

THE IGNEOUS HORIZONS OF THE SOUTH PENNINE OREFIELD
AND THEIR INTERACTIONS WITH MINERALIZATION

by

Stephen Geoffrey Walters B.Sc., A.M.I.M.M., F.G.S.

Thesis submitted in fulfilment
of the requirements for the
Degree of Doctor of Philosophy

DEPARTMENT OF GEOLOGY
UNIVERSITY OF SHEFFIELD

OCTOBER 1981

Therefore a miner, since we think he ought to be a good and serious man, should not make use of an enchanted twig, because if he is prudent and skilled in the natural signs, he understands that a forked stick is of no use to him, for as I have said before, there are the natural indications of veins which he can see for himself without the help of twigs.

De Re Metallica, Georgius Agricola 1556.

(from translation by Hoover and Hoover, 1912)

SUMMARY

Over forty igneous horizons of Dinantian age are recorded. The major Lavas occur as 'scutulum-type' shields reaching diameters of 10 km and thicknesses of 1-200 m with central vents marked by boss-like tuff cones. Subordinate pyroclastic intercalations and discrete cones represent phraeatomagmatic interactions but extrusive activity was predominantly subaerial. 'Clay-wayboards' also associated with emergent surfaces, represent air-fall ash of distal, acidic, origin, but also include local degraded tuffs.

The basalts display a restricted petrography and all are microphyric with olivine, augite and labradorite. Eight petrographic types based on phenocryst assemblage and textures are defined. Selection criteria were developed to avoid weathered or hydrothermally altered samples although deuteric affects are ubiquitous. Despite their phyric-nature, geochemical variations encompass well defined trends. Geochemical evolution was controlled by restricted eutectic fractionation in a periodically replenished magma chamber. The basalts are of a 'transitional' nature between typical alkali or tholeiitic types.

The basalts are not 'barren' with regard to mineralisation but fundamental changes in the style of mineralisation within basalt hosts are noted. Hydrothermal interactions result in zoned wall-rock alteration the development of which correlates with the attainment of wall-rock diffusion equilibrium, while geochemical variations correspond with fluid-inclusion data.

K-Ar isotopic dating indicate complex relationships, with devitrification and smectite replacement of interstitial phases resulting in systematic argon loss. Samples yielding true stratigraphic ages can

only be selected on an empirical basis. Deuteric smectite phases persist during incipient hydrothermal alteration and exert an older 'contaminating' influence resulting in a spread of 'apparent' ages. This is negated during 'advanced' alteration reflecting in relative potassium saturations and resolves the spread of ages into two distinct mineralising events at 240 ± 5 m.y. and 170 ± 5 m.y. These correlate with widespread episodes of Mesozoic mineralisation in the United Kingdom.

The Sills and Lavas are consanguineous, it is envisaged that replenishment of a number of shallow magma chambers was accompanied by ascensive injections of magma which in places reached the surface as extrusive lavas, but elsewhere formed high-level Sills often localised by intrusion along the 'line of weakness' afforded by older Lava interfaces.

ACKNOWLEDGEMENTS

This research project was carried out with the tenure of a Natural Environment Research Council/CASE Award with N.C.C. Minerals Ltd.

Numerous individuals in the Department of Geology at the University of Sheffield provided invaluable assistance throughout its duration, in particular the guidance of Dr. R. Kanaris-Sotiriou, Dr. F.G.F. Gibb and Mr. S. Reynolds concerning the application of X-ray Fluorescence, Electron Microprobe and Atomic Absorption analytical techniques are acknowledged.

Dr. N.J.D. Butcher of Dresser Minerals International Inc. allowed access to unpublished borehole logs and provided core sampling facilities and his continued enthusiasm and helpful discussions are greatly appreciated.

Dr. J.G. Mitchell at the School of Physics, University of Newcastle undertook K-Ar isotopic age determinations and his critical comments and advice on aspects of the dating technique are acknowledged. Dr. R.A. Ixer at the University of Aston is thanked for discussions concerning reflected light (ore) microscopy.

Numerous friends provided assistance in the field during the initial stages of research, in particular H.A. Armstrong and A.V. Bristow assisted with underground mapping and sampling in adverse conditions.

The following individuals and institutions allowed access to unpublished borehole information and sampling facilities: Mr. I.P. Stevenson (Institute of Geological Sciences), Dr. P.H. Dagger (ICI - Mond Division), Mr. J. Hedges (Laporte Industries Ltd.), Dr. D.P. Jefferson (Blue Circle Technical) Mr. R. Simons (Tarmac Roadstone Ltd.), and the Severn Trent Water Authority.

This research project was carried out under the supervision of Dr. P.R. Ineson without whose continued support, enthusiasm, critical comments and patient reading of the manuscript it would not have been possible.

