series of faults some of which contain barite. The general structure is a series of tightly folded anticlines. The axial planes of these anticlines dip at 80° in a westerly direction. The crest of the hill shows that a structural trend with a dip of 45° in a direction of 145° predominates in the limestones and sandstones. A fault of some magnitude is inferred, which may have caused this sudden structural change in the attitude of the sediments.

Standards Hush

The Whin Sill and dyke form the north wall of Standards Hush against which is a broad rib of brecciated ground (the presumed continuation of the North fault dyke). The 30 feet wide belt contains numerous barite stringers in an altered dolerite, sandstone and shale matrix.

The south face of Standards hush exposes bedding planes of a massive sandstone. The base of each plane is characterised by ripple marks while the upper surface is indicated by a red zone between 1 and 3 inches. The present attitude of these bedding planes is with the ripple marked surface uppermost and the reddened surface lying on another series of ripple marks. The general structure would indicate that the sandstone has been overturned in a southerly direction next to the fault zone.

A series of sink holes in the overburden, traced from the crest of the hill into Standards hush indicates the position of a thin limestone. The limestone is exposed in the south face of the hush and is terminated next to the fractured ground in the hush.

The geology of the hushes is illustrated in fig.10 (see folded map at the rear).

The Magnetic Survey

A magnetic survey was conducted to assist in the interpretation of the geological structure of the Lunedale fault at Closehouse mine. The aim of the survey was to locate and estimate the thickness and dip of the dolerite dykes and their relationship to the Whin Sill.

The Littlemore Proton Magnetometer (Type 592) was used and found to give satisfactory results for the total field strength. Thanks are due to Dr. R.A. Stacey and Mr.A.K.Chakrabarti, for assistance in this operation.

The Profiles

The profiles, aligned in a N.S. direction are illustrated in Fig.3. The approximate position of the dyke was initially located by one or two extended traverses. Once the anomaly associated with the dyke and the Whin Sill had been found, detailed readings were taken over this region at a spacing of 15 feet, between stations. Whenever possible the traverses were extended beyond the anomaly until the field had resumed a constant background value. A base station was situated in this region and on completion of each traverse, a reading was taken at this position to estimate diurnal variation.

Figs. 4 and 5 respectively, illustrate the observed anomalies from the areas to the west and the east of Closehouse mine.

A portion of the ground to the east of the mine and close to the East hush was found to show strong local variations. A detailed survey was therefore carried out over this area, the approximate boundaries of which are illustrated on fig.5. The resultant anomalies are shown on fig.6.

Interpretation

Instrument readings were converted to Oersted according to the following equation:-

MAGNETIC TRAVERSES NEAR CLOSEHOUSE MINE.

