A

THESIS

entitled

THE REGIONAL GEOCHEMICAL DISTRIBUTION OF ARSENIC IN SOUTH WEST ENGLAND

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ABSTRACT

The geochemical distribution of arsenic in south-west England was investigated by means of stream sediment, soil and rock sample analysis.

At the outset of this research, interpretation of data from an earlier broadscale geochemical reconnaissance stream sediment survey, indicated the existence of a marked contrast in the distribution of arsenic in the region. According to this interpretation, the geochemical background appears to have mainly been affected by contamination from surrounding anomalous areas, and to a lesser extent by the influence of secondary environment. Anomalous patterns are classified in relation to:-

a) known mineralisation, and consequently contamination;
b) possible undiscovered mineralised bodies, and
c) lithological units surrounding the granitic masses.

In order to discern the origin and significance of these patterns, both regional-scale and detailed investigations were carried out in selected areas. Thus the close relationship between geochemical background and bed-rock geochemistry was established, and the sources of the anomalies were confirmed.

Detailed lithogeochemical studies revealed that:-

a) the anomalous patterns of arsenic within the metamorphic aureole surrounding the Dartmoor granite, and within the granite itself, are related to primary dispersion of arsenic introduced during the emplacement of the granitic batholith; and

b) the origin of relatively high arsenic concentrations in stream sediments and soils derived chiefly from

the Permian rocks are related to primary distribution from the underlying parent-rocks.

The role played by early magmatic fluids as well as by the pneumatolitic and hydrothermal solutions in the deposition of arsenic both within and without the metamorphic aureole, and in the granite is described. The possible relationship between arsenic anomalies and possible undiscovered ore deposits is examined.

The sulphur content in sulphide-bearing rocks was determined by means of a new rapid, semi-quantitative colorimetric method. Primary relationships between the arsenic and sulphide sulphur of the rocks and mineral veins were thus established.

Lastly, the significance of correlations between arsenic and selected trace-elements analysed during this study is discussed.

ACKNOWLEDGMENTS

The investigation described in this thesis forms part of the studies associated with the Wolfson Geochemical Atlas of England and Wales which is being compiled by the Applied Geochemistry Research Group at the Imperial College of Science and Technology, University of London, under the direction of Professor J. S. Webb.

Grateful acknowledgment is given to the Ministry of Mines and Hydrocarbons of the Venezuelan Republic, the institution that provided the writer with constant financial support.

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TABLE OF CONTENTS

		Page
ABSTRACT		i
ACKNOWLEDGMENT		iii
TABLE OF CONTENTS		v
LIST OF FIGURES		ix
LIST OF TABLES		xv
CHAPTER 1 - INTRODUCTION		1
1.1	Purpose of the Research	1
1.2	Scope and Limitations of the Work	3
1.3	Presentation of the Thesis	5
CHAPTER 2 - PHYSICAL FEATURES OF SOUTH-WEST ENGLAND		6
2.1	Location	6
2.2	Climate	6
2.3	Topography and Drainage	6
2.4	Soils	
CHAPTER 3 - GENERAL GEOLOGY		13
3.1	Stratified Rocks	13
3.2	Armorican Granite	17
3.3	Metalliferous Minerals	19
3.4	Arsenic Mineralisation	19
CHAPTER 4 - GEOCHEMISTRY OF ARSENIC		24
4.1	Basic Principles	24
4.2	Arsenic in Meteorites	24
4.3	Arsenic in Magmatic Rocks	25
4.4	Arsenic in Sedimentary Rocks	26
4.5	Arsenic in Soils	26
4.6	Arsenic in Stream Sediments	28
4.7	Arsenic in Ore Forming Minerals	29

		Page
CHAPTER 5 - SAMPLING METHODS, ANALYTICAL TECHNIQUES AND DATA PROCESSING		31
5.1	Introduction	31
5.2	Sampling Methods	31
5.2.1	Stream Sediment Sampling	31
5.2.2	Soil and Rock Sampling	32
5.3	Analytical Techniques	32
5.3.1	Sample Preparation	32
5.3.2	Analysis of Samples	33
5.3.3	Precision Control	37
5.4	Data Processing	37
CHAPTER 6 - INTERPRETATION AND CLASSIFICATION OF REGIONAL GEOCHEMICAL PATTERNS		40
6.1	Introduction	40
6.2	Interpretation of Patterns	41
6.2.1	Arsenic	42
6.2.2	Copper	42
6.2.3	Iron	45
6.2.4	Lead	47
6.2.5	Manganese	49
6.2.6	Tin	49
6.2.7	Zinc	52
6.3	Classification of Geochemical Patterns of Arsenic	52
6.4	Summary	59
CHAPTER 7 - GEOCHEMICAL INVESTIGATIONS IN SELECTED AREAS		65
7.1	Introduction	65
7.2	Devon Area	66
7.2.1	Location	66
7.2.2	General Geology	68
7.2.3	Soil Traverses	68
7.2.4	Soil Characteristics	68

		Page
7.3	Results of the Investigations	73
7.3.1	Secondary Distribution of Arsenic and Selected Trace-Elements	73
7.3.2	Summary	129
CHAPTER 8 - DETAILED GEOCHEMICAL INVESTIGATIONS		131
8.1	Introduction	131
8.2	Hatherleigh - Yeoford Area	133
8.2.1	Location	133
8.2.2	General Geology	133
8.2.3	Geochemical Investigations	135
8.2.4	General Description of Patterns	135
8.2.5	Correlation between Arsenic and Selected Trace-Elements	144
8.2.6	Interpretation of Arsenic Patterns	152
8.2.7	Summary	158
8.3	Dartmoor Area	159
8.3.1	Generalities	159
8.3.2	Primary Distribution of Arsenic in the Dartmoor Area	165
8.3.3	Correlation between Arsenic and Selected Trace-Elements	182
8.3.4	Discussion of the Results	186
8.3.5	Summary	201
8.4	Corscombe Area	203
8.4.1	Introduction	203
8.4.2	Results of Investigations	206
8.4.3	Summary	218
8.5	Kit Hill Area	219
8.5.1	Introduction	219
8.5.2	Soil Traverse	220
8.5.3	Result of the Investigations	222
8.5.4	Interpretation of Patterns	229
8.5.5	Summary	234

		Page
CHAPTER 9 - POLDICE MINE-BORE HOLE		235
9.1	Introduction	235
9.2	General Description of the Bore Hole	235
9.3	Sampling and Analysis	238
9.4	Distribution of Arsenic in the Poldice Mine-Bore Hole	239
9.5	Correlation between Arsenic and Selected Trace-Elements	248
9.6	Summary	253
CHAPTER 10 - SUMMARY AND CONCLUSIONS		255
10.1	Geochemistry of Arsenic	255
10.2	Regional Geochemical Reconnaissance Survey of South-West England	256
10.3	More Detailed Geochemical Investigations in Selected Areas	256
10.3.1	Sampling and Analytical Techniques	256
10.3.2	Data Processing	257
10.4	Secondary Dispersion of Arsenic	257
10.4.1	Stream Sediments	257
10.4.2	Soils	258
10.5	Primary Dispersion of Arsenic	261
10.5.1	Arsenic Patterns as Related to Geology	261
10.5.2	Arsenic Patterns as Related to the Metamorphic Aureole	263
10.5.3	Arsenic Patterns as Related to Mineralisation	265
10.5.4	Arsenic Content in Mineralised Veins	266
10.5.5	Correlation between Arsenic and Selected Trace-Elements	267
REFERENCES		269
APPENDIX I	Determination of Sulphur in Sulphide Bearing Rocks and Minerals	284
APPENDIX II	Poldice Mine-Bore Hole Log.	293

LIST OF FIGURES

		Page
1.1	Conceptual Diagram	4
2.1	Location of Reconnaissance Area	7
2.2	Rainfall 1965	8
2.3	Main Topographic Features of South-West England	9
2.4	Drainage Map	11
2.5	Distribution of Major Soil Groups in South-West England	12
3.1	Geology of South-West England	14
3.2	Simplified Geological Map showing the Distribution of the Permian Rocks	16
3.3	Major Granite Bodies in South-West England	18
3.4	Sketch Map of Cornwall and South Devon showing the Distribution of the Mineral Lodes	20
3.5	Mineralisation of South-West England	23
5.1	Precision Control Chart for Duplicate Results: Copper	38
5.2	Precision Control Chart for Duplicate Results: Zinc	38
5.3	Precision Control Chart for Duplicate Results: Arsenic	39
5.4	Precision Control Chart for Duplicate Results: Tin	39
6.1	Regional Stream Sediment Reconnaissance in South-West England: Arsenic	43
6.2	Regional Stream Sediment Reconnaissance in South-West England: Copper	44
6.3	Regional Stream Sediment Reconnaissance in South-West England: Iron	46
6.4	Regional Stream Sediment Reconnaissance in South-West England: Lead	48
6.5	Regional Stream Sediment Reconnaissance in South-West England: Manganese	50
6.6	Regional Stream Sediment Reconnaissance in South-West England: Tin	51
6.7	Regional Stream Sediment Reconnaissance in South-West England: Zinc	53

		Page
6.8	Regional Geochemical Background of Arsenic	55
6.8a	Distribution of Arsenic in Dartmoor Granite Related to Soil Types and Physiography	57
6.9	Anomalous Geochemical Patterns of Arsenic	58
6.10	Anomalies of Arsenic Related to Arsenic Mineralisation	60
6.11	Anomalies of Arsenic Related to Possible Mineralisation	61
6.12	Anomalies of Arsenic Related to Contamination and Metamorphic Aureole	62
7.1	Regional Investigation Areas	67
7.2	Geology of the Dartmoor Area	69
7.3	Main Geological Features of Traverse AA1, North Devon	71
7.4	Main Geological Features of Traverse BB1, South Devon	72
7.5	Relationship between Soil Type and Topography over Upper Carboniferous Shales in Devon	74
7.6	Soils of Dartmoor	75
7.7	Distribution of Arsenic in Soils and Stream Sediments from Traverse AA1	77
7.8	Distribution of Copper and Zinc in Stream Sediments from Traverse AA1	79
7.9	Distribution of Manganese and Iron in Stream Sediments from Traverse AA1	80
7.10	Distribution of Tin and Lead in Stream Sediments from Traverse AA1	81
7.11	Distribution of Copper and Lead in Sub-Soil from Traverse AA1	82
7.12	Distribution of Tin in Sub-Soil from Traverse AA1	83
7.13	Distribution of Manganese and Iron in Sub-Soil from Traverse AA1	85
7.14	Distribution of Zinc in Sub-Soil from Traverse AA1	86
7.15	Traverse AA1 - Anomalous Areas	89
7.16	Area I - Stream Sediment Sampling	90

		Page
7.17	Area II - Stream Sediment Sampling	91
7.18	Dartmoor - Anomalous Area (Tin)	92
7.19	Dartmoor - Anomalous Area (Arsenic)	93
7.20	Range and Mean Trace-Element Contents of Soils from the Inside of the Metamorphic Aureole	94
7.21	Range and Mean Trace-Element Contents of Soils from the Outside of the Metamorphic Aureole	94
7.22	Devon Area - Stream Sediment and Soil Sampling (Traverse AA1)	97
7.23	Range and Mean Arsenic Content of Soils Related to the Main Geological Formations (Traverse AA1)	99
7.24	Arsenic Content of the Soils Related to the Granite	101
7.25	Devon Area - Soil Sampling	104
7.26	Corscombe Area - Soil Sampling	106
7.27	Distribution of Arsenic in Soils and Stream Sediments from Traverse BB1	108
7.28	Devon Area - Stream Sediment Sampling (Zn & Cu)	109
7.29	Devon Area - Stream Sediment Sampling (Sn & Pb)	110
7.30	Devon Area - Stream Sediment Sampling (Fe & Mn)	111
7.31	Devon Area - Soil Sampling, Traverse BB1 (Zn & Cu)	113
7.32	Devon Area - Soil Sampling, Traverse BB1 (Sn & Pb)	114
7.33	Devon Area - Soil Sampling, Traverse BB1 (Fe & Mn)	115
7.34	Devon Area - Soil and Stream Sediment Sampling (Traverse BB1)	117
7.35	Traverse BB1, Anomaly V	119
7.36	Area V - Stream Sediment Sampling	120
7.37	Devon Area - Soil Sampling	122
7.38	Range and Mean Trace-Element Contents of Soils from the Inside of the Metamorphic Aureole (Traverse BB1)	124
7.39	Range and Mean Trace-Element Contents of Soil from the Outside of the Aureole (Traverse BB1)	124

		Page
7.40	Range and Mean Arsenic Content of Soils Related to the Main Geological Formations (Traverse BB1)	126
8.1	Detailed Investigation Areas	132
8.2	Hatherleigh-Yeoford Area	134
8.3	Hatherleigh-Yeoford Area - Rock Sampling (Arsenic)	140
8.4	Hatherleigh-Yeoford Area - Rock Sampling (Sulphur)	143
8.5	Hatherleigh-Yeoford Area - Rock Sampling (Tin)	145
8.6	Hatherleigh-Yeoford Area - Rock Sampling (Manganese)	146
8.7	Hatherleigh-Yeoford Area - Rock Sampling (Zinc)	147
8.8	Hatherleigh-Yeoford Area - Rock Sampling (Iron)	148
8.9	Hatherleigh-Yeoford Area - Rock Sampling (Copper)	149
8.10	Hatherleigh-Yeoford Area - Rock Sampling (Lead)	150
8.11	Correlation between Arsenic and Selected Trace-Elements in the Permian Sediments	151
8.12	Correlation between Arsenic and Selected Trace-Elements in Volcanic Rocks	151
8.13	Correlation between Arsenic and Selected Trace-Elements in Lamprophyre Dykes	151
8.14	Dartmoor Area - Sampling Sites	164
8.15	Dartmoor Area - Rock Sampling (Arsenic)	171
8.16	Dartmoor Area - Rock Sampling (Tin)	173
8.17	Dartmoor Area - Rock Sampling (Zinc)	175
8.18	Dartmoor Area - Rock Sampling (Lead)	176
8.19	Dartmoor Area - Rock Sampling (Sulphur)	177
8.20	Dartmoor Area - Rock Sampling (Copper)	178
8.21	Dartmoor Area - Rock Sampling (Iron)	179
8.22	Dartmoor Area - Rock Sampling (Manganese)	180
8.23	Correlation between Arsenic and Selected Trace-Elements in Rocks from the Dartmoor Area (metamorphic aureole)	183

		Page
8.24	Correlation between Arsenic and Selected Trace-Elements in Rocks from the Dartmoor Area (outside of the Aureole)	183
8.25	Correlation between Arsenic and Selected Trace-Elements in Granitic Rocks from the Dartmoor Area	185
8.26	Relationship between Arsenic Anomalies and Arsenic Mineral-Bearing Areas	195
8.27	Arsenic, Tin and Copper Anomalies (Presumably Related to Undiscovered Mineralisation)	198
8.27a	Arsenic and Tin Anomalies in Rocks (Presumably Related to Mineralisation	200
8.28	Main Geological Features of the Corscombe Area	205
8.29	Corscombe Area - Soil Sampling: Arsenic in Sub-Soils	208
8.30	Corscombe Area - Soil Sampling (Pb and Sn)	209
8.31	Corscombe Area - Soil Sampling (Zn and Fe)	210
8.32	Corscombe Area - Soil Sampling (Cu and Mn)	211
8.33	Corscombe - Anomalous Areas	214
8.34	Kit Hill Area: Geological Map	221
8.35	Kit Hill Area - Soil Sampling (Arsenic in Top and Sub-Soils)	223
8.36	Kit Hill Area - Soil Sampling (Tin in Top and Sub-Soils)	226
8.37	Kit Hill Area - Soil Sampling (Copper, Zinc and Lead)	227
8.38	Kit Hill Area - Soil Sampling (Iron and Manganese)	228
8.39	Kit Hill Area: Anomaly C	231
8.40	Kit Hill Area: Anomaly D	232
8.41	Kit Hill Area: Anomaly E	233
9.1	Geology Around Poldice Mine	236
9.2	Poldice Mine-bore Hole	240
9.3	Arsenic as Related to Bed-Rock Geology	241
9.4	Arsenic and Tin Anomalies in Granite	243
9.5	Poldice Mine-bore Hole (Copper)	245

		Page
9.6	Poldice Mine-bore Hole (Lead)	246
9.7	Poldice Mine-bore Hole (Zinc)	247
9.8	Poldice Mine-bore Hole (Iron)	249
9.9	Poldice Mine-bore Hole (Manganese)	250
9.10	Poldice Mine-bore Hole (Tin)	251
9.11	Correlations between Arsenic and Selected Trace-Elements in Rocks from the Poldice Mine-bore Hole	252

LIST OF TABLES

		Page
4.1	Arsenic Content in Igneous Rocks	27
5.1	Instrument Parameters for Atomic Absorption Spectrophotometry	35
7.1	Geological Formations Present in the Devon Area	70
7.2	Range and Mean Trace Element Contents of Soils from Traverse AA1, North Devon, Inside and Outside of the Metamorphic Aureole	95
7.3	Mean Trace-Element Contents of Rocks, Soils and Stream Sediments from the Inside and the Outside of the Metamorphic Aureole	98
7.4	Range and Mean Trace-Element Contents of Soils Related to Bed-Rock Geology	102
7.5	Mean Metal Content of Rocks, Soils and Stream Sediments from Corscombe Area	105
7.6	Range and Mean Trace-Element Contents of Soils from Traverse BB1, South Devon, Inside and Outside of the Metamorphic Aureole	125
7.7	Range and Mean Trace-element Contents of Soils Related to Bed-Rock Geology, Traverse BB1	127
8.1	Classification and Distribution of Characteristic Detritus in the Permian Deposits	136
8.2	Hatherleigh-Yeoford Area: Location of the Sampling Sites	137
8.3	Average Trace-Element Contents of Rocks for Individual Sampling Sites from the Hatherleigh-Yeoford Area	138
8.4	Range and Mean Trace-Element Contents of Rocks from the Hatherleigh-Yeoford Area	141
8.5	Range and Mean Trace-Element Contents of Rocks from the Hatherleigh-Yeoford Area (Carboniferous and Permian)	142
8.6	Mean Trace-Element Contents of Breccia-Forming Pebbles from the Bow Conglomerates Unit	153
8.7	Arsenic Content of Sediments from the Copplestone Quarry, Bow Conglomerates	156

		Page
8.8	Dartmoor Area: Location of the Sampling Sites of Prime Importance	161
8.9	Range and Mean Trace-Element Contents of Rocks from the Dartmoor Area	166
8.10	Range and Mean Trace-Element Contents of Rocks from the Dartmoor Area	168
8.11	Mean Arsenic Content of Rocks from the Dartmoor Area (Outside of the Aureole)	169
8.11a	Mean Trace-Element Contents of Rocks from the Dartmoor Area (Metamorphic Aureole)	181
8.12	Mean Trace-Element Contents of Rocks Related to Bed-Rock Geology from the Dartmoor Area (outside the Aureole)	189
8.13	Mean Trace-Element Contents in the Eastern and Western Zones of the Corscombe Area	207
8.14	Threshold Trace-Element Values in the Corscombe Soil Traverse	213
8.15	Range and Mean Trace-Element Contents of Soils from the Kit Hill Area	224

CHAPTER 1

INTRODUCTION

1.1 PURPOSE OF THE RESEARCH

> "Modern geochemistry studies the distribution and amounts of the chemical elements in minerals, ores, rocks, soils, waters and the atmosphere and the circulation of the elements in nature on the basis of the properties of their atoms and ions ..... From a human point of view, geochemistry is of the greatest practical importance, especially in its applications to mining, metallurgy, chemical industry, agriculture ....."
>
> Goldschmidt

Research in geochemical exploration was initiated at Imperial College in 1949 by Professor J. S. Webb, and expanded and re-organised in 1954, when the Geochemical Research Centre was established. The aims of the Centre were:-

i) The critical investigation of geochemical prospecting methods under a variety of conditions;

ii) The development of new analytical and field techniques to meet different demands; and

iii) Research on the fundamental principles involved in the formation and detection of geochemical dispersion patterns.

At present that Centre - now called the Applied Geochemistry Research Group - is involved in an extensive programme of geochemical investigation of multi-element stream sediment data in the British Isles.

The regional geochemical reconnaissance stream sediment survey of south-west England, which forms part of this programme, has been undertaken by staff and students of the Applied Geochemistry Research

Group under a grant from the Wolfson Foundation. The main purposes of this survey were:-

i) To produce a Geochemical Atlas of England and Wales;

ii) To evaluate areas of mineral potential;

iii) To provide information to delineate lithological units and geological formations;

iv) To establish geochemical patterns in relation to agricultural problems and medical geography; and

v) To delineate areas and to establish sources of metal pollution.

The present research is part of this extensive programme. The main objectives of this project were:-

i) To interpret and classify the regional geochemical patterns of arsenic in stream sediments from south-west England, as displayed on maps produced for the Wolfson Geochemical Atlas of England and Wales;

ii) To study the distribution of Arsenic in rocks, soils, and stream sediments from selected areas in south-west England;

iii) To determine the significance and origin of anomalies unrelated to known mineralisation or contamination that surround the granitic bodies in the area;

iv) To establish the relationships existing between the distribution of trace-element and geological formations; and

v) To determine the relationship between arsenic and selected trace-elements.

During part of the research, the author was involved in developing a rapid method for the determination of reducible sulphur in sulphide-bearing rocks in order to establish whether there is a primary relationship between the arsenic and sulphide content of the country rocks in south-west England.

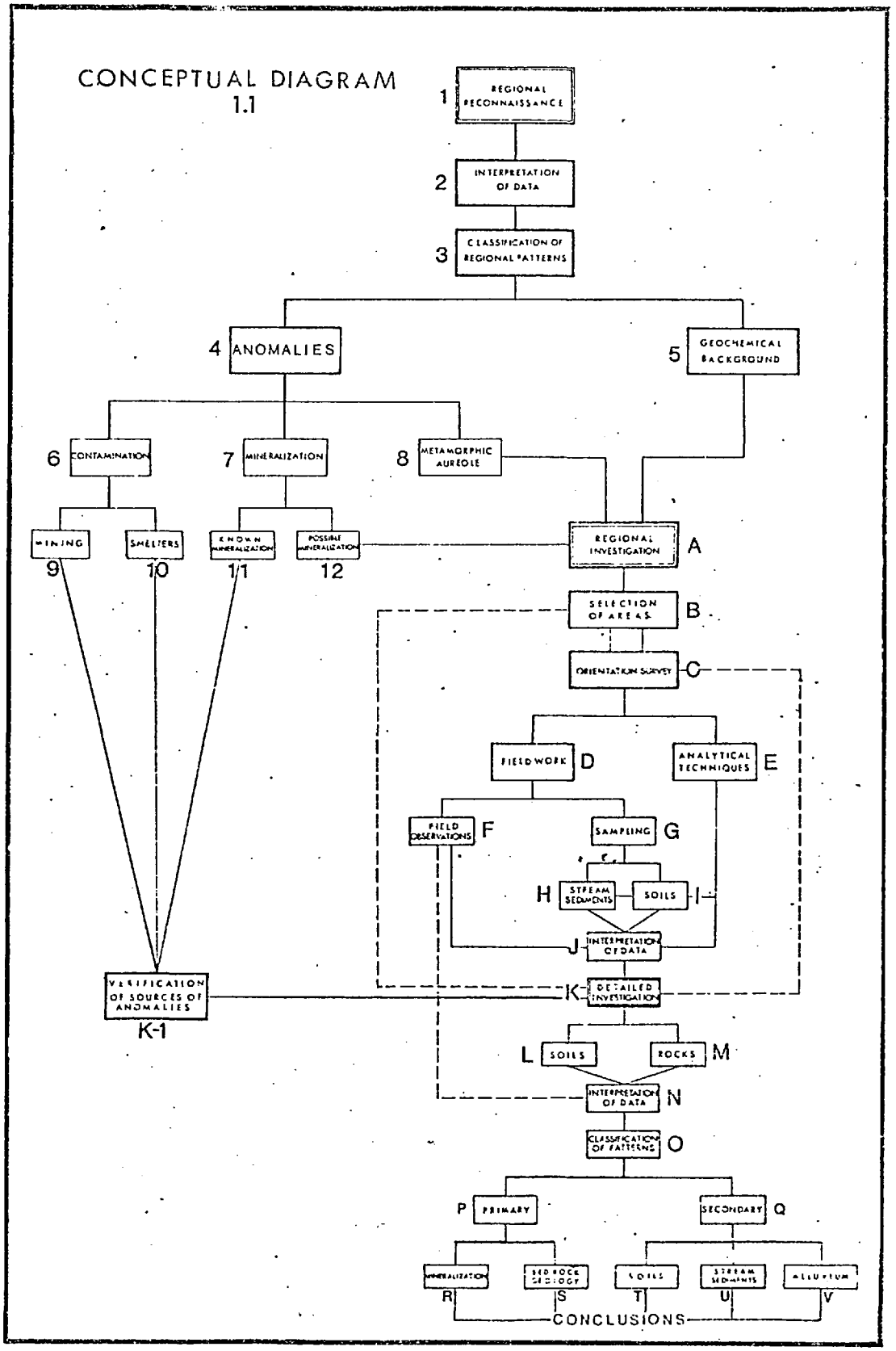
1.2 SCOPE AND LIMITATIONS OF THE WORK

The scope of this research is summarised on the conceptual diagram 1.1.

Based on the results of earlier geochemical reconnaissance (1) interpretation and classification (2 and 3) of geochemical patterns was done by comparative studies between geological and geochemical maps of the region. Thus, geochemical background patterns (4) were established in relation to bed-rock geology, the anomalous patterns (5) being classified according to suspected sources (6, 7 and 8 in the diagram). Regional investigations (A) were carried out on the basis of the geochemical background and anomalous patterns distinguished (8 and 12 in the diagram). A selection of areas and orientation surveys (B and C) were carried out following the steps D to I, resulting in the establishment of significant anomalous patterns (J). These patterns were the object of detailed investigations (K), as were the anomalies 9, 10 and 11 (K - I). The purpose of the investigation (K - I) has been to verify the sources of these anomalies.

Finally, the geochemical patterns were classified (P and Q). These are discussed further in Chapter 10.

A broad distribution of mineral veins in south-west England with a major concentration in the southern part of the region has historically stimulated intensive mining exploration, which according to Dines (1964) has been going on for at least 2500 years. Mining and smelting activities along with mills placed on riversides, have been the main sources of widespread contamination, creating a great problem in geochemical prospecting in the region. Contamination of this sort was one of the chief problems faced by the author during the development of the present research.


CONCEPTUAL DIAGRAM
1.1
1 REGIONAL RECONNAISSANCE
2 INTERPRETATION OF DATA
3 CLASSIFICATION OF REGIONAL PATTERNS
4 ANOMALIES
5 GEOCHEMICAL BACKGROUND
6 CONTAMINATION
7 MINERALIZATION
8 METAMORPHIC AUREOLE
MINING 9
SMELTERS 10
KNOWN MINERALIZATION 11
POSSIBLE MINERALIZATION 12
REGIONAL INVESTIGATION A
SELECTION OF AREAS B
ORIENTATION SURVEY C
FIELD WORK D
ANALYTICAL TECHNIQUES E
FIELD OBSERVATIONS F
SAMPLING G
H STREAM SEDIMENTS
SOILS I
INTERPRETATION OF DATA J
VERIFICATION OF SOURCES OF ANOMALIES K-1
DETAILED INVESTIGATION K
L SOILS
ROCKS M
INTERPRETATION OF DATA N
CLASSIFICATION OF PATTERNS O
P PRIMARY
SECONDARY Q
MINERALIZATION R
BEDROCK GEOLOGY S
SOILS T
STREAM SEDIMENTS U
ALLUVIUM V
CONCLUSIONS

1.3 PRESENTATION OF THE THESIS

This thesis has been divided into four main parts:

1 Part one, sub-divided into four chapters includes the general introduction, physical and geological features of south-west England, mineralisation of the region, and the most important characteristics of the geochemistry of the arsenic.

2 Part two, including chapters 5 and 6, describes the sampling and analytical techniques employed during the research, the analytical method developed during the work and the interpretation of data of regional geochemical reconnaissance in south-west England, as well as a classification of regional patterns of arsenic and selected trace-elements.

3 In part three (chapters 7, 8 and 9) the regional geochemical investigation and detailed geochemical studies in selected areas, as well as preliminary results are discussed.

4 Summary and conclusions of the research are presented in part four (chapter 10). A selected bibliography is included in this last part.

CHAPTER 2

PHYSICAL FEATURES OF SOUTH-WEST ENGLAND

2.1 LOCATION

The part of south-west England studied here lies between the Bristol, and English Channels, west of co-ordinate 300000 E, of the National Grid Reference System (Fig. 2.1) and embraces most of Devon and Cornwall.

It is an essentially rural area where the main activities are engineering industries, agriculture, pottery, etc. The larger populated centres are located mainly near the coast or along the A-30 main road.

2.2 CLIMATE

South-west England is an area with a maritime climate characterised by mild winters and cool summers. However, strong westerly winds create a heavy rainfall with an annual average of 40 inches in low lying inland areas, and between 60 to 100 inches over the high ground.

The distribution of the rainfall as a percentage of the average for the years 1916-1950 is indicated in Fig. 2.2 (British Rainfall, 1965).

2.3 TOPOGRAPHY AND DRAINAGE

The region displays a marked contrast in its topography. Rugged cliffs on the north and west coast, and high ground (up to 2000 feet) formed mainly by the granitic masses bound a relatively flat area characterised by gentle undulations dissected by river valleys. The slopes show considerable variation, though an average of 20^{o} could be assumed in the northern part and a little higher in the south, causing the eroded materials from the higher land to have a relatively short transport. (Fig. 2.3)

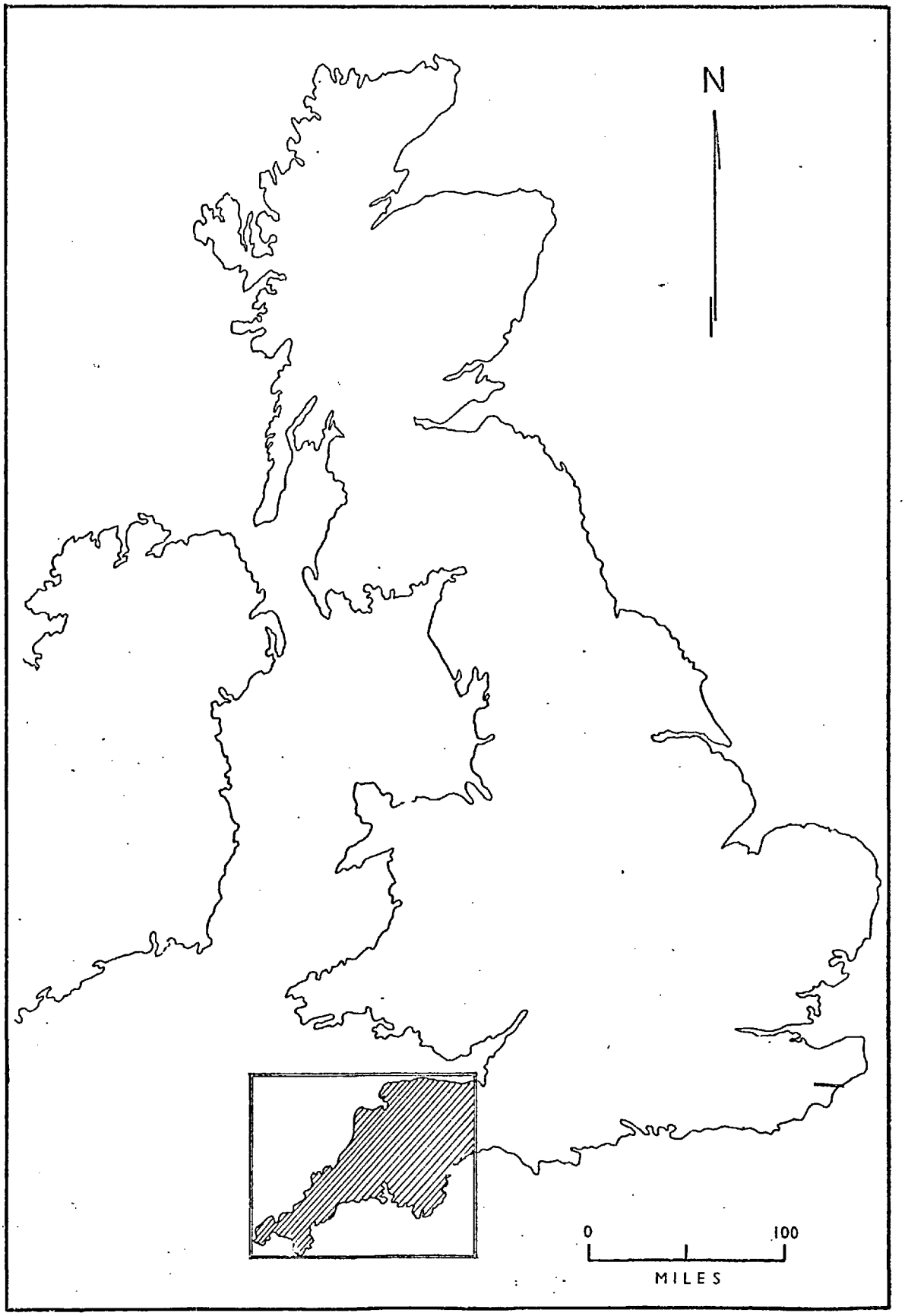


FIG.2.1. LOCATION OF RECONNAISSANCE AREA

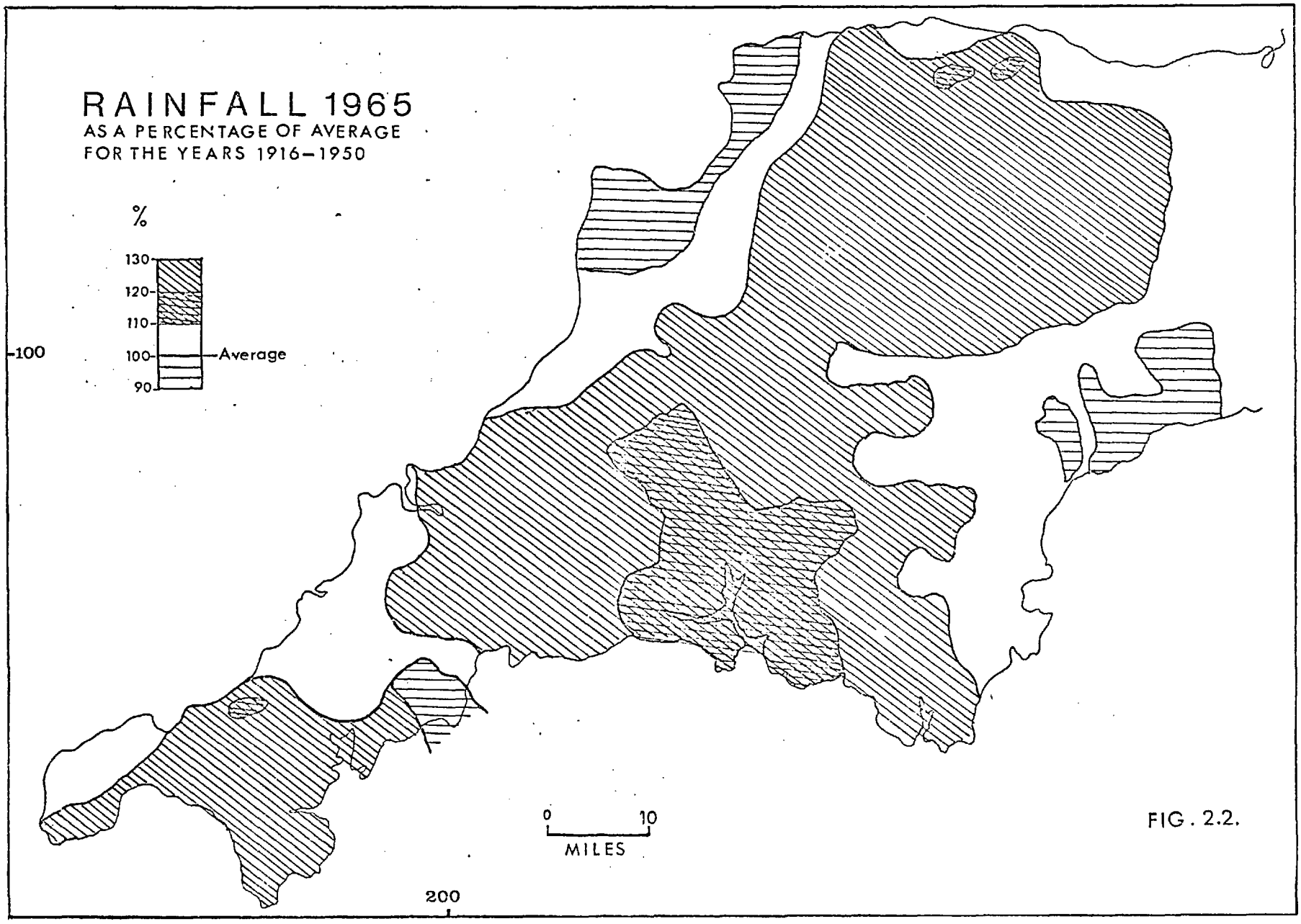

RAINFALL 1965
AS A PERCENTAGE OF AVERAGE
FOR THE YEARS 1916–1950
%
130
120
110
100
90
Average
100
0
10
MILES
200

FIG. 2.2.

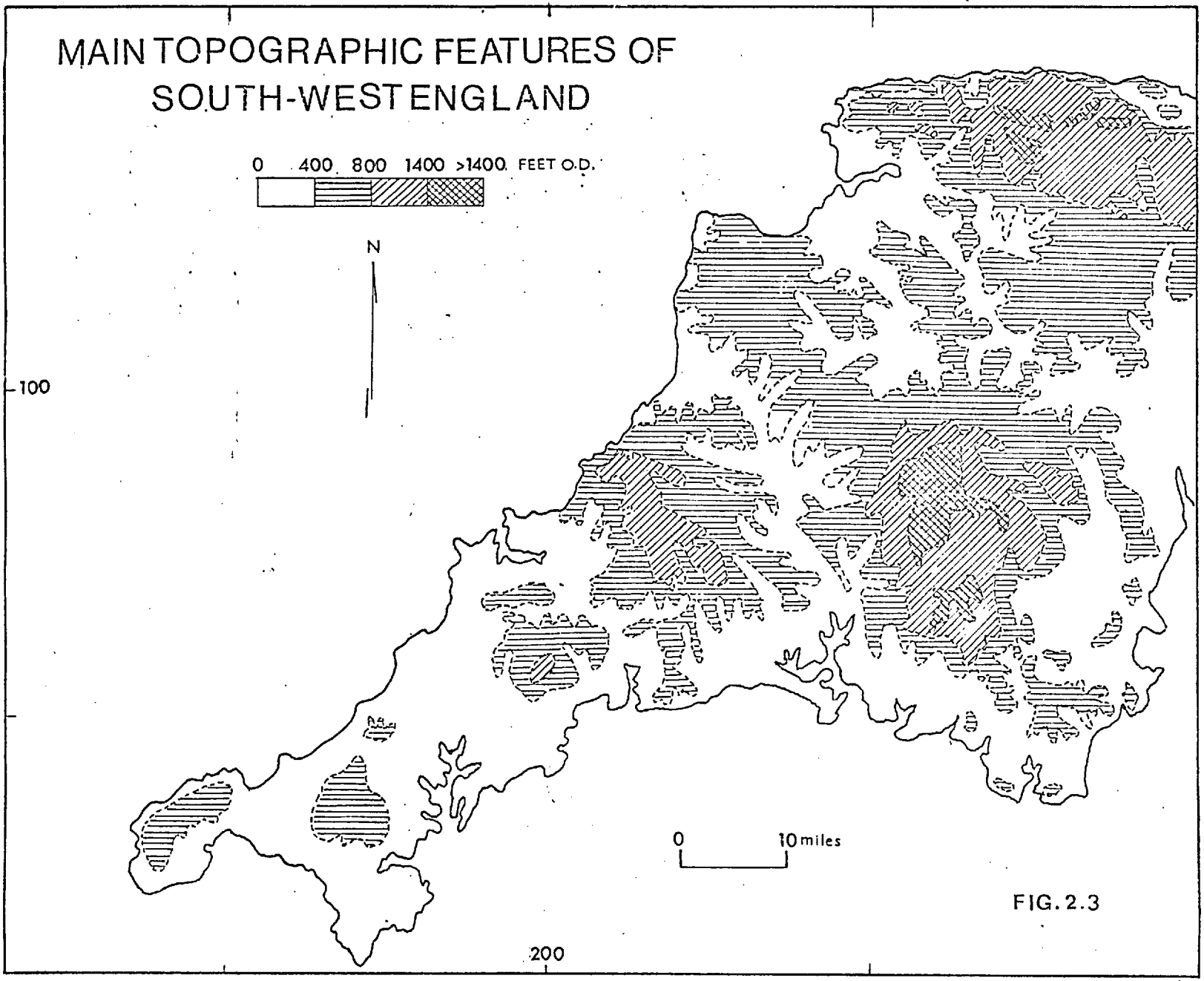

MAIN TOPOGRAPHIC FEATURES OF
SOUTH-WEST ENGLAND
0 400 800 1400 >1400 FEET O.D.
N
100
200
0 10 miles

FIG. 2.3

The drainage system is formed by numerous streams which flow in different directions being dominated by rivers flowing mostly southward to the English Channel (Fig. 2.4).

2.4 SOILS

The soils are poorly developed and are characterised by their close relationship to bed-rock geology. They are frequently mantled by a thin layer of autochtonous rock waste (head) originated from mass-movement under periglacial conditions. The Agricultural Advisory Council (1970) has distinguished four main soil groups in south-west England (Fig. 2.5) as follows:-

i) Medium textured mineral soils (Brown Earths, Clayden 1964) cover the wetter lowlands, high plateaux and upper low land valleys and are naturally acid and well drained, depending on site conditions and sub-stratum. These soils are shallow and stony, and they present uniform colours.

ii) Peaty soils of the uplands, developed under particular topographic and climate conditions (high altitude and rainfall), are characterised by very poor, or impeded drainage, and excessive surface wetness. They are found mainly on Dartmoor, Exmoor, Wendon and Bodmin Moors.

iii) Medium or heavy textured soils developed mainly over Devonian rocks are characterised by good or moderate drainage, and naturally acid conditions.

iv) Deep heavy or medium textured soils with impeded drainage are found over Upper Carboniferous rocks, and on parts of the Lizard Complex.

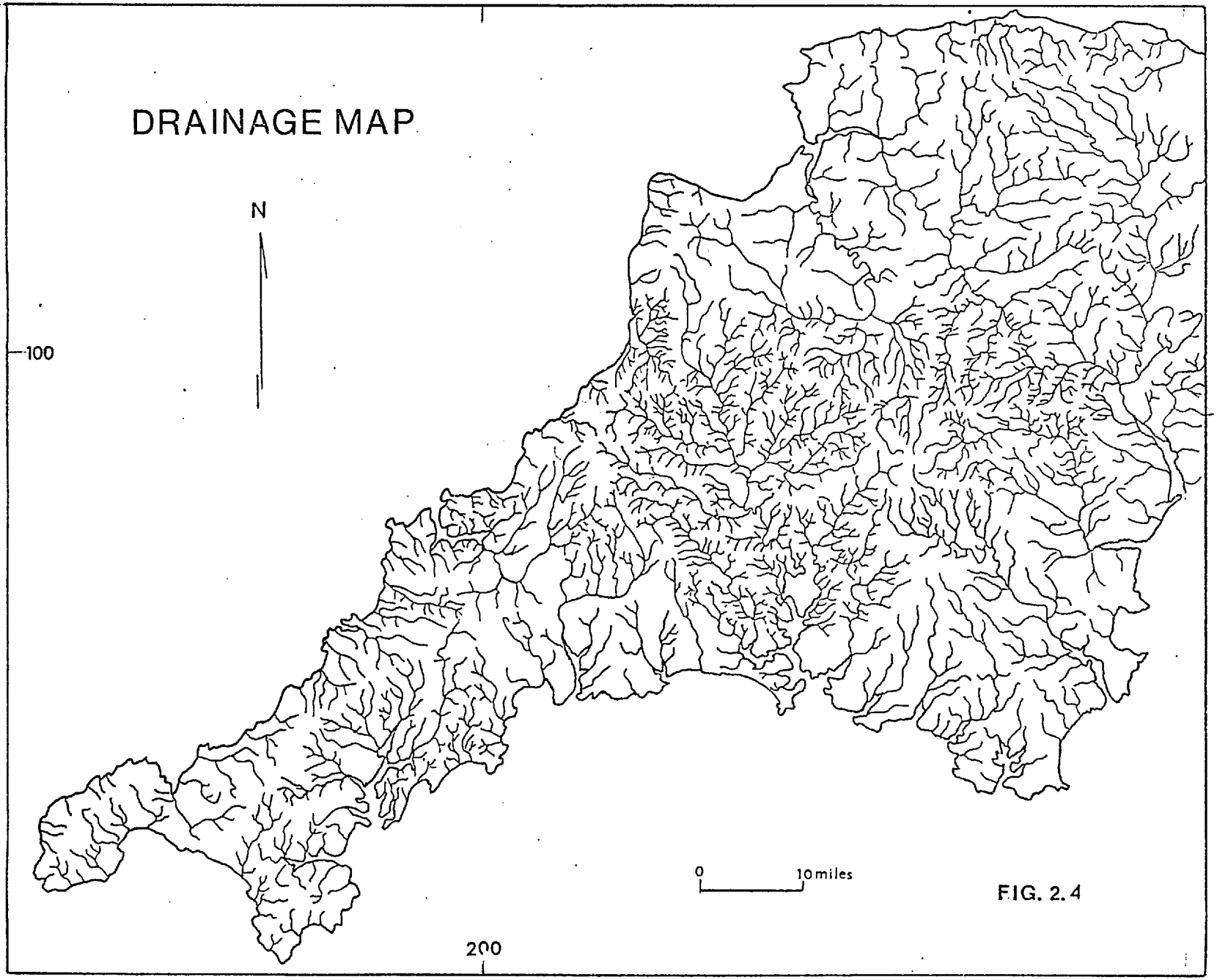


FIG. 2.4

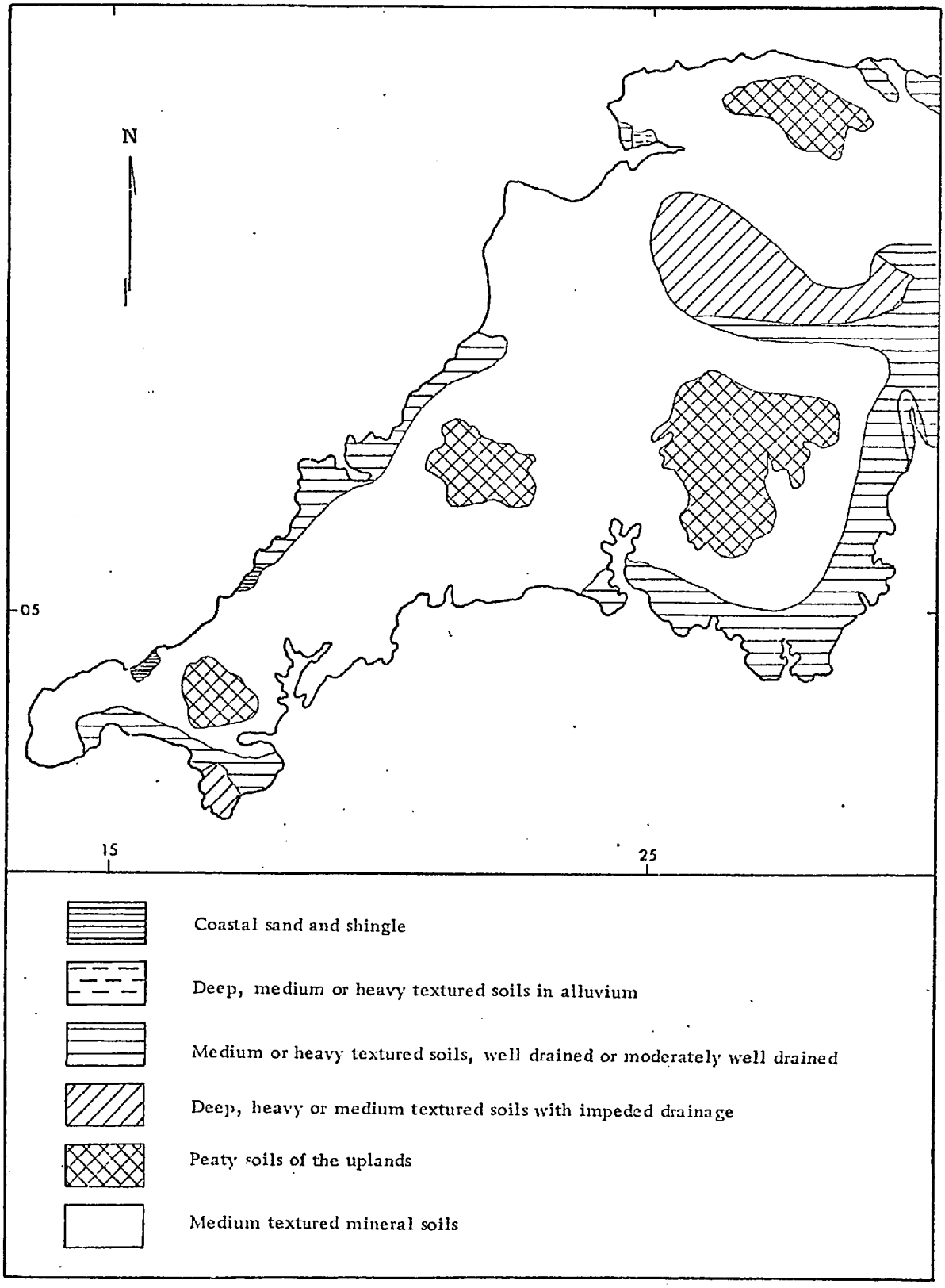


Fig. 2.5 DISTRIBUTION OF MAJOR SOIL GROUPS IN SOUTH-WEST ENGLAND (After A.A.C. 1970)

CHAPTER 3

GENERAL GEOLOGY

3.1 STRATIFIED ROCKS

A generalised account of the geology of south-west England is given below as a synthesis of the outstanding, relevant, geological features, based principally on the publications of the Institute of Geological Sciences (Edmonds et al, 1968, and 1969) and of the Royal Geological Society of Cornwall (Hoskings and Shrimpton, 1964). A generalised geological map of south-west England is shown in Fig. 3.1.

The majority of the area under consideration is covered by a variety of sediments which, from a geochemical standpoint, fall within Goldschmidt's modified classification (Rankama and Sahama, 1950 page 198), with a predominance of resistate and hydrolyzate sediments.

The bulk of the sediments of south-west England formed during Paleozoic times are mainly composed of slaty shales, mudstones and sandstones with subordinate bands of grits and conglomerates which are of Devonian and Carboniferous age. Both Devonian and Carboniferous sediments contain contemporaneous beds of lava and tuffs, and pene-contemporaneous sills, dykes and bosses of basic greenstones. In the eastern part of the area the Carboniferous rocks are overlain by sediments of the Permian age which extend westward (filling the Crediton trough), to the Hatherleigh area, north of Dartmoor.

Devonian rocks occur over most of Cornwall, throughout southern Devon and over the extreme northern section of north Devon and west Somerset. The Lower Devonian sediments in south Devon and Cornwall consist principally of slates with interbedded sandstones, conglomerates and pyroclastic rocks, the latter being particularly prominent in Devon. A succession of slates, siltstones, sandstones and occasional limestones is found overlying these sediments, followed by a sequence of sandstones,

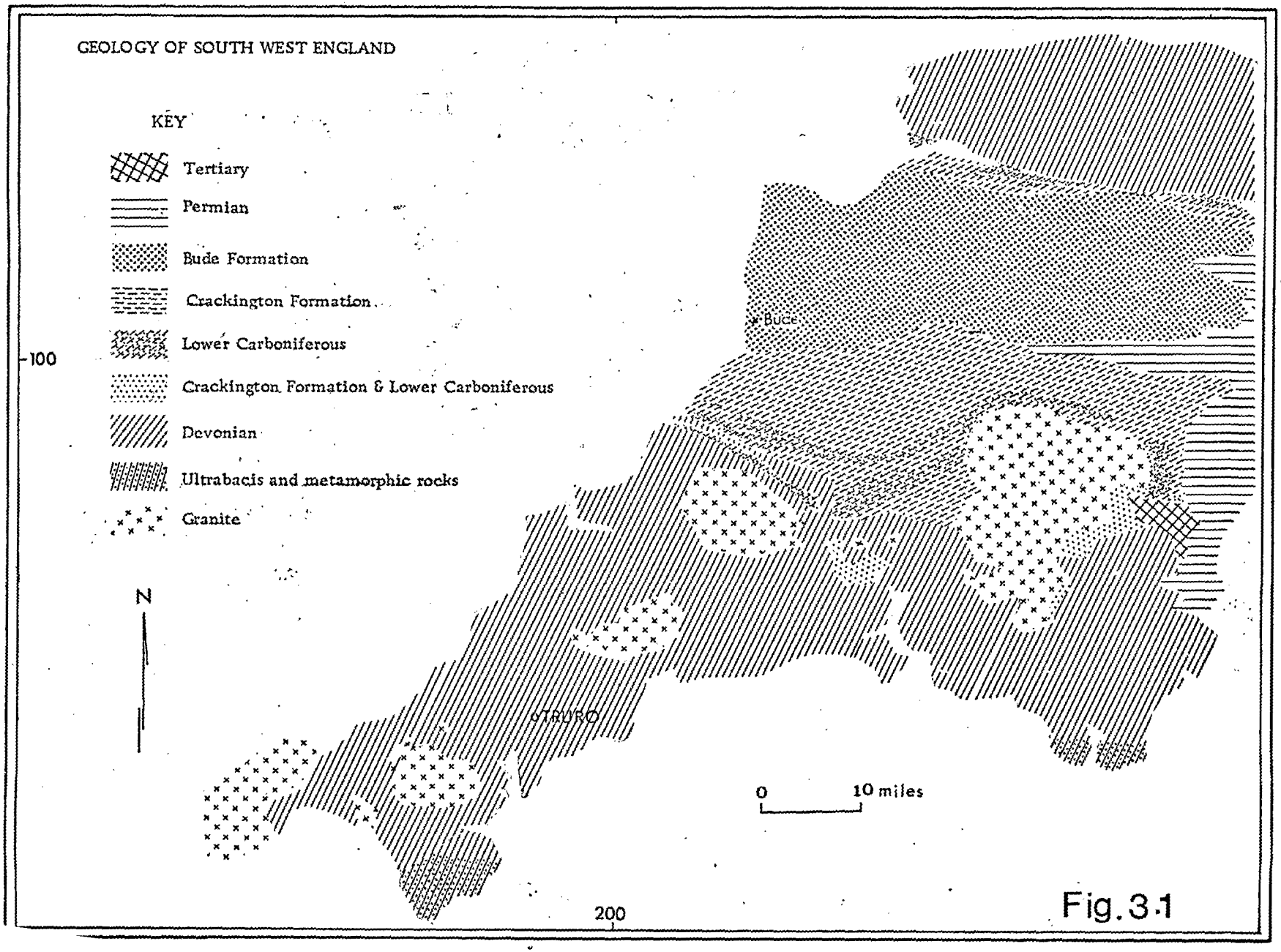

GEOLOGY OF SOUTH WEST ENGLAND
KEY
Tertiary
Permian
Bude Formation
Crackington Formation
Lower Carboniferous
Crackington Formation & Lower Carboniferous
Devonian
Ultrabacis and metamorphic rocks
Granite
N
100
200
Bude
TRURO
0
10 miles

Fig. 3.1

intraformational conglomerates and thin limestones. The Middle Devonian sediments in south-west Cornwall consist of interbedded greywackes and slates with sporadic limestones, conglomerates, cherts, spilitic lavas, siltstones and slates with a few sandstones. North and east Cornwall, and south Devon are characterised by a sequence of black slates, lavas and tuffs, and minor thin limestones. The Upper Devonian in southern Cornwall consists of breccias and conglomerates with interbedded greywackes, slates and limestones, whilst in north Cornwall and south Devon it consists of grey-green slates, and phyllites which are overlain by slates with silty and calcareous bands accompanied by basic volcanic rocks.

A wide tract of Carboniferous sediments occurs throughout central Devon and parts of north Cornwall and north Devon. The Lower Carboniferous (Dinantian) consists of black shales, fine sandstones, cherts, lenticular limestones, basic tuffs, agglomerates and basic intrusive rocks. Pyrite-bearing black shales and cherts are frequently found in the neighbouring areas of the granitic bodies. The lowermost Upper Carboniferous (Crackington Formation) is dominantly argillaceous and consists of a sequence of shales with subordinate sandstones and siltstones, which is succeeded by thickly bedded massive sandstones with subordinate shales and slates (Bude Formation).

The Permian sediments lie with a marked unconformity on Carboniferous strata. The predominant Permian rocks in the area consist of red beds and minor associated volcanic rocks (Exeter Volcanic Series) outcropping along a narrow east-west belt (Crediton Valley) which extends for approximately 25 miles (Fig. 3.2). The sequence is formed at the base by sporadic (and in many cases almost undifferentiated) outcrops of the Cadbury Breccia which is succeeded by the Bow Conglomerates group consisting of breccias and conglomerates with local variations of finer sediments ranging from pebbly sandstones to silts (Edmonds et al, 1968). Thus in the eastern margin the Bow Conglomerates unit is characterised by a normal sequence of sandy and gravelly breccia resting on red sandstones and pebbly sandstones. The coarser sediments occur mainly in the western

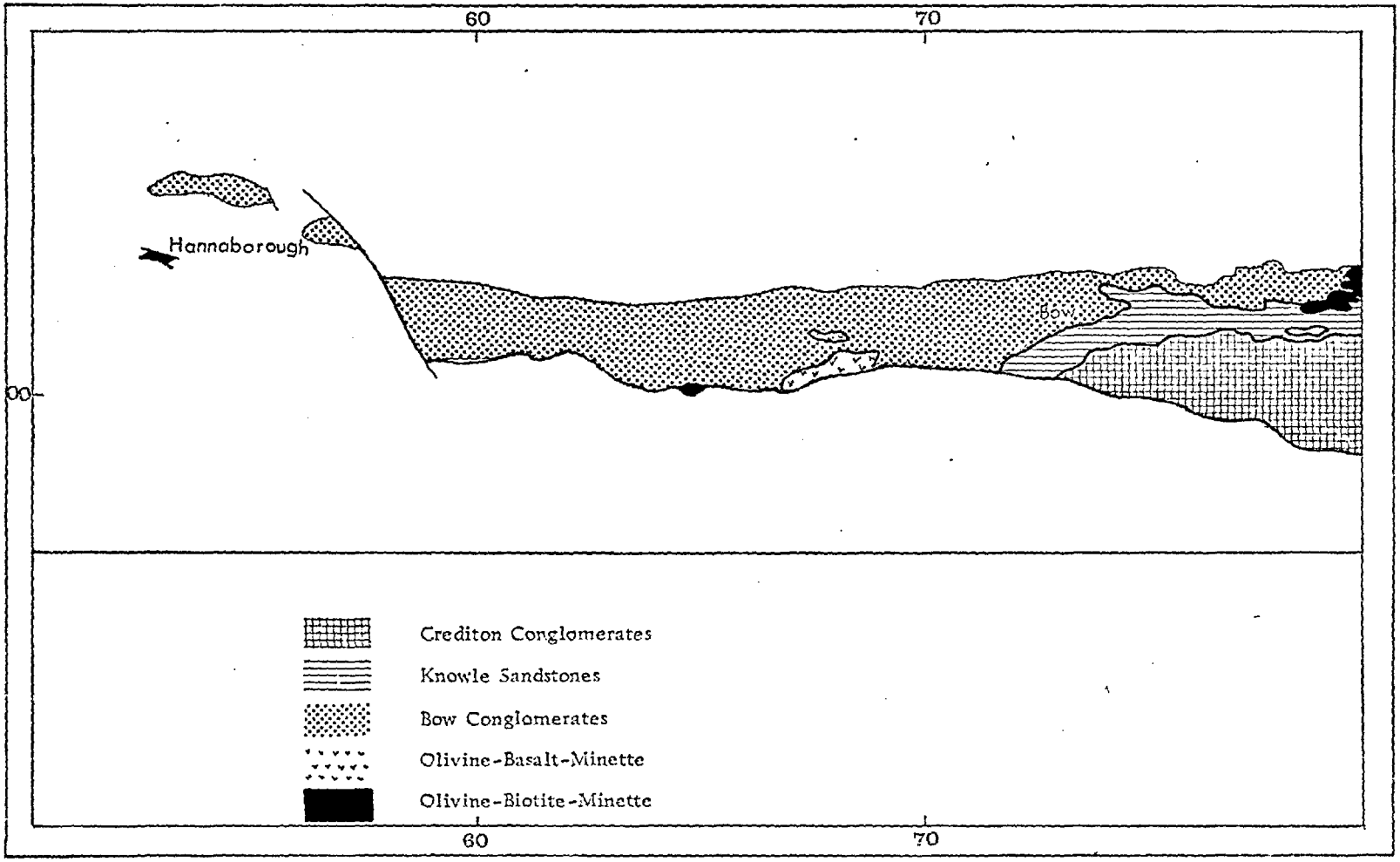


Fig. 3.2 SIMPLIFIED GEOLOGICAL MAP SHOWING THE DISTRIBUTION OF THE PERMIAN ROCKS

part of the area where fine breccia is accompanied by coarse breccia-conglomerates with boulders of limestones and volcanic rocks. Generally, the fragments forming the breccias consist of debris of Culm sandstones, quartz veins, metamorphosed mudstones and lamprophyric and basaltic lavas. Abundant fragments of lava of the Hannaborough-type (olivine-biotite-minette) and lamprophyre dykes can be seen incorporated in the strata. The Knowle Sandstones group consists of fine to coarse sandstones with clay and/or sericitic matrices, interbedded pebbly sandstones and fine gravelly conglomerates. In the eastern part of the area two lava flows are interbedded with the sandstones (olivine-biotite, and olivine-basalt). The Crediton Conglomerates formed mainly by coarse conglomeratic and breccia debris unconformably overlain on the Knowle Sandstones and in specific areas on the Bow Conglomerates group.

3.2 ARMORICAN GRANITE

Intrusion of the granitic batholith occurred after the culmination of the Hercynian orogeny at the end of the Carboniferous Period. Isotopic age determinations have fixed the granite emplacement at about 290 million years ago. The composition of the granite is generally adamellite with common porphyritic and fine grained marginal phases. The granite batholith is represented by six major bodies namely: Dartmoor, Bodmin Moor, St. Austell, Carnmenellis, Lands End and the Scilly Isles. Smaller masses occur in areas between Dartmoor and Bodmin Moor and around the major bodies located in south Cornwall. Each of the granitic masses outcropping in the region is surrounded by an aureole of thermal metamorphism (Fig. 3.3) whose affects and extension is mainly determined by the nature of the country rock and the angle of dip of the granite surface at the contact. The metamorphic changes induced by the granitic intrusion were caused by an increase of temperature and the presence of chemically active vapours, gases and solutions emanating from the intrusive magma.

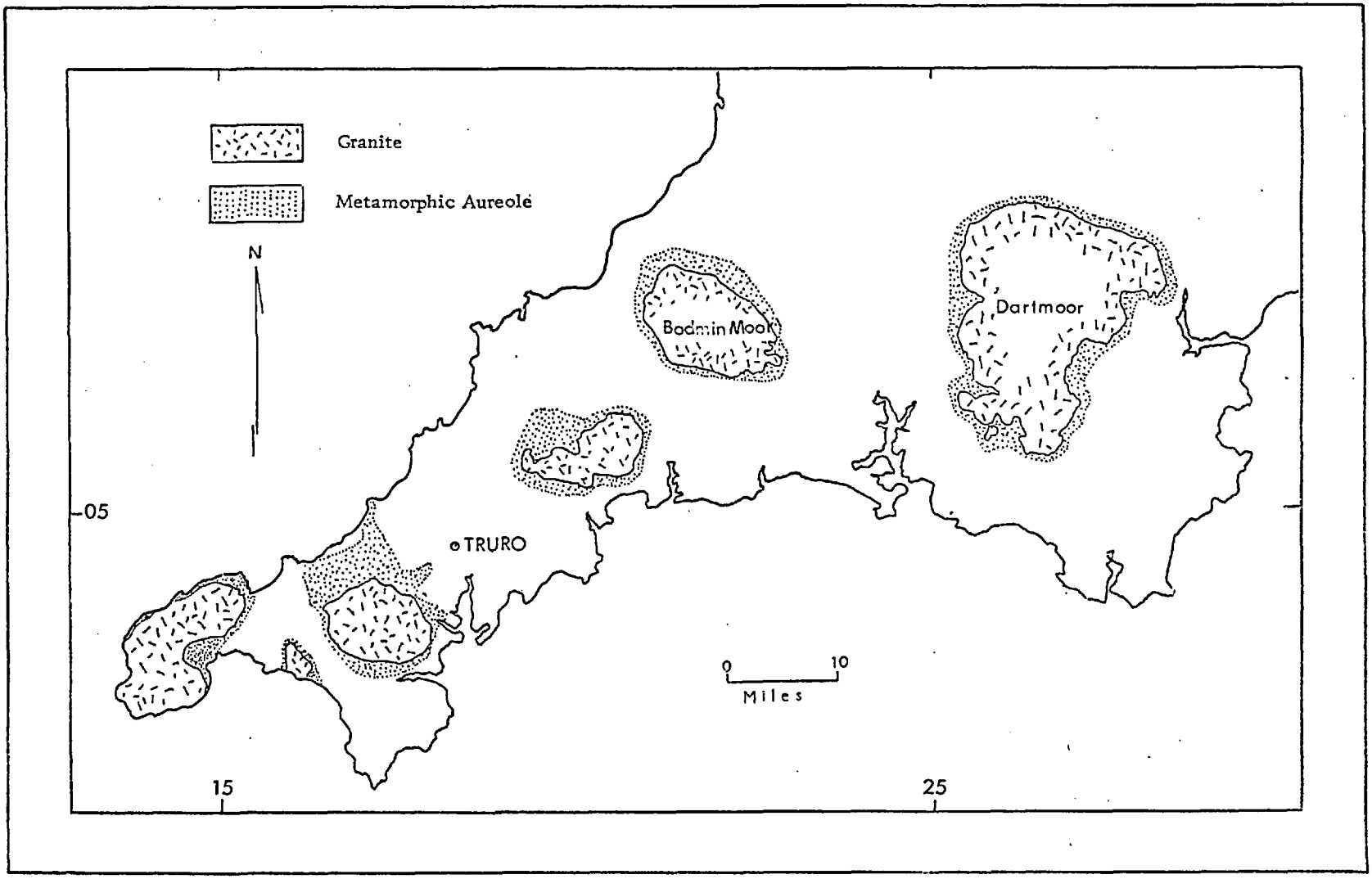


Fig. 3.3 MAJOR GRANITE BODIES IN SOUTH-WEST ENGLAND

3.3 METALLIFEROUS MINERALS

The sources and distribution of the metalliferous deposits of south-west England are genetically related to the intrusion of the granite batholith, although later orogenic movements seem to have produced primary mineralisations. Mineralising emanations escaped upwards from the magma through a fracture system developed in the consolidated granitic crust and in the overlying parent-rock where these fluids deposited their metalliferous content. Hypothetically the mineralising emanations may have been the last product of the consolidating magma. The sequence of deposition was controlled by temperature and pressure and by the crystallising temperature of each mineral type. Thus tin and tungsten (two metals of high temperature) are found in deeper zones whilst copper, lead, zinc and iron were deposited in the cooler zones above.

The mineral deposits commonly known as 'lodes' are predominantly of the fracture-filling type, and they occur within a diagonal belt approximately 10 miles wide which seems to follow the long axis of the granite batholith. The lodes are mainly concentrated in the metamorphic aureole and, to a lesser extent, they occur in the granite, and in neighbouring areas on the outer side of the aureole. The trends of the main lode systems are generally east/north east, but in some areas veins termed 'caunter lodes' sharply differ from these general trends; and yet lodes trending north-south named 'cross courses' are very common in the region (Fig. 3.4). According to Edmonds et al (1969) the main fracture systems have developed during the initial period of folding and granitic intrusion, whilst the fractures forming the cross courses developed later, possibly during a period of relaxation of regional pressures caused by the cooling of the granite.

3.4 ARSENIC MINERALISATION

Arsenic mineralisation is widespread in the lodes of south-west England and it appears to be associated with a majority of the minerals occurring in the region. Arsenopyrite or mispickel is the most common arsenic mineral and the only one of economic significance in south-west

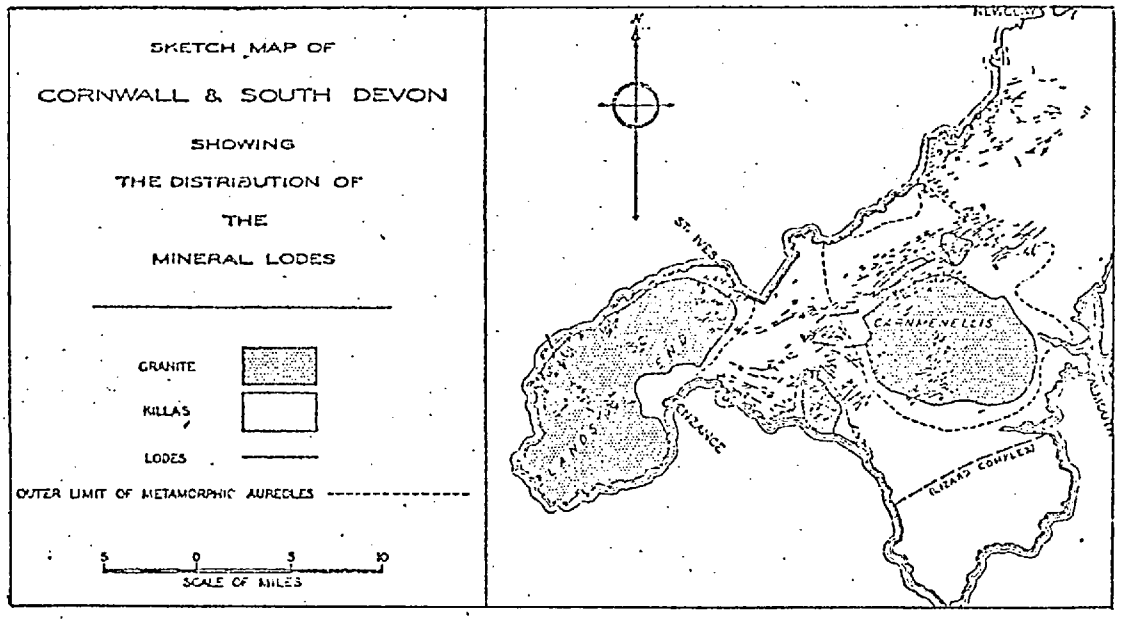


Figure 3.4 (After Dines 1956)

England. It is a primary sulphide and occurs principally in the sulphide zone generally associated with pyrite. Arsenopyrite-bearing lodes are found distributed along the general fracture patterns of the region but there are exceptions where the ore lies in north-south cross courses. The distribution of arsenopyrite in the lodes is variable. In some cases it is limited to the walls of the copper lodes, whilst in others the ore may be mixed with copper and iron sulphides, cassiterite and wolframite. Arsenopyrite has been extracted from lodes mainly located within the metamorphic aureole, although in some cases rich deposits were found both outside the aureole and within the granite where arsenopyrite is found in the higher tin zones.

Although in some areas arsenic constituted the predominant mineral in the whole region it has been worked mainly as a by-product in association with numerous minerals of both high and low temperature. Thus, in the Mount's Bay mineralised district arsenic occurs together with cassiterite, stannite, blende, argentiferous galena, argentite and native silver in the Wheal Darlington Mine, and with pyrite, nickel, cobalt, pitchblende, uranochre, chalcopyrite, galena and stannite in the Wherry Mine. In the Camborne-Redruth-St. Day district arsenopyrite is associated firstly with cassiterite, chalcopyrite, pyrite and wolframite (South Crofty Mine), secondly with tin, copper, tungsten, silver, nickel, cobalt and bismuth ores (Dolcoath Mine) and thirdly with tin, copper, pyrite, tungsten, uranium, cobalt, bismuth and nickel ores (Pool East and Agar Mine), Dines (1956).

Arsenopyrite has also been found associated with gold and antimony in the Wadebridge district in which the Treore Mine was worked almost exclusively for arsenic. Here lenticular masses of jamesonite and antimonite with silver, gold, pyrite, galena and chalcopyrite have been found. In the St. Just district arsenic was found to occur along with silver, gold and copper ores in the Levant Mine (Dines, op. cit.).

Kingsbury (1964) reports an unusual occurrence of scheelite associated with pyrite, stibnite, jamesonite, galena, arsenopyrite and

gold occurring in a carbonate matrix in a vein near St. Teath (in north Cornwall). Cobaltiferous lollingite has been recorded in Devon in the Okehampton mineralised district (Edmonds et al. 1968).

A generalised map of arsenic-bearing areas in south-west England is shown in Fig. 3.5.

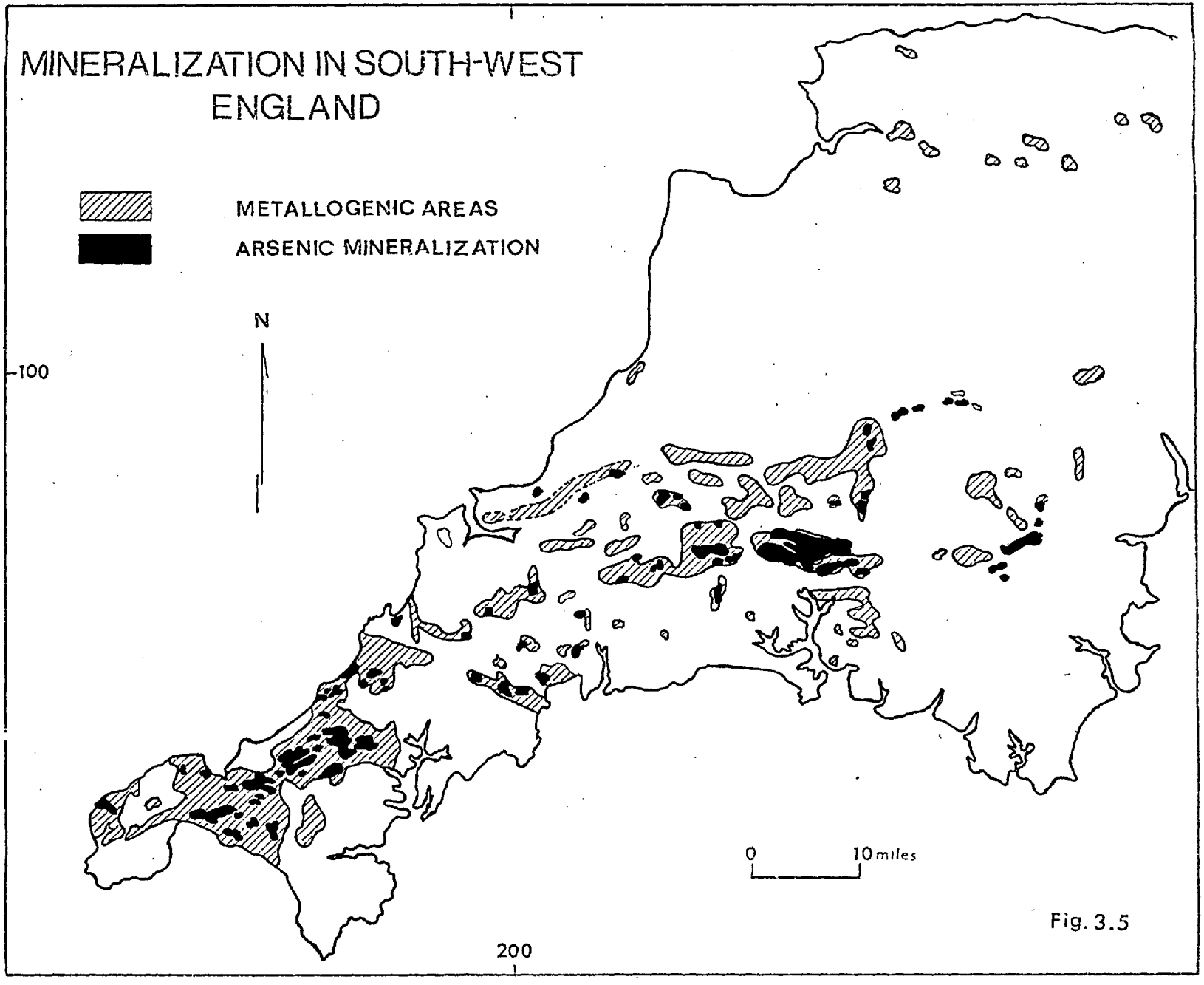

MINERALIZATION IN SOUTH-WEST ENGLAND
METALLOGENIC AREAS
ARSENIC MINERALIZATION
N
100
200
0
10 miles

Fig. 3.5

CHAPTER 4

GEOCHEMISTRY OF ARSENIC

This section outlines the basic features of the geochemistry of arsenic, gained principally from the published investigations of Clarke(1924 Fersman (1939), Rankama and Sahama (1950), Onishi and Sandell (1955 a) Esson et al.(1965) and Boyle and Jonasson (1973).

4.1 BASIC PRINCIPLES

Arsenic is considered to be a non-metallic element constituting the third member of Group VA of the periodic system along with nitrogen, phosphorous, antimony and bismuth. Its principal physical properties are: atomic number 33; atomic weight 74.91; density ($20^{o}C$) 572, and melting point $613^{o}C$. In dry air arsenic has a steel grey appearance but in the presence of moisture it is covered with oxide and then it takes on a black aspect.

Arsenic is recognized as a rare, but ubiquitous element in the upper lithosphere. It has been reported to be present in the solar atmosphere but its presence in the stellar atmosphere is doubtful. Arsenic is regarded as a chalcophile element and is enriched in the sulphide phase of meteorites. However, its occurrence in telluric and meteoritic irons suggests its siderophile character. In nature, arsenic in its native state is found mostly in mineral veins. It most frequently occurs combined with sulphur, selenium, tellurium and as sulpho-salts and arsenides of heavy metals such as copper, iron, nickel and cobalt. Arsenic forms a number of pentavalent arsenate minerals that bear a close geochemical relationship with phosphates and vanadates which are often isomorphic. The trioxide (As_2O_3) occurs in two mineral forms: arsenolite and claudite.

4.2 ARSENIC IN METEORITES

Among the existing analytical data on the abundance of arsenic in meteorites there is considerable variation. Noddack and Noddack (in

Goldschmidt 1954) found 1020 ppm of arsenic associated with the troilite phase and 360 ppm of this element associated with the nickel-iron phase. Onishi and Sandell (1955 a) reported an average of about 2 ppm in chondrites in general of which 12 ppm is found in the metal phase, 10 ppm in the troilite and less than 0.5 ppm in the silicate phase.

4.3 ARSENIC IN MAGMATIC ROCKS

Arsenic in magmatic rocks is reported to be present in arsenides which are associated with very different rocks of the magmatic sequence and it is considered to be an electron donor and acceptor in igneous and metamorphic systems.

In basic magmas arsenic appears to follow sulphides closely. Hypothetically, arsenic poses as an electron acceptor in basic magmas in which the oxidation potential is low and the separation of sulphide-melts collects much of the arsenic as well as the sulphur in the system. Esson et al.(1965) discussed the geochemical behaviour of arsenic during the fractionation of a basic magma and reported that As^{3+} is probably accepted into octahedral lattice sites usually occupied by Fe^{3+}, Mg^{3+}, Ti^{4+} and Al^{3+} and that there is also some substitution of As^{5+} for Si^{4+} and Al^{3+} in the tethedral sites. Goldschmidt (1954) reported that sulphide segregations associated with gabbroic rocks have been estimated to contain high arsenic concentrations.

In intermediate and acid igneous magmas the arsenic content in the liquid increases with the degree of crystallisation, especially near the terminal stage. Probably in the partitional stage arsenic is contained almost completely in an aqueous fluid in the form of sulpho-arsenite complexes.

Determinations of arsenic in igneous rocks reported by Clarke and Steiger, Noddack and Noddack (both in Onishi and Sandell 1955 a). Verhoogen (1948), Odman (1950), Onishi and Sandell (op. cit.) and Boyle and Jonasson (1973) range from very low (4.5 ppm) to anomalous values (2000 ppm). Onishi and Sandell found that the average arsenic content in

common igneous rocks does not differ greatly: basalts and diabases, 2 ppm; gabbros, 1.4 ppm; and granitic rocks 1.5 ppm. Boyle and Jonasson also found little difference in arsenic content between the various types (Table 4.1).

4.4 ARSENIC IN SEDIMENTARY ROCKS

In sedimentary rocks, shales and argillites were found to be the richest in arsenic, especially in pyritiferous types and phosphorites whose mean values are 17 and 14 ppm respectively (Boyle and Jonasson, 1973). According to Onishi and Sandell (1955 a) shales are richer in arsenic than igneous rocks, due to the fact that shales contain sulphide and carbonaceous matter which tend to be arsenic collectors. Sandstones and limestones normally contain less arsenic than shales and their mean values (4 and 2 ppm respectively) do not show much difference from that of igneous rocks (1.5 to 4.3 ppm).

Goldschmidt and Peters (in Goldschmidt, 1954) found arsenic in sediments that are rich in iron, manganese and aluminium and in which arsenic is concentrated through absorption processes. From 65 to 650 ppm of arsenic was found in oxide and hydroxide iron ores. Sedimentary manganese ores were found to contain less arsenic than iron ores. Bauxite rich in iron contains detectable arsenic (320 ppm).

4.5 ARSENIC IN SOILS

The concentration of arsenic in soils is widespread and is believed to have been precipitated principally through the medium of ferric hydroxide and probably fixed as the arsenate ion in the upper part of the soil profile (Goldschmidt, 1954). According to Boyle and Dass (1967) the A horizon of some soils bears a high arsenic content in relation to the lower horizons; however, the element is usually more concentrated in the B horizon. In common soils and glacial material the arsenic concentration is low but it becomes higher in those soils located in the vicinity of arsenical deposits.

TABLE 4.1 ARSENIC CONTENT OF IGNEOUS ROCKS IN PARTS PER MILLION

(After Boyle and Jonasson, 1973)

Rock type	Number of values	Range	$\bar{X}$	S	$\bar{X}g$	Sg($\log_e$)
Ultrabasic rocks (peridotite, pyroxenite, dunite, kimberlite, etc.)	40	0.034–15.8	1.5	1.6	0.9	1.1
Basic rocks:						
extrusives (basalt, etc.)	78	0.18–113	2.3	2.6	1.5	0.90
intrusives (gabbro, diabase, etc.)	112	0.061–28	1.5	1.6	0.85	1.20
Intermediate rocks:						
extrusives (latite, trachyte, andesite, etc.)	30	0.5–5.8	2.7	1.8	2.1	0.80
intrusives (granodiorite, syenite, diorite, etc.)	39	0.091–13.4	1.03	1.48	0.57	1.06
Acid rocks:						
extrusives (rhyolite, etc.)	2	3.2–5.4	4.3	1.6	4.2	0.37
intrusives (granite, aplite, etc.)	116	0.18–15.0	1.29	1.38	0.93	0.78
Feldspathoid rocks (nepheline syenite, phonolite, etc.)	no data					

Note: In this and subsequent tables $\bar{X}$ is the arithmetic mean; S, the standard deviation; $\bar{X}g$, the geometric mean; and Sg($\log_e$) the logarithmic standard deviation.

Here the arsenic is primarily concentrated in the B and C horizons. Arsenic has been found to develop well-defined secondary dispersion halos and trains in soils derived from arseniferous deposits. Anomalous arsenic concentrations related to mineralised bodies have been detected in many parts of the world. Thus, Rodgers (1956), James (1957), Webb (1958), Mather (1959), Mazzucchelli and James (1966), Erickson et al.(1964), Presant and Tupper (1966), Boyle and Dass (1967), and Presant (1971) established that arsenic anomalies occur in soils which are related to polymetallic ore deposits, especially those bearing gold, silver, tin, tungsten and sulphide ores. Anomalous arsenic concentrations in soils related to alluvial terrain and copper-tin type ore deposits from south-west England have been reported by Hosking et al.(1959), Dearman and El Sharkawi (1965) and Dunlop (1973).

Soils treated with arsenic-bearing fertilisers and insecticides tend to fix the arsenic chiefly in the B horizon (Boyle and Jonasson, 1973), the concentrations ranging from 11 to 290 ppm.

4.6 ARSENIC IN STREAM SEDIMENTS

As in the soils, arsenic occurs in anomalous levels in sediments from streams draining mineral deposit-bearing areas. Extensive stream sediment surveys carried out in many places of the world have shown that high arsenic values may occur in relation to mineralised areas yielding gold, silver, tungsten, tin, copper, nickel, cobalt, etc. This fact has been demonstrated by many workers such as Nichol et al.(1966), Elliot (1962), Viewing (1963), James (1965), Garret and Nichol (1967), Reed and Mill (1971) and Boyle (1972). Similar results were obtained in England by Hosking et al (1962, 1964, 1965, 1966 and 1968), Horsnail (1968) and Nichol et al.(1971). Nichol (1967), Nichol et al. and Horsnail (op. cit) found that high arsenic (in addition to zinc and cobalt) occurs in association with iron and manganese, probably because of the retention effects of iron and manganese oxides. Horsnail, and Nichol et al. also found anomalous

arsenic and zinc concentrations in areas surrounding the Dartmoor and Bodmin Moor granitic bodies of south-west England and they indicated the possible relationship between these anomalies and high background levels of arsenic in the bed-rock.

4.7 ARSENIC IN ORE FORMING MINERALS

During the stages of geochemical separation the concentration of arsenic is low in the early magmatic sulphides, becoming more significant in the late magmatic sulphides. During the pegmatitic stage further concentration of arsenic occurs but the largest number of arsenic minerals are formed when the pneumatolitic and hydrothermal stages are reached.

Arsenopyrite is the most abundant and widespread mineral of arsenic. It is found in pegmatites but most frequently in high temperature gold-quartz and tin veins, and in contact with metamorphic sulphide deposits. Native arsenic is relatively common in some ore deposits; however, due to its chalcophile character it forms sulphides and sulpho-salts particularly with copper, silver, mercury, lead and iron (Boyle and Jonasson, 1973). Realgar (arsenic sulphide) and orpiment (arsenic tri-sulphide) are found in hydrothermal veins and volcanic sublimates.

Many sulphide minerals contain appreciable amounts of arsenic probably in lieu of sulphur or as a solid solution valency compensation. Arsenic has been found in small quantities in galena by spectrographic analysis. El Shazly et al.(1956) detected arsenic in three samples of epigenetic galena from Ireland, Portugal and England (Cornwall). Although arsenic is reported to be present in many sphalerite samples, it is believed that its presence is due to impurities in the sulphide mineral; nevertheless, arsenic in pure sphalerite may occur at least in moderate amounts. Hohene and Noddack and Noddack (both in Fleischer, 1955) and El Shazly et al.(op. cit.) discovered arsenic in some chalcopyrite samples. The presence of arsenic in pure pyrite has been reported by many authors. Newhouse and Hohene

(in Fleischer, op. cit.) reported that homogeneous pyrite contained about 5 and 2.7% of arsenic respectively. Arsenic has been found in both sedimentary and hydrothermal pyrite, as well as in pyrite samples of eruptive origin. According to Fleischer (1955) Hawley found more arsenic in low temperature rather than high temperature pyrite. El Shazly et al.(1956) analysed thirteen samples of pyrite and six of marcasite, and detected arsenic in all of them. According to Boyle and Jonasson (1973) the main carrier of arsenic in rocks and in many mineral deposits is pyrite, which may contain up to 6000 ppm or more arsenic, the arsenic probably occurring in lattice sites substituting for sulphur.

CHAPTER 5

SAMPLING METHODS, ANALYTICAL TECHNIQUES AND DATA PROCESSING

5.1 INTRODUCTION

The original regional geochemical reconnaissance of south-west England for the Wolfson Geochemical Atlas of England and Wales comprised the sampling and analysis of active stream sediments for six major and twenty trace elements. Sites were located at road/track and tributary drainage intersections at an approximate density of one sample per square mile. Sampling procedures and analytical techniques were based on the results of earlier geochemical reconnaissance surveys in the United Kingdom carried out by Nichol et al.(1969 - 1970), Young (1971), and Davies (1971). Computerised methods were used to process the analytical data, and to compile geochemical maps. The sampling, analytical work and data processing were undertaken by members of the Applied Geochemistry Research Group at Imperial College.

The more detailed investigations undertaken for this study consisted of the collection and analysis of soil, rock and a few stream sediment samples.

5.2 SAMPLING METHODS

5.2.1 Stream Sediment Sampling

The regional geochemical reconnaissance of south-west England was undertaken in the summer of 1969 during which approximately 10,000 stream-sediments were collected by eleven two-man crews who gathered duplicate samples at each site. Sample sites were chosen at road/track and stream intersections and recorded on 1"/1m map. In a more detailed stream sediment sampling, sample sites were selected at the stream-soil traverse crossing point.

The stream sediment samples were collected in most cases from the centre of the stream. Fine silty material was selected and care was taken to avoid collapsed bank material and organic litter as well as domestic and industrial sources of contamination.

5.2.2 Soil and Rock Sampling

Systematic soil sampling was carried out in selected areas along traverses in which top-soil and sub-soil samples were collected using a 'T' one inch diameter hand-operated screw auger. Position and location of the soil sampling traverses and rock sampling sites were recorded on 1 and $2\frac{1}{2}$ inch/mile maps respectively. Two soil samples were collected at each site, the first of top-soil below the zone of matted grass roots and the second of sub-soil in an attempt to get the B soil horizon. During the soil sampling, rocks were taken nearby wherever they were exposed.

Chip rock samples for detailed investigations were taken in quarries and surface outcrops where relatively fresh bed-rock is frequently exposed. Weathered rocks were avoided while sampling rocks during the investigations and the possible relationship between bed-rock and mineralisation was carefully observed.

Stream sediment, soil and rock samples were placed in numbered kraft paper bags.

5.3 ANALYTICAL TECHNIQUES

5.3.1 Sample Preparation

Stream sediment and soil samples were dried in a portable electrical oven at about $60^{o}C$. The samples were placed into the oven in their original paper bags previously opened to facilitate evaporation of moisture. Dried samples were lightly broken up in a porcelain mortar by pestle action and then sieved through an 80-mesh (nominal aperture of 0.204 mm) bolting cloth mounted in an acrylic frame. The minus 80 mesh fraction was kept in numbered kraft paper bags.

Rock samples were carefully washed with deionised water and air dried. Altered material was removed by hammering. A sledge hammer was used to reduce the rock samples to gravel size chips which were then fed into a stainless steel jaw-crusher. The crushed sample was ground in an agate mortar and sieved through an 80-mesh sieve.