CONTENTS

	<u>Page</u>
<u>CHAPTER ONE</u>	
<u>Historical Review and Scope of Proposed Research</u>	1
1:1 Introduction	1
1:2 Historical Review	1
1:3 Aims of the Present Research	4
<u>CHAPTER TWO</u>	
<u>Analytical Techniques</u>	5
2:1 Grinding	5
2:2 'Wet Chemistry'	5
2:3 X-ray Fluorescence Spectrometry	6
2:4 Electron Microprobe Analyses	6
2:5 Atomic Absorption Spectrophotometry	6
2:6 Accuracy and Precision of A.A. Techniques	10
2:7 X-ray Diffraction	11
2:8 Petrological Techniques	
<u>CHAPTER THREE</u>	
<u>Stratigraphy, Distribution and Styles of Igneous Activity</u>	13
3:1 Stratigraphy and Distribution	13
3:2 Styles of Extrusive Activity	13
3:3 Styles of Pyroclastic Activity	17
3:4 The Paleoenvironment of Vulcanicity	19
3:5 Igneous Activity in the South Pennine Orefield in its Regional Context	21
<u>CHAPTER FOUR</u>	
<u>Mineralogy of the Basalts and Dolerites</u>	23
4:1 Introduction	23
4:2 Plagioclase Feldspars	23
4:3 Pyroxenes	25
4:4 Olivines	30
4:5 Olivine Alteration	32

4:6	Interstitial Alteration Phases	37
4:7	Opaque and Minor Phases	38
4:8	The Status of 'Chlorites'	40
4:9	Mineralogical Evidence for the Magmatic Affinities of the Derbyshire Basalts	41
<u>CHAPTER FIVE</u>	<u>Petrography of the Basalts</u>	42
5:1	Introduction	42
5:2	Petrographic Types	42
5:3	Petrographic Variations within Lavas	46
<u>CHAPTER SIX</u>	<u>Selection of Unaltered Basalts - Petrographic Selection Criteria</u>	51
6:1	Sampling Criteria	51
6:2	Petrographic Criteria	51
6:3	Constraints on the Validity of the Geochemical Data	53
6:4	Iron Oxidation Ratios	53
6:5	CIPW Norm Calculations and Readjustments	55
6:6	A Weathering Index	56
<u>CHAPTER SEVEN</u>	<u>Geochemistry of the Basalts</u>	58
7:1	Readjustments and Fractionation Index	58
7:2	Major Element Variations	59
7:3	Low Pressure Fractionation	61
7:4	Trace and Minor Element Variations	64
7:5	A Model for the Magmatic Evolution of the Basalts	67
7:6	Relationships between Geochemistry and Stratigraphy	70
7:7	Geochemical Evidence for the Validity of the Major and Trace Element Results	72
7:8	Comparisons with the Duffield Sill	74

	<u>Page</u>
<u>CHAPTER EIGHT</u>	
<u>Nomenclature and Magmatic Affinities of the Derbyshire Basalts</u>	80
8:1 Introduction	80
8:2 The Concept of Magma Series	80
8:3 A Normative Classification of the Derbyshire Basalts	82
8:4 Discrimination Based on 'Immobile' Trace Elements	83
 <u>CHAPTER NINE</u>	
<u>Geochemistry, Mineralogy and Origin of Wall-Rock Alteration in Basalts</u>	85
9:1 Introduction	85
9:2 Mineralisation and Wall-Rock Alteration in Basalts	85
9:3 Selection of Sampling Localities and Presentation of Geochemical Data	86
9:4 Locality and Sampling Details	87
9:5 Geochemistry and Mineralogy of Hydrothermal Alteration	90
9:6 Previous Geochemical Research	98
9:7 Geochemical Variation and Hydrothermal Zonation	100
9:8 Geochemical Interactions between Hydrothermal Fluids and Wall-Rock Alteration	103
9:9 Geochemistry of Mississippi Valley Type Hydrothermal Brines and Specific Wall-Rock Interactions	106
9:10 Hydrothermal Versus Deuteric Alteration	111
9:11 Alteration of the Ible Sill	113
 <u>CHAPTER TEN</u>	
<u>Occurrence, Geochemistry and Mineralogy of 'Toadstone Clays'</u>	118
10:1 Introduction and Previous Research	118
10:2 Sampling Localities	119
10:3 Geochemistry and Mineralogy	120
10:4 The Origin of the Toadstone Clays	123
10:5 Comparisons of Toadstone Clay and Wall-Rock Alterations within Basalts	125