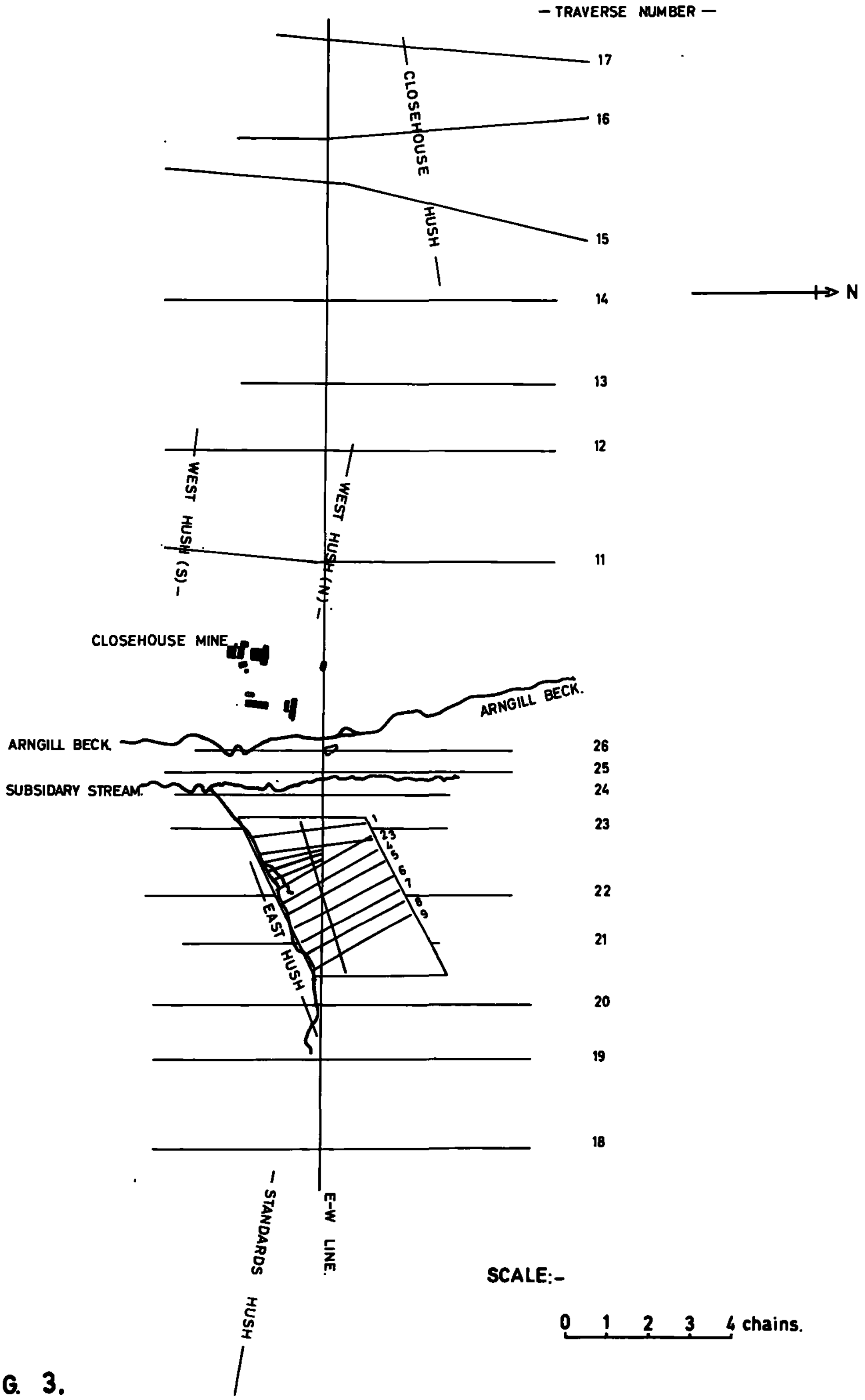


FIG. 3.

TOTAL FORCE MAGNETIC PROFILES TO THE WEST OF CLOSEHOUSE MINE.