5.3.2 Analysis of Samples

Stream sediment samples from the regional Wolfson Atlas reconnaissance survey were analysed by direct reading emission spectrometer (ARL 29000 B Quantometer), atomic absorption, and colorimetric techniques. Stream sediments, soil and rock samples from the more detailed investigations have been analysed by atomic absorption spectrophotometry (Cu, Pb, Zn, Mn and Fe) and by colorimetric methods (As and Sn).

Sulphur from sulphide-bearing rocks was determined by a semi-quantitative colorimetric method developed by the author during the present research (Appendix I).

Description of the operating techniques of the ARL 9000 B Quantometer have been given by Newman and Foster (1968) and Young (1971) and descriptions of sample preparation and analysis for the Wolfson Geochemical Atlas have also been given by Urquidi (1973) and Dunlop (1973). The present account only deals with a brief outline of the atomic absorption and colorimetric techniques as they were used in this research.

a) Atomic Absorption Spectrophotometry Analysis

Stream sediment, soil and rock samples were analysed by this method for the following elements: Cu, Pb, Zn, Mn and Fe.

A Perkin Elmer 403 (double beam) Atomic Absorption Spectrophotometer was used for the determinations of the above elements after acid digestion of the samples with an $HNO_3/HClO_4$ mixture, followed by leaching with 6M HCL.

A deuterium background correction was used in the determination of Pb and Zn for non-atomic interferences (molecular absorption plus light scattering). The operating conditions used with the instruments are presented in Table 5.1.

b) Colorimetric Analysis

Arsenic Determination

The determination of the total arsenic content in stream sediment, soil and rock samples was carried out, in the present research, by means of the modified Gutzeit method described in the AGRG technical communication No. 49 (March 1965).

Briefly, the method consists of a fusion of the sample with potassium hydrogen sulphate. Decomposition of the sample results in the oxidation of arsenic,substances such as sulphides,and organic carbon. Arsenic is oxidated to pentavalent arsenic. The arsenic thus formed is subsequently reduced to arsenic III by the addition of potassium iodide. Cupric and ferric ions are also reduced. The iodine thus released is reduced by addition of stannous chloride. The reaction of hydrochloric acid with metallic zinc pellets liberates hydrogen which in its nascent state converts arsenic III into arsine. The arsine obtained is swept up the test tube through a glass tube into which glass wool, saturated with lead acetate has been packed. The lead acetate removes any hydrogen sulphide that may have been liberated.

Arsine reacts with mercuric chloride paper placed at the top of the Gutzeit tube to form a coloured spot. The colour intensity of the spot depends on the amount of arsine which reacts with the $HgCl_2$ to form different arseno-mercury compounds. The production of a dark brown spot on the mercuric chloride paper indicates that the amount of arsenic present in the sample exceeds the useful range of the method.

TABLE 5.1

INSTRUMENT PARAMETERS FOR ATOMIC ABSORPTION SPECTROPHOTOMETRY

Element	Wave length (mm)	Slit	Flame	Spectral Interference (Molecular Absorption)
Cu	324.7	4	Oxidising	None
Fe	371.9	3	Oxidising	None
Pb	283.3	4	Oxidising	Ca
Zn	213.8	5	Oxidising	Ca, Na
Mn	279.4	4	Oxidising	None

Tin Determination

The method employed for determination of tin in the samples is described in the AGRG technical communication No. 18 (January 1966).

Briefly, the method consists of attacking the sample by heating it with ammonium iodide. Cassiterite is converted into stannic iodide which together with the excess of ammonium iodide, sublimes on the upper, cooler parts of the test tube. The sublimate is dissolved with diluted hydrochloric acid and then leached in a hot sand-tray in order to prevent hydrolysis of tin.

Chloroacetic buffer solution, which is prepared from chloroacetic acid and sodium hydroxide, keeps the pH value of the final solution within the range 2.0 to 2.5. This range must be maintained during the reaction of tin with gallein since the reduction of ferric ions is incomplete above pH 2.5. Below pH 2.0 the reaction of tin with gallein is not quantitative.

Hydroxyammonium chloride reduces the iodine liberated during the sample attack. This result is obtained by gently heating the solution on a sand tray. Gelatine is included as a protective colloid. The standard series ranges from green to colourless through grey to purple and then pink.

Determination of Sulphide Sulphur

This method consists of an attack on the sample with diluted (3M) hydrochloric acid in the presence of free sulphur metallic zinc pellets and a small quantity of metallic chromium powder. This attack permits the reduction and liberation of sulphide sulphur from the sulphide-bearing sample, in a sulphide form (H_2S). The hydrogen sulphide thus liberated is passed through a thin glass tube previously filled with silica powder impregnated with lead acetate. Sulphur reacts with the lead acetate to give a black stain of varied height depending on the content of sulphur in the sample. The results are then compared with artificial standards and the concentration of sulphur is measured in parts per million.

A detailed description of this method is presented in Appendix I.

5.3.3 Precision Control

In order to assess the precision of the analysis, one sample was analysed in duplicate every five samples for the atomic absorption analysis and every ten samples for the colorimetric determinations.

Precision was then assessed graphically (Figs. 5.1 - 5.4) using the method described by Thompson and Howarth (1973). It was found that this method was adequate for monitoring the precision of all the techniques used in the laboratory including atomic absorption and colorimetry.

Results were within $\pm$ 25% at 95% confidence level over different ranges, according to the analytical method used.

5.4 DATA PROCESSING

The samples collected during this research produced 24,200 analytical determinations for eight selected trace elements. Essential statistical parameters for interpretation (mean, standard deviation, product moment correlation matrix) were calculated using the GESTAT programme (Garret, 1968) on the CDC 6400 computer at the Imperial College Computer Centre.

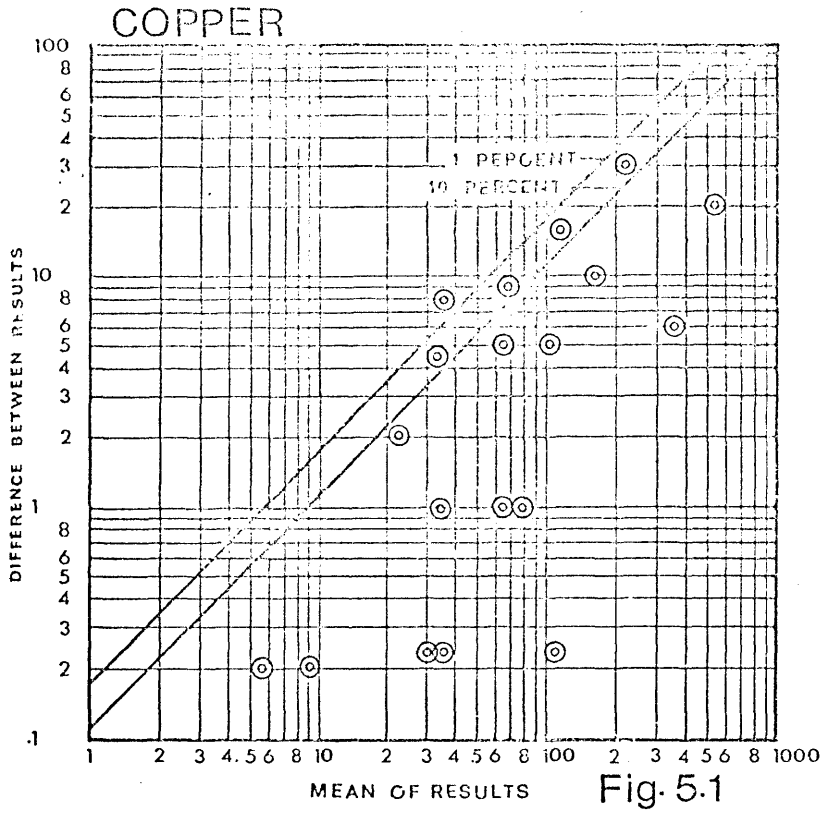


Fig. 5.1

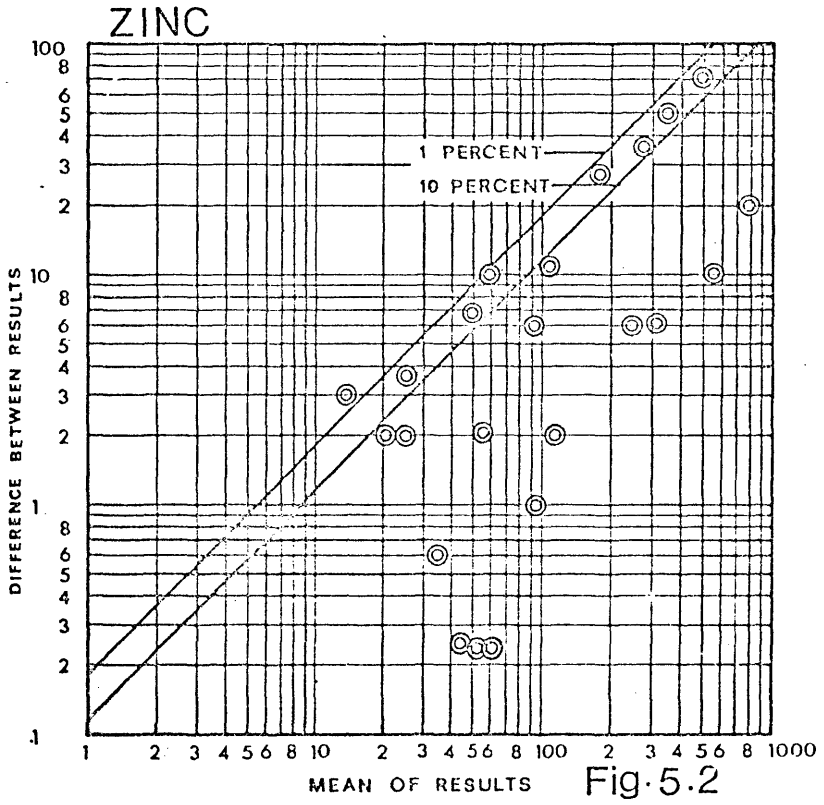


Fig. 5.2

PRECISION CONTROL CHART FOR DUPLICATE RESULTS

In a set of duplicate measurements on many samples where for each sample the precision of measurement is 10 per cent at the 95 per cent confidence limit (i.e. $\sigma/\mu = 0.05$) the indicated proportion of points will fall above the diagonals. The scale of the means must be 10 times greater than the scale of the differences.

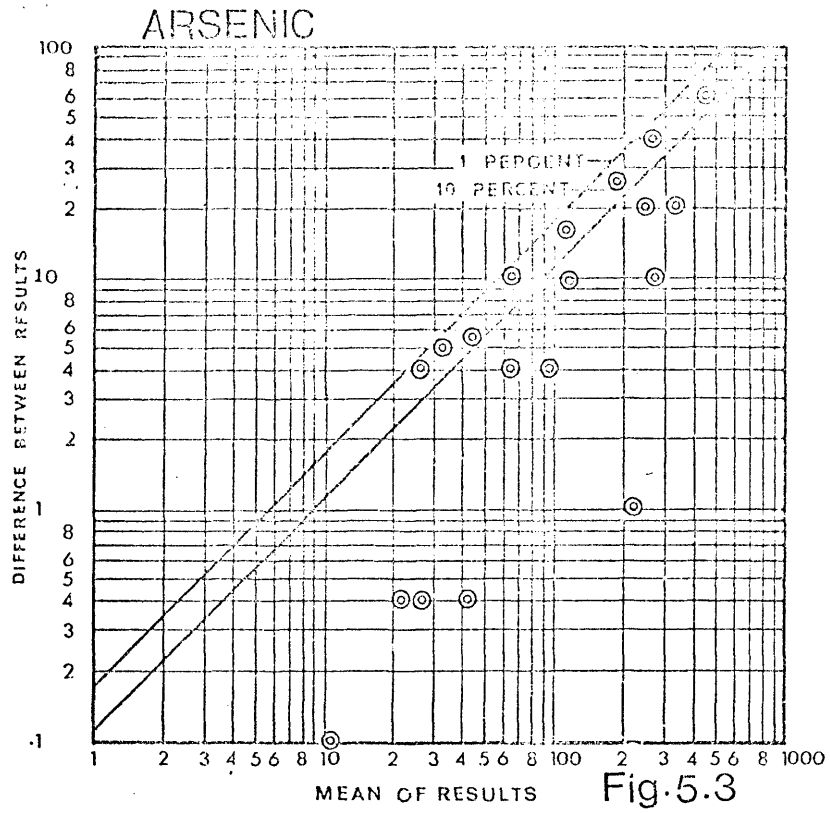


Fig.5.3

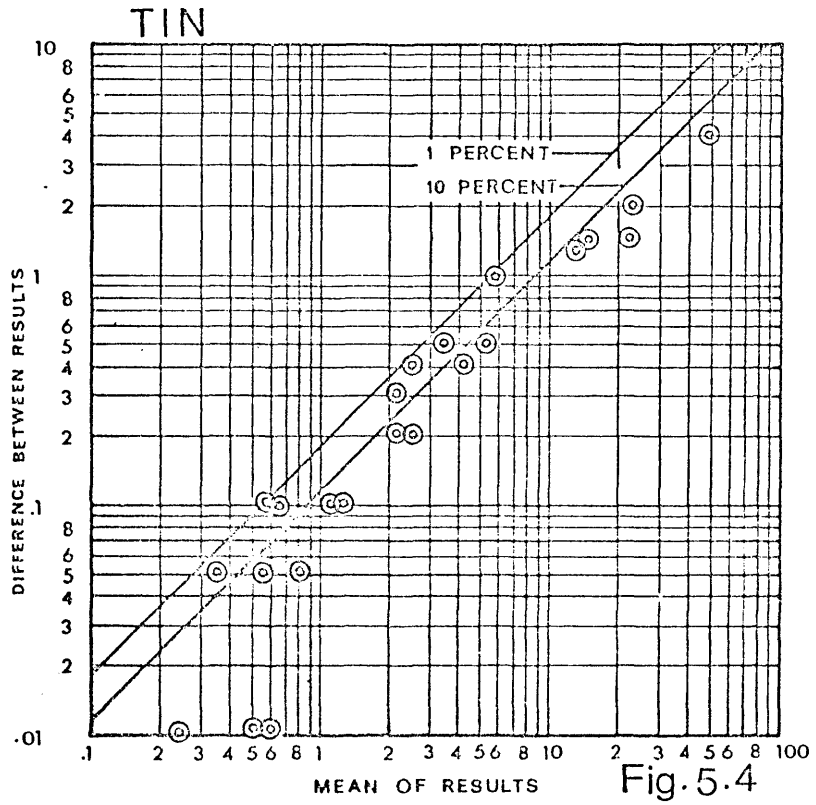


Fig.5.4

PRECISION CONTROL CHART FOR DUPLICATE RESULTS

In a set of duplicate measurements on many samples where for each sample the precision of measurement is 10 per cent at the 95 per cent confidence limit (i.e. $\sigma/\mu = 0.05$) the indicated proportion of points will fall above the diagonals. The scale of the means must be 10 times greater than the scale of the differences.

CHAPTER 6

INTERPRETATION AND CLASSIFICATION OF REGIONAL GEOCHEMICAL PATTERNS

6.1 INTRODUCTION

Interpretation and classification of the geochemical As patterns and the other selected trace-elements was based on the provisional geochemical maps (Data: June 1972) produced for the geochemical Atlas of south-west England.

Data from the geochemical reconnaissance stream sediment survey have been transposed onto maps by means of a computer program to produce maps on the line printer (Howarth, 1971), in order to develop a multi-element geochemical Atlas of England and Wales.

Because of the fixed size of the character positions on the line printer (eight lines per inch vertically, and ten columns per inch horizontally) any data points falling into one character position (cell) at the map scale chosen are averaged, using the arithmetic or geometric mean, as appropriate. The symbols printed on the map vary in grey-level, the progressive darkening being achieved by overprinting. The print character chosen corresponds to the class interval into which the averaged value falls. The cell-averaged values are smoothed prior to print-out by a variant of the moving average technique, to eliminate the 'noise' caused by sampling and analytical errors as well as small-scale geochemical fluctuations.

As mentioned previously, this research deals chiefly with the interpretation and classification of regional geochemical patterns of As in active stream sediments from south-west England.

Attention was also given to the patterns of Cu, Pb, Sn and Zn (due to the genetic ties between these elements and As) as they appear in the mineralised ores of south-west England.

In addition, Fe and Mn patterns were studied in an attempt to determine whether or not they played a significant role in the dispersion and distribution of As and the other selected trace-elements in active stream sediments from the area.

The compilation of the maps used in the interpretation of the already mentioned patterns was done using class intervals, so that ten per cent of the data values fell into each class. These percentile values were based on the data following elimination of the top one per cent to avoid distorting effects of outliers on the interpretation of the percentile intervals over the rest of the data range. With the large number of samples used, this effect was eliminated (Howarth, Personal Communication 1973).

In order to facilitate the interpretation of the data, the maps were smoothed by moving average methods which greatly accentuate the regional geochemical trends present in the raw-data.

The interpretation and classification of geochemical patterns has been performed by rigorous comparative studies between the smoothed grey scale map and a geological overlay at the same scale (10 miles to the inch). Physiographic, pedological and climatological maps of the region were also used as a complement to the latter. Secondary environmental and contamination effects were also taken into consideration. Features of the element distributions are presented in Figs. 6.1 to 6.7.

6.2 INTERPRETATION OF PATTERNS

As stated before, the advantage offered by the type of geochemical map used in the interpretation and classification of patterns is that it shows very clearly all the trends that might exist in the sub-anomalous areas. Thus facilitating the recognition of contrast between low and high patterns as displayed in the geochemical map of the region.

6.2.1 Arsenic (Fig. 6.1)

The regional distribution of As demonstrates a marked differentiation in the region. High values located in West Devon and Cornwall exhibit an evident contrast with the low to moderate values mainly distributed in North Devon, West Somerset and in some scattered areas along the northern and southern coasts of Cornwall, and in the southern coast of Devon.

High As levels show a strong relationship with the mineralised and contaminated areas of the region, although some individual high anomalies occur in areas of relatively low As concentrations. The highest As values are mainly concentrated in the mineralised-contaminated low lands between Ludgvan and Porthleven, and Uny Lelant and St. Day in the Gwinear Mounts Bay and Camborne-Redruth-St. Day mineralised districts of West Cornwall. In East Cornwall and West Devon, the highest As concentrations are found between the Liskeard and Callington-Tavistock districts. Less extensive areas of high As values are located between the St. Austell and Bodmin Moor granites, and around Dartmoor. Anomalous As levels are found within the Dartmoor granite south of Birchy Lake, and in the area around Tintagel in North Cornwall.

6.2.2 Copper (Fig. 6.2)

Cu patterns show clearly distinguishable distribution in the region. High Cu concentrations follow a north-east south-west trend in a close relationship with the mineralised belt of Cornwall and Devon. However, those high levels extend laterally in some places beyond the mineralised area. The most prominent feature of Cu distribution is the broad area of high levels of this element located in the Callington-Tavistock, and Liskeard mineralised districts, where significant Cu values extend away to the south of these districts. In the Wadebridge district high Cu levels are found in the northern part of Bodmin Moor and a broad area of these levels extends from the southern border of the moor southward to the St. Just mineralised district. In North Devon high Cu values are found in a limited area south of Ilfracombe.

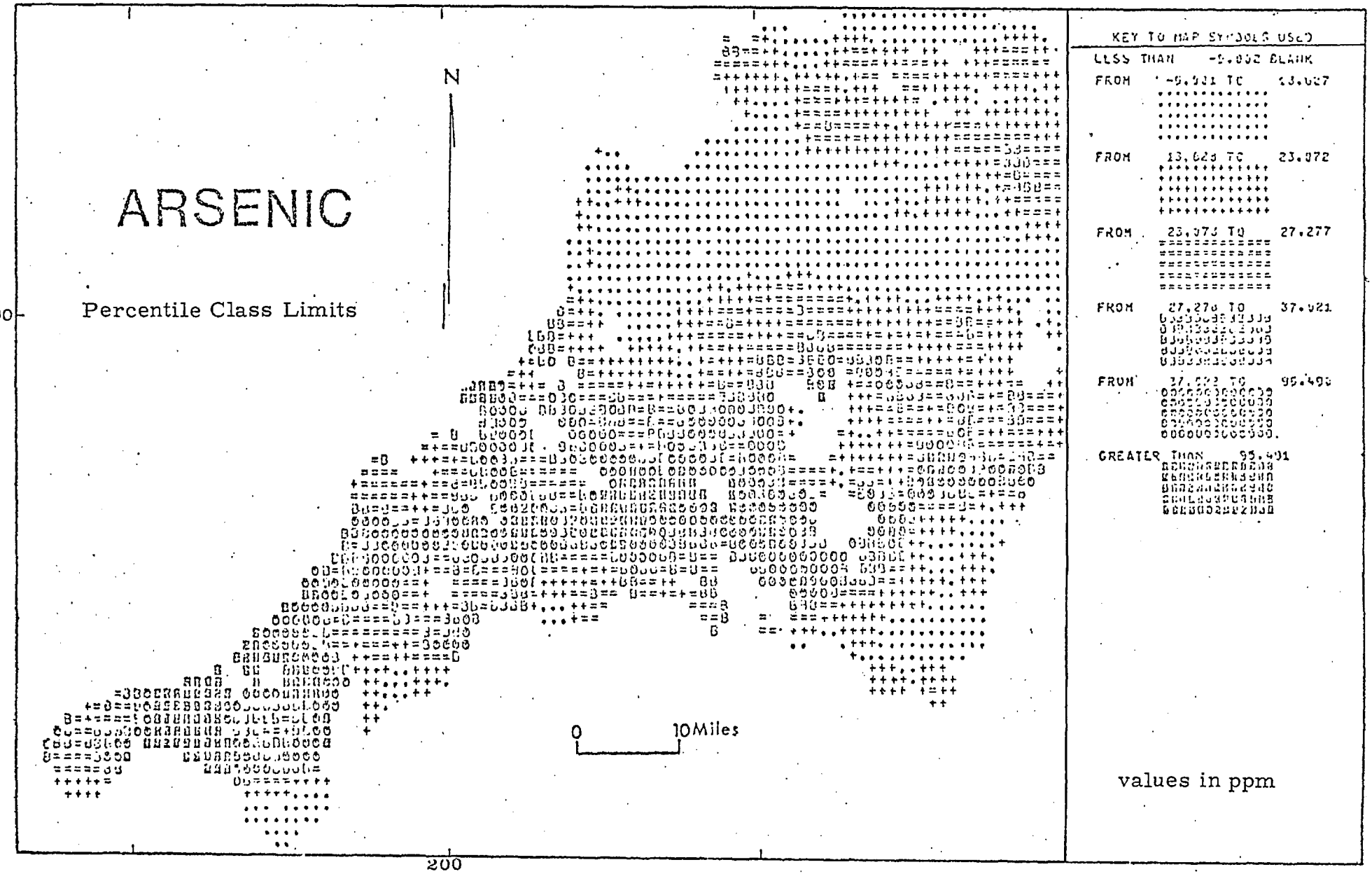


Fig. 6.1 REGIONAL STREAM SEDIMENT RECONNAISSANCE IN SOUTH-WEST ENGLAND

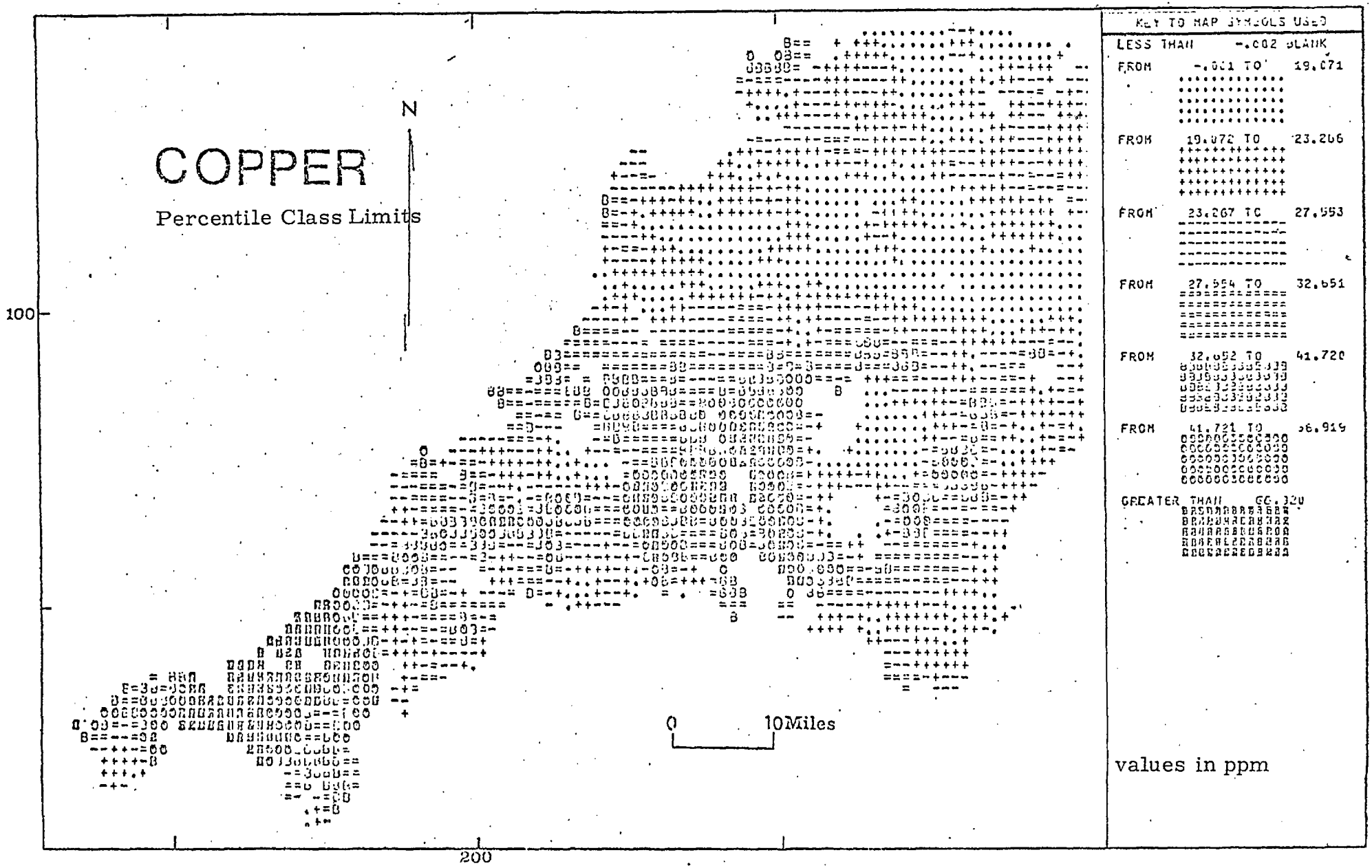


Fig. 6.2 REGIONAL STREAM SEDIMENT RECONNAISSANCE IN SOUTH-WEST ENGLAND

Devonian and Upper Carboniferous sediments display low Cu concentration whilst the Lower Carboniferous and the Permian (in the west) sediments show slightly higher levels. Dartmoor, Bodmin Moor and St. Austell granitic masses present low Cu values whilst Carnmenellis granite exhibits high levels which extend southward into the Lizard Peninsula.

6.2.3 Iron (Fig. 6.3)

Extensive areas of high Fe content can be distinguished principally around the Dartmoor granite and in the northern part of St. Austell granite. The latter extends northward to the western and northern areas of Bodmin Moor. Less extensive areas are found in North Devon and West Somerset, in the northern part of the Carnmenellis granite, and in the south-east of the Lizard Peninsula.

The highest Fe levels are mainly located in zones of known Fe mineralisation such as those of the Wadebridge and St. Austell mineralised districts where the occurrence of Fe bearing-lodes has been reported.

In the Camborne-Redruth-St. Day mineralised district the high Fe values may reflect contamination chiefly derived from the gossans of sulphide-bearing lodes. On the other hand, those located in and to the south of the Callington-Tavistock district may have originated because of contamination derived from mineralisation.

Most of the high Fe concentration in and around Dartmoor and in North Devon and West Somerset may be related to Fe-bearing-lodes. Although in the eastern border of Dartmoor, these values seem to be connected with basic rocks and Lower Carboniferous sediments. Low Fe levels are found over the Land's End, Carnmenellis, and Bodmin Moor granites, and over Westphalian and Permian sediments. Slightly higher values are located in the Dartmoor granite and in the Devonian and Namurian sediments.

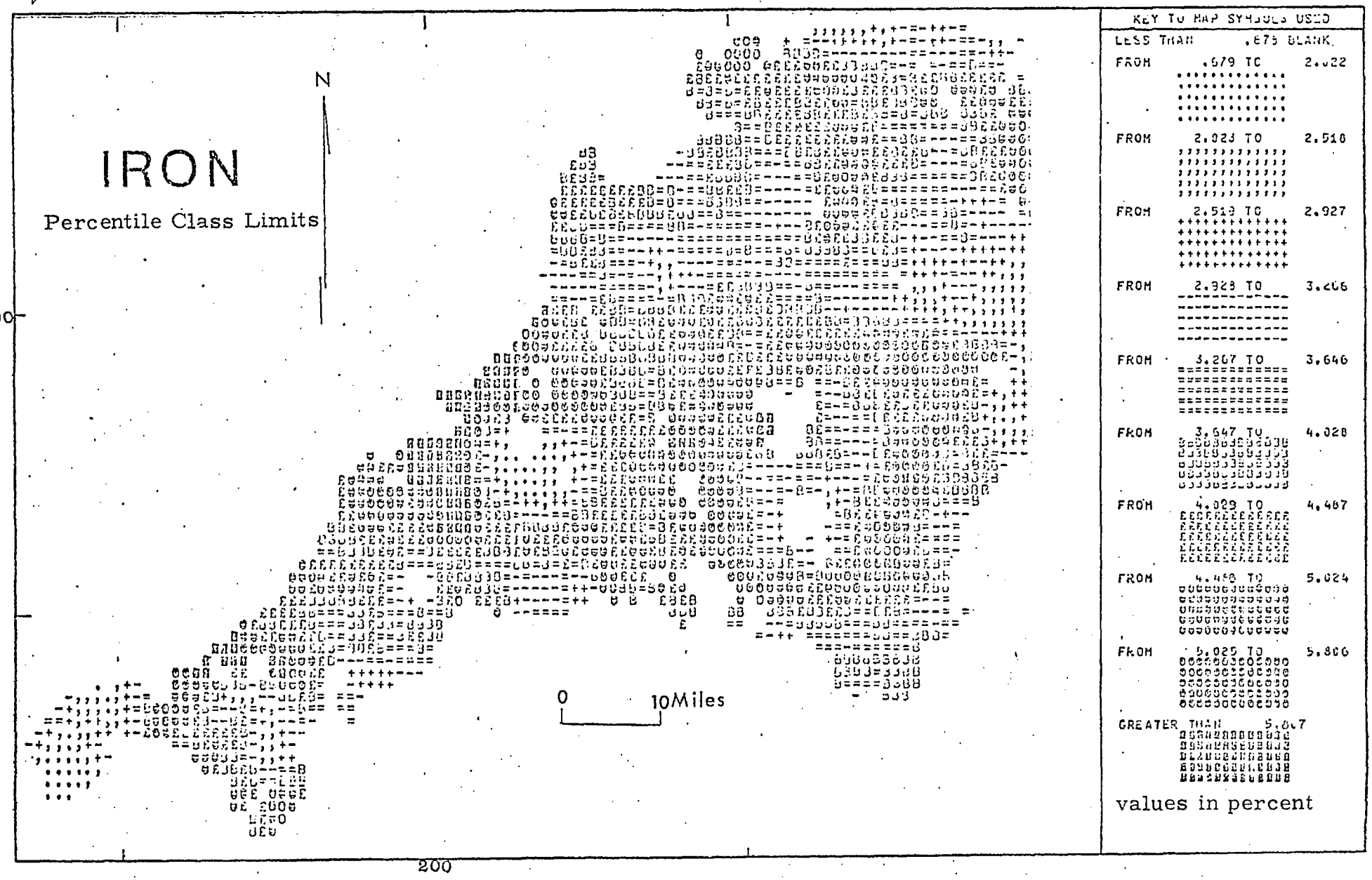


Fig. 6.3 REGIONAL STREAM SEDIMENT RECONNAISSANCE IN SOUTH-WEST ENGLAND

6.2.4 Lead (Fig. 6.4)

Moderate to high Pb levels are located in West and South Devon, and in Cornwall, whilst low values are found in North Devon and West Somerset. High Pb concentration, however, can be found in some scattered areas in the western part of North Devon east of Morte Bay, and in the south of Ilfracombe where these levels may be related to the mineralised lodes situated between Ilfracombe, Barnstaple and Bideford. The highest values are mainly concentrated in East and West Cornwall and West Devon. In West Cornwall these levels are closely related to the rich Sn-Cu mineralised areas of the Gwinear, Mounts Bay and Camborne-Redruth-St. Day districts, and to the Zn-Pb mineralisation of the St. Agnes district. In East Cornwall and West Devon high Pb values are especially related to the mineralised zones of the Callington-Tavistock district, while in the western area of Bodmin Moor they are related to the north-south lead-bearing-lodes of the Wadebridge district. Less extensive areas of high Pb concentrations can be found on the north-east and north-west borders of Dartmoor granite, and in the north-east, to the east of the St. Austell granite. All these values are related to Pb-Zn and Cu mineralisation. Some high Pb patterns seem to have been created by contamination in urban centres such as in Plymouth and Exeter. Those located in the latter may be related to the mineralised ores of Newton, St. Cyres and Upton Pyne (north-west and north of Exeter).

Vis-à-vis bed-rock geology the distribution of Pb patterns is irregular. Low Pb values are mainly concentrated in Upper Carboniferous, Devonian and Permian sediments of North Devon and West Somerset. Slightly higher levels are concentrated over the Lower Carboniferous and Devonian, and other geological units of the southern and northern coasts of Cornwall. Over the Dartmoor and Carnmenellis granites, relatively high levels are found being highest in the eastern part of Carnmenellis which can be related to the mineralised lodes of this area.

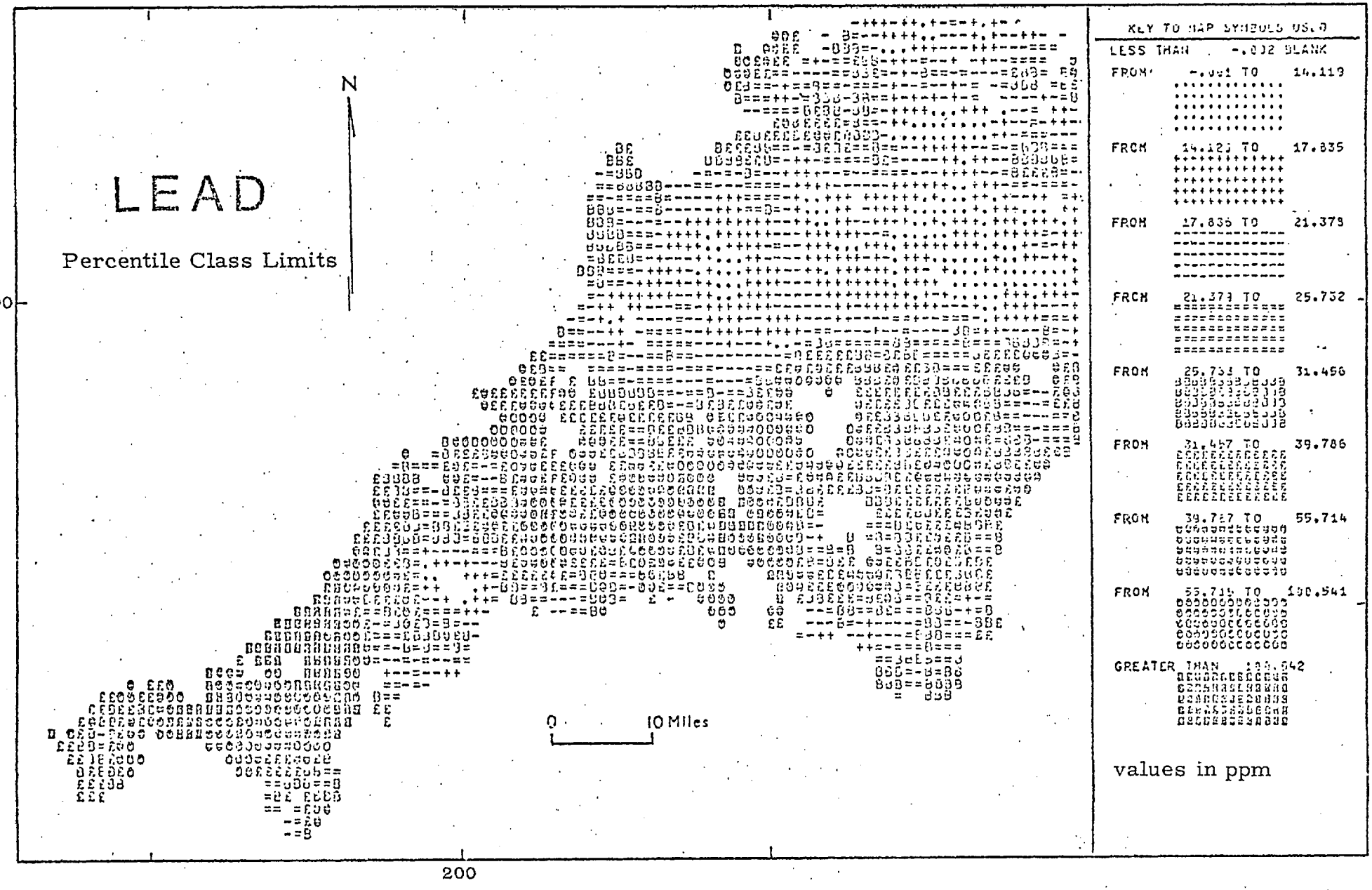


Fig. 6.4 REGIONAL STREAM SEDIMENT RECONNAISSANCE IN SOUTH-WEST ENGLAND

6.2.5 Manganese (Fig. 6.5)

High Mn values are mostly located in North and West Cornwall, West Devon and in areas surrounding the Dartmoor granite. In West Cornwall high Mn concentration seems to be related to poorly drained soils, although in the northern part of this area high levels lay over Fe-Mn bearing-lodes such as the Perran Iron Lode and the Indian Queens lodes of St. Agnes and St. Austell districts, respectively. In the northern area of the St. Austell Moor high Mn values are related to mineralised areas where Mn ores occur as oxide and silicate, probably as a result from alteration of siderite.

Occurrences of high levels in the northern zone of Callington-Tavistock district show a close relationship with the cherty beds of Culm Measures, with the basic rocks, and with the Mn ore deposits of this area (Howarth, 1971). On the eastern and western borders of Dartmoor granite high Mn values are related to both Mn mineralisation and basic rocks although earlier studies in these areas have reported those values to be connected to a secondary environment. (Horsnail, 1968; Nichol et al. 1971).

In North Devon and West Somerset the highest values are also connected to Mn bearing-lodes. Granitic masses, Devonian, Upper Carboniferous and Permian sediments show low Mn concentrations.

The Lizard Peninsula presents significant levels especially in the eastern part of the area.

6.2.6 Tin (Fig. 6.6)

The distribution of Sn reveals two well defined patterns: a long broad zone of high Sn values extends along the line of the mineralised belt of the region, whilst the areas of barren bed-rock geology show uniform Sn values.

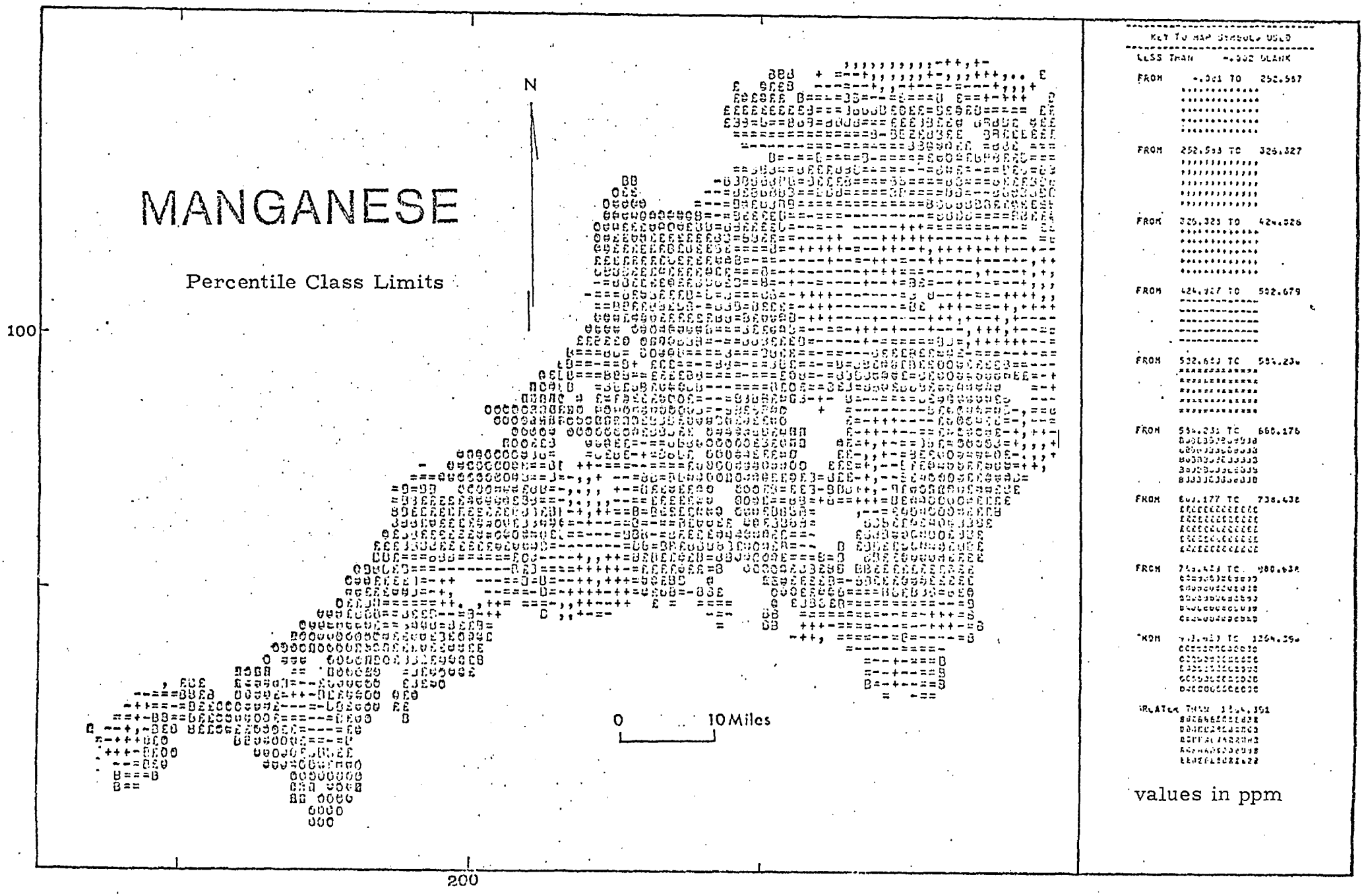


Fig. 6.5 REGIONAL STREAM SEDIMENT RECONNAISSANCE IN SOUTH-WEST ENGLAND

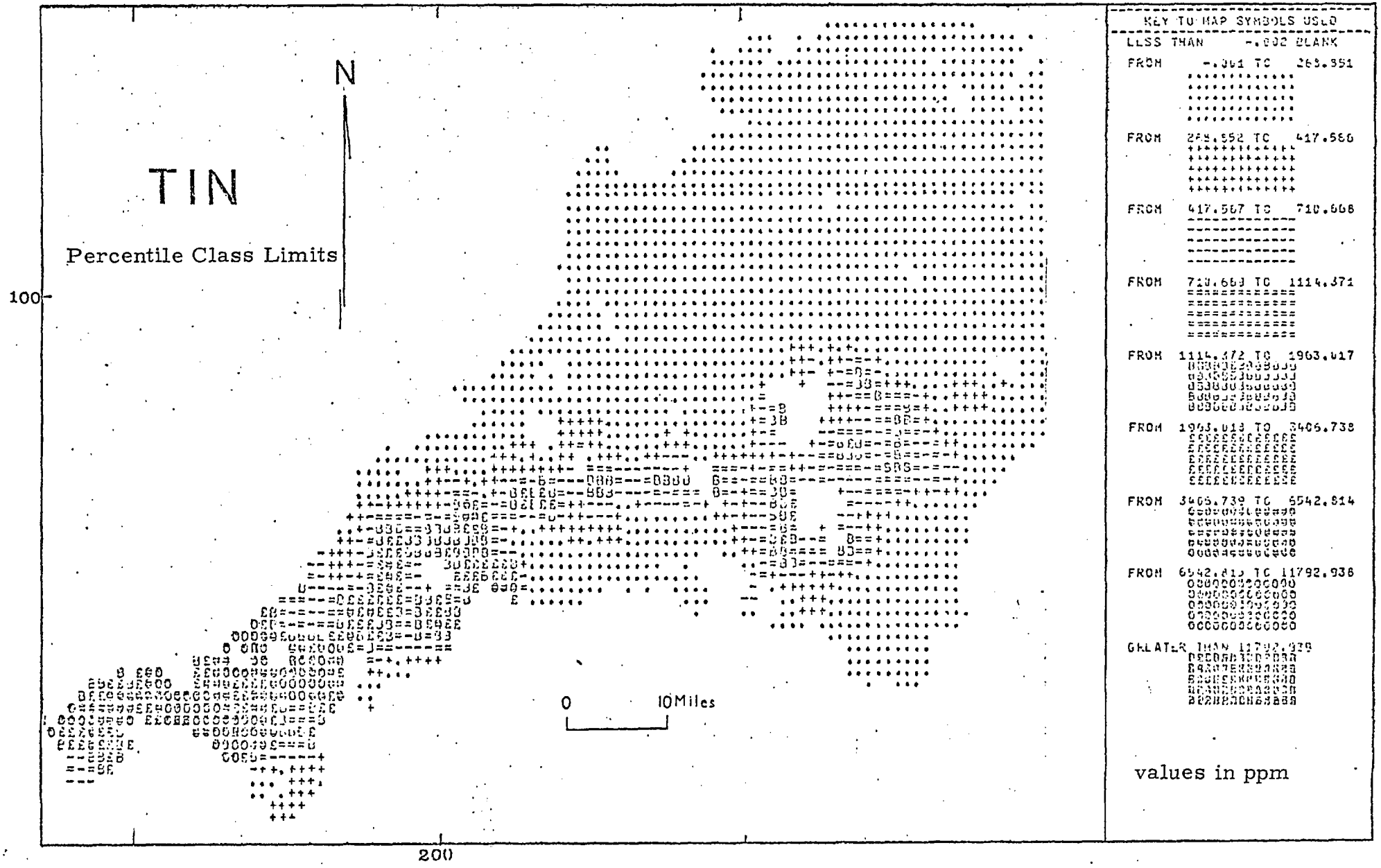


Fig. 6.6 REGIONAL STREAM SEDIMENT RECONNAISSANCE IN SOUTH-WEST ENGLAND

The highest Sn levels are located close to areas of Sn mineralisation. The largest areas of high Sn content are found in Mid and West Cornwall where these values extend mainly southward beyond the Sn mineralised zones. According to Dunlop (1973) this extension has been interpreted as being a detrital dispersion pattern formed since the exposure of the granitic bodies during the Permian Period.

With the exception of some areas in Dartmoor, all the granitic masses are associated with high Sn values. The Devonian, Carboniferous and Permian sediments exhibit uniform low Sn patterns. Slightly high levels are located in the central part to the east of the Lizard Peninsula.

6.2.7 Zinc (Fig. 6.7)

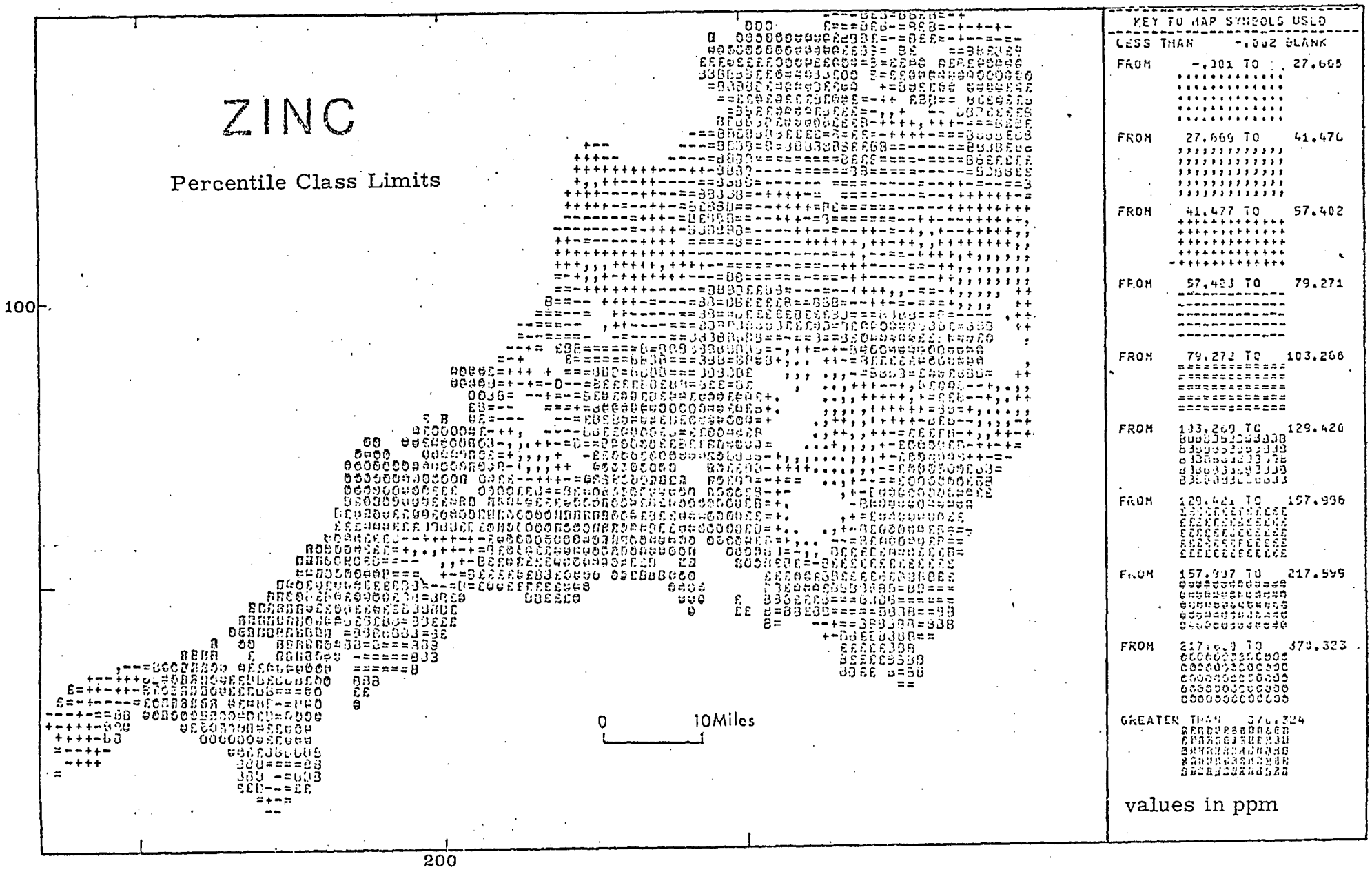
The main features of the distribution of Zn in stream sediments from south-west England are: the occurrence of high Sn levels in zones of Sn-Zn and Pb-Zn mineralisation, and the moderate high values over barren country-rock surrounding the granitic masses.

In North Devon and West Somerset, zones of high Zn concentration seem to be related to Pb and Cu-Pb mineralisation such as at West Challacombe and Combe Martin mines where the presence of blend has been reported (Dines, 1956). Most of the Upper Carboniferous and Permian sediments, and the granitic masses are characterised by low Zn content, while Devonian and Lower Carboniferous sediments are characterised by higher values.

6.3 CLASSIFICATION OF GEOCHEMICAL PATTERNS OF ARSENIC

Interpretation of the geochemical patterns of As in stream sediments of south-west England has indicated the existence of a marked contrast in the distribution of this element.

A broad zone of high As content mostly bearing a close relationship with mineralised and contaminated areas has been distinguished in contrast to zones of low levels which are related to the barren-earth material of the region.



6.7 REGIONAL STREAM SEDIMENT RECONNAISSANCE IN SOUTH-WEST ENGLAND

On the basis of the results of the above interpretation, complemented by a brief field examination of some areas, an attempt has been made to classify these patterns in order to facilitate a better understanding of their significance.

For this purpose the geochemical patterns have been classified into two main groups:-

A Gecchemical background, and

B Anomalous patterns

A Geochemical Background

Geochemical background is determined in terms of the normal geochemical distribution of As in relation to the barren bed-rock geology of the region (Fig. 6.8). As the concentration limits (percentiles) displayed in the area are not uniform, they have been grouped into three classes: low, medium and high background concentrations.

Although some geological units show more or less uniform background levels, most of them display an indiscriminate distribution (low, medium and high levels within the same unit) which makes it difficult to determine if these levels reflect the real content of the element in the parent-rock or whether they were affected by some sort of secondary factors such as the modifying influences of topography, the degree of weathering, the nature of drainage, etc. This problem is mainly found in the southern coastal areas of Cornwall and Devon where the distribution patterns seem to bear a zonal arrangement in a close relationship with the drainage system and topography. Zones of higher background levels mainly occur down drainage from the anomalous areas. Because of this fact, it is obvious that the normal background concentration of the parent-rock underlying those zones have been affected by contamination effects derived from the anomalies.

North Devon and West Somerset are the only areas where it is possible to delineate to some degree the geochemical features of the bed-rock geology. Perceptible associations of low background levels with

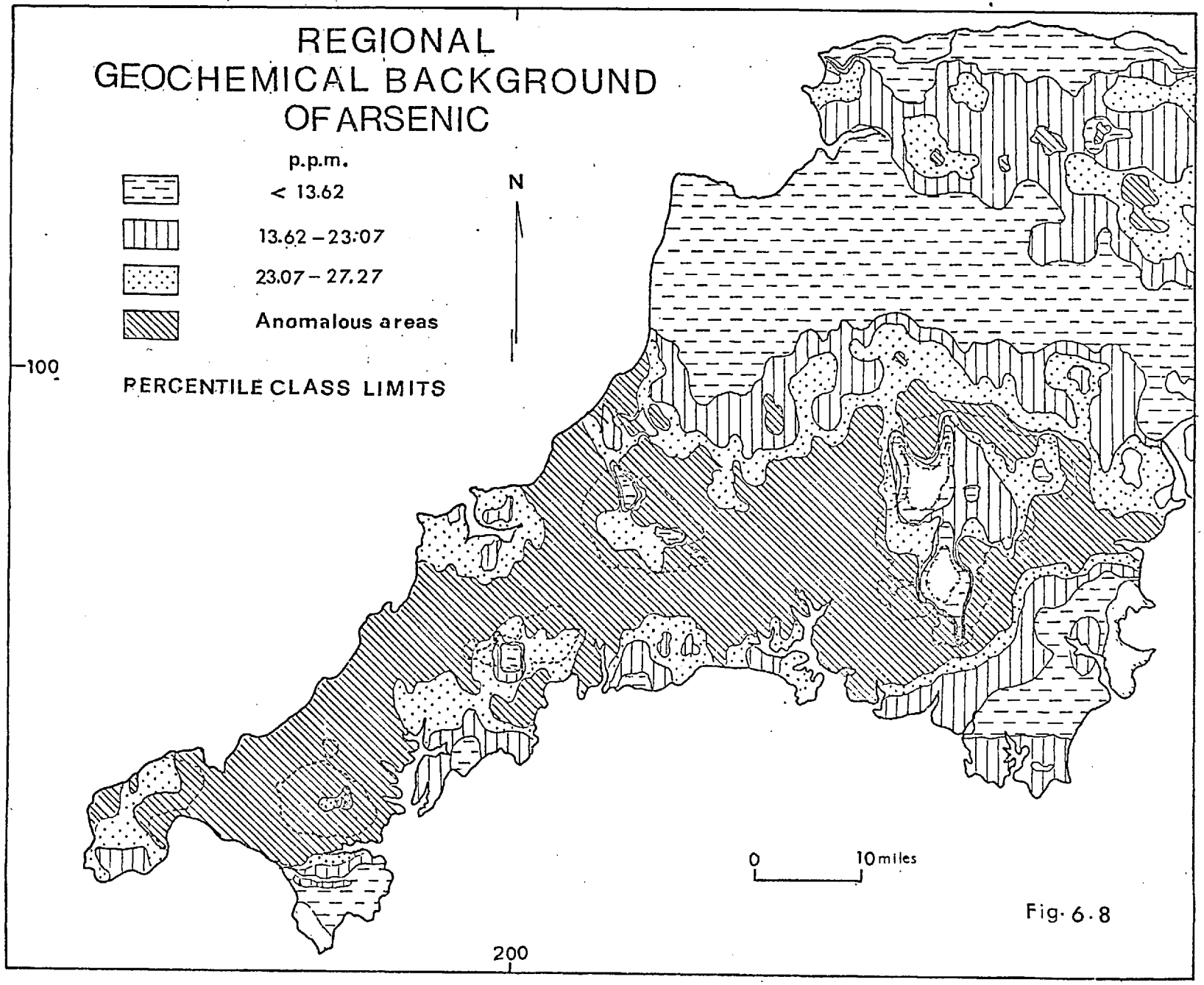

REGIONAL
GEOCHEMICAL BACKGROUND
OF ARSENIC
p.p.m.
< 13.62
13.62 – 23.07
23.07 – 27.27
Anomalous areas
PERCENTILE CLASS LIMITS
N
100
200
0
10 miles

Fig. 6.8

the Lower Devonian and Westphalian sediments differ from the association of medium values with the Middle-Upper Devonian, Namurian and Permian rocks.

Distribution of geochemical patterns of As (background levels) in stream sediments from the Dartmoor granite bear a close relationship to the soil types and topographic relief of the area (Fig. 6.8a). Low background concentrations are found in the highest areas of the moor (1400 feet O.D.) which are covered by poorly drained peaty soils. Medium background levels are located in areas between 800 and 1400 feet O.D. covered by peaty gleyed podzol. High background levels are mainly found in areas between 400 and 800 feet O.D. where the soils are freely drained, brown earths.

B Anomalous Patterns

The high As values which are in clear contrast with the geochemical background already established are referred to here as anomalous patterns. (Fig. 6.9) Interpretation of the geochemical patterns in stream sediments in south-west England showed that most of the anomalous patterns of As are related to the following: the mineralised belt, contamination, alluvial deposits and to areas where neither mineralisationnorcontamination have been reported before.

On the basis of these results, suspected anomalies have been classified according to:

1 Mineralisation
   a) Known mineralisation
   b) Possible mineralisation

2 Contamination
   a) Mining
   b) Smelters

3 Geology
   a) Metamorphic aureole
   b) Undefined sources

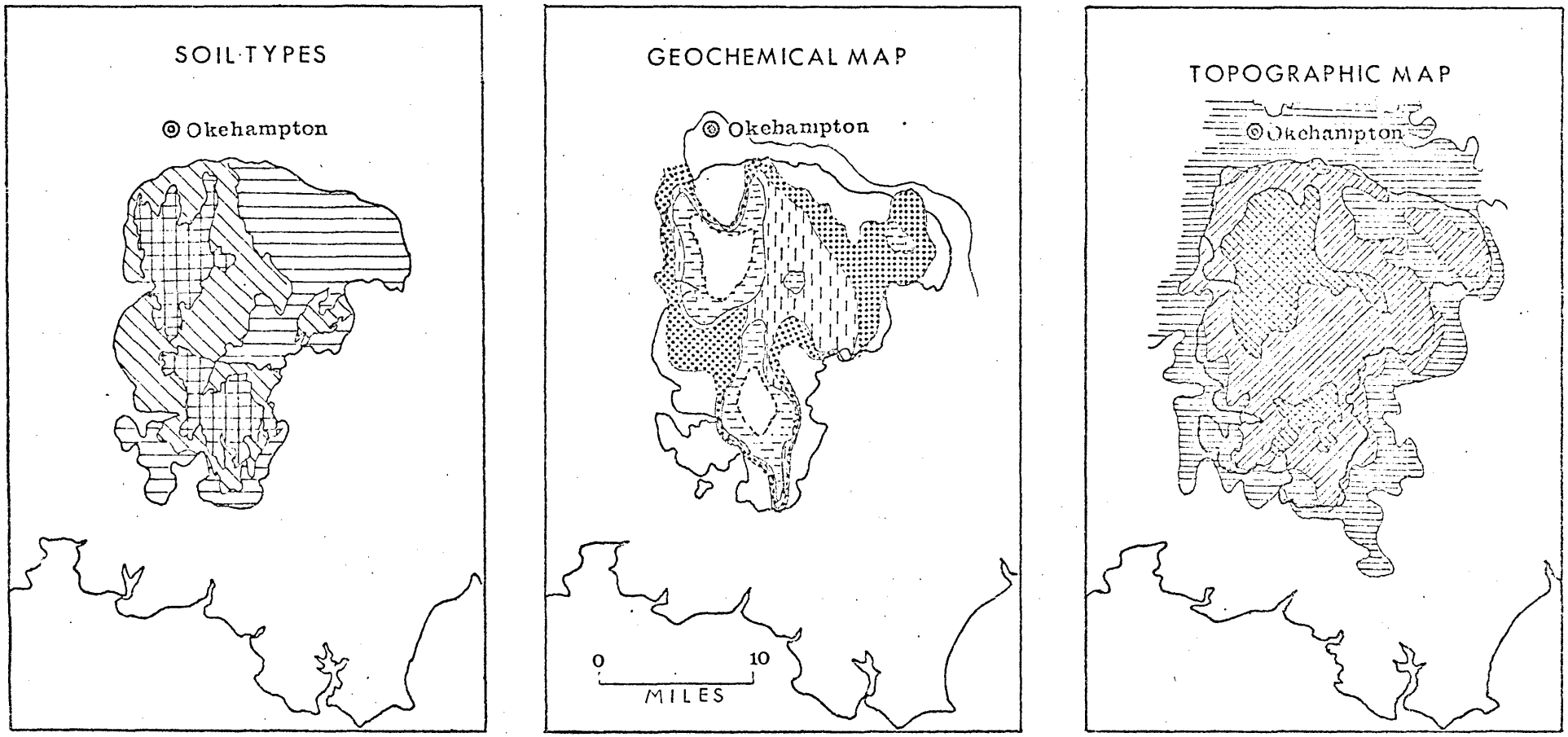


FIG. 6.8a. DISTRIBUTION OF ARSENIC IN DARTMOOR GRANITE RELATED TO SOILTYPES AND PHISIOGRAPHY. (1) POORLY DRAINED SOILS; (2) PEATY GLEYED PODZOL; (3) BROWN EARTHS.

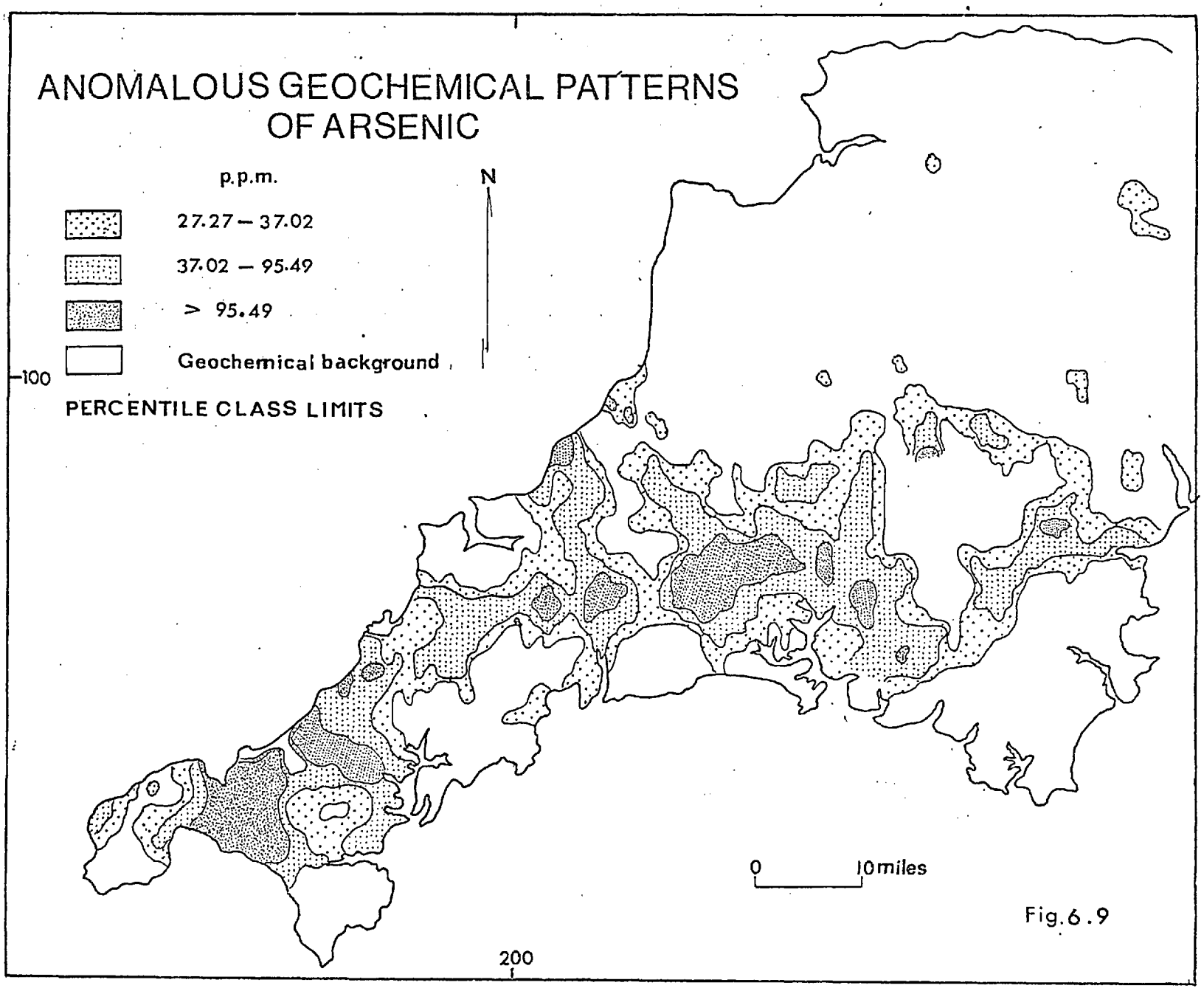

ANOMALOUS GEOCHEMICAL PATTERNS
OF ARSENIC
p.p.m.
27.27 – 37.02
37.02 – 95.49
> 95.49
Geochemical background
100
PERCENTILE CLASS LIMITS
N
0
10 miles
200

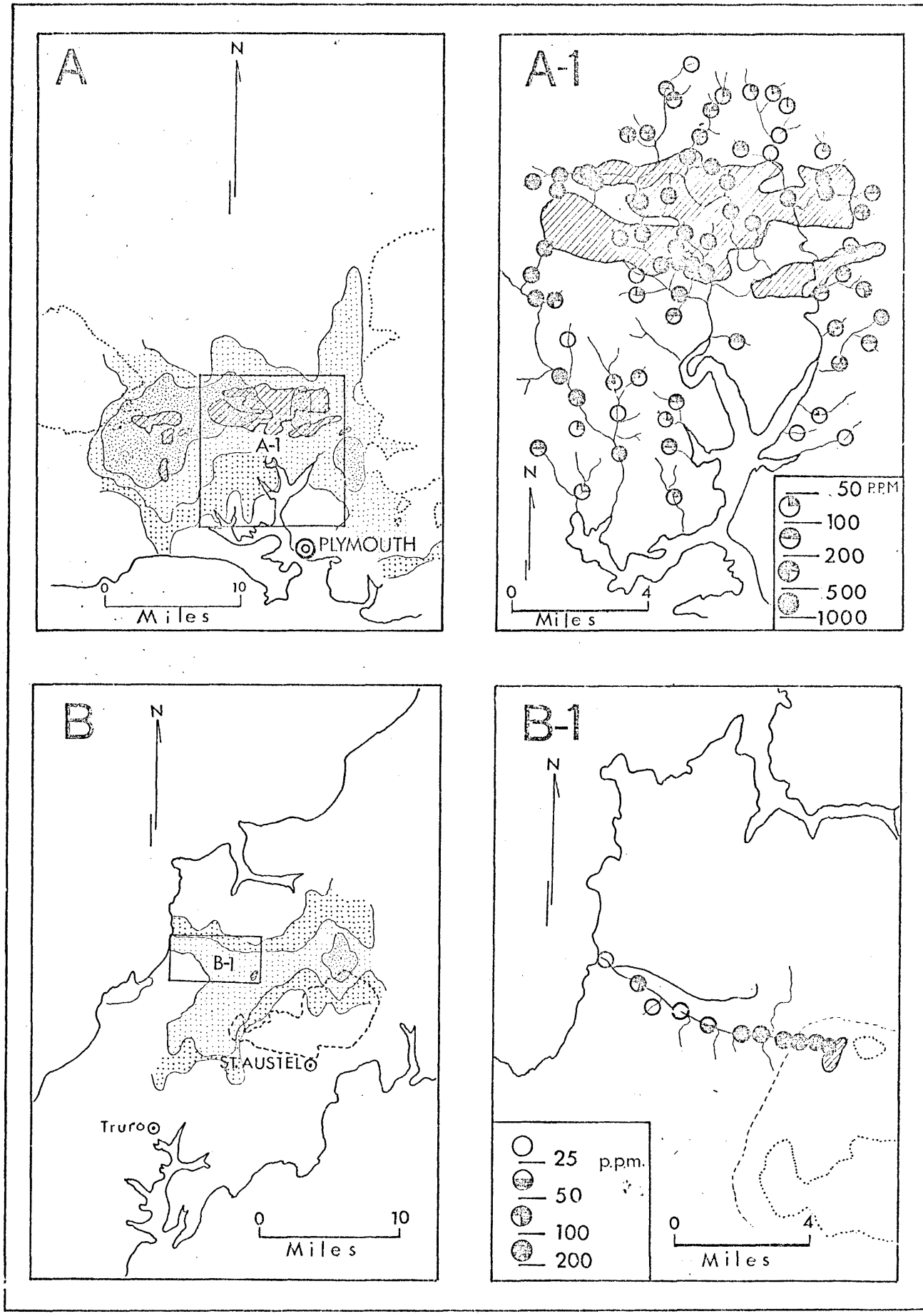
Fig. 6.9

Areas representing each type of anomaly have been selected from the smoothed grey scale map and they are presented in figures 6.10 to 6.12 (A, B, C, D and E).

Each anomaly is accompanied by a map (on a magnified scale) of the values of individual stream sediment samples expressed in parts per million (A.1, B.1, C.1 and 2, D.1 and E.1 in the figures). The purpose of this being to further clarify and explain the significance of the types set forth on the smoothed grey scale map. Thus in the Callington-Tavistock mineralised district where a broad As anomaly appears closely related to mineralisation (A and D) geochemical data from the individual stream sediment samples revealed that anomalous As patterns have originated in addition to As mineralisation-bearing areas (A.1), from contamination from mine dumps and smelters (D.1), and probably from high As background bed-rock. On the other hand, the anomalous As values in a stream from Anomaly B seem to bear a close relationship with As mineralisation (B.1). In the Anomaly C, in which two areas appear highly enriched in As content (Corscombe and Dartmoor) only the values from one of the streams (Dartmoor Area, C.2) is probably the result of contamination derived from mining activities in areas located up-stream in the western flank of the Steepertor Tor Hill. The anomalous concentrations in the other streams from this anomaly were classified as related to possible mineralisation. The varied range of anomalous As levels surrounding the Dartmoor granite (Anomaly E) were confirmed by examination of the As values in samples from the numerous streams draining the area. Although most of them are clearly in close relationship to mineralised areas, there exists broad zones of moderately high values which seem to indicate high background bed-rock.

6.4 SUMMARY

The most outstanding features of the regional geochemical distribution of As and selected trace-elements in stream sediments from south-west England are summarised below:



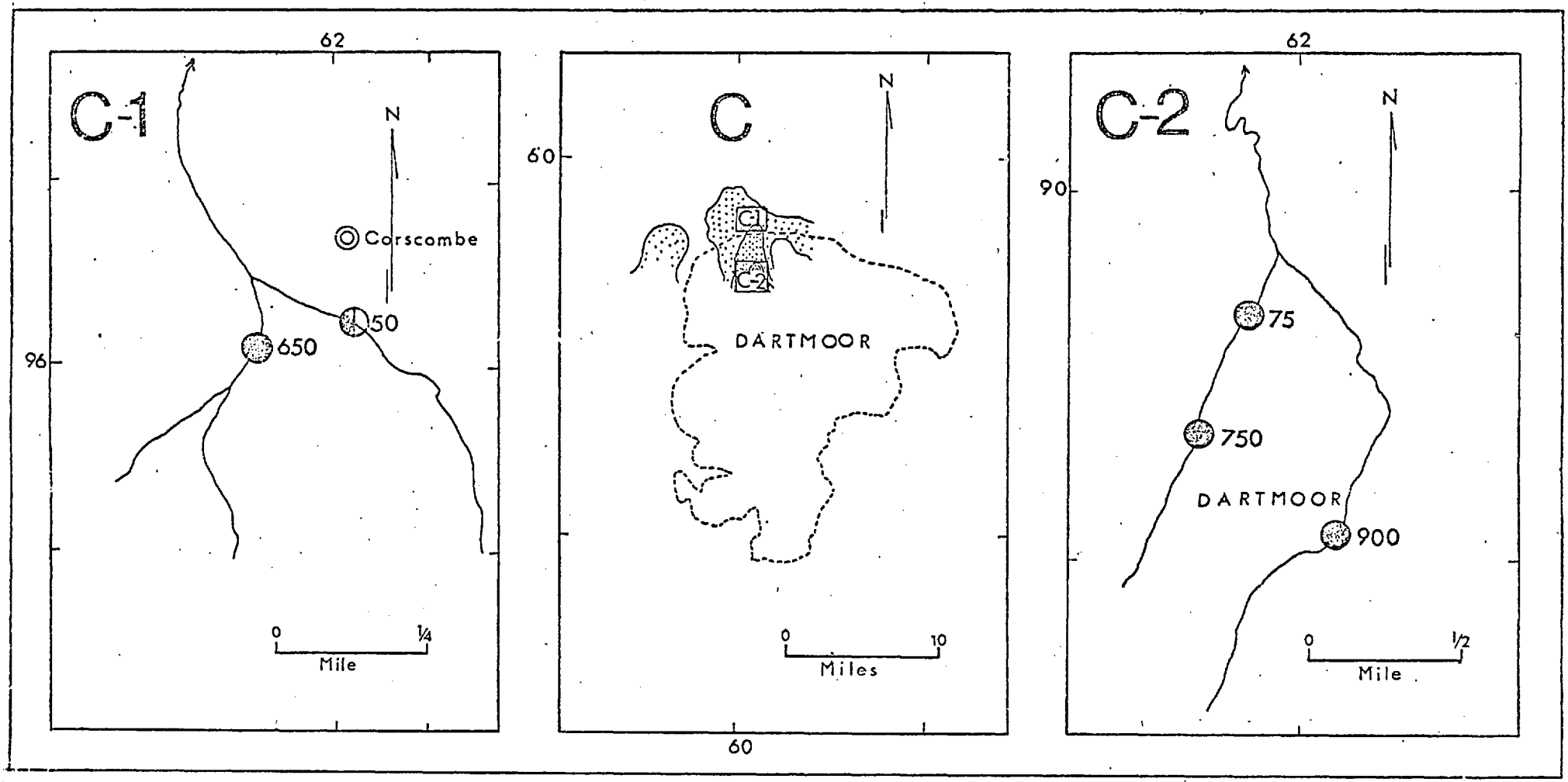
Arsenic mineralization

27 37 95 >95 p.p.m.

Arsenic Anomalies (Percentile).

A & B Grey scale map; A-1 & B-1 Values for indivual stream sediment samples.

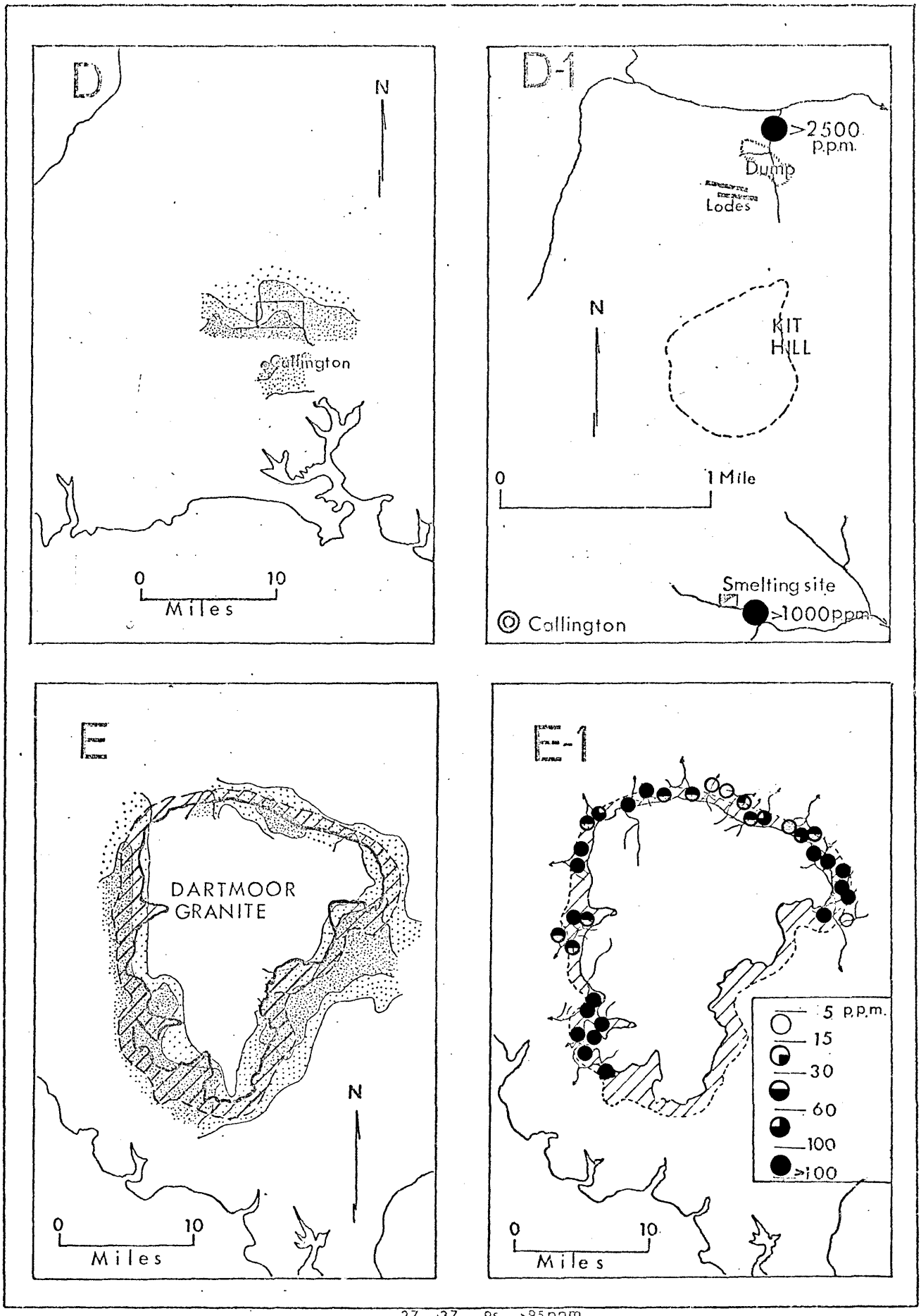
Fig.6.10. ANOMALIES OF ARSENIC RELATED TO ARSENIC MINERALIZATION



27 37 95 >95 p.p.m.

Anomalies of arsenic; C Grey scale map; C-1 & C-2 Values for individual stream sediment sample(p.p.m.).

Fig.6.11. ANOMALIES OF ARSENIC RELATED TO POSSIBLE MINERALIZATION



Metamorphic aureole; 27 37 95 >95 p.p.m. Anomalies of arsenic.

D & E Grey scale map; D-1 & E-1 Values for individual stream sediment samples.

Fig. 6.12 ANOMALIES OF ARSENIC RELATED TO CONTAMINATION AND METAMORPHIC AUREOLE

Geochemical Background

Granitic masses are characterised by low Cu, Fe, Mn, Zn and to a lesser extent As levels, where high Pb and Sn values are located.

The Lower Devonian sediments display low As, Cu, Pb and Mn patterns, these elements being higher in the Middle-Upper Devonian of North Devon.

As, Cu, Fe, Pb, Mn and Zn exhibit high levels in the Lower Carboniferous showing a general decrease northward on passing to the Upper Carboniferous.

Over the Permian sediments almost all elements are uniformly low, the exception being the high As and Mn levels located in the western part, around Exbourne and Hatherleigh.

Over the Dartmoor granite the distribution of As shows a close relationship with the topographic features, and with the soil types of the region.

Over the Lizard Complex As is low whilst Cu and Sn show higher levels.

Anomalous Patterns

High anomalous patterns of As, Cu, Pb, Sn and Zn are mainly related to mineralised and/or contaminated areas of the region.

Fe and Mn anomalies are connected with the occurrence of mineral ores of these elements and in some restricted areas they are related to sulphide ores, to contamination and to secondary environments.

Anomalous As concentrations found in small areas in the Dartmoor granite, in Corscombe and in the southern part of Hatherleigh, appear to reflect undiscovered mineralisation in

the case of the Corscombe and Dartmoor areas, whilst in the Hatherleigh area, the origin of these high As levels seems to have a lithological relationship.

The high As, Mn, and Fe values around Tintagel were found to be related to the abundant pyrite mineralisation occurring in the grey and black slates of the Tintagel Group at Bossiney Haven (Lower Carboniferous).

High As and to a lesser extent the Zn and Pb concentrations which surround the granitic masses are associated with the metamorphic aureole.

CHAPTER 7

GEOCHEMICAL INVESTIGATIONS IN SELECTED AREAS

7.1 INTRODUCTION

The mineralised area of south-west England can be represented by a wide, metal-rich belt with zones of apparent barren land in it. A high concentration of mineral-veins primarily distributed around the granite bodies in addition to a number of former mining and smelting sites, have contributed to the broad pattern of high metal values in the region. Consequently, the interpretation of geochemical patterns of trace-elements, as displayed in the geochemical Atlas of the region, showed that most of the regional, anomalous, distinguishable metal patterns bear a close relationship to the mineralised belt, to contamination arisen from mineral dumps and smelting sites and to some alluvial deposits. However, some anomalous patterns lie in areas where neither mineralisation, nor contamination have been previously recognised.

As As was found to be one of the outstanding anomalous elements, and since it was widespread in the region, investigations to determine the nature of the distribution, and the origin of this element were considered worthwhile. The results of the interpretation of regional geochemical reconnaissance data have established that:-

1 Anomalous patterns of As are strongly related to mineralised and/or contaminated areas, and to lithological units surrounding the granitic bodies;

2 The existence of some scattered anomalies which are located in areas of low regional As levels, and

3 The normal distribution of As in relation to barren material of the region does not bear a clear relationship with the bed-rock geology, but it appears that it has been mainly distorted by secondary anomalous areas and industrial activities, soil types, etc.

On the basis of these findings a regional geochemical investigation was considered desirable in order to:

1 Establish the relationship between drainage sediment reconnaissance patterns of As and the geology of the region;

2 Establish the significance and origin of As anomalies unrelated to mineralisation or contamination that surround the granitic bodies, and

3 To elucidate, to some degree, the significance of some anomalies that might be related to possible mineralisation, and to contamination.

For these purposes areas were selected taking into consideration the following features:

1 Occurrence of extensive and varied geological units;

2 No evidence of known mineralised areas and subsequently contamination, and

3 Existence of a wide range of primary and secondary dispersion patterns.

These criteria were found in zones within Devon, to the north and south of Dartmoor granite. In these areas, the distribution of As and selected trace-elements in soils and in some stream sediments and rock samples were investigated.

7.2 DEVON AREA

7.2.1 Location

The areas chosen for the regional geochemical investigations are entirely located in the County of Devonshire, lying between the co-ordinates 250,000 to 280,000 E, and 47,000 to 106,000 N of the National Grid Reference System (Fig. 7.1).

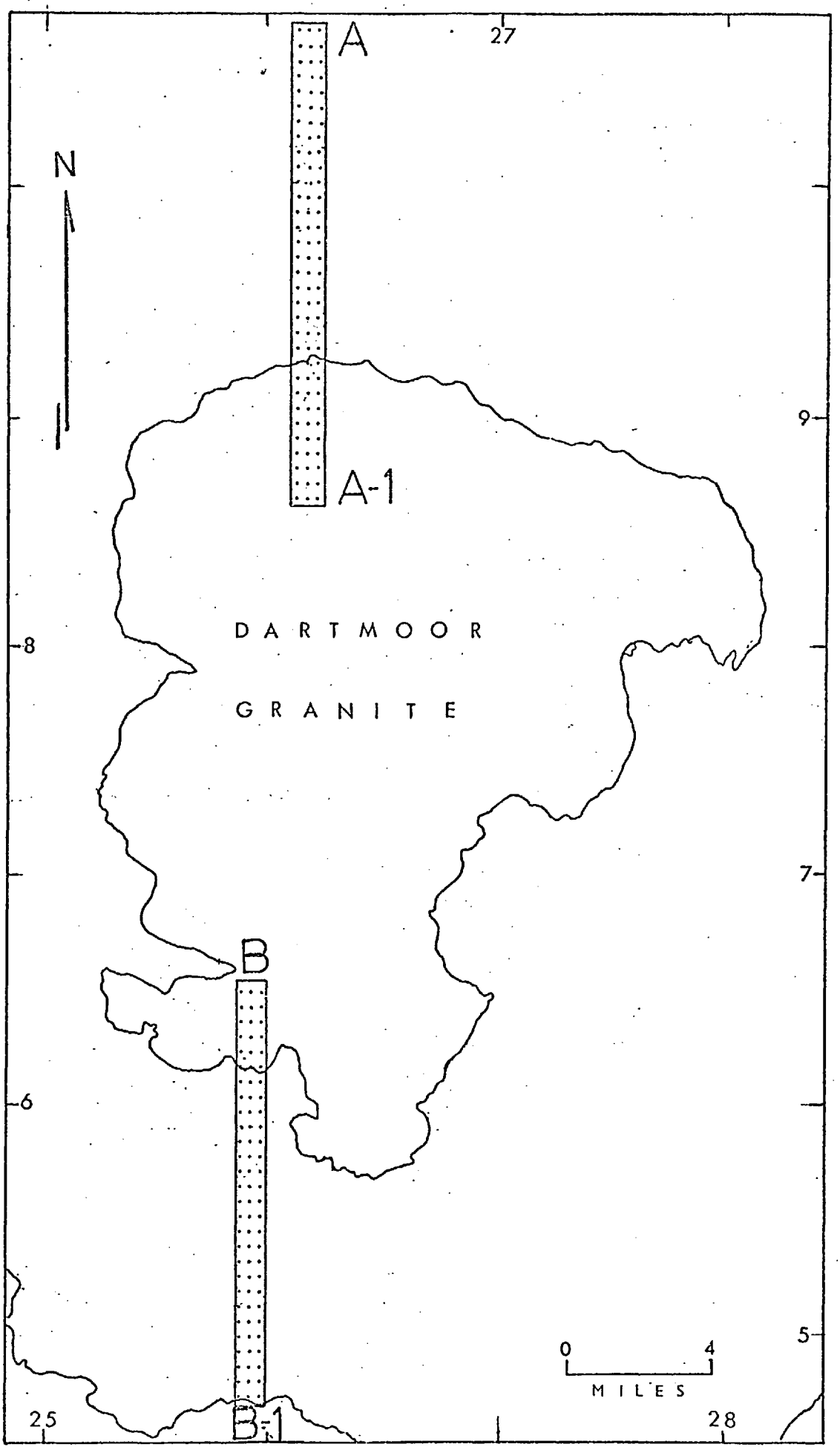


FIG. 7.1. REGIONAL INVESTIGATION AREAS

7.2.2 General Geology

The central part of the area is underlain by the Dartmoor granitic mass which is surrounded by sediments of Devonian and Carboniferous age. Permian rocks underlie a narrow east-west strip in the northern part of the area, and some outcrops of basic intrusive igneous rocks are found mainly bordering the granitic body. The major lithological units of the area are presented in Fig. 7.2 and Table 7.1.

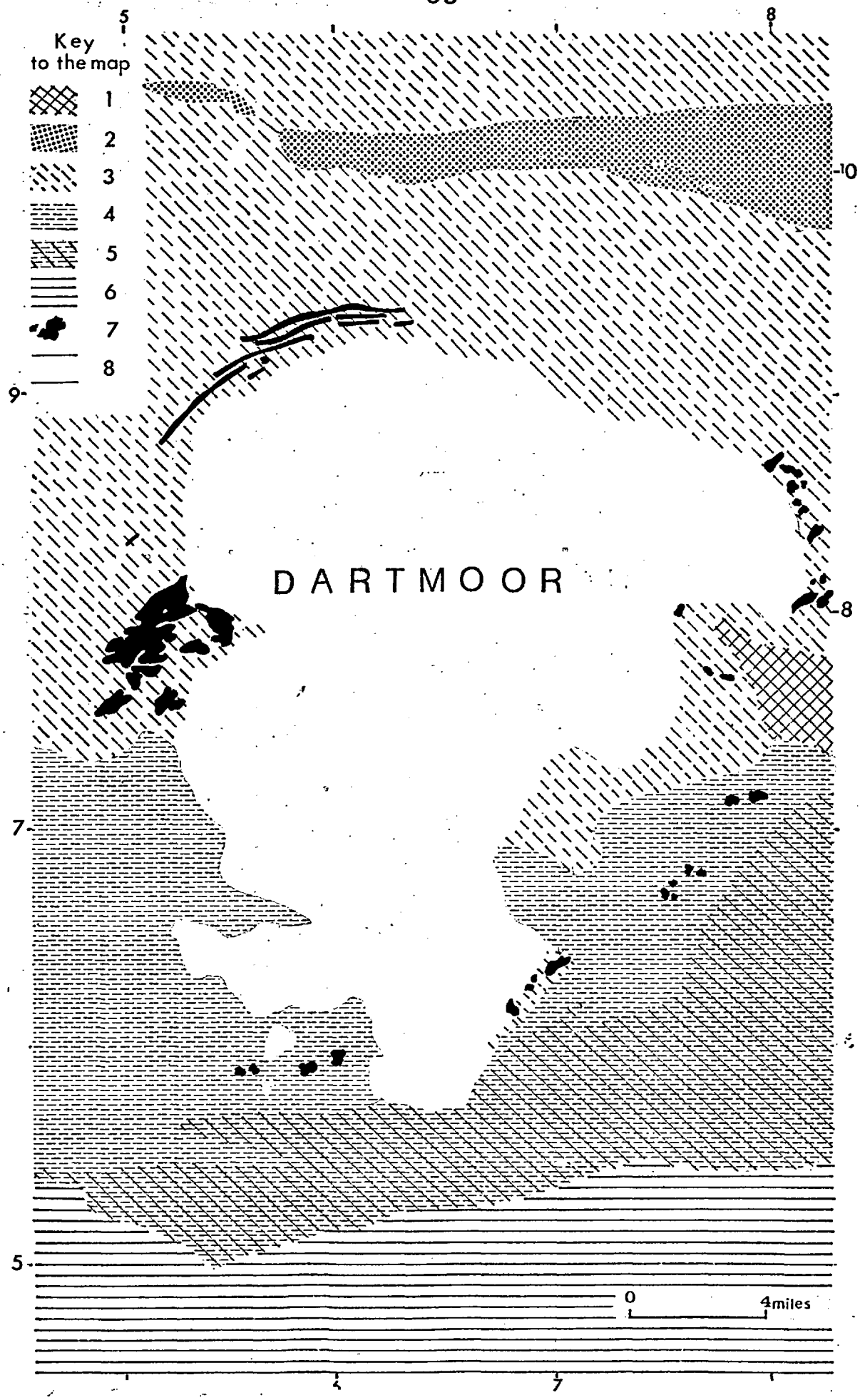
7.2.3 Soil Traverses

Studies in the areas consisted of systematic soil sampling in two twelve mile north-south traverses in which top-soil and sub-soil samples were collected at approximately two hundred yard intervals, and at six to twelve inches depth. An exception was made of the sampling within narrow geological units and the metamorphic aureole, where soil samples were taken at hundred yard intervals. Streams were sampled up-stream from their traverse crossing point (one sample per stream). Rock samples were collected along the traverses wherever they were exposed.