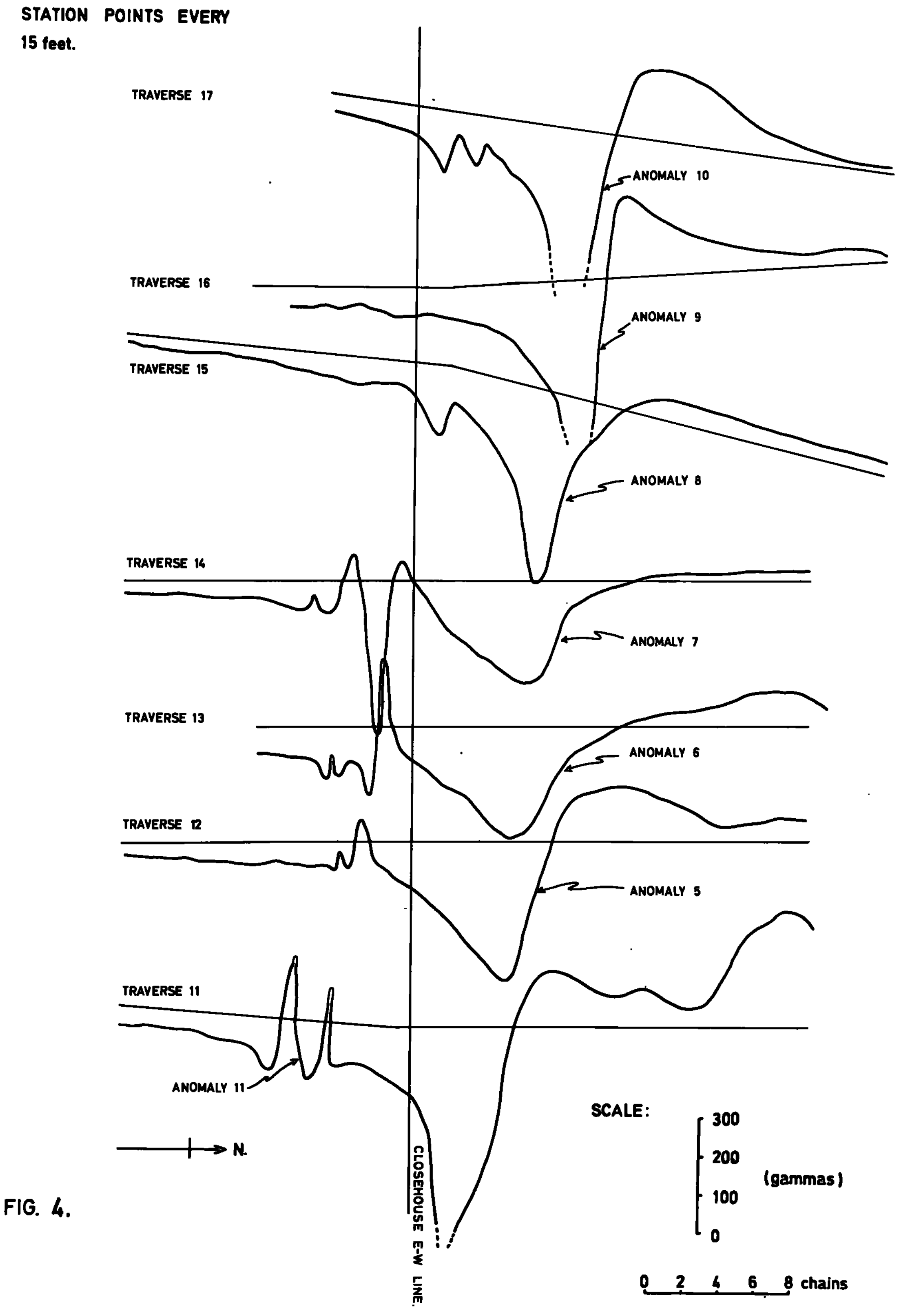


FIG. 4.

TOTAL FORCE MAGNETIC PROFILES TO THE EAST OF CLOSEHOUSE MINE.

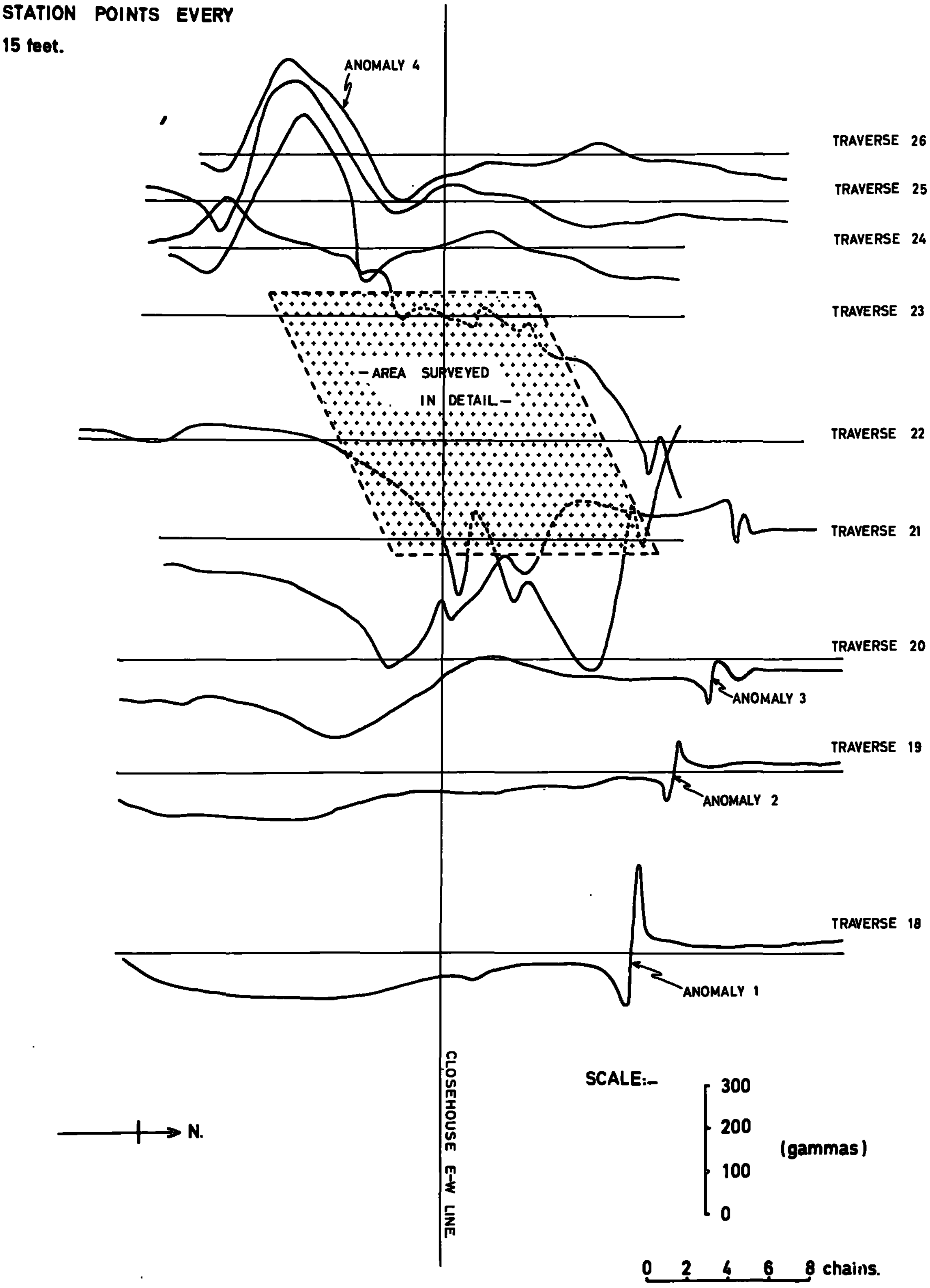


FIG. 5.

MAGNETIC TRAVERSES TO THE EAST OF CLOSEHOUSE MINE.

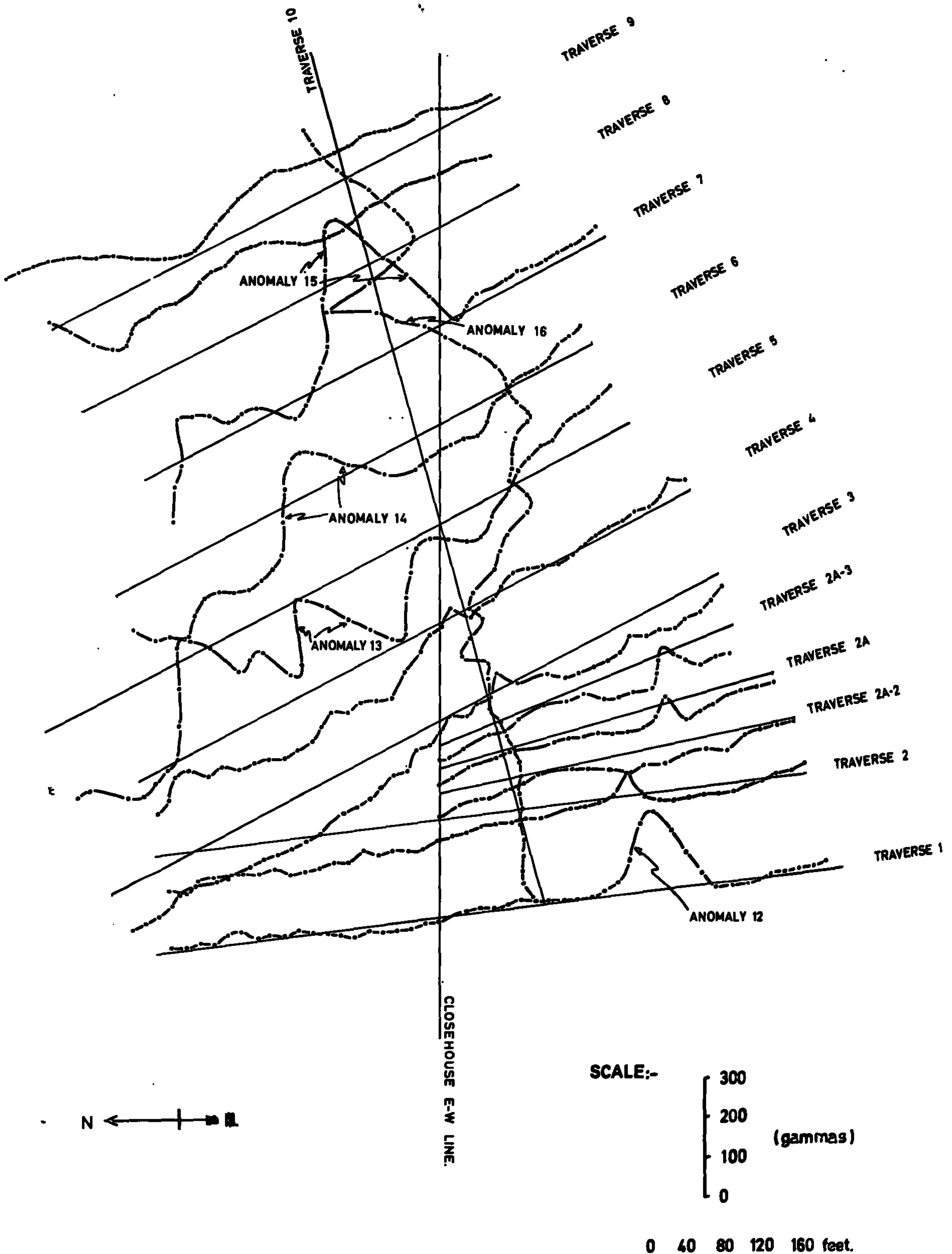


FIG. 6.

$$\text{Magnetic field} = \frac{24050}{\text{reading}}\ \text{oersted}$$

The following assumptions were made when plotting and calculating the observed and theoretical profiles:- Longitude corrections, negligible in 500 yard traverses, and daily variations in the total field strength were ignored in plotting and calculating the observed and theoretical profiles.