The samples thus collected were prepared and analysed by means of the methods already described in Chapter 5. Plotting of the data obtained took the form of profile curves at horizontal scale one-inch to the mile which was reduced to page-size presentation. The profiles were compared to geological cross-sections which underlaid the sampling traverse. Main features of the soil traverses are shown in Figs. 7.3 and 7.4

7.2.4 Soil Characteristics

The main characteristics of soils observed during the sample collection coincide with the Clayden's soil-types classification (1964). Soil types in the area are varied. They are generally residual and closely related to the underlying parent-rock. However, in some areas it is difficult to distinguish between soil formed on weathered parent-rock material, and those derived from transported material. In many areas, either consolidated bed-rock or shattered rock debris are found at a very shallow depth.



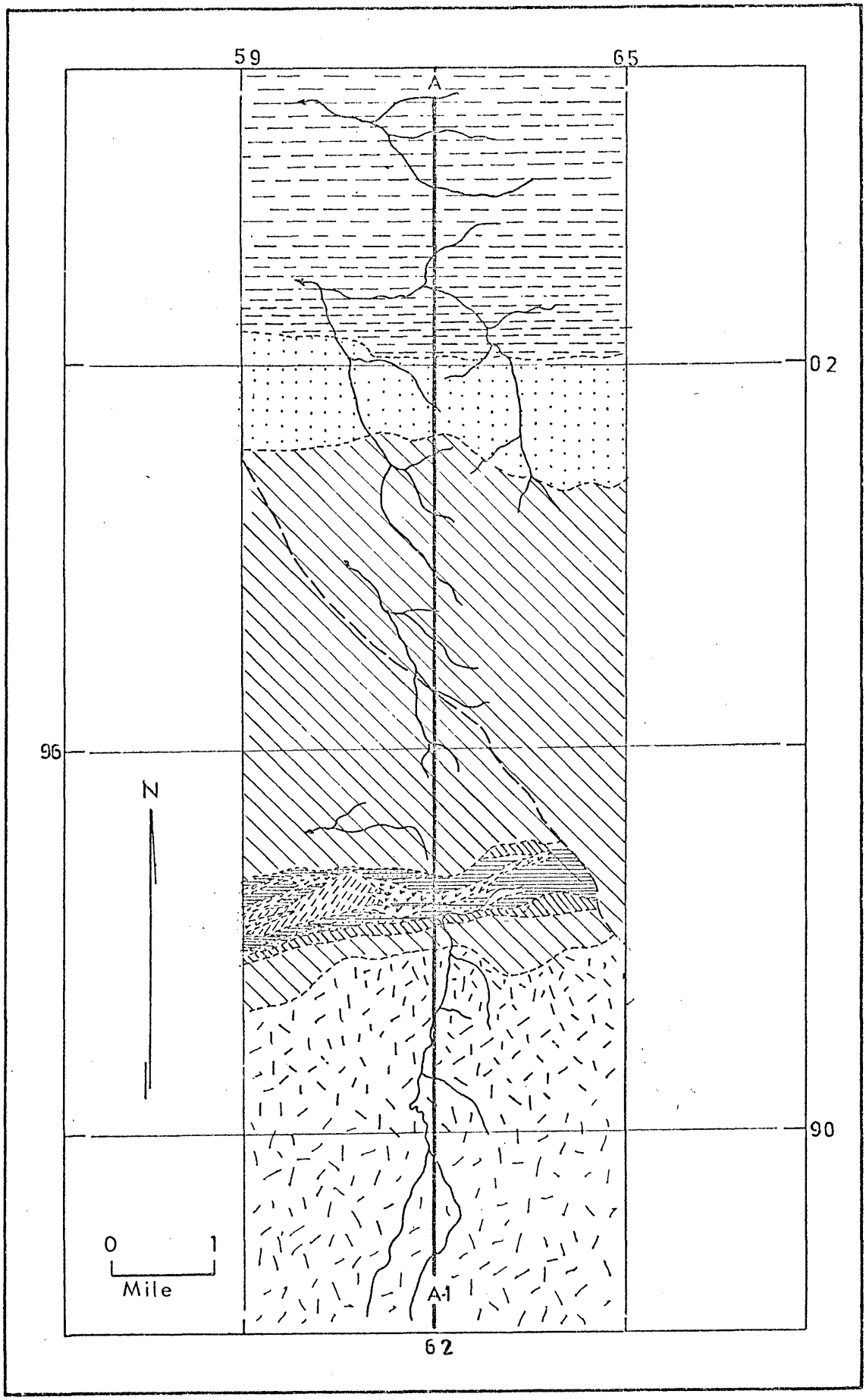
1 Tertiary
2 Permian
3 Carboniferous
4 Upper Devonian
5 Middle Devonian
6 Lower Devonian
7 Dolerite
8 Granite

Fig. 7.2 GEOLOGY OF THE DARTMOOR AREA

TABLE 7.1

GEOLOGICAL FORMATIONS PRESENT IN THE DEVON AREA

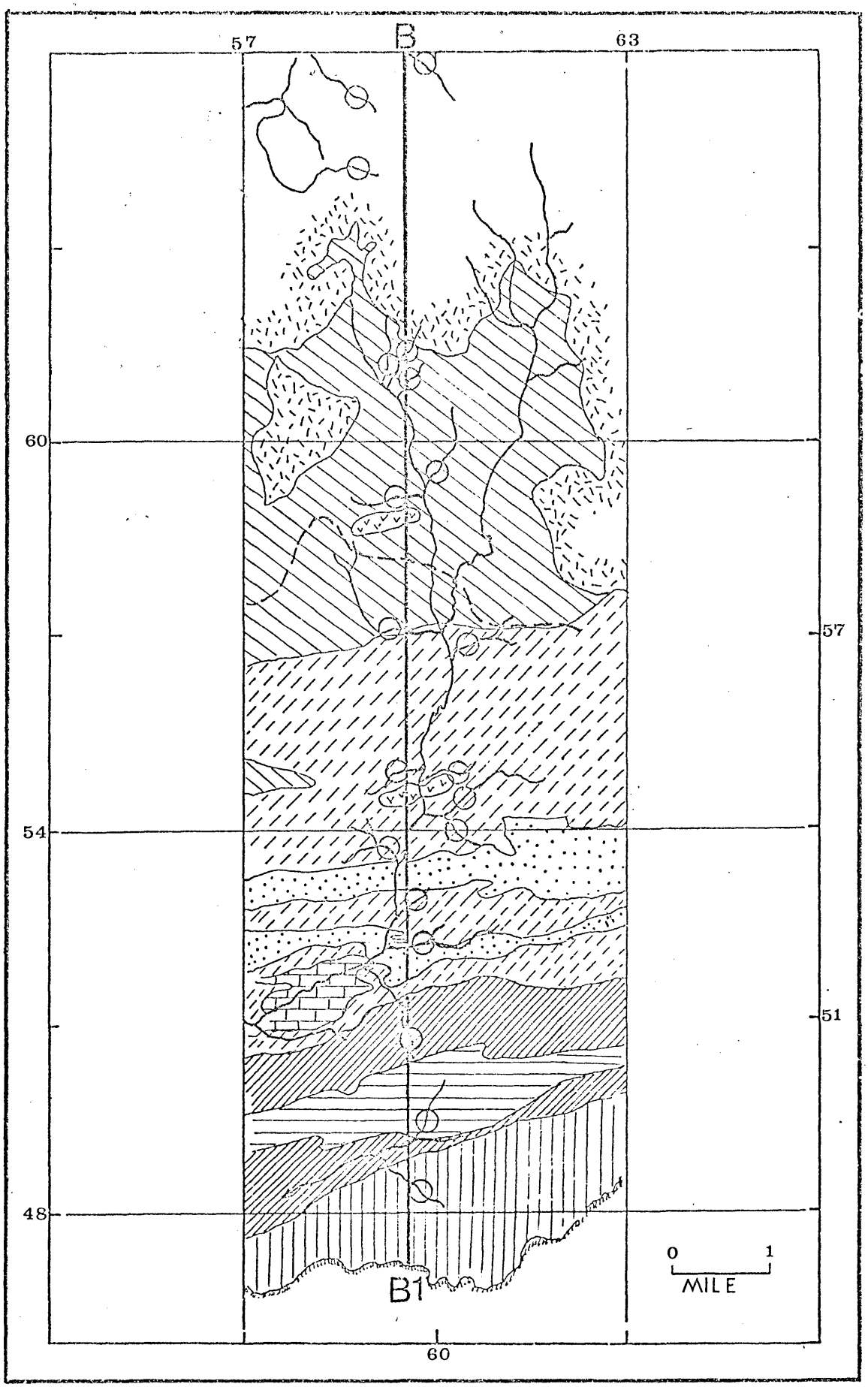
	PERMIAN		Crediton Conglomerates	
			Knowle Sandstones	
			Bow Conglomerates	
CARBONIFEROUS (CULM MEASURES)	UPPER CARBONIFEROUS	Westphalian		Bude Formation
		Namurian		Crackington Formation
	LOWER CARBONIFEROUS	Dinantian		Meldon Chert Formation
				Meldon Shale and Quartzite Formation including Meldon Volcanic Beds
DEVONIAN	UPPER & MIDDLE DEVONIAN		Slates, Mudstones, Sandstones and Limestones	
	LOWER DEVONIAN		Sandstones, Shales Conglomerates	
IGNEOUS	EXTRUSIVE		Tuff, Ash, Lava	
			Dolerite	
	INTRUSIVE		Lamprophyre	
			Agglomerate	
			Aplite	
			Granite	



1, 2, 3, 4, 5, 6, 7, 8, 9, 10

1, Permian; 2, Westphalian; 3 Namurian; 4, 5, 6, 7, Dinantian; 8 Granite; 9, Fault; 10, Streams

Fig. 7.3. MAIN GEOLOGICAL FEATURES OF TRAVERSE A, A' NORTH DEVON



1, Upper Devonian; 2,3, Middle Devonian; 4,5,6, Lower Devonian; 7, Tuffs; 8, Diabase, 9 Granite; 10, Outer limit of metamorphic aureole.

Fig. 7.4. MAIN GEOLOGICAL FEATURES OF TRAVERSE B,B', SOUTH DEVON

In the northern part of the area (Traverse A. A1), the Carboniferous sediments display two main soil types: well drained brown soils, (Brown Earths, Clayden.1964), located on moderate or steep slopes, and gley soils developed on flat or gently sloping places. (Fig. 7.5). Brown soils are considered naturally acid and show brown colour due to the presence of ferric oxides, while gley soils on flatter slopes are characterised by a grey colour with ochreous motting, due to water logging which gives rise to reducing conditions (Nichol et al. 1971). The latter type of soil is mainly found in areas underlain by shales of Namurian sediments (Crackington Formation).

Over Devonian rocks (Traverse B, B1) soil patterns developed on slates present very similar characteristics of those formed over Carboniferous. These soils are predominantly well drained, brown earths; gleyed brown soils and gley soils are restricted to low-lying areas of subdued relief and footsteps sites.

Black concretions of manganese and iron oxide, as well as tiny coal fragments, are sporadically found in the sub-soil.

Soils of Dartmoor granite are formed by peaty gleyed podzol and blanket bog and peaty gleys. Clayden and Manley (1964) have recognised four major soil types covering the granite which are strongly related to topography, climate and vegetation (Fig. 7.6).

7.3 RESULTS OF THE INVESTIGATIONS

7.3.1 Secondary Distribution of Arsenic and Selected Trace-Elements

Studies in the area consisted of systematic collection of top-soil and sub-soil samples, complemented by stream sediments and rock sampling. It was found that the content of most of the elements showed little if any difference in both top, and sub-soil media, the exception being the alluvial material over the granite, where As and Sn present a great contrast with their major concentration in the sub-soil. The interpretation of the distribution of the elements was made on the basis of their concentration in the latter medium.

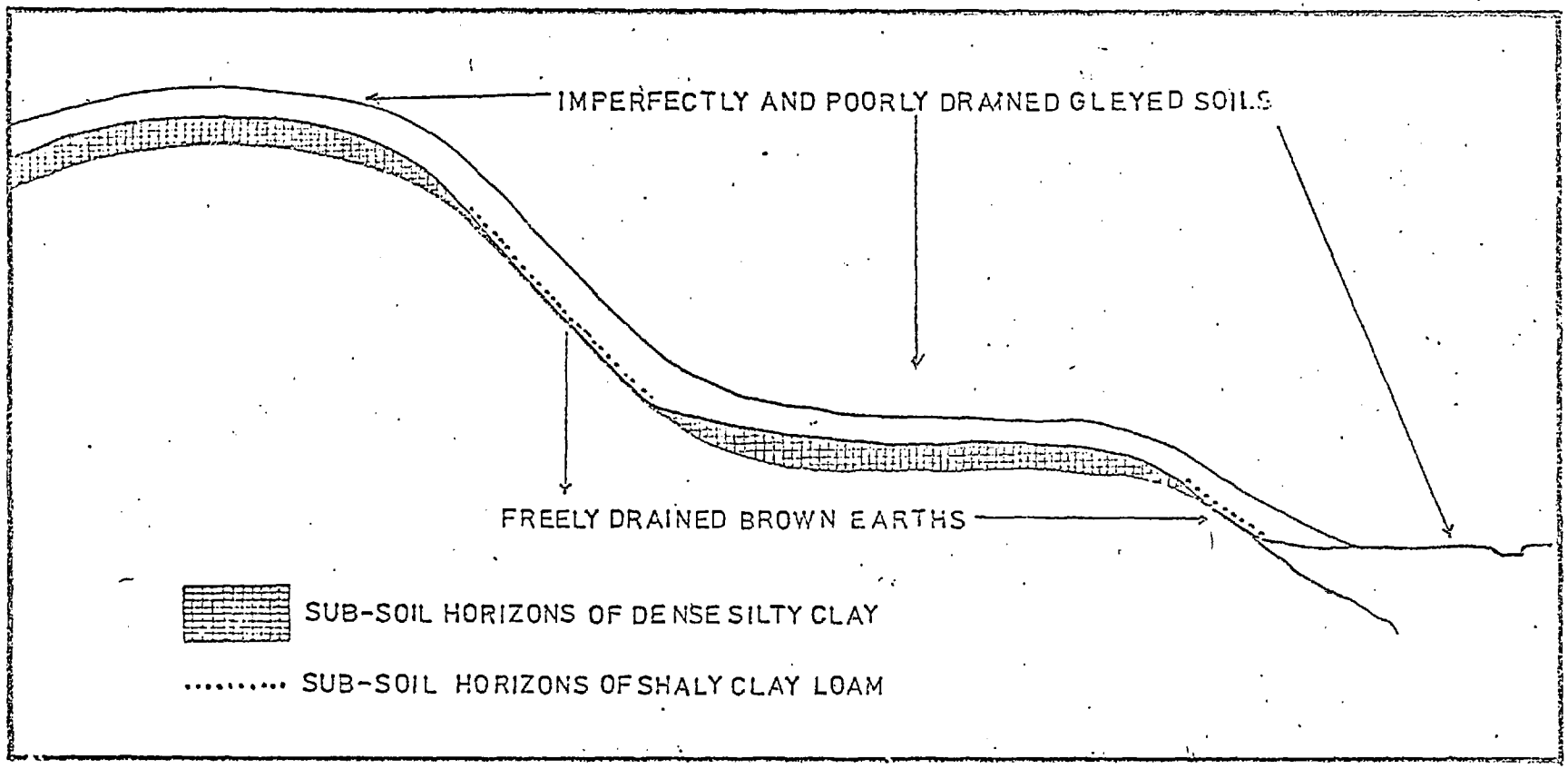


Fig. 7.5 RELATIONSHIP BETWEEN SOIL TYPE AND TOPOGRAPHY OVER UPPER CARBONIFEROUS SHALES IN DEVON (After Horsnail, 1968)

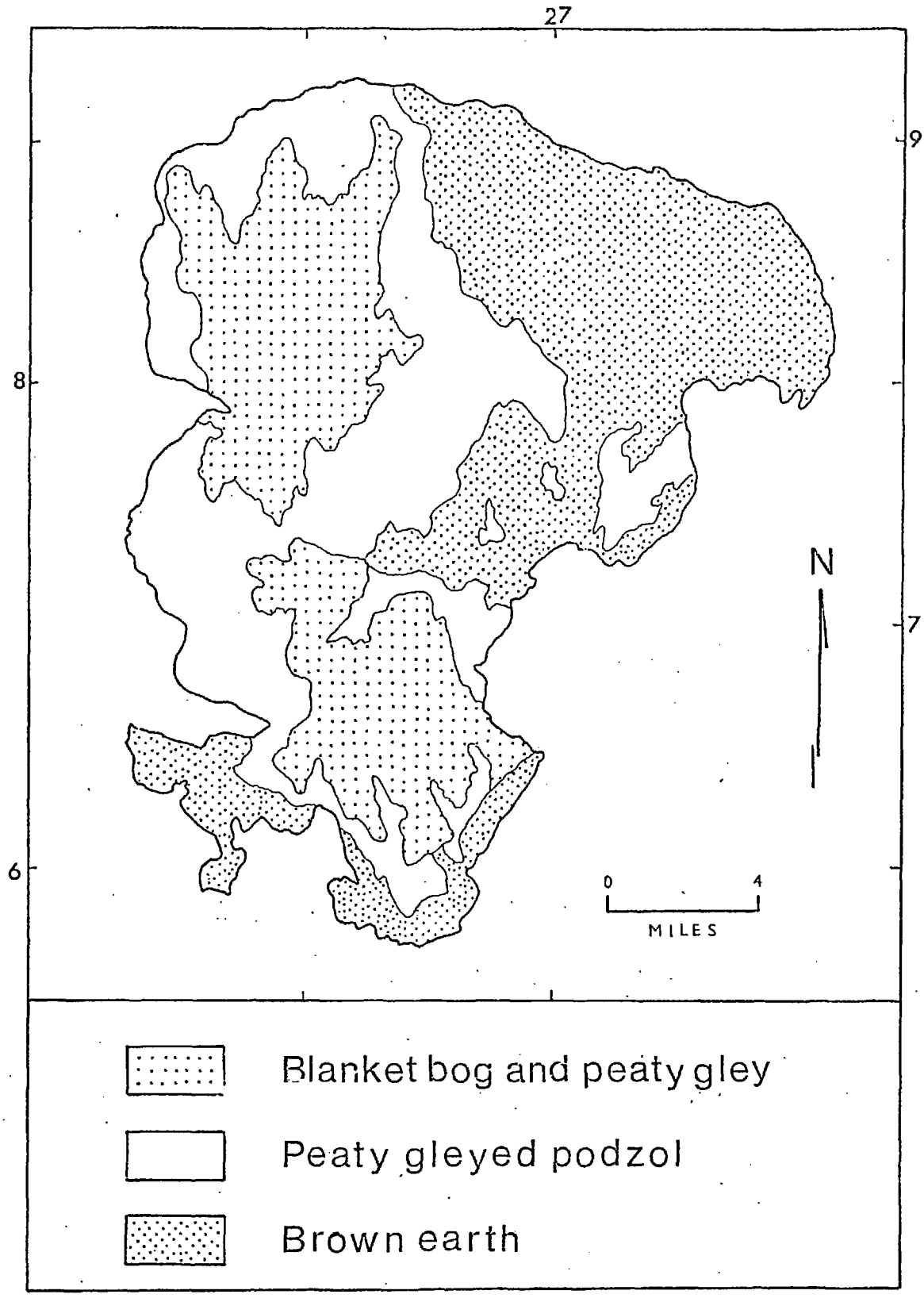


FIG 7.6. SOILS OF DARTMOOR
AFTER HORSNAIL, 1968.

Streams which were sampled during the soil sample collection generally drain into a limited catchment area, and each geological unit is represented by at least two streams. Exposure of bed-rock was very limited and the outcrops generally are located along the stream borders, where, obviously they display the effects of strong weathering.

1 Traverse A, A1, North Devon

The underlying parent-rock in this traverse is characterised by a normal sequence of steeply dipping brown and/or green sandstones, and grey shales of the Bude Formation (2.8 miles length); red Permian conglomerates (0.8 miles), shale and sandstones (mainly shale), of the Crackington Formation (4.4 miles); sediments and basic rocks of Lower Carboniferous (0.5 miles), and by igneous rocks of Dartmoor granite (3.5 miles). Fig 7.3.

The topographic profile shows a sequence of gentle undulations, some steep hills and flatter land mainly located in areas underlain by the Crackington Formation (Fig. 7.7). A great part of the granitic area covered by the traverse is characterised by river deposits, (7th terrace), and swamps. As values obtained from these media have been excluded from the soil traverse profile presentation.

a) General Description of the Distribution of the Elements

i) Stream Sediments

Distribution of As and selected trace-elements is shown in Figs. 7.7a to 7.10.

As, Cu, Pb and to a lesser extent Zn, display a fairly regular dispersion. On the contrary, Fe, Mn and Sn are irregularly distributed. As with values rising from 5 to at least 2,500 ppm presents the best distribution pattern in the area. Low concentrations are found over the Upper Carboniferous with the lowest values located within sediments of the Bude Formation which slightly increase southward almost over all the Crackington Formation. Permian sediments display moderately high values

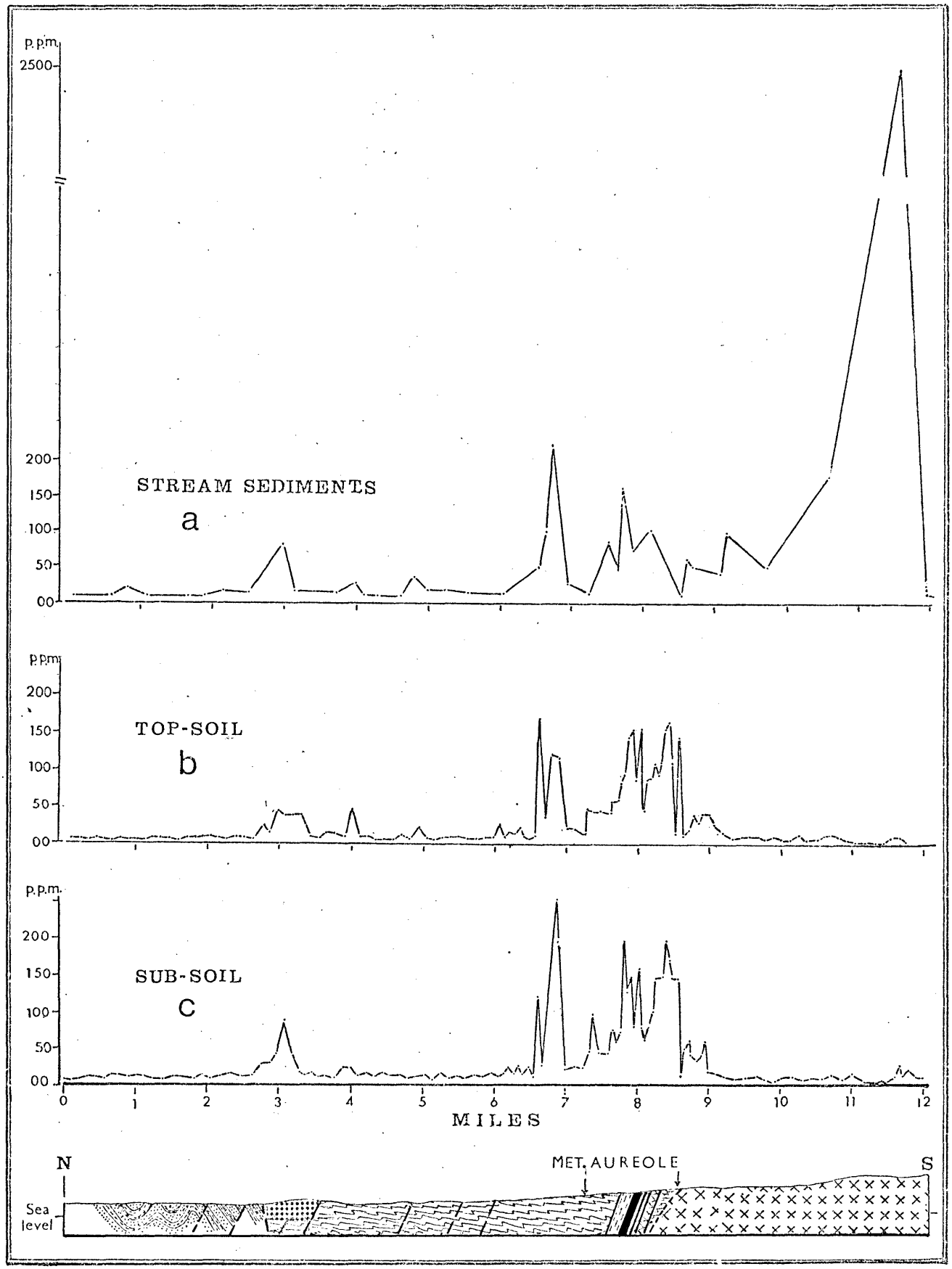


Fig. 77. DISTRIBUTION OF ARSENIC IN SOILS AND STREAM SEDIMENTS FROM TRAVERSE 'A'

1, Permian; 2, Westphalian; 3, Namurian; 4, 5, 6, Dinantian. 7, Dolerite; 8, Granite; 9, Fault; 10, Granite–boundary.

(80 ppm), and within the granitic mass the concentration of this element ranges from 10 to 2,500 ppm. Anomalous As levels are found in the Corscombe area; right through the metamorphic aureole, and over the granite (Fig. 7.7a). Cu, Pb and Zn values demonstrate very little contrast over the Carboniferous sediments being slightly higher within the Crackington Formation than those of the Bude Formation. The lowest Cu levels are found over almost all the granite, and the higher values of this element, together with those of Zn, Pb and Mn are concentrated in the metamorphic aureole (Fig. 7.8 to 7.10). The distribution of Sn shows a peculiar characteristic: very low concentration (2 ppm) is noted in part of the Bude Formation increasing this level southward passing over the Permian to the northern part of the Crackington Formation. Higher Sn concentration is located within the metamorphic aureole being limited to the metamorphosed sediments from the Upper Carboniferous and showing low values over the Lower Carboniferous rocks. (Fig. 7.10)

ii) Soils

The distribution of As in soils is shown in Fig. 7.7b and c and of selected trace-elements in Figs. 7.11 to 7.14.

The As content in soils presents a well defined distribution within the overall pattern, and keeps a close relationship to its distribution in stream sediments. The exception is the anomalous stream sediment value (>2500) over the granite which is not reflected in the soils. The most prominent characteristics of the distribution of As in soils are: very low values within the granitic mass and the Upper Carboniferous sediments; moderately high concentration in the Permian, and anomalous values in the Corscombe area and through the whole metamorphic aureole.

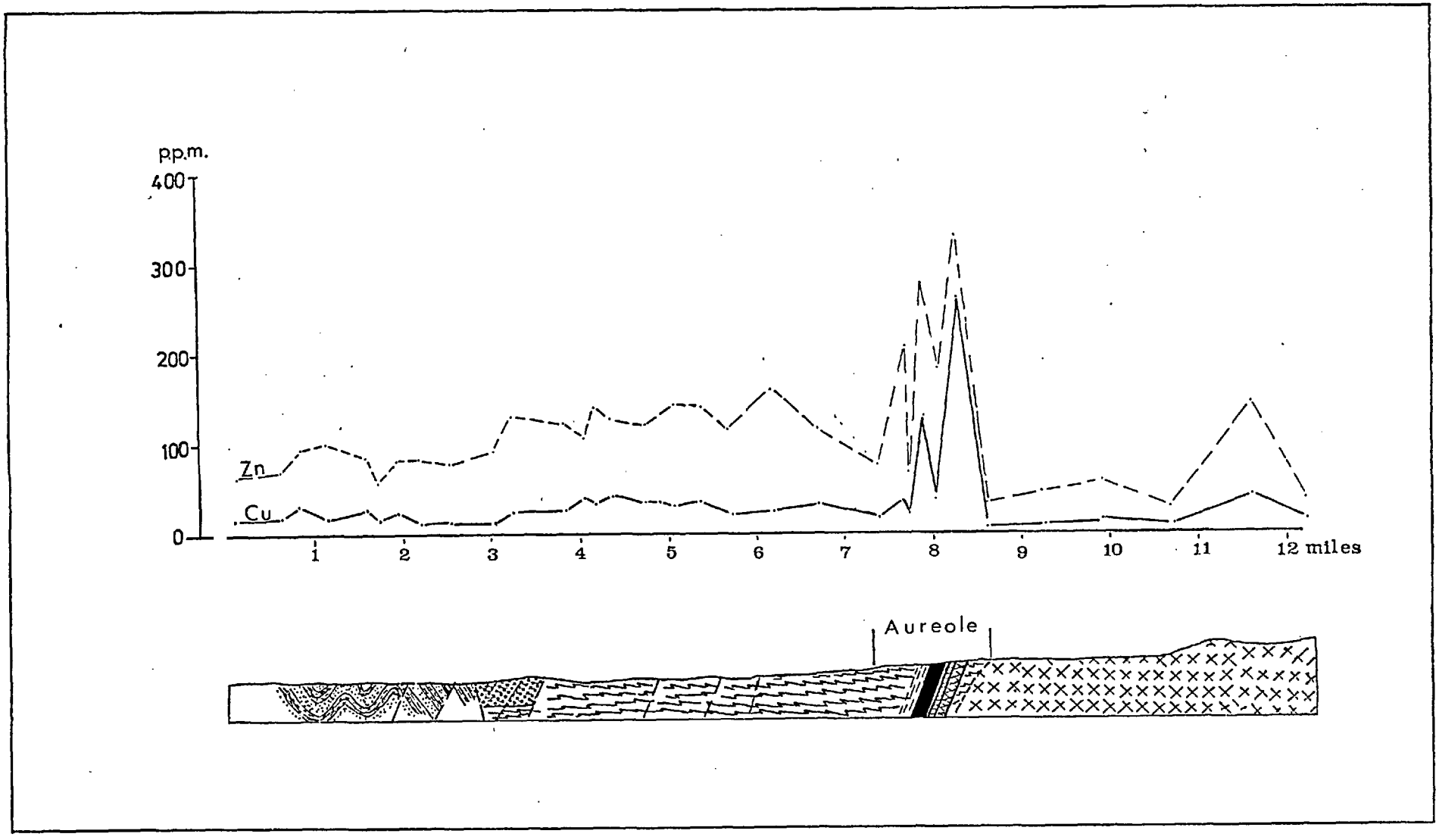


Fig. 7.8. DISTRIBUTION OF COPPER AND ZINC IN STREAM SEDIMENTS FROM TRAVERSE A A1

(Explanation as for fig. 7.7.)

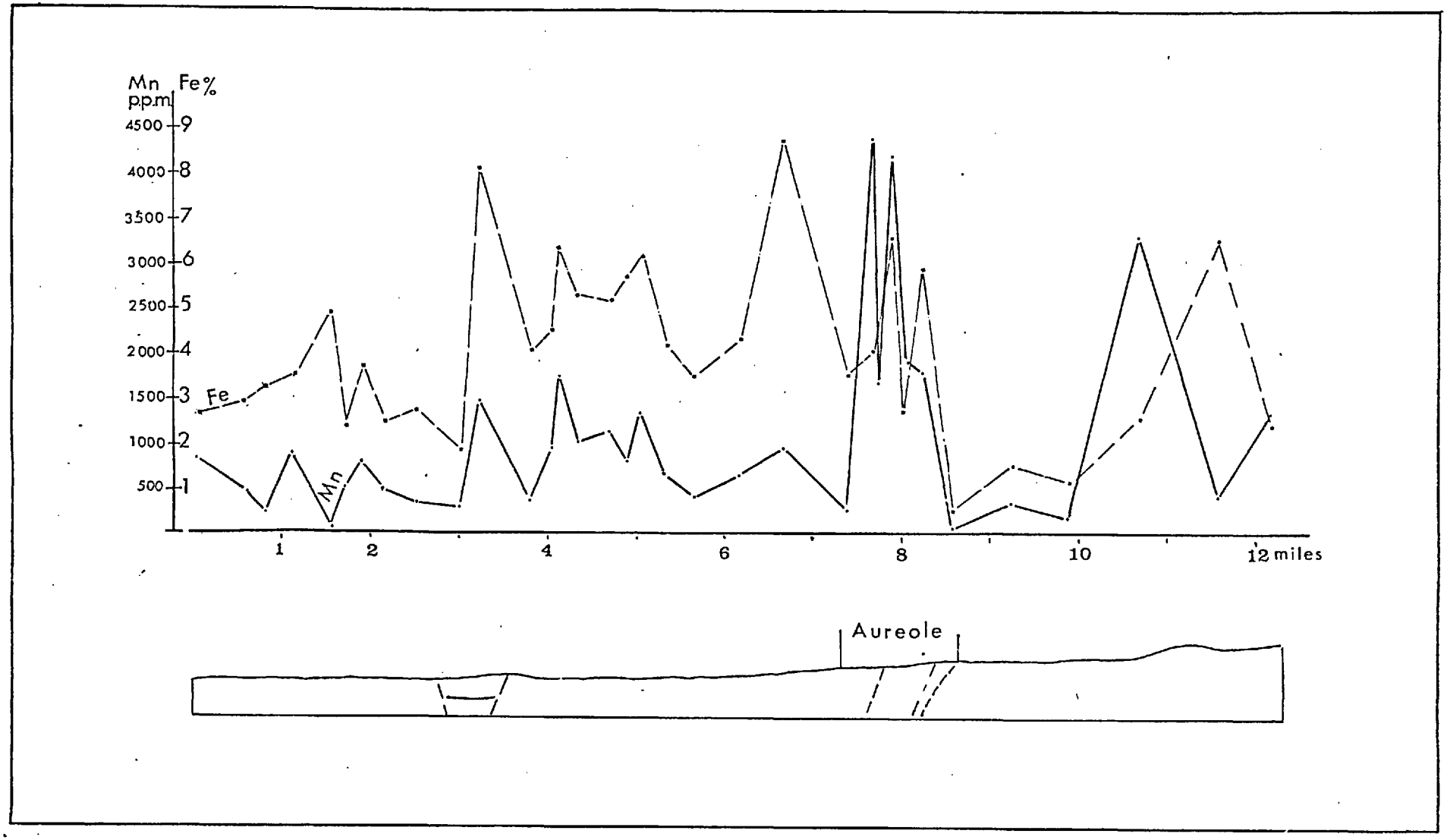


Fig. 7.9 DISTRIBUTION OF MANGANESE AND IRON IN STREAM SEDIMENTS FROM TRAVERSE AA1 NORTH DEVON
(Explanation as for Fig. 7.11)

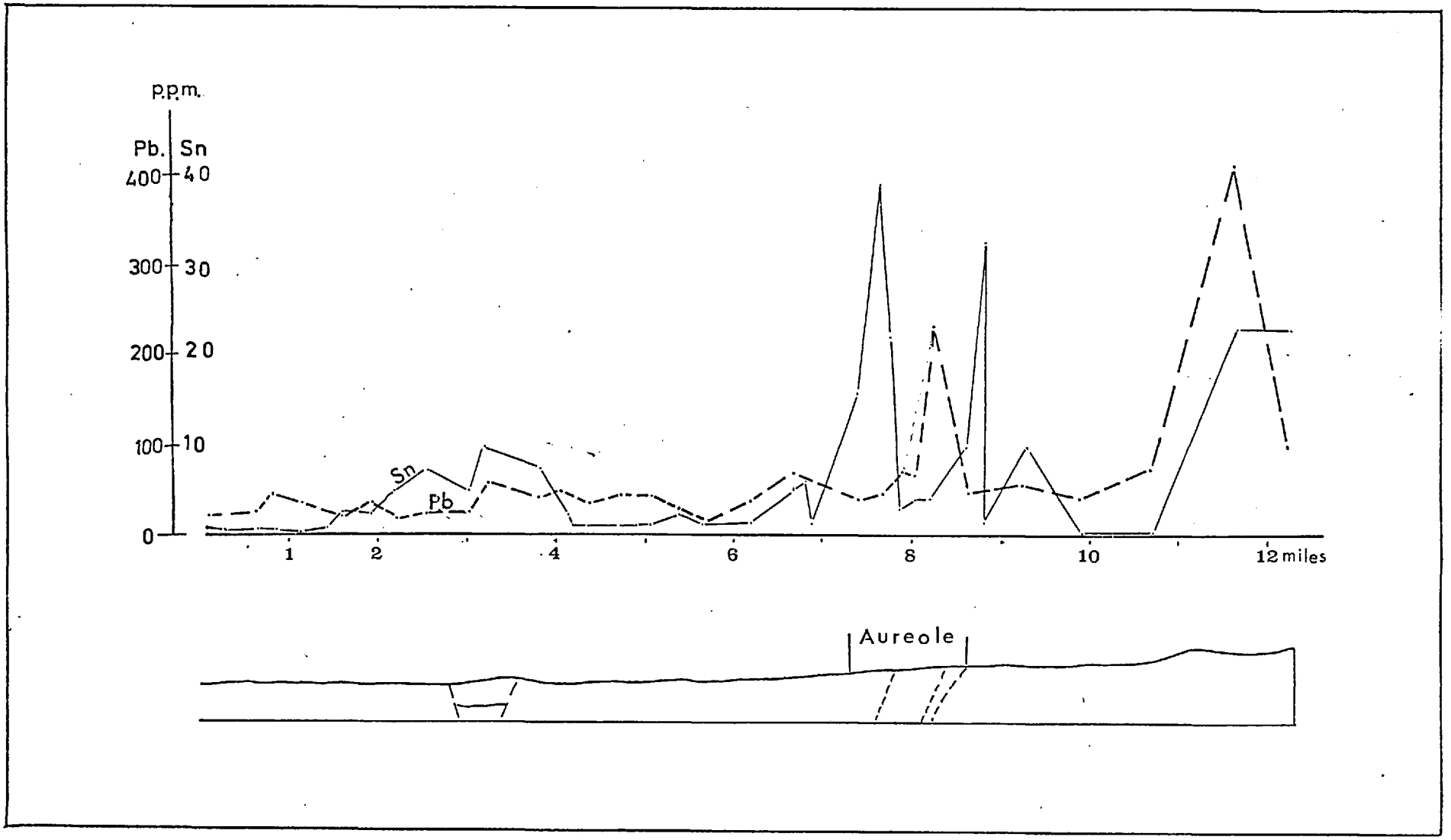
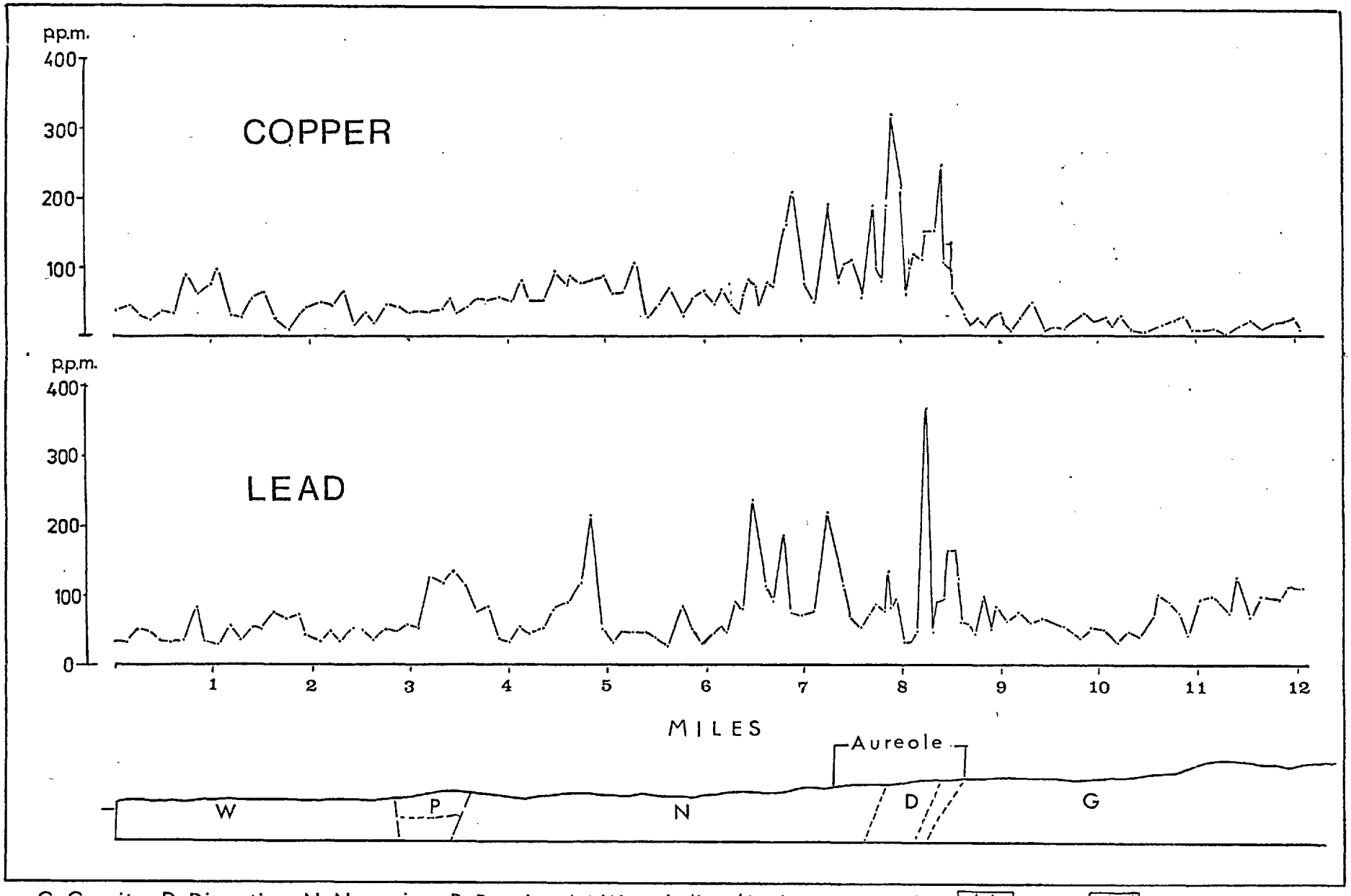


Fig. 7.10 DISTRIBUTION OF TIN AND LEAD IN STREAM SEDIMENTS FROM TRAVERSE AA1 NORTH DEVON
(Explanation as for Fig. 7.11)



G, Granite; D, Dinantian; N, Namurian; P, Permian; W, Westphalian, (Bude Formation); Faults; Contacts.

Fig. 7.11. DISTRIBUTION OF COPPER AND LEAD IN SUB-SOILS FROM TRAVERSE A, A' - NORTH DEVON.

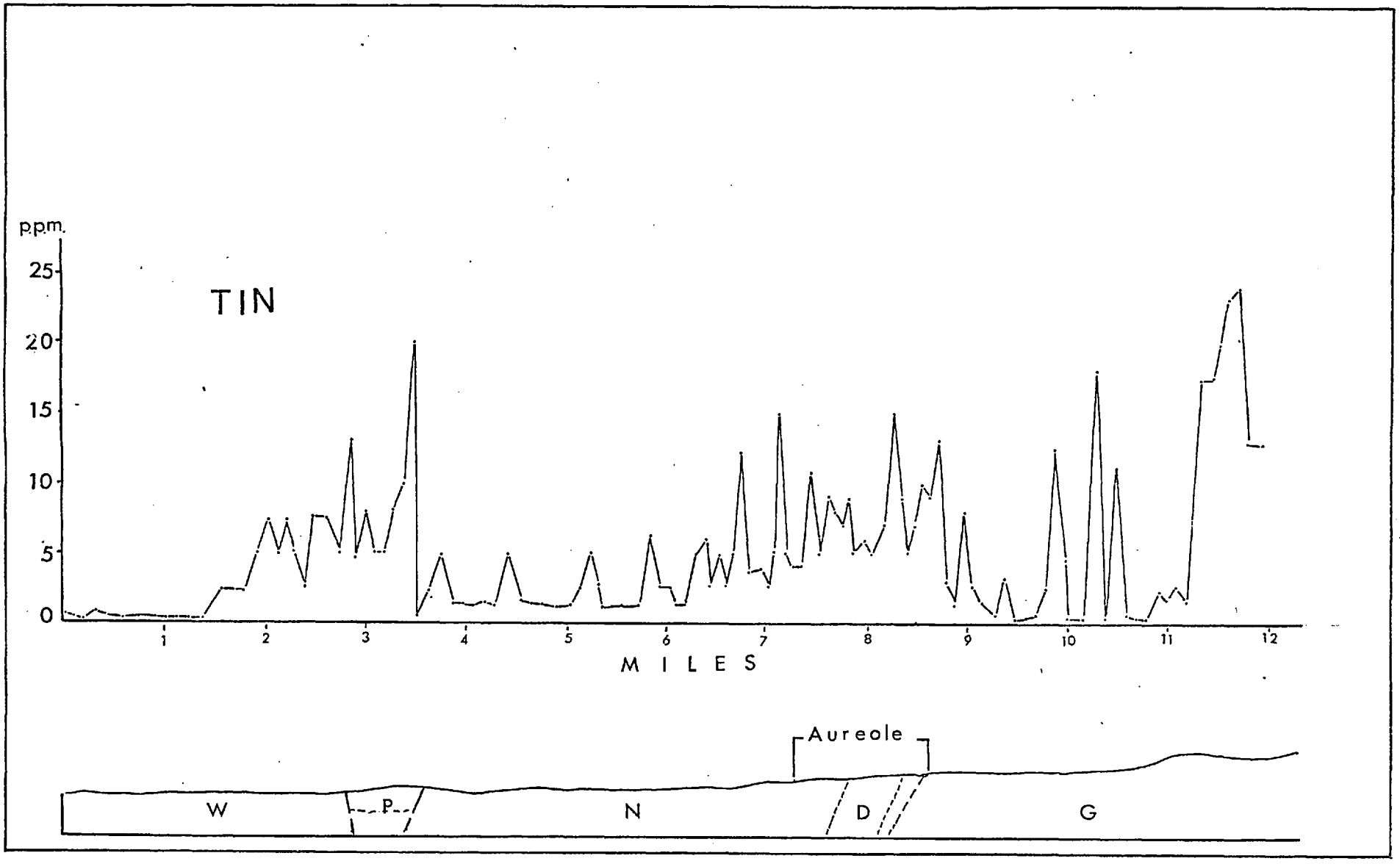


Fig. 7.12 DISTRIBUTION OF TIN IN SUB-SOILS FROM TRAVERSE AA1

(Explanation as for Fig. 7.11)

Cu, Fe, Pb, Mn and Zn patterns present irregularity within the whole area, the distribution of Sn being a little more conspicuous. The lowest contents of Cu, Fe, Mn and Zn are found in the area underlain by the granite. Over the Namurian (Crackington Formation) and the Permian sediments Cu is almost uniformly distributed, where Mn is ranging between low and moderately high values. The best Mn distribution pattern is found over the metamorphic aureole with its highest value related to doleritic and cherty rocks. (Fig. 7.13) Fe shows its highest concentration within the Namurian, getting lower in the Permian and very erratic in the Westphalian (Bude Formation). Sn levels out with its lowest concentration in the northern part of the latter formation and tends to be higher over the Namurian. The highest Sn values are found over the whole Permian and the southern half of the Westphalian, and on the metamorphic aureole. Dartmoor granite presents a contrasting Sn distribution: very low values (2 ppm) are found alternating with high peaks which reach up to 25 ppm. Zn concentration shows its highest levels over the Corscombe area, and this element together with Fe and to a lesser extent Cu and Pb, presents high values within the metamorphic aureole.

b) Interpretation of Patterns

i) Stream Sediments

The interpretation of the essential features of the distribution patterns of As and selected trace-elements in stream sediments has been performed as follows:-

a) Examination of the occurrence of trace-elements within the overall pattern displayed in the area in relation to bed-rock geology and

b) Examination of single sample values in areas whose importance has been suggested before. (See Summary Chapter 6). In the

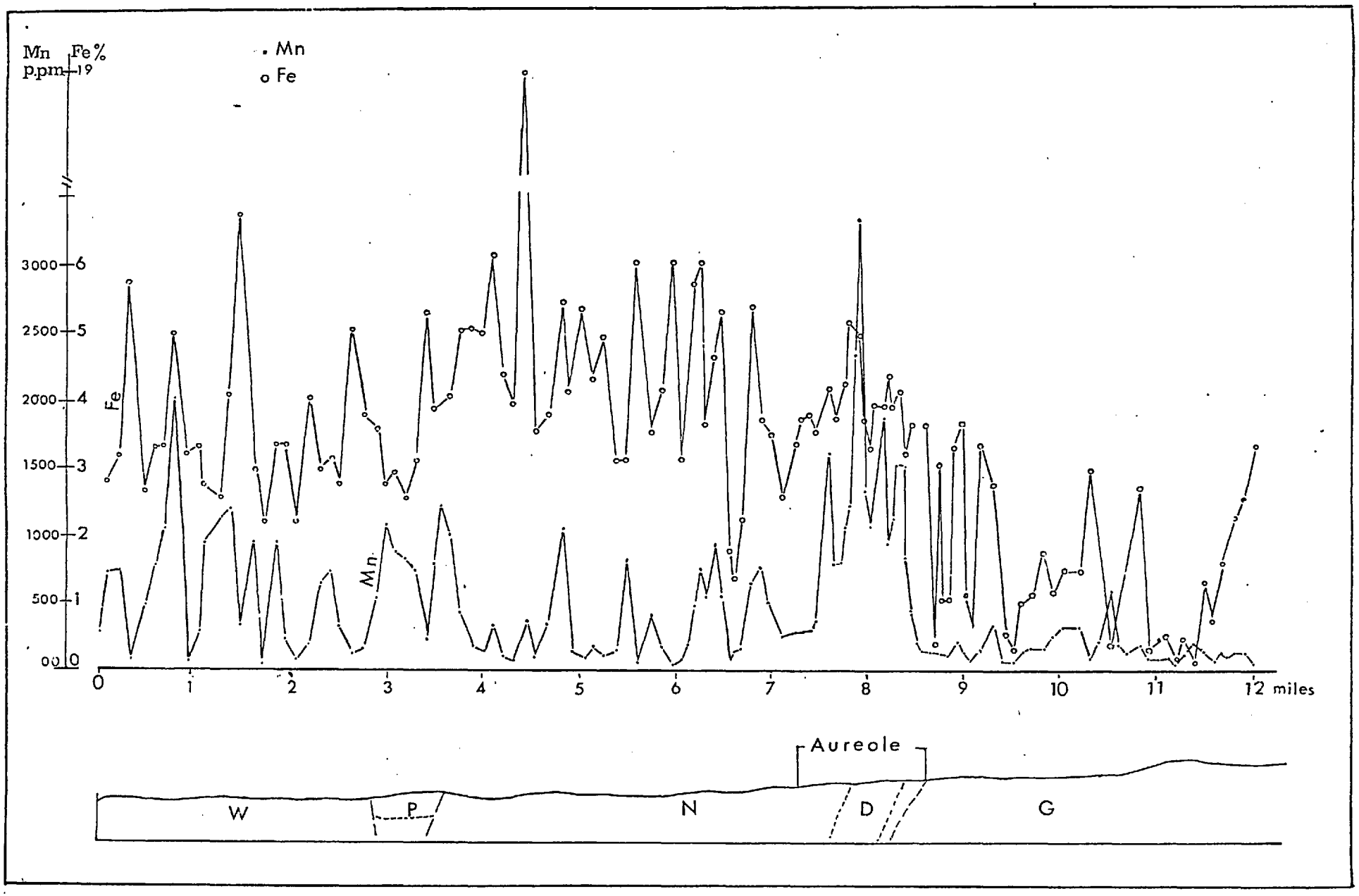


Fig. 7.13 DISTRIBUTION OF MANGANESE AND IRON IN SUB-SOILS FROM TRAVERSE AA1 (Explanation as for Fig. 7.11)

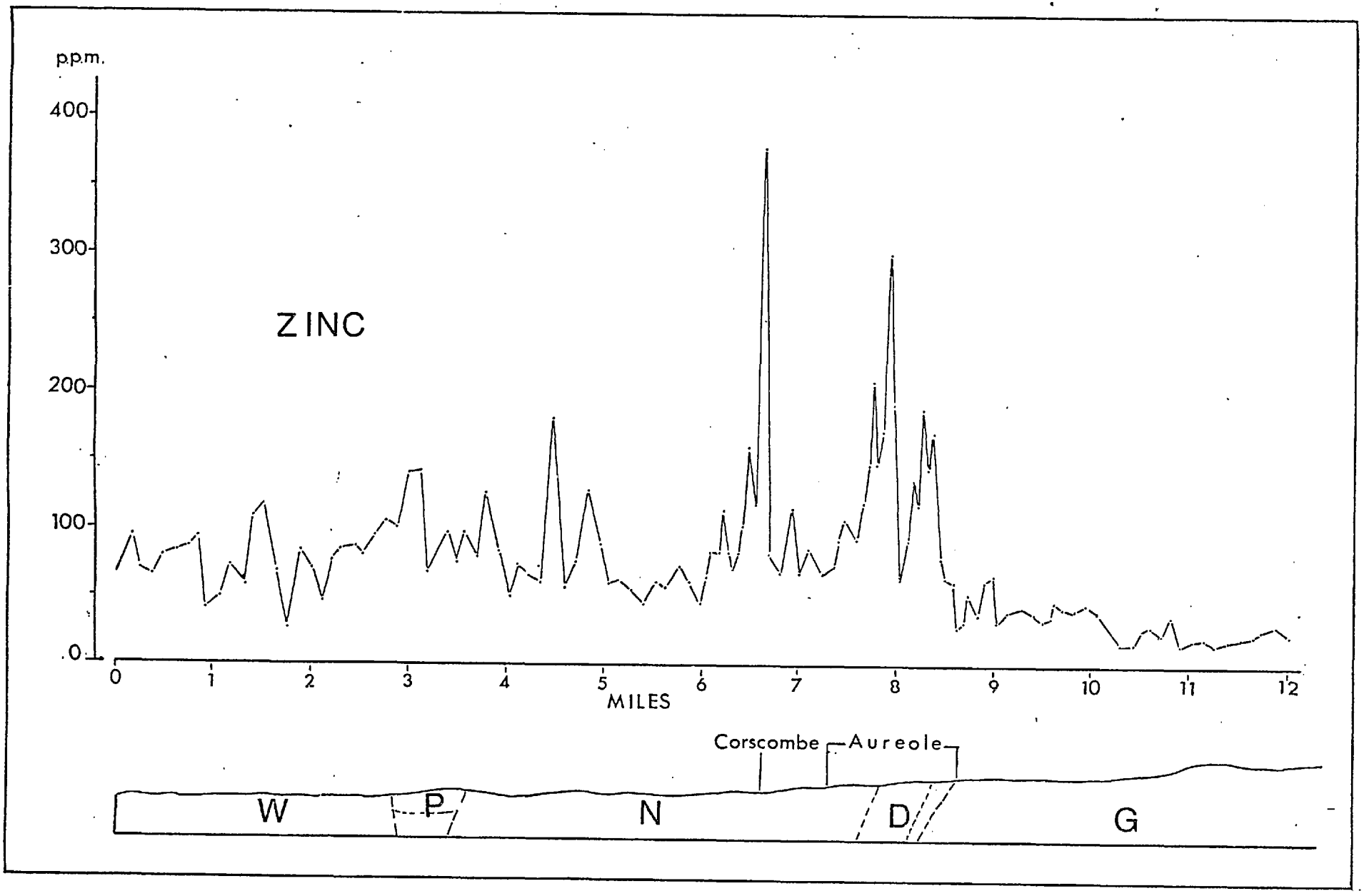


Fig. 7.14 DISTRIBUTION OF ZINC IN SUB-SOILS FROM TRAVERSE AA1
(Explanation as for Fig. 7.11)

first case, it was found that despite a varied distribution, the metal patterns show specific characteristics when related to individual geological units. High As concentration over the granitic mass are related to alluvium deposits composed by roughly bedded gravel, and to contamination derived from mineralisation. The latter source is assumed to have had the same effect on the high concentration of Sn, Fe, Pb and Zn in this area.

The marked variation in, ~~and major~~ Fe content between the Crackington and Bude Formations is related to secondary environmental effects, in particular, poorly drained soils. An examination of As, Pb and Cu values in some rock samples from both Crackington and Bude Formations showed that the distribution of these elements in the sediments of the streams within these geological units, is mostly related to bed-rock geochemistry rather than to Fe and/or Mn content in the area. The same assumption can be made with respect to the moderately high As and Sn concentrations from the Permian sediments. Sn values extending over great part of the Carboniferous sediments bordering the Permian Formation may be at least in part, due to secondary dispersion derived from this geological unit.

On the other hand, an examination of single stream sediment sample values allows a confirmation, to some degree, of: (1) the significant anomalous patterns in the Corscombe and the Dartmoor granite areas (see Fig. 6.11), and (2) the high background levels of As within the Permian which were found during the interpretation of the regional geochemical reconnaissance patterns (Chapter 6). High Sn values (1,000 ppm) were found over Dartmoor which seem not to be related to known mineralised areas.

All these findings were classified in four single groups (I to IV) (Fig. 7.15). Areas I and II are situated within the Permian and Corscombe zones, respectively, and they were the objective of further detailed investigations (Fig. 7.16 and 7.17). Areas III and IV located over the granitic mass (Fig. 7.19), demonstrate a high concentration of Sn (Area III, Fig. 7.18) with values of over 1,000 ppm, whilst an average of 1,800 ppm of As was obtained from four samples in area IV (Fig. 7.19). These values suddenly change up-stream from 2,500 to 10 ppm of As content. In the absence of any sort of known mineralisation and contamination, it is speculated that these levels originated from possible hidden ores which might be the prolongation of the mineral deposits located in the western flank of the Steepertor Tor Hill (Fig. 7.19).

ii) Soils

The distribution of As and selected trace-elements within the overall pattern has been examined as related to:

a) Metamorphic Aureole
b) Bed-rock Geology, and
c) Mineralisation

a) Metamorphic Aureole

Despite the heterogeneity of bed-rock types underlying the metamorphic aureole, a persistent range of high values of As and some other elements in soils are found in this particular area (Fig. 7.7 and 7.11 to 7.14) The distribution of As which appears to be similarly dispersed both outside and inside the metamorphic aureole, exhibits a considerable contrast in mean values (1:7) from both media. This contrast in mean levels can be found in the distribution of the other elements but in varied proportions. After As, the highest contrast in mean values is found in Mn and Cu (1:3), and Sn (1:25) (Fig. 7.20 and 7.21, Table 7.2).

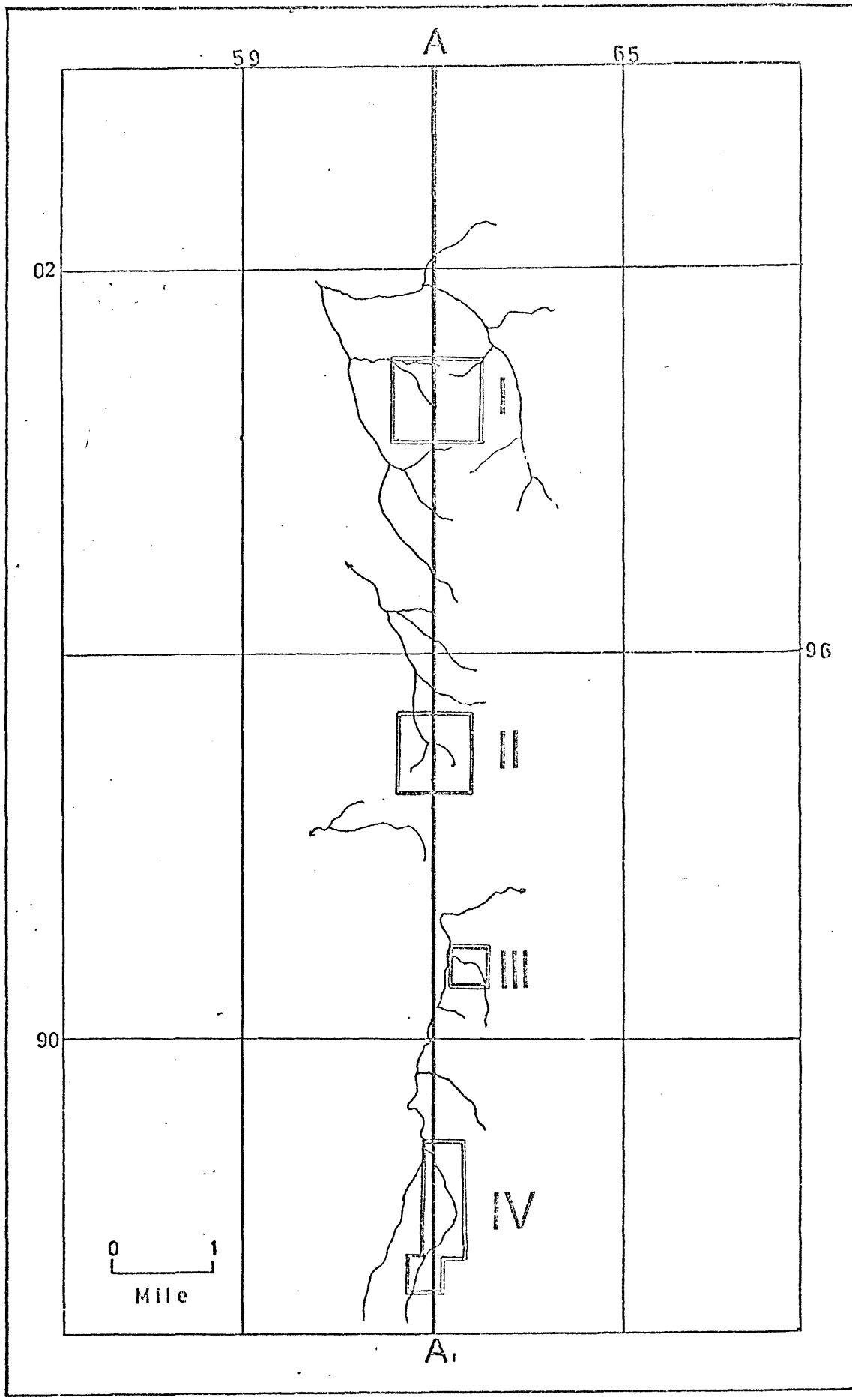


Fig.7.15. TRAVERSE A, A_1 - ANOMALOUS AREAS

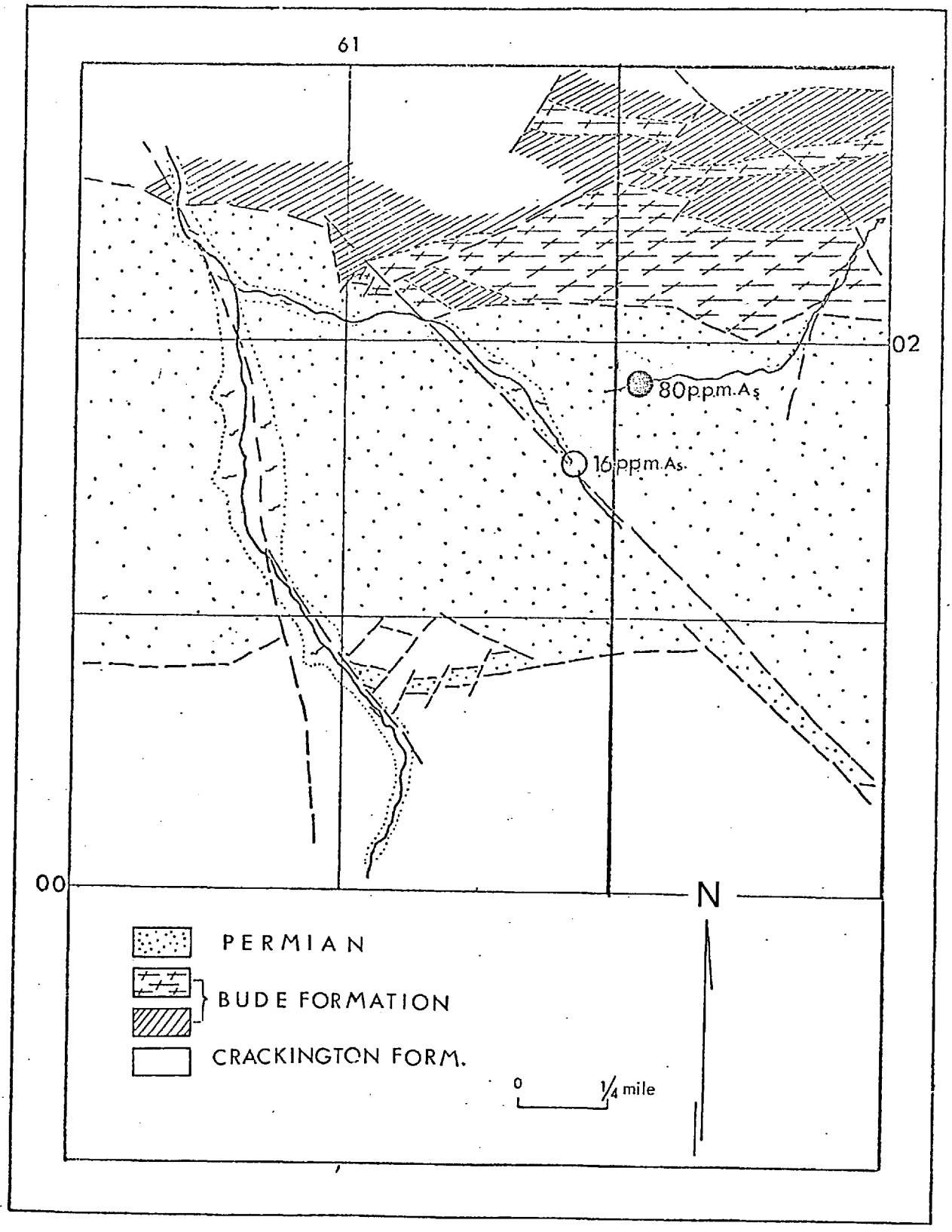


Fig. 7.16. AREA I-STREAM SEDIMENT SAMPLING

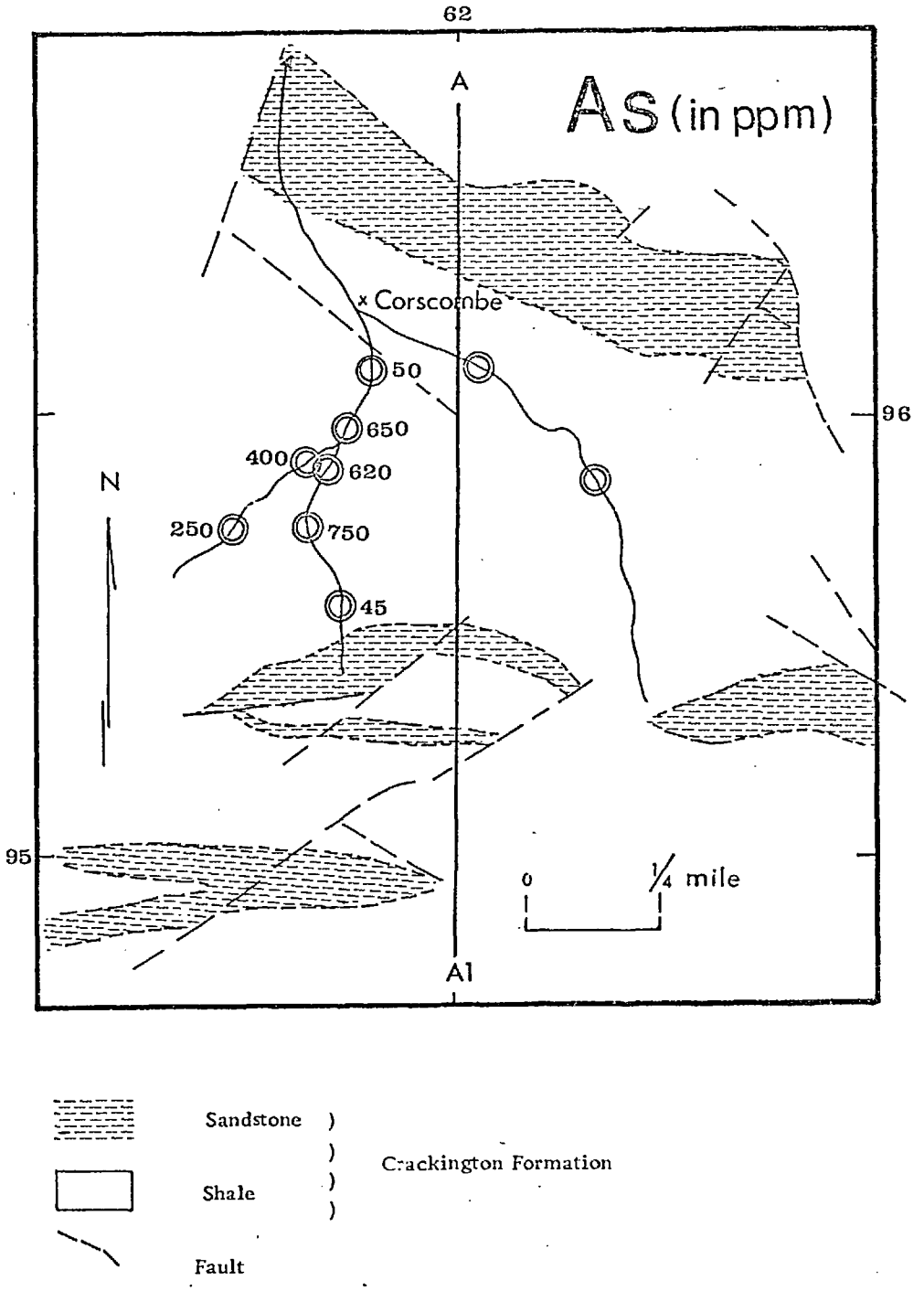


Fig. 7.17 AREA II - STREAM SEDIMENT SAMPLING

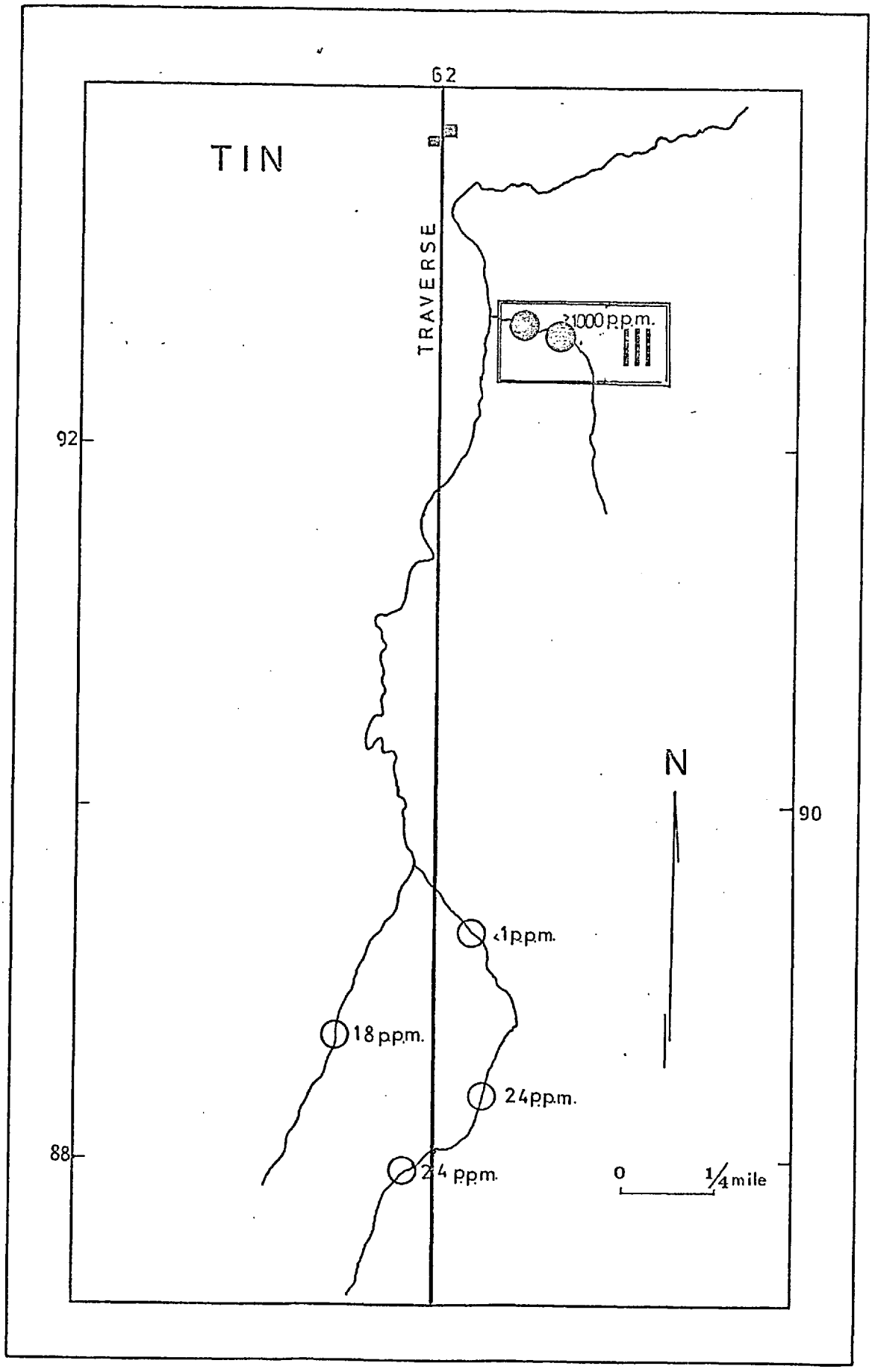


Fig. 7.18 DARTMOOR - ANOMALOUS AREA

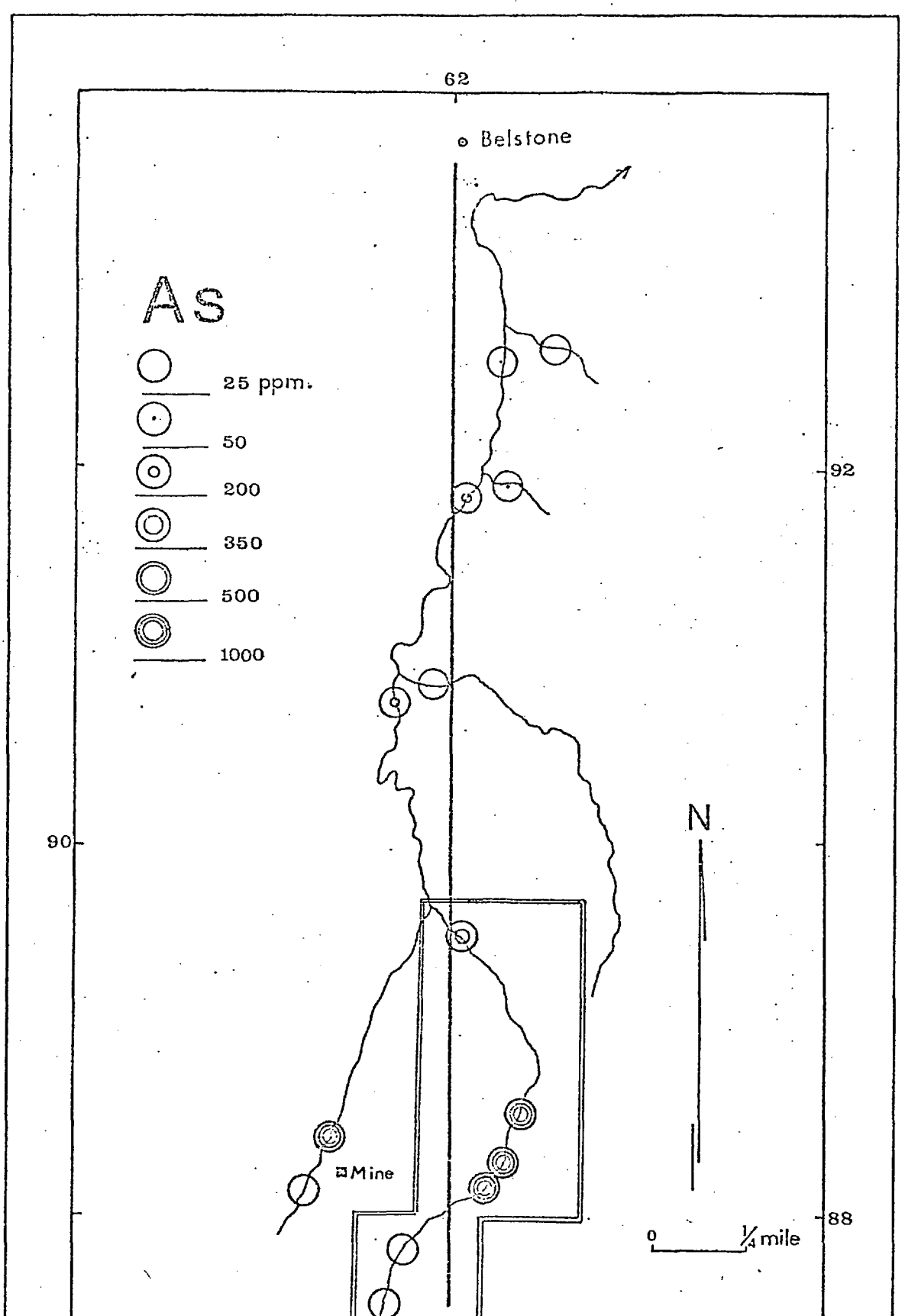
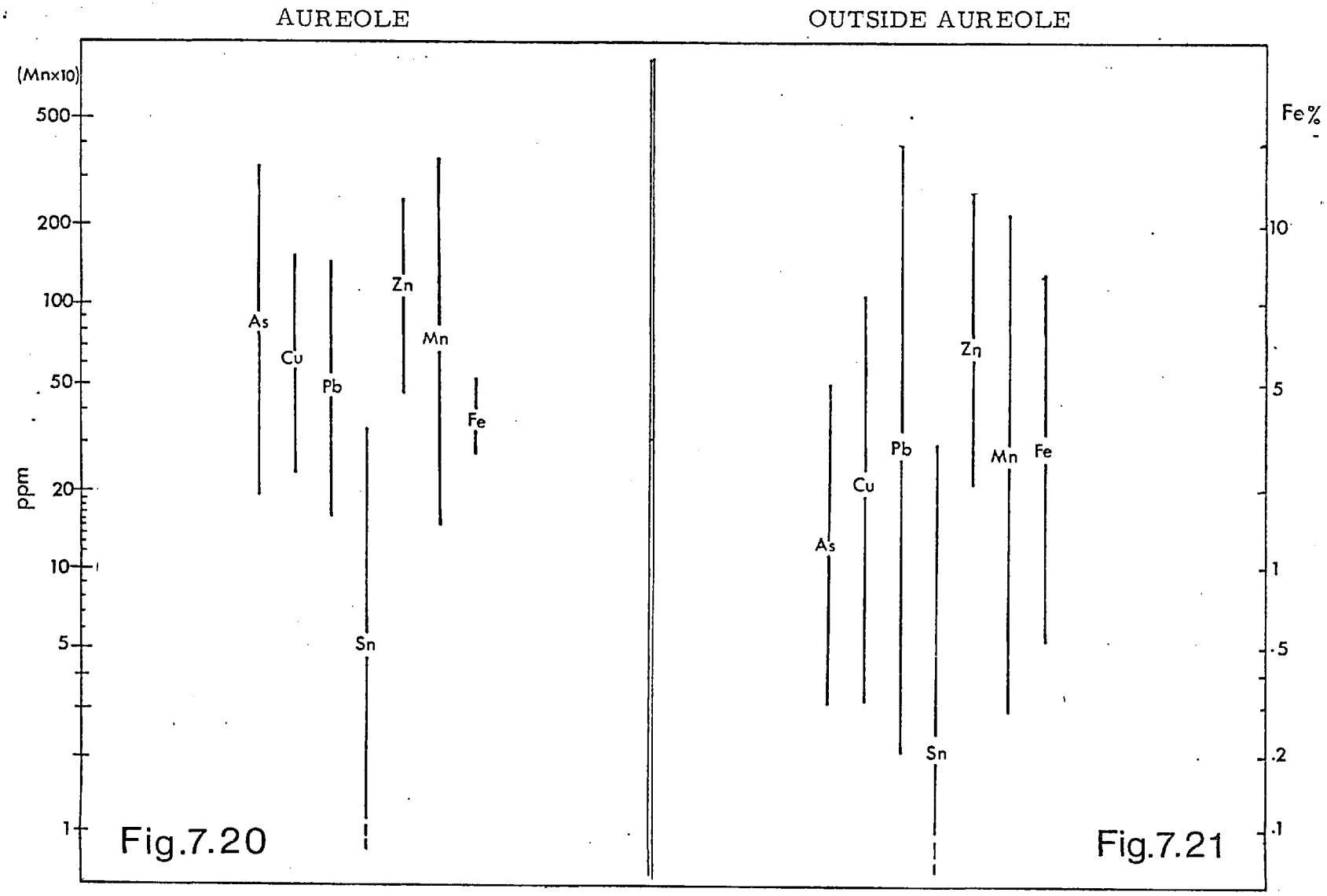


Fig. 7.19. DARTMOOR - ANOMALOUS AREA



RANGE AND MEAN TRACE-ELEMENT CONTENTS OF SOILS FROM THE INSIDE AND THE OUTSIDE OF THE METAMORPHIC AUREOLE (TRAVERSE AA1)

TABLE 7.2

RANGE AND MEAN* TRACE-ELEMENT CONTENTS OF SOILS FROM TRAVERSE A, A1, NORTH DEVON, INSIDE AND OUTSIDE OF THE METAMORPHIC AUREOLE (values in ppm)

Element	Aureole	Outside Aureole**
As	81* 19-338	12 3- 49
Cu	61 23-162	20 3-104
Fe %	3.7 2.6-5.1	2.8 0.5-13.8
Mn	725 144-3630	252 29-2188
Pb	48 16-144	28 2-380
Sn	5 1- 35	2 1- 29
Zn	105 46-239	65 20-204

* Geometric Mean ($\bar{x}$)

Range = $\bar{x} \pm 2S$ (log standard deviation)

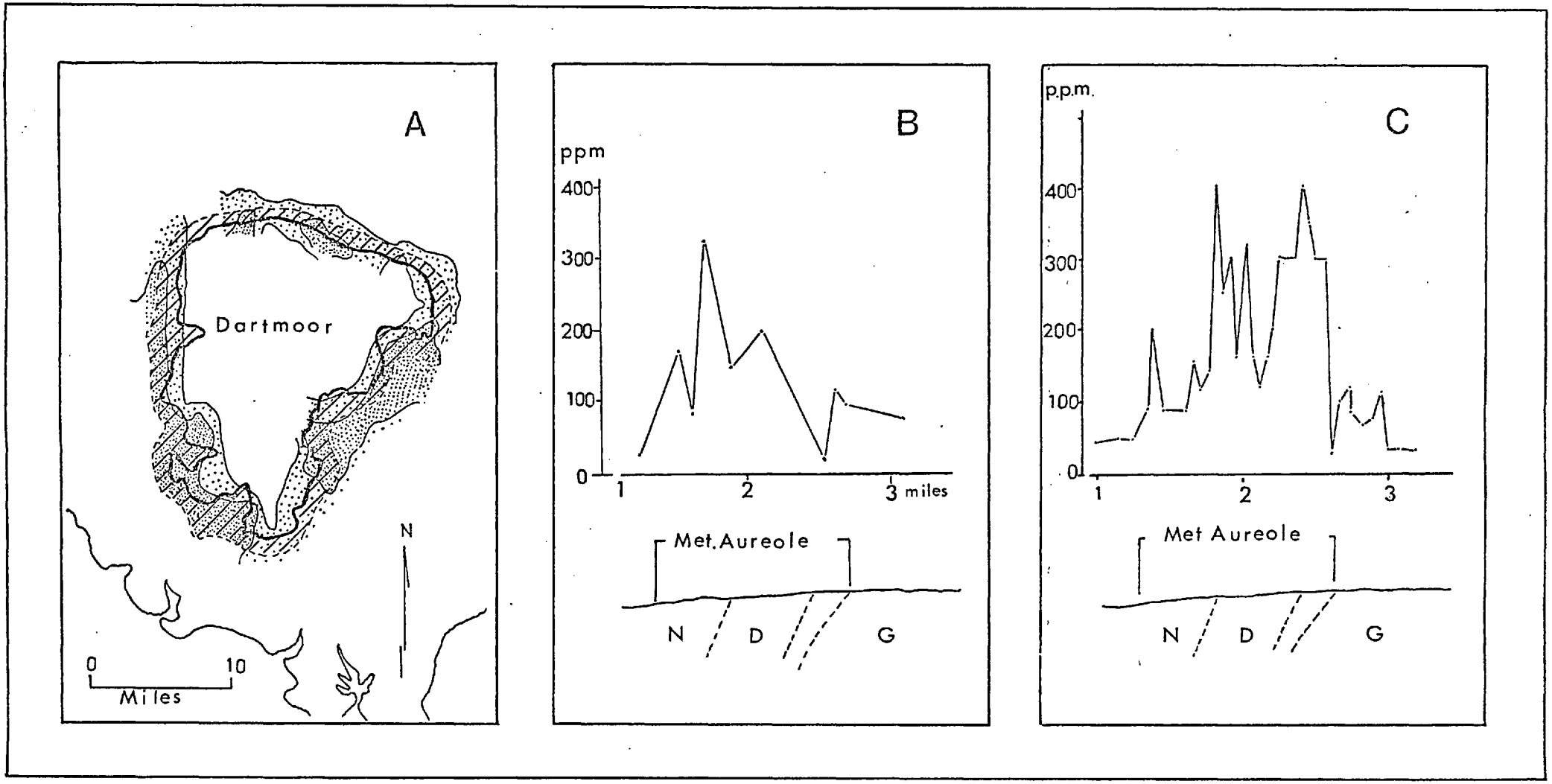
** Granite not included

The interpretation of stream sediment reconnaissance patterns revealed the presence of anomalous concentrations of As accompanied by other trace-elements over areas surrounding the granitic masses, specifically, within the metamorphic aureole. These concentrations have been confirmed by the stream sediment and soil investigations which showed the same features within such an area (Fig. 7.22). Examination of soil characteristics, which appear closely related to bed-rock geology, and some rock samples from the area suggested that the anomalous values of As and the other elements are directly related to primary dispersion derived from rocks which have undergone thermal metamorphism during the granite emplacement. Nevertheless, those soil values over the Lower Carboniferous which lie entirely within the metamorphic aureole differ from the rest of the soil levels found in the aureole, being higher in this Formation. The exception is Pb whose mean value is lower over the Lower Carboniferous. Mn shows its highest value over the igneous basic rock from this Formation while Cu, Pb, Sn and Zn tend to be lower. At the same time it was disclosed that Cu, Fe and Zn, which show high concentration in stream sediment and soils' samples from the metamorphic aureole, are lower in rocks from this area in relation to those from the outside of the aureole (Table 7.3). This last assumption however, must be considered cautiously due to the fact that it is based on the analysis of a small number of rock samples.

b) Bed-Rock Geology

Mean and range Arsenic content related to geology are shown in Fig. 7.23 and Table 7.4.