Estimation of the shape of sills and dykes is possible by comparison of observed profiles with those calculated for theoretical models. The direction and intensity of magnetisation are assumed to be 070° and .003 respectively (Creer et. al. 1959).

The data was reduced by computer using a programme devised by Stacey (1965) and a number of theoretical anomalies attained. Figs. 7 and 8 illustrate the observed and theoretical anomalies derived from this study.

Hallimond and Butler (1949) had indicated the position of the faulted margin of the Whin Sill and the approximate position of the top and base of the sill, suggesting a possible displacement of the Whin Sill to the east (op.cit. p.268).

The present study confirmed some of their conclusions, and in addition provided further detailed information.

OBSERVED AND CALCULATED MAGNETIC ANOMALIES
CLOSEHOUSE MINE.

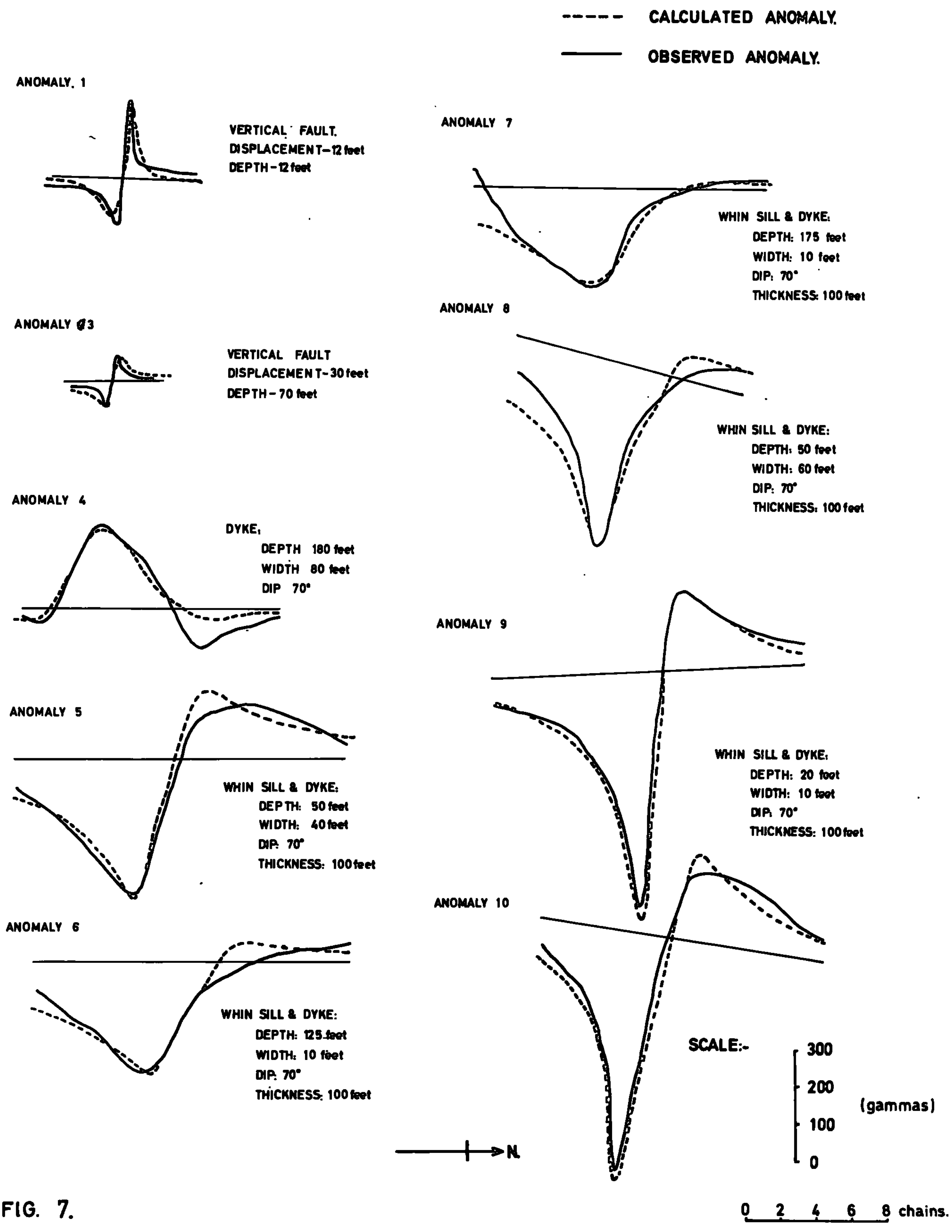


FIG. 7.

Anomalies 1 to 3 result from a small fault in the Whin Sill downthrowing to the south, with a depth of 12 feet to the top of the sill on the upthrow side, and a displacement of 12 feet. The displacement appears to increase westwards, since anomalies 2 and 3 indicate a displacement of 30 feet and a depth to the top of the Whin Sill of 70 feet.

The continuation of the South Fault dyke in an easterly direction, under the Arngill Valley was observed. The dyke appears to have a thickness of 80 feet a dip of 70° to the North and to be buried (presumably by boulder clay and river gravel) to a depth of 180 feet. Traverse 22 and the corresponding traverses further east did not indicate the continuation of this dyke beyond the commencement of the East Hush. The disappearance of the dyke suggests a major fault, trending approximately NNW-SSE, which has displaced or terminated the dyke.

The North Fault dyke, exposed and mined to the west was traced into Closehouse Hush (fig.7) and anomalies 5 to 10.

The dyke, initially 40 feet wide, decreases to a width of 10 feet, between the West Hush and Closehouse Hush. It then increases to 60 feet wide before contracting again as it is traced along Closehouse Hush, where the westerly profiles indicate that a thickness of 10 feet has been attained.

Along the strike of the North Fault dyke, it is calculated that the footwall of the dyke is, in part, the Whin Sill. Anomaly 11, the only profile which was interpreted for the westerly continuation of the South Fault dyke, indicated that a bifurcation of the dyke had occurred near the surface. The southerly portion is 24 feet wide, the northerly one 12 feet wide and both are buried to a depth of 15 feet.

Fig. 8 illustrates the observed and calculated anomalies shown in fig. 6 for the area examined in detail. The North Fault dyke is traced across the Arngill Valley and is shown in anomaly 12, which indicates a dip of 70°S, a width of 15 feet and a depth of burial of 20 feet. The dyke then decreases in width and is displaced to the south. The inferred fault which terminated the South Fault dyke may be responsible for this movement. The continuation of the North Fault dyke is illustrated in traverses 5 to 7 and 10, and anomalies 13 to 16. Within this region, the dyke has been displaced in a northerly direction and has parted from the southern margin of the Whin Sill. Initially 22 feet deep and 10 feet wide, the dyke is 60 feet in width, while eastwards it contracts to 35 and 25 feet in width. The overburden illustrates the same tendency for a greater thickness on the slope and a thinning on the crest of the hill.

Traverses 8 and 9 are not anomalous and indicate that the dyke is absent between the East Hush and Standards Hush. The dyke reappears in Standards Hush adjacent to the Whin Sill.

OBSERVED AND CALCULATED MAGNETIC ANOMALIES

CLOSEHOUSE MINE.