Almost all the elements display their highest mean values within the Lower Carboniferous as compared to other geological units. The expections are: Pb, whose mean level presents almost no difference with that of this Formation, and yet being slightly lower



A Grey Scale Map

B Stream Sediment

C Soil

Fig. 7.22 DEVON AREA - STREAM SEDIMENT AND SOIL SAMPLING (TRAVERSE AA1)
(Explanation as for Fig. 7.11)

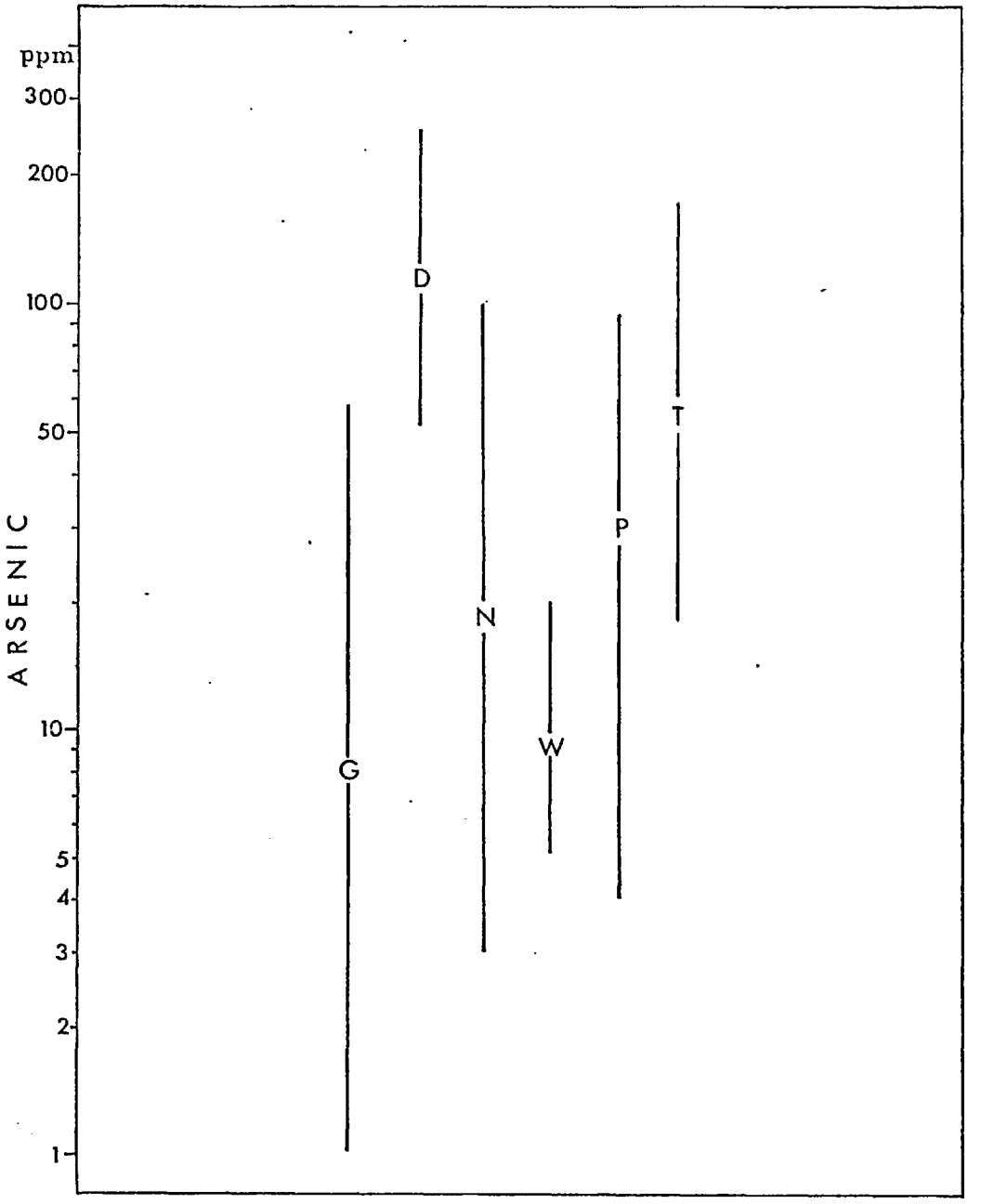
TABLE 7.3

MEAN* TRACE-ELEMENT CONTENTS OF ROCKS (R), SOILS (S), AND STREAM SEDIMENTS (SS) FROM THE INSIDE AND THE OUTSIDE OF THE METAMORPHIC AUREOLE, TRAVERSE A, A1 (values in ppm)

Element	AUREOLE			OUTSIDE AUREOLE**		
	R	S	SS	R	S	SS
As	77	81	62	10	12	14
Cu	12	61	68	18	20	20
Fe %	1.6	3.7	2.3	3.6	2.8	3.6
Mn	538	729	525	390	252	490
Pb	49	48	50	32	28	36
Sn	5	5	7	1	2	2
Zn	55	105	71	73	65	89
No. of Samples	10	39	32	12	88	31

* Geometric Mean

** Granite not included



G = Granite
D = Dinantian (Lower Carboniferous)
N = Namurian (Crackington Formation)
W = Westfalian (Bude Formation)
P = Permian
T = Pleistocene (Ta. Terrace)

Fig. 7.23 RANGE AND MEAN ARSENIC CONTENT OF SOILS RELATED TO THE MAIN GEOLOGICAL FORMATIONS (TRAVERSE AA1)

than that of the Permian; and Fe whose mean value only manifests a high contrast within the granite. Because the Lower Carboniferous is entirely situated within the metamorphic aureole, and thus has undergone thermal metamorphism, it has not been included in the present interpretation. Its main features have been mentioned previously in the discussion of the metamorphic aureole.

Although some kind of secondary environmental effects have influenced the distribution of As in some areas (poorly drained soils in the Crackington Formation, for instance), the concentration patterns of this element closely correspond to the local geological units and it is obvious that such patterns have originated from the underlying parent-rock. This assumption is supported by rock sample analysis which shows little difference in the As content in relation to the soils. The most outstanding features of the distribution of As in soils related to bed-rock geology are: the contrast in mean values between the Bude and Crackington Formations (1:2); the high mean level in the Permian sediments relative to surrounding country rock, and the moderately high As concentration within the area located over the granite immediately after its contact with the country-rock (Fig. 7.23, 7.24 and Table 7.4)

The difference in the As content in the Crackington and Bude Formations has already been established in sediment patterns. This contrast is reflected in the As levels of the rocks from these geological units although in these samples the difference is less than in the soils. The relatively high As concentration over the Permian occupies two thirds of the northern part of this Formation, with values ranging from 25 to 90 ppm. The southern area is characterised by low As levels ranging from 8 to 12 ppm. It is possible that a topographic profile which is deeper to the north, has played an important role in this particular dispersion, however, variation in lithology might be considered.

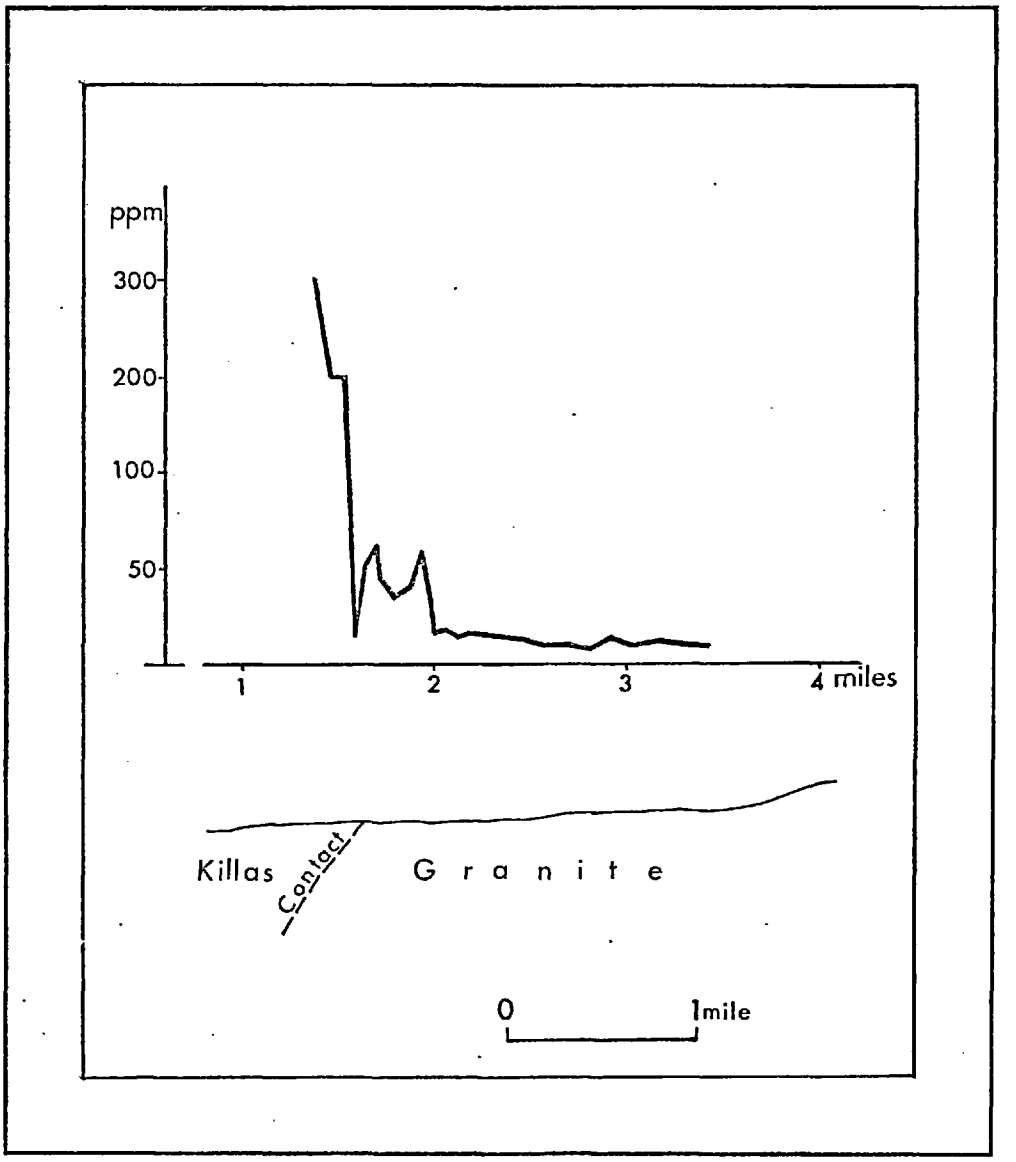


Fig. 7.24 ARSENIC CONTENT OF THE SOILS RELATED TO THE GRANITE

TABLE 7.4

RANGE* AND MEAN** TRACE-ELEMENT CONTENTS OF SOILS RELATED TO BED-ROCK GEOLOGY, TRAVERSE A, A1, NORTH DEVON (values in ppm)

ELEMENT	GRANITE	CARBONIFEROUS			PERMIAN	PLEISTOCENE
		Lower Carboniferous	Crackington Formation	Bude Formation		7th Terrace
As	8** 1- 58*	113 51-257	18 3-102	9 5- 19	30 4- 95	55 17-173
Cu	7 1- 35	80 30-302	33 15- 72	20 6- 65	21 14- 32	11 3- 22
Fe %	0.4 0.2-6.7	4.2 2.6-6.0	4 1.7-9.0	3.4 2.0-6.0	3.4 2.1-5.5	2.2 0.2-10
Mn	70 31-371	1150 289-4580	252 38-1650	372 35-1074	725 229-2291	175 28-691
Pb	25 10- 30	38 8-152	39 13-112	34 15- 38	41 17-109	41 23- 69
Sn	2 <1- 85	8 <1- 28	2 <1- 14	1 <1- 17	5 <1- 87	3 <1- 35
Zn	26 13- 72	139 55-347	89 35-199	24 35-141	93 54-162	45 18- 95
No. of Samples	48	24	41	25	19	17

* Range = $\bar{x} \pm 2$ (log standard deviation)

** Geometric mean ($\bar{x}$)

Four granite samples were collected in the area where As shows its major concentration (near the contact) within the granitic soils. The values found in these rocks exceeded those of the soils. Thus it can be assumed that the As content in soils from this particular area has originated from the parent-rock, and that soils have been depleted of this element to some degree.

A relatively high concentration of Sn is located over the Permian sediments, and this concentration extends northward and continues half-way into the Bude Formation before falling off. (Fig. 7.25) These high Sn values within the Permian were reported in early studies (Horsnail, 1968; Nichol et al. 1971), and they have been associated with the presence of cassiterite in this unit. The high concentration of Sn in the Bude Formation might be due to clastic dispersion from the Permian in which topography and river capture seem to have played the most important role. However, in some areas this concentration is reflected in the underlying parent-rock. This phenomenon has not been explained and further investigations are considered worthwhile.

c) Mineralisation

On interpreting the regional geochemcial reconnaissance patterns in south-west England, (Chapter 6), the Corscombe area was found to be high in As content. These high levels were classified as anomalous values related to possible mineralisation (Fig. 6.11, C-1). During this study these concentrations were confirmed in the analysis of stream sediment, soil and rock samples from the area (Table 7.5). In the soil traverse, this anomaly is reflected in both top-soil and sub-soil, with values ranging from 25 to 250 ppm in the latter medium. Zn concentration reaches its highest peak within this area, its value being about 20 times the mean level from the general soil traverse (Fig. 7.26).

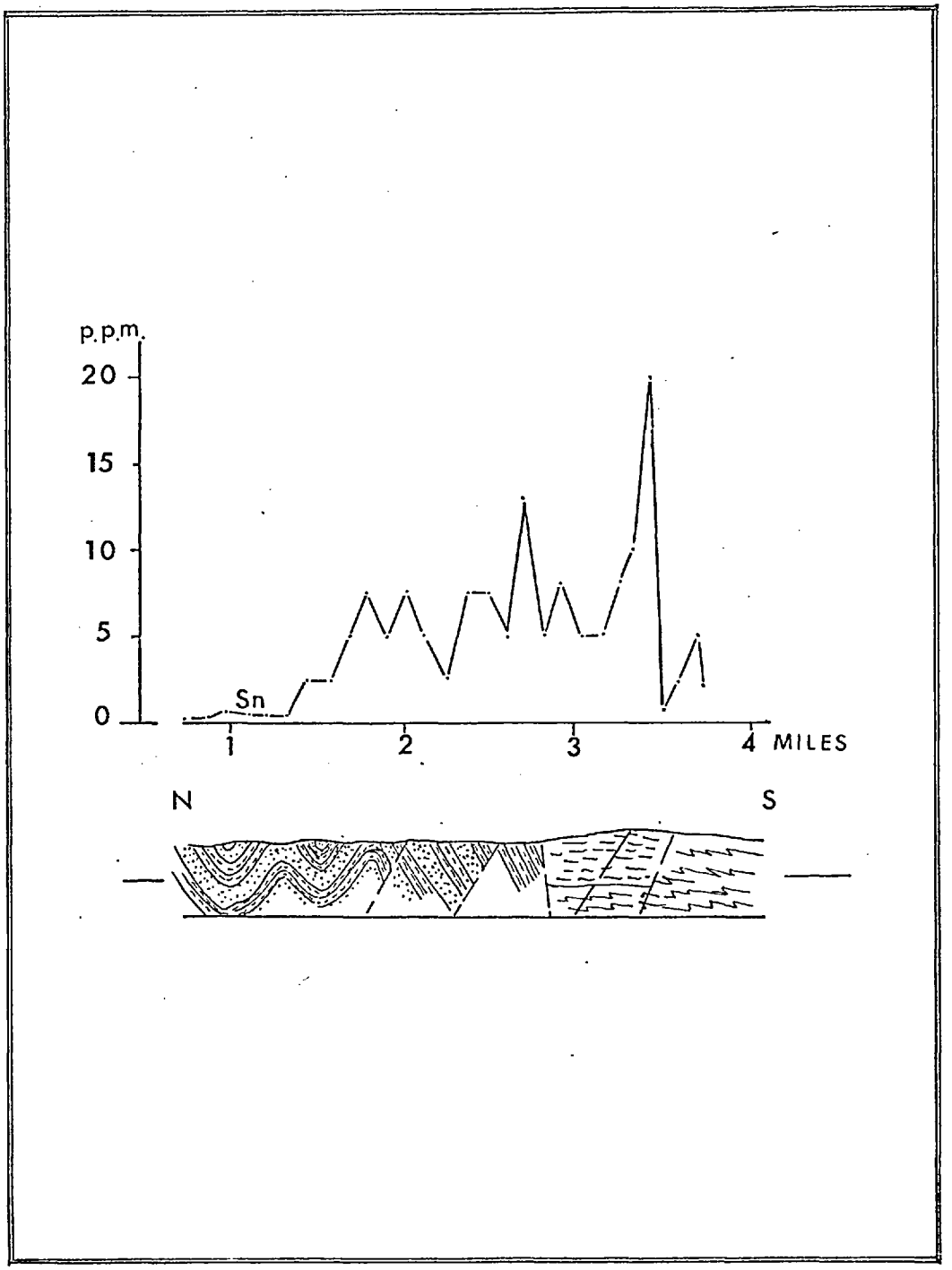


Fig. 7.25 DEVON AREA - SOIL SAMPLING
(Explanation as for Fig. 7.7)

TABLE 7.5

MEAN* METAL CONTENT OF ROCKS, SOILS AND STREAM SEDIMENTS FROM CORSCOMBE AREA (values in ppm)

Element	Rocks	Soils	Stream Sediments
As	112	182	400
Cu	40	55	132
Fe %	2.3	4.2	8.16
Mn	860	914	524
Pb	60	91	45
Sn	9	14	25
Zn	246	400	914
No. of Samples	12	15	7

* Arithmetic mean

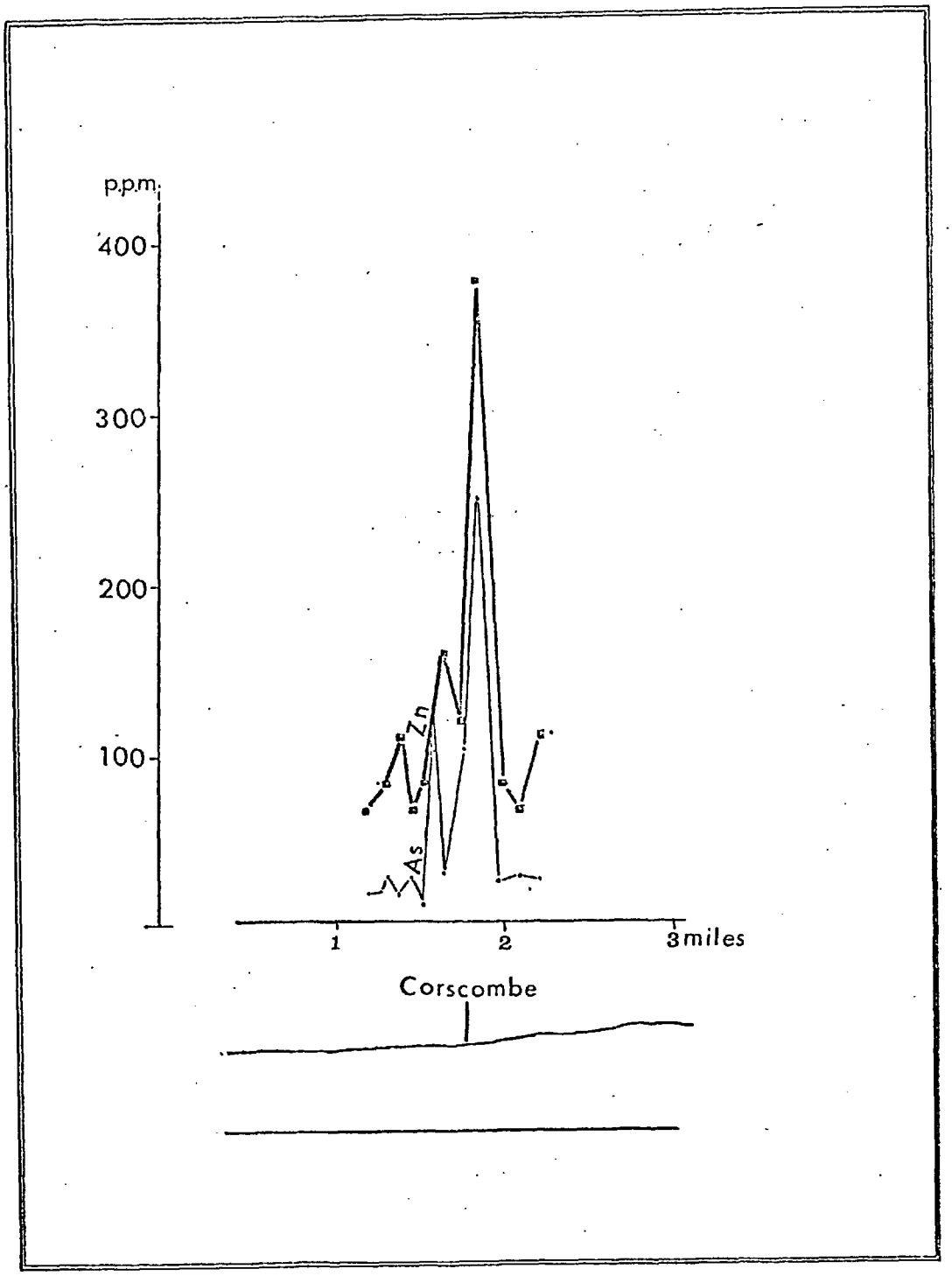


Fig 7.26. CORSCOMBE AREA-SOIL SAMPLING

2 Traverse B, B1 South Devon

This twelve-mile north-south soil traverse is underlain by igneous rocks and sediments of Devonian age. (Fig. 7.4). The igneous rocks are composed of Dartmoor granite (2.8 miles); two small laccolithic masses of basic igneous rocks (0.3 miles), and two narrow east-west strips of spilitic lava (0.5 miles). Devonian sediments are represented by slates and grits of the Lower and Middle Devonian (3.0 and 2.8 miles respectively), as well as slates of the Upper Devonian (2.6 miles). The latter lies almost entirely within the metamorphic aureole which surrounds the Dartmoor granite.

River gravel and head material derived from the Dartmoor overlays a broad area of the northern part of the Upper Devonian where it comes in contact with the granite. Narrow strips covered by this material together with alluvium are restricted to zones bordering the streams.

The topographic profile is characterised by flatter lands alternating with hills whose slopes range from 10^{o} to 25^{o}, the granitic surface being the steeper in the whole traverse (Fig. 7.27).

The metamorphic aureole underlying this traverse is totally composed of slates of the Upper Devonian; the only exception is a small intrusion of basic igneous rock (diabase). In this area the aureole is wider than in the northern part (Traverse A, A1), with an approximate ratio of 2:1.

a) General Description of the Distribution of the Elements

i) Stream Sediments

Distribution patterns of As and selected trace-elements in stream sediments are shown in Figures 7.27a, to 7.30.

As exhibits almost regular low distribution over the granite and in the Lower and Middle Devonian. The higher concentrations are restricted to the Upper Devonian, with its major content near

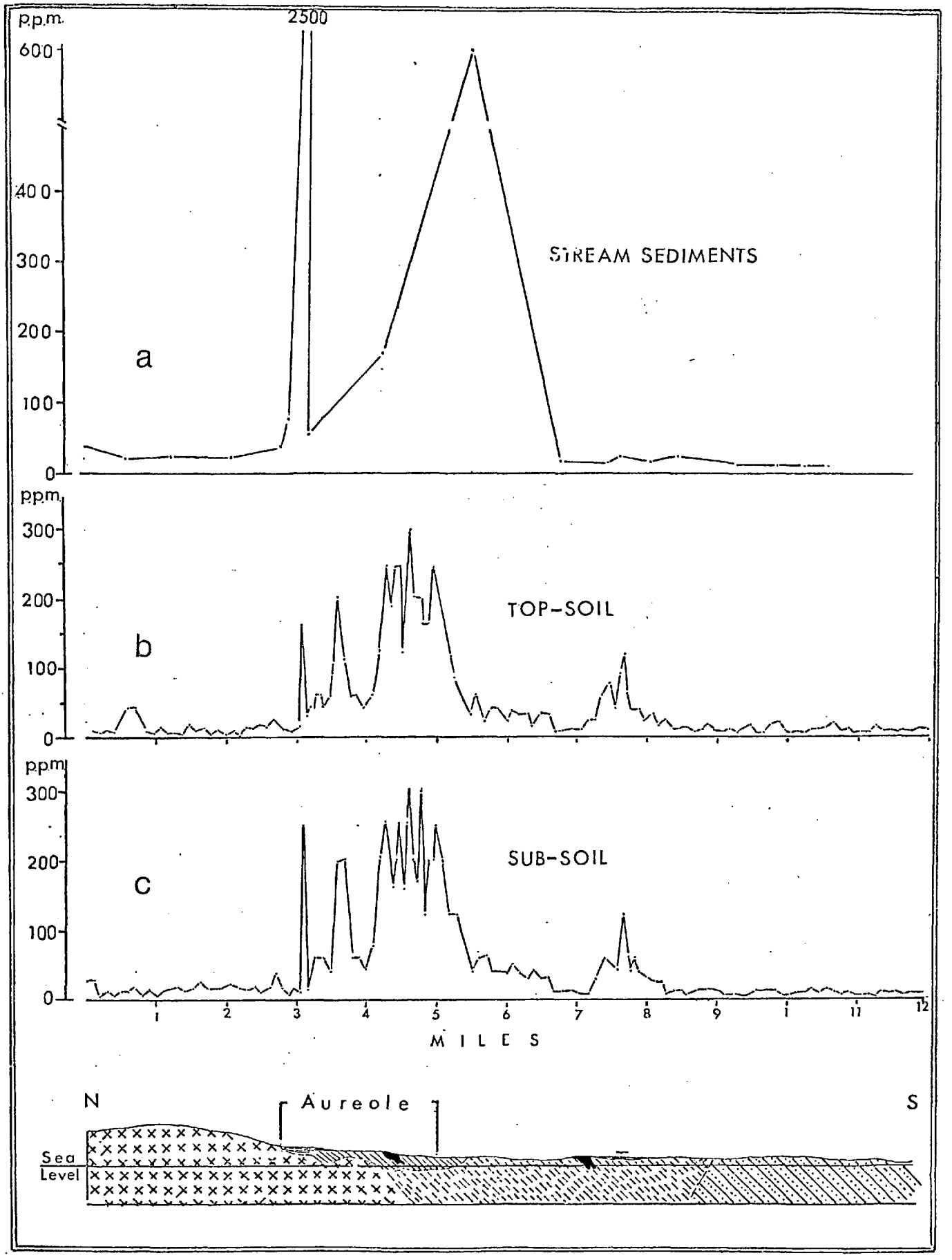


Fig. 7.27. DISTRIBUTION OF ARSENIC IN SOILS AND STREAM SEDIMENTS FROM TRAVERSE B'

1, Alluvium; 2, River gravel & Head; 3, Upper Devonian; 4, Middle Devonian; 5, Lower Devonian; 6, Tuffs; 7, Diabase; 8, Granite.

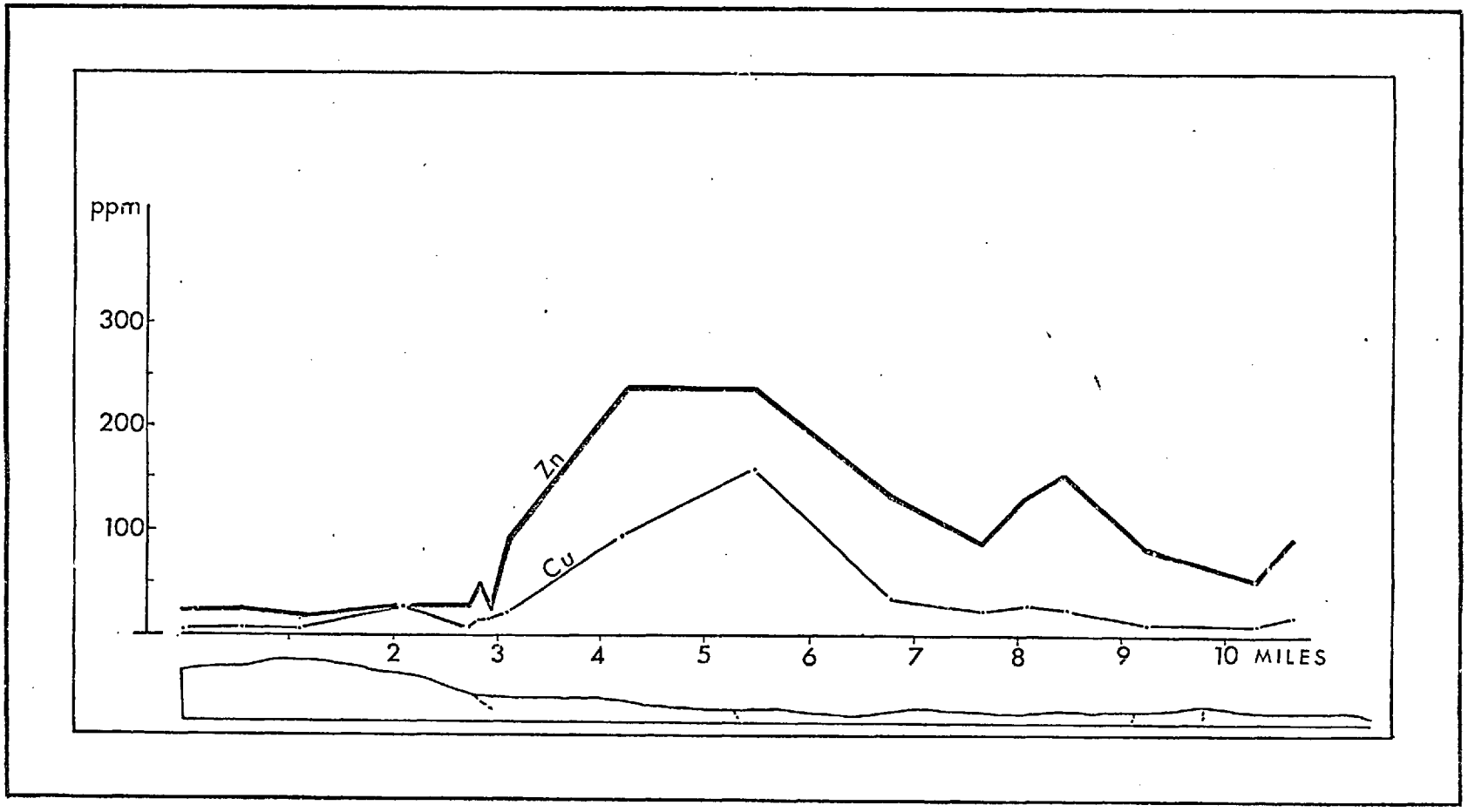


Fig. 7.28 DEVON AREA - STREAM SEDIMENT SAMPLING (TRAVERSE BB1)
(Explanation as for Fig. 7.27)

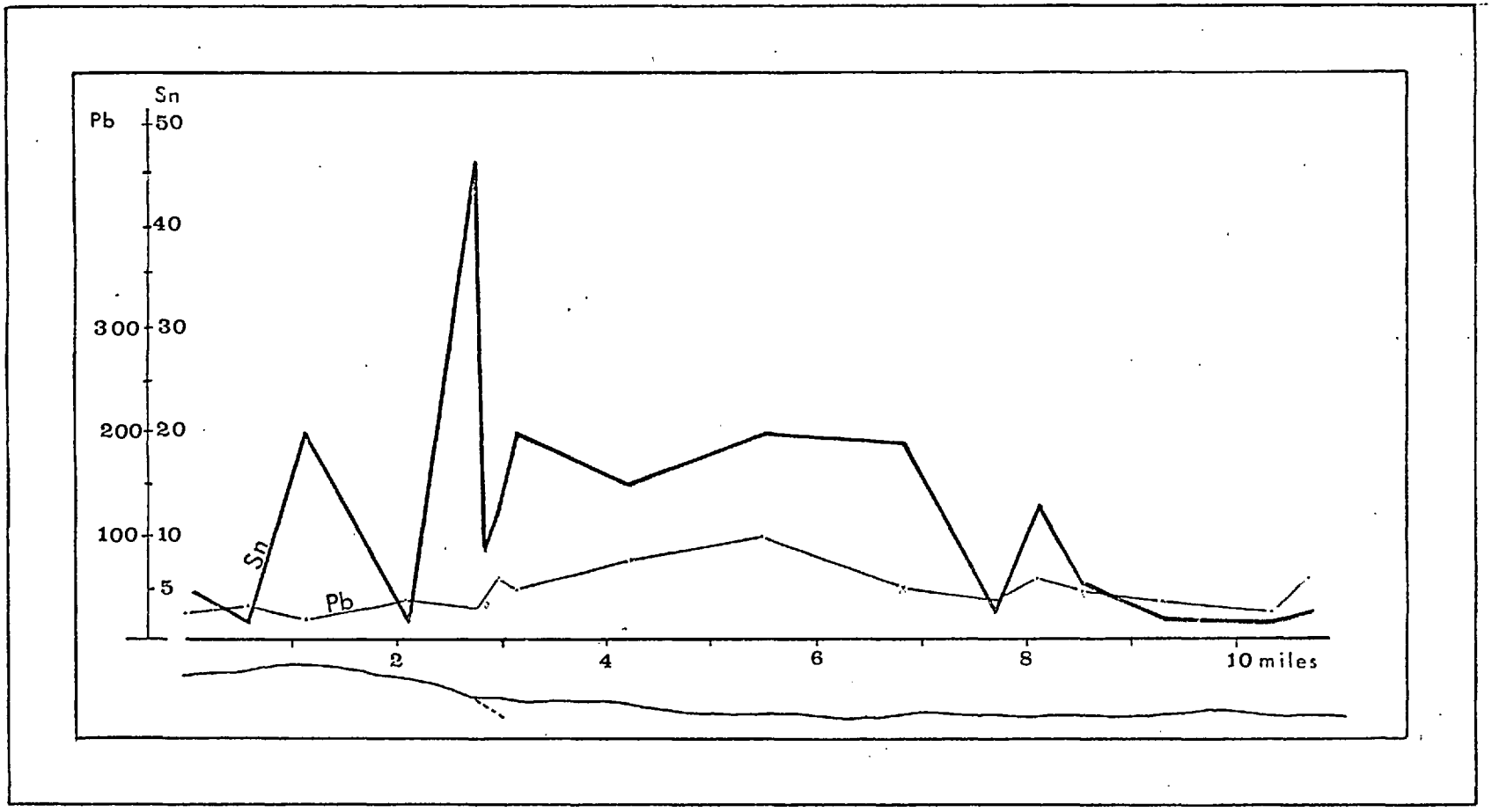


Fig. 7.29 DEVON AREA - STREAM SEDIMENT SAMPLING (TRAVERSE BB1)
(Explanation as for Fig. 7.27)

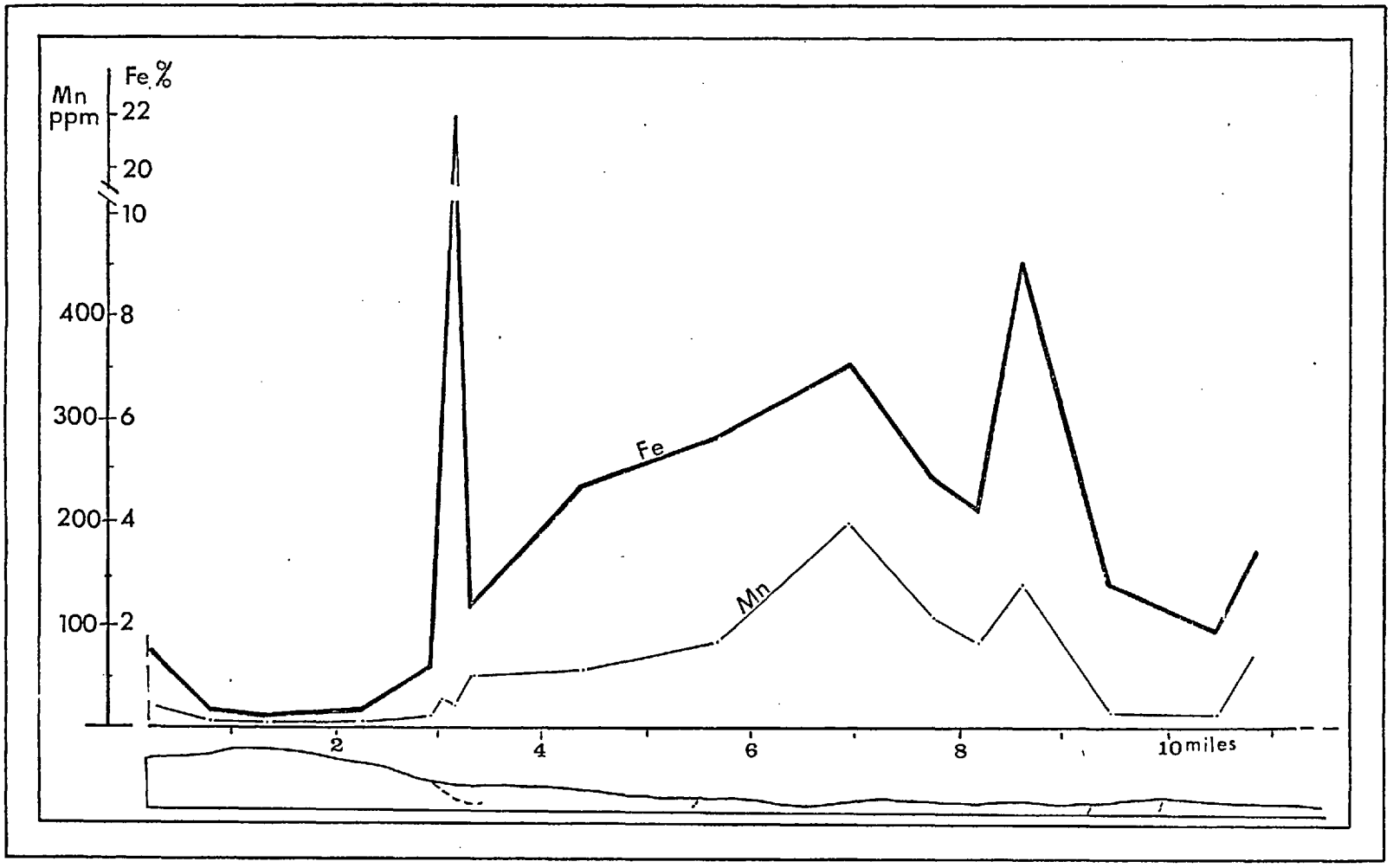


Fig. 7.30 DEVON AREA - STREAM SEDIMENT SAMPLING (TRAVERSE BB1)
(Explanation as for Fig. 7.27)

both northern and southern contacts. In the former area As reaches its highest value (2,500 ppm). The lowest concentration of this element is found almost uniformly distributed in the Lower Devonian, slightly increasing northward to the Middle Devonian.

Cu, Pb and Zn are very similar in their distribution. The lowest values are located over the granite, Lower Devonian, and southern part of Middle Devonian, although Zn becomes erratic in the latter units. The highest levels of these elements are found entirely over the Upper Devonian and in the northern section of the Middle Devonian. Fe and Mn also show a similar distribution along the whole traverse, with the exception of the high Fe peak (22%) over the northern section of the Upper Devonian. These two elements are low over the granite, increasing southward within Upper and Middle Devonian. The higher concentration of Mn and Fe is found within the Middle Devonian with Fe showing a high peak in the Middle-Lower Devonian contact. Over this latter unit both Fe and Mn are lower than in the former.

Sn is one of the most irregularly distributed elements. Low Sn values alternate with higher concentrations over the granite. The highest Sn content is located near the granite - Upper Devonian contact. This element gets more uniformly distributed in the Upper Devonian, and in a great part of the Middle Devonian, becoming lower southward into the Lower Devonian.

ii) Soils

Distribution of As in soils is shown in Fig. 7.27 (b and c), and selected trace-elements in Figures 7.31 to 7.33.

The distribution pattern of As is characterised by (1) its low concentration over the granitic mass, and within the Lower Devonian sediments, (2) broad areas of relatively high values alternating with less extensive zones of low levels in the Middle Devonian, and (3) high concentration over the Upper Devonian.

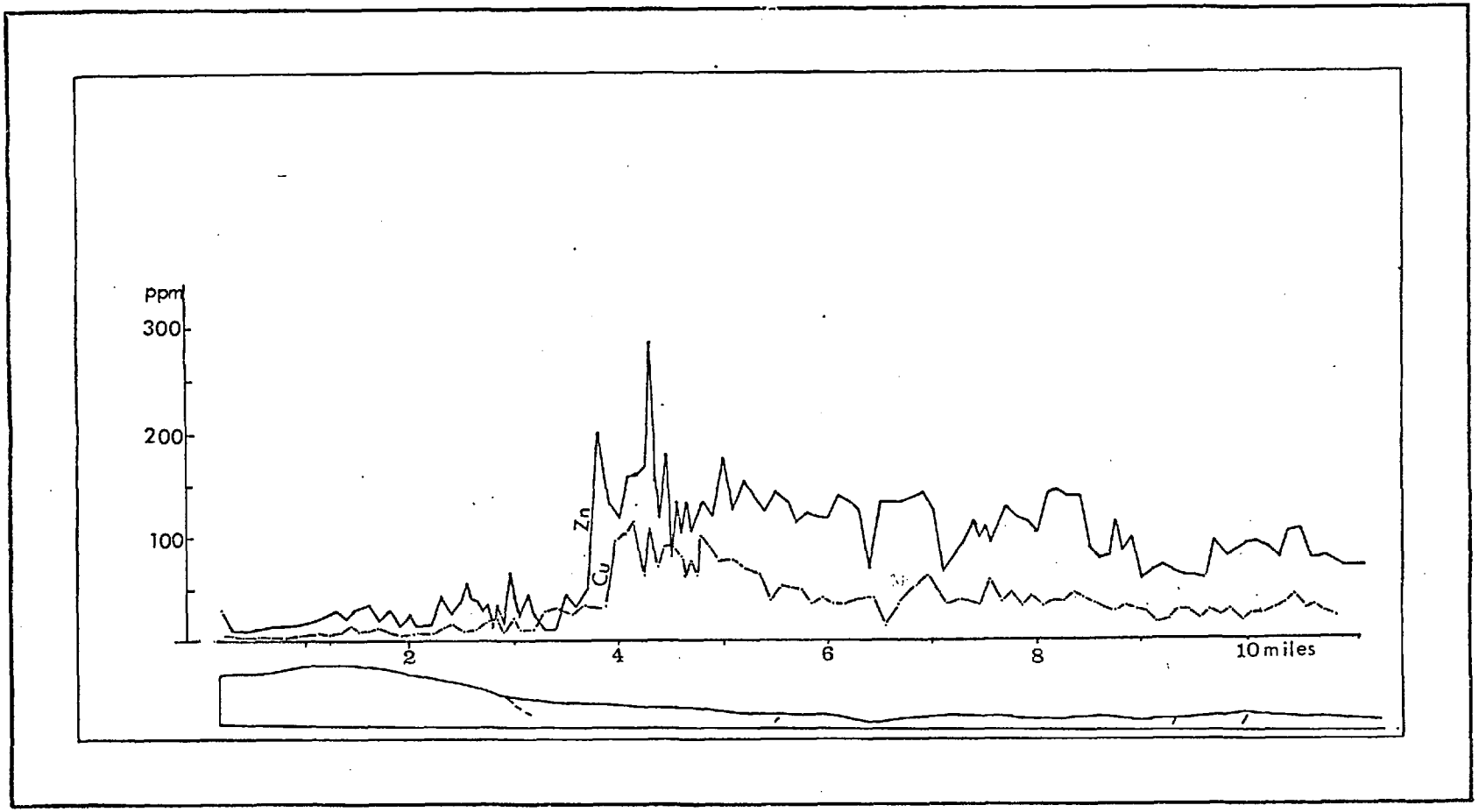


Fig. 7.31 DEVON AREA - SOIL SAMPLING, TRAVERSE BB1

(Explanation as for Fig. 7.27)

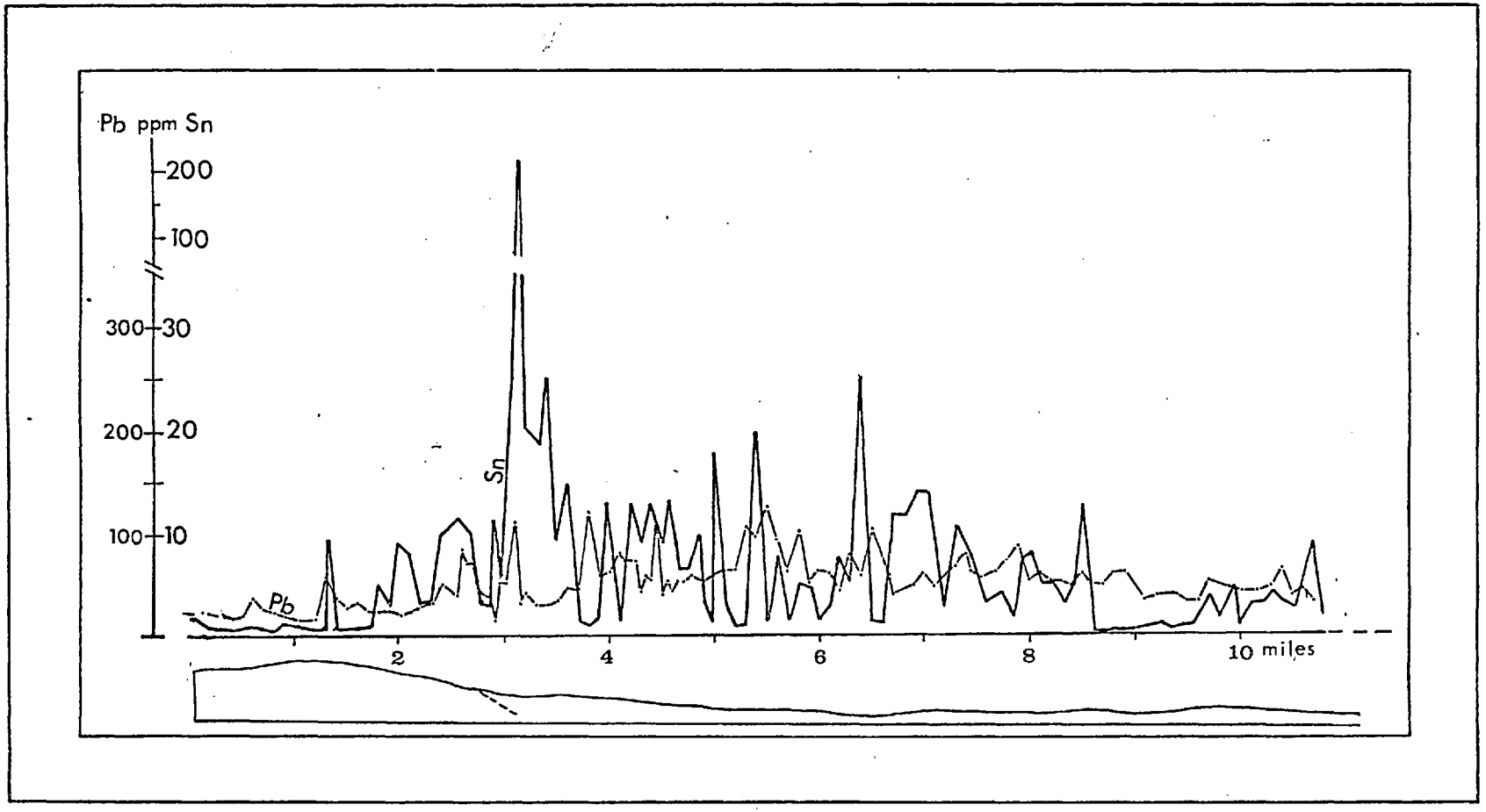


Fig. 7.32 DEVON AREA - SOIL SAMPLING TRAVERSE BB1

(Explanation as for Fig. 7.27)

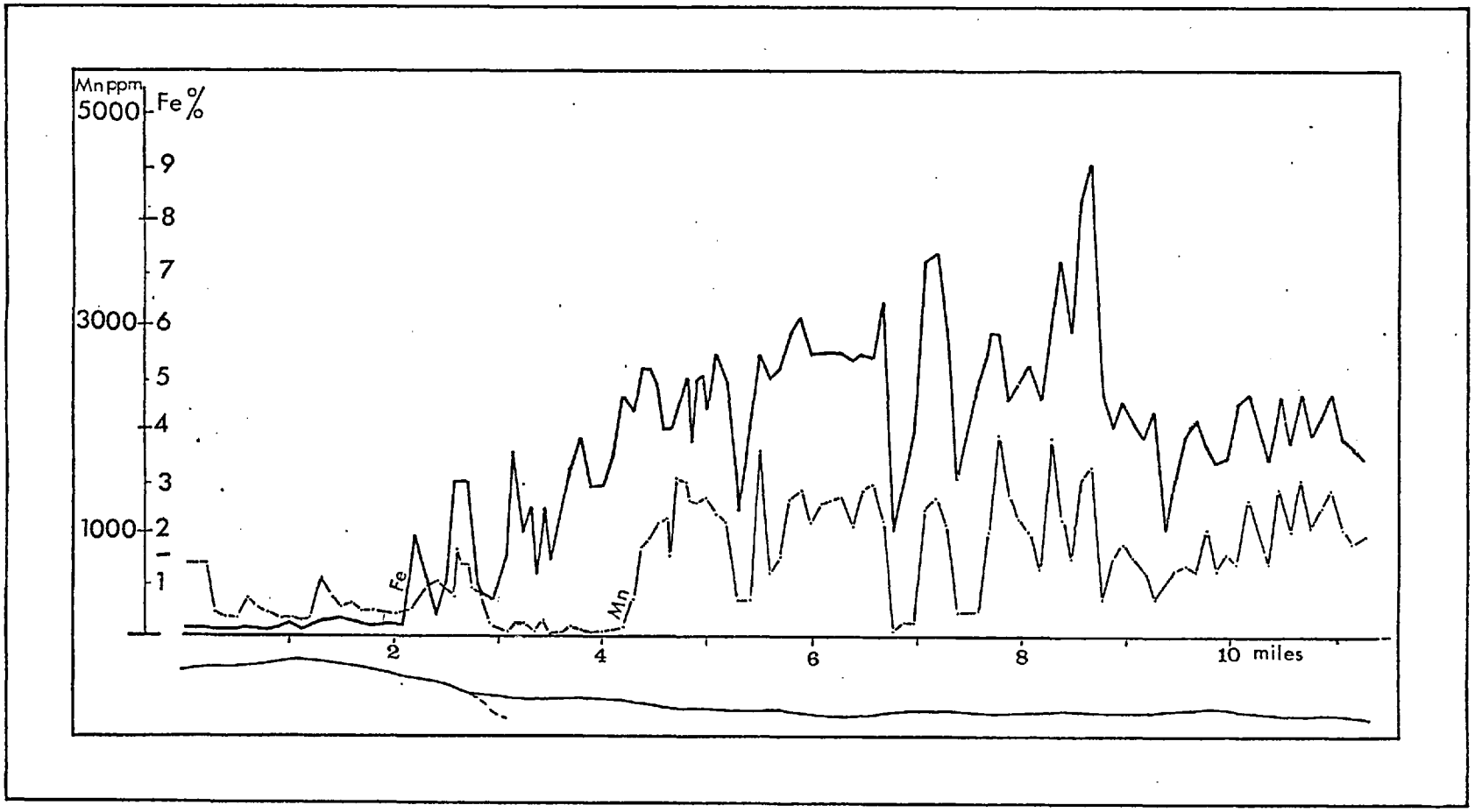


Fig. 7.33 DEVON AREA - SOIL SAMPLING TRAVERSE BB1

(Explanation as for Fig. 7.27)

In addition, distribution of As within the metamorphic aureole shows the peculiarity of being very high over the southern half of this area and extends into the Upper Devonian, while in the northern half relatively low values alternate with high levels of this element. This peculiarity is reflected in both top and sub-soil media, and in stream sediments. The high As concentration located over the northern section of the Upper Devonian is also found in stream sediments accompanied by high Sn and Fe content. (Fig. 7.34).

Cu, Fe, Mn, Pb, Sn and Zn display very irregular concentrations along the whole traverse. Their lowest values are located over the granite except Mn whose lowest levels are found in the northern half of the metamorphic aureole where Sn shows its highest concentration. Zn presents its highest content within the southern half of the metamorphic aureole. This element, along with Pb and Fe, is high over the Middle Devonian getting lower in the Lower Devonian. Sn, and Mn are very erratic throughout the whole Devonian although Sn is less irregular over the Lower Devonian. Cu displays its highest concentration within the metamorphic aureole; its values decrease southward as it passes through the Middle Devonian to the Lower Devonian.

b) Interpretation of Patterns

i) Stream Sediments

The limited data from stream sediments do not allow a clear assessment of the patterns displayed by most of the trace-elements in the area. This situation is especially noticeable in the Upper Devonian, particularly within the metamorphic aureole.

The low As patterns found in the granite, and in the Lower Devonian most likely reflect the bed-rock geochemistry, although it is difficult to discriminate individual local lithological units.

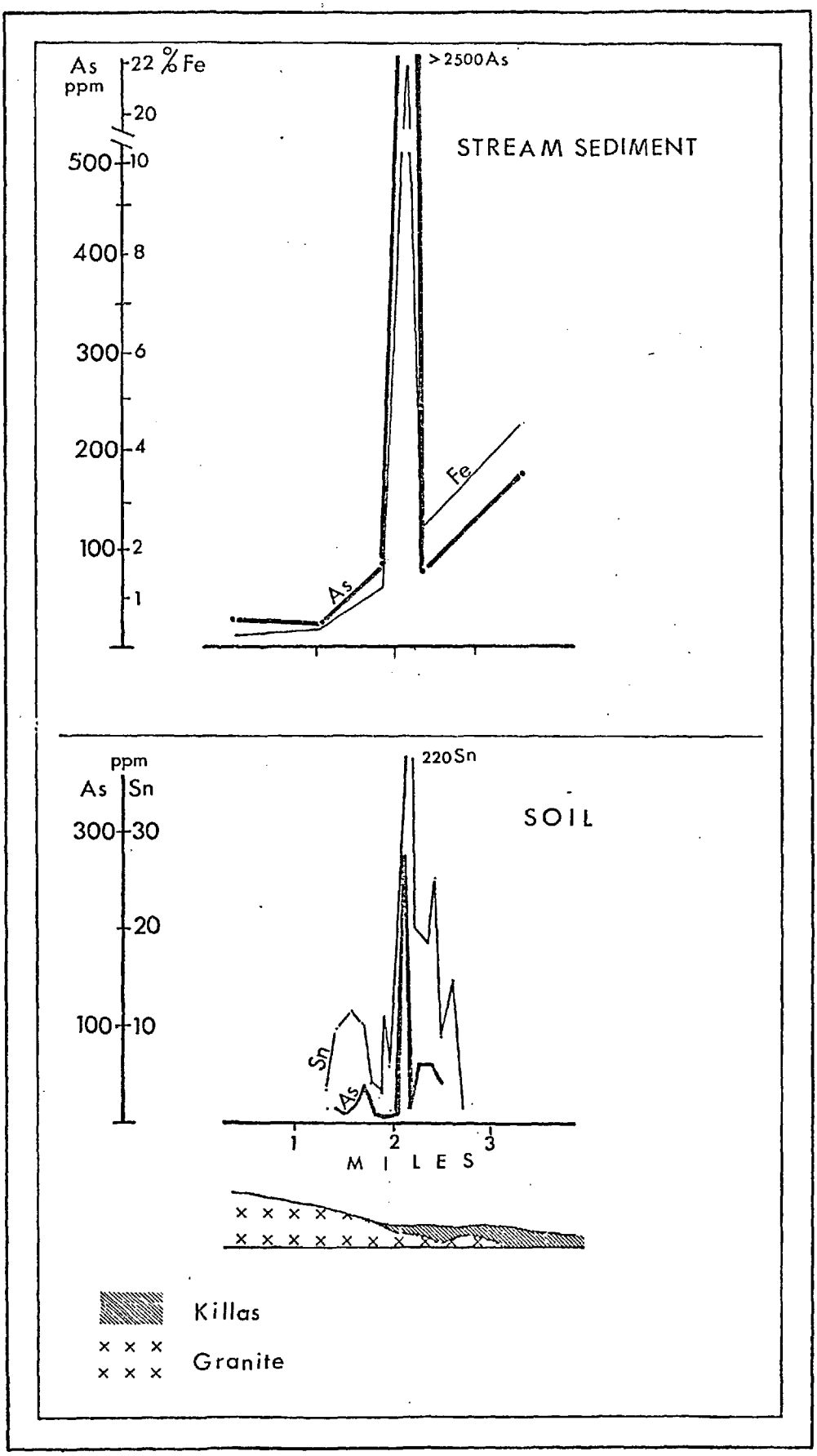


Fig. 7.34 DEVON AREA-SOIL AND STREAM SEDIMENT SAMPLING (TRAVERSE BB1)

The high As values (2,500 ppm) near the granite-Devonian contact are of significance (Fig. 7.27a). Detailed sampling in two small streams showed high concentration of As and Fe (2,500 ppm, and 22% respectively) downstream, the high values falling off up-stream to 40 ppm As and 1% of Fe. These anomalous levels might suggest possible mineralisation into the area; more detailed studies are necessary to clarify the significance of this anomaly. The area has been classified as anomalous Area V. (Figs. 7.35 and 7.36). The high As level located in the Upper-Middle Devonian contact (800 ppm) seems to have originated as a result of contamination rather than by the influence of mineralisation of bed-rock geochemistry. The high concentration of Sn within the granite closely located to the granite-Devonian contact possibly originated because the clastic concentration of this element in the stream which drains through a blocky granitic area. Mn and Fe show high values within the Middle Devonian and they probably are related to basic igneous rocks and/or to poorly drained soils. Low patterns of Cu, Pb and Zn over the granite, Middle and Lower Devonian seem to be connected to bed-rock geology, and the relatively high peak of Zn in the latter Formation can be related to the high Fe or Mn concentrations in this point. Although most of the elements show their higher concentrations over Upper Devonian, no correlation can be established between these concentrations and the parent-rock from this unit.

ii) Soils

Interpretation of the distribution patterns of As and selected trace-elements has been assessed as it relates to:

a) Metamorphic Aureole

b) Bed-Rock Geology

c) Mineralisation

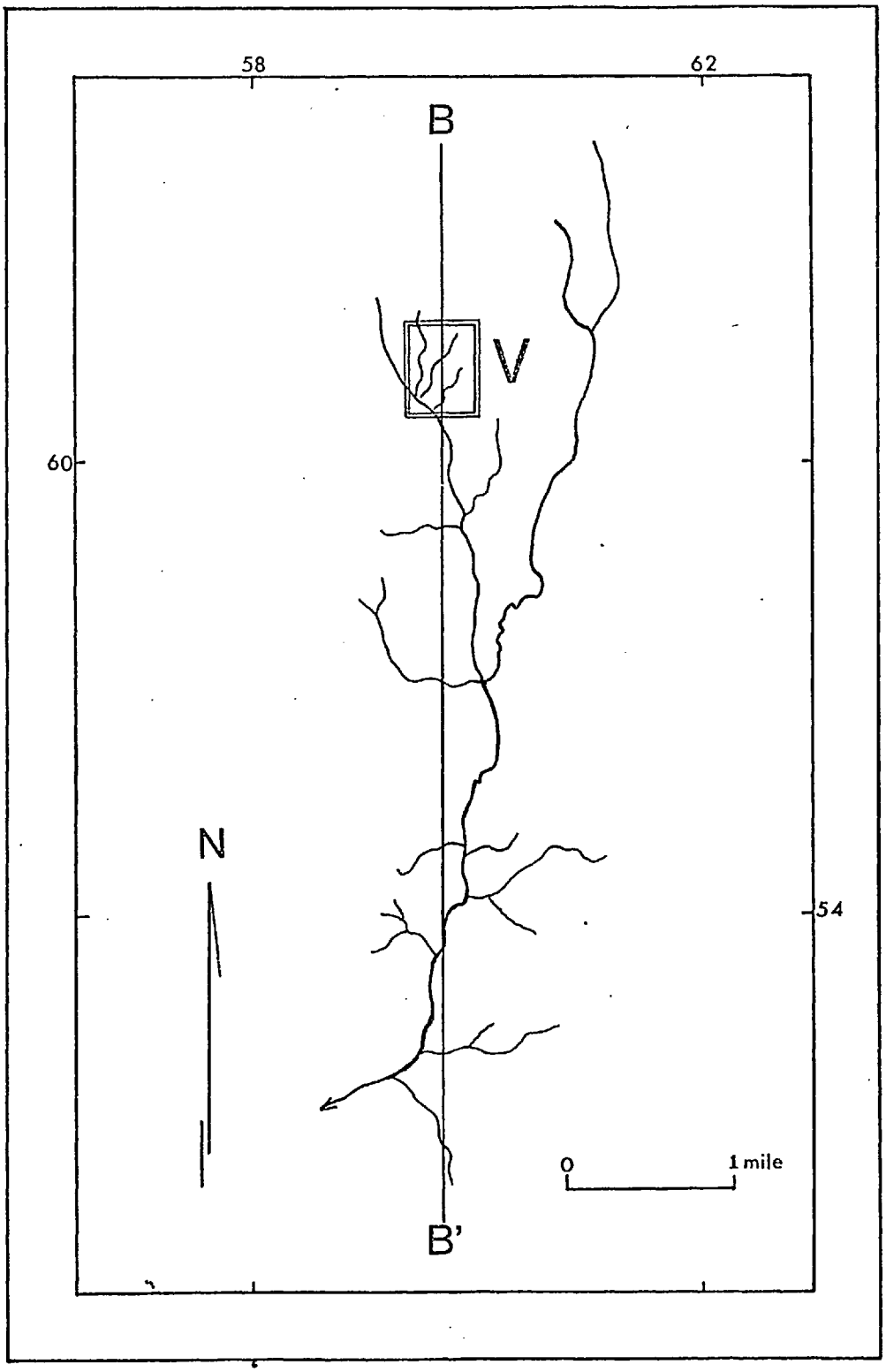
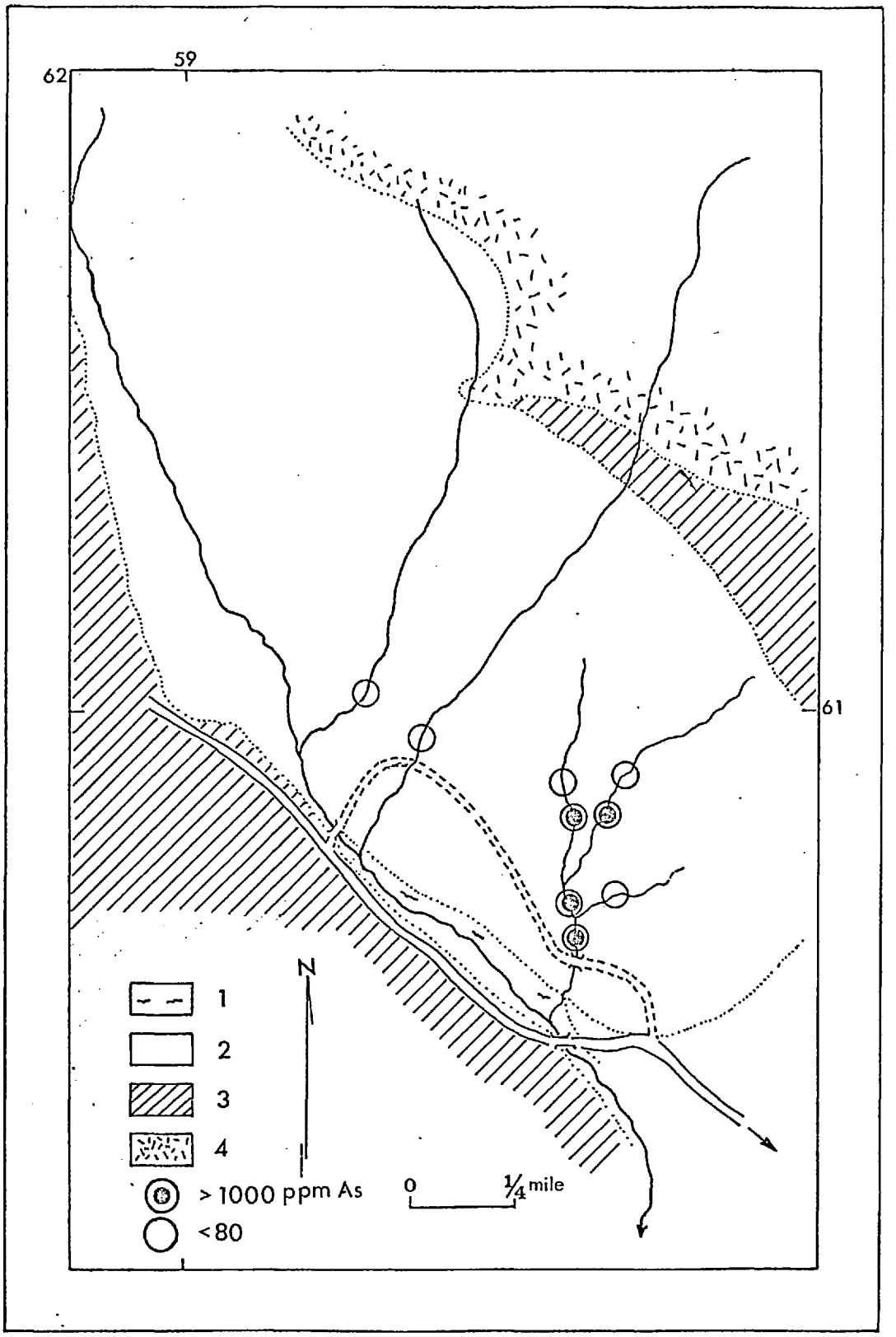


Fig. 7.35 TRAVERSE BB1, ANOMALY V



1 Alluvium
2 River, head and gravel
3 Devonian
4 Granite

Fig. 7.36 AREA V- STREAM SEDIMENT SAMPLING

a) Metamorphic Aureole

As previously mentioned, the metamorphic aureole covered by the traverse occupies a broad area lying entirely over sediments of Devonian age. Within this area As exhibits a striking distribution pattern which greatly differs from that found in the former traverse (Figures 7.7 and 7.27). This As pattern, described above, is supposed to have been affected by three primary factors:-

i) A large area in the northern section of the aureole, close to the contact, is covered by river gravel, head, and alluvium material mainly arising from the granitic body. Thus the concentration patterns of the elements cannot be associated with the underlain parent rock. It is over this area that As in addition to Cu, Mn, An and to a lesser degree Fe displays its lowest values, while Pb and Sn show high concentration, with Sn reaching its highest level there (225 ppm).

ii) On the assumption that trace-element patterns in soils are directly related to the underlying metamorphosed parent-rock, and consequently to the granite emplacement, the disparity of As patterns in soils over the aureole might be related to the following facts:

a) The granitic mass extending outward to the south from its country-rock contact seems to be very shallow beneath most of the metamorphic aureole.

b) The granitic body, with a roof displaying a waving 'topographic relief', generated a varied temperature gradient which affected the dispersion of the element into the host-rock (Figs. 7.27 and 7.37)

The hypothesis concerning granitic shallowness is supported by early gravimetric studies carried out in the area. Thus Bott et al (1958) and Bott and Scott (1964) reported that negative anomalies over

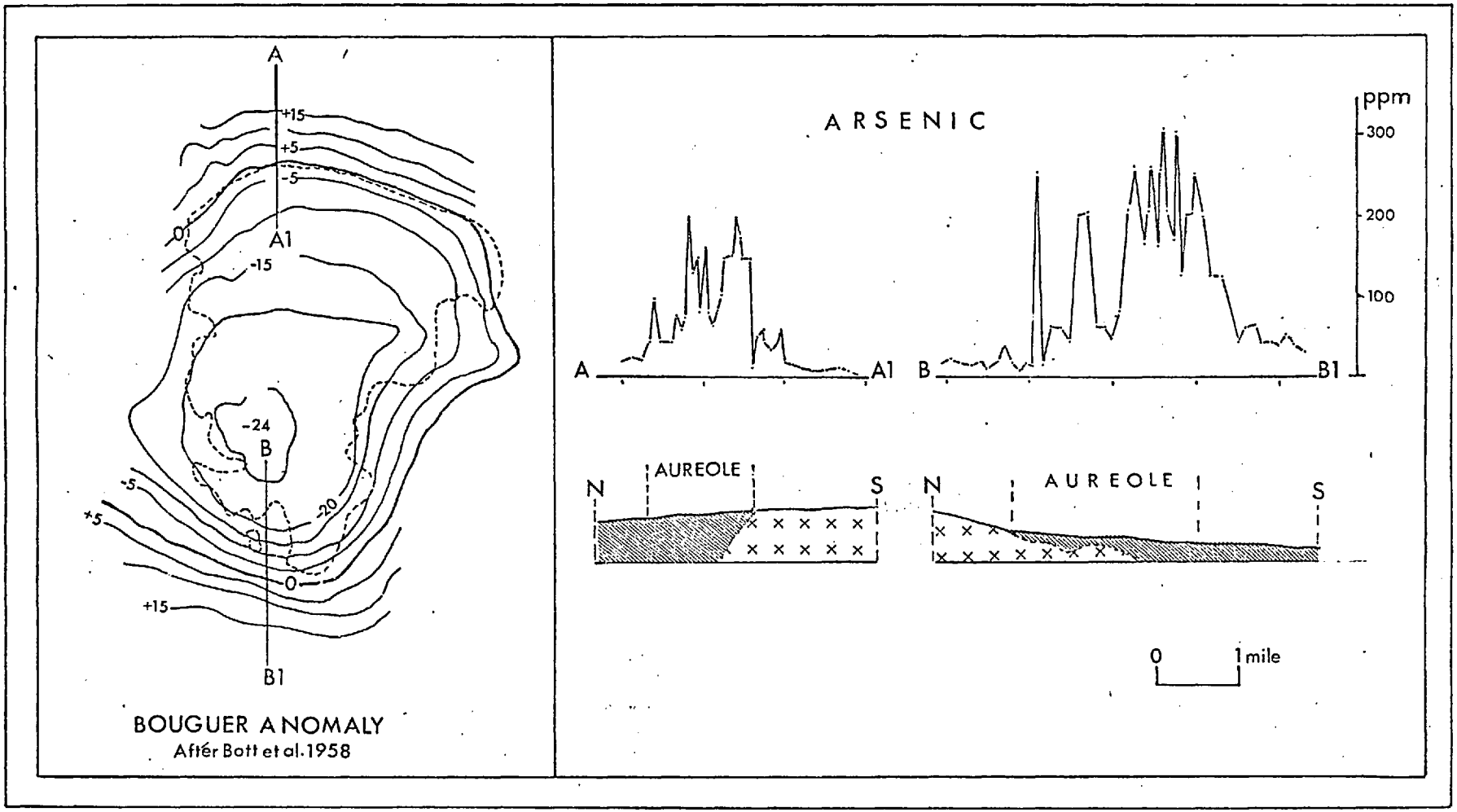


Fig. 7.37 DEVON AREA - SOIL SAMPLING

(Explanation as for Fig. 7.34)

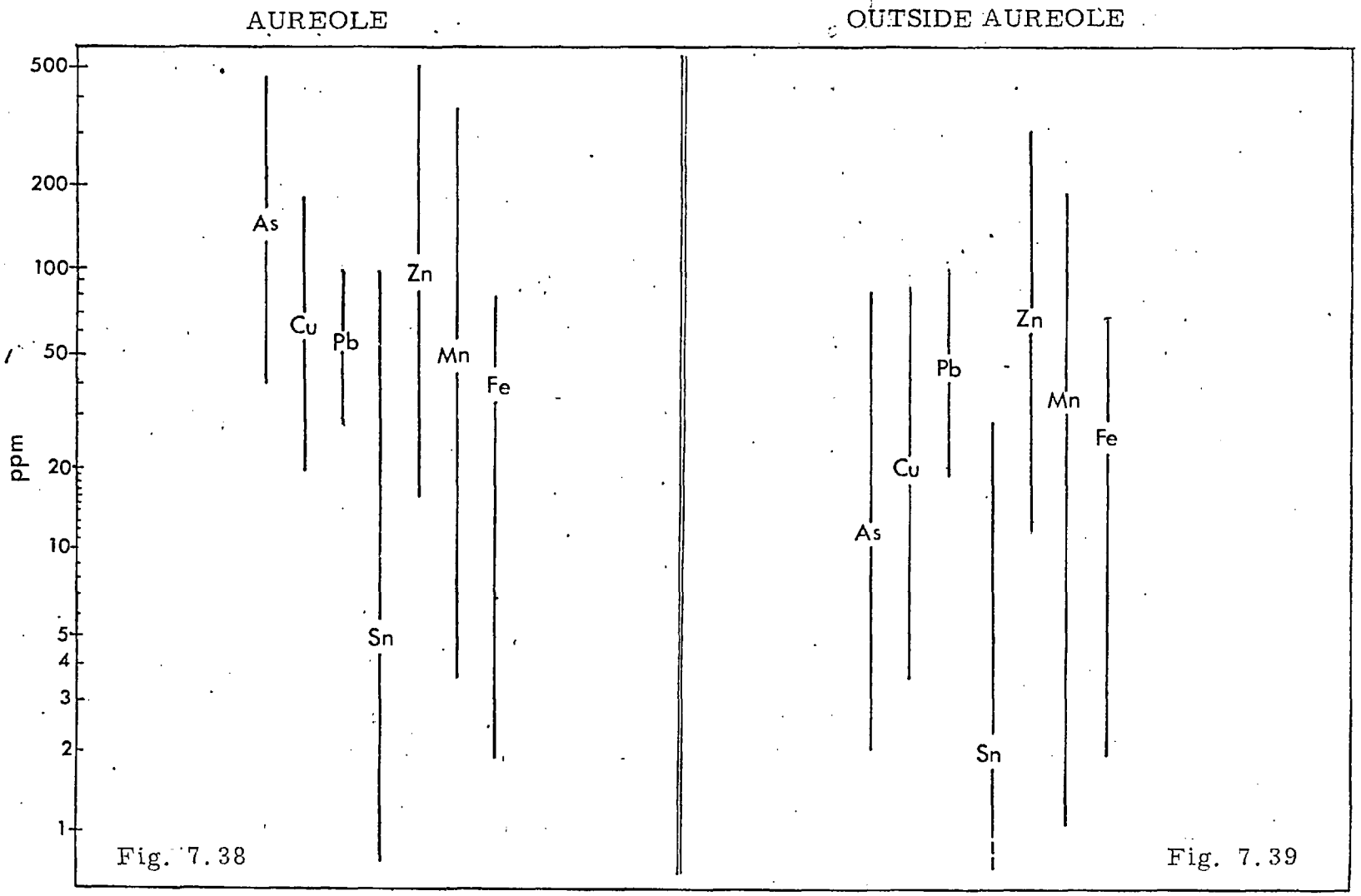
the granite can be attributed to the low density of the granite as compared to the country-rocks. Furthermore, on the basis of the gravity anomalies, the contact of the granite may be divided into relatively flat lying (but undulating) roof region, and walls which normally slope steeply outwards. (Fig. 7.37).

iii) Topographic relief might have influenced the major As concentration over the southern section of the aureole, and within the Upper Devonian area situated outside the aureole. Distribution patterns of Cu, Pb, Fe, Mn, Sn and Zn in the metamorphic aureole are similar to that of As within the same area, with higher mean levels than those from outside the aureole (Fig. 7.38 and 7.39 and Table 7.6).

b) Bed-Rock Geology

Mean and range levels of the As related to the geology are shown in Fig. 7.40 and in Table 7.7.

The best exposed pattern of As bearing a mean value of 7 ppm is found over the Lower Devonian. The lithological groups from this Formation (Dartmouth slates, Meadfoot Group, and Staddon Grits), do not show any difference in their As content. Concentration of this element within the Middle Devonian, with a mean level of 22 ppm, has been affected by the high values derived from the metamorphic aureole, and river-deposit material. These relatively high levels are exposed over a great part of this unit, southward from its Upper Devonian contact, and over a broad area located in roughly the central section of the Middle Devonian. The latter As concentration has been recognised as having originated in soils from river-deposit material. As concentration over igneous rocks outcropping in Middle Devonian is well distributed, and exhibits low mean levels: diabase 11 ppm and tuffs 12 ppm. The limited Upper Devonian area located outside the metamorphic aureole



RANGE AND MEAN TRACE-ELEMENT CONTENTS OF SOILS FROM THE INSIDE AND THE OUTSIDE OF THE METAMORPHIC AUREOLE (TRAVERSE BB1)

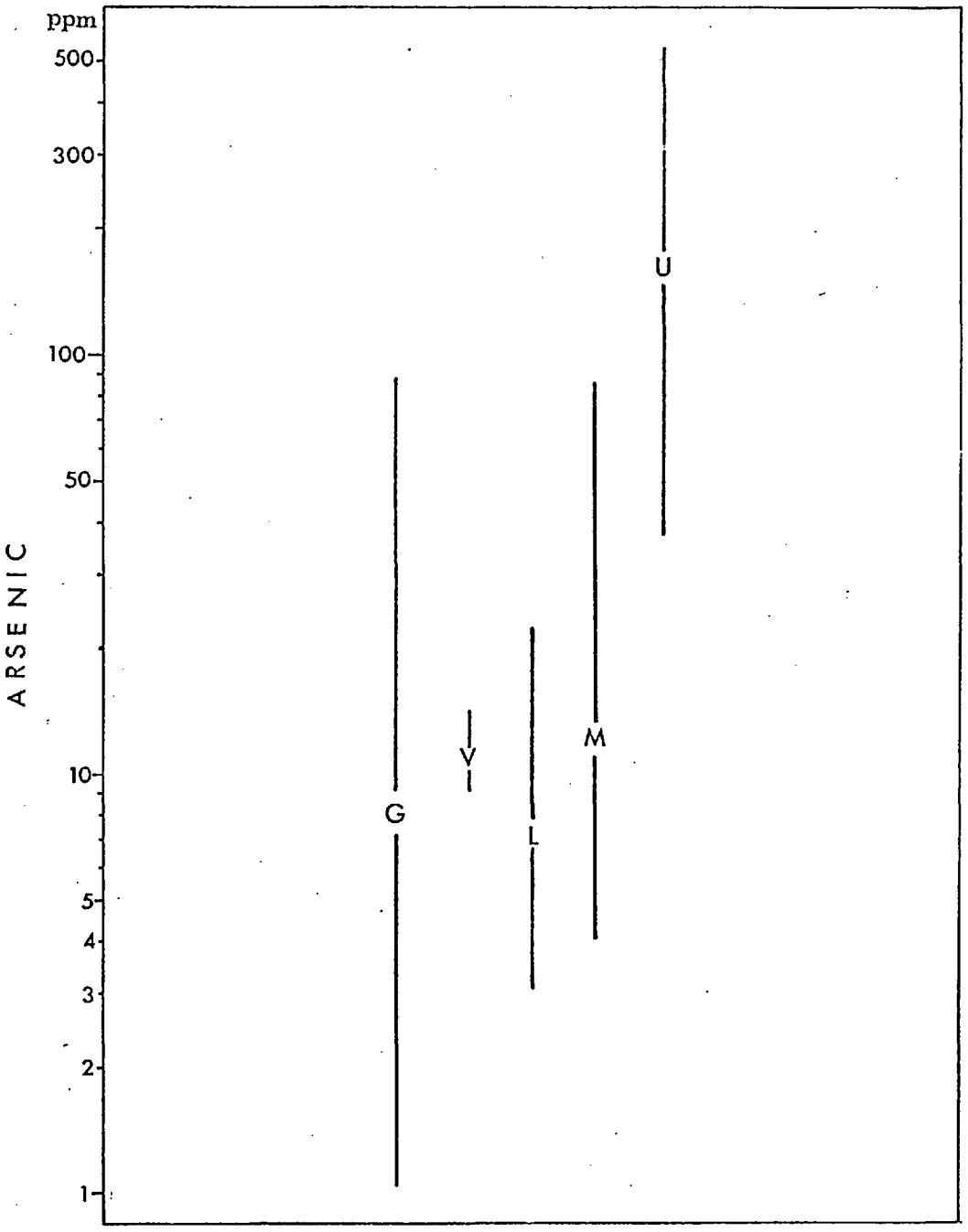
TABLE 7.6

RANGE AND MEAN* TRACE-ELEMENT CONTENTS OF SOILS FROM TRAVERSE B, B1, SOUTH DEVON INSIDE AND OUTSIDE OF THE METAMORPHIC AUREOLE (values in ppm)

Element	Aureole	Outside Aureole
As	150* 43-512	12 2-83
Cu	63 20-199	20 4- 96
Fe %	3.9 1.8-8.1	2.5 0.2-6.9
Mn	479 38-4026	324 11-1933
Pb	56 27-117	47 20-107
Sn	5 1- 91	2 1- 40
Zn	94 16-537	65 13-323
No. of Samples	35	80

* Geometric mean ($\bar{x}$)

Range = $\dot{\bar{x}} \pm 2$ (log standard deviation)



G = Granite
V = Dolerite
L = Lower Devonian
M = Middle Devonian
U = Upper Devonian

Fig. 7.40 RANGE AND MEAN ARSENIC CONTENT OF SOILS RELATED TO THE MAIN GEOLOGICAL FORMATIONS (TRAVERSE BB 1)

TABLE 7.7

RANGE AND MEAN* TRACE-ELEMENT CONTENTS OF SOILS RELATED TO BED-ROCK GEOLOGY, TRAVERSE B, B1 SOUTH DEVON (values in ppm)

ELEMENT	GRANITE	DOLERITE	DEVONIAN		
			Lower	Middle	Upper
As	8* 1- 89	11 9- 14	7 3- 22	12 4- 85	160 37-537
Cu	8 2- 30	53 42- 66	30 13- 40	33 18- 60	81 29-223
Fe %	0.2 0.1-6.2	7.3 6.3-8.3	4.8 2.7-6.2	5.3 3.0-9.1	4.5 2.4-8.1
Mn	55 8-346	1260 1097-1446	881 29-7390	892 201-3900	1050 315-3470
Pb	34 13- 85	38 24- 60	43 29- 66	63 35-115	55 42- 68
Sn	2 <1- 42	9 <1- 74	2 <1- 14	1 <1- 16	4 <1- 45
Zn	24 7- 74	139 109-173	110 54-123	118 74-187	132 87-200
No. of Samples	27	8	30		

* Geometric mean ($\bar{x}$)

Range = $\bar{x} \pm 2$ (log standard deviation)

bears the highest mean concentration: 160 ppm, which obviously cannot be related to bed-rock from this formation but might instead have been caused by contamination from the aureole. Granitic soils are characterised by low As concentration and the mean level in this unit (8 ppm) can be considered as a value reflecting bed-rock geochemistry. Sn, Fe, and Pb concentrations over the granite show their higher values in a steeper area mostly covered by altered granitic blocks (mean levels: 2 ppm, 0.2% and 34 ppm, respectively). These elements together with Cu, Mn and Zn in the Lower Devonian demonstrate little contrast in mean values when related to those of the Middle Devonian, yet they are slightly higher in the latter Formation. Sn is an exception, its mean level being higher in the Lower Devonian. The highest Sn, Zn, Mn and Fe means are found in soils overlying basic igneous rocks (9 ppm, 139 ppm, 1,260 ppm and 7.3% respectively), while Cu is better concentrated in the Upper Devonian and Pb over the Middle Devonian.

The erratic distribution of most of the elements within the whole Devonian unit makes it difficult to discriminate between lithological units from this Formation. However, it does allow a determination of a slight enhancement of the elements within the Middle Devonian in relation to the Lower Devonian.

c) Mineralisation

The high As level in the northern and southern parts of the Upper Devonian (which is also found in stream sediment patterns) are the only concentrations that might be considered of economic importance. Although the high Sn contents in the same areas could also be regarded as significant anomalies, as stated earlier, more detailed studies would be required in these zones in order to elucidate the significance of these anomalies.

7.3.2 Summary

During the more detailed investigations in selected areas of south-west England most of the varied As patterns shown by the earlier regional geochemical reconnaissance were confirmed. The overall pattern of distribution of As in stream sediments and soils from these areas appears to be related to the nature of the underlying parent rock. The range of values varies from low to anomalous concentrations.

Low As levels characterise the Lower and Middle Devonian, Upper Carboniferous, and most of the granitic mass. These concentrations approximate the normal background expected in soils developed over these rock types.

Stream sediment sampling revealed the existence of As anomalies in the area. These anomalies are associated with the Permian, the Corscombe area, the metamorphic aureole and the granite. The anomalous values within the Permian, and in the metamorphic aureole reflect the high As background of the underlying parent-rock, although some anomalies in the latter could be related to mineralisation. The high As values in the Corscombe area probably represent undiscovered mineralised bodies, whilst the anomalous As concentrations in the granite represent alluvial material, contamination derived from known mineralisation, and probable hidden ore deposits.

Soil investigations lead to a confirmation of these anomalies, with the exception of the highest values in the granite, which were not detected in soils. Depletion of this element from soils of this particular zone might be caused by the effects of the physico-chemical conditions prevailing in the area (leaching).

Anomalous As values in soils overlying the Permian are not uniform, and they seem to represent a variation in local bed-rock types. This anomaly extends northward within part of the Bude Formation, probably due to clastic dispersion of Permian material. The high As values located over the Middle Devonian, and the Middle-Upper Devonian contact, are considered to originate from alluvial material.

High As concentrations in soils within the granite close to its country-rock contact appear to be related to the underlying bed-rock. As anomalies in the northern aureole of the granite greatly differ from those in the southern part, the values in the latter being higher and more erratic and seem to have been influenced by the shallowness of the granite in this area.

The lithological units lying within the metamorphic aureole, although being anomalous in As values, show contrast in their element content. In the northern aureole the Lower Carboniferous is higher in As than the Upper Carboniferous (Crackington Formation). In the southern aureole, where the underlying parent-rock is entirely of Devonian age, the As patterns appear to have been distorted by the presence of river gravel, head and alluvium material (all of which are mainly derived from the granitic body), in addition to the granitic intrusion effects.

The As-Sn anomalies located in the northern and southern parts of the Upper Devonian most likely indicate undiscovered mineralisation.

High concentrations of Cu, Mn, Pb, Sn, Zn and Fe are found within the metamorphic aureole, becoming lower over the granite and the other geological units, the exceptions being Fe, Zn and Sn, which display anomalous values in specific areas outside the aureole. Thus, Fe is highly concentrated in stream sediments draining into the Crackington Formation and, along with Sn, is also of high value over the granite. Badly drained soils in the case of Fe, and alluvium deposits in that of Sn, appear to have influenced these high values.

Sn anomalies in soils over the Permian reflect bed-rock geochemistry, and the extension of the anomaly towards the Bude Formation was probably the result of clastic dispersion of material from the Permian. Zn anomalies accompany the high As concentrations in the Corscombe area, and they are also related to mineralisation.

CHAPTER 8

DETAILED GEOCHEMICAL INVESTIGATIONS

8.1 INTRODUCTION

Detailed geochemical studies were carried out in selected areas (Fig. 8.1), the importance of which was established during the interpretation of previous geochemical data (Chapters 6 and 7).

The studies within these areas consisted of systematic soil and rock sampling and analysis by means of the methods already described. The main geochemical features of the areas chosen for detailed investigations are outlined below.

i) HATHERLEIGH-YEOFORD AREA

This area is characterised by:-

a) Anomalous As and Mn concentrations which are located in the western part of the area, south of Hatherleigh;

b) High As background levels located around Exbourne and Hatherleigh, and

c) Relatively high As concentrations accompanied by other elements within the Permian sediments.

The two former patterns were identified from the regional reconnaissance data, and the latter was found during the regional investigation. The significance of the As - Mn anomalies was not explained, although it is suspected that they are directly related to bed-rock geology. The high As background values around Exbourne were confirmed by soil and stream sediment regional investigations. They too are assumed to bear a lithological connection.

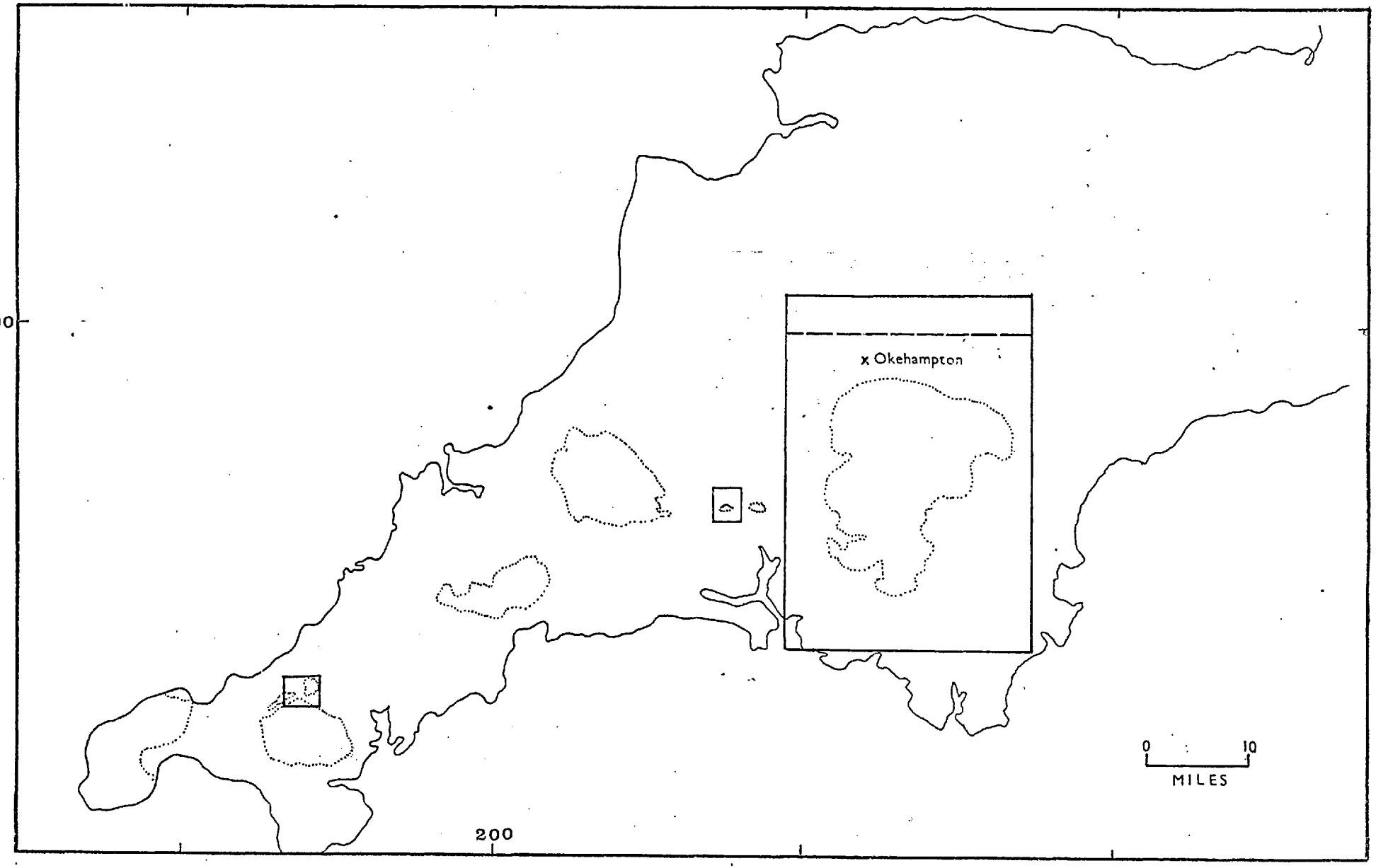


FIG.8.1. DETAILED INVESTIGATION AREAS

ii) DARTMOOR AREA

The anomalous values in stream sediments and soils from the metamorphic aureole constitute the outstanding aspect of this area. The significance of these anomalies has been broadly treated in former chapters. The detailed investigations were chiefly carried out in order to confirm the stream sediment-soil-bed-rock relationships already established in the regional investigations, and to explain the origin of the high As patterns.

iii) CORSCOMBE AREA

The significance of this anomaly has been discussed at length in Chapters 6 and 7. As and Zn anomalies were detected in soils during the regional investigations, and detailed studies were carried out in a very limited area in order to delineate the magnitude of the anomaly.

iv) KIT HILL AREA

This area lies within a broad mineralised-contaminated area and displays very high, anomalous, patterns of As and the other selected trace-elements. Investigations within this area were carried out with the purpose of verifying the sources of the anomalies.

8.2 HATHERLEIGH-YEOFORD AREA

8.2.1 Location

With a surface covering of approximately 54 square miles this area lies entirely in North Devon (north of Dartmoor). Its boundaries being the National Grid Reference System co-ordinates 250, 000E; 280, 000E; 96, 000N and 105, 000N (Figure 8.2).

8.2.2 General Geology

The Crackington Formation in the south, and the Bude Formation to the north enclose a narrow strip of Permian sediments which strikes in an east-west direction.