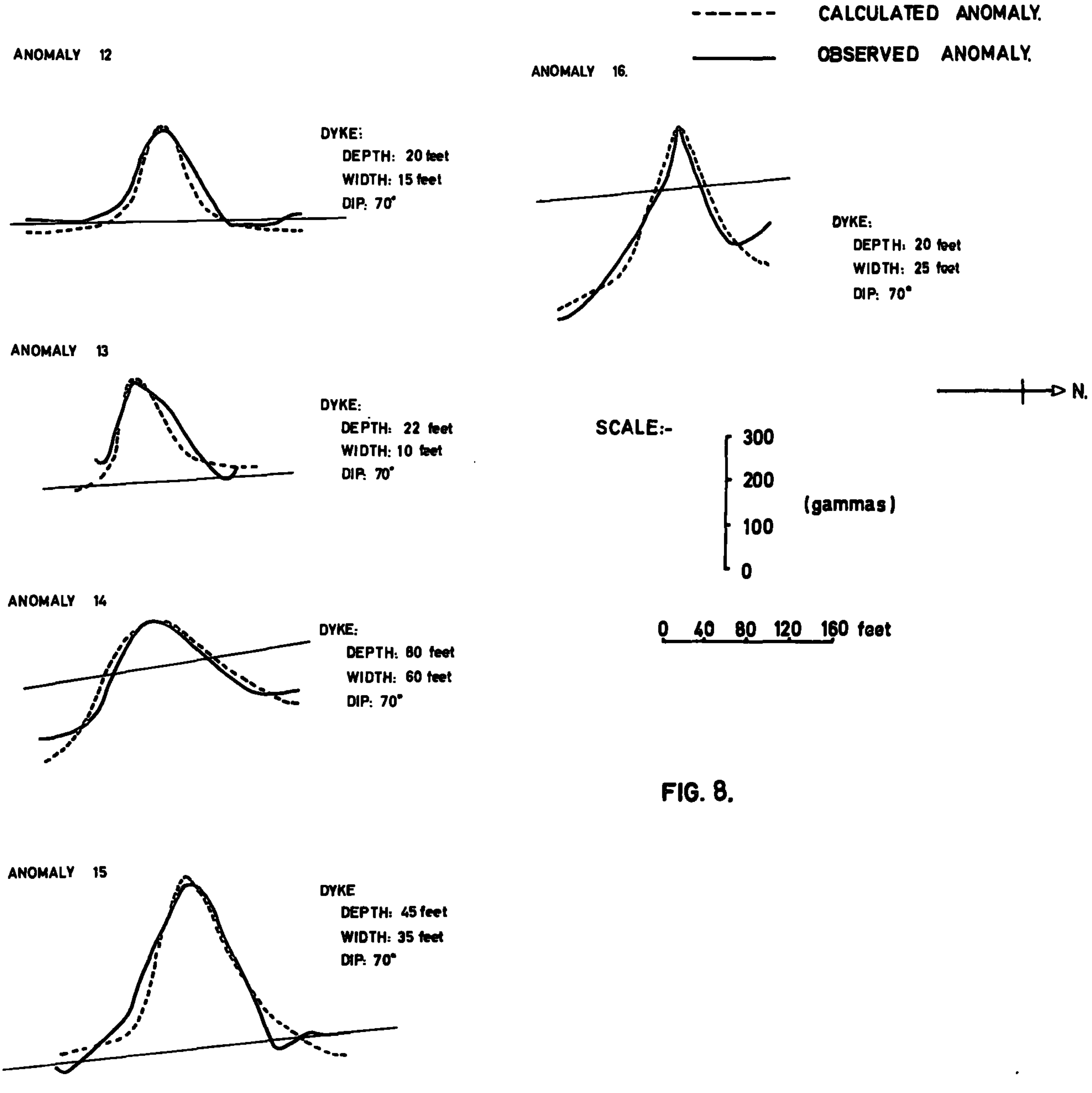


FIG. 8.

A buried water pipe is situated in this area and resulted in a local magnetic anomaly. The anomaly associated with this pipe has been removed from the profiles, however a larger anomaly was found in traverse 3 than in the other traverses which intersected the pipe. It is possible that quartz-dolerite is present in this area.

The results of this survey are included on the geological map of the area where the geophysical interpretation of the structure is superimposed on the field mapping.

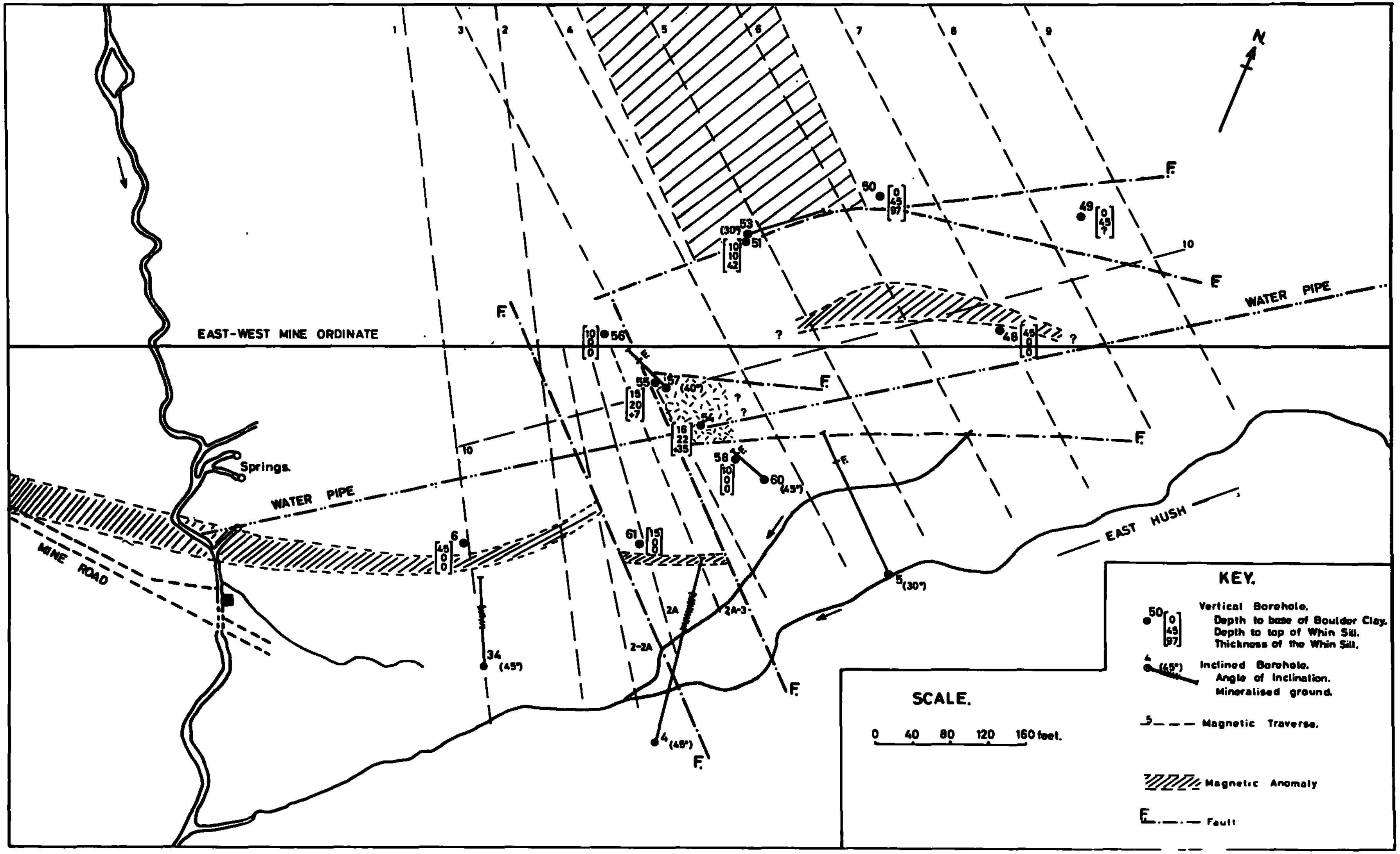
Recent exploration in the Arngill Valley