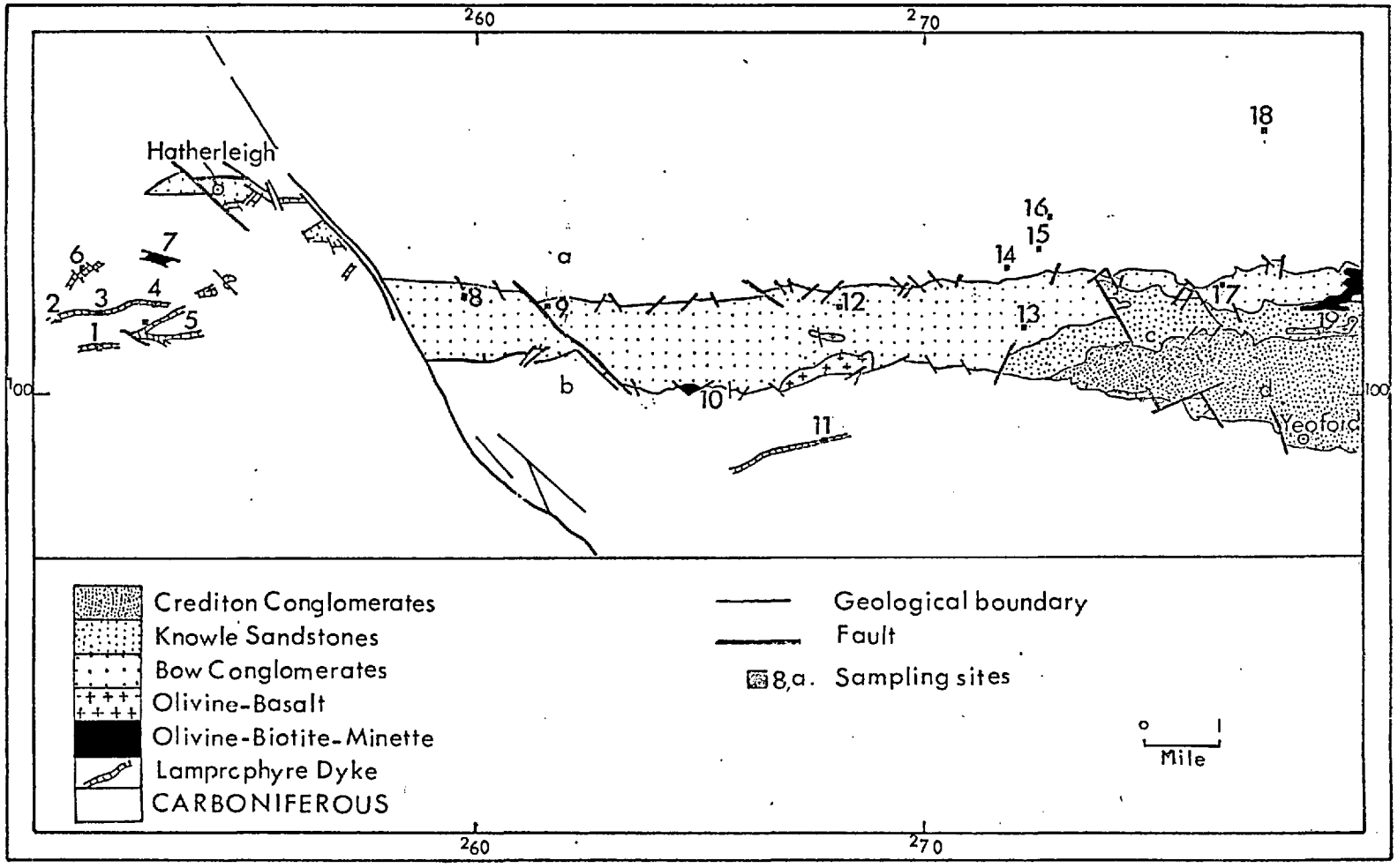


Fig. 8.2. HATHERLEIGH - YEOFORD AREA

The Crackington Formation consists of a sequence of shales with subordinate sandstones whereas the Bude Formation is formed by brown to green sandstones and subordinate dark shales.

The Permian sequence is formed by the Crediton Conglomerates and the Knowle Sandstones in the east, and the Bow Conglomerates which outcrop throughout the area. The igneous rocks in the zone are represented by lavas which form part of the Exeter Volcanic Series and by lamprophyre dykes intruding the Crackington Formation sediments. The Exeter Volcanic Series in this area (Permian Volcanics of Devonshire) have been re-defined by Cosgrove (1972) as belonging to the high-potassium shoshonitic suite of rocks commonly associated with a late or post-orogenic tectonic setting.

The geological units of the area are shown in figure 8.2 and table 8.1.

8.2.3 Geochemical Investigations

Geochemical investigations in the Hatherleigh-Yeoford area included systematic rock sampling and analysis for eight trace-elements. The samples were analysed for As, Cu, Pb, Zn, Mn, Sn and Fe by atomic absorption spectrophotometry and colorimetric methods. In addition, the presence of sulphur in sulphide-bearing rocks was determined by a colorimetric method which is described in Chapter 5 and Appendix I.

Seventy two rock samples were collected in nineteen quarries (Qy-1 to Qy-19), and four surface outcrops (a, b, c and d). The locations of the sample sites are described in table 8.2 and shown in relation to the geology in figure 8.2.

Pebbles sampled from some of the Bow Conglomerates were separated from their matrix with the aid of a microscope. They were analysed individually.

8.2.4 General Description of Patterns

The distribution of As and selected trace elements is shown in figures 8.3 to 8.10. Table 8.3 lists the averages of sample values from

TABLE 8.1

CLASSIFICATION AND DISTRIBUTION OF CHARACTERISTIC DETRITUS IN THE PERMIAN DEPOSITS

(After Edmonds et al. 1968)

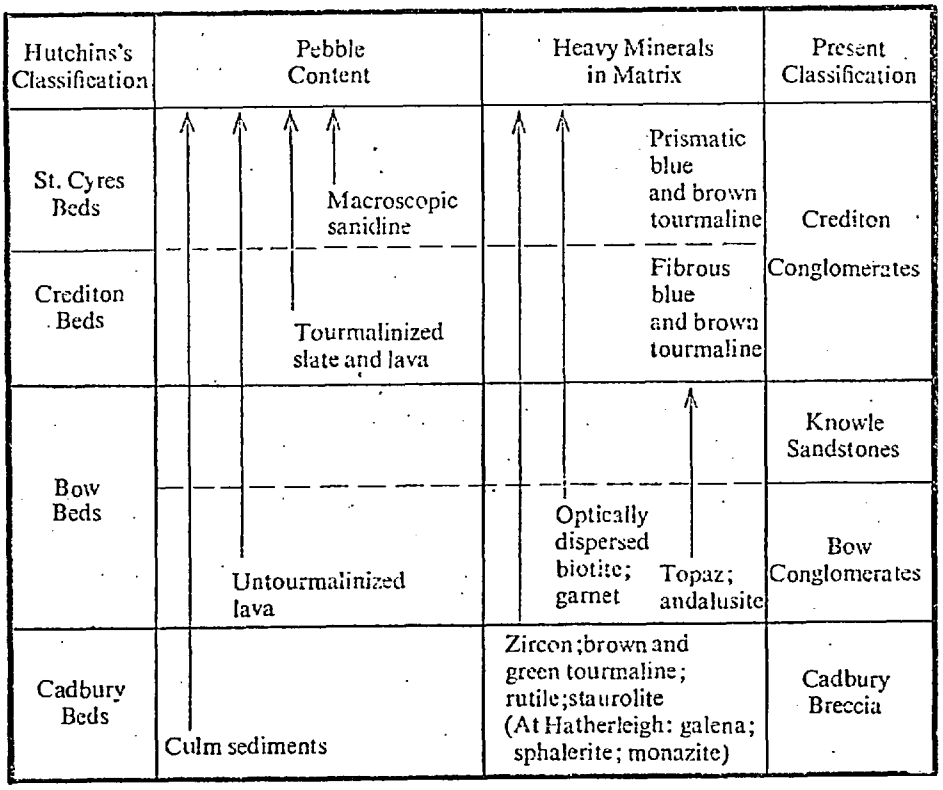


TABLE 8.2

HATHERLEIGH-YEOFORD AREA

LOCATION OF THE SAMPLING SITES

Sample Site	E	N	Quarry Name	Locality
Qy-1	514	009	Great Rutleigh	Hatherleigh
Qy-2	509	017	Rutleigh Ball	Hatherleigh
Qy-3	519	018	Lydbridge	Hatherleigh
Qy-4	530	020	Cleave Farm	Hatherleigh
Qy-5	536	018	River Low	Hatherleigh
Qy-6	513	026	Lewmoor Farm	Hatherleigh
Qy-7	529	029	Hannaborough Quarry	Hatherleigh
Qy-8	604	022	Exbourne Quarry	Exbourne
Qy-9	615	020	Solland Quarry	Exbourne
Qy-10	648	001	Greenslade Quarry	Nr. Tawton
Qy-11	678	989	Itton Quarry	Nr. Tawton
Qy-12	684	023	Westacott Quarry	Nr. Tawton
Qy-13	722	017	Bow	Bow
Qy-14	718	030	Clapper Cross	Zeal Monachorum
Qy-15	725	034	Tuckingmill	Zeal Monachorum
Qy-16	724	039	Waie	Zeal Monachorum
Qy-17	765	023	Copplestone Quarry	Copplestone
Qy-18	775	062	Oldborough	Morchard Bishop
Qy-19	787	017	Knowle Quarry	Knowle

TABLE 8.3

AVERAGE TRACE-ELEMENT CONTENTS OF ROCKS FOR INDIVIDUAL SAMPLING SITES FROM THE HATHERLEIGH-YEOFORD AREA (values in ppm)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	a	b	c	d
As	64	20	22	236	60	24	190	56	32	4	50	22	12	1	4	8	9	1	2	8	16	10	8
Cu	30	16	16	8	76	13	44	36	20	25	12	15	20	25	8	75	16	40	26	75	20	20	10
Fe%	2.7	6.6	7.6	4.1	3.4	4.3	6.4	4.8	3.5	5.7	4.7	3.4	3.6	1.6	3.8	4.0	2.9	3.1	8.6	3.5	2.7	6.3	6.0
Mn	360	510	1260	800	1150	810	1400	200	900	1960	940	2000	1830	75	200	405	420	122	760	950	360	800	560
Pb	60	70	120	115	60	180	51	70	60	65	90	85	90	22	55	85	60	35	80	80	19	65	20
Sn	<1	3	2	<1	5	<1	4	14	12	<1	2	18	6	3	<1	<1	<1	<1	3	5	2	5	5
S	222	110	222	300	666	64	440	20	25	13	306	20	16	40	26	25	20	8	28	20	40	20	24
Zn	66	75	110	110	49	127	48	220	90	170	110	200	150	75	125	165	120	126	166	120	146	95	80
No. of Samples	3	3	3	6	3	3	12	4	4	6	3	4	4	3	3	3	6	3	6	2	4	3	3

each sampling site, and tables 8.4 and 8.5 list the arithmetic mean and range for concentration of eight trace-elements in the lithological units. Mean values from Bow Conglomerate pebbles are shown in table 8.6.

The distribution of As within the overall area is characterised by contrasting patterns which range from very low to anomalous levels, the latter being located in the western section of the area, south of Hatherleigh (Fig. 8.3). Within the Carboniferous sediments the Bude Formation exhibits the lowest concentration (1 to 10 ppm) whilst in the Crackington Formation the As levels reach up to 16 ppm (Table 8.4). The Permian manifests a contrast in the As content of its lithological units (Table 8.5). Thus, the basal group (Bow Conglomerates) displays the highest concentration (average: 56 ppm) located in the western part of this formation (Qy-8, table 8.3). This relatively high concentration appears to decrease in an easterly direction the values falling sharply to 1 ppm in Qy-17. Both the Knowle Sandstones and Crediton Conglomerates are low in As content, (being slightly higher in the former) with mean values of 10 and 8 ppm respectively (Table 8.5).

The best distribution of As patterns is found in the intrusive igneous rocks (lamprophyre dykes) which display values ranging from 24 to 240 ppm and a mean level of 119 ppm. Within the Exeter Volcanic Series the olivine-basalt-minette shows very low As content with an average of 2 ppm (Qy-19, table 8.3) in contrast with the olivine-biotite-minette from Qy-7 whose As values reach up to 400 ppm. These high levels are not found in the olivine-biotite-minette from Qy-10 where As averaged only 4 ppm.

S displays two distinct patterns in the area: Low S concentration (less than 50 ppm) characterises the Permian and Carboniferous Formations. In contrast, moderate to high values are evident within the igneous rocks (64 to 666 ppm) the exception being the very low concentrations found in Qy-10 and Qy-19 where values range from 11 to 22 ppm. (Fig. 8.4; table 8.3 to 8.5).

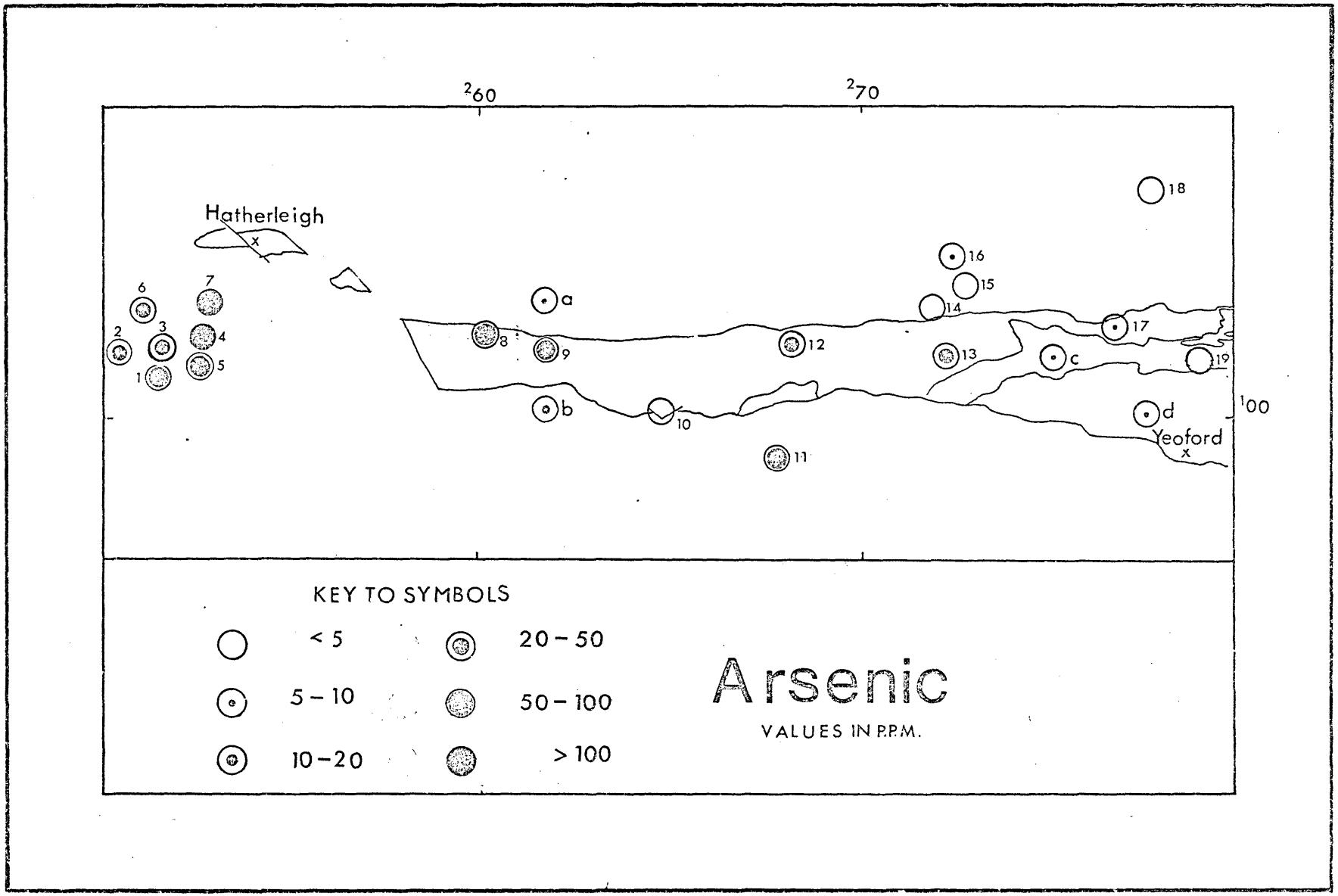


Fig. 8.3. Hatherleigh-Yeoford Area-rock sampling

TABLE 8.4

RANGE* AND MEAN** TRACE-ELEMENT CONTENTS OF ROCKS FROM THE HATHERLEIGH-YEOFORD AREA (values in ppm)

Element	Carboniferous		Permian	
	Crackington Formation	Bude Formation	Sediments	Igneous+
As	8** 4- 16*	4 1- 10	16 1-110	45 1-400
Cu	38 8- 54	54 8- 75	25 8-107	28 3- 92
Fe%	1.6 .6- 2.0	4 2.0-4.5	3.2 .4-6.8	4.9 3.0-8.6
Mn	260 150-480	186 20-950	890 180-3950	940 740-3840
Pb	22 18- 24	48 25-100	77 20-130	62 40-100
Sn	<1	1 <1- 10	3 <1- 28	2 <1- 10
S	24 8- 50	22 5- 50	16 10- 32	151 11-444
Zn	135 95-146	124 95-180	119 30-270	56 12-210
No. of Samples	12	14	28	24

** Arithmetic mean
* General range
+ Lamprophyre dykes not included

TABLE 8.5

RANGE* AND MEAN** TRACE-ELEMENT CONTENTS OF ROCKS FROM THE HATHERLEIGH-YEOFORD AREA

(values in ppm)

Element	Permian Red Beds			Permian Volcanic Series		Post Carboniferous Dykes
	Crediton Conglomerates	Knowle Sandstones	Bow Conglomerates	Olivine Basalt	Olivine Biotite minette	Lamprophyres
As	8**	10	20 1-110*	2 1- 4	59 4-400	119 24-240
Cu	10	20	24 8-107	26 8- 72	25 10- 51	24 6- 92
Fe %	6.0	6.3	3.4 2.9-6.8	5.9 1.4-8.6	6.4 2.2-7.4	3.8 2.3-7.6
Mn	560	800	1093 250-3950	950 80-1650	1036 1400-3840	720 200-1870
Pb	20	65	71 16-130	72 30-120	72 40-100	94 60-210
Sn	5	5	3 <1- 28	3 2- 4	1 <1- 4	1 <1 - 6
S	24	20	17 11- 25	15 5- 45	101 11-444	260 100-666
Zn	80	95	121 80-270	166 79-270	198 57-180	84 30-130
No. of Samples	3	3	22	6	18	24

* General range
** Arithmetic mean

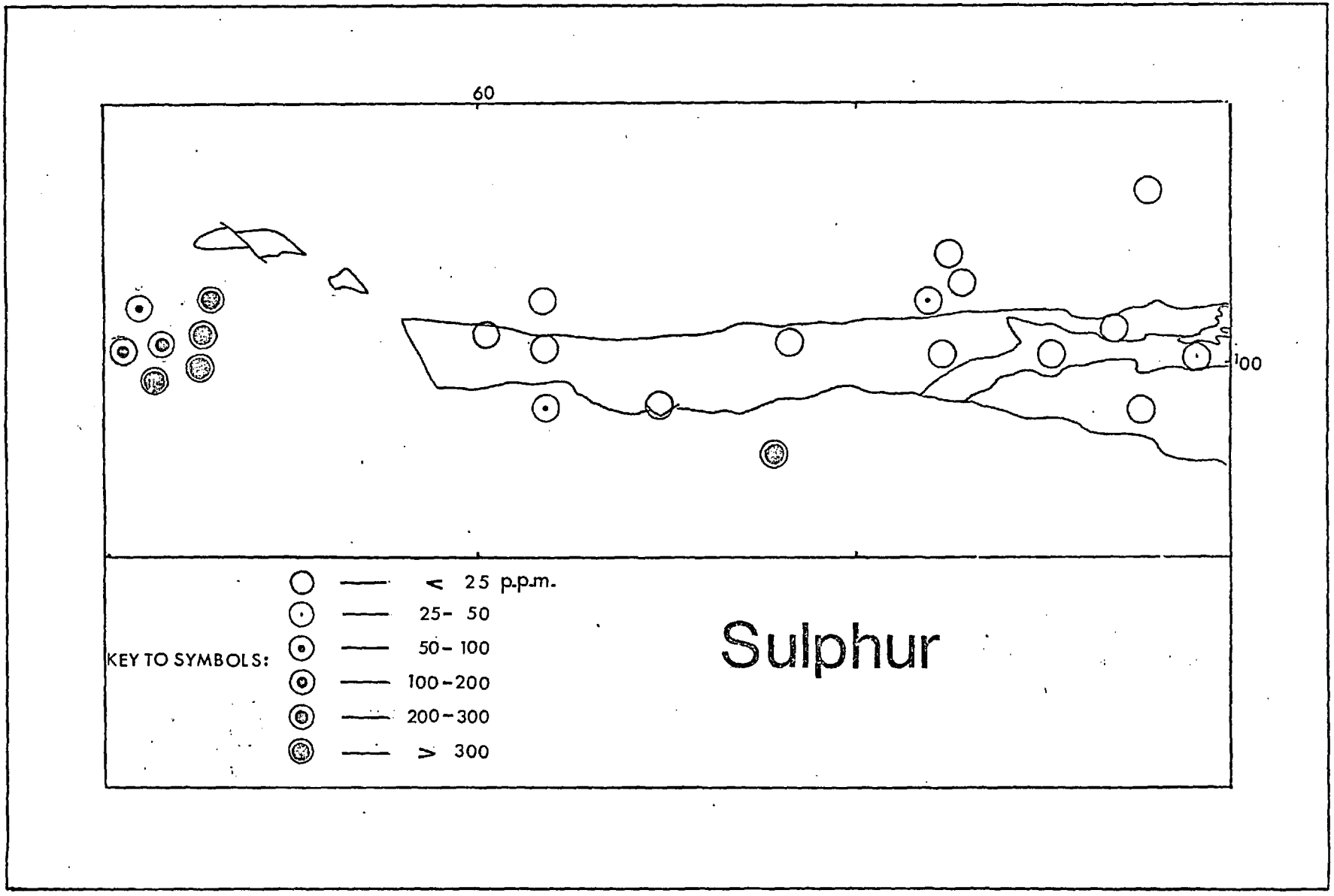


Fig. 8.4 HATHERLEIGH-YEOFORD AREA - ROCK SAMPLING (Explanation as for Fig. 8.2)

The outstanding characteristics of the distribution of the other selected trace-elements are:

i) Low to high levels of Mn and Fe within the igneous rocks and Permian sediments (Table 8.4 and Figs. 8.6 and 8.8)

ii) High Sn concentration in the Bow Conglomerates (Qy-8, 9 and 12, table 8.3, Fig. 8.5)

iii) Uniform distribution of Pb within the Permian Formation including the igneous rocks outcropping in this unit. This element shows high to moderate levels within the igneous rocks located within the Crackington Formation (Table 8.5 and Fig. 8.10)

iv) The Cu distribution is relatively low over the whole area (Fig. 8.9)

8.2.5 Correlations between Arsenic and Selected Trace-Elements

Correlation coefficients were calculated for three rock types: Permian sediments, Exeter Volcanic Series, and the intrusive rocks (lamprophyre dykes). The results are shown in Figures 8.11 to 8.13.

The only strong, positive correlations within these three groups are: As-S and Zn-Mn in the Volcanic Series, and Pb-Zn in the intrusive dykes. To a lesser degree sympathetic Fe-Pb correlations are found in both volcanics and in the dykes; Sn-Cu, and Fe-Mn in the latter; Mn-Pb within the Permian.

A weak relationship is found between Zn and Fe-Mn in the Permian, and this same low degree of correlation is found between As-S and Fe-Pb-Zn in the intrusive rocks. Sn displays a low negative correlation with As and S in the Volcanic Series whereas Cu appears to be unrelated to the other elements. This state of non-relationship is also manifested by Sn and Cu in the Permian.

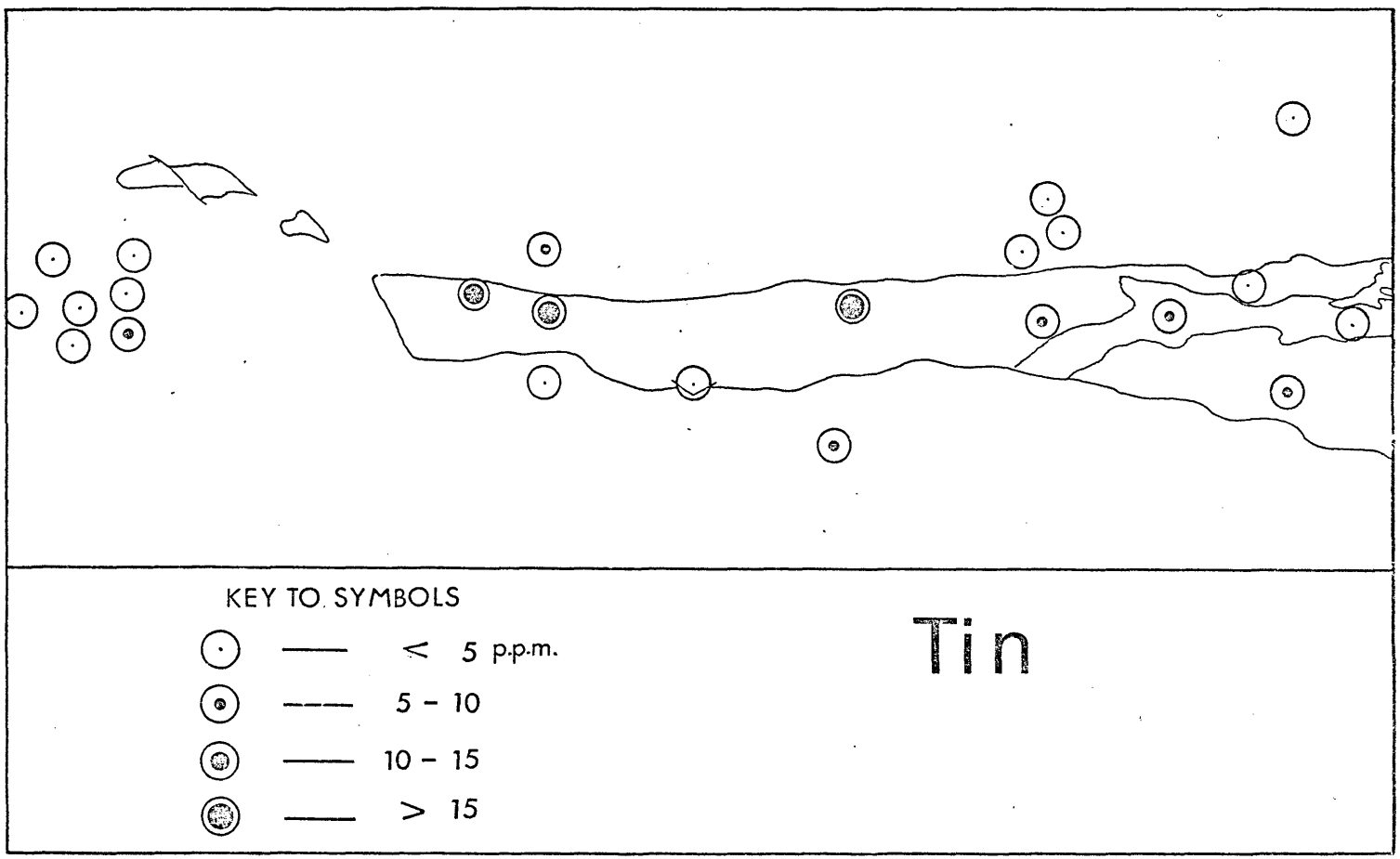


Fig. 8.5 HATHERLEIGH-YEOFORD AREA - ROCK SAMPLING (Explanation as for Fig. 8.2)

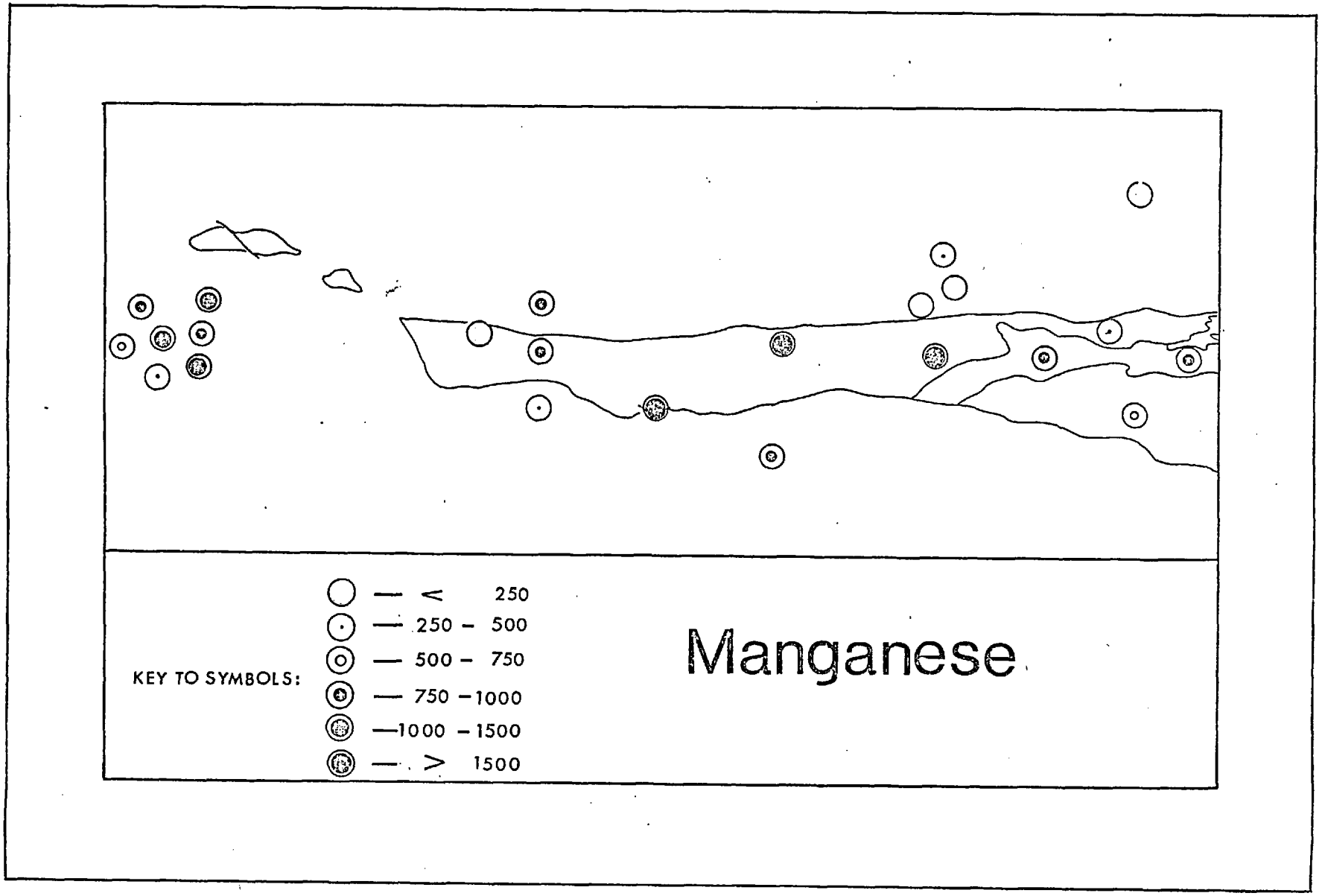


Fig. 8.6 HATHERLEIGH-YEOFORD AREA - ROCK SAMPLING (Explanation as for Fig. 8.2)

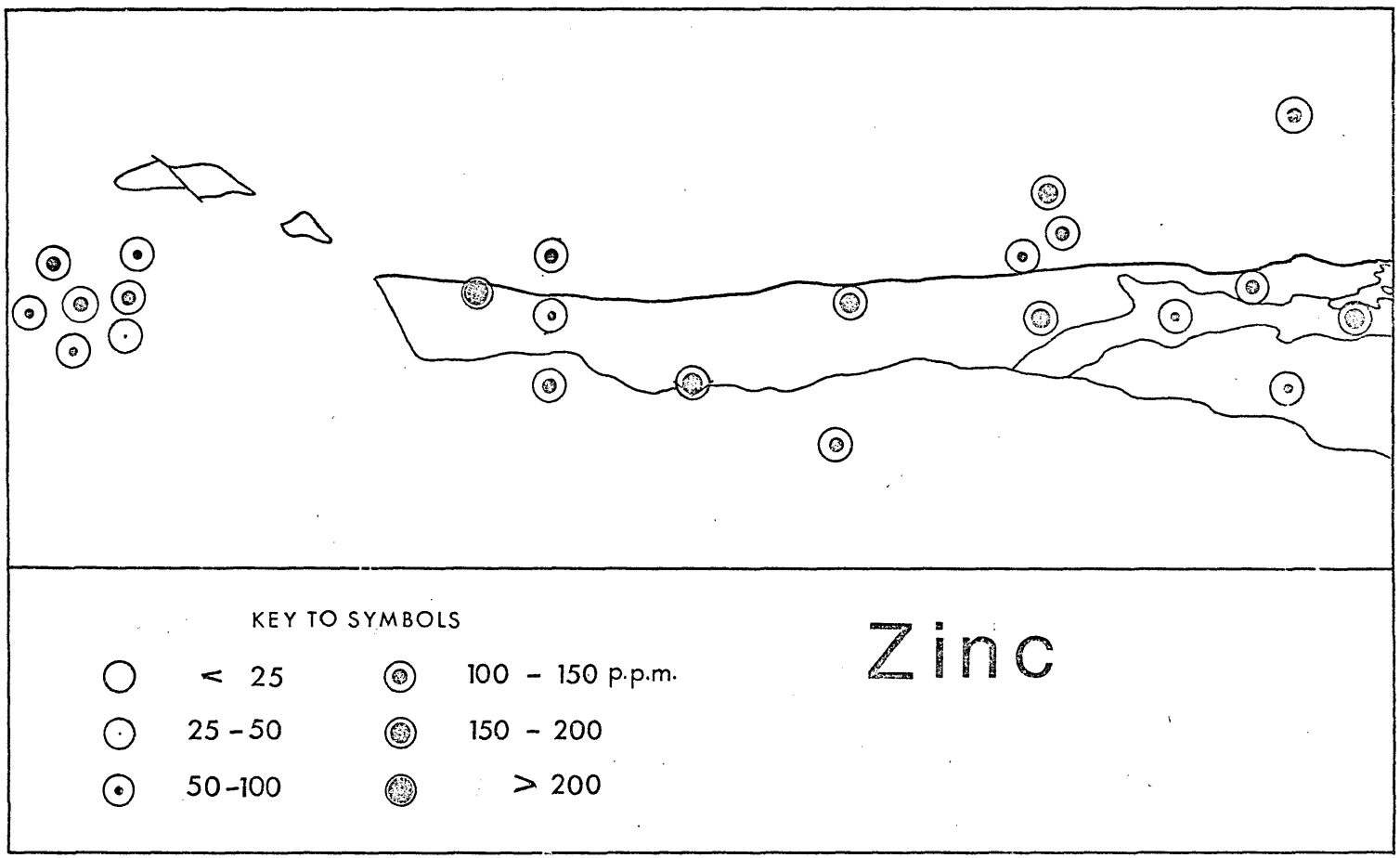


Fig. 8.7 HATHERLEIGH-YEOFORD AREA - ROCK SAMPLING (Explanation as for Fig. 8.2)

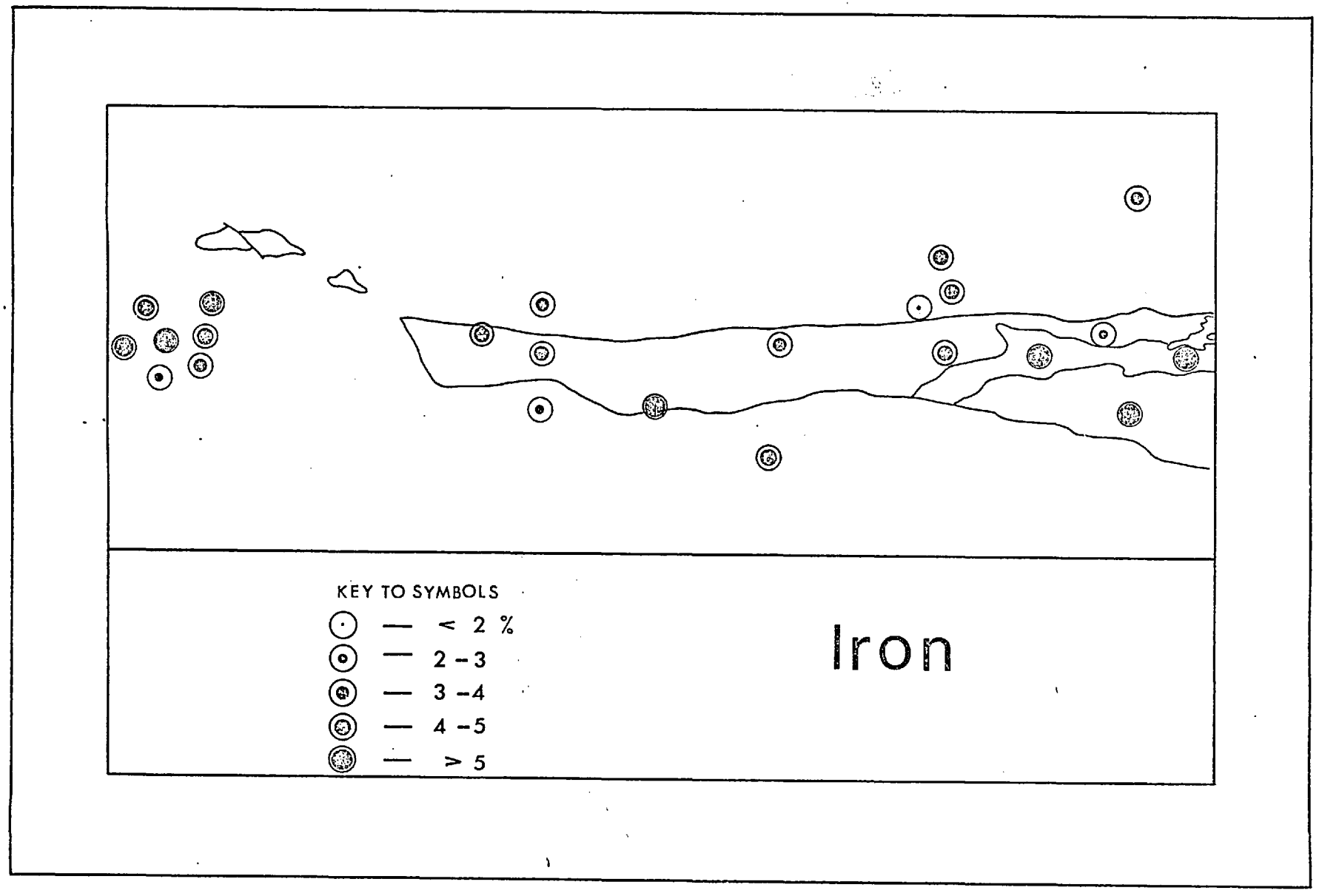


Fig. 8.8 HATHERLEIGH-YEOFORD AREA - ROCK SAMPLING (Explanation as for Fig. 8.2)

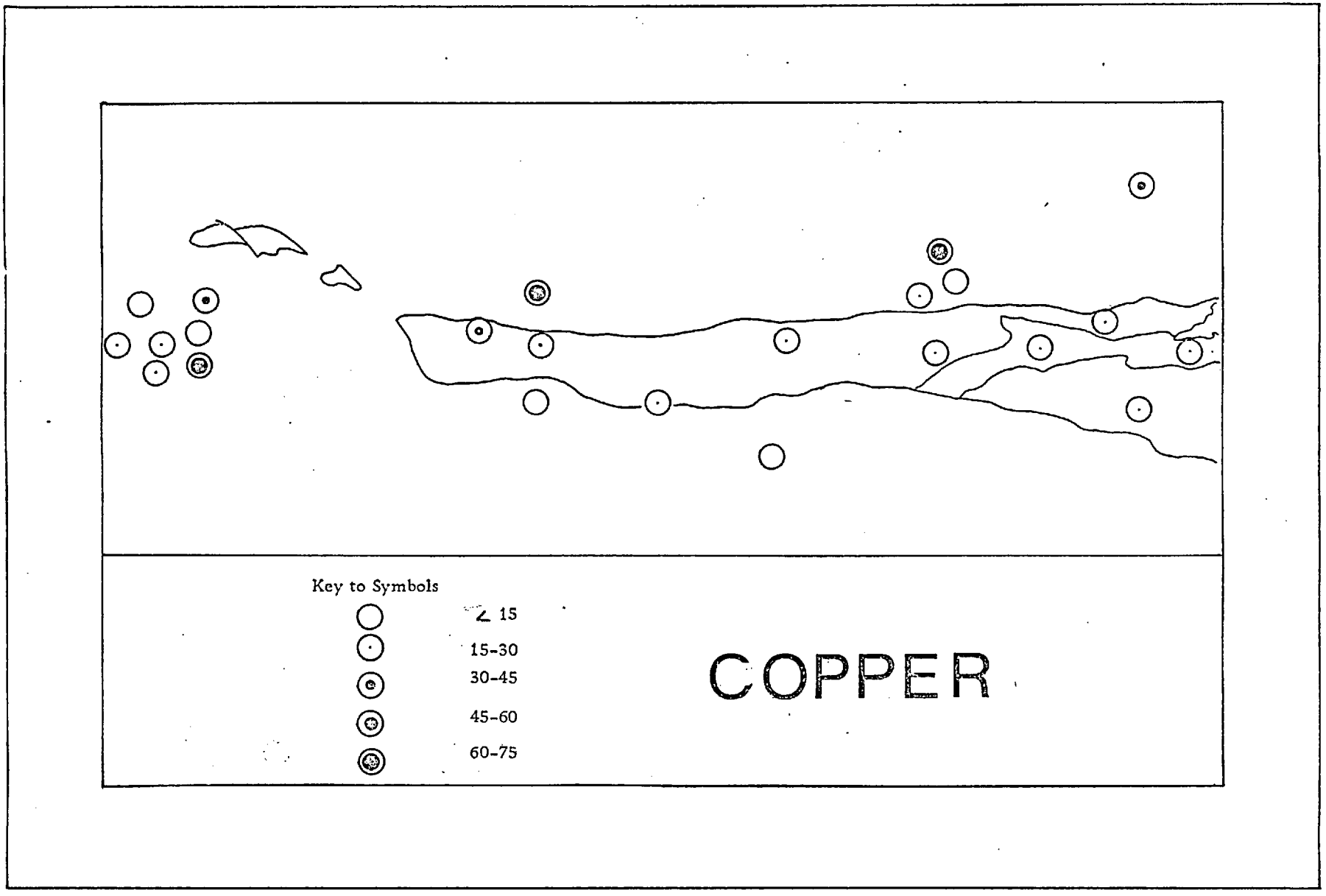


Fig. 8.9 HATHERLEIGH-YEOFORD AREA - ROCK SAMPLING (Explanation as for Fig. 8.2)

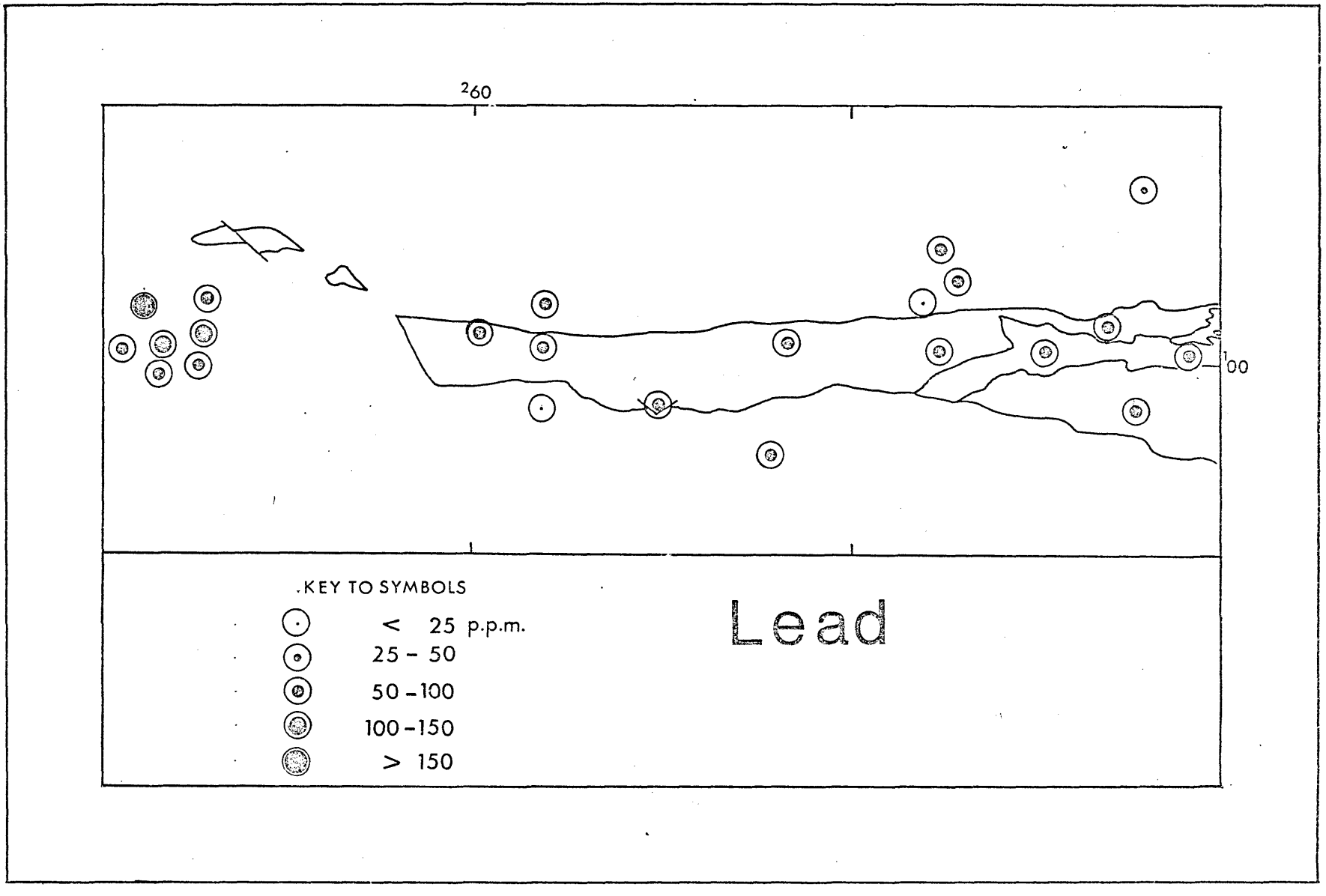
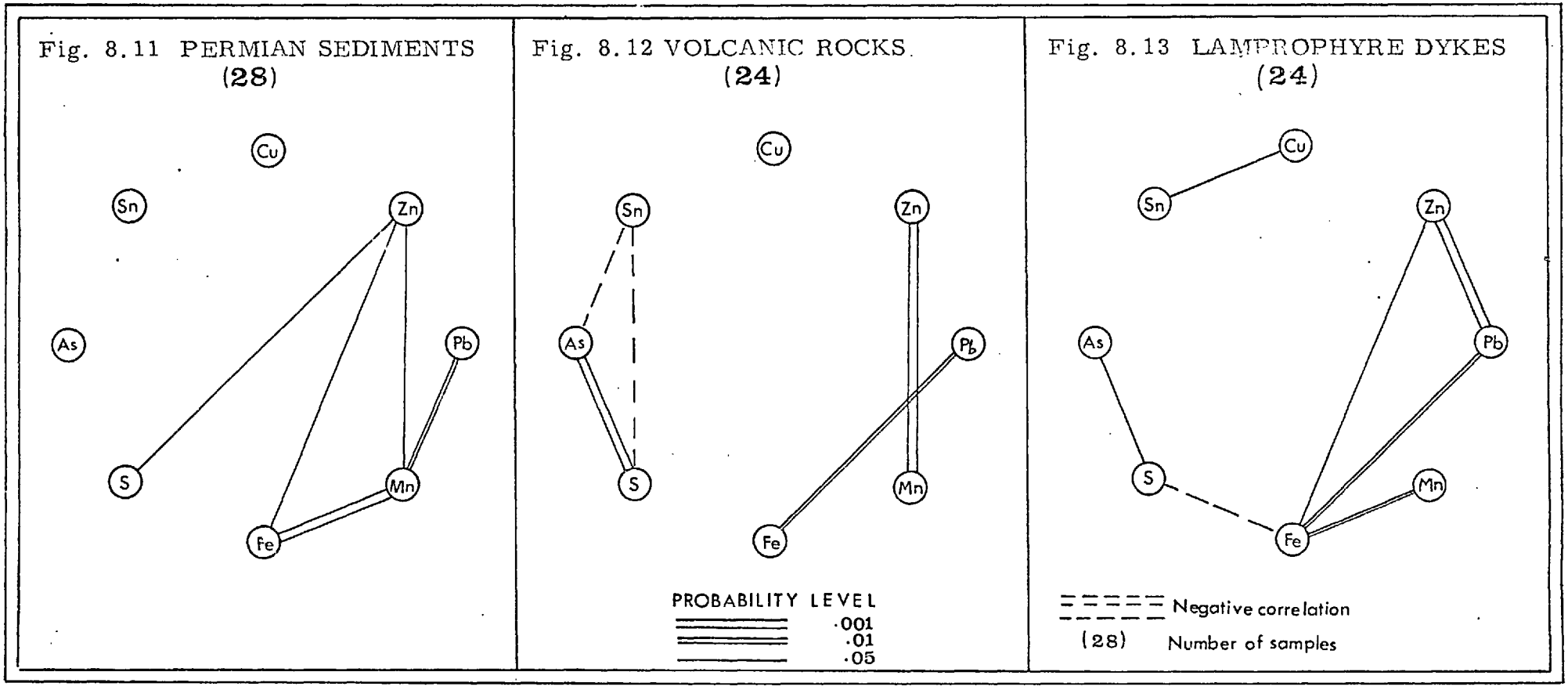


Fig. 8.10 HATHERLEIGH-YEOFORD AREA - ROCK SAMPLING (Explanation as for Fig. 8.2)



CORRELATION BETWEEN ARSENIC AND SELECTED TRACE-ELEMENTS IN ROCKS FROM THE HATHERLEIGH-YEOFORD AREA
(values expressed as probability level of significance)

8.2.6 Interpretation of Arsenic Patterns

In order to obtain a better understanding of the distribution of As, the geochemical data have been interpreted as they relate to three main rock types outcropping in the area:

i) Permian sediments;

ii) Exeter Volcanic Series

  a) Olivine-biotite-minette

  b) Olivine-basalt-minette

iii) Lamprophyre dykes.

Concentrations of the elements are shown in Figures 8.4 to 8.10 and tables 8.3 to 8.7.

i) Permian Sediments

The bulk of the data from this Formation corresponds to the Bow Conglomerates. Data from the other two units were not considered because of their high state of weathering.

The As patterns within the Bow Conglomerates appear to bear a close relationship with the very nature of the bed-rock geology. Thus, in the western section, where As reaches its highest value the outcropping parent-rock predominantly consists of coarse and fine breccia, and boulders of volcanic rock (Qy-8). On the other hand, the eastern section, where As values range from 1 to 16 ppm. (Qy-17), is characterised by a normal sequence of sandy and gravelly breccia resting on red sandstone and on pebbly sandstone.

Analytical data from Qy-8 and Qy-9 indicate that As content in breccias and sandstones varies according to:-

a) Nature of the Breccia-Forming Pebbles

Analytical data from the main breccia-forming pebbles (coarse breccia) have demonstrated that As concentration in this rock-type is mainly determined by the nature of the rock-fragments forming the breccia. Thus, it was found that in Qy-8 and Qy-9 (Table 8.6) where

TABLE 8.6

MEAN* TRACE-ELEMENT CONTENTS OF BRECCIA-FORMING PEBBLES FROM THE BOW CONGLOMERATES UNIT, HATHERLEIGH-YEOFORD AREA (values in ppm)

Element	Volcanic	Mudstone	Sandstone	Limestone
As	95	44	9	1
Cu	37	30	28	9
Fe%	2.5	3.8	6.7	0.14
Mn	180	160	658	150
Pb	30	70	91	15
Sn	3	1	5	<1
S	88	89	18	<10
Zn	86	180	121	46
No. of Samples	12	9	14	10

* Arithmetic mean

As is relatively high, the major As concentration is located in the volcanic and mudstone pebbles, whilst in sandstone and limestone fragments the As is lower. On the basis of their As content and their suggested short transport (Edmonds et al., 1968) these volcanic pebbles may be related to the As - rich lamprophyres located to the south and west of Hatherleigh, and southward of Exbourne (Berrydown Plantn). Edmonds et al., (Op. cit.) report a vast amount of contemporaneous lava debris in the Bow Conglomerates, and that a westerly derivation of debris and the abundance of fragments of lava of Hannaborough-type in this lithological unit implies that there was a broad early Permian lava field in the Hannaborough area. However, in breccias in which there is an abundance of lava fragments of the Copplestone/Knowle-type a low As content is detected. Thereby contradicting the above conclusion that volcanic pebbles contain high As concentration. The contradiction is due to the difference between the Hannaborough and Copplestone/Knowle-types. (See below: Exeter Volcanic Series).

Assuming that mudstone and sandstone fragments are derived from the eroded Carboniferous sediments, the contrast in As content between the two has already been established: As is higher in the former than in the latter. Limestones are distinguished by their low As content.

Edmonds et al. (Op. cit.) define the main fragments included in the breccias as debris of Culm sandstones, indurated and metamorphosed mudstones, hornfelses, etc.

b) Texture of the Bed-Rock

It has been found that the coarse breccia is higher in As content than the finer. Although the nature of the material which forms the fine breccia had not been entirely determined, it is probable that most of the

fragments are derived from the Carboniferous sediments. Due to the size of the pebbles it is clear that the fine rock-fraction was more easily depleted of its As content than coarser fragments. Furthermore, volcanic pebbles rarely appear in the finer breccia. Another factor which appears to influence the difference in As content in both rock-types is the calcite cement of the breccias. It has been analysed and very low As was found (2 ppm). The abundance of cement is higher in the fine than in the coarse breccia.

c) Nature of Bed-Rock

The As concentration is higher in the fine breccia than in the fine sandstones. This difference might be the result of the hetereogeneity of the material forming the breccia. The sandstones exhibit whitish circular spots which probably indicates reduction.

All of these characteristics are regarded as being local rather than general. This can especially be seen at Westacott (Qy-12) where volcanic pebbles are not found, and Solland (Qy-9) where the coarser breccia mainly bears sandstones and limestones, two elements of low As content.

In Qy-17 distribution of As is also variable although here the texture of bed-rock does not seem to be related to these variations. In this sample site the red sandstone reaches up to 16 ppm of As, whilst the pebbly sandstone (chert and slates inclusions) give only 1 ppm, and gravelly breccia is lower than sandy breccia in As concentrations (12 and 16 ppm respectively). See table 8.7.

The decreasing As values in an easterly direction in the Bow Conglomerates may be caused mainly by the influence of the As - rich volcanic pebbles which are restricted to the ~~east~~ western half of the zone.

The As values found in the Knowle Sandstones and Crediton Conglomerates are unreliable because of the intense weathered state of the samples. Nevertheless there is a clear possibility of higher As values. Cosgrove (1973) found that As along with Sn and chlorine

TABLE 8.7

ARSENIC CONTENT OF SEDIMENTS FROM THE COPPLESTONE QUARRY (Qy-17), BOW CONGLOMERATES

ROCK TYPE	As ppm	No. of Samples
Sandy Breccia	16	2
Gravelly Breccia	12	2
Pebbly Sandstone (Abundant feldspar)	2	2
Red Sandstone	16	2
Coarse pebbly Sandstone (Chert and Slate Pebbles)	1	2
Red Sandstone	16	2

are enriched in all phases of the Permian red beds, and states that this fact probably reflects the provenance in the case of As and Sn from the adjacent Cornubia.

ii) Exeter Volcanic Series

The As content in Qy-10 (Olivine-biotite-minette) and Qy-19 (Olivine-basalt-minette) falls within the general range of As content in such rock types.

The anomalous As concentration and its possible origin in rocks from Hannaborough (Qy-7) is discussed by Cosgrove (1972) in his study of the volcanic rocks from Devonshire. Cosgrove classifies the rocks from Qy-7 (Pv-3, Cosgrove 1972) as a shoshonitic type coming into being as a result of the partial melting of the sinking slab of oceanic crust at approximately 300 km depth. Complex processes involving partial melting during the origin of shoshonitic rocks is proposed by Jackes and White (1969), Jopling (1968), and Jopling et al. (1972). Cosgrove (Op. cit) found the shoshonitic-type rocks from Hannaborough to be rich in As along with other 'incompatible elements' (P, Rb, Sr, Zr, Ba, La, etc.), and to explain this Cosgrove resorted to the studies of Harris (1957), later modified by Green and Ringwood (1967). Briefly, Green and Ringwood apply the term 'incompatible elements' to these elements unable to substitute significantly in the major minerals of the upper mantle. They explain the incidence of the 'incompatible elements' in the magma by 'wall-rock reaction' and conveyance to the magma of the elements from the wall-rock by selective melting processes and extraction of the lowest melting fraction.

On the other hand, the strong positive correlations between As and S in the volcanic rocks (Fig. 8.12) suggest that the As occurs in sulphides, probably in pyrite.

Analytical data from two host-rock samples (shale) collected at 15 and 30 yards from the volcanic-sedimentary contact in Qy-7, gives high As and S concentrations (120 ppm As, and 444 ppm S). This fact

might indicate that lateral migration of As in sulphur-bearing sulphide (pyrite) took place during the extrusion of the magma. Dispersion of As in syngenetic sulphide from the country-rock cannot be assumed to be due to the low S content in rocks from the Upper Carboniferous rocks.

iii) Lamprophyre Dykes

Distribution of As in these rock-types is shown in table 8.5.

Analysis of the lamprophyre dykes gathered in the area produced As values ranging from 24 to 240 ppm. However, the low As levels from Qy-2, 3 and 6 must cautiously be considered due to the fact that the rocks from these sites outcrop in quarries which are water-filled during the wet season. These changes of environment might have caused reduction and oxidation of the As - bearing sulphide. Thus, part of the As was leached and part was fixed in the weathered rock in an oxidised state. This hypothesis is supported by the fact that As and S show a low positive correlation (Fig. 8.13) and by the very weak negative correlation (-.35) between Fe and S. This last phenomenon might indicate the formation of limonite at the expense of FeS_2.

Samples from the host-rock were collected in Qy-1 and Qy-11, at approximately 15 and 20 yards from its dyke-contact. As levels in the host-rock were slightly higher than normal. This finding might indicate low temperatures during the emplacement of the magma.

The sources of As dispersion within the lamprophyre dykes is supposedly the same as that suggested by Cosgrove (1972) for the high As content in the olivine-biotite-minette.

8.2.7 Summary

As appears to be enriched in almost all the Permian sediments with the highest values concentrated in the western area. The Cornubia sediments and certain types of lamprophyres are the main source of this enrichment.

Bow Conglomerates display the highest As values among the other sedimentary units, the As content generally being higher in the breccia than in the sandstones. As concentration in the breccia is determined by the nature of the breccia-forming pebbles. High As values were found in volcanic pebbles in breccias from the western area, and they appear to have derived from the neighbouring As - rich lamprophyres.

Lamprophyre dykes manifest anomalous As patterns in which As seems to occur in pyrite. Some lamprophyres appear to have been depleted of their As content due to secondary environmental effects.

The volcanic rocks belonging to the Exeter Volcanic Series exhibit a high contrast in As patterns. Anomalous values in the western area contrast with normal As concentrations in most of these rock types.

Correlations between As and S - sulphide indicate that As occurs in sulphides, probably in pyrite.

Lateral dispersion of As from As - rich magma seems to have been greater in rocks containing volcanic lavas than in those containing intrusive dykes.

Selected trace elements display a varied distribution within the overall area, the exception being Pb and Cu which show almost uniform concentration patterns.

8.3 DARTMOOR AREA

8.3.1 Generalities

The Dartmoor area covers a surface of approximately 840 square miles and lies within the southern, centraland part of the northern section of Devon, its boundaries being the National Grid Reference System co-ordinates 250, 000E; 280, 000 E; 52, 000N and 95, 000N. A major

part of this area was the subject of regional geochemical investigations (Chapter 7). Thus, a general account of the geology of this area is given in Chapter 7, and the main geological units are shown in Figure 7.2 and table 7.1.

Detailed studies in the Dartmoor area consist of the sampling and analysis of 280 rock samples which were collected in 80 quarries and 102 surface outcrops gathered within and around the granitic body. The locations of the sampling sites of prime importance are described in table 8.8 and shown in relation to the geology in Fig. 8.14.

The data were grouped into concentration ranges and they are represented by contours. As in most of the sample sites more than one type of rock was sampled at each site, the values in the map represent the average of the data obtained.

In order to facilitate the interpretation of geochemical data, the samples were grouped according to the following media:

i) Metamorphic aureole
ii) Outside the metamorphic aureole, and
iii) Granite.

i) Metamorphic Aureole

This group includes a variety of sedimentary, intrusive and volcanic rocks which are of Devonian and Carboniferous age. These rocks have undergone thermal metamorphism due to the rise in temperature occasioned by the intrusion of the granite. The grade of metamorphism and its lateral extension is mainly determined by:-

a) The nature of the host rock, and
b) the depth and angle of slope of the granite surface at its country rock contact.

A small number of rocks located in the outer edge of the aureole which, due to their nature have suffered the effects of hydrothermal alteration, have been included in this group.

TABLE 8.8

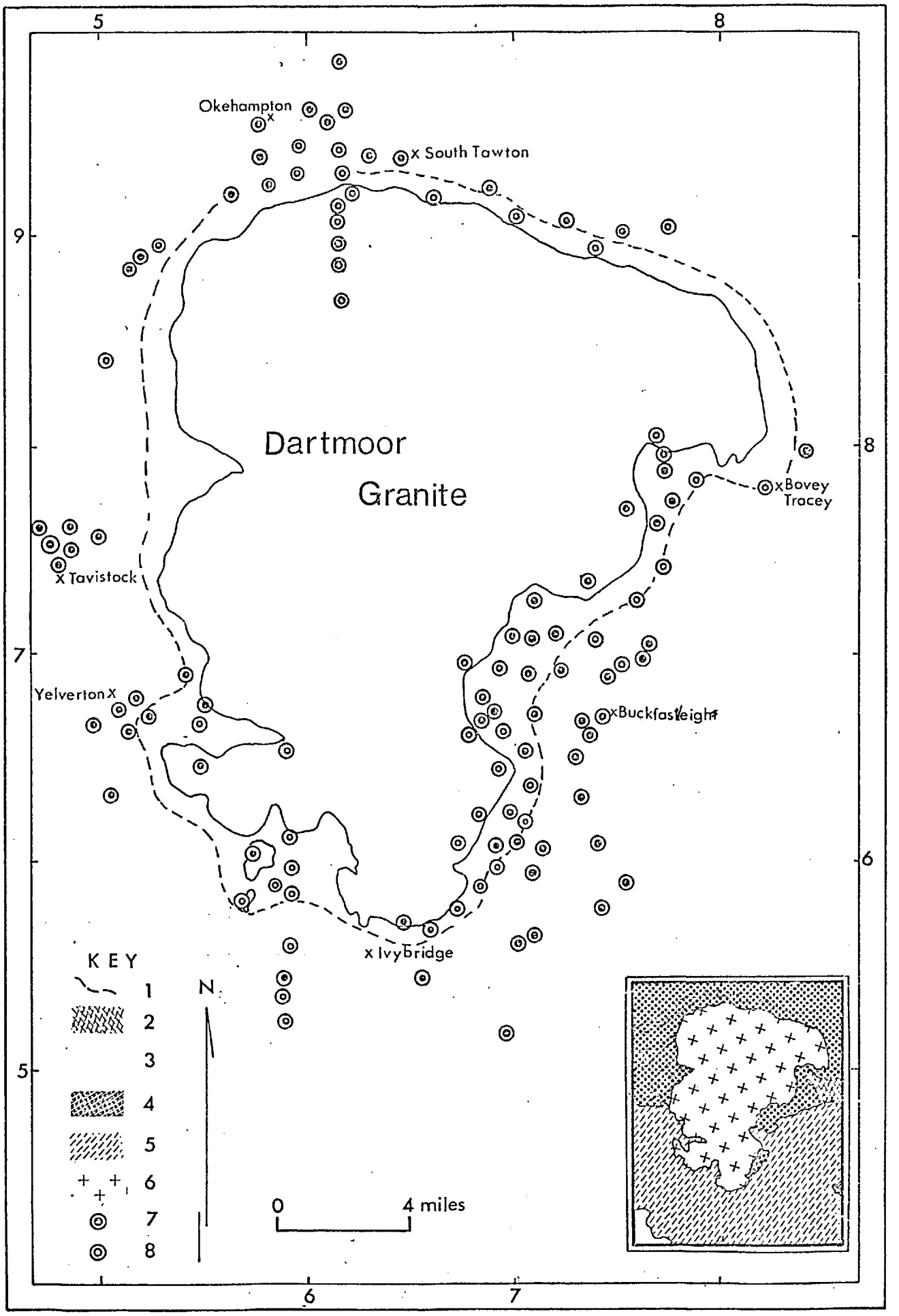
DARTMOOR AREA

Location of the Sampling Sites of Prime Importance

	N	S	QUARRY NAME	LOCALITY
Dt- 1	608	966	Webber Hill Farm	Okehampton
Dt- 2	624	965	Corscombe Lane	Okehampton
Dt- 3	636	943	Greenhill	Sticklepath
Dt- 4	655	950	South Tawton Qy.	South Tawton
Dt- 5	695	922	Hobhouse	Whiddon Down
Dt- 6	666	932	Fire Stone Cross	South Zean
Dt- 7	731	912	Drewsteignton	Drewsteignton
Dt- 8	620	919	Irishman's Wall	Belstone
Dt- 9	620	912	River Taw	Belstone
Dt-10	620	929	Belstone Common	Belstone
Dt-11	620	935	Belstone	Belstone
Dt-12	620	988	Sampford	Sampford Courtenary
Dt-13	620	946	Priestacott	Belstone
Dt-14	490	755	Indescombe	Tavistock
Dt-15	453	748	Millhill	Tavistock
Dt-16	474	766	Kilworthy	Tavistock
Dt-17	503	762	Pitts Cleave	Tavistock
Dt-18	568	925	Meldon Qy.	Okehampton
Dt-19	524	896	Sourton Qy.	Bridestowe
Dt-20	780	908	Clifford	Drewsteignton
Dt-21	777	793	Trendlebere Down	Lustleigh
Dt-22	620	976	Lydcott	Sampford Courtenary
Dt-23	583	944	Okehampton	Okehampton
Dt-24	847	807	Grocombe	Kenton
Dt-25	781	778	Ullacombe	Haytor Vale
Dt-26	760	775	Haytor	Haytor Vale
Dt-27	776	760	Smallcombe	Haytor Vale

	N	S	QUARRY NAME	LOCALITY
Dt-28	770	710	Balland	Ashburton
Dt-29	784	858	Blackingstone	Moretonhampstead
Dt-30	651	569	Rutt House	Bittaford Bridge
Dt-31	620	988	Sampford	Sampford Courtenary
Dt-32	620	996	Chapple Moor	Sampford Courtenary
Dt-33	742	740	Cold East Cross	Buckland
Dt-34	590	955	Home Farm	Okehampton
Dt-35	713	712	Deeper Marsh	Ashburton
Dt-36	704	713	Aish Tor	Ashburton
Dt-37	726	114	Ausewell Wood	Ashburton
Dt-38	725	696	Green Down	Holne
Dt-39	752	694	Ashburton	Ashburton
Dt-40	772	694	Dipwell	Ashburton
Dt-41	713	676	Brook Manor	Combe
Dt-42	698	699	The Shanty	Holne
Dt-43	742	665	Church Cross	Buckfastleigh
Dt-44	712	658	Kings Wood	Buckfastleigh
Dt-45	737	656	East Buckfastleigh	Buckfastleigh
Dt-46	738	636	Dean Prior	Dean Prior
Dt-47	719	612	Marley Farm	South Brent
Dt-48	716	599	South Brent	South Brent
Dt-49	706	616	Beara Common	South Brent
Dt-50	692	678	Scae Wood	Combe
Dt-51	696	608	Weir	South Brent
Dt-52	665	571	Bittaford	Bittaford Bridge
Dt-53	676	582	Moorlands	Cheston
Dt-54	702	521	Churchland	Brownston
Dt-55	716	570	North Huish	Diptford
Dt-56	707	564	Butterford	North Huish
Dt-57	581	630	Heddon Down	Cornwood
Dt-58	749	582	Lincombe Cottages	South Brent

	N	S	QUARRY NAME	LOCALITY
Dt-59	660	548	Quarry Farm	Ugborough
Dt-60	759	595	Yeo Bridge	Harberton
Dt-61	546	695	Peekhill	Horrabridge
Dt-62	549	677	Yemadon Down	Meavy
Dt-63	553	652	Wigford Down	Meavy
Dt-64	509	636	Combe Park	Bickleigh
Dt-65	502	671	Stokehill	Yelverton
Dt-66	518	669	Down Park	Yelverton
Dt-67	528	676	Lower Lake	Meavy



1 Aureole Limit
2 Tertiary
3 Upper Carboniferous
4 Lower Carboniferous
5 Devonian
6 Granite
7 & 8 Sampling Sites (7 Quarry)

Fig. 8.14 DARTMOOR AREA-SAMPLING SITES

ii) Outside the Metamorphic Aureole

Sediments and basic igneous rocks of Devonian and Carboniferous age are included in this group. In contrast to the metamorphic aureole these rocks are supposed not to have undergone thermal alteration. Sampling was conducted in areas both near, and at varied distances from the outer limit of the aureole.

iii) Granite

The granitic mass occupies the major part of this area. Samples of this type of rock were collected in and near to its country rock contact. Fine and coarse grained granite as well as tourmaline-rich granite were sampled separately.

8.3.2 Primary Distribution of Arsenic in the Dartmoor Area

Characteristics of the distribution of As and other selected trace-elements are shown in figures 8.15 to 8.22. Tables 8.9 to 8.12 list the means and general ranges for concentrations of eight trace-elements in different media as well as in specific rock types from the area.

The abundance of As in the igneous and sedimentary rocks of the area is more pronounced than in the general background established for these rock types. The As concentration greatly increases when related to the metamorphic aureole surrounding the granite body. The high As content within the aureole has already been established in stream sediments and soils from this particular area (chapters 6 and 7). In this medium the primary distribution of As reaches its highest mean level (66 ppm) contrasting sharply with those from the outer side of the aureole (8 ppm) and from the granite whose mean value is the lowest (7 ppm). See table 8.9.

Examination of the occurrence of As in the main geological units from the area has disclosed that the Carboniferous Formation yields greater As concentration than the Devonian units both within and without

TABLE 8.9

RANGE AND MEAN* TRACE-ELEMENT CONTENTS OF ROCKS FROM THE DARTMOOR AREA (values in ppm)

Element	Aureole	Outside Aureole	Granite
As	66* 19-810	8 1-270	7 1- 65
Cu	36 53-235	36 4-389	16 2-170
Fe%	3.9 .2- 17	2.5 .2- 21	0.8 .05-3.8
Mn	460 34-3900	625 30-4270	132 -
Pb	42 72-200	58 8-339	19 5- 53
Sn	5 1- 21	3 <1- 28	7 <1- 26
S	280 16-14000	41 <5-3390	7 <5- 95
Zn	89 21-347	100 11-413	25 5-113
No. of Samples	138	119	23

* Geometric mean ($\bar{x}$)

Range = $\bar{x}$ + 2 (log standard deviation)

the metamorphic aureole (Table 8.10). Although this contrast is not entirely reflected in the actual rock types from both units it is obvious that this discrepancy is directly related to the nature of the parent rock. Thus, shales and slates from the Carboniferous and the Devonian unit located outside the aureole, display relatively high mean values (16 and 10 ppm; respectively) the Carboniferous black shales being those which show high concentrations (up to 280 ppm), and yet the pyritic shales exhibit the highest mean value (51 ppm). These concentrations (as well as those from tuffs, sandstones, limestones, etc.) fall within the general range and background expected of such rock types (Table 8.11).

In the metamorphic aureole the parent rock appears to have been indiscriminately enriched in its As content although in some specific areas it displays normal As concentrations. Nevertheless, some of the rocks are totally depleted of the element in question.

The outstanding features of the As distribution in the metamorphic aureole are listed below:-

i) Low As levels are found in rocks located along their immediate granite contact. These rocks appear to have been partially or totally depleted of their As content by the effects of the granite intrusion.

ii) Devonian and Carboniferous dolerites show a marked contrast in their As concentration. High As values (up to 250 ppm) characterise the former whilst the latter exhibits values ranging from 1 to 13 ppm. According to Fitch (1932) Devonian dolerites were 'relaxed' as a result of dynamic metamorphism before the intrusion of the granite whilst the Carboniferous dolerites escaped the Devonian and early Carboniferous earth movements. This fact may suggest that the concentration of As in these rocks was controlled by structural factors.

iii) Analytical data of 7 axinite samples collected in axinite-bearing veins in the Meldon Quarry (Dt-18) and in the Weir Quarry (Dt-51) average 520 ppm of As. On the other hand tourmaline-bearing rocks and

TABLE 8.10

RANGE* AND MEAN** TRACE-ELEMENT CONTENTS OF R[illegible]S FROM THE DARTMOOR AREA (values in ppm)

Element	Aureole		Outside Aureole	
	Devonian	Carboniferous	Devonian	Carboniferous
As	62** 1-260*	78 1-450	6 <1- 25	9 <1-360
Cu	27 8- 58	70 10-980	18 5- 59	94 25-320
Fe %	4.6 .43- 10	3.8 .1-14.4	3.6 .1-9.8	2.5 .2-6.8
Mn	389 336-1488	592 130-4400	460 -1333	980 72-11300
Pb	25 19- 91	70 20-660	50 17-530	87 -220
Sn	6 1- 80	4 <1- 85	2 <1- 25	1 <1- 13
S	36 <5-1000	590 20-6800	29 <10-267	368 <10-7104
Zn	67 19-232	95 41-1700	76 5-137	188 20-864
No. of Samples	64	74	47	72

* General range

** Geometric mean

TABLE 8.11

MEAN* ARSENIC CONTENT OF ROCKS FROM THE DARTMOOR AREA (Outside of the Aureole) (values in ppm)

Rock Type	Devonian	Carboniferous	No. of Samples
Grey-green shale	-	10	31
Black shale	-	16	28
Pyritic black shale	-	51	12
Sandstone	-	2	12
Slate	10	-	16
Limestone	1**	1.5***	(7, 7)
Greenstone (Dolerite, diabase)	3	3	(8, 7)
Tuff	1	-	5

* Geometric mean

** Upper Devonian

*** Lower Carboniferous

tourmaline-bearing veins were found to contain high As concentrations ranging from 150 to 320 ppm. On the assumption that some, if not all, of these minerals (axinite and tourmaline) originated from magmatic gases it is obvious that As was deposited during the pneumatolitic stage.

iv) Anomalous As-bearing areas are found scattered around the granite and most of them coincide with mineralised areas (Fig. 8.15). These anomalies have been classified in four groups:-

a) A broad area in the east with values ranging from 40 to 480 ppm extends in a north-east/south-west direction bordering the granite, from the southern part of Bovey Tracey to the northern section of Ivybridge.

b) A less extensive anomaly is located to the north of Belstone and it seems to extend to the west into the Meldon area (south-west of Okehampton).

c) A limited anomaly is found to the south-west of Yelverton, the As values ranging from 50 to 260 ppm.

d) Moderately high As levels are located in the western part of Cornwood, south of Lutton, where the concentration reaches up to 250 ppm.

As previously indicated the outer edge of the metamorphic aureole is characterised by its low mean levels. However, in some areas the anomalies described above extend beyond the limits of the aureole, as is the case with the As anomaly to the north of Tavistock which is wholly located outside the metamorphic aureole.

The granitic body manifests the following outstanding features in its As content:

a) Anomalous levels were determined in three samples from the eastern section (Dt-26), the values of which averaged about 400 ppm;

b) Very low concentrations were found in samples collected in the actual country rock contact (Dt-62) showing maximum values of 2 ppm;

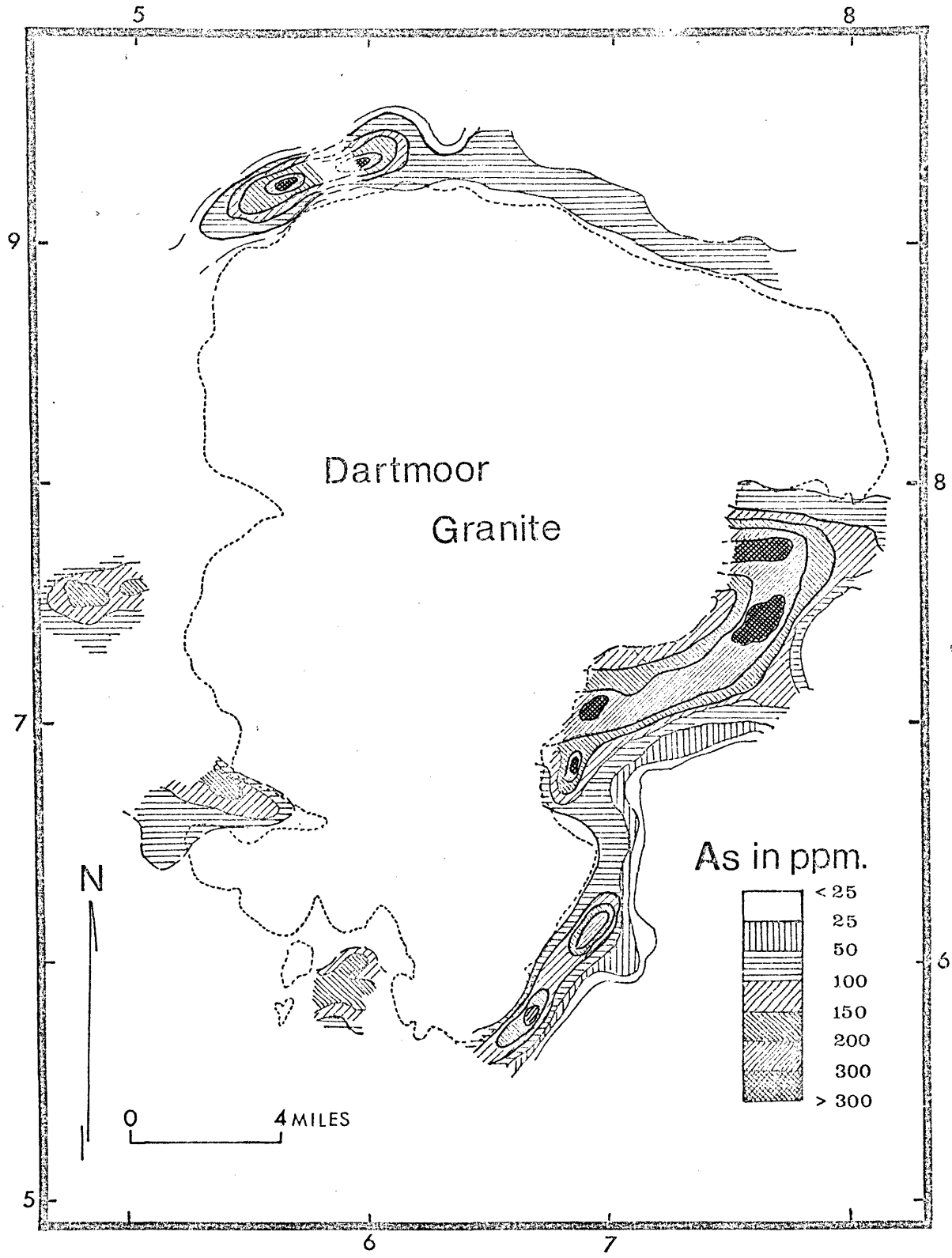


Fig. 8.15 DARTMOOR AREA - ROCK SAMPLING

c) Relatively high concentrations (up to 56 ppm) were found in areas close to the contact. These values decrease as the distance from the contact increases (in towards the granite), the As levels falling off to 4 ppmat their lowest point.

d) In relation to the granite texture no difference has been found in the As content between fine grained and coarse grained granite.

e) Detailed studies in the granite-country rock contact revealed that both rock types are depleted of their As content in, and very close to their contact.

f) Tourmaline-rich granite samples were analysed and As concentrations up to 150 ppm were found. The main characteristics of the distribution patterns of the other selected trace-elements are:-

i) Sn shows almost uniformly low concentrations in the whole area, the exceptions being:-

a) the anomalous values (up to 85 ppm) bordering on the south-eastern part of the granite between South Brent and Buckfastleigh;

b) some sporadic high levels within the granite, and

c) high Sn concentrations found to the west of Cornwood (fig. 8.16).

ii) Zn Pb, S and Cu display high levels in areas located on the northern margin of the granite between Corscombe and Drewsteington to the east, and between Meldon and Bridestowe to the west. In the eastern part of the area Zn, Pb, Cu and S exhibit high concentrations in the western section of Holne. S extends southward within the western part of Combe where it reaches its highest peak (6800 ppm). In this area Cu displays anomalous patterns with values ranging from 330 to 500 ppm. In a section striking north-south between Ashburton

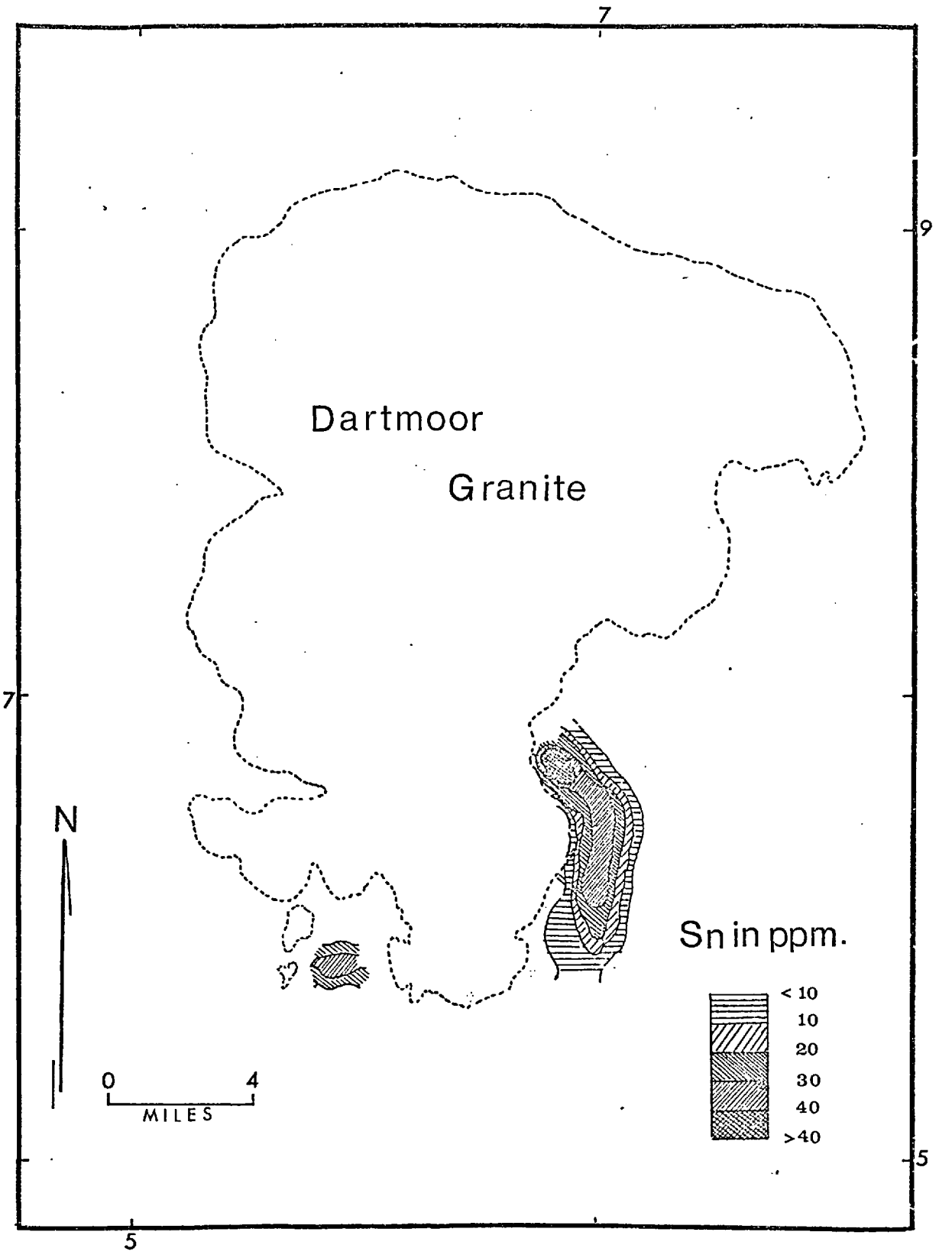


Fig. 8.16 DARTMOOR AREA-ROCK SAMPLING

and Dipford Zn demonstrates high levels (up to 360 ppm) whilst Cu, Pb, and S are relatively low. S.is found highly concentrated in an area located between South Brent and the northern section of Ivybridge with values reaching up to 1,000 ppm. In the west around Tavistock, high Zn (up to 580 ppm) is accompanied by S whose levels range from 500 to 800 ppm. (Figures 8.17 to 8.20).

iii) Fe and Mn patterns exhibit three main characteristics:

a) a broad area of high Fe-Mn concentrations is found on the eastern border of the granite between Ashburton and Dipford,

b) a less extensive zone of high Fe-Mn levels is located in the north between Corscombe and Belstone, and to the south of Wheddon Down, and

c) a limited area of high Fe-Mn values is found in the west, in the northern part of Tavistock. In addition high Fe concentration is shown to the south of Yelverton (Figures 8.21 to 8.22).

In relation to the geological units most of the trace-elements are more concentrated in the Carboniferous than in the Devonian unit with the exception of Sn and Fe which are higher in thelatter (Table 8.10). The granite contains a high Sn mean value (higher than that of the Carboniferous and Devonian) and is low in all the other trace elements. (Table 8.9).

The metamorphic aureole displays the highest Fe, Sn and S mean concentrations with respect to the outside of the aureole, but is lower in the Mn, Pb and Zn. Cu appears equally distributed in both media (Table 8.9). Among the rock types, shales exhibit the highest Cu, Zn and S mean values; Sn is most concentrated in slates, and Mn and Fe in dolerites (Table 8.11a).

Mineralised Veins

In attempt to find out any influence of the mineralising fluids in the country rock during their deposition in the structures, rocks from

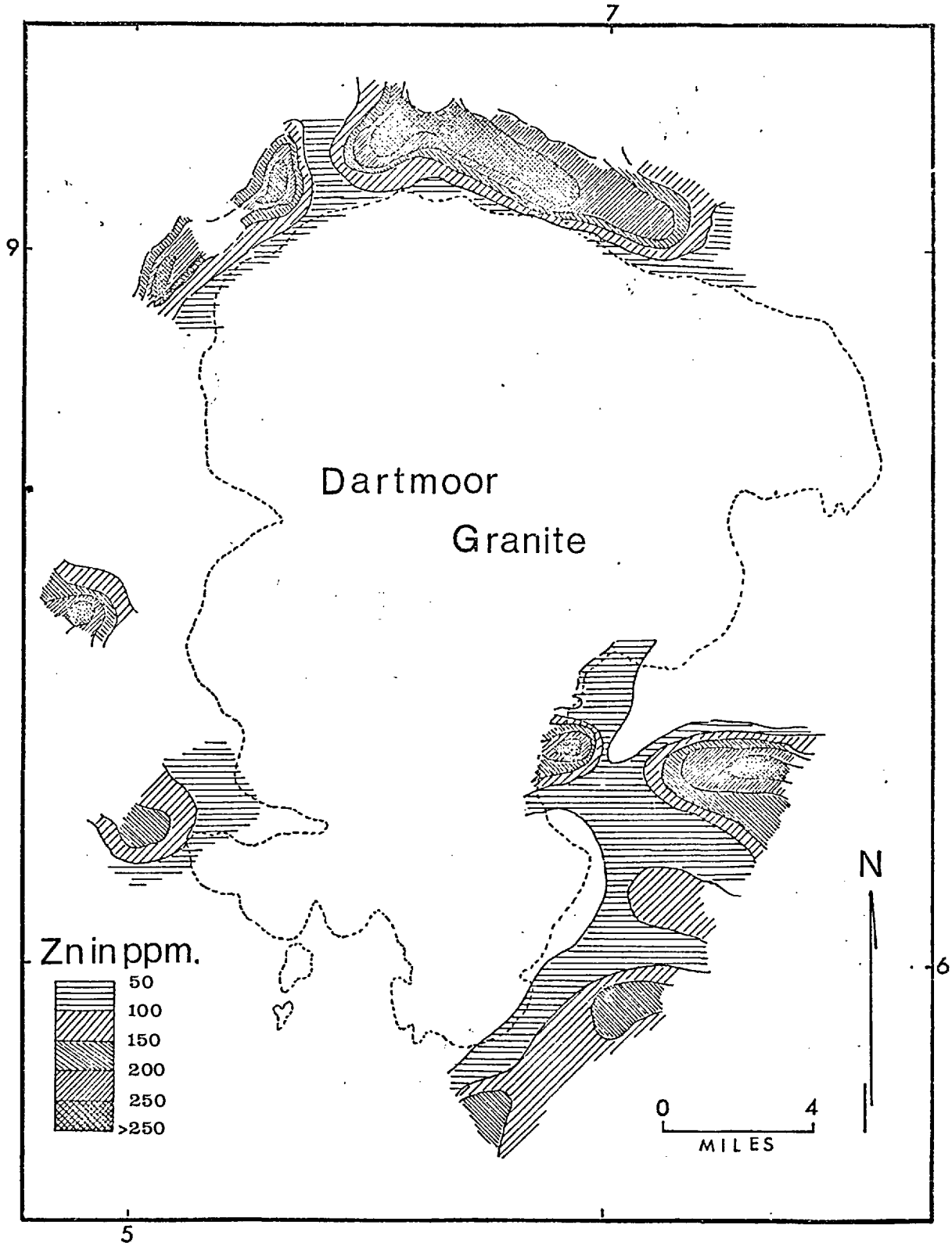


Fig. 8.17 DARTMOOR AREA - ROCK SAMPLING

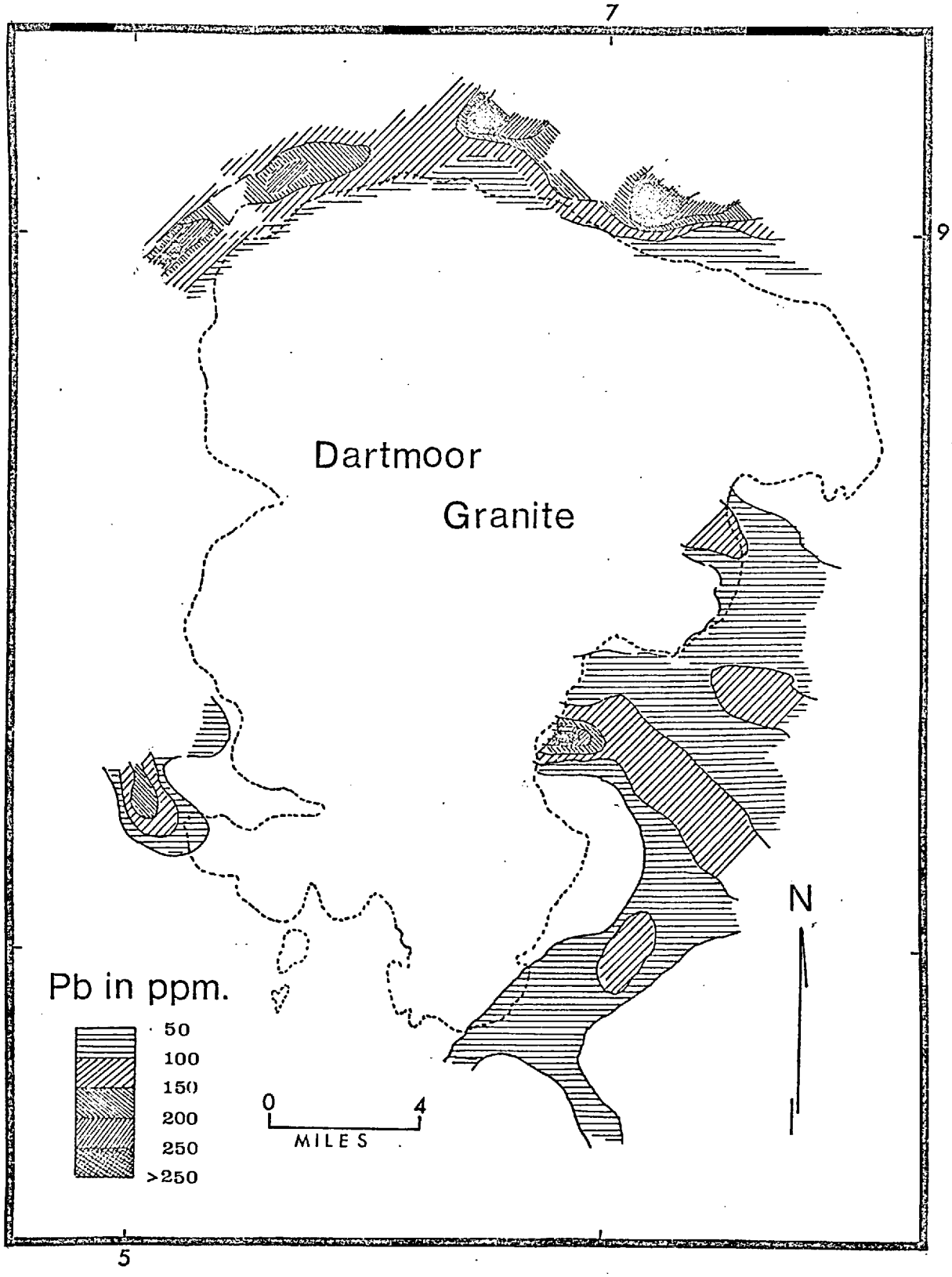


Fig. 8.18 DARTMOOR AREA - ROCK SAMPLING

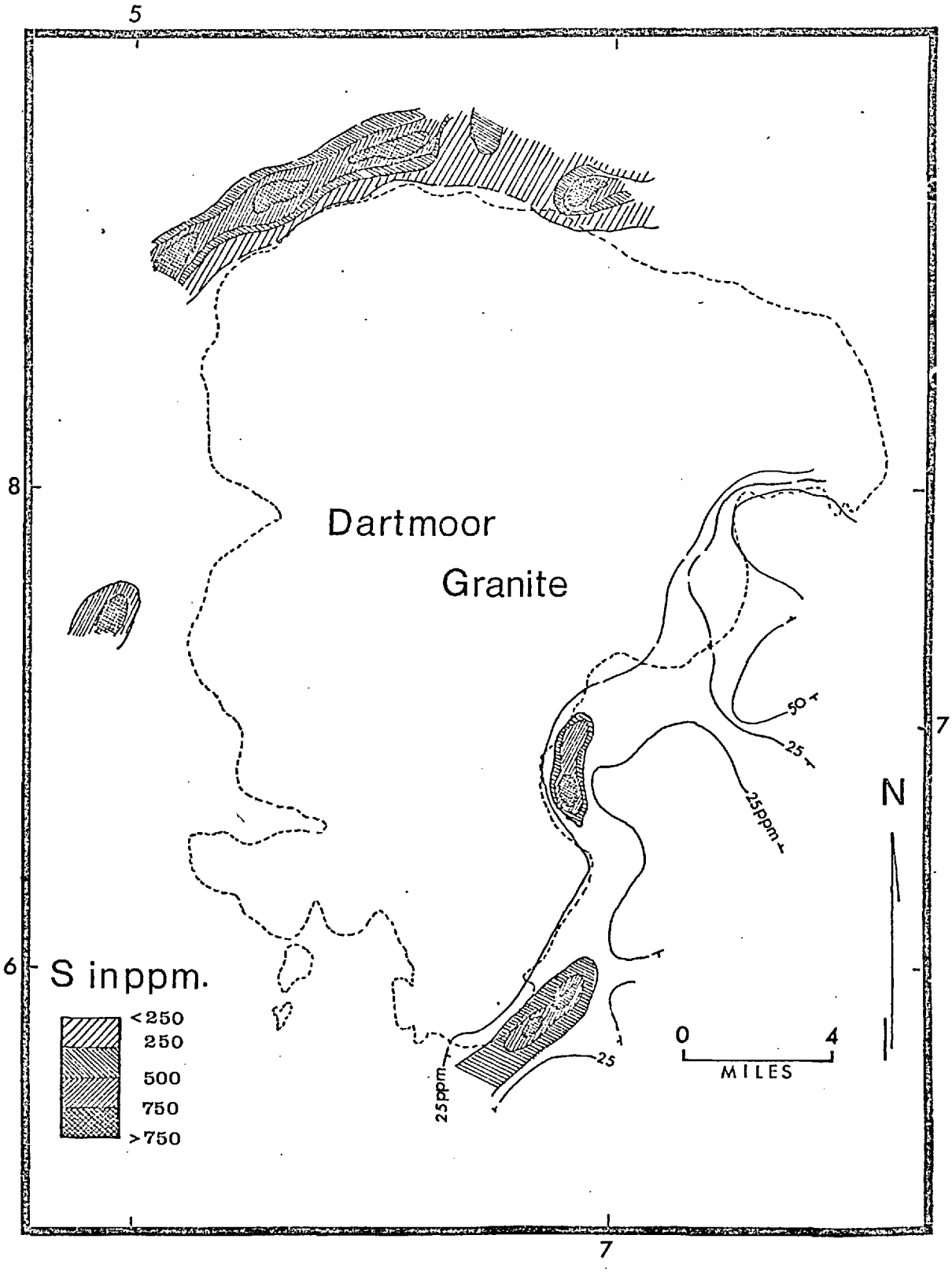


Fig. 8.19 DARTMOOR AREA-ROCK SAMPLING

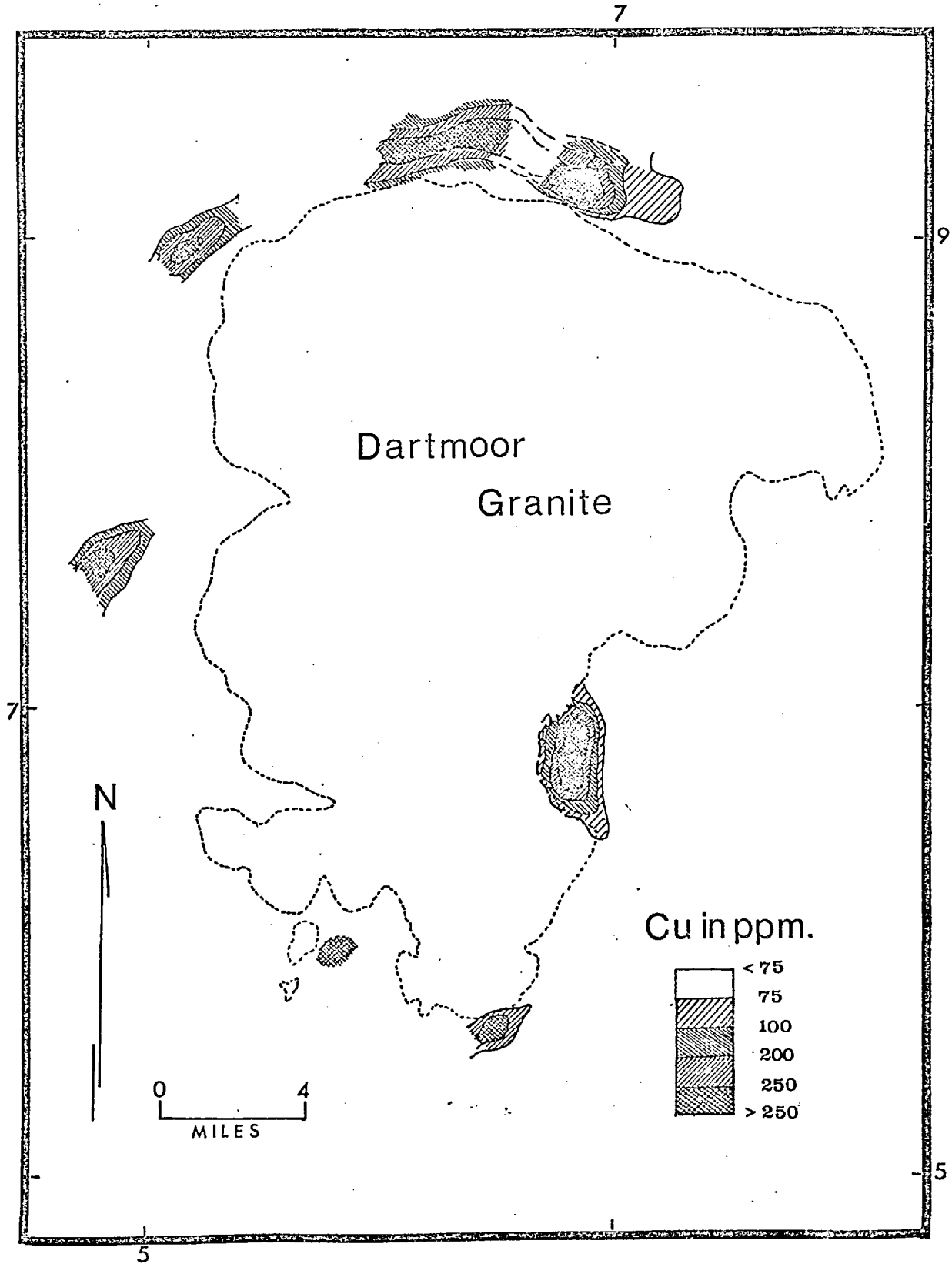


Fig. 8.20 DARTMOOR AREA-ROCK SAMPLING

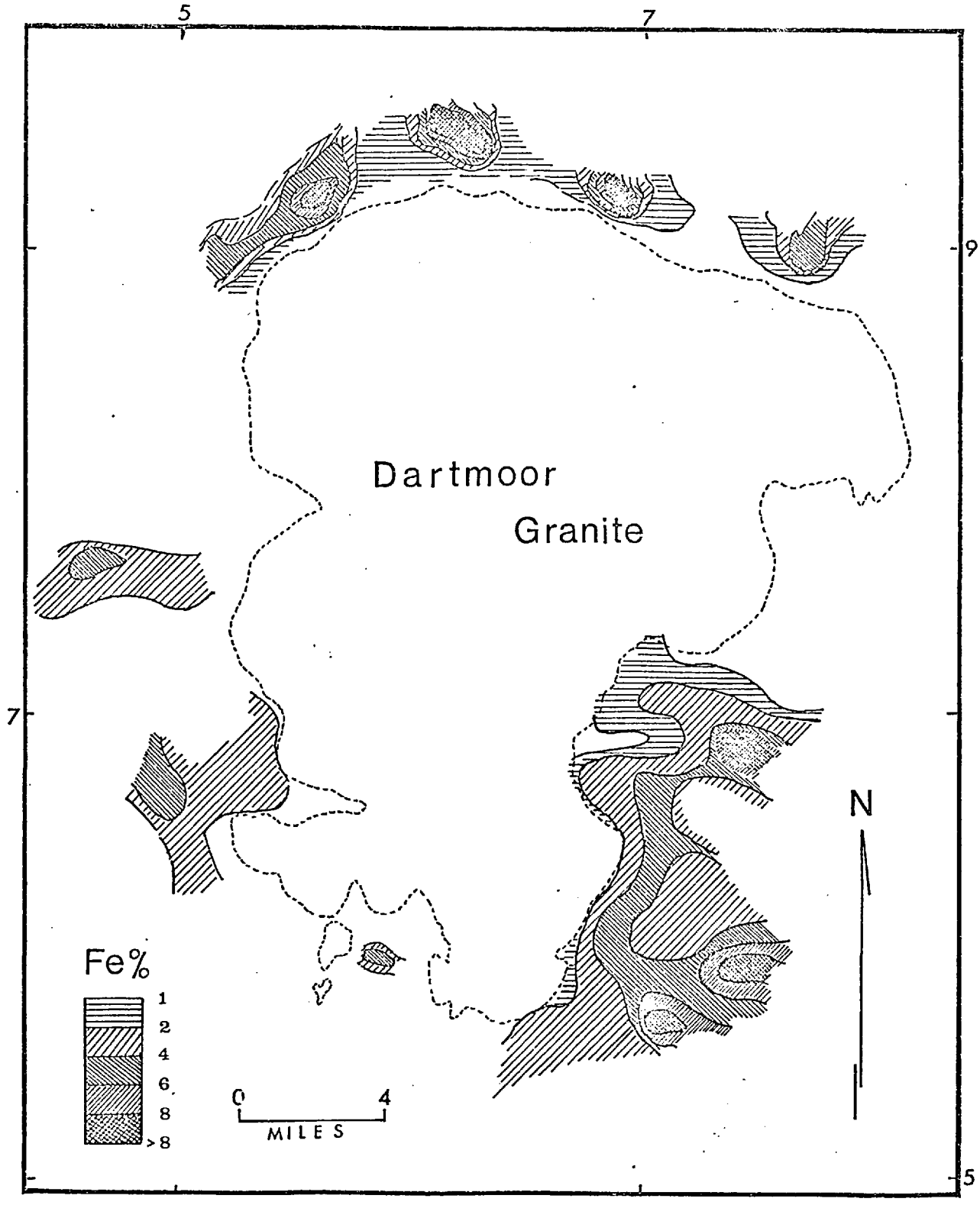


Fig. 8.21 DARTMOOR AREA - ROCK SAMPLING

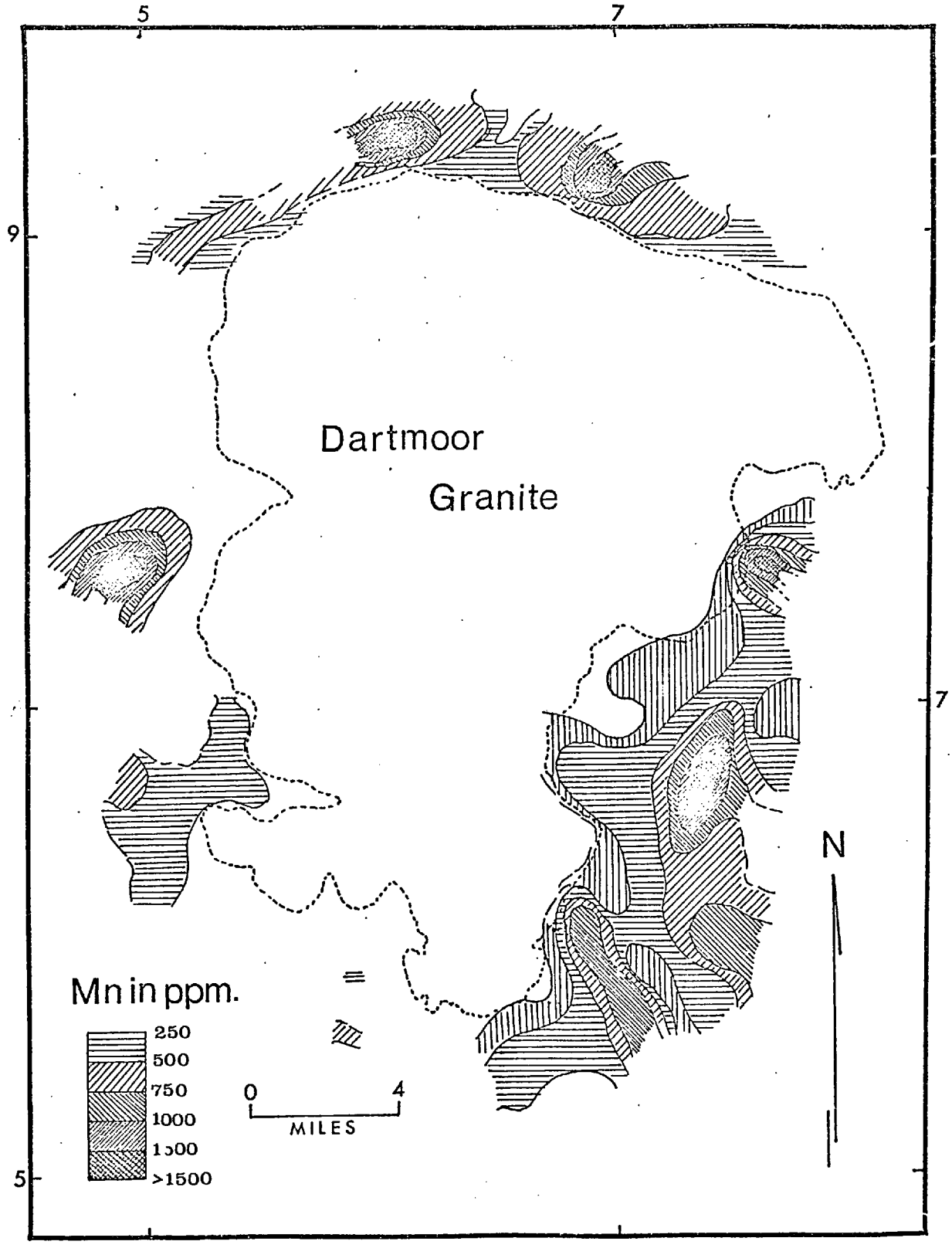


Fig. 8.22 DARTMOOR AREA-ROCK SAMPLING

TABLE 8.11 (a)

MEAN* TRACE-ELEMENT CONTENTS OF ROCKS FROM THE DARTMOOR AREA (Metamorphic Aureole)(values in ppm)

Element	Shales	Sandstones	Slates	Greenstones (Dolerite & Diabase)
As	100	45	35	20
Cu	38	33	36	27
Fe%	3.8	3.2	2.5	9.9
Mn	381	275	525	630
Pb	49	36	51	35
Sn	12	5	18	2
S	180	23	95	125
Zn	105	66	100	52
No. of Samples	48	20	40	15

* Geometric mean

mineralised ore-bearing areas were analysed, although samples from the immediate vicinity of the ores were excluded. Some mineral veins were analysed separately. As a result of these investigations the following facts were established:

i) As is the only element which shows anomalous concentrations in rocks from lode-bearing areas.

ii) Examination of analytical data from individual rock samples disclosed that despite the fact that the anomalous values are distributed indiscriminately within the different parent rocks, a considerable contrast in As levels is found when related to some specific rock types. That is the case with two dolerite samples collected at the same sample site (Dt-51) whose As concentration changes from 240 to 4 ppm in a horizontal interval of approximately 6 feet.

iii) In the Meldon quarry (Dt-18) three samples were collected in a Zn-vein which was exposed during recent quarry works. The ore has been classified by the author as marmatite, a variety of sphalerite (dark brown sphalerite, Edmonds et al., 1968) originated at a high temperature. The As content in these samples averaged 2 ppm whilst Zn, Fe, and S averaged 15, 19 and 18% respectively. Cu and Sn are relatively low.

iv) Four quartz samples carrying pyrite and chalcopyrite from a dump at Combe mine were analysed. These samples averaged: 2,800 ppm As, 1.4% Cu, 15% Fe and 22% S.

8.3.3 Correlation between Arsenic and Selected Trace-Elements

To calculate the correlation coefficients the data were grouped in relation to the following media:-

Metamorphic aureole;
outside the metamorphic aureole, and
the granite mass.

The results of these calculations are shown in Figures 8.23 to 8.25.

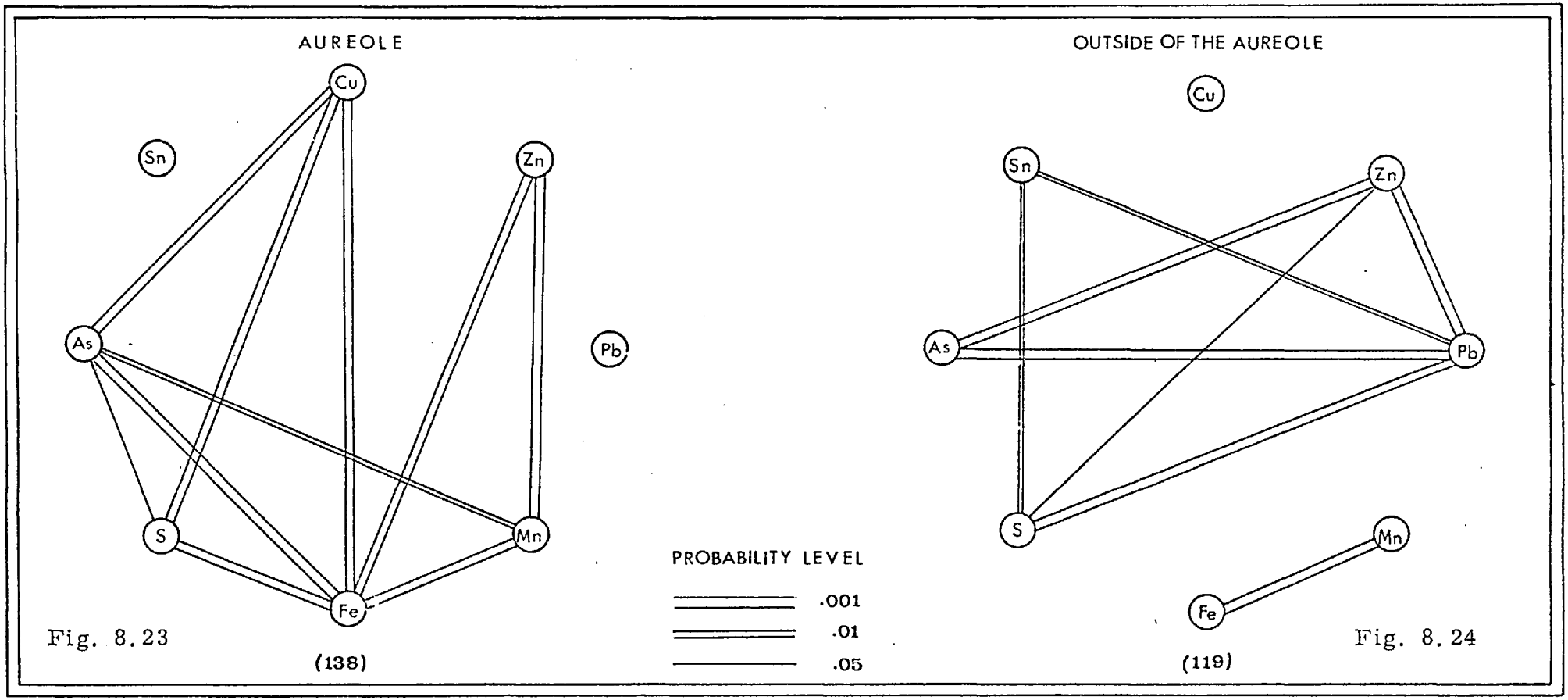


Fig. 8.23

Fig. 8.24

CORRELATION BETWEEN ARSENIC AND SELECTED TRACE-ELEMENTS IN ROCKS FROM THE DARTMOOR AREA
(values expressed as probability level of significance)

The varied groups of associated trace-elements within and outside the metamorphic aureole seem to represent almost exclusively mineralogical assemblages.

The associated As-Cu-Fe group may be related to sulphide ores from the area. Among the elements in this group, Cu and Fe are strongly related to S whilst As shows a weak correlation with this element. Since the analytical method for the determination of S in sulphides does not attack As sulphides, no As-S correlation is expected. From these facts it can be assumed that the As-S correlation corresponds to As-bearing pyrite and/or pyrrhotite and reducible sulphides in rocks and veins, and that the As-Cu-Fe association represents chalcopyrite ores yielding arsenopyrite. The association of pyrrhotite, chalcopyrite, pyrite and arsenopyrite in deposits from south-west England is well known. However, other As compounds have been reported to occur in addition to these minerals. Edmonds et al. (1968) report the presence of lollingite ($FeAs_2$) and gersdorffite (NiAsS) in rocks and veins from the Okehampton district. They explain that, since lollingite is easily mistaken for arsenopyrite, it may prove to be a relatively common component in the mineralised rocks.

The Fe-Zn-Mn correlations and the presence of marmatite might be related to each other. In effect, the high Fe content in this mineral (19%) indicates its high temperature origin. On the other hand it is known that Mn is incorporated in sphalerite, and that the highest Mn content is found in sphalerites formed at an elevated temperature (Rankama and Sahama, 1950; El Shazly et al. 1956; Goldschmidt, 1954). El Shazly et al. (1956) report that blends from veins near the granite masses contain relatively large amounts of In, Mn and Sn. However, the Fe-Zn-Mn association in the granite is most probably due to the presence of ferromagnesian minerals (biotite).

The As-Mn correlation may in part be caused by the axinite which has been found to be rich in As content, and in part by manganese oxide in cherts from the Lower Carboniferous unit.

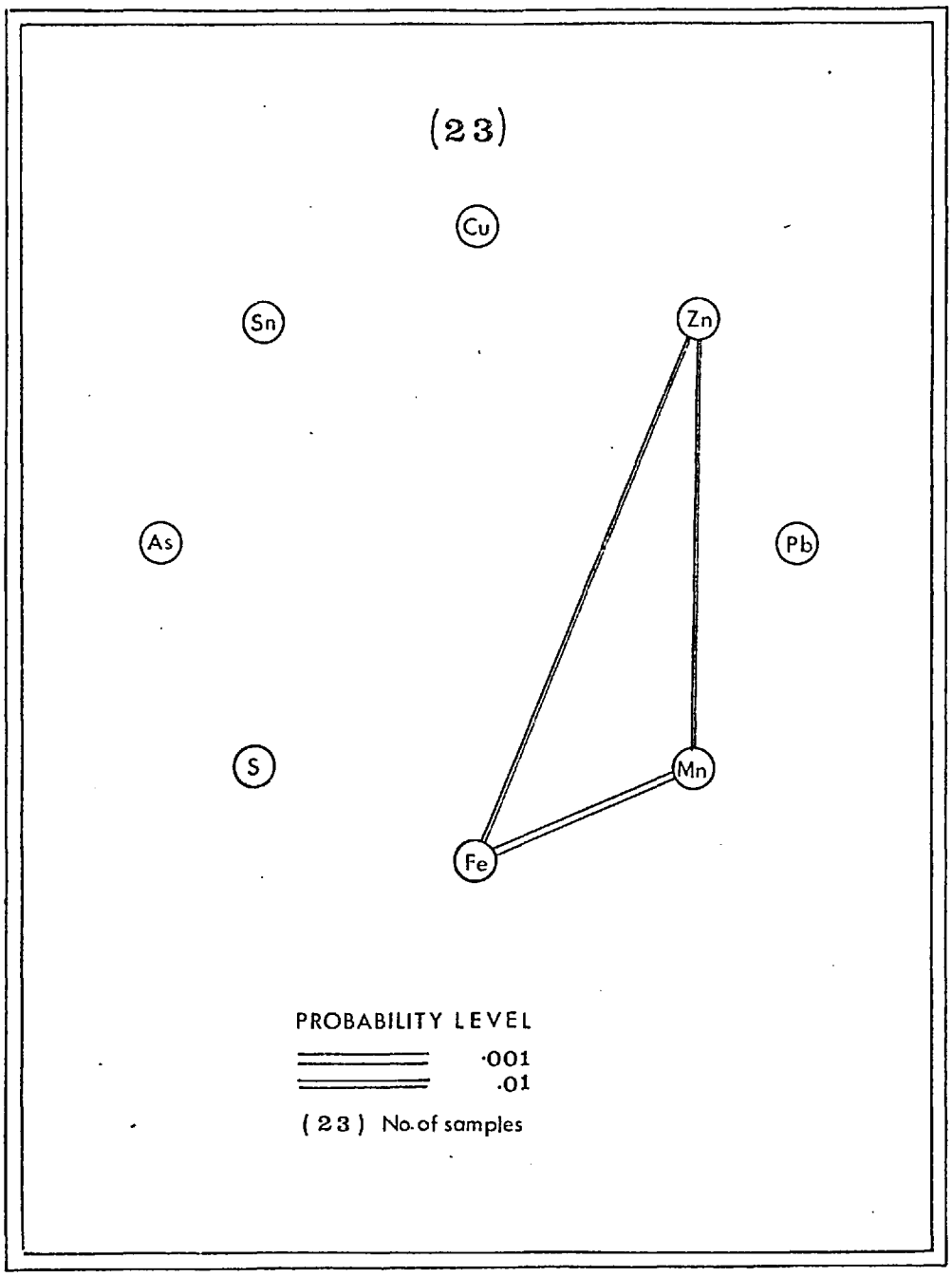


Fig. 8.25 CORRELATIONS BETWEEN ARSENIC AND SELECTED TRACE ELEMENTS IN GRANITIC ROCKS FROM THE DARTMOOR AREA
(values expressed as probability level of significance)

The As-Pb-Zn correlation outside the metamorphic aureole can be related to black shales, and the association of Sn, Pb and S is related to the marked affinity of galena for Sn.

The uncorrelated state of As in the granite suggests the occurrence of this element in its sulphide form. However, in certain areas, As is found to be correlated to S. This correlation is probably due to the presence of As-carrying pyrite.

8.3.4 Discussion of the Results

i) Generalities

The primary geochemical distribution of As in the Dartmoor area is characterised by a normal concentration which varies according to the nature of the bed rock. In specific areas this normal concentration has been altered and in most cases enriched by endogenous agents associated with the phase of the granite intrusion. As and its compounds were intruded into the neighbouring rocks in the gaseous and liquid media emanating from the magma, especially during the pneumatolitic and hydrothermal stages.

A tentative résumé of the possible events which might have occurred during the migration and deposition of As is given below. The discussion is mainly based on field and chemical evidence, and the available information concerning the behaviour of As during the magmatic activity.

At the end of the Carboniferous Period the area presently under consideration was composed of sediments from the Devonian and Carboniferous age which originated under continental and marine environments. Igneous activity took place at times ranging from early Devonian to early Carboniferous, producing the emplacement of intrusive and extrusive basic rocks. During the final stage of the Carboniferous, the Devonian - Carboniferous sediments were folded by movements of the Armorican orogeny, producing overfolding, thrusting, faulting and the development of slaty cleavages and jointing. At this stage, the occurrence

of As in the whole area was characterised by several distinct patterns which were closely related to the existing parent rock. These patterns fell within the limits of normal As background.

Intrusion of the granite batholith occurred after the Hercynian orogeny had induced metamorphic changes in the host-rock. These changes were manifested by thermal effects caused by an increase of temperature, and by chemical effects due to chemically active vapours, gases, and solutions emanating from the intrusive rock.

To a certain extent, the early escaping gases bearing low As concentrations were capable of penetrating pores and cracks of the neighbouring rocks where As might have been deposited. Due to the high temperature along with the volatile character of As this element was not only not deposited in areas at the immediate contact, but the rocks from these areas were depleted of their normal As content. On the other hand, the heat transferred by the magmatic emanations baked and hardened the invaded rock creating an impermeable 'screen' at the contact which, supported by the lithostatic pressure, impeded the migration of further fluids within the host rock. These fluids were subject to a 'reflux process' between the 'screen' and the melted magma. During this phase, part of As in the refluxing fluid was gradually deposited within the granite along its country rock contact. However, the consolidation of the granite crust, the relaxation of the regional pressure, and the accumulated pressure of the gases produced fracture patterns which, in addition to those originated by early movements (Armorican orogeny), created the channels for the accumulated gases and new solutions. During the pneumatolitic and hydrothermal stages As-rich solutions escaping through suitable fissures in both the consolidating granitic crust and overlying country rock deposited (under favourable physical and chemical conditions) all or part of their metalliferous content. At the end of these events the area was characterised by a normal As background yielding anomalous As patterns located almost totally within the metamorphic aureole.

ii) Primary Distribution of Arsenic as related to the Lithology

(Outside the metamorphic aureole)

The concentration patterns of As in the Devonian Formation shows contrast in mean values between Middle and Upper Devonian, being higher in the former (Table 8.12). This variation is due to the low As content in limestones from the Upper Devonian whose mean level is 1 ppm. In slates from this unit As is slightly higher than those from the Middle Devonian (11 and 12 ppm respectively), this little difference might be due to analytical variations.

Carboniferous sediments also display variation in As content within the units. The Crackington Formation appears higher than Lower Carboniferous (15 and 9 ppm, respectively) and as in the Devonian, this difference is caused by the low As concentration (1.5 ppm) in the limestones (Lower Carboniferous).

The contrast already established in As levels between Devonian and Carboniferous rocks is due to the high As values in the Carboniferous black shales (mean:16 ppm). In effect, limestones and basic igneous rocks (dolerites) from both the Devonian and Carboniferous show no/or little difference in their As content. Devonian slates and Carboniferous green shales exhibit no difference at all.

The As mean value in granitic rocks (7 ppm) greatly differs from that expected of such rock types. Thus, the As mean for granite given by Boyle and Jonasson (1973) scarcely reaches 0.93 ppm, whilst Onishi and Sandell (1955a) give an average of 1.5 ppm. However, despite the high mean level the As concentration is not uniform in the granite, the range varying from very low to anomalous values. According to its As content, the granite can be classified into three types:-

a) 'Uncontaminated' granite which is mainly found in the central area with As content ranging from 4 to 10 ppm;
b) 'Contaminated' granite which is located near the country rock contact, and mineral veins, with values reaching up to 450 ppm; and

TABLE 8.12

MEAN* TRACE-ELEMENT CONTENTS OF ROCKS RELATED TO BED-ROCK GEOLOGY FROM DARTMOOR AREA

(Outside Aureole)

(values in ppm)

Element	Devonian		Carboniferous	
	Middle	Upper	Lower	Upper
As	10	6	9	15
Cu	19	22	96	78
Fe %	1.2	4.6	2.1	2.8
Mn	296	708	1260	1550
Pb	60	36	178	64
Sn	3	1	2	<1
S	41	7	195	163
Zn	65	89	276	160
No. of Samples	20	24	30	40

c) 'Barren' granite which is found at the contact, the As content being very low.

In the first type the abundance of As is considered as syngenetic, the values falling within the normal range established in granitic rocks. The As-S correlation suggests that As probably occurs in pyrite. This mode of occurrence of As is well known and has been mentioned by many authors such as Rankama and Sahama (1950), and Goldschmidt (1954). Boyle and Jonasson (1973) concluded:- "In these studies we have found that the bulk of As in igneous, sedimentary and metamorphic rocks occurs in pyrite".

In the 'contaminated' granite the occurrence of As is mainly considered to be of an epigenetic primary origin. Its deposition might have occurred in two main phases:

a) As-bearing fluids emanating from the uprising magma deposited part of their As content in the margin of the granite along its country rock joining. As previously indicated, this deposition resulted as a consequence of a 'refluxing process' to which early magmatic fluids were subjected, between the melted magma and the impermeable 'screen' of baked country rock at the contact (see section 8.3.4. Generalities). However, field evidence reveals that this 'screen' does not extend along the entire contact, therefore in some areas the fluids were able to flow into the host-rock. In this case other 'refluxing processes' might have developed within the country rock. These processes may resemble those suggested by Phillips (1973) when explaining the formation of some porphyry ~~porphyre~~ ore deposits. Phillips postulates that during the process of absorption of volatile components by a magma intruding permeable rocks which contains pore fluids, convective circulation may occur, and that the rate and extent of the conventional circulation will depend, respectively on the permeability of the envelope rocks, and the presence of impermeable barriers.

The As concentration in the 'contaminated' granite of this first phase ranges from 15 to 56 ppm. This fact, and the moderately high As values in the aureole (see below: Section (iii), Metamorphic Aureole), may indicate that the As content was low in the early magmatic fluids. Low correlation between As and S suggests that in addition to pyrite, As occurs in other forms, as sulphide, for instance.

b) Emplacement of ore deposits in the granitic crust was accompanied by lateral migration of volatile compounds into the wall-rock. Dispersion halos originated in hanging walls, and the extension of these halos depended on multiple, complex factors such as pressure and temperature gradients, nature of the migrating material, porosity of the rock, etc. Dispersion halos of As may be found in deposits where this element constitutes either the major or the minor constituent. The As content in lode-bearing areas within the granite averages 400 ppm, whilst S only reaches 7 ppm, therefore the absence of pyrite and other reducible sulphides is obvious. It can be assumed that As occurs in the sulphide state, although other forms of occurrence should be considered.

In the third type, ('barren' granite) the maximum As value found was only 2 ppm, and in many cases no As was detected. The possibility of the existence of a 'impermeable screen' of granitic rock (migmatite?) can be considered.

Since the theoretical considerations concerning the 'refluxing processes' are speculations based solely on limited field and analytical data no conclusive evidence can be given, and such a hypothesis must be considered cautiously.

iii) Primary Distribution of Arsenic as related to the Metamorphic Aureole

The As concentration within the metamorphic aureole can be classified in two major patterns:

a) Local background, and

b) Anomalous patterns

a) Local Background

This pattern groups three different As levels:-

i) very low concentrations in rocks along the contact;

ii) 'normal' content in specific rock types, and

iii) relatively high values in definite areas.

In the first group, as previously discussed, the rocks at their granite contact were depleted of their As content by heat transmitted from the magma. In the second group, the rocks maintained their normal As concentrations despite the thermal metamorphism. Such is the case of the Devonian and Carboniferous dolerites which only show high As values when related to ore deposits. For instance, the high contrast in As content in the dolerite samples from Dt-51 (see mineralised veins) may be an indication that high As levels in this rock type occur in very limited zones, and probably in association with mineralisation. This phenomenon has also been observed in the Carboniferous dolerites and cherts at Dt-3, Dt-17 and Dt-18.

In the third group are those rocks which seem to have been enriched in As by endogene agents during the granitic intrusion. Examination of analytical data suggests the existence of super-imposed As patterns, and that the distribution of this element in the parent rock might have occurred in two main phases:-

a) Early magmatic gases penetrated the pores and/or the pore-walls and could even have entered into the crystal lattice of some syngenetic minerals of the rocks. Despite the lack of sufficient

data, it might be assumed that uniform physical-chemical conditions prevailed during this phase, and that the nature of the parent rock was responsible for the concomitant variation in the metal content of the rocks. However, the factors which control the accumulation and dispersion of trace elements in rocks are so numerous and complicated that considerable difficulty is encountered in arriving at a clear understanding of the circumstances in which As was deposited in this particular area. The fact that As is highly related to S leads to the assumption that pyrite is the main As-carrier, and the moderate As levels in this phase suggests that the early magmatic gases were relatively low in As content.

b) Later, As-rich magmatic fluids (gases and liquids) penetrated the rocks and deposited their As content. The relatively high values do not characterise the whole area; rather they are concentrated in specific zones where As is distributed indiscriminately within the varied lithologies of the parent-rock. Analytical data from some 'baked' rock samples collected in a very restricted area at the contact show that As values range from 1 to 280 ppm. This characteristic is also found in some white calc-flinta rocks near the contact. Therefore, it seems that As was deposited in microfractures rather than in pores of the host-rock.

The low As-S correlation suggests that the incidence of As in pyrite is low and that As might occur as sulphide or other As compounds.

b) Anomalous Patterns

The anomalous patterns within the aureole are classified in relation to:-

i) Known mineralisation

ii) Possible mineralisation

i) Known Mineralisation

The spatial super-imposition of As anomalies and ore mineral-bearing areas constitutes an indication of a close relationship between mineralisation and the anomalous As patterns (Fig. 8.26). In effect, in the northern and eastern part of the area where most of the anomalies have been located the occurrence of sulphide-bearing veins is well known. However, in the northern section where Sn-Cu-As, and Cu-As mineral deposits occur in a broad area surrounding the granitic mass, the As anomalies are confined to the mineralised zones of Belstone and Meldon, whilst eastward of the Belstone zone the As concentrations are moderately high.

In this area the ore minerals (veins) which are mainly located in the Lower Carboniferous cherts, almost lack dispersion halos, and lateral migration of the element into the host rock is insignificant.

In addition to these mineral deposits the area is characterised by a pattern of several thin sulphide-bearing veins, veinlets, and joints distributed in the metamorphosed rocks. According to Edmonds et al. (1968) pyrite, chalcopyrite and arsenopyrite can be seen in veins in the different aureole rocks. It is probable that an imperceptible pattern of micro-veins originated in the parent rock and that lateral dispersion (if there was any) of the element from the major structures was controlled by these micro-veins patterns. Furthermore, foliation structures might have played an important role in the dispersion of the element in pelitic rocks. However, these micro-structure patterns have barely developed in cherts and dolerites from the area.

In the eastern area the anomalous As concentrations connected to known mineralised area, lie in a broad zone between Bovey Tracey and Buckfastleigh where ore veins bearing Sn, Fe, Cu and As occur (Dines, 1956). In this zone the relationship between As anomalies and mineralised areas is more conspicuous than in the northern section. The anomalies extend outside the metamorphic aureole into the granitic mass and killas, and seem to follow the mineralised structures trend (Fig. 8.26).

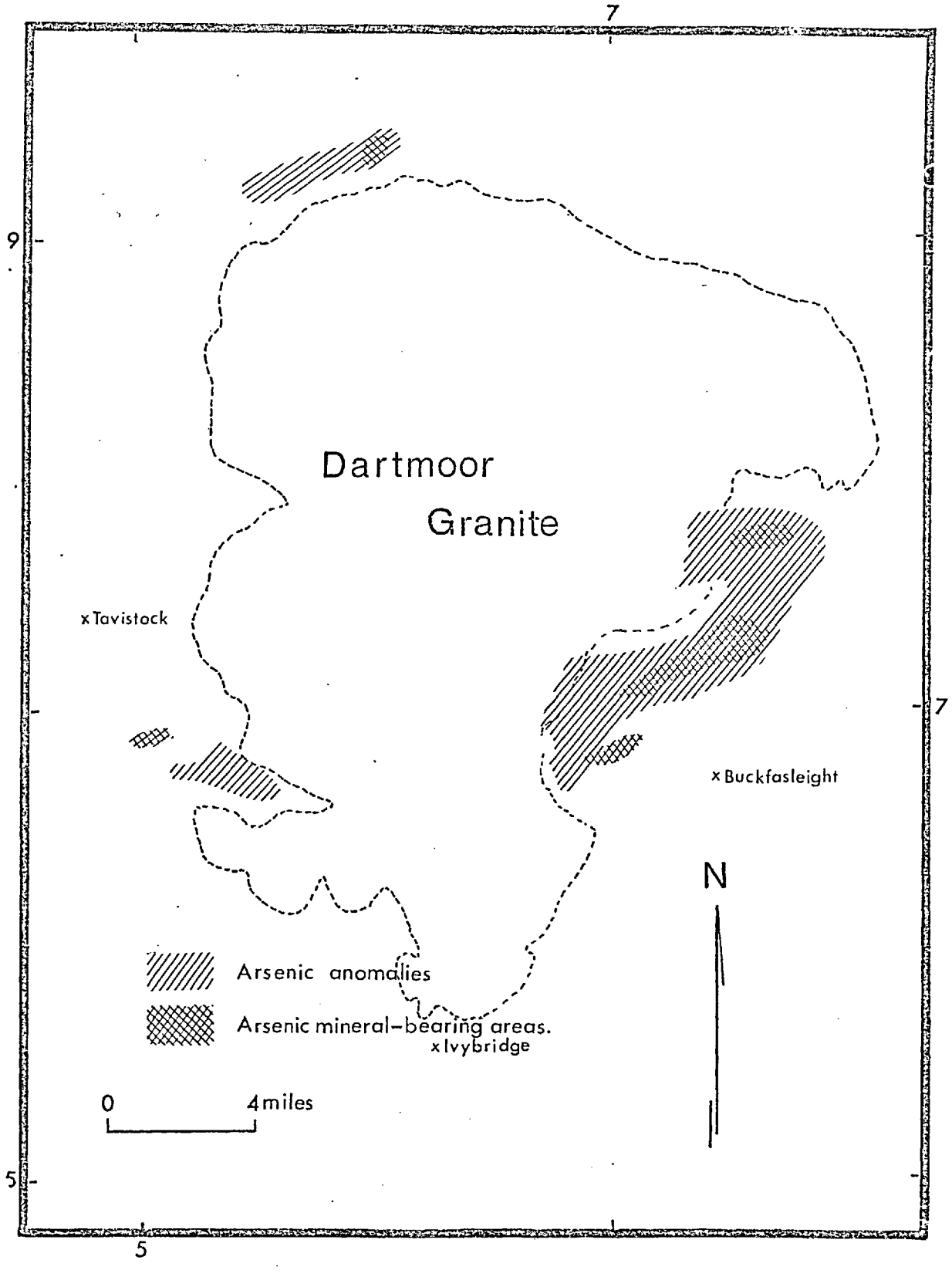


Fig. 8.26 RELATIONSHIP BETWEEN ARSENIC ANOMALIES AND ARSENIC MINERAL-BEARING AREAS

In an attempt to exclude any influence from wall rock alteration no analytical data from the immediate vicinity of the ores were considered while drawing up the geochemical maps of this area, the only exception being those from the western part of Buckfastleigh where samples were collected near the ore body. Shales, black shales, sandstones and granitic rocks display indiscriminate anomalous As values. Dolerites show the same characteristics from those in the northern area. With the exception of the dolerites, it seems that no lithological control has influenced the concentration of the element, and it can be assumed that in addition to fracture and micro-fracture patterns, dispersion halos from the ore bodies greatly contributed to the anomalous concentrations of As in this region.

ii) Possible Mineralisation

Two As anomalies were found in the southern aureole of the granite in areas which are considered metallogenically barren. In effect, no mineralisation has been reported in this area with the exception of the silver-lead and blend ore deposits located one mile south-east of Ivybridge (Dines 1930, 1956).

In the absence of sufficient lithological and structural evidence (among other important factors) mainly due to poor exposure, it becomes difficult to extract a clear understanding of the significance of these anomalous concentrations. However, on the basis of the geochemical data and some field relationships these anomalies have tentatively been regarded as relating to undiscovered ore deposits.

The first anomaly (termed Anomaly A) extends in a south-west direction from Brent Hill to the eastern section of Ivybridge, whilst the second one (termed Anomaly B) lies in a limited area to the south of Lutton, westward of Cornwood (Fig. 8.27).

Anomaly A

The parent rock in this area is formed of metamorphosed Culm and Devonian sediments, and some basic igneous rocks (tuff and dolerites) outcropping in the north-eastern part of the area.

The significant characteristic of this anomaly is that most of the high As values are related to the Devonian-Carboniferous calc-silicate rocks. The occurrence of metalliferous minerals, especially sulphides, in these rock types have been pinpointed in many mineralised districts of Cornwall and Devon. In the northern margin of the Dartmoor granite, as mentioned before, the main concentrations of sulphides seem to occur in the calc-silicate rocks (cherts) of the Lower Carboniferous. Edmonds et al. (1968, 1969) reported that in this zone concentrations of minerals of economic significance were largely confined to calc-silicate-bearing rocks.

In the dolerites the distribution of As is very similar to those of the northern aureole. Their values contrast with very low levels in an interval of a few feet. Analytical data from dolerites at Dt-3, 17 and 18 have demonstrated that these rocks are high in As only when they are closely related to mineralisation. Shales and slates, all high in As concentrations, show no great difference in their metal content.

In addition to As, this area exhibits anomalous Cu, S and Sn concentrations. Cu is highly concentrated in a small zone north-east of Ivybridge, whilst S extends over the whole area in an apparent close relationship to the As anomalies. However, despite this spatial As-S correlation, the S appears to arise from pyritic black cherts, and from pyrrhotitic dolerites. On the other hand, it has been found that the As-pyrite/pyrrhotite relationship in these rocks is relatively low.

In the north-east section of this anomaly, the anomalous Sn concentrations are in part related to dolerites, and extend north/north-west into the mineralised Devonian-Carboniferous sediments. Occurrence of Sn in dolerites is not uncommon in the area, and the possibility of Sn anomalies relationship with ore bodies must be considered.

Anomaly B

The parent rock in this area is composed of sediments and dolerites of Devonian age (Upper-Devonian). Analytical data from these rocks clearly show that practically the bulk of anomalous As concentrations are located in the doleritic mass outcropping southward of Lutton (Fig. 8.27). High As values in this area already have been determined during the soil and

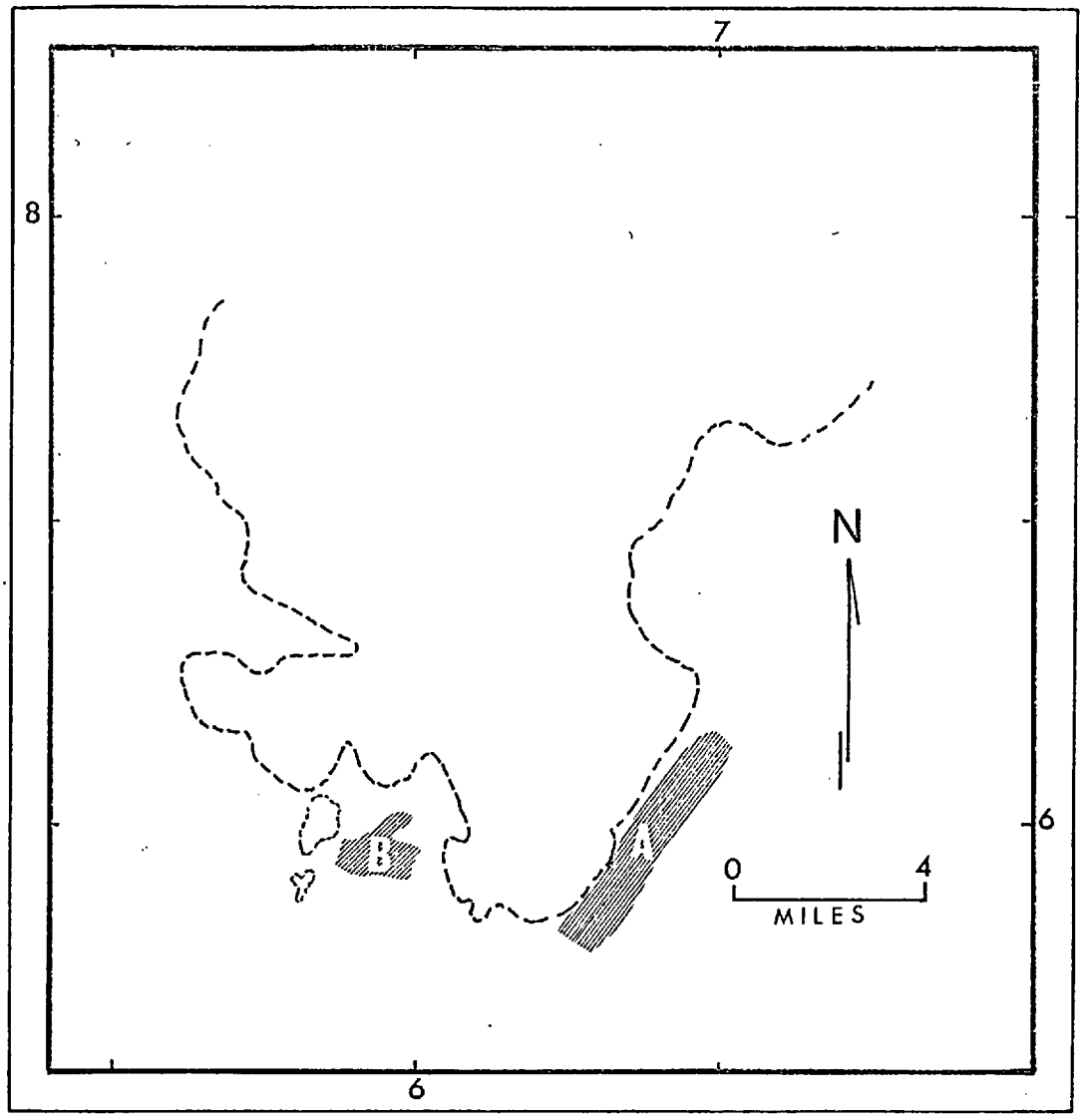


Fig. 8.27 ARSENIC, TIN AND COPPER ANOMALIES (PRESUMABLY RELATED TO UNDISCOVERED MINERALISATION)

stream sediment investigations (Chapter 7). Along with As high Cu, Sn, Mn and Fe were found in this rock type, S is erratic with values ranging from low to anomalous values.

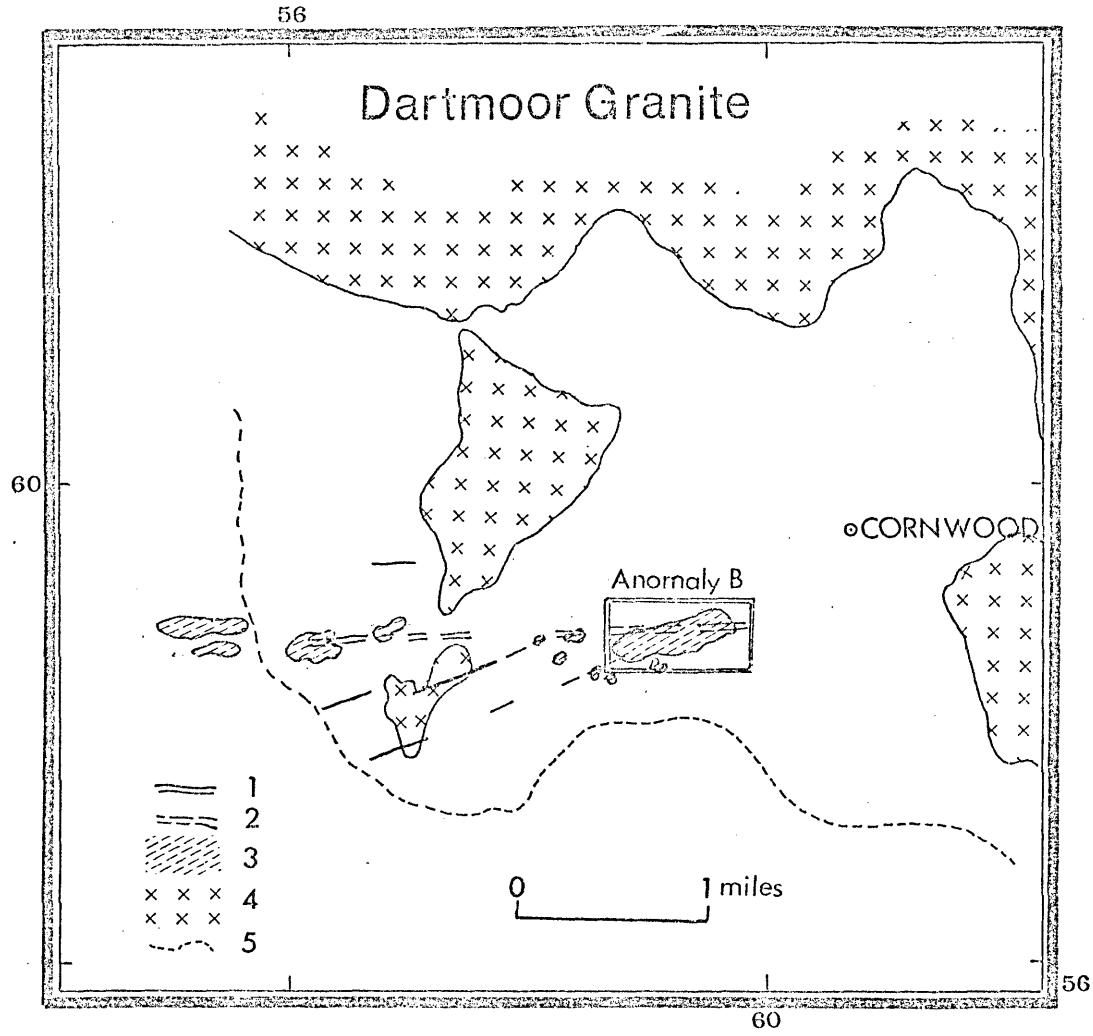
The doleritic body in which As appears highly concentrated seems to constitute the major boss of a group outcropping westward in an adjacent, mineralised zone where Sn, Cu, As and W occur in lodes emplaced in Devonian killas and dolerites, and in the granite. Especial attention is given to the Bottle Hill mineralised area where As, along with Cu and Sn has been reported to occur in killas and dolerites in lodes striking in an east-west direction. According to Dines (1956) in this specific area four east-west Sn and Cu lodes occupy a belt of country about 200 yards wide. Assuming that this geochemical anomaly could represent mineralisation, it is possible that an eastward extention of this mineralised belt is a factor to be considered (Fig. 8.27a).

Other Anomalies

The As, S, Cu and Zn anomalies located in the western area, north of Tavistock (outside the aureole) are regarded as having arisen from the pyritic black shales and cherts rather than from known or undiscovered mineralisation. The anomaly south-east of Yelverton seems to be related to mineralisation, but the weathered nature of the rock samples makes this possibility doubtful.

The Zn, Cu, Pb and S anomalies found on the northern border of the granite appear to be related to the sulphide ore deposits scattered in the area. However, in the case of Cu, Pb and Zn, part of these anomalous concentrations are connected to black shales, whilst S anomalies appear to arise mainly from pyritic rocks. Anomalous values of these elements in the western part of Buckfastleigh are entirely related to sulphide ore deposits.

Mn and Fe minerals in rocks and veins from the northern margin of the granite are reported to occur in different states. Edmonds et al. (1968) report the existence of axinite, rhodonite, ilmenite haematite,



1 Lodes
2 Projection of Lodes
3 Dolerite
4 Granite
5 Metamorphic Aureole Boundary

Fig. 8.27a ARSENIC AND TIN ANOMALIES IN ROCKS (PRESUMABLY RELATED TO MINERALISATION)

garnet spessartine, etc. within the varied rocks from this area. The presence of some of these minerals has been confirmed during the present study. Fitch (1932) recounts of abundant specular haematite-bearing lodes, and wad manganese and axinite associated with spilites and other rock-types in the eastern area of the granite. Dines (1956) reports the presence of Fe and Mn around the granitic mass. The Fe and Mn anomalies in the Dartmoor area appear to be closely related to these mineral occurrences.

8.3.5 Summary

Detailed geochemical investigations into the primary distribution of As and selected trace-elements in rocks from the Dartmoor area which is underlain by Devonian, Carboniferous, and granitic rocks, revealed the existence of varied As patterns in this area which range from very low to anomalous concentrations.

The geological units (Devonian and Carboniferous) show varied As values which are closely related to the nature of the bed-rock forming the units. These values fall within the normal range levels expected in such rock types. However, the As content from these geological units greatly increases when related to the metamorphic aureole, and/or to mineralised lode-bearing areas.

The granitic mass displays normal As content with local variations of relatively high values located in specific zones near its country rock contact. Anomalous As values are found in the granite when related to mineralised veins.

As anomalies were discovered to be mainly confined to the metamorphic aureole surrounding the granitic body. In some specific areas these anomalies extend into the granite, and into the sediments located outside the metamorphic aureole. The origin of the As anomalies is closely related to the phases of the granitic intrusion, although this intrusion produced baking and hardening of the rocks at the contact zone, and consequently depleted the rocks of their As content.

Gases and liquids emanating from the magma were responsible for the gradual enrichment in As concentrations of the neighbouring rocks as well as the granite. Deposition of As which involved numerous, complex endogene and exogene processes lasted from the early magmatic activity to the later stage of the granitic consolidation. Analytical data suggest that early magmatic fluids were low in As content, the concentration being higher in the pneumatolitic and hydrothermal stages which were capable of forming ore deposits of economic significance.

High As values are found indiscriminately within the varied country rock. Although some rock-types appear more enriched than others in As content no lithological control seems to have influenced the As concentration in the host-rock. Primary dispersion of As within the rocks seems to have been controlled mainly by fracture and micro-fracture patterns developed before, during, and after the granitic intrusion. However, concentration of the element in pores, wall-pores, and even in the crystal lattice of certain rock-types might occur during the early magmatic stage, and from lateral migration of solutions from the fluid-filling veins.

Tourmaline, axinite, quartz, and sulphide-bearing veins were found to be high in As values. However, marmatite ores of the Meldon area (dark brown sphalerite) exhibit a very low As content.

Analytical data from mineralised lode-bearing areas demonstrate that halo dispersions of As from the ore-bodies are better developed in shales, sandstones, slates and granitic rocks. In calc-silicates and doleritic rocks the halos are either restricted to a very limited area or they are insignificant. Dispersion halos might develop in these rocks only through structures and micro-structures (infiltration).

Four significant As anomalies were located bordering the granitic mass, and they were regarded as having been caused by mineralisation. The anomalies located between Belstone and Meldon in the northern

margin of the granite, and between Bovey Tracey and Buckfastleigh in the east were found to be related to Sn and sulphide-bearing veins within the killas and the granite.

Two As anomalies lying between South Brent and Ivybridge (Anomaly A) and to the west of Cornwood (Anomaly B) are thought to represent undiscovered mineralisation. The high As values from Anomaly B, mainly concentrated in dolerites, might represent the continuation of the east-west mineralised belt located $1\frac{1}{2}$ miles westward from the anomalous area.

Anomalous concentrations of Sn, Cu and S were found along with As in the anomalous areas A and B. However, S is related to pyrite and/or pyrrhotite from the rocks rather than to As or Cu sulphides.

The varied degree of As-S correlations revealed that As in rocks and veins from the area may occur in reducible sulphides (mainly in pyrites) and as As-sulphides and other As compounds. In ore deposits arsenopyrite is considered to be the primary constituent.

Cu, Pb, Zn and S anomalies in the northern margin of the granite, to the west of Buckfastleigh, and to the south of Yelverton show a close relationship with mineralised areas, (particularly with sulphide deposits) and with black shales.

Occurrence of Mn and Fe minerals is widespread in varied states within rocks and veins from the area. The anomalous values of these elements are related to this occurrence and their significance is relative.

8.4 CORSCOMBE AREA

8.4.1 Introduction

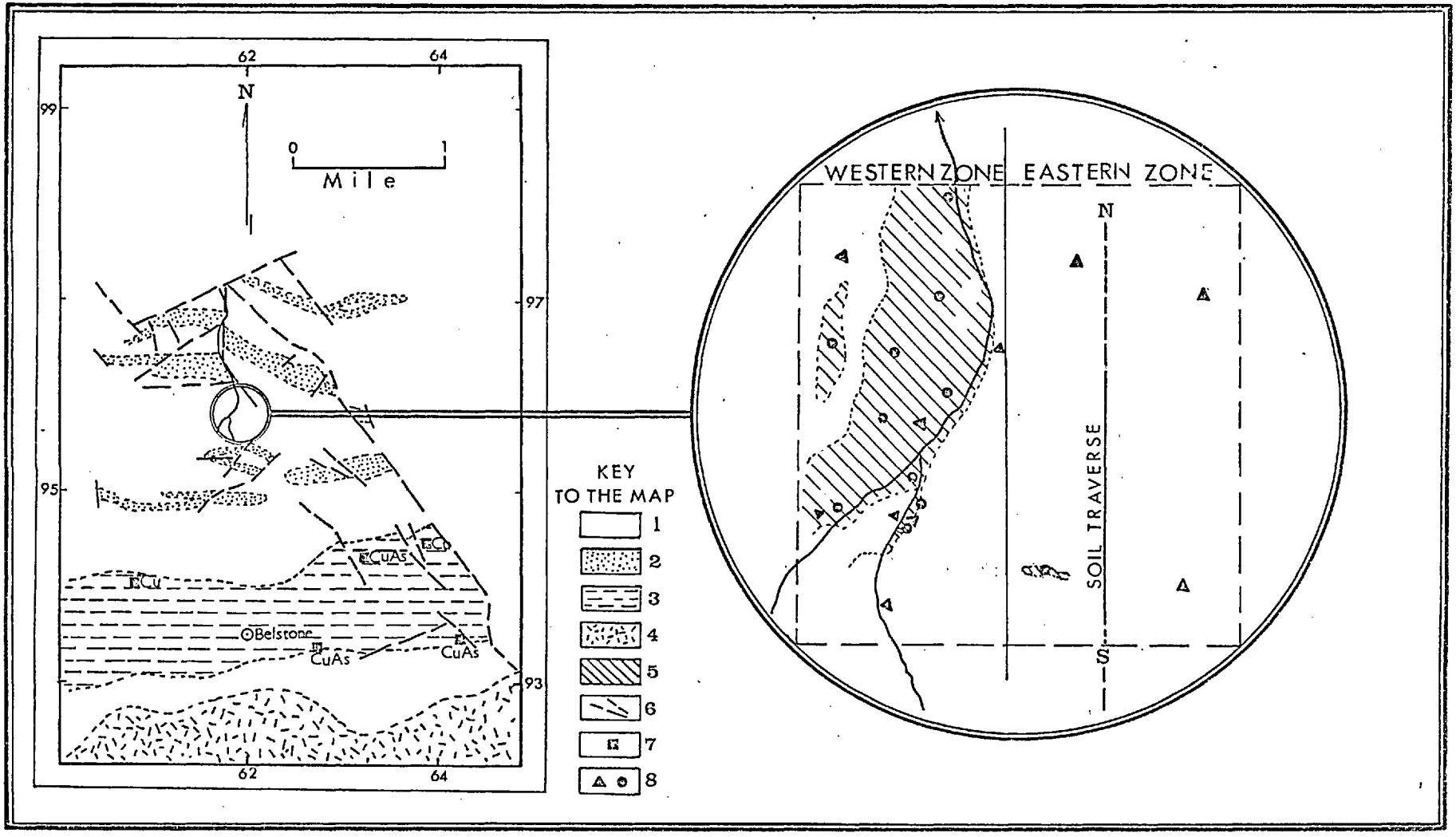
The importance of this As-Zn anomaly was established during the geochemical investigation of the regional distribution of As and selected trace-elements in stream seidment and soil samples. Detailed studies were considered desirable in order to confirm and document the origin of the As-Zn anomaly and its possible relationship with undiscovered mineralisation.

The area under consideration is located $2\frac{1}{2}$ miles north of Belstone, between Corscombe in the north, and Corscombe Down in the south (Fig. 8.28). The area is characterised by a broad zone of poorly drained soils located in the western part of the area, poor geological exposure, and by intensely weathered outcrops of parent-rock. Well drained soils are confined primarily to the eastern section of the area.

Although the area appears to lie entirely over Carboniferous shales (Crackington Formation) some field evidence indicates the possible occurrence of hardened pyritic rocks under the surface. Limonitic material is widespread in the western zone, and it is considered to be a farming 'trouble maker' (Fig. 8.28). The existing limonite is characterised by a yellow to brick-red colour which might indicate pyritic provenance. However, the occurrence of three small limonitic outcrops in the eastern zone of generally well drained soils is suspected to be related to sulphide-bearing veins.

During the detailed geochemical survey rock and soil samples were collected and analysed for seven trace-elements by means of the methods already described in earlier chapters. Because of the nature of most of the soils (i.e. badly drained), the sampling activities were mainly limited to a very restricted area of well drained soils (eastern zone), where the As-Zn anomaly was detected. In this zone, soil sampling was carried out along a short north-south traverse in which sub-soil samples were obtained at approximately six yard intervals, and at a twelve-inch depth. The purpose of this traverse was to determine the extent of the As-Zn anomaly. In addition to the soil sampling, a small number of rock and residual limonite (gossan) samples were collected.

Sampling in the western zone consisted of collection of limonitic material (limonite, and limonitic soils), shales and black cherty pyritic rocks. However, the outcrops of the cherty rocks were inconspicuous and therefore their autochthonous origin is uncertain.



1,2, Shale & Sandstone (Upper Carboniferous); 3. Lower Carb.; 4, Granite; 5, Limonitic material; 6, Fault, 7, Ore; 8, Sampling site, (▲ rock)

Fig. 8.28. MAIN GEOLOGICAL FEATURES OF CORSCOMBE AREA

8.4.2 Results of the Investigations

i) Eastern Zone

The distribution of As in soils from the traverse is shown in Figure 8.29 and that of selected trace-elements in Figures 8.30 to 8.32.

The As concentrations on this traverse show two clearly defined patterns: relatively low values ranging from 10 to 30 ppm sharply contrasting with those anomalous concentrations whose As values reach up to 680 ppm. Along with the As anomaly a range of high concentrations of the other selected trace-elements occurs in this traverse; the peak values of these concentrations being 610 ppm Zn; 260 ppm Pb; 245 ppm Cu; 78 ppm Sn;6000 ppm Mn; and 9% Fe. All the anomalous elements are concentrated within a sixty-six yard width south of the centre of the traverse.

The analysed parent-rock from the area consisted of shales which are relatively poor in most of the trace-elements, their mean levels being: 10 ppm As, 1 ppm Sn; 25 ppm Cu; 300 ppm Mn and 14 ppm Pb. Fe and Zn show higher concentrations with values ranging from 160 to 256 ppm Zn and 3.2 to 4% Fe.

The residual limonite displays very high trace-elements concentrations which contrast with those values from the shales underlying the eastern zone (Table 8.13).

Interpretation of Patterns: Soil Traverse

Hawkes and Webb (1962) consider that interpretation of geochemical soil data involves four primary problems:-

i) Determination of background and threshold values;
ii) Discrimination between significant and non-significant anomalies;
iii) Discrimination between lateral and superjacent anomalies; and
iv) Estimation of the significance of anomalies as an indication of possible ore, with the purpose of selecting those which might merit further investigations.

TABLE 8.13

MEAN* TRACE-ELEMENT CONTENTS IN THE EASTERN AND WESTERN ZONES OF CORSCOMBE AREA

Element	Eastern Zone		Western Zone	
(Values in ppm)	Shales	Residual Limonite (Gossan)	Pyritic Cherts	Transported Limonite
As	10	865	210	180
Sn	1	45	1	5
Cu	25	385	293	76
Zn	176	710	276	225
Pb	14	180	48	67
Mn	300	10500	760	460
Fe %	3.6	21.5	3.6	21.76
No. of Samples	12	15	6	16

* Arithmetic Mean

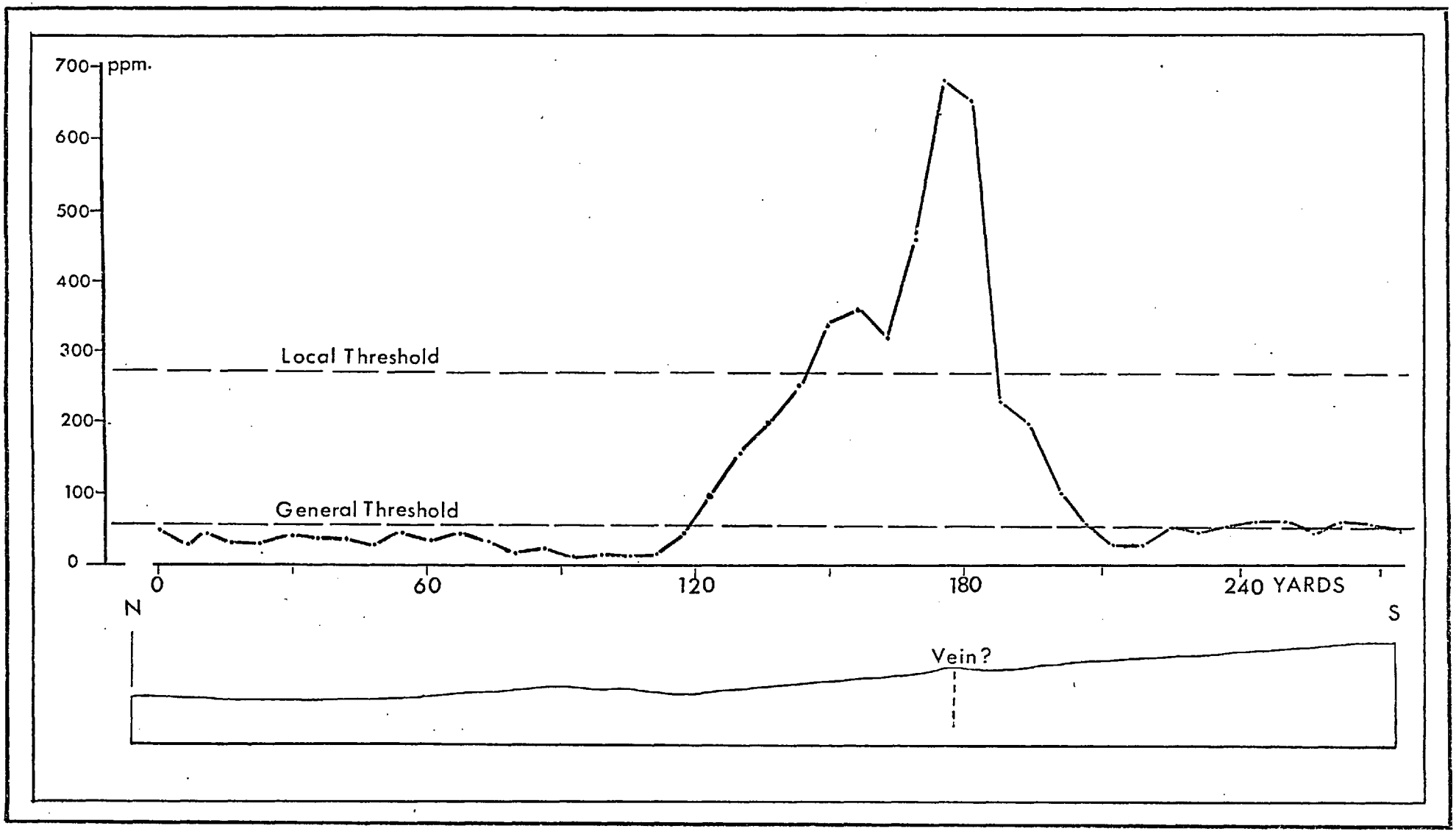


Fig.8.29. CORSCOMBE AREA-SOIL SAMPLING. ARSENIC IN SUB-SOILS

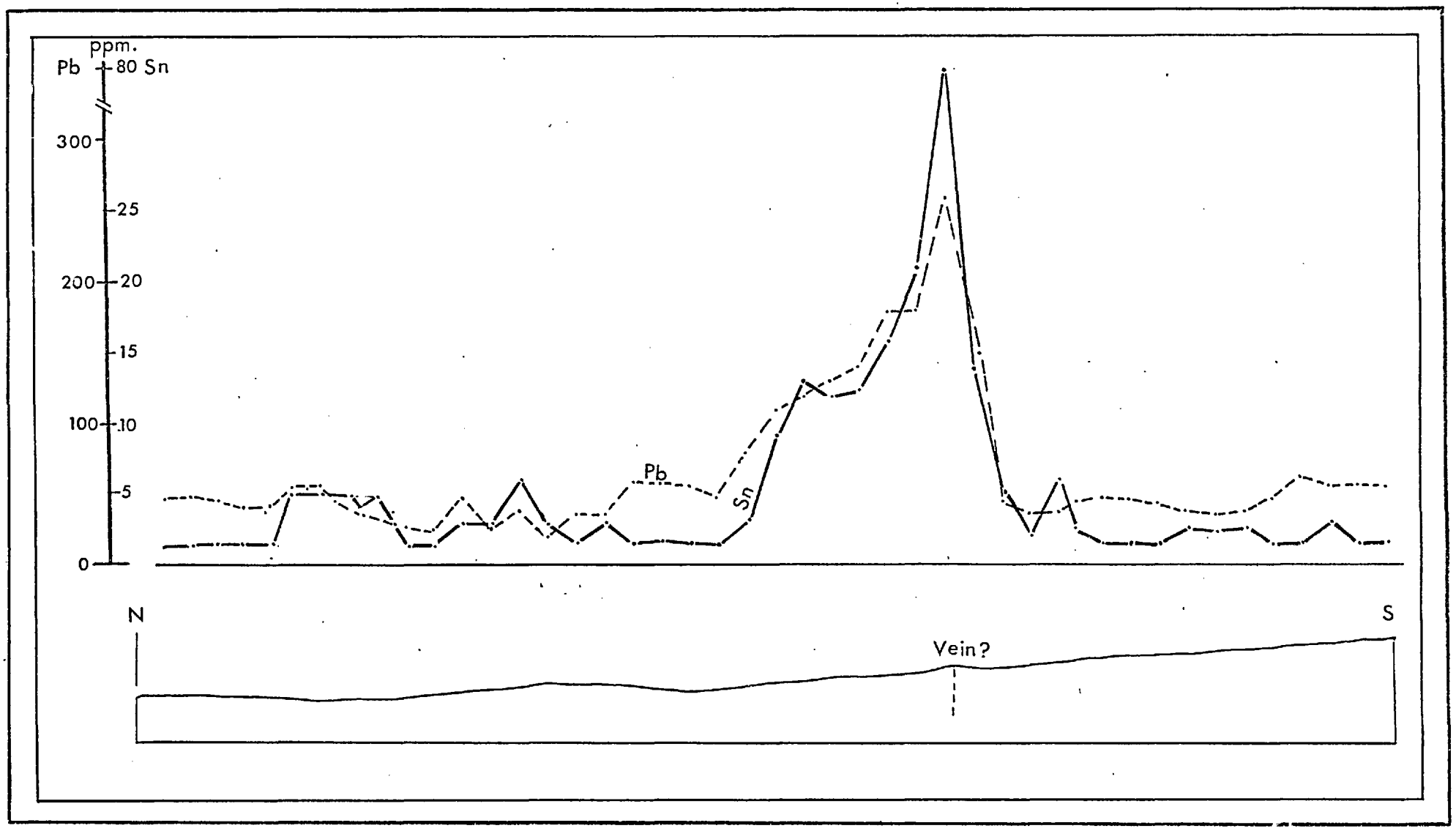


Fig. 8.30. Corscombe Area - Soil Sampling

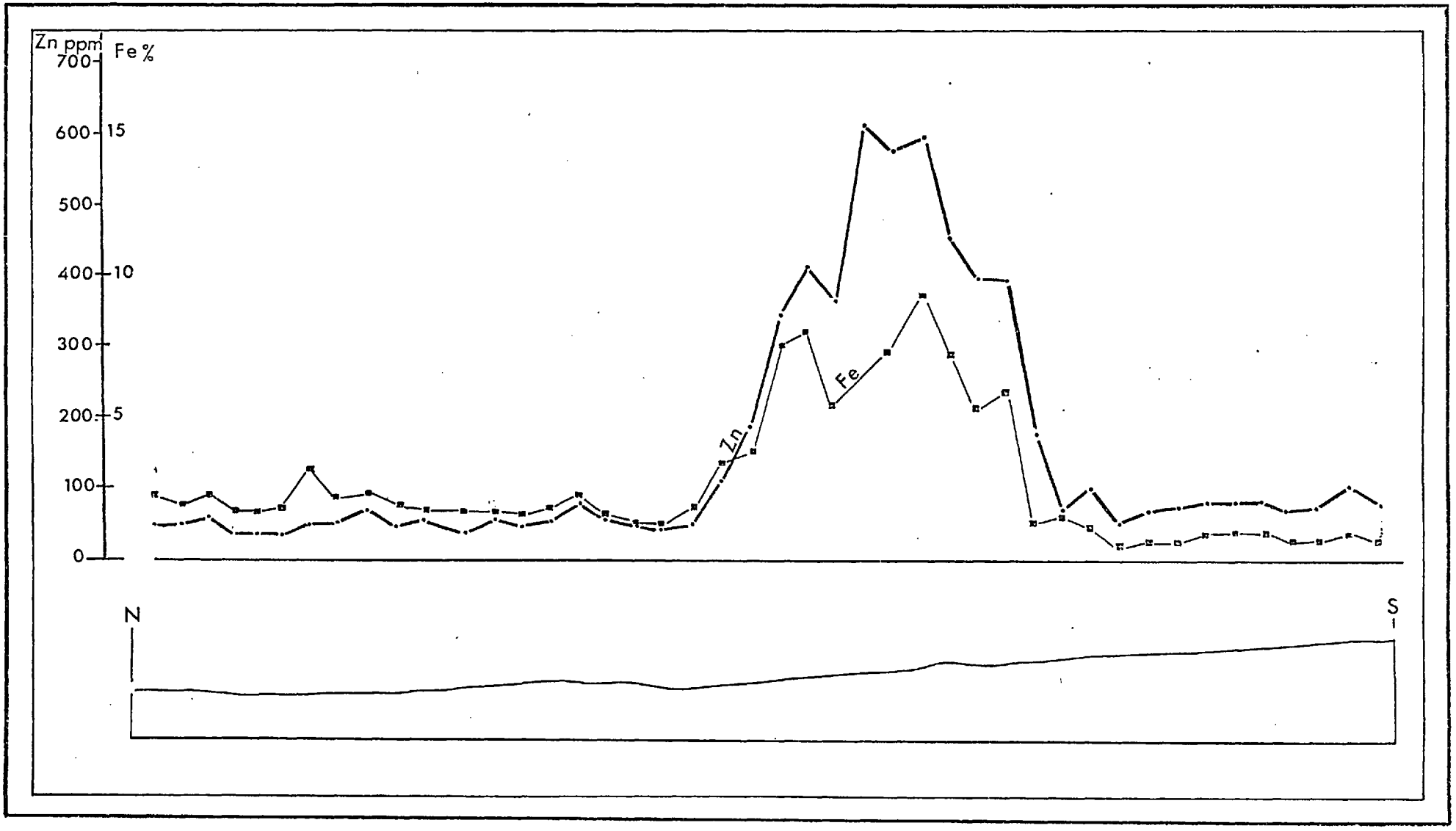
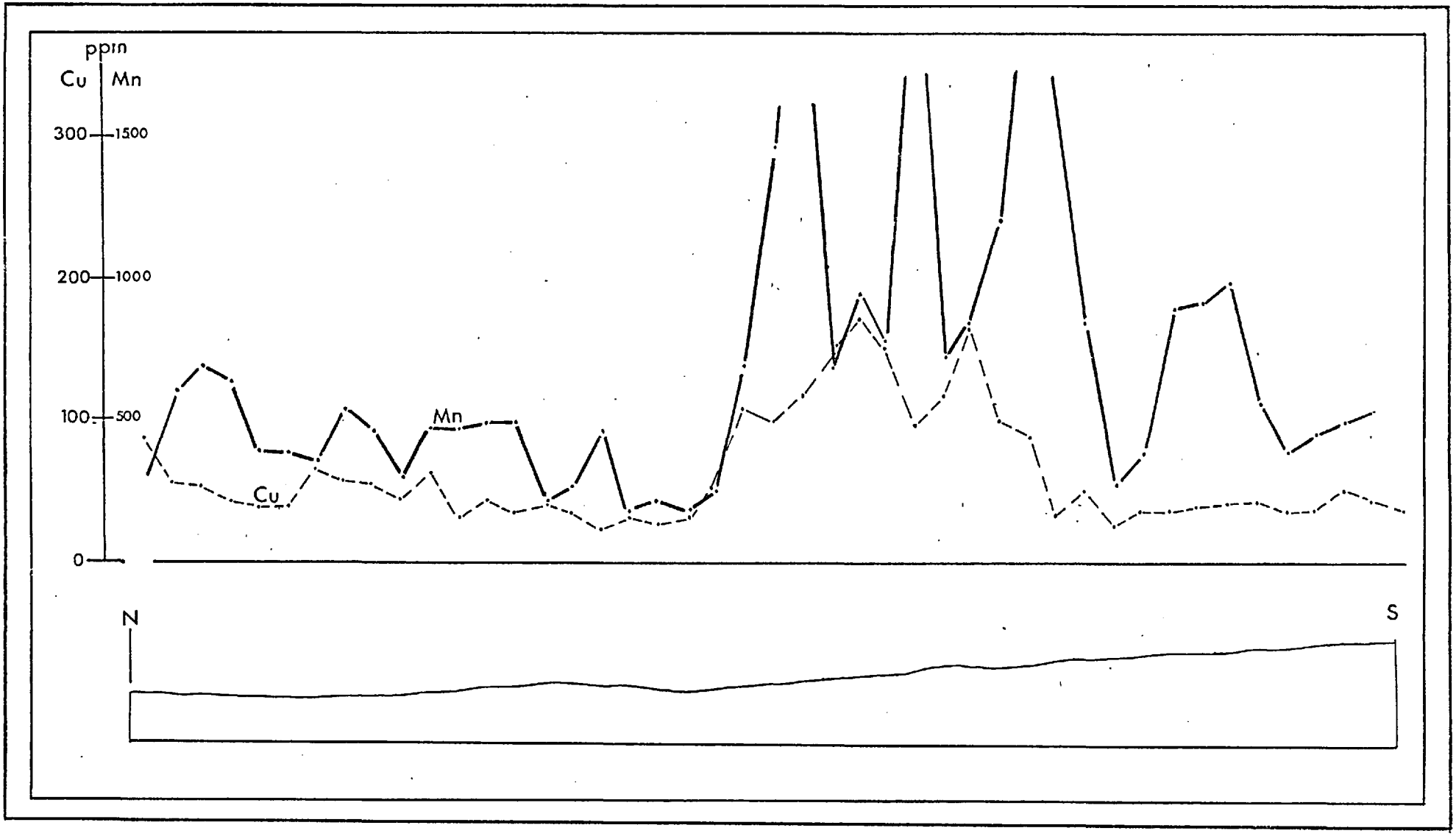


Fig.8.31. Corscombe Area - Soil Sampling



Fig, 8.32. Corscombe Area - Soil Sampling

In the interpretation of the geochemical data from the Corscombe-soil traverse the above problems have been confronted and are discussed as follows:-

i) Determination of Background and Threshold Values

Examination of the geochemical data has revealed the existence of two distinctive patterns in the area: a range of relatively low values which are considered as the normal background, and a range of high concentrations which are recognised as anomalous values. In order to define the boundaries between the background and the anomaly, statistical methods were used to determine these parameters. By these means the background was defined as being the values falling within the range limits determined by $X \pm 2S$, where X is the geometric mean, and S the standard deviation. The upper limit of the background is defined as the threshold value ($X + 2S$), and it constitutes the starting point of the positive deviation of the values from the normal concentrations. As the anomalous values reveal lateral dispersion, a local threshold was calculated in order to discriminate between lateral and superjacent anomalies. General and local threshold values for the elements are given in Table 8.14.

ii) Discrimination between Significant and Non-Significant Anomalies

Based on field and analytical evidence two anomalous patterns have been determined in the whole area: A significant anomaly which is located in the Eastern Zone (soil traverse), and a non-significant anomaly which is found related to the limonitic material in the Western Zone (Fig. 8.33).

Significant Anomaly

This anomaly is located in an area characterised by well drained residual soils developed over barren parent-rock. The most

TABLE 8.14

THRESHOLD* TRACE-ELEMENT VALUES IN THE CORSCOMBE SOIL TRAVERSE

Element	Threshold Values (ppm)	
	General	Local
As	54	275
Sn	6	11
Cu	50	131
Zn	71	289
Pb	46	125
Mn	360	2827
Fe %	6.8	1.7
No. of Samples	56	15

* Threshold Value: $\bar{X} + 2S$ ($\bar{X}$ = Geometric Mean)

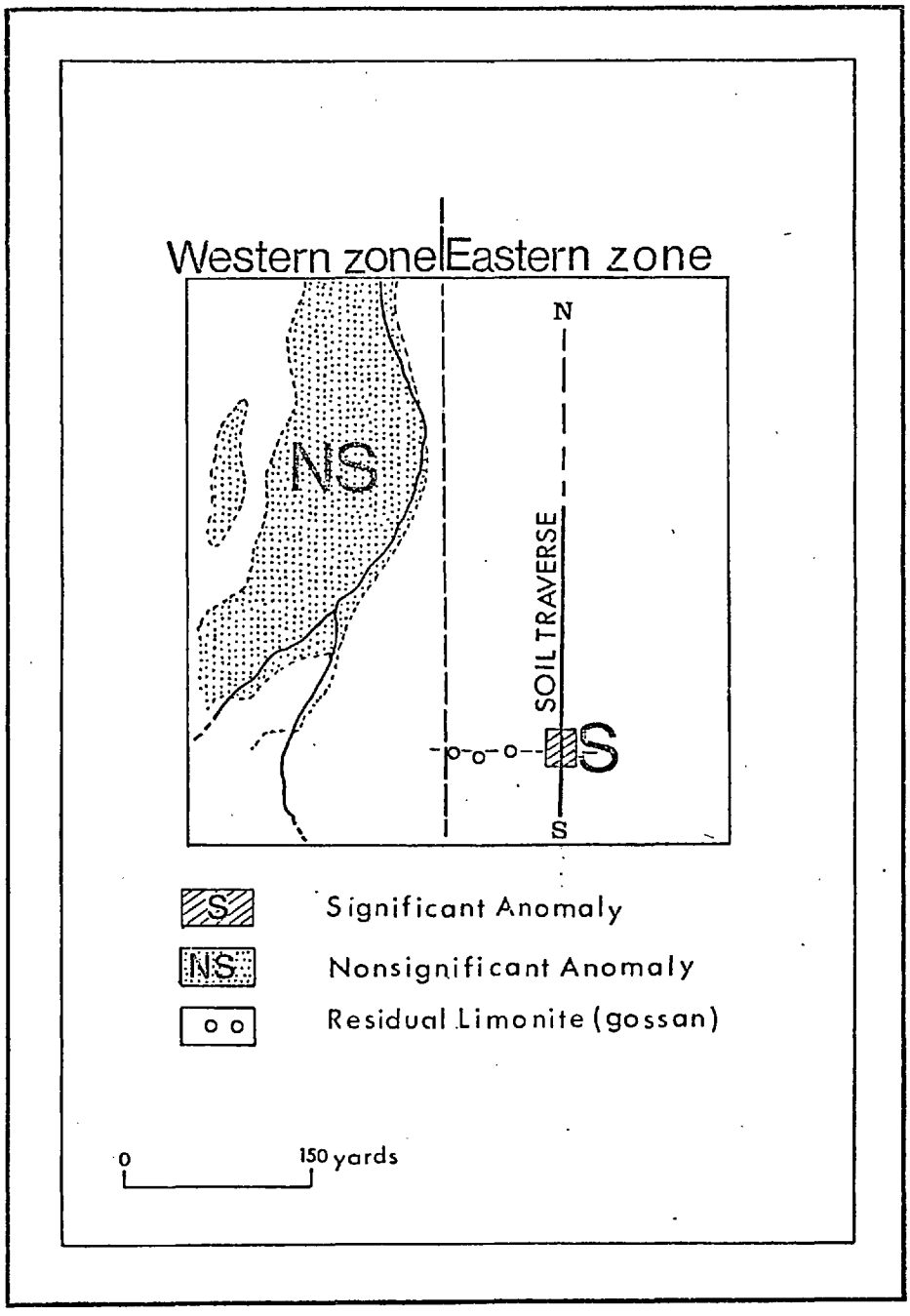


Fig. 8.33. CORSCOMBE-ANOMALOUS AREAS

important features of this anomaly are:- (1) Very high contrast between the general threshold value and the peak concentrations of the elements: 1:12 As, 1:20 Sn, 1:5 Cu, 1:10 Zn, 1:5 Pb, 1:10 Mn and 1:3 Fe, respectively; (2) The geometrical shape of the anomaly is varied: Asymmetrical As, Pb, and Sn concentrations contrast with the symmetrical Zn, Cu and Fe anomalies, and with the heterogeneous Mn pattern. These facts indicate that dispersion of the elements has been imposed primarily by differential mobility in which the topographic relief had played a very important role; (3) The As, Sn and Pb anomalies, three elements of very low mobility, exhibit well defined peak values rising sharply over a width of eighteen yards. These values, which are in sharp contrast with the local threshold values, gradually fall off for a relatively short distance, downslope in a northerly direction. The section where the high As, Sn and Pb peak values are concentrated is regarded as a superjacent anomaly which has been distorted by the effects of the elements' mechanical movements by soil creeping (Figure 8.29 and 8.30). On the other hand, Zn, Mn, Fe and Cu are considered, for the most part, to have been dispersed by chemical processes (solution and precipitation). The dispersion of Zn and Cu whose peak levels are concentrated in the centre of the anomaly, seems to have been controlled by the Fe content in the soils (Figure 8.31); (4) The anomaly is located 400 yards westward from the area where the As-Zn anomaly was found in earlier investigations (Chapters 6 and 7). On the other hand, residual limonite (gossan) superimposed by transported limonite outcrops to the west of the anomaly and then is perpendicularly aligned with the anomaly in approximately a western direction. Concentrations of trace-elements in the

limonite are higher than in the soil-traverse anomaly with the exception of Pb, and Sn which have been found to be lower. These trace-elements averaged (in limonite) 865 ppm As, 710 ppm Zn, 45 ppm Sn, 385 ppm Cu, 10500 ppm Mn, 180 ppm Pb, and 21.5% Fe.

iii) Significant Anomaly as Related to Ore Deposits

The several facts cited above, complemented by field observations, leads to the assumption that the significant anomaly is directly related to an undiscovered ore deposit. The principal considerations in assessing the possible economic significance of this geochemical anomaly are considered below:-

A) Geological Relationships

The anomaly rises in an area underlain by shales which were found to be relatively barren in trace-elements. The soils that have developed in the zone are entirely residual, and the trace element content of the bed-rock and soils is very similar. The area is located near the metamorphic aureole of the granite and within a known mineralised district where Cu, As, Pb, Sn, Zn, etc. deposits have been recognised (Fig. 8.28). Minor structures (i.e. local faults) striking in different directions are indigenous to the area. The topographic relief, which is characterised by a gentle sloping surface, exhibits a wave crest-like east-west structure along which the anomaly and the gossan-bearing outcrops are aligned.