In 1966, Athole G. Allen Ltd. explored the ground to the north of the East Hush. The results of this investigation are shown on fig.9. Previous diamond drill holes (numbers 4,5,6 and 34) are included on the diagram.

Boreholes 4 and 34 prove the presence of mineralised ground while borehole 5 indicates a fault to the north of the Hush. Borehole 6 situated near Arngill Beck contains 45 feet of boulder clay. The recent boring programme has contributed the following additional information. An overburden of 45 feet of boulder clay, sandstone and shale rests on the Whin Sill. The presence of a fractured area is indicated between boreholes 48, 49, 50 and 51. Boreholes 56, 57, 58, 60 and 61 did not intersect quartz-dolerite, although 57 and 60 indicated the presence of fractured ground, Boreholes 54 and 55 cut dolerite at a depth of 22 feet, indicated a horizontal upper surface and an unknown thickness of quartz-dolerite.

BOREHOLE AND MAGNETIC RESULTS TO THE EAST OF CLOSEHOUSE MINE.

FIG. 9.



These results confirm the approximate position of the Whin Sill, the presence of numerous faults in this area, the altered and mineralised dolerite dyke in boreholes 4 and 34, and the unaltered and unmineralised dolerite in boreholes 54 and 55.

The magnetic survey and the exploratory programme have indicated that this area has a very complex series of faults and quartz-dolerite intrusion. Neither of the methods have resolved the structure, however they have provided additional information, which it is hoped, will be advantageous if exploration is undertaken in this area.

Conclusions

The geological mapping indicates a complex series of folds and faults which preceded the intrusion of the dolerite dykes along the line of the Lunedale fault. The fault and fold structure extends eastwards for 3 miles to Greengates Quarry, but economic mineralization is only known in the neighbourhood of Closehouse mine.

The faulting and folding are such that exposures in one hush cannot be traced into the adjoining hush, a few hundred yards distant. Exposures are infrequent, due to the peat, boulder clay and mine operations and add to the difficulties in interpreting the structure.

The magnetic survey has indicated that the North fault dyke continues into Standards Hush, with minor disturbances, while the South fault dyke terminates against a fault to the east of the Fish Lake.

The fractured nature of both dykes and the absence of a fault 1,100 feet N.W. of the East Hush (Dunham, 1948 p.316) are also evident from the survey.

The following sequence of events must be considered tentative with the evidence at present available. Subsequent to the deposition of the Carboniferous sediments, the area was folded and the Lunedale fault initiated. This was followed by the injection of the Whin Sill into the sediments and the dykes along the fault planes. A previous fracture pattern, imposed on the dykes, is responsible for the vertical attitude of the mineralization and the concomittent alteration of the dykes.

Movement prior to, and during, alteration and mineralization of the dykes had formed an impervious boundary at certain localities on the footwall and hangingwall. The degree of alteration of the wallrocks is a result of the presence or absence of this boundary. Blocks of partly altered dolerite in the North Fault dyke are considered to have been included at a late stage when movement was more active than metasomatism.

Renewed movement along the same structural lines would explain the displacement of the dykes.

References

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Hallimond, A.F. and Butler, A.J.	1949	Magnetic Survey in Teesdale. Mining Mag. **80**, 265-278.
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THE GEOLOGY OF THE AREA TO THE EAST AND WEST OF CLOSEHOUSE MINE.

FIG. 10.