B) Magnitude of the Concentrations

As stated before, the contrast between the general threshold level and the anomalous concentrations is of great magnitude, and yet this contrast persists even when the peak values are

compared to local threshold values. Despite the fact that most of the elements display high peaks in relation to local threshold, only As, Sn and Pb have been regarded as the most significant elements. Their low rate of mobility, and the geometrical shape in which they are concentrated resemble the particular characteristic of the superjacent anomalies.

C) Extension of the Anomaly

It has been found that anomalous patterns covering very large areas can rarely be considered as significant anomalies because they originate from the weathering of high background rocks (Hawkes and Webb 1962). On the contrary, anomalies resulting from mineralised veins are in close relationship with the dimensions of the ore bodies. In the present case the whole anomaly extends along a sixty-six yard width, whilst the suggested superjacent anomaly rises over a width of eighteen yards.

D) Other Factors

Residual limonite (gossan) was found to contain fragments of arsenopyrite-bearing quartz veins. Similar fragments were found in the surface downslope from the suspected ore deposits. These facts may indicate a breaking up of the vein before it was affected by the weathering agents.

Contamination, and sampling and analytical errors are not considered to have influenced the high concentrations of the trace-elements in this zone.

ii) Western Zone

The analysed parent-rock from this zone consisted of shales, and cherty pyritic rocks, the average values of the elements in the shales being very similar to those from the eastern area. In contrast to the shales, the pyritic rocks exhibit higher average levels: 210 ppm As, 1.3 ppm Sn, 293 ppm Cu, 276 ppm Zn, 48 ppm Pb, 760 ppm Mn, and 3.7% Fe.

Non-Significant Anomaly

Anomalous As concentrations were determined in limonite and limonitic soils from the western area. Limonite is dominant in the soils of this zone, and probably originated from the pyrite-bearing cherts located in the area. The anomalous As levels along with the other selected trace-elements have been classified as a non-significant anomaly (Fig. 8.33). This classification has been done according to the following facts:

i) Medium in which the anomalous values occur: These values were found in transported limonite, and/or limonitic soils in a zone which is waterlogged during the wet season. As a consequence of this seasonal variation the elements are subjected to processes of solution and precipitation. Limonite which originated at the expense of the pyrite-bearing rocks had played an important role in the fixation of the trace-element in the surface,

ii) The suspected relationship between the anomalous values and pyritic rocks: the pyritic cherts which are characterised by a relatively high concentration of trace-elements are suspected to underlie a part of the Western Zone. Analytical data revealed the existence of a close relationship between the trace-element content in these rocks, and the content in the overlying material (limonite and soils). This contrast in values is given in Table 8.13.

8.4.3 Summary

The Corscombe area which lies entirely over Carboniferous sediments is characterised by an extensive area of poorly drained soils, a small area of well drained soils, and by the occurrence of abundant limonitic material. According to its origin, the limonitic material has

has been classified in two types: Transported limonite, which is related to pyritic cherty rocks, and residual limonite (gossan) which is suspected to be related to ore deposits.

Detailed investigations in soils, rock and limonitic material from the area have led to the confirmation of the anomaly detected during the regional, geochemical stream sediment and soil surveys.

On the basis of statistical determinations of background and threshold values the trace-elements occurring in the area were classified in two main categories: Normal background, and anomalous concentrations. The normal background is characterised by a range of relatively low values which are reflected in the underlying parent rock. The anomalous concentrations have been grouped in two types: non-significant, and significant anomalies. The non-significant anomaly is extensively located in the western part of the area and it appears to have originated from the weathering of pyritic cherty rocks occurring in this zone. The significant anomaly which is located in the eastern part of the area is characterised by high As, Sn, Pb, Cu, Zn, Mn and to a lesser degree Fe concentrations.

The highest peak values of As, Sn and Pb are considered as superjacent anomalies which have been distorted by mechanical movement by soil creeping.

The residual limonite outcrops which has undergone superimposition of transported limonite by seasonal ground water is geographically related to the occurrence of anomalous values for most of the trace-elements.

Based on their geological relationships, the magnitude and extension of the anomaly along with other factors, the significant anomalous concentrations have been considered as related to existing ore deposits.

8.5 KIT HILL AREA

8.5.1 Introduction

The Kit Hill area is located in the south-western part of the Callington-Tavistock mineralised district, and covers a surface of

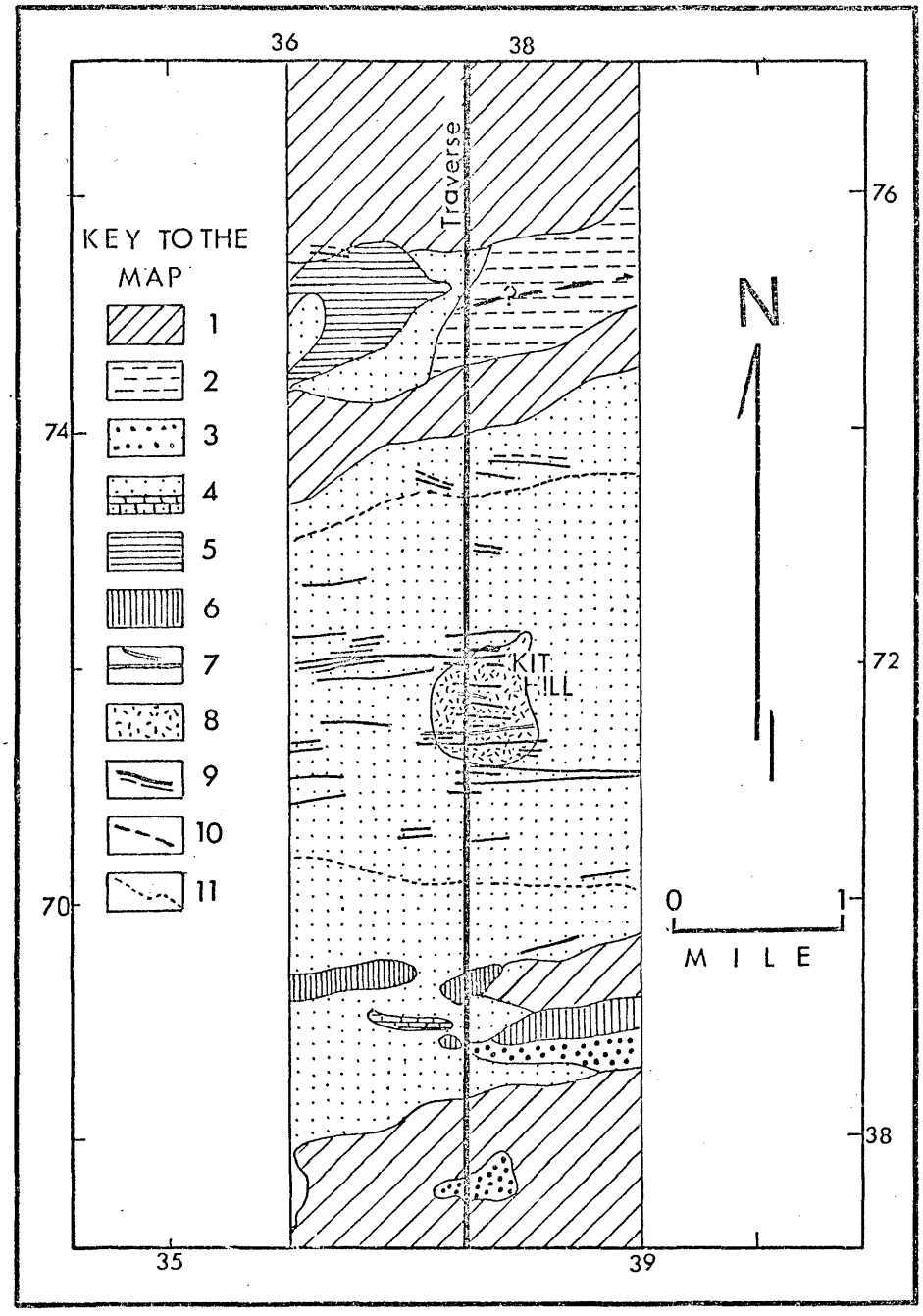
approximately twelve square miles. The underlying parent rock is composed of Devonian sediments which surround a small granite mass (Kit Hill granite) situated in the central part of the area. Carboniferous sediments, consisting of shales and cherty rocks, are found in the northern and southern sections of the zone. Intrusive greenstones outcrop in the southern and south-eastern part of Callington, whilst elvan dykes traverse the granitic body in an east-west direction (Fig. 8.34)

The metalliferous lodes with a general east-west trend form part of a mineralised belt of twelve miles east-west length and four miles width, extending from the border of the Dartmoor granite westward across the Gunnislake and Kit Hill granites. In this area the bulk of the lodes occur within both the granite and the metamorphosed killas (metamorphic aureole) in which cassiterite, wolfram and sulphide ores were worked. Arsenic-sulphide (mispickel) arose from lodes located within and without the granite frequently associated with Sn, W, Cu and occasionally with Fe and Zn. Silver-bearing lead is reported to have been found in lodes situated to the north, and east of Callington (Dines 1968, p. 624).

Interpretation of geochemical patterns of trace-elements as displayed in the geochemical Atlas of south-west England, revealed the existence of a broad zone of anomalous As, and the other selected trace-element concentrations covering the Kit Hill area. Analytical data from specific zones (Chapter 6, Anomalous Patterns) demonstrated that As anomalies in this area mainly derived from the mineralised veins, from mineral dumps and from smelter sites in the region. The collection and analysis of soil samples were carried out with the purpose of verifying the sources of these anomalies.

8.5.2 Soil Traverse

Studies in the area consisted of systematic soil sampling in a six-mile north-south traverse in which top and sub-soil samples were



1,2, Carboniferous; 3, Chert (Lower Carb.); 4, Devonian; 5. Pillow Lava; 6, Diabase; 7, Elvan; 8, Granite; 9, Lodes; 10, Projection of lodes; 11, Aureole boundaries.

Fig. 8.34. KIT HILL AREA: GEOLOGICAL MAP.

taken at approximately one hundred yard intervals, and at a depth of six to twelve inches. The samples were prepared and analysed according to the methods already described in Chapter 5. Plotting of the analytical data took the form of profile curves at a horizontal scale, one inch to the mile. The profiles were compared to geological cross-section of the underlying parent rock.

The topographic relief is characterised by altitudes ranging from 300 to 1100 feet O.D. Ridges and plains located in the northern and southern parts of the area contrast with the steep inclinations developed on the metamorphosed killas intruded by the granitic body.

The soils are generally residual, poorly developed and well drained. Poorly drained soils are rare even on the flatter land, the exception being in the extreme northern part of the area where badly drained soils are confined to Carboniferous shales. In much of the area the soils have been disturbed by mining activities, and in some places, they are coated by a laterite-like layer probably resulting from the weathering of mining-waste material.

8.5.3 Result of the Investigations

The distribution of As and selected trace-elements in soils from the Kit Hill area is shown in Figs. 8.35 to 8.38, Table 8.15 lists the mean and range values of these elements.

Both top, and sub-soils exhibit little difference in their As content (Fig. 8.35). This characteristic was discovered during the study of the soils overlying the varied lithological units from Devon (Chapter 7). The interpretation of the As patterns, and of the other selected trace-elements was made on the basis of their occurrence in the sub-soil.

The distribution of As along the soil traverse is characterised by a broad zone of anomalous values with pronounced peaks which reach up to 3800 ppm. These high concentrations contrast sharply with the relatively low values located within the Carboniferous sediments. However, the

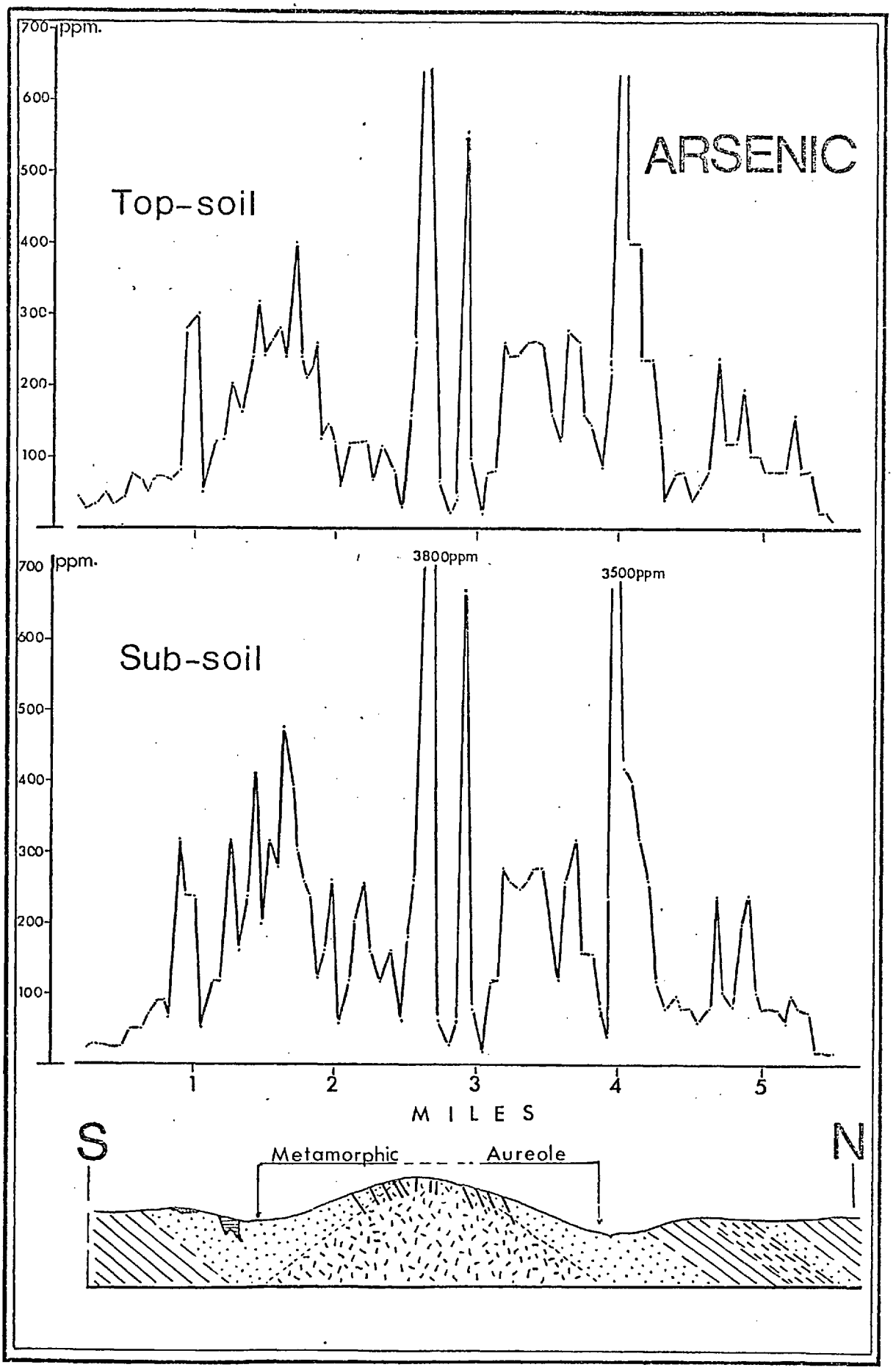


Fig. 8.35. Kit Hill Area-Soil Sampling

Expl. as for fig. 8.34

TABLE 8.15

RANGE AND MEAN* TRACE-ELEMENT CONTENTS OF SOILS FROM THE KIT HILL AREA

(values in ppm)

Element	Mean & Range	General Range
As	145* 21-1000	18-3800
Cu	47 11-195	6-940
Fe %	3.6 1.3-9.3	.67-9.1
Mn	437 63-3010	20-3810
Pb	105 36-301	29-552
Sn	17 1-813	1-1190
Zn	124 39-389	44-1060
No. of Samples	97	

* Geometric mean ($\bar{x}$) Range = $\bar{x} \pm 2$ (log standard deviation)

Lower Carboniferous units display high concentrations with values ranging from 80 to 280 ppm. The Devonian sediments, most of which lie within the metamorphic aureole, demonstrate a range of high As levels whose peak value reaches 3500 ppm. In relation to the igneous rocks, As occurs in uniformly high concentrations (420 ppm) over the intrusive greenstones, whilst over the granite the As content varies from low (18 ppm) to very high (3800 ppm).

Sn concentrations like As are almost equally distributed in both top-soil and sub-soil (Fig. 8.36). The distribution of Sn is characterised by two marked patterns: a range of low values distributed over the Carboniferous and Devonian sediments contrast with the very high concentrations over the granite where the values range from 32 to 1190 ppm. Scattered peak values ranging from 60 to 160 ppm can be observed over the Devonian and Carboniferous units and within the basic igneous rocks (greenstones).

Cu, Pb and Zn are erratically distributed along the traverse (Fig. 8.37). Cu and Pb show their highest values over the granite (940 and 580 ppm respectively). Both elements are also highly concentrated in specific areas on the northern and southern parts of the traverse, although to a lesser degree than in the granite. Zn appears also to be highly concentrated along the whole traverse with several peaks whose values reach up to 1060 ppm. The lowest Zn levels are found over the Carboniferous sediments, although a peak of 480 ppm can be observed over the Lower Carboniferous unit (northern section of the traverse).

Fe and Mn appear similarly concentrated, the Mn being more erratically distributed (Fig. 8.38). Both elements tend to be low within the northern part of the granite whose values are 0.6% Fe, and 80 ppm Mn. Fe appears in a broad high concentration over the Devonian and Carboniferous sediments, the highest values being concentrated over the Lower Carboniferous where Mn also displays its highest value (9% Fe, 3810 ppm Mn). Southward from the granite Mn ranges from low (20 ppm) to high (1640 ppm) concentrations whilst in the northern part the distribution of this element is more uniform.

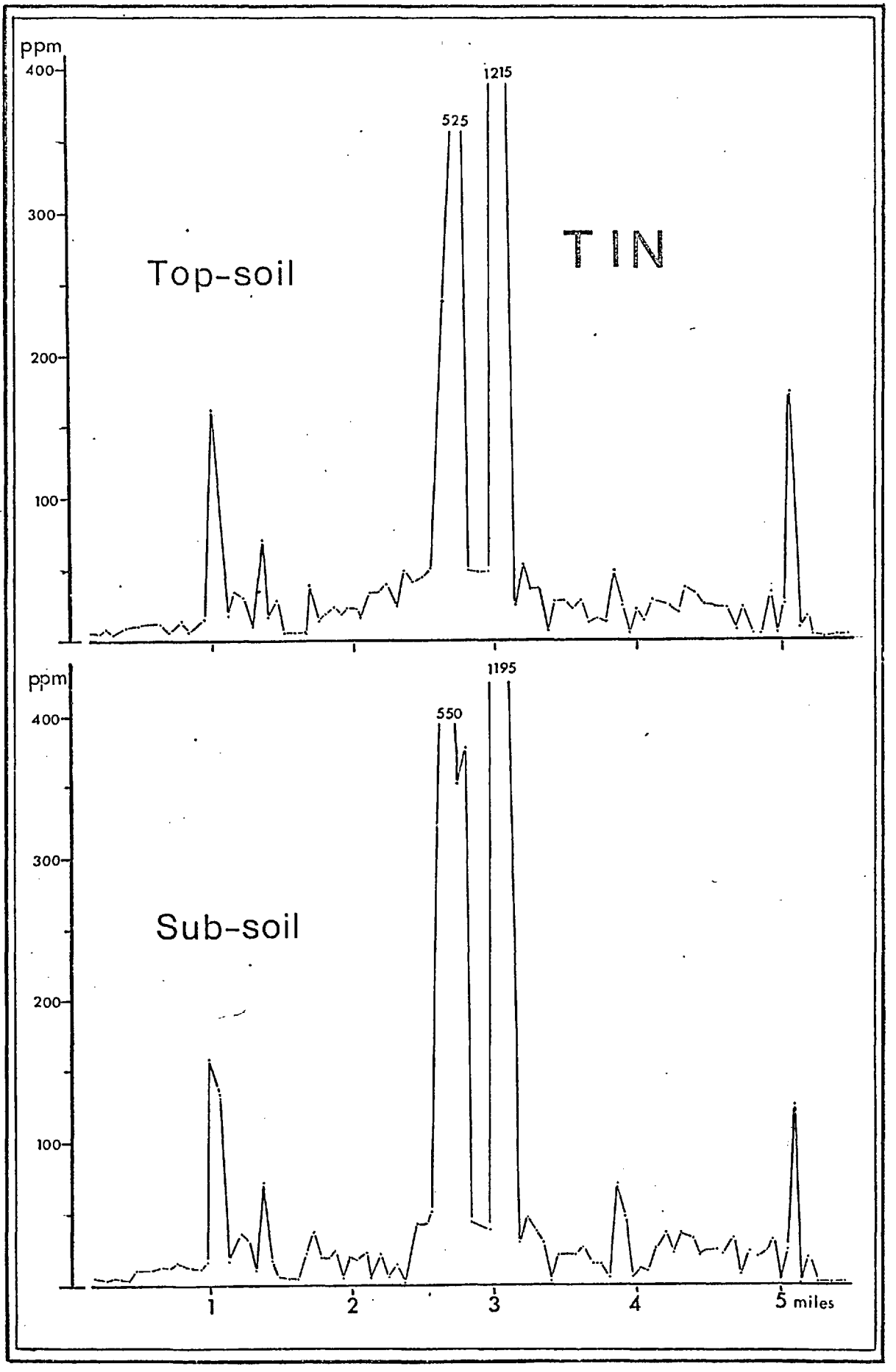


Fig.8.36. Kit Hill Area - Soil Sampling

(Explanation as for fig.8.34)

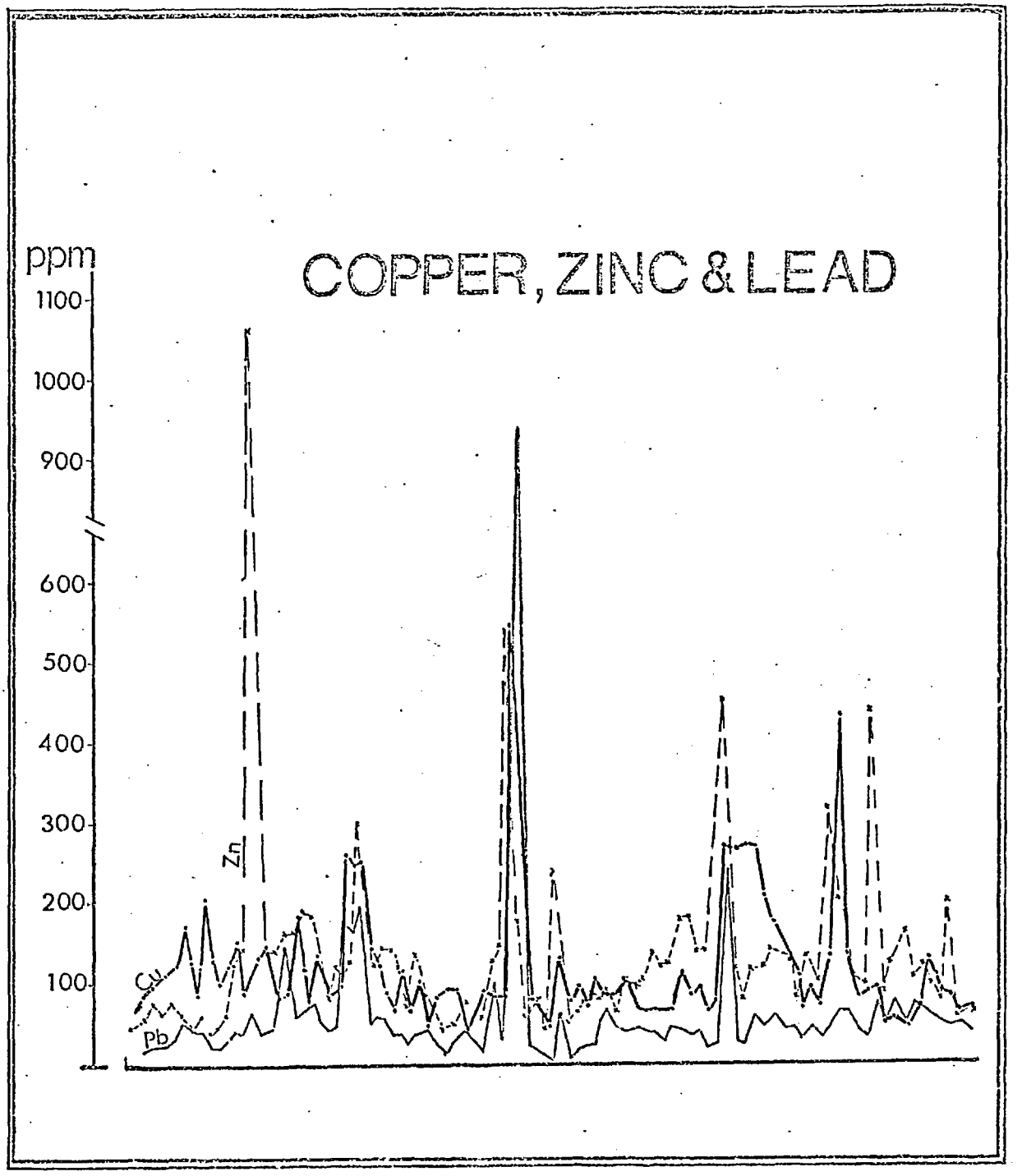


Fig.8.37. Kit Hill Area-Soil Sampling

Explanation as for fig. 8·34 & 35

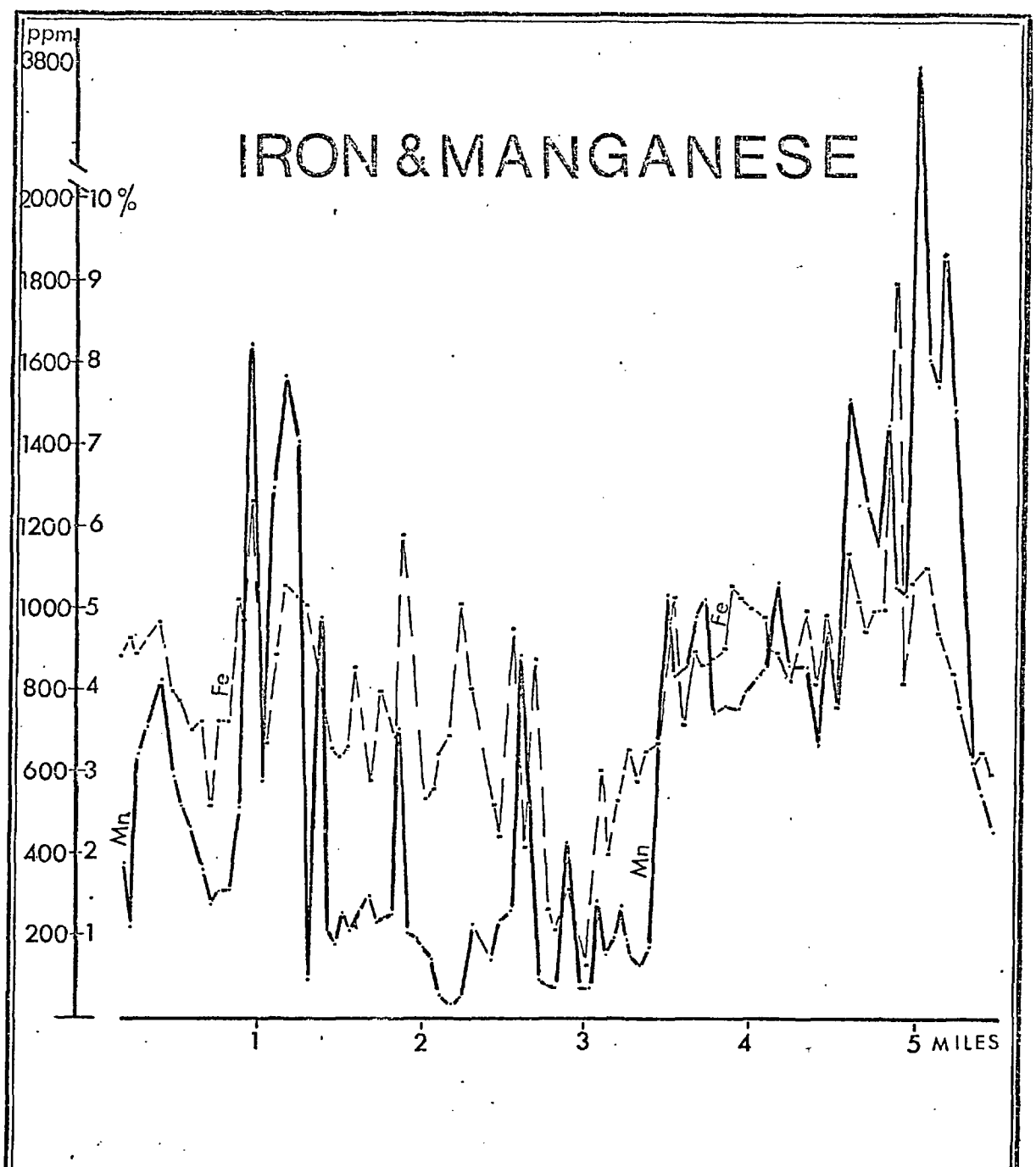


Fig.8.38. Kit Hill Area-Soil Sampling

(Explanation as for fig. 8.34)

8.5.4 Interpretation of Patterns

The interpretation of the anomalous patterns of As in soils from the Kit Hill area has revealed that these anomalies have originated from the following sources:-

i) Metamorphic Aureole

High As concentrations can be observed to be closely related to the metamorphic aureole surrounding the granitic body. A similar phenomenon was discovered during the geochemical investigations in the Dartmoor area where As anomalies in soils were found to be related to the underlying parent-rock in which As had been deposited by fluids emanating from the consolidating granite (see 8.3 Dartmoor Area). Analytical data from rock samples collected in the aureole of the Kit Hill granite indicate that the high As values in soils from this particular area are not entirely reflected in the underlying bed-rock but they have been enriched by transported material, probably derived from the existent ore-bearing areas.

ii) Ore Deposits

The spatial relationship between geochemical profile, and the geological cross-section (Fig. 8.35) shows that some of the highest As levels are directly related to mineralised vein-bearing areas. As-rich material derived from the weathering of both ore body and wall rock had been fixed in the residual soil, and/or dispersed downslope from their point of origin creating a first phase of superimposition of As patterns over the adjacent parent-rock (aureole).

iii) Contamination

Mining activity, mine-dumps, and smelting sites appear to be the main sources of As contamination in the area. Mine-waste, and mine dump materials are widespread in the zone, specially in the upper parts. These materials were sampled, and the analytical data revealed high As concentrations, the average values being: 2500 ppm for the dumps, and 15000 ppm for the mining-waste materials. Dispersion of the element

downslope from these media might have been imposed by gravitational movement of the material and by aqueous transportation, thus creating a second phase of superimposition of As patterns over the metamorphic aureole. In addition, soils from the neighbouring smelting sites were analysed and a peak value of 2800 ppm was found.

iv) Undefined Sources

Anomalous As patterns have been located in soils overlying rocks which are supposed to be barren. In effect, in these anomalous zones neither mineralisation nor contamination is evident. In the southern part of the traverse approximately $1\frac{1}{2}$ miles from the granite-killas contact, an As anomaly (named: Anomaly C) can be seen in soils overlying Carboniferous cherts (Fig. 8.39). Along with As, high Sn (160 ppm), Zn (1060 ppm), Mn (1660 ppm), and Fe (6.5%) concentrations occur in this specific section. Adjacent to this anomaly a second anomaly (named: Anomaly D, Fig. 8.40) extends northward for six hundred yards with As values ranging from 120 to 480 ppm. In its southern part this anomaly seems to be associated with the underlying basic igneous rocks (greenstones). In addition to As, other selected trace-elements show high concentrations (although to a lesser degree than in Anomaly C), the peak values being: 75 ppm Sn, 300 ppm Zn, 280 ppm Pb, 200 ppm Cu, 1000 ppm Mn and 5.4% Fe (Fig. 8.40). Field evidence suggests the possibility of this anomaly being related to an underlying ore deposit which might be the continuation of the Langford lode (Dines 1968, P.634) located one quarter mile eastward from the basic igneous rock. The lode appears to strike directly towards the anomaly at approximately N 70°E angle. According to Dines (1956) this lode has yielded Ag, Pb, Zn and Mn ores.

Another broad area bearing high As, Mn, Cu, Pb, Zn, Sn and Fe concentrations can be observed in the northern part of the traverse extending northward for about two miles. Like Anomaly D the As anomalous pattern

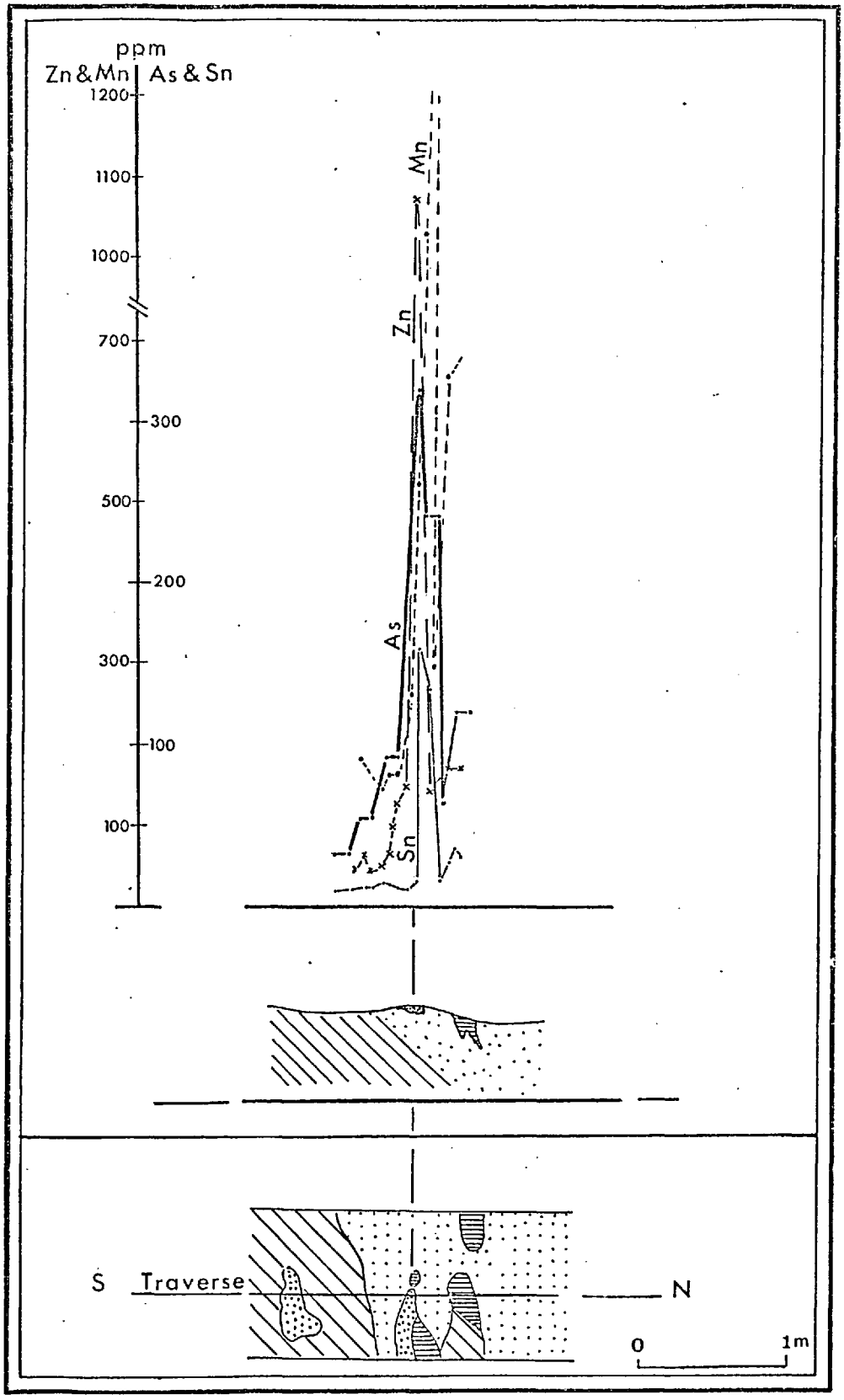


Fig.8.39. KIT HILL AREA, ANOMALY 'C'

Expl. as for fig. 8.34

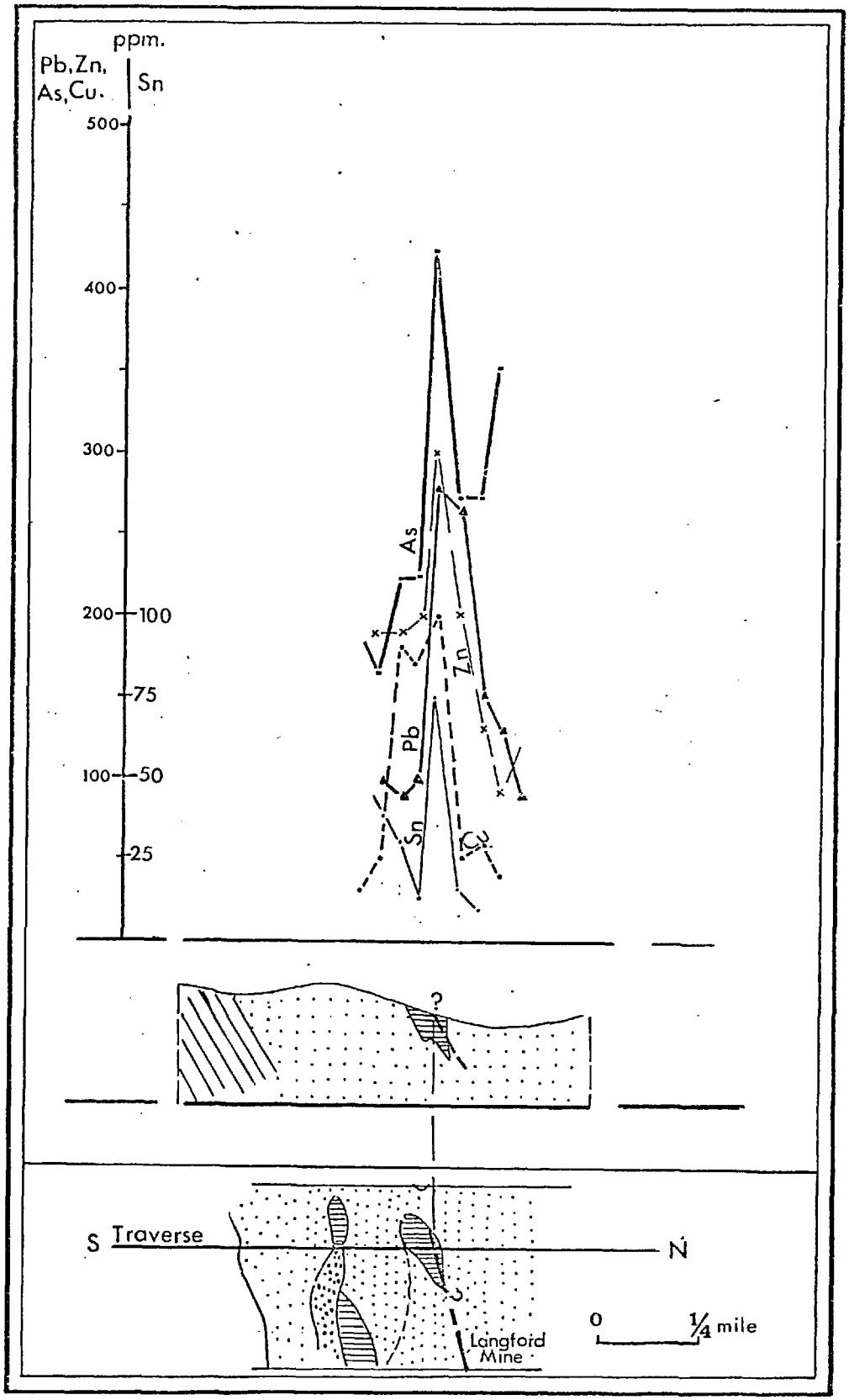
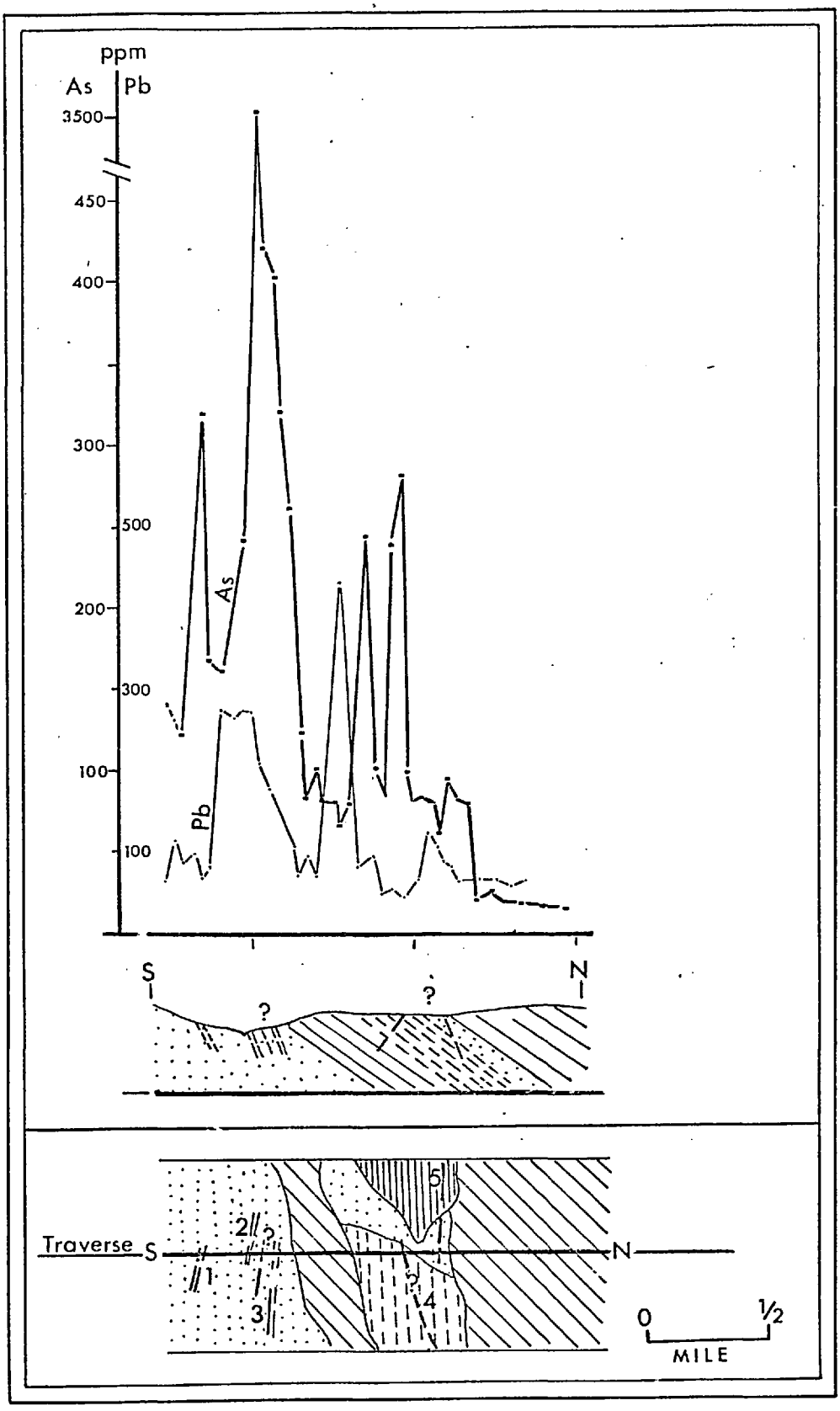


Fig. 8.40. KIT HILL AREA. ANOMALY "D"

Explanation as for fig. 8.34



1, TOM MINE; 2, SHEBA MINE; 3 MARTHA MINE; 4, CAPUNDA MINE; 5, KINGSTON CONSOLS MINE; (4 & 5, PROJECTION OF THE LODES)

Fig. 8.41. KIT HILL AREA. ANOMALY "E"

Explanation as for fig. 8.34

(termed: Anomaly E, Fig. 8.41) might suggest projection of the neighbouring lodes from the Sheba, Martha, Tom, Capunda and Kingston Consols mines.

8.5.5 Summary

The Kit Hill area which lies over Devonian, Carboniferous and instrusive igneous rocks is characterised by an extensive mineralised area in which lode-bearing ores have been intensively worked during the past.

The results of the present investigation indicate that anomalous As concentrations are widespread in soils overlying the varied lithological units from the area. Interpretation of these anomalous patterns has revealed that the high As levels are related to high background bed-rock (metamorphic aureole), to ore deposits, to contamination arisen from mining-waste and dump materials, to smelting sites and to undefined sources.

The anomalies whose sources have not been defined, have been tentatively related to undiscovered ore bodies which may be the continuation of neighbouring lodes striking almost perpendicular to the anomalies.

In addition to As, anomalous levels of Cu, Pb, Zn, Sn, Mn and Fe can be observed along the traverse mainly associated with the mineralised contaminated area, although most of these elements show peak values in zones where no mineralisation and/or contamination have been found.

CHAPTER 9

POLDICE MINE-BORE HOLE

9.1 INTRODUCTION

As indicated in Chapter 8, the varied rock types within the metamorphic aureoles surrounding the granitic masses, and to some extent the granite itself, are mainly characterised by a range of anomalous As concentrations whose origin has been linked to As-bearing fluids coming from the consolidating granite. This hypothesis has been primarily based on geochemical data obtained from the analysis of the outcropping parent rocks of the area. In order to gain further information about the As distribution below the surface in the metamorphosed and granitic rocks, detailed geochemical investigations were carried out by means of sampling and analysis of a deep (951 feet) drill-core provided by the Cornwall Tin & Mining Corporation. The Poldice Mine-Bore hole (originally termed C. T. M. C. Hole C-51) is located within the Gwennap area which forms part of the Camborne-Redruth-St. Day mineralised district (Dines ~~1968~~ 1956, p. 392). The underlying parent rock in the Gwennap area is composed of Devonian sediments (Mylor, and Falmouth Series) traversed by elvan dykes generally trending east-north-east to north-east, and a granitic mass (Carn Marth) outcropping in the western part to the south of the Zone (Fig. 9.1). Mineralised lodes with a similar trend to that of the elvan dykes, and cross-courses trending north-west, south-east occur extensively within the area.

9.2 GENERAL DESCRIPTION OF THE BORE HOLE

The main characteristics of the bore hole and the lithological description of the drill-core are briefly outlined below.

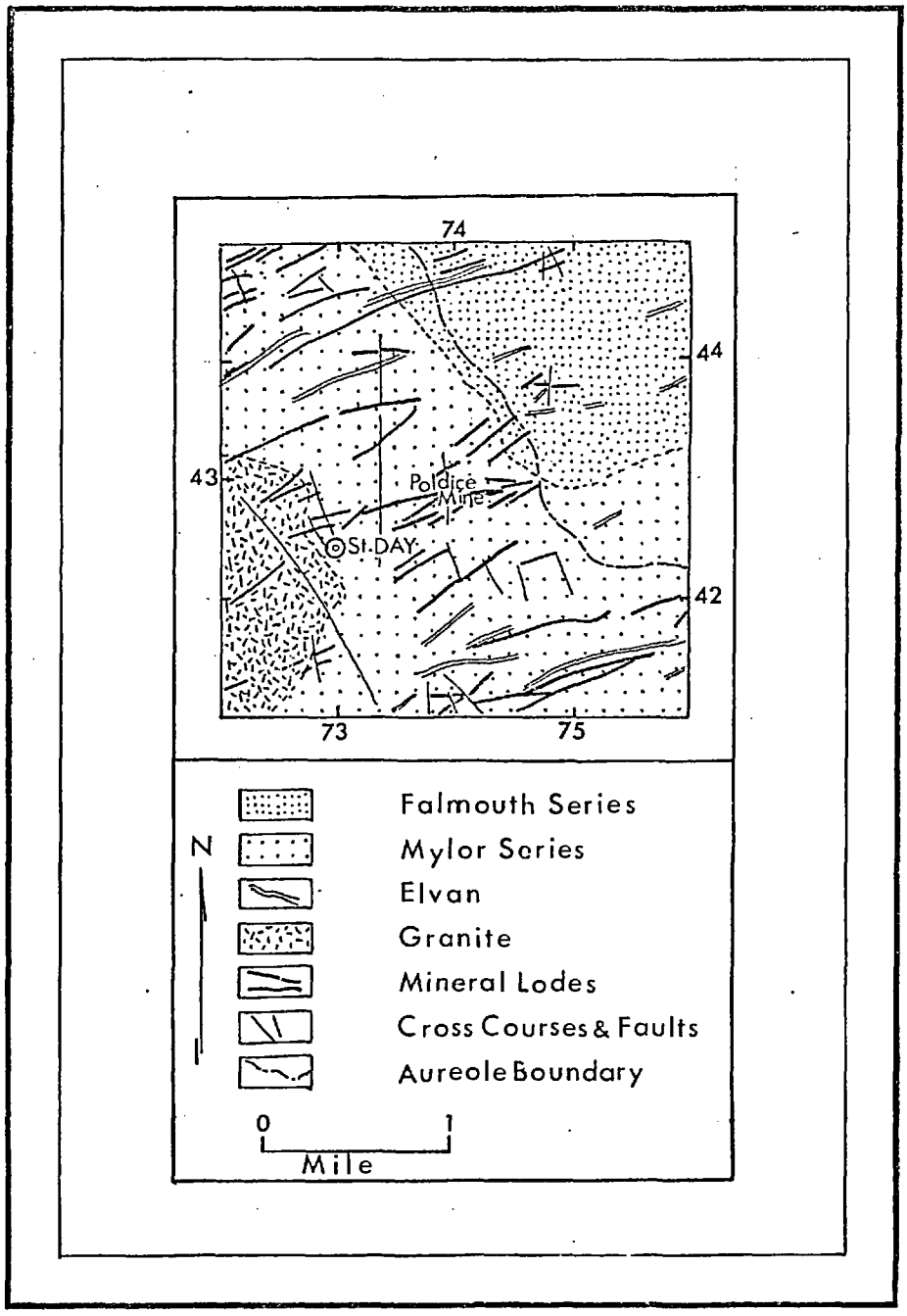


Fig. 9.1. GEOLOGY AROUND POLDICE MINE

A detailed log of the lithology and mineralisation of the drill-core (which is mainly based on the information provided by the Cornwall Tin & Mining Corporation) is presented in Appendix 2.

Location: Poldice Mine, Little Beside, St. Day
National Grid Reference 7378E, 4307N.

Collar: dip - 55°, bearing 160° T

Elevation Collar: About 270 feet above O. D.

Depth Reached: 951'5".

Lithology: No core was recovered from the first 77 feet of drilled rock, but from a depth of 77 feet down to the bottom of the hole (951'5") core recovery was almost 99 per cent. It should be noted, however, that when the present research was in process samples from the core from a depth of 498 to 520 feet were missing, and were thus unavailable for examination by the author.

The bed-rock penetrated by the hole consists of metamorphosed killas, and intrusive igneous rocks (greenstone and granite) the greenstones being present at different depths in the form of four dykes whose thickness varies from 3'4" to 13 feet. The metamorphosed killas is characterised by a thick section (from 77 to 228 feet) of brick-red colour shales, the red colour probably being imposed by supergene alteration of the light grey-green, uniformly well bedded, cherty shale. Bedding is mostly folded with axial planes at roughly 45° to the core axis. From 228 feet down to the granite contact the sediments consist of inter-bedded light and dark grey shales, with occasional fawn sections. At 800 feet the sediments become harder, and they take on the appearance of intensely spotted hard phyllite as they approach the contact. The igneous rock penetrated by the hole consists of a 20'11" section (from 930'6" to 951'5") of the fine granite near the contact but becoming progressively coarser with depth. Mineralisation is almost completely confined to the killas, within which thin sulphide bearing veins frequently occur at

all depths. Quartz and schorl-bearing veins are common in the core, and in many cases these veins contain sulphide minerals both disseminated and in veinlets. The various sulphide minerals recognised in the drill-core are pyrite, chalcopyrite, sphalerite, arsenopyrite and galena. The geological column of the bore hole is shown in Figs. 9.2 and 9.3.

9.3. SAMPLING AND ANALYSIS

Systematic rock sampling was carried out along the drill-core at intervals which varied according to the thickness of each rock type. In the metamorphosed killas, chip samples were collected along every five feet of the core, except in a section near the granite contact (900 to 930 feet) where the interval was reduced to two feet. This interval was also applied to the granitic mass. Sampling of greenstone rocks varied from one to four feet along the drill-core. Quartz, schorl and sulphide-bearing veins were studied separately, taking five-inch core samples which were individually cut in half along the core axis with the aid of a core splitter. Sediments traversed by mineralised veins were sampled at intervals of $\frac{1}{2}$, 1, 2, 3 and 4 feet away from the vein in order to determine the possible lateral influence of the mineralised fluids within the host rock.

The samples were carefully washed with deionised water and air dried, and then reduced to a finer material firstly in a stainless steel-jaw crusher and lastly in an agate mortar. The material thus obtained was sieved through an 80-mesh Schindler nylon bolting cloth. The fine samples were analysed for eight elements: As, Sn, Pb, Cu, Zn, Mn, Fe and S by means of the methods described in Chapter 5 and Appendix I.

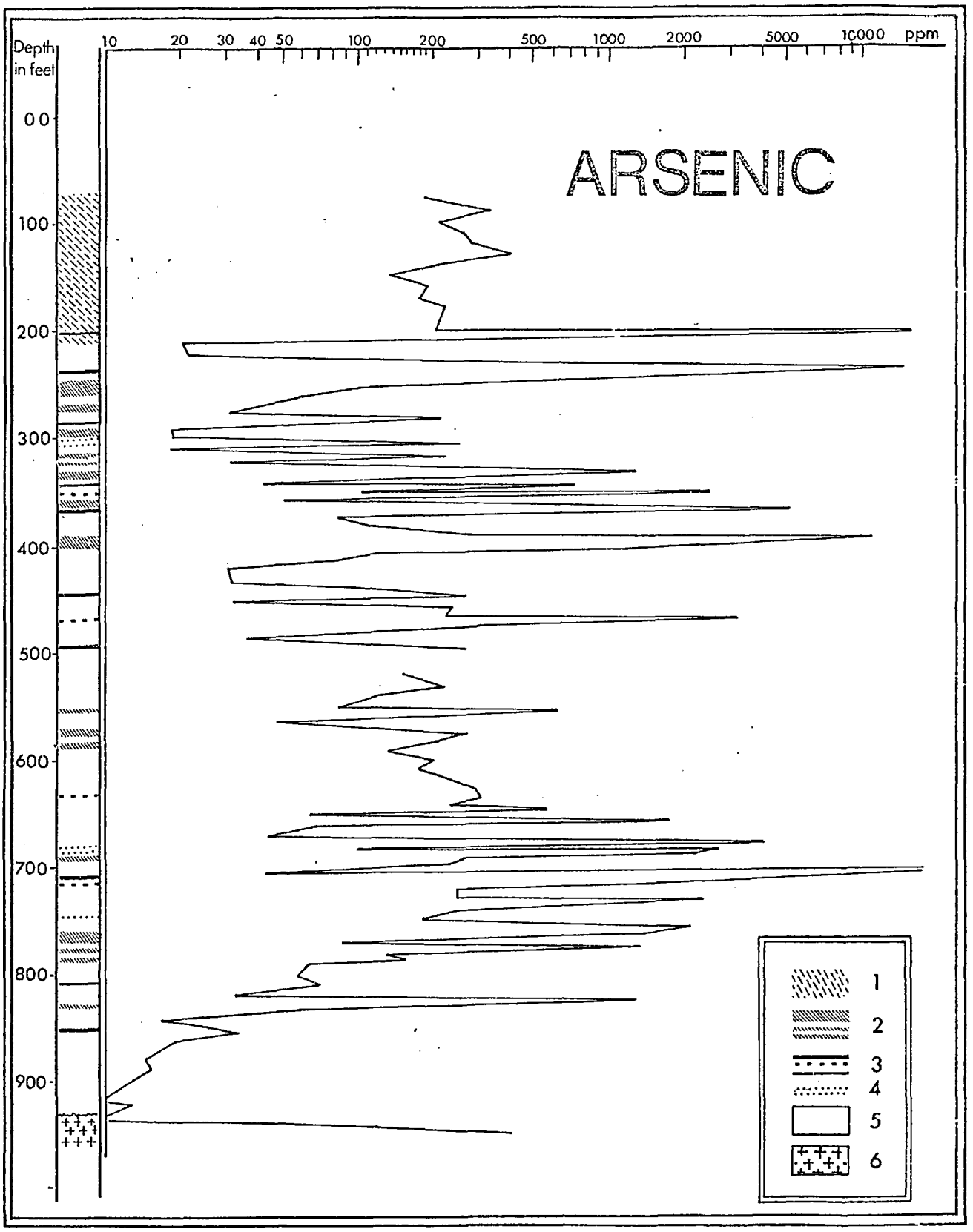
Plotting of the analytical data took the form of profile curves at an original vertical scale of one inch to 100 feet. Because of some extremely high As and other trace-elements concentrations, the metal content expressed in parts per million (ppm) was plotted on a logarithmic scale. In order to discriminate between the As content in rocks versus

veins, the geochemical data of the rocks (whose As concentration apparently has not been influenced by the mineralised veins) were drawn separately (Fig. 9.3) using an arithmetic scale.

9.4 DISTRIBUTION OF ARSENIC IN THE POLDICE MINE BORE HOLE

The overall pattern of the As distribution along the Poldice Mine-Bore Hole is characterised by a broad range of concentrations which vary from 1 to 60,000 ppm (Fig. 9.2). In the metamorphosed killas As exhibits a large section of anomalous As values. The most uniform patterns can be observed along the section (77 to 228 feet) which seems to have undergone the effects of supergene alteration. Here the As levels range from 100 to 400 ppm. From 228 feet down to approximately 840 feet As becomes more erratic with low values down to 5 ppm near to the granite contact. The higher As concentrations (of several hundred ppm) are found in the sulphide-bearing veins. Greenstones are relatively low in As content (15 ppm) becoming anomalous (260 ppm) when they bear disseminated sulphides. The granitic mass shows a high contrast in its As concentration: less than 1 ppm was detected at its country rock contact, then suddenly increases downwards to reach 520 ppm. The granitic dyke located at approximately 917 feet was found to be barren of As content. Some quartz veins in which no As mineralisation has been distinguished were found to contain up to 4000 ppm.

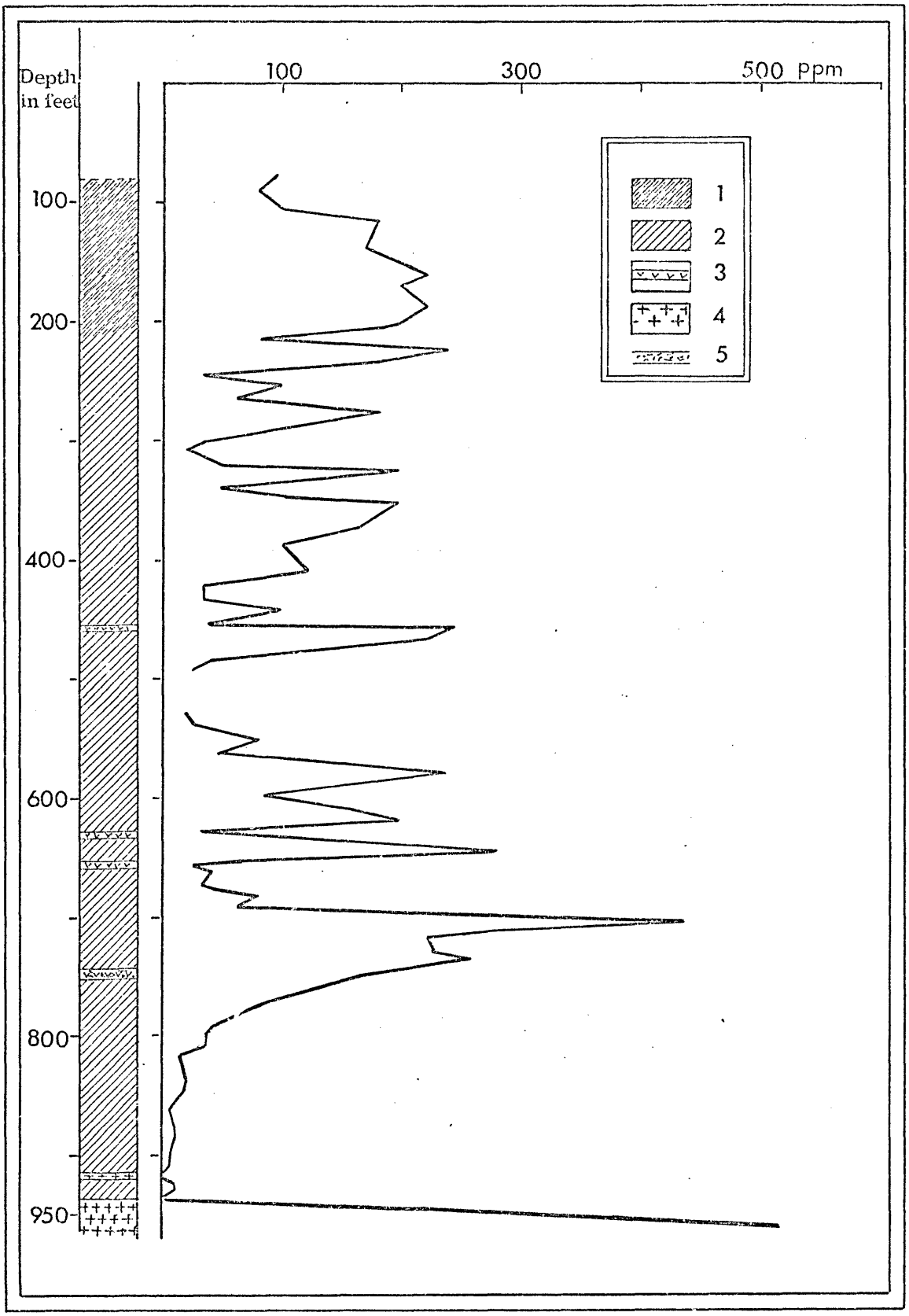
Although highly anomalous As concentrations have been found to relate to the mineralised veins (with the highest concentrations obviously located in arsenopyrite-bearing veins) examination of individual ore mineral samples has revealed that in veins in which arsenopyrite has not been detected, high As contents (up to 5000 ppm) occur in chalcopyrite and/or pyrite-bearing veins. In veins in which sphalerite and galena are dominant the As content is relatively low (260 ppm).



1 Zone of Supergene alteration
2 Quartz veins
3 Sulphide veins
4 Disseminated sulphide in killas, quartz veins and schorl veins
5 Killas
6 Granite

FIG. 9.2. POLDICE MINE - BOREHOLE

Poldice Mine - Bore Hole (C-51)



1 Zone of supergene alteration
2 Killas
3 Greenstones
4 Granite
5 Disseminated sulphide

Fig. 9.3 ARSENIC AS RELATED TO BED-ROCK GEOLOGY

Plotting of the geochemical data of rock samples collected along the drill-core, excluding that of mineralised veins and adjacent parent-rock, has allowed one to establish, to some degree, the As distribution pattern within the metamorphosed killas. This pattern (Fig. 9.3) displays As concentrations which vary from 5 to 480 ppm. In addition to the suggested supergene altered zone, other sections along the drill core show a range of anomalous As values. Although no visible mineralisation appeared in the analysed parent-rock, it is probable that the mineralised fluids which filled the veins greatly influenced the high As concentrations within these apparently barren rocks. Lateral migration of fluids within the wall rock from the veins was found to be insignificant (less than 6"), therefore no dispersion halos can be related to the high As levels in the parent-rock.

The lowest As concentrations in the metamorphosed killas have been found in the hardened rocks adjacent to the granite junction, the values ranging from 5 to 18 ppm. A similar phenomenon was found in the Dartmoor area where As concentrations in sediments along the granite contact display very low levels. The most outstanding characteristic of the As distribution in the Poldice Mine-Bore hole is the anomalous pattern which occurs within the granitic body.

As described above, the As concentration is very low at the killas junction (1 ppm) then it increases till it reaches anomalous values ranging from 120 to 520 ppm (Fig. 9.4). Although anomalous As levels have been found in the Dartmoor granite in areas near its country rock contact, (see Chapter 8) the form of occurrence of this element greatly differs between Dartmoor and the bore hole and suggests that the As anomaly in the granite from the borehole may be related to the dispersion halo of an undiscovered mineralised vein, rather than to the 'refluxing' processes proposed as an explanation for the As concentration in the Dartmoor granite. The supporting facts for this hypothesis are:-

Poldice Mine - Bore Hole

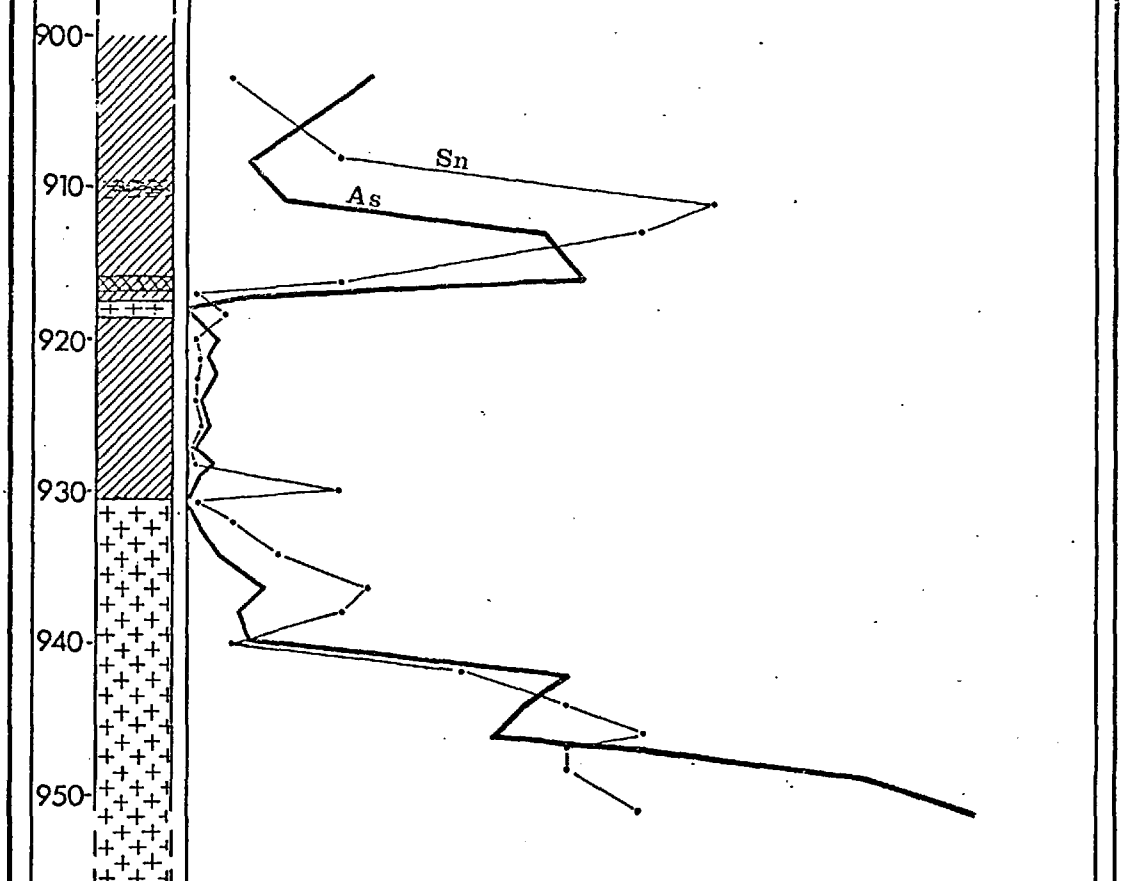


Fig.9.4. Arsenic and Tin anomalies in Granite

(Explanation as for Fig. 9.3)

i) In the Dartmoor granite the As concentrations close to the country rock contact decrease as the distance from the contact increases into the granite, whilst in the drill core As values in the granite body increase as the distance from the contact increases. The highest As concentration in the former medium reaches up to 56 ppm, whilst in the latter the As content is approximately 10 times higher.

ii) In the Dartmoor granite the positive As-S correlation suggests that As may occur mainly in pyrite. The correlation between these elements in the granite from the bore hole is very weak. On the other hand, mocroscopic examination of granite samples from the drill core revealed the existence of arsenopyrite.

iii) Analytical data from granite samples collected in lode-bearing areas within the Dartmoor granite averaged 400 ppm As, the average in the drill core granite being 340 ppm.

However, despite all of these facts it is possible that superimposed patterns within the granite near its country rock contact might occur. The weak As-S correlation could indicate that As-bearing pyrite was deposited during the early stages of the granitic intrusion.

On the basis of the data obtained from this study it could be theorised that the dispersion of As in rocks and mineral veins from the metamorphic aureole in this area occurred under the same conditions of those already indicated in Chapter 8. The only difference may be that in the area of the bore hole the parent rock was more enriched due to the intense hydrothermal activity; activity which was more violent here than in the Dartmoor area.

The other selected trace-elements also display a varied range of values especially along the metamorphosed sediments. High Cu, Pb, and Zn values reaching up to 20,000 ppm. (Fig. 9.5 and 9.7) appear closely related to the mineralised veins, with the highest values

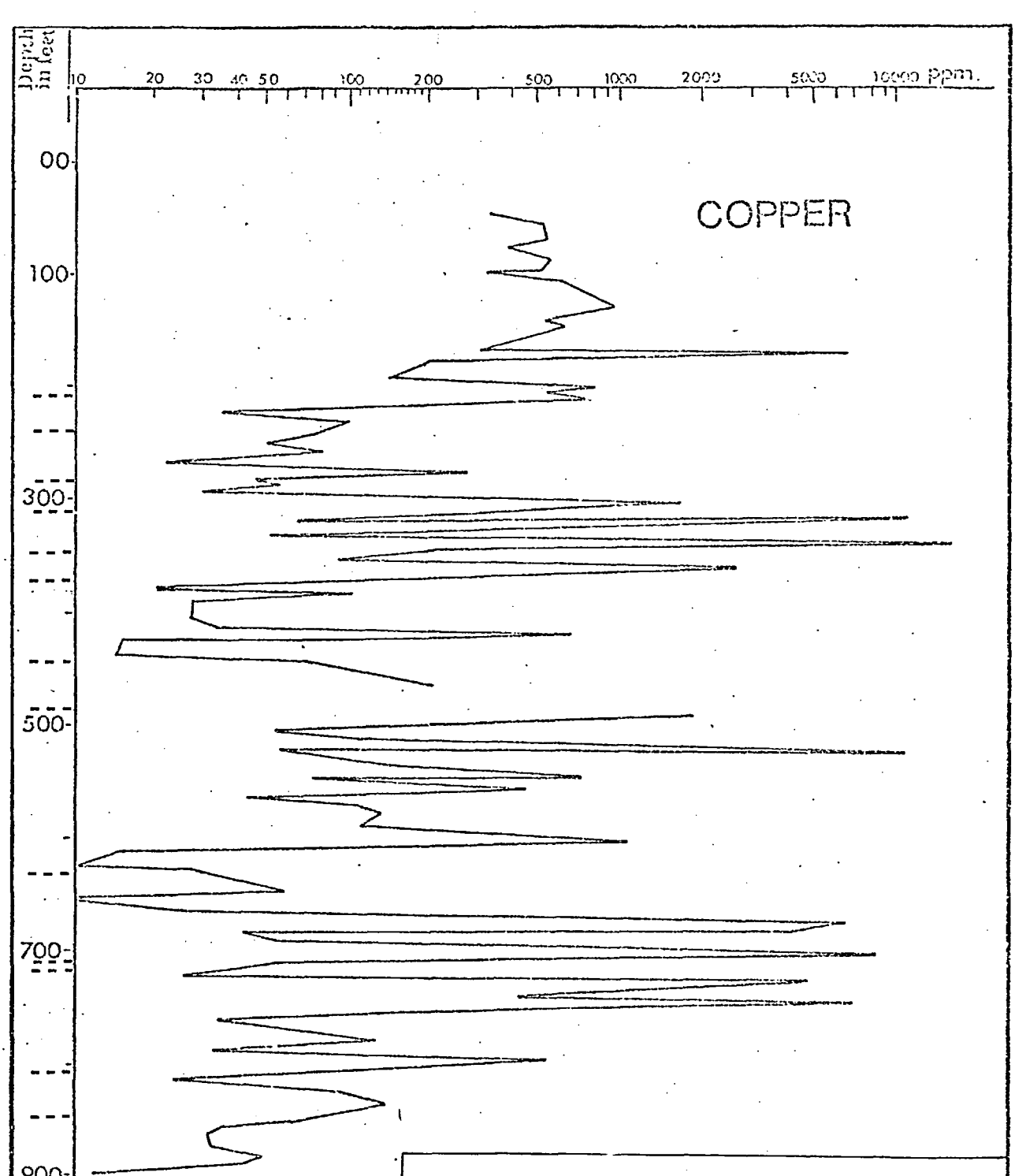


FIG. 9.5 POLDICE MINE-BORE HOLE

EXPLANATION AS FOR FIGS. 9.2&3.

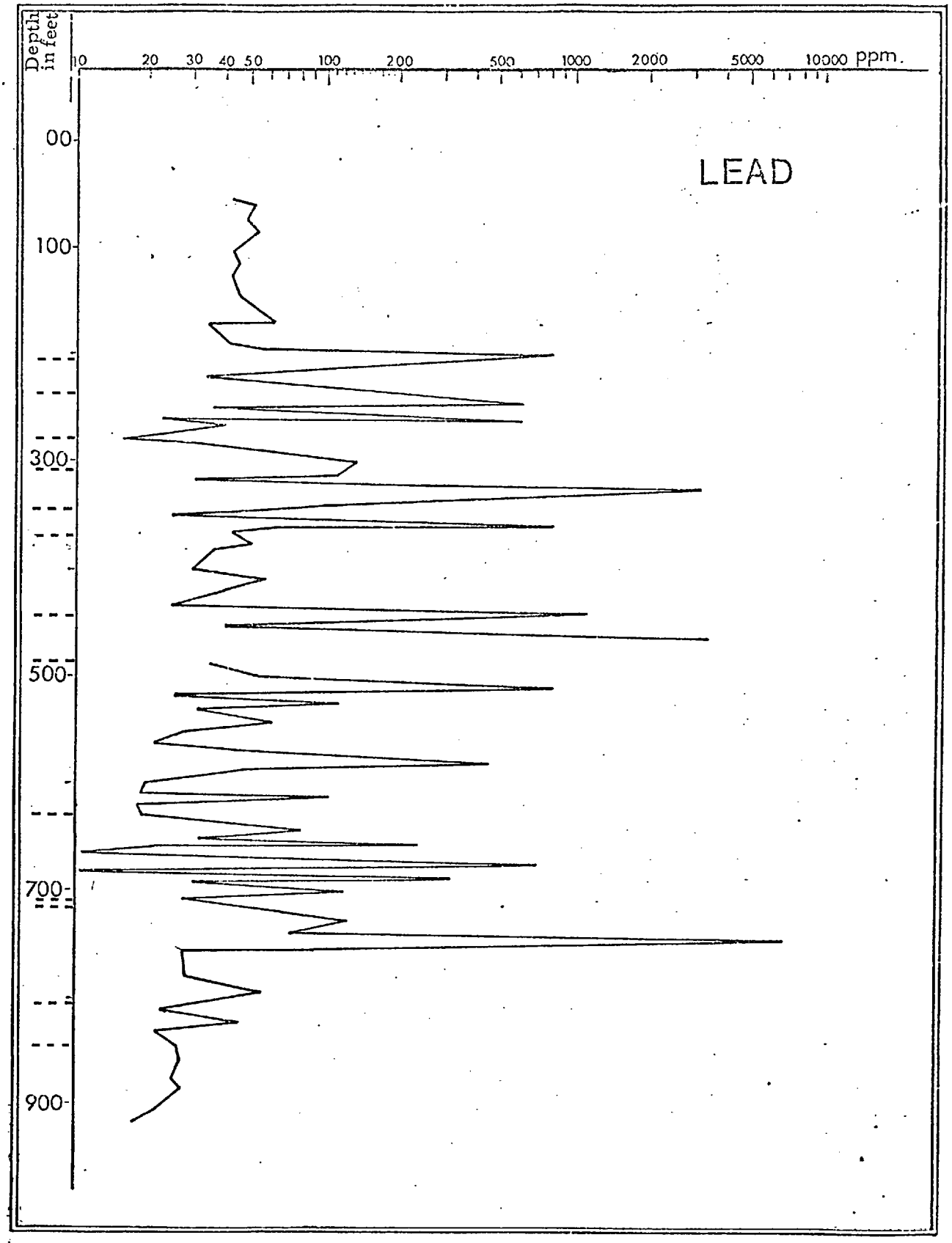


Fig.9.6. PoldiceMine-Bore Hole

(Explanation as for Figs. 9.2, 3 & 5)

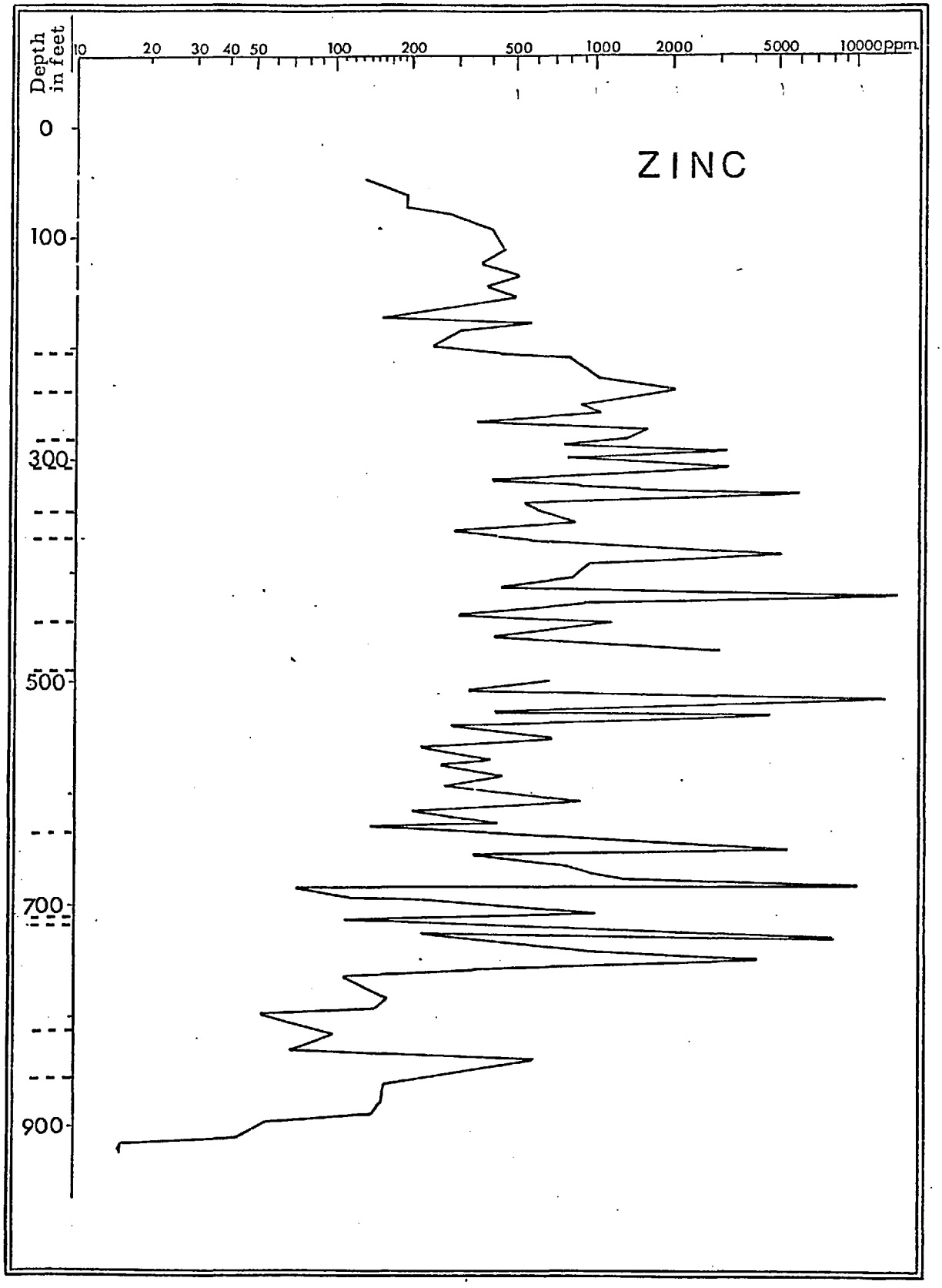


Fig. 9.7. Poldice Mine-Bore Hole

(Explanation as for Figs. 9.2, 3 & 5)

associated with the occurrence of chalcopyrite, galena and sphalerite. The Zn concentrations along the drill core display a broad section of anomalous values, these values becoming lower near and within the granite. Like the As, these three elements show their best distribution pattern within the indicated section of supergene alteration the values ranging from: 40 to 100 ppm Pb; 300 to 1000 ppm Cu; and 120 to 500 ppm Zn.

Sn, Mn and Fe display a range of high to low concentrations in both rocks and mineralised veins. Fe and Mn exhibit their high values (up to 15% and 5800 ppm respectively) within the killas, both elements being low in the granite: 0.8% Fe, and 120 ppm Mn (Fig. 9.8 and 9.9). Sn is more erratically distributed with values varying from 1 to 35 ppm (Fig. 9.10). The most important feature of this element is its mode of occurrence within the granitic body. The values, increasing away from the country-rock contact in toward the granite (1 to 30 ppm), seem to follow the distribution pattern displayed by As in this specific section (Fig. 9.4).

S shows the most contrasting distribution pattern. Only traces of this element were found in the supergene altered zone, the values becoming higher (although erratic) in fresher rocks, whilst in the sulphide-bearing veins extremely high concentrations (up to 38%) were located. Because of the insoluble character of the arsenopyrite and other As sulphide in relation to the analytical method for S determination, these anomalous levels detected in the veins are often directly related to the Cu, Zn, Pb and Fe sulphides.

9.5 CORRELATIONS BETWEEN ARSENIC AND SELECTED TRACE-ELEMENTS

Correlation coefficients were calculated for the overall data, and the results are shown in Fig. 9.11.

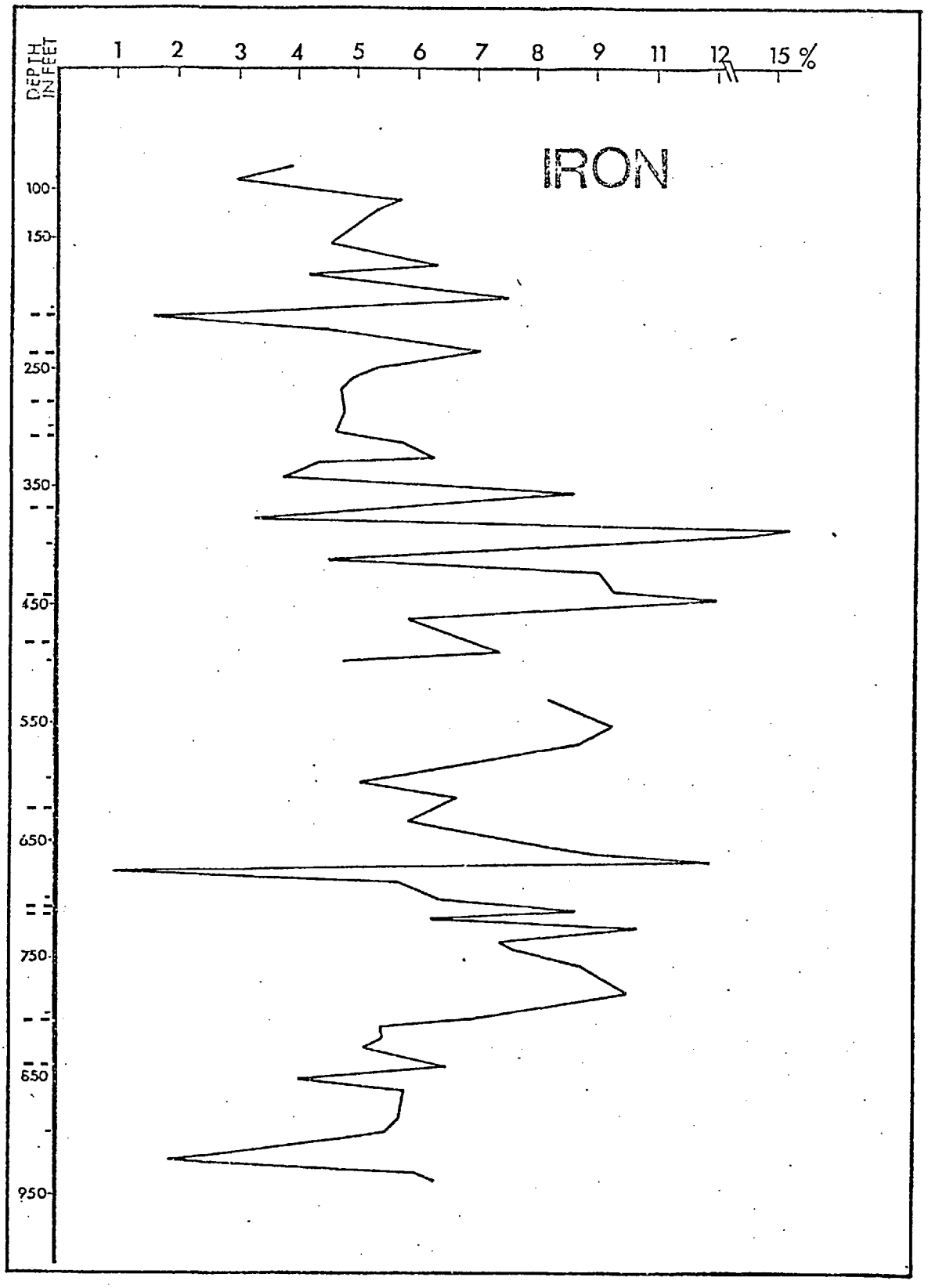


Fig. 9.8 POLDICE MINE-BORE HOLE

(Explanation as for Figs, 9.2, 3 & 5)

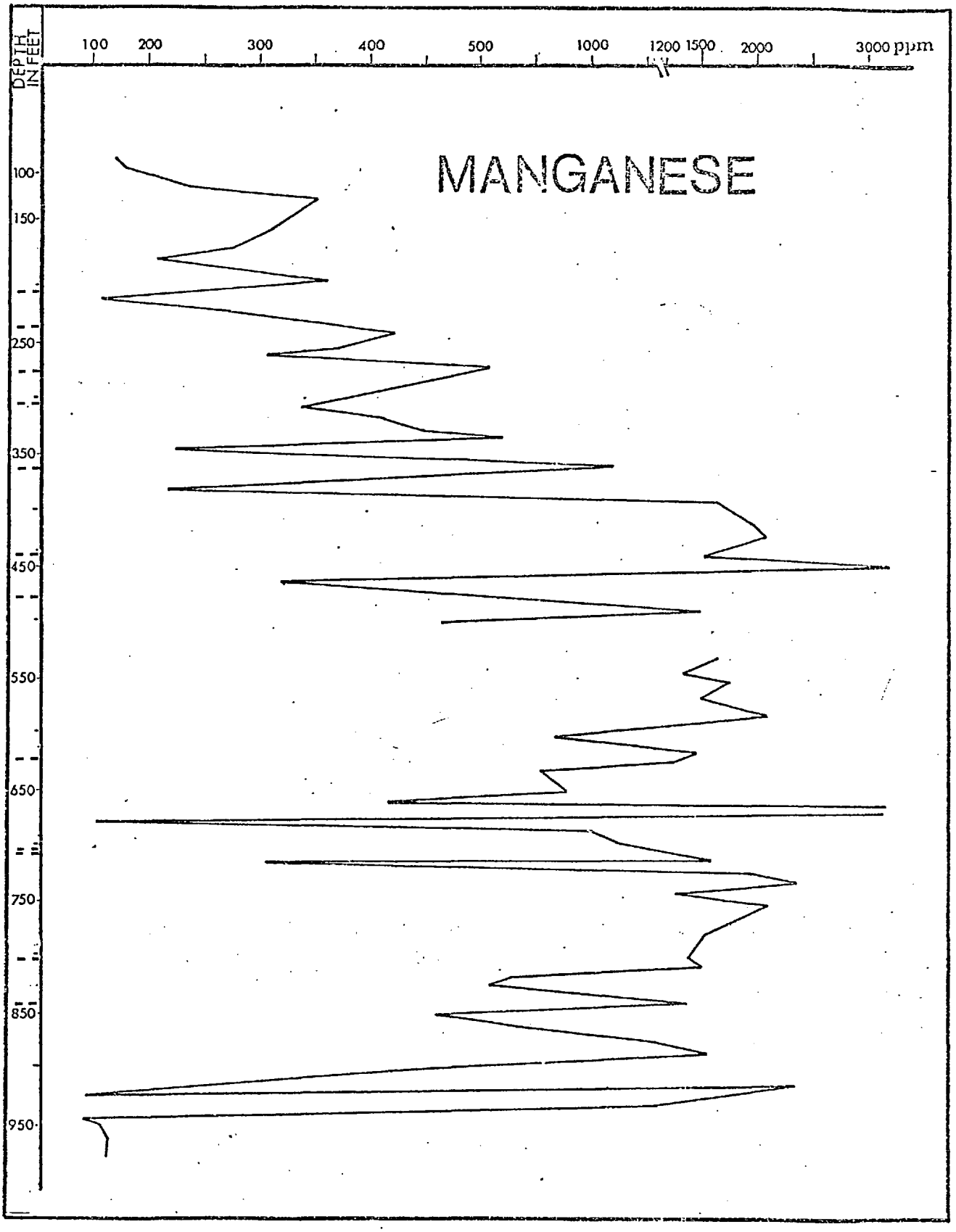


Fig. 9.9 POLDICE MINE-BORE HOLE

(Explanation as for Figs. 9.2, 3 & 5)

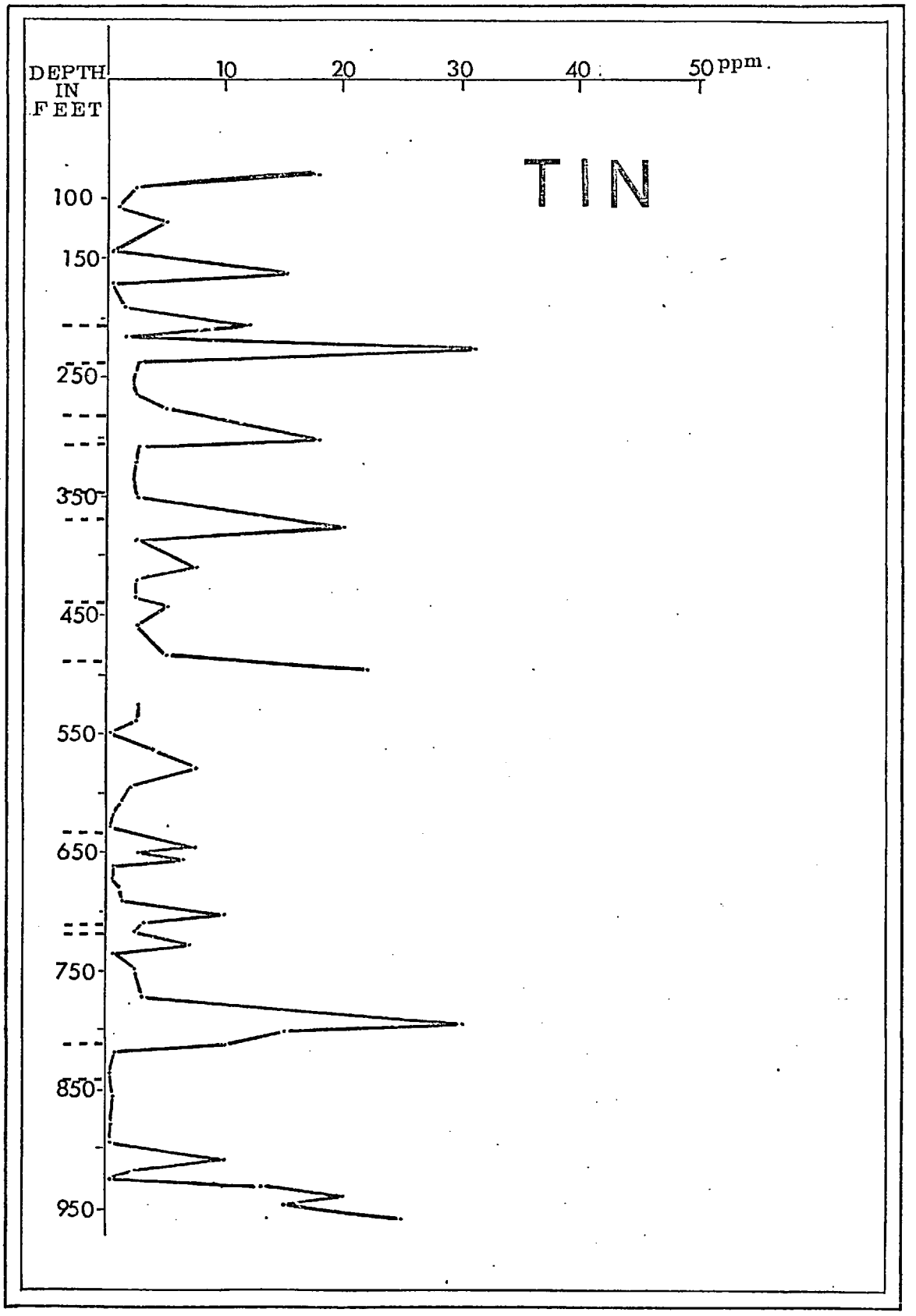


Fig.9.10.POLDICE MINE-BORE HOLE

(Explanation as for Fig. 9.3)

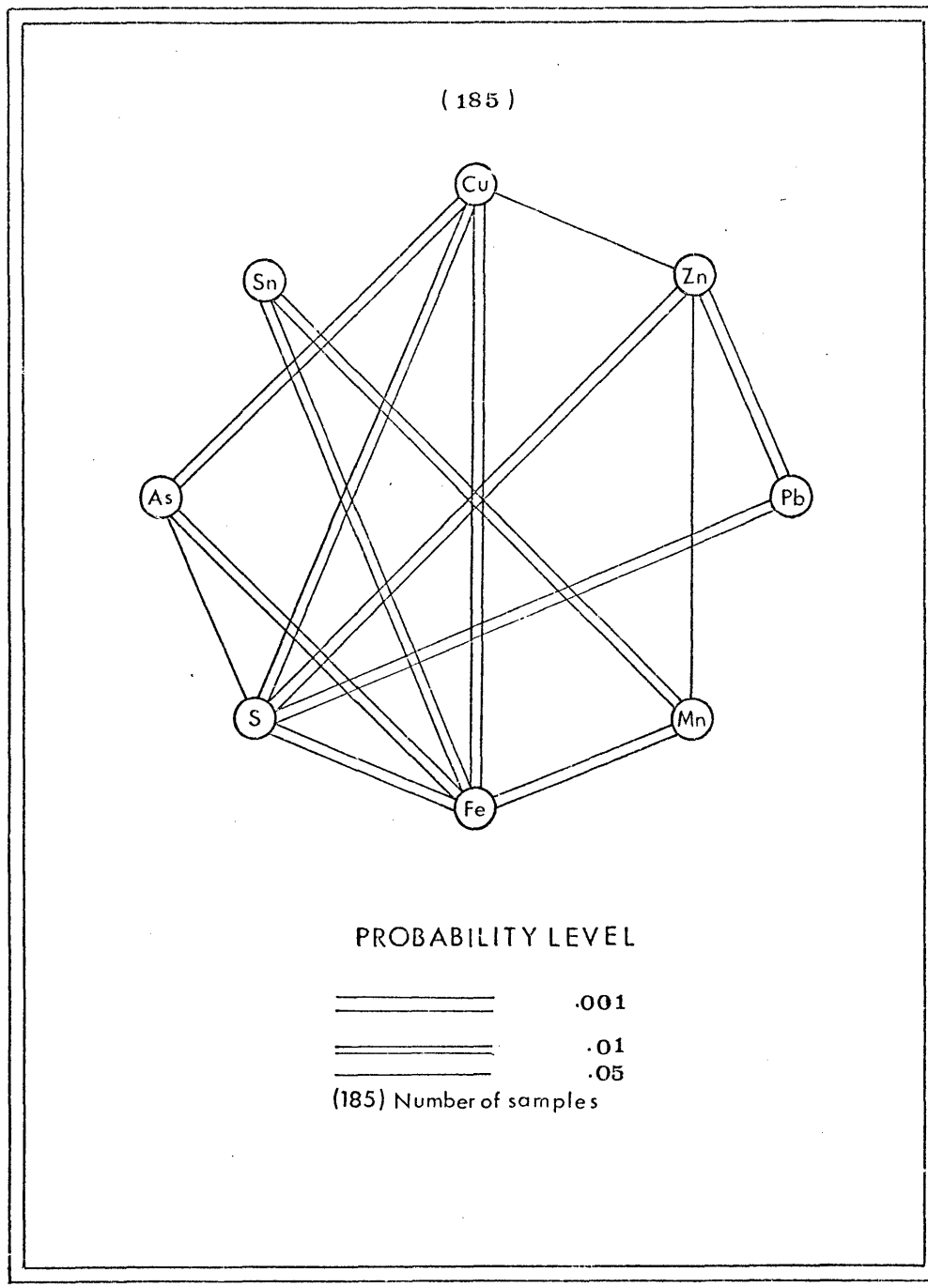


Fig. 9.11 CORRELATION BETWEEN ARSENIC AND SELECTED TRACE-ELEMENTS IN ROCKS FROM THE POLDICE MINE-BORE HOLE
(values expressed as probability level of significance)

As it can be expected from an intensely mineralised area, correlations between the selected trace-elements from the Poldice Mine-Bore hole mainly represent mineral assemblages. Most of the associated groups present in the area belong to the general associations of chalcophile elements occuring in sulphide ores (Hawkes and Webb, 1962). Thus the As-Cu-Fe, Cu-S-Fe, S-Zn-Pb and S-Fe associations represent the form of occurrence of sulphide ores in the mineral deposits from south-west England. On the other hand, the strong positive correlation between Mn, Fe and Sn may be related to wolframite yielding Sn. The weak As-S, and Mn-Zn correlations probably reflect As-bearing pyrite, and ferromagnesian minerals, respectively.

9.6. SUMMARY

The Poldice Mine-Bore hole is located within an area whose underlying parent-rock has undergone thermal metamorphism and has been subjected to an intense mineralising activity.

The bed-rock penetrated by the hole is characterised by a thick section of sediments traversed by greenstone and granite dykes, and by numerous mineralised veins. Mineralisation occurs mainly as fissure-fillings, and in a few cases it occurs disseminated in greenstones, shales and in pre-existent quartz veins. The ores are represented by Cu, Zn, Fe, As, Fe and Pb sulphides, and occasionally by wolframite. Almost 21 feet of granite were penetrated at the bottom of the hole.

Detailed geochemical investigations about the distribution of As in the drill-core revealed the existence of varied patterns which can be related to:-

i) Sulphide-bearing veins: Very high concentrations were found closely related to chalcopyrite and/or pyrite-bearing veins. Occurrence of As in sphalerite and galena-bearing veins was found to be relatively low. The highest As values obviously were located in veins yielding arsenopyrite.

ii) Bed-rock geology: A varied range of As patterns was found in rocks from the bore hole. Anomalous As concentrations alternating with low values characterise the bulk of sedimentary rocks. These sediments display uniform low As values as they approach the granite contact.

iii) Probable mineralisation: anomalous As concentrations within the granitic mass, along with high Sn values probably represent dispersion halo of an undiscovered mineralised vein.

The mode of occurrence of As in rocks and veins of the Poldice Mine-Bore hole resembles that of the Dartmoor Area discussed in an earlier chapter.

Anomalous concentrations of Cu, Pb, S and Zn are directly related to sulphide ores, the Zn being also high within the sedimentary rocks. Low, and high Fe and Mn concentrations are found indiscriminately located within the rocks and mineralised veins.

Correlation coefficients between the elements principally reflect the common minerals occurring in the ore bodies from the region.

CHAPTER 10

SUMMARY AND CONCLUSIONS

10.1 GEOCHEMISTRY OF ARSENIC

On the basis of an examination of selected literature a brief account of arsenic's geochemistry has been given. As is considered to be a non-metal element, it constitutes the third member of Group VA of the periodic system, and is regarded as a chalcophile element with a certain siderophile character.

As is universally widespread and is present in the solar atmosphere, meteorites, igneous, sedimentary and metamorphic rocks, and in many types of mineral deposits.

During the stages of geochemical fractionation As is of low concentration in the early magmatic sulphides but is predominant during the pneumatolitic and hydrothermal stages. Arsenopyrite is the most abundant and widespread As-bearing mineral, and is found most frequently in high temperature gold-quartz, and Sn veins. It occurs in sulphide and sulpho-salt deposits in association with Cu, Ag, Au, Zn, Cd, Hg, U, Pb, P, Sb, S, Te, Fe, Ni, Co, and Pt.

As has a marked tendency to enter into a sulphide lattice, and its presence as trace and minor quantities in common sulphides is well known. It was found that pyrite is the main As carrier in rocks and many types of mineral deposits.

As is widely diffused in soils and stream sediments being especially rich in areas of As-bearing deposits. Its presence has been detected in hot spring, stream, river and sea waters as well as in the atmosphere and biosphere.

10.2 REGIONAL GEOCHEMICAL RECONNAISSANCE SURVEY OF SOUTH-WEST ENGLAND

The geochemical interpretation of As and other selected trace-elements has been based on single-element, percentile interval, grey-scale maps together with geological, physiographic, pedological and climatological maps. The As patterns have been classified into two main groups (see Chapter 6, Sections A and B: Geochemical Background and Anomalous Patterns, pp 54-56).

a) Geochemical background (which is characterised by a varied range of As values), determined in terms of the normal distribution of the element in relation to the barren lithological units.

b) Anomalous patterns, in clear contrast to the geochemical background, are related to mineralised and /or contaminated areas, to bed-rock lying within the metamorphic aureoles, and to possible hidden mineral deposits.

The geochemical patterns of Cu, Pb, Zn, Fe, Mn and Sn are broadly influenced by mineralisation and contamination, and to a lesser extent by bed-rock geology and secondary environmental effects (Section 6.4; Summary).

10.3 MORE DETAILED GEOCHEMICAL INVESTIGATIONS IN SELECTED AREAS

10.3.1 Sampling and Analytical Techniques

The regional geochemical investigations were carried out in areas which are characterised by the occurrence of extensive and varied lithology, no evidence of known mineralisation and subsequent contamination, and by the existence of a wide range of primary and secondary dispersion patterns.

The survey in these areas was based on conventional geochemical exploration techniques which included stream sediment, soil and rock sampling and the analysis of the minus 80-mesh fraction of the samples for eight trace-elements by means of atomic absorption spectrophotometry, and colorimetric methods.

A new method for the determination of sulphur in sulphide-bearing samples was successfully employed in the analysis of rocks and common sulphides such as pyrrhotite, marcasite, sphalerite, chalcopyrite, galena and pyrite (Chapter 5: Analytical Techniques and Appendix I).

10.3.2 Data Processing

Analysis of the frequency distribution of the data from each lithological unit and other specific areas showed that the bulk of elements approximate to a lognormal distribution.

The use of the product-moment correlation matrix at different levels of significance was found to satisfactorily establish the relationship between the primary distribution of As and the other selected trace-elements.

10.4 SECONDARY DISPERSION OF ARSENIC

10.4.1 Stream Sediments

Analytical data from stream sediments of the Devon Area disclosed the existence of a contrasting range of As values which varied from low (5 ppm) to anomalous (over 2500 ppm) concentrations. Because of the limited analytical data it was not possible to obtain a clear picture of most of the As patterns displayed in the area. However on the basis of the available data, and the examination of single stream sediment values, the As patterns were tentatively related to barren bed-rock geology (5 to 35 ppm); to high background parent-rock (Permian unit 80 ppm and metamorphic aureole 50 to 160 ppm); to contamination derived from lode-bearing areas (800 to 2500 ppm) and to possible undiscovered ore deposits (220 to 2500 ppm). See Chapter 7, Section 7.3.1 (b); Interpretation of Patterns (pp 84-88 and 116-118).

10.4.2 Soils

a) Distribution of Arsenic Related to the Metamorphic Aureole

A varied pattern of anomalous As values was located in soils over the metamorphic aureole surrounding the granite. The distribution of As in the soils (which appears closely related to bed-rock geology) and rocks indicated that these concentrations are directly related to primary dispersion derived chiefly from the metamorphosed, underlying parent-rock. The mean As level from the aureole (115 ppm) exhibits considerable contrast when related to those from areas located outside the aureole (12 ppm) and from the granite (8 ppm).

The As content in the northern aureole (Traverse AA1, North Devon) whose mean level reaches 82 ppm greatly differs from that in the southern part (Traverse BB1, South Devon) the values in the latter (mean 150 ppm) being higher and more erratic and seem to have been influenced by the shallowness of the granite and by the presence of alluvial material (Chapter 7, Section 7.3.1 (a) Metamorphic Aureole and Tables 7.2 and 7.6; pp 88-96 and 121-124).

Detailed studies in soils and rocks from areas where intense mineralisation took place revealed that the anomalous As concentrations within the aureole (up to 3500 ppm) are not entirely reflected in the underlying parent-rock but they were enriched by transported material probably derived from the existing ore-bearing areas and subsequent mining and smelting activities. (Chapter 8, Kit Hill Area, Section 8.5.4 Interpretation of Patterns, pp 229-230)

Along with As, high Cu, Zn, Pb, Mn, Sn and Fe levels occur in soils from the metamorphic aureole. The sources of these elements are not solely related to bed-rock geochemistry but they are associated with mineralisation, contamination and secondary environmental effects.

b) Distribution of Arsenic in Relation to Geology

Geochemical investigations within the Devon Area showed that both stream sediments and soils have similar As content when related to the geological units. Concentrations of As in soils within these units mainly reflect bed-rock geochemistry. Comparison of mean values outlined anomalous As values over the Pleistocene (65 ppm), and over the Permian (30 ppm). As appears in lower concentrations in the Carboniferous and Devonian sediments. It is low over the Upper Carboniferous (Crackington Formation 18 ppm, and Bude Formation 9 ppm); in the Lower and Middle Devonian (7 and 12 ppm, respectively), and in basic igneous rocks (11 ppm). In the granite As values range from low (5 ppm) to relatively high (58 ppm) levels, the higher values being located near its country rock contact then falling off inwards from the contact towards the centre of the granitic mass (Fig. 7.24, p 101). The Lower Carboniferous (113 ppm) and the Upper Devonian (160 ppm) rocks lying within the metamorphic aureole are characterised by a varied range of high As patterns which vary from 50 to 320 ppm. See Chapter 7, Section 6 pp 96-103 and 123-128.

c) Arsenic Patterns Related to Mineralisation

Significant anomalous As concentrations located during the regional geochemical investigations (Chapter 7) indicate the possible presence of undiscovered mineral deposits, they are:

i) Corscombe Area

This anomaly whose significance was established during the interpretation of the geochemical reconnaissance patterns (Chapter 6, Section 6.3.1 Anomalous Patterns), displays high mean As concentrations in soils (182 ppm); stream sediments (400 ppm), and rocks (112 ppm). Chapter 7, Section 7.3.1 Mineralisation and Table 7.5 pp 103-106.

Detailed investigations in soils complemented by analysis of rocks and limonitic material (Chapter 8, Corscombe Area) confirmed the occurrence of As anomalies in this area detected during previous geochemical stream sediment, soil and rock surveys (Chapter 6 and 7). On the basis

of statistical determinations of background and threshold values the As levels occuring in the area were classified into two main groups:

1 normal background, and

2 anomalous concentrations whose peak value reaches up to 680 ppm.

The anomalous concentrations were grouped in two categories:-

1a significant anomaly, which is located within a barren zone in the eastern part of the area, and

2a non-significant anomaly which is extensively located in the western part of the area and appears to have originated from underlying pyrite-bearing rocks.

(Section 8.4.2 Eastern, and Western Zones, Figure 8.33, pp 206-218). The high As concentrations in the Eastern Zone are accompanied by anomalous Sn (78 ppm), Cu (245 ppm), Zn (610 ppm), Pb (260 ppm), Fe (9%) and Mn (6000 ppm) contents. On the basis of their geological relationships, the magnitude of the concentrations, and the extension of the anomaly among other things, these concentrations were regarded as having originated from unknown, buried mineral deposits (Section 8.4.2 (iii) Significant Anomaly, pp 216-217)

ii) Kit Hill Area

Detailed studies in soils from the Kit Hill Area (Chapter 8.5) revealed the occurrence of anomalous As values (up to 3800 ppm) together with other selected trace-elements which are related to mineralised and/or to contaminated areas (Section 8.5.4 (ii) Ore Deposits, and Contamination pp 229-230). In addition to these anomalous levels other As anomalies were found in areas where neither mineralisation nor contamination was evident. Therefore, it was assumed that they were related to unknown, buried mineral veins which may be the continuation of neighbouring lodes striking almost perpendicular to the anomalies (Section 8.5.4 (iv) Undefined Sources, and Figures 8.39 to 8.41, pp 230-234). These anomalies termed Anomaly C, D, and E, with peak As values reaching up to 320, 450 and 3500 ppm respectively, are accompanied by high Sn, Zn, Mn, Cu, Pb and Fe concentrations.

10.5 PRIMARY DISPERSION OF ARSENIC

The abundance of As in rocks from south-west England appears more pronounced than in the general background established for these rock types elsewhere. The As concentrations greatly increase in the metamorphic aureole surrounding the granite. However, examination of the As occurrence in individual lithological units, and rock types showed that the element is, in some cases, normally concentrated while in others the rocks were depleted of their As values.

10.5.1 Arsenic Patterns as Related to Geology

Geochemical studies on the primary dispersion of As within the Permian Formation outcropping in the Hatherleigh-Yeoford Area (Chapter 8, Section 8.2) disclosed that As is enriched in almost all the sedimentary sequence (mean 16 ppm), and in igneous rocks from the Exeter Volcanic Series (mean 45 ppm). Within the sedimentary rocks the Crediton Conglomerates and Knowle Sandstones showed the lowest mean levels (8 and 10 ppm, respectively), the higher values occurring in the Bow Conglomerates unit (mean 20 ppm). The wide variation in As content in the Bow Conglomerates, with levels ranging from 1 to 110 ppm, is mostly due to:-

i) The nature of the breccia-forming pebbles,
ii) the texture of the bed-rock, and
iii) the nature of the parent-rock.

(Section 8.2.6 (i) Permian Sediments, pp 152-157)

Examination of the breccia and conglomerate-forming pebbles from the western zone of the area (where As is highly concentrated) revealed that the major occurrence of As in the Bow Conglomerates is found in volcanic and mudstone pebbles, the former belonging to neighbouring As-rich lamprophyres, and the latter being probably derived from the Cornubia (Table 8.6 p153).

Within the Exeter Volcanic Series a high contrast in As content is found: low values (2 ppm) characterise the olivine-basalt-minette while

the olivine-biotite-minette show a mean level of 59 ppm. However, a contrast is also found within the olivine-biotite-minette themselves: low concentrations (mean 4 ppm) located in the Coplestone quarry (Qy-10) sharply differ with the anomalous values (up to 400 ppm) found in the Hannaborough quarry (Qy-7). See Section 8.2.6 (ii) Exeter Volcanic Series, and Tables 8.3 and 8.5 (pp 138, 142 and 157-158).

The Carboniferous Formation displays greater As concentrations than the Devonian both within and without the metamorphic aureole (Chapter 8, Table 8.10, p 167). The mean values from both units (6 ppm Devonian, and 9 ppm Carboniferous) located outside the metamorphic aureole fall within the normal range of such rock types. Within the Devonian, the Middle Devonian is higher in As than the Upper Devonian (mean levels 10 and 16 ppm respectively). This discrepancy was also found in the Carboniferous where As in the Upper Carboniferous (Crackington Formation, mean value 15 ppm) is much higher than in the Lower Carboniferous (mean 9 ppm). The contrast established between Devonian and Carboniferous (1:1.5) was determined to be mainly due to the high As content in the Carboniferous black shales (Section 8.3.4 (ii) Arsenic related to Lithology, p 188)

Among the intrusive igneous rocks, the granite has a high mean value (7 ppm) with anomalous concentrations located near its country-rock contact, and around mineralised bodies. According to its As content the Dartmoor granite was tentatively classified into three types:-

i) 'Uncontaminated' granite with values ranging from 1 to 10 ppm;

ii) 'Contaminated' granite whose levels reach up to 450 ppm, and

iii) 'Barren' granite whose As content is insignificant (<1 ppm).

To explain the occurrence of anomalous As values in the granite two hypotheses were proposed:-

i) As-bearing fluids emanating from the magma gradually

deposited part of their As content in the margin of the granite (15 to 56 ppm) as a consequence of a 'refluxing process' to which early magmatic fluids were subjected between the melted magma and an impermeable 'screen' of baked country-rock at the contact (Section 8.3.4 (i) Generalities pp 186-191);

ii) Emplacement of ore deposits in the granitic crust was accompanied by lateral migration of volatile compounds into the host-rock thus creating dispersion halos of high As concentration.

In the Poldice Mine-bore hole the granite is characterised by a low As content at its country-rock contact (1 ppm) the values increasing downwards to reach up to 520 ppm. (Chapter 9, Poldice Mine-Bore hole, Section 9.4, pp 242-244 and 248)

Lamprophyre dykes intruding into the Upper Carboniferous sediments (Crackington Formation) showed values ranging from relatively high (24 ppm) to anomalous levels (250 ppm), and appear in some areas to have been depleted of As by action of weathering processes (Chapter 8, Section 8.2.6 (iii) Lamprophyre dykes, p 158)

10.5.2 Arsenic Patterns as Related to the Metamorphic Aureole

As a result of the investigations on the primary distribution of As in selected areas, varied patterns of anomalous concentrations were found to characterise the metamorphic aureole surrounding the granite. The parent rock lying within the aureole was found to be indiscriminately enriched in As, although some rock types showed normal concentrations, while others in specific areas, seem to have been depleted of their As content.

The origin of the As anomalies within the aureole is primarily related to the phases of the granitic intrusion. Gases and liquids emanating from the magma were responsible for the gradual enrichment in

As of the neighbouring country-rock, and to some extent of the granite itself. Primary dispersion of As within the host-rock appears to have been controlled principally by fracture and micro-fracture patterns developed before, during and after the granitic intrusion. The deposition of As began with the early magmatic activities and lasted until the later stage of the granitic intrusion. However, in specific areas migration of early fluids into the host-rock was interrupted (by impermeable rocks at the contact), therefore, deposition of this element took place in the granite margin (see above, Section 10.5.1, Arsenic patterns as related to Geology). Early magmatic fluids were of low As concentrations, the As content becoming higher in the pneumatolitic and hydrothermal stages which were capable of forming ore deposits of economic significance (Chapter 8, Section 8.3.4 (i) Generalities pp 186-188). The As concentrations within the metamorphic aureole in the Dartmoor Area were classified into two major patterns:-

a) Local background which includes: (1) rocks at the granite contact that were depleted of their As content by heat transmitted from the magma; (2) rocks which, despite the thermal metamorphism, maintained their As values, and (3) rocks which seem to have been enriched to some degree by endogene agents during the granitic intrusion (Section 8.3.4 (a) Local background pp 192-198)

b) Anomalous patterns which are related to known mineralisation and to possible unknown hidden ore deposits (see discussion below: Section 10.5.3).

The general levels (mean 66 ppm) within the metamorphic aureole sharply contrast with those outside the aureole (8 ppm) and from the granite (7 ppm). The amount of As in the Carboniferous (mean 78 ppm) was found to be higher than in the Devonian (62 ppm). Among the individual rock types As is highly concentrated in shales, sandstones, slates and

greenstones their mean values being 100, 45, 35 and 20 ppm respectively. However, in some rock such as greenstones, the high As concentrations are confined to very specific areas, and in many cases closely related to mineralisation (Section 8.3.2 Mineralised Veins, Table 8.11a pp 174 and 181).

The sampling and analysis of rocks from a deep drill-core penetrating the metamorphic aureole and the granite showed that:-

i) As is enriched in a large section of the metamorphosed sediments (up to 480 ppm) with uniform high values in the zone of supergene alteration;

ii) The lowest and most uniform As concentrations are located in the hardened rocks adjacent to the granite junction,

iii) Greenstones are relatively low in As content (15 ppm) becoming anomalous when they bear disseminated sulphides (Chapter 9, Poldice Mine-bore hole, Section 9.4 pp 239-242).

Analysis of the rocks around the As-rich lamprophyres of the Hatherleigh-Yeoford Area indicated the occurrence of high As and S values (120 ppm As,444 ppm S) extending laterally for at least 30 yards away from the contact in the case of the extrusive rocks, and 16 yards in the case of the dykes. This fact was regarded as being an indication of the presence of a geochemical aureole in which As was deposited probably in sulphides. The extension of the aureole may indicate difference in grade of temperature between the extrusive and the intrusive magma (Section 8.2.6: Interpretation of Arsenic Patterns, pp 157-158).

10.5.3 Arsenic Patterns as Related to Mineralisation

The classification of anomalous As patterns in the metamorphic aureole permitted the discrimination between anomalies related to known mineralised areas, and those which might be related to possible mineralisation.

Broad areas of anomalous As concentrations found in the metamorphic aureole are closely related to mineral ore-bearing areas. In the eastern part of the Dartmoor granite where the relationship between As anomalies and mineralised areas is more conspicuous, these anomalous values extend into the granite and the killas, and appear to follow the trend of the mineralised structures (Section 8.3.4 (b) Anomalous Patterns pp 193-196). The two anomalies located in the southern aureole of the Dartmoor granite (termed Anomalies A, and B) in areas considered metallogenically barren, are thought to represent hidden ore deposits. Anomaly A which arises on metamorphosed Culm and Devonian sediments and on some basic igneous rocks displays its highest As values (360 ppm) in the Devonian-Carboniferous calc-silicate rocks. On the other hand, Anomaly B showed its peak level (200 ppm) concentrated in basic intrusive rocks (dolerite), and might represent the continuation of mineralised ores located westward from the anomalous area (Section 8.3.4 (ii) Possible Mineralisation, Anomalies A and B; Fig. 8.27 and 8.27a pp 196-200). Both anomalies were also found to be high in Sn (30 ppm), Cu (248 ppm) and S(888 ppm), although S seems mostly related to pyrite and/or pyrrhotite occurring in the parent-rock (dolerites).

In the Poldice Mine-bore hole anomalous As and Sn values occur in the granite. Both As and Sn are low in the granite-killas junction and increase downward into the granite reaching up to 520 ppm As, and 30 ppm Sn. These values probably represent the dispersion halo from an undiscovered mineralised vein which was not intersected by the drill-hole (Chapter 9, Section 9.4, Fig. 9.4 pp 242-244).

10.5.4 Arsenic Content in Mineralised Veins

Anomalous As concentrations found in axinite and tourmaline-bearing veins collected in different parts of the Dartmoor Area averaged 520 and 320 ppm respectively. The presence of As in these minerals suggested that the element might have been deposited during the pneumatolitic stage. Quartz samples bearing pyrite and chalcopyrite were found to be

rich in As (up to 2800 ppm), while in high temperature blende-bearing veins the occurrence of As is insignificant (average 2 ppm). See Section 8.3.2 Mineralised Veins, pp 174 and 182.

In the Poldice Mine-bore hole very high As concentrations (up to 5000 ppm) were found in chalcopyrite and pyrite-bearing veins, and in some apparently barren quartz veins the As reaches up to 4000 ppm. The concentrations of As in sphalerite and galena-carrying veins were found to be relatively low (260 ppm). The highest As levels were obviously found in veins containing arsenopyrite (over 6% As). See Chapter 9, Section 9.4 p. 238.

10.5.5 Correlations between Arsenic and Selected Trace-Elements

In the Hatherleigh-Yeoford Area As was found to be strongly related to S within the Volcanic Series while in the intrusive lamprophyre dykes the As-S correlation is weak. In both cases these correlations are an indication that As occurs in sulphides (probably pyrite). The weak positive As-S correlation in the dykes, together with a weak negative Fe-S relationship, suggests that pyrite is weathering and the formation of limonite at the expense of pyrite (Section 8.2.6 (ii) and (iii) Exeter Volcanic Series and Lamprophyre Dykes, pp 157-158)

In the Dartmoor Area and Poldice Mine-bore hole the variety of associated elements seems to principally represent mineralogical assemblages which belong to the general association of chalcophile elements. The outstanding As associations found in these areas were:-

a) As-Cu-Fe — This group might be related to chalcopyrite-yielding As sulphides (most probably arsenopyrite).

b) As-S — This strong positive correlation suggests As-bearing pyrite, pyrrhotite or other reducible sulphides.

c) As-Mn — This correlation might be in part caused by axinite which was found to be rich in As, and in part by Mn oxide occurring in cherts from the Lower Carboniferous.

d) As-Pb-Zn — determined in rocks adjacent to the outer edge of the metamorphic aureole and could be related to the black shales.

e) As — The uncorrelated state of As in the granite suggests the occurrence of this element in its sulphide form. However, in specific areas As is found correlated with S at varied levels of significance. This fact was regarded as an indication that part of the As occurs in reducible sulphide (Chapters 8 and 9, Sections 8.33 and 9.5 Correlations pp 182 and 248)

REFERENCES

AGRICULTURAL ADVISORY COUNCIL ON SOIL STRUCTURE AND SOIL FERTILITY, 1970. Modern Farming and the Soil: Ministry of Agriculture, Fisheries and Food, HMSO.

AHERENS, L. H. 1954, The Lognormal Distribution of the Elements: Geochm. et Cosmochim. Acta v. 5 pp 49-73; v 6 pp 121-131.

ALMOND, Hy. 1953b, Field Method for the Determination of Traces of Arsenic in Soils: Anal. Chemistry, v. 25, pp 1766-1777.

ANDERSON, D. H. and HAWKES, H. E. 1958, Relative Mobility of the Common Elements in Weathering of Some Schist and Granite Areas: Geochm. et Cosmochim. Acta, v. 14, pp 204-210.

APPLIED GEOCHEMISTRY RESEARCH GROUP, 1965, Determination of Arsenic in Soils and Stream Sediments. Technical Communication No. 49.

APPLIED GEOCHEMISTRY RESEARCH GROUP, 1966, Determination of Tin in Soils and Stream Sediments: Technical Communication No. 18.

ARMOUR-BROWN, A. 1971, Provincial and Regional Geochemical Studies in Zambia: Unpublished Ph. D. Thesis, University of London.

ARMOUR-BROWN, A. and NICHOL, I. 1970, Regional Geochemical Reconnaissance and the Location of Metallogenic Provinces: Econ. Geol. v. 65, pp 312-330.

BAIRD, A. K., McINTYRE, D. B., WELDAY, E. E. and MADLEM, K. W. 1964, Chemical Variations in a Granite Pluton and its Surrounding Rocks: Science, v. 146, pp 258-259.

BARTON, D. B. 1967, A History of Tin Mining and Smelting in Cornwall: D. Bradford Barton Ltd. Truro.

BARTON, P. B. Jr. 1969, Study of the System Fe-As-S: Geochm. et Cosmochim. Acta v. 33, pp 841-857.

BATEMAN, A. M. 1950, Economic Mineral Deposits: Willey, New York, NY.

BATEMAN, A. M. 1951, The Formation of Mineral Deposits: Chapman and Hall, London.

BICHAN, W.J. 1941, The Nature of Ore-Forming Fluids: A Discussion: Econ. Geol. v.36, pp 212-217.

BLANCHARD, R. 1942, Leached Derivatives of Arsenopyrite and Chromite: Econ. Geol. v.37, pp 596-626.

BOLVIKEN, B. 1970, A Statistical Approach to the Problem of Interpretation in Geochemical Prospecting: In Geochemical Exploration 1970, Montreal: CIM, 1971, pp 564-567 (CIM Spec. Vol. II).

BOTT, M.H.P., DAY, A.A. and MASSON-SMITH, D. 1958, The Geological Interpretation of Gravity and Magnetic Surveys in Devon and Cornwall: Phil. Trans. Roy. Soc. 251A, pp 161-191.

BOTT, M.H.P. and SCOTT, P. 1964, Recent Geophysical Studies in South-West England: In Present Views of Some Aspects of the Geology of Cornwall and Devon, pp 25-44. Hosking, K.F.G. and Shrimpton, G.J. Eds. Royal Geol. Soc. of Cornwall, Penzance.

BOYLE, R.W. 1972, The Geology, Geochemistry and Origin of the Barite, Manganese, and Lead-Zinc-Copper-Silver Deposits of the Walton-Cheverie Area, Nova Scotia: Geol. Surv. Can. Bull. v.166: 181 pp.

BOYLE, R.W. and DASS, A.S. 1967, Geochemical Prospecting - Use of A Horizon in Soil Surveys: Econ. Geology, v.62, pp 274-276.

BOYLE, R.W. and JONASSON, I.R., 1973, The Geochemistry of Arsenic and its use as an Indicator Element in Geochemical Prospecting: J. Geochem. Explor. v.3, pp 251-296.

BRADSHAW, P.M.D., 1967, Distribution of Selected Elements in Feldspar, Biotite and Muscovite from British Granites in Relation to Mineralisation: Trans. Inst. Min. Metall. v.76, pp B137-148.

BRADSHAW, P.M.D. and STOLEY, A.J. 1968, Exploration for Blinde Ore Bodies in South-West England by Use of Geochemistry of Fluid Inclusions: Trans. Inst. Min. Metall. v. 77 pp B144-152.

BRAMMALL, A. and HARWOOD, H.F. 1925, Tourmalinisation in the Dartmoor Granite: Miner Mag. v 20, pp 319-330.

BRAMMALL, A. and HARWOOD, H.F. 1932, The Dartmoor Granites: Quat. J. Geol. Soc. v. 88, pp 171-237.

BRINDLEY, J.C. and CONNOR, B.P. 1972, The Minor Acid Intrusions of the Aughrim-Ballinaclash Area, Co. Wicklow: Proc. Royal Irish Academy, v. 72, sect. B. No. 10, pp 166-183.

BROOKS, R.R. 1972, Geobotany and Biogeochemistry in Mineral Exploration: Harper and Row, London, 290 pp.

BURHAM, C.W. 1967, Hydrothermal Fluids at the Magmatic Stage: In Geochemistry of Hydrothermal Ore Deposits, Barnes, H.L. Ltd. Ed. New York, pp 34-76.

BUTCHER, N.E. 1961, Age of the Orogeny and Granites in South-West England: Nature, v.190, p 253.

CLARK, A.H. 1970, Arsenian Sphalerite from Mina Pampa Larga, Copiapo Shile: Am. Mineral. v. 55 pp 1794-1797.

CLARKE, F.W. 1924, The Data of Geochemistry, U.S. Geol. Surv. Bully, v. 770: 841 pp.

CLARKE, G.I. 1957, Encyclopaedia of Chemistry, Reinhol Pub. Co., N.Y.

CLARKE, L.A. 1960, The Fe-As-S System: Phase Relations and Applications: Econ. Geology v.55, pp 1345-1381 and 1631-1652.

CLAYDEN, B. 1964, Soils of Cornwall. In Present Views of Some Aspects of the Geology of Cornwall and Devon, pp. 311-330. Hosking, K.F.G. and Shrimpton, G.I. Eds. Royal Geol. Soc. of Conrwall, Penzance.

CLAYDEN, B. and MANLEY, D.J.R. 1964, The Soils of the Dartmoor Granite: In Dartmoor Essays, Ed. Simmons, I.G. Devon Ass. Adv. Sci.

CLEWS, D.R. 1962, The Secondary Dispersion of Copper in the Drainage System of the Kilembe Mine Area, Uganda: Unpubl. Ph.D. Thesis, University of London.

COPE, F.W. 1973, Woodele Borehole Near Buxton-Derbyshire; Nature v.243, No. 124, pp 29-30.

COSGROVE, M.E. 1972, The Geochemistry of the Potassium-rich Permian Volcanic Rocks of Devonshire, England: Contr. Mineral. Petrol v.36, pp 155-170.

COSGROVE, M.E. 1973, The Geochemistry and Mineralogy of the Permian Red Beds of South-West England: Chem. Geol. v.11, pp 31-47.

CURTIS, C.D. 1969, Trace Elements in some British Carboniferous Sediments: Geochm. et Cosmochim. Acta, v.33, pp 519-523.

DANA, E.S. 1966, A Textbook of Mineralogy, with an Extended Treatise on Crystallography and Physical Mineralogy: 4th Edition, Ford, W.E. Ed. Wiley, New York.

DAVIES, W.C. 1971, Regional Geochemistry of Stream Sediment Derived from an Area Underlain by the English Permo-Triassic: Unpubl. Ph.D. Thesis, University of London.

DEARMAN, W.R. 1959, The Structure of the Culm Measures at Meldon, near Okehampton, North Devon. Quat. J. Geol. Soc. v.115, pp 65-106.

DEARMAN, W.R. and BUTCHER, N.E. 1959, The Geology of the Devonian and Carboniferous Rocks of the North-West Border of the Dartmoor Granite, Devonshire. Proc. Geol. Assoc. v.70 pp 51-92.

DEARMAN, W.R. and EL SHARKAWI, M.A.H. 1965, A Newly Discovered Emanative Centre Associated with the Dartmoor Granite: Proc. Ussher Soc. v.1, pp 164-165.

DEARMAN, W.R. and EL SHARKAWI, M.A.H. 1965, The Relationship between Iron-Metsomatism and Emanative Centres on Dartmoor: Proc. Ussher Soc. v 1, pp 183-185.

DEER, W.A., HOWIE, R.A. and ZUSSMAN, J., Rock Forming Minerals: v.5, Longmans, London.

DEWEY, H. 1948, South-West England: 2nd Edition. Br. Reg. Geol., Geol. Surv. Mus. 72 pp.

DINES, H.G. 1934, Lateral Extent of Ore Shoots: Trans. Roy. Geol. Soc. Corn. v. 16, pp 279-296.

DINES, H.G. 1956, The Metalliferous Mining Region of South-West England: Mem. Geol. Surv. Great Britain, 2 vols. HMSO. London.

DRURY, S.A. 1972, The Chemistry of some Granitic Veins from the Lewisian of Coll and Tiree, Argyllshire, Scotland: Chem. Geol. v.9, 175-193.

DUNHAM, K.C., DUNHAM, A.C., HODGE, B.L. and JOHNSON, G.A.L. 1965, Granite Beneath Visean Sediments with Mineralisation at Rookhope, Northern Pennines: Quat. Journ. Geol. Soc. London, v.121, pp 383-417.

DUNLOP, A.C. 1973, Geochemical Dispersion of Tin in Stream Sediments and Soils in South-West England: Unpubl. Ph. D. Thesis, University of London.

EDMONDS, E.A., McKEOWN, M.C. and WILLIAMS, M. 1969, South-West England, 3rd Ed. British Regional Geology, 130 p. HMSO.

EDMONDS, E.A., WRIGHT, J.E., BEER, K.E., HAWKES, J.R. WILLIAMS, E.C., FRESHNEY, E.C. and FENNING, P.J. 1968, Geology of the Country around Okehampton: Mem. Geol. Surv. Great Britain, 256 pp.

EL SHARKAWI, M.A.H. and DEARMAN, W.R. 1966, Tin-bearing Skarns from the North-West Border of the Dartmoor Granite, Devonshire, England: Econ. Geol. v.61, pp 362-369.

EL SHAZLY, E.M., WEBB, J.S. and WILLIAMS, D. 1957, Trace Elements in Sphalerite, Galena and Associated Minerals from the British Isles: Ext. Trans. Inst. Min. Metall. v.66, pp 241-271 (1956-1957).

ELLIOT, I.L. 1962, Dispersion of Arsenic and Molybdenum in Surface Drainage, Sierra Leone: Unpubl. Ph. D. Thesis, University of London.

ELLIOT, J.E. and WELLS, J.D. 1968, Anomalous Concentrations of Gold, Silver and other Metals in the Mill Canyon Area, Cortez Quadrangle, Eureka and Lander Counties, Nevada:U.S. Geol. Surv. Circ. No. 606, 20 pp.

ERICKSON, R.L., MARRANZINO, A.P., UTEANA, O.D.A. and JANES, W.W. 1964, Geochemical Exploration near the Getchell Mine, Humboldt County, Nevada:U.S. Geol. Surv. Bull. v 1198-A: 26 pp.

ERICKSON, R.L., VAN SICKLE, G.H., NAKAGAWA, H.M., McCARTHY, J.H. and LEONG, K.W., 1966, Gold Geochemical Anomaly in the Cortez District, Nevada:U.S. Geol. Surv. Circ. 534, 3 pp.

ESSON, J., STEVENS, R.H. and VINCENT, E.A. 1965, Aspects of the Geochemistry of Arsenic and Antimony, Exemplified by the Skaergaard Intrusion: Min. Mag. v. 35 pp 88-107.

EXLEY, C.S. 1959, Magmatic Differentiation and Alteration in the St. Austell Granite: Quat. Geol. Soc. v 114, pp 197-230.

EXLEY, C.S. and STONE, M. 1964, The Granitic Rocks of South-West England: In Present Views of Some Aspects of the Geology of Cornwall and Devon, pp 121-184. Hosking, K.F.G. and Shrimpton, G.J. Eds. Royal Geol. Soc. of Cornwall, Penzance.

FEIGL, F. 1967, Qualitative Analysis by Spot Tests: Elsevier, N. Y.

FERSMAN, A. E., 1939, Arsenic. In: Geochemistry Vol. IV. Akad. Sci. USSR. Leningrad, pp 162-166.

FLOYD, P. A., 1972, Geochemistry, Origin and Tectonic Environment of the Basic and Acid Rocks of Cornubia, England: Proc. Geol. Ass. v 83, pp 385-404.

FITCH, A. A. 1932, Contact Metamorphism in South-Eastern Dartmoor: Quat. Geol. Soc. London, v 88, pp 576-609.

FLEISCHER, M. 1955, Minor Elements in Some Sulphide Minerals: Econ. Geol. 50 II, pp 970-1024.

FLETCHER, W. K. 1968, Geochemical Reconnaissance in Relation to Copper Deficiency in Livestock in the Pennines and Devon: Unpubl. Ph. D. Thesis, University of London.

FOUCH, K. F. and SMALES, A. A. 1967, The Distribution of Trace Elements in Chondritic Meteorites, (2) Antimony, Arsenic, Gold, Palladium and Rhenium: Chemical Geology, v. 2, pp 105-134.

FRESNEY, E. C., McKEOWN, M. C. and WILLIAMS, M. 1972, Geology of the Coast between Tintagel and Bude: Mem. Geol. Surv. Great Britain, HMSO.

FUGE, R. and POWER, G. M. 1969, Chlorine and Flourine in Granite Rocks from South-West England: Geochem. et Cosmochim. Acta. v. 33, pp 888-893.

GARRELS, R. M. 1944, Solubility of Metal Sulphides in Dilute Vein Forming Solutions: Econ. Geol. v. 39, pp 472-483.

GARRET, R. G. 1966, Regional Geochemical Reconnaissance of Eastern Sierra Leone: Unpubl. Ph. D. Thesis, University of London.

GINZBURG, I. L. 1960, Principles of Geochemical Prospecting (Techniques of Prospecting for Non-Ferrous Ores and Rare Metals): Pergamon Press, London.

GOLDSCHMIDT, V. M. 1937, The Principles of the Distribution of Chemical Elements in Minerals and Rocks: Jour. Chem. Soc. London, v. 1 pp 655-673.

GOLDSCHMIDT, V. M. 1954, Geochemistry: Alex Muir Ed. Oxford, Claredon Press.

GREEN, J. 1959, Geochemical Table of the Elements for 1959: Geol. Soc. Am. Bull. v. 70, pp 1127-1184.

GREEN, D. H. and RINGWOOD, A. E. 1967. The Genesis of Basaltic Magmas. Contr. Mineral and Petrol v. 15, pp 103-190.

HALL, W. E. 1971, Minor Element Contents of the Sulphide Minerals, Darwin Lead-Silver-Zinc Mine: Soc. Mining. Geol. Japon. Spec. Issue, No. 2 pp. 119-126.

HAMAGUCHI, H. ONUMA, N., HIRAO, Y., YOKOYAMA, H., BANDO, S., and FURUKAWA, M., 1969, The Abundances of Arsenic, Tin and Antimony in Chondritic Meoteorites: Geochm. et Cosmochim. Acta, v. 33 pp 507-518.

HARDEN, G. and TOOMS, J. S., 1965, Efficiency of the Potassium Bisulphate Fusion in Geochemical Analysis: Extr. Trans. Inst. Min. Metall. v. 74(3), 1964-1965, pp 129-141.

HARRIS, P. G. 1957, Zone Refining and the Origin of Potassic Basalts: Geochm. et Cosmochim. Acta. v. 12, pp 195-208.

HAWKES, H. E., and WEBB, J. S. 1962, Geochemistry in Mineral Exploration: Harper and Row, London.

HENLEY, R. W. 1973, Some Fluid Dynamics and Ore Genesis: Trans. Inst. Min. Metall. v. 82, pp B1-7.

HOLLAND, D. H. 1972, Granites, Solutions and Base Metal Deposits: Econ. Geol. v. 67 pp 281-301.

HORSNAIL, R. F., 1968, The significance of Some Regional Geochemical Patterns in Northwest and Southwest England: Unpubl. Ph. D. Thesis, University of London.

HOSKING, K. F. G., 1959, Applied Geochemistry, Studies in Cornwall: Trans. Roy. Geol. Soc. Cornwall, v. 19, pp 52-83.

HOSKING, K. F. G., 1964, Permo-Carboniferous and later Primary Mineralisation of Cornwall and South-West Devon: In Present Views of Some Aspects of the Geology of Cornwall and Devon, pp 201-245, Hosking, K. F. G. and Shrimpton, G. J. Eds., Royal Geol. Soc. of Cornwall, Penzance.

HOSKING, K. F. G., NAIK, S. M., BURN, R. G. and ONE, P. 1962, A Study on the Distribution of Tin, Tungsten, Arsenic and Copper in the Sediments and of the Total Heavy-Metals in Water of the Mehalhyl River, Mid-Cornwall: Camborne Sch. Mines Mag. v. 62, pp 49-59.

HOSKING, K.F.G. and OBIAL, R., 1966, A Preliminary Study of the Distribution of Certain Metals of Economic Interest in the Sediments and Waters of the Carrick Roads (West Cornwall) and of its Feeder Rivers: Camborne Sch. of Mines Mag. v.66, pp 17-37.

HOSKING, K.F.G., OLINZE, S.K., LEE, J.Y., MITCHEL, D., and MUGENYI, Y.H.K., 1965, A Reconnaissance Survey of the Distribution of Tin, Copper, Zinc and Arsenic in the Sediments of the Rivers to the South of the St. Austell Granite Mass, Cornwall: Camborne Sch. Mines Mag. v.65, pp 30-42.

HOWARTH, R.J. and LOWENSTEIN, P.L. 1971, Sampling Variability of Stream Sediments in Broad-Scale Regional Geochemical Reconnaissance: Trans. Inst. Min. Metall. v. 80, pp B363-372.

HOWARTH, R.J. 1971, Fortran IV Program for Grey-Level Mapping of Spatial Data: Math. Geol. 3, pp 95-121.

HOWARTH, R.J. 1971, Empirical Discriminant Classification of Regional Stream Sediment Geochemistry in Devon and East Cornwall: Trans. Inst. Min. Metall. v. 80, pp B142-149. Discussion: 81 : 115-119 (1972)

HOWARTH, R.J. 1972, The Pattern Recognition Problem in Applied Geochemistry: In Geochemical Exploration 1972 (London Institute of Mining and Metallurgy, 1973) pp 259-273 (Proc. 4th Int. Geochm. Expl. Symp. 1972).

HUTCHINS, P.F. 1963, The Lower New Red Sandstone of the Crediton Valley: Geol. Mag. v. 100 pp 149-163.

JAMES, C.H. 1957, Applied Geochemical Studies in Southern Rhodesia (I) Geochemical Dispersion Patterns Related to Arsenical and Antimonial Deposits in Southern Rhodesia: Geochm. Prospect. Res. Cont., Imperial College, London, Tech. Comm. 12, 237 pp.

JAMES, L.D., 1965, Regional Geochemical Reconnaissance in the Northern and Southern Sections of the Sula Mountains Schist Belt Sierra Leone. Unpubl. Ph.D. Thesis, University of London.

JENKINSON, S.D. 1968, A Tritrimetric Method for Determining Total Sulphur in Mineral Soils: Analyst, v.93, pp 535-539.

JONES, R.H.B., 1934, Temperature Relations to Ore Deposition: Econ. Geol. v.29, pp 711-724.

JOPLIN, G.A., 1964, The Shoshonitic Magma, The Near-undersatured Magma: In a Petrography of Australian Igneous Rocks, pp 90-111. Angus and Robertson Ltd. Sydney.

JOPLIN, G.A., 1968, The Shoshonitic Association: A Review J. Geol. Soc. Australia, v. 15 pp 275-294.

JOPLIN, G.A., KISS, E., WARE, N.G., and WIDDOWSON, J.R., 1972, Some Chemical Data on Members of the Shoshonite Association: Mineral Mag. v.38, pp 936-945.

KHALEELEE, J. 1969, The Application of Some Data Processing Techniques in the Interpretation of Geochemical Data: Unpubl. Ph.D. Thesis, University of London.

KINGSBURY, A.W.G., 1964, Some Minerals of Special Interest in South-West England: In Present Views of Some Aspects of the Geology of Cornwall and Devon, pp 247-266. Hosking, K.F.G. and Shrimpton, G.J. Eds., Royal Geol. Soc. of Cornwall, Penzance.

KOTHOFF, I.M. and SANDELL, E.B., 1952, Textbook of Quantitative Inorganic Analysis: Third Edition. The Macmillan Company New York 334 pp.

KRAUSKOPF, K.B., 1967, Introduction to Geochemistry, McGraw-Hill, New York.

LAMING, D.J.C., 1965, Age of the New Red Sandstones in South Devon: Nature, v.207, pp 624-625.

LEPELTIER, C. 1969, A Simplified Statistical Treatment of Geochemical Data by Graphical Representation: Econ. Geol. v.64, pp 538-550.

LEVINSON, A.A. 1974, Introduction to Exploration Geochemistry: Applied Publishing Ltd. Calgary.

MACLAUGHLIN, R.J.W., 1955, Geochemical Changes due to Weathering under Varying Climatic Conditions: Geochm. et Cosmochm. Acta. v.8 pp 109-130.

McCONNEL, D. 1970, Arsenic in Phosphorite and Apatite: Econ. Geol. v.65 pp 64-65 (Discussions).

MASKE, S. and SKINNER, B.J., 1971, Studies of the Sulfosalts of Copper, I. Phases and Phase Relations in the System Cu-A-S: Econ. Geol. v.66, pp 901-918.

MASON, B. 1966, Principles of Geochemistry: John Wiley, New York.

MATHER, A. L. 1959, Geochemical Prospecting Studies in Sierra Leone: Unpubl. Ph. D. Thesis, University of London.

MAXWELL, J. A. 1968, Rock and Mineral Analysis: 3rd Edition, Interscience Publishers, New York.

MAZZUCCHELLI, R. H. and JAMES, C. H. 1966, Arsenic as a Guide to Gold Mineralisation in Laterite - Covered Areas of Western Australia: Trans. Inst. Min. Metall. v. 75, pp B 286-294.

MENSCHUTKIN, N. 1903, Determination of Sulphur and Hydrogen Sulphide in Metallic Sulphides: Analytical Chemistry, MacMillan & Co. Ltd. Eds.

MILLMAN, A. P. 1957, Biochemical Investigations in Areas of Copper-Tin Mineralisation in South-West England, Geochm. et Cosmochim. Acta, v. 12 pp 85-93.

MORRIS, H. T. and LOVERING, T. S., 1952, Supergene and Hydrothermal Dispersion of Heavy Metals in Wallrocks near Orebodies, Tintic District, Etah: Econ. Geol. v. 47 pp 685-716.

MURTHY, A. R. V., NARAYAN, V. A. and RAO, M. R. A., 1956, Determination of Sulphide Sulphur in Minerals: Analyst, v. 81, pp 373-375.

MURTHY, A. R. V. and SHARADA, K. 1960, Determination of Sulphide Sulphur in Minerals: Analyst, v. 85, pp 299-300.

NEWMAN, E. and FOSTER, R. 1968, Internal Report on Direct Reading Spectograph. AGRG.

NICHOL, I. JAMES, L. D. and VIEWING, K. A., 1966, Regional Geochemical Reconnaissance in Sierra Leone: Trans. Inst. Min. Metall. v. 75 pp B146-61.

NICHOL, I., HORSNAIL, R. F. and WEBB, J. S. 1967, Geochemical Patterns in Stream Sediment Related to Precipitation of Manganese Oxides: Trans. Inst. Min. Metall. v. 76, pp B113-115.

NICHOL, I., GARRET, R. G. and WEBB, J. S., 1969, The Role of some Statistical and Mathematical Methods in the Interpretation of Regional Geochemical Data: Econ. Geol. v. 64 (2) pp 204-220.

NICHOL, I., THORNTON, I., WEBB, J.S., FLETCHER, W.K., HORSNAIL, R.F. and KHALEELEE, J., 1971, Regional Geochemical Reconnaissance of Part of Devon and North Cornwall: Inst. Geol. Sci. Report 71/2. 26 pp.

NOCKOLDS, S.R. and ALLEN, R. 1953, The Geochemistry of some Igneous Rocks Series: Geochm et Cosmochim Acta, v.4 pp 105-142.

ODMAN, O.H. 1950, Sver. Geol. Undersokn. Arsbok 44, (2), Ser.C. 516 pp 1-28.

OHMOTO, H., 1972, Systematics of Sulphur and Carbon Isotopos in Hydrothermal Ore Deposits: Econ. Geol. v.67, pp 551-578.

ONISHI, H. and SANDELL, E.B., 1955a, Geochemistry of Arsenic: Geochem et Cosmochim. Acta. v.7 pp 1-33.

ONISHI, H. 1970, Arsenic: In K.H. Wedepohl Ed., Handbook of Geochemistry II/1, Springer, Berlin 38 pp.

PHILLIPS, F.C. 1964, Metamorphism in South-West England: In Present Views of some Aspects of the Geology of Cornwall and Devon, pp 185-200, Hosking K.F.G. and Shrimpton, G.I. Eds. Royal Geol. Soc. of Cornwall, Penzance.

PHILLIPS, W.J. 1973, Mechanical Effects of Retrograde Boiling and its Probable Importance in the Formation of some Porphyry Ore Deposits: Trans. Inst. Min. Metall. v.82, pp B90-98.

PLANT, J. 1971, Orientation Studies on Stream Sediment Sampling for a Regional Geochemical Survey in Northern Scotland: Trans. Inst. Min. Metall. v.80, pp B324-345.

POUGH, F. 1970, A Field Guide to Rocks and Minerals: London Constable.

PRESANT, E.W., 1971, Geochemistry of Iron, Manganese, Lead, Copper, Zinc, Arsenic, Antimony, Silver, Tin and Cadmium in the Soils of the Bathurst Area, New Brunswick: Geol. Surv. Can. Bull v.174, 93 pp.

PRESANT, E.W. and TUPPER, W.M. 1966, The Distribution of Arsenic in the Soils of Bathurst Area, New Brunswick District: Econ. Geol. v.61, pp 760-767.

PRUDEN, G. and BLOOMFIELD, C., 1968, The Determination of Iron (II) Sulphide in Soil in the Presence of Iron (III) Oxide: Analyst, v.93 pp.

QUASTEL, J.H. and SCHOLEFIELD, P.G., 1953, Arsenite Oxidation: Soil Science, v.75 pp 279-287.

RADTKE, A.S., TAYLOR, C.M. and HEROPOULOS, C., 1973, Antimony-bearing Orpiment, Carlin Gold Deposits Nevada: Journal of Research, U.S. Geol. Surv. v.1 pp 85-87.

RAMDOHR, P. 1969, The Ore Minerals and their Intergrowths: Pergamon Press Oxford.

RANKAMA, K. and SAMAMA, Th. G. 1950, Geochemistry, Univ. Chicago Press, Chicago Ill. 912 pp.

RAYMENT, B.D., DAVIS, G.R. and WILSON, J.D. 1971, Controls to Mineralisation at Wheal Jane, Cornwall: Trans. Inst. Min. Metall. v. 80, pp B224-237.

REED, B.L. and ELLIOT, R.L., 1968, Geochemical Anomalies and Metalliferous Deposits between Windy Fork and Post River South Alaska Range: U.S. Geol. Surv. Circ. 569, 22 pp.

REED, B.L. and MILLER, R.L. 1971, Orientation Geochemical Survey al Nixon Fork Mines, Medfra Quadrangle, Alaska: U.S. Geol. Surv. Bull. v.1312-K, 21 pp.

RINGWOOD, A.E., 1955, The Principles Governing Trace Element Behaviour during Magmatic Crystallisation: Geochem et Cosmochim. Acta, v.7, Part I pp 189-202, Part II, pp 242-254.

RIVALENTI, G. and SIGHINOLFI, G.P., 1971, Geochemistry and Differentiation Phenomena in Basic Dykes of the Frederikshab District South West Greenland: Grønlands Geol. Unders., Miscellaneous Papers, v.96, pp 358-380.

ROBSON, J. 1964, The Cornish 'Greenstones': In Present Views of some Aspects of the Geology of Cornwall and Devon, pp 115-130, Hosking K.F.G. and Shrimpton, G.I. Eds., Royal Geol. Soc. Cornwall Penzance.

RODGERS, T. 1957, Geology and Mineralisation of the Phoenix Mine, Southern Rhodesia, Unpubl. Ph.D. Thesis, University of London.

SAULL, V.A., 1958, Chemical Energy and Metamorphism: Geochm. et Cosmochim, Act, v8, pp 86-107.

SEN, N. 1959, Trace-Element in Minerals from Rocks of the South California Batholith: Geochm. et Cosmochim. Acta, v 16, pp 58-78.

SEN GUPTA, J.G. 1963, Determination of Microgram Amounts of Total Sulphur in Rocks: Analytical Chemistry, v 35, pp 1971-73.

SHAPIRO, L. 1973, Rapid Determination of Sulphur in Rocks: Journal Research, U.S. Geol. Surv. v1, pp 81-84.

SHNYUKOV, E.F. 1963, Arsenic in the Cimmeriam Iron Ores of the Azov-Black Sea Region: Geochemistry, v 1 pp 87-98.

SHORT, N.M. 1961, Geochemical Variation in Four Residual Soils: J. Geol. v 69, pp 534-571.

SHOULDS, M.M., RADULL, A.P. and RUGHEIM, M.E.H. 1968, A Study of the Distribution of Five Heavy Elements in the Streams Draining the Bodmin Granite: Camborne Sch. Mines Mag. v 68, pp 20-29.

SKINNER, B.J. 1965, The System Arsenic-Antimony: Econ. Geol. v.60, pp 228-239.

SMITH, F.G. 1954, Composition of Vein-Forming Fluids from Inclusion Data: Econ. Geology, v.49, pp 205-210.

SMITH, F.G. and MUTCH, A.D., 1950, Origin of the 'Ephythermal' Mineral Deposits: A Discussion: Econ. Geol. v.45, pp 701-703.

SMITH, F.G., PEACH, P.A., SCOTT, A.S., MUTCH, A.D., SPRINGER, G.D., BOYLE, R.W., and OGDEN, W.H.M. 1950, 'Pneumatolysis' and the Liquid Inclusion Method of Geologic Thermometry: A Discussion: Econ. Geol. v.45, pp 582-587.

SNELL, F.D. and SNELL, C.T., 1949, Colorimetric Methods of Analysis Including Some Turbidimetric and Nephelometric Methods: Third Edition, V.II, Van Nostrand Regional Offices, New York, 950 pp.

SØRENSEN, H. Ed. 1974, The Alkaline Rocks: A Wiley-Interscience Publication, London, 622 pp.

SPEARS, D.A. 1965, Chemical Logging of Strata from Boreholes: The Oil and Gas Journal.

STATON, R.E., 1946, The Field Determination of Arsenic in Soils and Sediments: Econ. Geol. v.59, pp 1599-1602.

SWIANE, D.J. and MITCHELL, R.L. 1960, Trace Elements Distribution in Soil Profiles: J. Soil Sci. v.11, pp 347-368.

TAUSON, L.V., 1965, Factors in the Distribution of the Trace Elements during the Crystallisation of Magmas: Physics and Chemistry of the Earth, v.6, pp 215-249, Aherens Press Runcornurey, Eds.

TAUSON, L.V. 1967, Geochemical Behaviour of Rare Elements during Crystallisation and Differentiation of Granitic Magmas: Geochm. Int. v.4, pp 1067-1075

TAYLOR, R.S. 1965, The Application of Trace Elements Data to Problems in Petrology: Physics and Chemistry of the Earth, v.6 pp 133-214, Aherens Press Runcornurey Eds.

TENNANT, C.B. and WHITE, M.L., 1959, Study of the Distribution of some Geochemical Data: Econ. Geol. v.54, pp 1281-1290.

THEODORE, T.G. and ROBERTS, R.J. 1971, Geochemistry and Geology of Deep Drill Holes at Iron Canyon, Lander County, Nevada: US Geol. Surv. Bull, v.1318, 32 pp.

THOMPSON, M. and HOWARTH, R.J. 1973, The Rapid Estimation and Control of Precision by Duplicate Determinations: The Analyst, v.98, pp 153-160.

TIDMARSH, W.G. 1932, The Permian Lavas of Devon: Quat. J. Geol. Soc. v.738, pp 712-73.

TISCHENDORF, G. 1973, The Metallogenetic Basis of Tin Exploration in the Erzgebirge: Trans. Inst. Min. Metall. v. 82, pp 9-24.

TOLL, R.W., 1953, Arsenic in West Devon and East Cornwall: Mining Mag. v.89, pp 83-88.

TOOMS, J.S., ELLIOT, I. and MATHER, A.L. 1965, Secondary Dispersion of Molybdenum from Mineralisation, Sierra Leone: Econ. Geol. v.60, pp 1478-1496.

TUREKIAN and WEDEPOHL, 1961, Distribution of the Elements in some Major Units of the Earth's Crust: Geol. Soc. Am. Bull, v.72, 175 pp.

URQUIDI-BARRAU, F. 1973, Regional Element Distribution in Stream Sediments in Wales in Relation to Mineral Exploration, Unpubl. Ph.D. Thesis, University of London.

VERHOOGEN, J. 1948, Inst. Parks Nat. Congo Belge, Exploration Parc. Nat. Albert. Missions J. Verhoogen (1938-1940).

VIEWING, K.A. 1963, Regional Geochemical Patterns Related to Mineralisation in Central Sierra Leone: Unpubl. Ph.D. Thesis, University of London.

VLISIDIS, A.C., 1966, The Determination of Sulfate and Sulfide Sulfur in Rocks or Minerals: US Geol. Surv. Bull, v.1214, pp D1-5.

WARREN, V.H., DELAVAUL, R.E. and BARASKO, J. 1964, The Role of Arsenic as a Pathfinder in Biochemical Prospecting: Econ. Geol. v.59, pp 1381-1389.

WEBB, J.S. 1947, The origin of the Tin Lodes of Cornwall: Unpubl. Ph.D. Thesis, University of London.

WEBB, J.S. 1958, Observations on the Geology and Origin of the San Domingo Pyrite Deposit, Portugal: Direccao Gen. Minas, Servicos Geologicos, Tomo 42, pp 129-143.

WEDEPOHL, K.H. 1971, Geochemistry: Holt Rinehart and Winston, London.

WELLS, J.D. and MULLENS, T.E. 1973, Gold-Bearing Arsenian Pyrite Determined by Microprobe Analysis, Cortez and Carlin Gold Mines, Nevada, Econ. Geol. v.68, pp 187-201.

WHITTAKER, E.J.W. and MUNTUS, R. 1979, Ionic Radii Use in Geochemistry: Geoch. et Cosmochim. Acta, v.34, pp 945-956.

WILSON, A.D., SERGEANT, G.A. and LIONNEL, L.J. 1963, The Determination of Total Sulphur in Silicate Rocks by Wet Oxidation: Analyst. v.88, pp 138-141.

WILSON, I.R. 1972, Wall-Rock Alteration at Geevor Tin Mine: Extract Proc. Ussher Soc. v.2, pp 425-434.

YERMAKOV, N.P., 1965, Studies of Mineral-Forming Solutions, In Research on the Nature of Mineral-Forming Solutions, International Series of Monographs, Earth Sciences, v.22, Pergamon Press. Inc.

YOUNG, R.D. 1971, The Interpretation of Regional Geochemical Patterns in Northern Ireland: Unpubl. Ph.D. Thesis, University of London.

ZIES, E.G., 1938, The Concentration of the Less Familiar Elements through Igneous and Related Activity: Geophysical Lab. No. 988, pp 386-404, Cornegie Inst. of Washington.

APPENDIX I

DETERMINATION OF SULPHUR IN SULPHIDE BEARING-ROCKS AND MINERALS

1 INTRODUCTION

Scientific literature abounds with methods for determining the presence of sulphur in sulphide, some of the most important of which are summarised below.

Sulphide sulphur has been routinely detected by oxidation of the sulphide to the corresponding sulphate, and subsequently precipitated as barium sulphate. In this analysis decomposition of the sample can be made by wet oxidation with reagents such as aqua regia, fuming nitric acid, etc., or by fusion with an alkaline oxidising agent such as sodium peroxide (Kothoff and Sandell, 1952).

Vlisidis (1966) analysed sulphate and sulphide sulphur in rocks and minerals, converting the sulphate sulphur to barium sulphate by digesting the sample with an acidified solution of barium chloride while cadmium chloride was used to precipitate the sulphide sulphur.

The wet oxidation method was used by Wilson et al. (1963) to separate total sulphur from silicate rocks, in which, according to Maxwell (1968) sulphur is low and usually occurs in the form of pyrite and pyrrhotite. For detecting sulphur in pyrite they used a combination of aqua regia with hydroflouric acid and perchloric acid.

In a method described by Murthy and co-workers (1956, 1960) the mineral sulphide is reduced by hydriodic acid to hydrogen sulphide which is swept into a suspension of cadmium hydroxide, the sulphide thus being determined iodimetrically. By this means galena and sphalerite were dissolved satisfactorily. Through the use of a more concentrated solution of hydriodic acid in addition to small mercury pellets they succeeded in dissolving sulphides such as pyrite, chalcopyrite, realgar and orpiment.

Smith et al. (1964) used a similar reduction for the analysis of sulphide sulphur in pyrites, reducing the pyrite sulphur to sulphide by the LAH (lithium aluminium hydroxide) treatment. The hydrogen sulphide evolved by acidification was determined by filtration of the free acid formed in a neutral cadmium sulphate absorbing solution.

Snell and Snell (1949) determined sulphide sulphur by the stain produced by it on lead acetate-impregnated paper. The sulphur is evolved by reaction of sulphur-free metal with hydrochloric acid and causes a stain of varying length on a lead acetate-strip paper.

The various analytical methods for the analysis of sulphur in sulphide-bearing rocks are not commonly used in geochemical exploration because they are relatively slow and demand a certain level of skill and frequently require extensive equipment. These requisites become particularly cumbersome when dealing with a large number of samples.

During the laboratory phase of the present research, a new, swifter, simplified technique for the determination of sulphide sulphur in rocks and minerals has been developed. The method is a rapid semi-quantitative, colorimetric technique adapted to the determination of sulphide sulphur in the geochemical analysis of rock samples. The technique (an approach related to the Gutzeit method for arsenic) consists of the reduction of sulphide sulphur from the sample in a hydrochloric acid medium in the presence of sulphur free metal (zinc or aluminium) and of a small quantity of metallic chromium powder. The metal reacts with the hydrochloric acid to give hydrogen which in its nascent state reduces the sulphide sulphur to form hydrogen sulphide. The hydrogen sulphide thus formed is passed through a narrow glass tube of standard bore containing silica powder impregnated with lead acetate, and reacts with the lead acetate to give a black stain of lead sulphate. The length of the stained silica produced will therefore depend on the content of sulphur liberated from the sample. The addition of metallic chromium powder makes the reactivity of the attacking solution towards the sulphide much

higher and particularly assures the reduction of sulphide sulphur in the sample (Professor A. J. E. Welch, pers. com.). According to Welch (who resorted to the studies of Radmacher and Mohrhauer, 1953 for his information), the chromium reacts with the acid to give a strong reducing chromous (Cr^{2+})ion in solution, and the reduced state of the chromium is maintained by the zinc/acid interaction. By this means the solution phase (not just the metal/acid interphase) is kept effectively reducing.

2 PROCEDURE

a) Apparatus

The method only requires the basic apparatus (Fig. 1) of a test tube (16 x 150 mm) to which a narrow glass tube of 4 mm internal diameter and 12 cm length (containing precipitated silica powder impregnated in lead acetate) is connected by a rubber bung. The lead acetate-silica powder (prepared as described below) is placed in the tube as follows:-

i) Place a wisp of cotton-wool in the lower end of the glass tube;

ii) Put into the tube a small amount of pure silica powder. Using a stirring rod press down the powder trying to get a uniform surface.

iii) Put into the glass tube 200 mg of the lead acetate-silica powder, which is obtained by saturation of the pure precipitated silica with lead acetate solution. Place the tube in a vibrator and leave for about 15 minutes or till the powder becomes compact.

iv) Place a wisp of cotton-wool in the upper end of the tube to avoid blowing the powder out by action of the pressure of the gas.

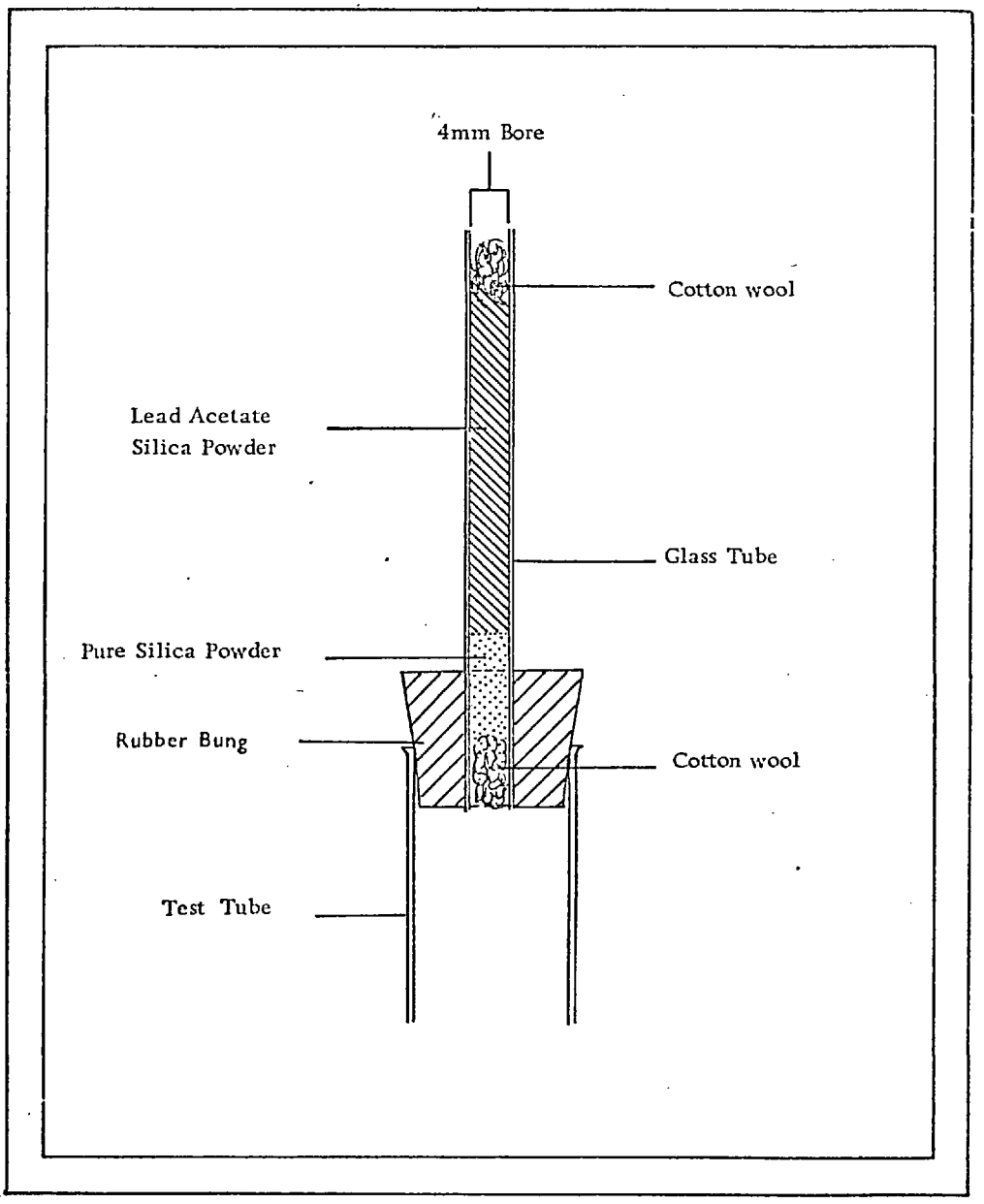


Fig. 1 APPARATUS FOR SULPHUR DETERMINATION
(not to scale)

b) Preparation of Reagents

3M Hydrochloric acid: mix 300 ml of acid (sp. gr. 18 AR) with 800 ml of water.

10% Cadmium sulphide: mix 1 g. of synthetic CdS with 9 g. of pure precipitated silica powder.

Lead acetate solution: dissolve 15 g. of the tri-hydrate in 100 ml of water containing 1 ml of glacial acetic acid.

c) Calibration

i) Weigh out 0.5, 1, 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 50, 60, 70, 80, 90 and 100 mg. of 10% Cadmium sulphide into numbered test tubes.

ii) Treat as indicated in section (d) below (analytical procedures).

iii) Calculation of sulphur content in ppm:

$$22.2 \times (\text{mg } 10\% \text{ CdS})$$

Use the length of the black stained silica powder as standards for the calculation of S content in the sample.

d) Analytical Procedures

Weigh out 0.25 g. of sample ground to pass a 80 mesh sieve (nominal aperture of 0.204mm) into a borosilicate test tube (16 x 150 mm). Add 10 ml of 3M HCl and zinc pellets in large size grains (5 g. approximately) together with a small amount of metallic chromium powder (50 mg.). Immediately fit the glass tube containing the lead acetate-silica powder onto the test tube with a rubber bung. Leave for 30 minutes then place the apparatus in a warm (50°C) sand-tray and leave for a further 15 minutes. Remove the glass tube and compare the length of the black stained silica powder with the artificial standards (above). If the stain is greater than the top standard take a lesser amount of sample.

The range covered is 90 to 8880 ppm for 250 mg. of sample. It may be increased to 44,400 ppm by using 50 mg samples. For values lower than 90 ppm make up standards using 1% CdS.

Calculation of sulphur content in ppm (250 mg sample)

$$\frac{4 \times 22.2 \times (\text{mg of matching standard})}{}$$

e) Evaluation of the Method

As the method involves solution of sulphide in HCl, and as it is well known that the response of sulphide minerals to the acid attack is varied (and in many cases nil), the solubility of 15 common sulphides was tested in concentrated and dilute (3 and 6M) HCl. Subsequently these minerals were analysed by the new method.

The sulphide specimens of British origin were in part, kindly supplied by the Geological Department at the Imperial College, and part were collected by the author in lodes from Cornwall and Devon. Each sulphide sample was carefully examined under a binocular microscope in order to separate other minerals that might be associated in the ore. The samples were ground in an agate mortar to pass an 80 mesh (0.204 mm) sieve. One gram of the powder was thoroughly mixed (on a roller mixer) with nine grams of silica powder, then analysed in batches of five samples of different weights. Rock samples were analysed in the same way as the sulphides in order to determine the more adequate sample weight for further analysis. Any residue was meticulously washed and re-analysed with the purpose of discovering whether or not the reduction of the sulphide sulphur was complete. As a result of these analyses it was found that:

a) the technique is effective for the analysis of a few sulphide minerals whilst others such as arsenic sulphides remained insoluble;

b) in rock samples the attack is more effective in 250 mg weight when the sulphide content is moderate.

For high sulphide-bearing samples 100 mg is recommended. In sum, the method was found suitable for the semi-quantitative analysis of pyrrhotite, marcasite, sphalerite, galena, pyrite and chalcopyrite. The results of these analyses are presented in Tables 1.1 and 1.2.

TABLE 1.1

SULPHUR CONTENT IN COMMON SULPHIDES

(Average of 5 Sulphide Samples)

Sulphide	Compositional Formula	Sulphur Sulphide (%)	Ideal Content* (%)
Argentite	Ag_2S	5.0	12.9
Galena	PbS	12.0	13.0
Bismuthinite	Bi_2S_3	11.10	18.8
Arsenopyrite	FeAsS	Tr.	19.7
Grennockite	CdS	Nil	22.2
Stibinite	Sb_2S_3	14.65	28.6
Realgar	AsS	Nil	29.9
Stannite	$CuFeSnS_4$	1.12	29.9
Sphalerite	ZnS	27.8	33.0
Chalcopyrite	$CuFeS_2$	31.1	35.0
Orpiment	As_2S_3	Nil	39.0
Pyrrhotite	Fe_7S_8	41.4	39.6
Molybdenite	MoS_2	Nil	40.0
Marcasite	FeS_2	50.2	53.4
Pyrite	FeS_2	46.8	53.4

*Data from Dana's Manual of Mineralogy (Dana, E.S., 1966, 4th Ed.)

TABLE 1.2

SULPHUR IN SULPHIDE-BEARING ROCKS

(Apparent Sulphur Content in ppm)

Sample: Rock Size Fraction: -80 mesh Reaction Time: 45 minutes

I = First Analysis II = Second Analysis (First residue) III = Third Analysis (Second Residue)

	0.100 grams			0.250 grams			0.500 grams		
	I	II	III	I	II	III	I	II	III
1596	6540	288	9	5228	888	44	3558	2664	333
1643	110	Tr.	Nil	115	Nil	Nil	118	22	Nil
1650	3330	188	8	2664	888	22	2220	1776	133
1657	333	8	Nil	330	44	Nil	355	88	Tr.
1660	89	Nil	Nil	85	Nil	Nil	133	9	Tr.
1667	22200	660	33	7600	5520	664	3800	3300	1770
1689	76	Nil	Nil	80	Nil	Nil	115	22	Tr.
1742	2886	88	Nil	1776	888	44	2218	888	133
1743	222	Nil	Nil	222	Nil	Nil	222	88	9
1748	7740	288	22	6216	1776	288	4228	3330	888
1774	1338	44	Tr.	1046	333	88	976	444	177
1776	Nil	Tr.	Nil	17	Nil	Nil	26	Nil	Nil
1789	76	Nil	Nil	96	Nil	Nil	88	40	Tr.
1790	89	Nil	Nil	112	Nil	Nil	122	9	Nil
1792	45	Nil	Nil	76	Nil	Nil	88	9	Nil
1837	9768	222	44	7104	2888	355	3216	3560	888
1838	222	Tr.	Nil	266	8	Nil	283	88	Tr.
1880	2220	88	Tr.	1953	288	22	1774	444	88
1889	2664	22	Tr.	2040	888	110	2218	888	97
1891	6660	133	Nil	5228	1976	177	4440	3550	330
1893	7770	222	Tr.	6482	1976	288	4440	3560	888

APPENDIX II

POLDICE MINE-BORE HOLE LOG

(C. T. & M. C., Hole C-51)

From	To	Rock Type	Description
0'	77' 0"		Open hole, no core recovered.
77' 0"	126' 0"	Killas	Brick red coloured shales. Red colour is imposed supergene alteration on light grey-green uniformly well bedded, cherty shale. Bedding mostly folded with axial planes at roughly 45° to core axis.
126'0"	126'3"	Vein	Quartz-chlorite vein at 45° to core axis. No visible mineralisation.
126'3"	149'0"	Killas	As above. Variagated red staining.
149'0"	176'0"	Vein	Several stringers of white quartz follow core. About 75% vein material in killas.
176'0"	200'0"	Killas	Medium grey shale with mottled red staining, occasional quartz stringers. Bedding at various dip angles, some cut by a cleavage at 40° to core.
200'0"	201'10"	Vein	Quartz-chlorite
201'10"	204' 6"	Killas	As above
204' 6"	206' 3"	Vein	Quartz-chlorite with ½" wide stringer containing arsenopyrite.
206' 3"	228' 0"	Killas	Red stained, silty shale. Fairly consistent bedding at about 40° to core axis. Axial planes of minor folds cut core at about 30°.
228' 0"	359' 8"		Light grey shale with well redeveloped spotting of sizes. Some lit-par-lit quartz. Very light coloured sections might be slightly kaolinised. From 237'3" to 240'0", 1'0" core recovered. Traces of chalcopyrite in quartz stringer. At 251'0", core size reduced from NQ to BQ. At 325'0", 1" quartz chlorite stringers with traces of pyrite, sphalerite and chalcopyrite. Quartz-chalcopyrite veins from 341'4" to 341'10", 334'8" to 345'1".
359' 8"	365' 0"	Vein	Massive white quartz. Killas band from 358'2" to 362'2".
365' 0"	452' 0"	Killas	As above. Interbedded light and dark grey shale. Bedding at about 45° to core axis. Spotting of various sizes irregularly developed.

From	To	Rock Type	Description
452' 0"	459' 0"	Greenstone	Massive, fine grained basic igneous rock. Upper and lower contacts at about 40° to core axis.
459' 0"	506' 0"	Killas	Well spotted, interbedded light and dark grey shales. Quartz stringer at 469' has traces of chalcopyrite and sphalerite. At 491'1", ½" stringer of massive galena, sphalerite and chalcopyrite.
506' 0"	511' 7"	Vein	Quartz and brecciated, silicified shale. Traces of chalcopyrite. Some chloritisation. Hole possibly follows vein. Walls are indistinct.
511' 0"	572' 6"	Killas	Finely interbedded light and dark grey shales with some chocolate brown in places. Irregular spotting throughout. No consistent bedding dip. Quartz veins and stringers throughout.
572' 6"	572'10"	Vein	Many sub-angular shale fragments less than ½" diameter in quartz-light brown matrix + epidote.
572'10"	624' 0"	Killas	Finely interbedded shales mainly light and dark grey but with irregular chocolate interbedded sections. Spasmodic quartz veining, associated with pyrite. ½" vein at 582'7" cutting core at 45° contains minor sphalerite and chalcopyrite. Whole length irregularly spotted.
624' 0"	629' 0"	Killas	Finely interbedded chocolate and light grey shales. Contorted but with bedding generally at 30° to core axis.
629' 1"	630' 3"	Greenstone	Fine grained with bottom contact at 35° to core axis.
630' 3"	642' 0"	Killas	Finely interbedded.
642' 0"	655' 0"	Greenstone	Bottom contact at 45° to core axis.
655' 0"	658' 0"	Killas	Finely interbedded fawn and grey shales and quartz. Planes at 45° to core axis.
658' 0"	659' 0"	Vein	Coarse grained schorl. Contains minor pyrite. Bottom contact 30° to core axis.
659' 0"	660' 9"	Vein	White quartz containing chocolate quartz tourmaline breccia.
661' 9"	675' 8"	Killas	Finely interbedded and spotted light grey and chocolate shales. Contains 10% interbedded quartz. Sporadic spotting. Much contorted.
675' 8"	677'10"	Vein	Schorl. Top contact 20° bottom 10° to axis. Contains several hair-thick veinlets of arsenopyrite which is also evident at contact. Top contact also has bunches of radiating brown tourmaline crystals in white quartz veinlet.

From	To	Rock Type	Description
677'10"	681' 9"	Killas	Interbedded fawn and light grey shales. Much folded with -$\frac{1}{4}$" quartz intrustions.
681' 9"	689' 0"	Vein	Schorl. Top contact 5° to core axis. Bottom 20° bounded by arsenopyrite quartz with chunks of solid brown tourmaline at top and bottom. From 683'0" to 683'6" is quartz and brown tourmaline bounded killas.
689' 0"	706' 5"	Killas	Finely interbedded chocolate and light and dark grey shales with occasional lit-par-lit quartz sheared at 45° to core axis. Occasional minor pyrite and sphalerite.
706' 5"	707' 5"	Vein	Schorl. Top contact against brown tourmalinised shale and white quartz stringers is at 30°. Bottom contact at 45°.
707' 5"	708' 9"	Vein	Green flourite with quartz and minor chalcopyrite.
708' 9"	709' 5"		Schorl. Bottom contact 30° to core axis.
709' 5"	712'10"	Killas	Much disturbed chocolate and grey shale with much quartz and minor pyrite.
712'10"	714' 2"	Vein	Fine grained schorl. Top contact 30°, borrom curved from 20° to 10°.
714 2"	715' 0"	Killas	Disturbed green and brown shales and quartz.
715' 0"	717' 6"	Vein	White quartz with 5% green chlorite associated with minor chalcopyrite and arsenopyrite. More abundant fine arsenopyrite with 1" of bottom content which is at 45° to core axis.
717' 6"	746' 6"	Killas	Interbedded green-grey and dark grey shales with occasional quartz veins containing minor arsenopyrite and less frequent chalcopyrite.
746' 6"	749'10"	Greenstone	Very fine grained and spotted.
749'10"	808' 3"	Killas	Finely interbedded light and dark grey shales. Silicified and containing fine lit-par-lit quartz. Much contorted in many sections but bedding and occasional shear generally at 45° to core axis. White quartz vein from 760'6" to 770'0" at 45° to core axis. White quartz vein from 770'8" to 771'3" contains minor pyrite and chlorite. White quartz vein from 773'9" to 776'0" which has rolling 10° top contact and 30° bottom contact contains minor chalcopyrite and pyrite. Small $\frac{1}{4}$" contorted, white fluorite vein at 806'6".
808' 3"	811' 7"	Vein	White quartz containing $\frac{1}{4}$" blades of wolfram, chalcopyrite, arsenopyrite, white and green fluorite and much chlorite. Top contact 45° bottom not distinct.

From	To	Rock Type	Description
811' 7"	852' 9"	Killas	Finely interbedded, hard, light and dark grey shales. Sporadic spotting and occasional minor chalcopyrite. Jointing at 30° to core axis.
852' 9"	853' 2"	Vein	Quartz with minor sphalerite and chalcopyrite at 30° to core axis.
853' 2"	917' 7"	Killas	Intensely spotted, hard phyllite, no consistent dip. Numerous minor folds have axial planes dipping at 60° to core axis.
917' 7"	918' 4"	Granite	Two dykes of fine grained granite separated by 2" of killas dipping at 40° to core axis.
918' 4"	930' 6"	Killas	As above.
930' 6"	951' 4	Granite	Muscovite-tourmaline granite. Several segregations of coarse tourmaline near contact. Contact dips at roughly 50-60° to core axis. Granite becomes progressively coarser in depth.