<u>CHAPTER ELEVEN</u>	<u>Geochemistry and Mineralogy of 'Clay-Wayboards - Geochemical Evidence for their Derivation</u>	127
	11:1 Nature and Occurrence of Wayboards	127
	11:2 Origin of Bentonites	128
	11:3 Possible Source Area for the Clay-Wayboards	129
	11:4 Comparisons of the Distribution Patterns of Recent Ash Falls with Clay-Wayboards	131
	11:5 The Application of Geochemistry to the Study of Volcanic Ash	135
	11:6 Objectives of the Present Study	136
	11:7 Mineralogy of the Clay Wayboards	137
	11:8 Application of Geochemical 'Fingerprinting' to the Study of Carboniferous K-Bentonites and Tonsteins	142
	11:9 Summary and Application of the Geochemical Results and Suggestions for Future Research	147
<u>CHAPTER TWELVE</u>	<u>K-Ar Isotopic Age Determinations</u>	149
	12:1 Introduction and Analytical Techniques	149
	12:2 Dating of Unaltered Basalts	150
	12:3 Dating of Hydrothermally Altered Basalts	155
	12:4 Discussion and Interpretation of Results	158
	12:5 South Pennine Mineralisation in a Regional Chronological Context	162
<u>REFERENCES</u>		164
<u>APPENDICES</u>		
<u>APPENDIX ONE</u>	<u>Atomic Absorption and XRF Major Element Data</u>	188
	1:A Atomic Absorption Major and Trace Element Analyses	188
	1:B XRF Major Element Analyses	

		<u>Page</u>
<u>APPENDIX TWO</u>	<u>XRF Trace Element Data</u>	198
<u>APPENDIX THREE</u>	<u>CIPW Norms</u>	202
<u>APPENDIX FOUR</u>	<u>Modal Analyses of 'Fresh' Basalts</u>	206
<u>APPENDIX FIVE</u>	<u>Sample Location Details</u>	208
<u>APPENDIX SIX</u>	<u>Electron Microprobe Data</u>	222
	6:A Plagioclases	222
	6:B Pyroxenes	224
	6:C Olivines	227
<u>APPENDIX SEVEN</u>	<u>Detailed Borehole Core 'Lithologs' and Abridged Borehole Logs</u>	228
<u>APPENDIX EIGHT</u>	<u>Black Hillock or Clear-The-Way Mine, Tideswell Moor (Bull. Peak Dist. Mines Hist. Soc., 7, 327-332, 1980)</u>	
<u>APPENDIX NINE</u>	<u>Mineralisation within the Igneous Rocks of the South Pennine Orefield (Bull. Peak Dist. Mines Hist. Soc. 7, 315-325, 1980)</u>	
<u>APPENDIX TEN</u>	<u>The Geology of Hallicar Wood Adit, Via Gellia, Derbyshire. (Bull. Peak Dist. Mines Hist. Soc. 7, 353-356, 1980)</u>	
<u>APPENDIX TWELVE</u>	<u>A Review of the Distribution and Correlation of Igneous Rocks in Derbyshire, England. (Mercian Geol., 8, 81-132)</u>	
<u>APPENDIX THIRTEEN</u>	<u>Geochemistry and Petrology of the Water-swallows Sill.</u>	

LIST OF FIGURES

Facing Page

3.1	General Map of the Igneous Horizons in the Matlock-Wirksworth-Ashover-Crich Area	13
3.2	General Map of the Igneous Horizons in the Alport-Bakewell-Taddington Dale Area	13
3.3	General Map of the Igneous Horizons in the Buxton-Tideswell-Castleton Area	13
3.4	General Map of the Igneous Horizons in the Eyam-Longstone-Litton Area	13
3.5	Simplified Summary of the Volcanic Stratigraphy of the South Pennine Orefield	13
3.6	Height-Diameter Relationships of Basaltic Shields	14
3.7	Internal Structures of the Cressbrook Dale and Haddonfields Lower Lavas	14
3.8	Internal Structures of the Millers Dale Lower Lava, Tunstead Boreholes 21 and 22	14
4.1	Compositional Variations of Zoned Phenocryst and Groundmass Plagioclase	25
4.2	CaO-MgO-FeO Plot of Clinopyroxene Analyses	27
4.3	SiO ₂ versus Al ₂ O ₃ Discriminant Diagram for Pyroxene Magma Types	30
4.4	Triangular Plot of TiO ₂ -MnO-Na ₂ O for Discriminating between Pyroxenes from Different Magma Types	30
7.1	Major Element Geochemical Variations versus Solidification Index	60
7.2	Three-Phase Phenocryst Extract Triangles	61
7.3	TiO ₂ and Y versus Zr	64
7.4	Trace Element Variations versus Zirconium	64
7.5	Nickel and Chrome Variations versus Modal Olivine	65
7.6	Volcanic Stratigraphy of the South Pennine Orefield Indicating the Relationships between the Main Sampled Lava Horizons	70

7.7	'Average' Trace and Minor Element Geochemical Variations	71
7.8	Rb and K ₂ O Variations versus H ₂ O ⁺	73
7.9	A Comparison of the CaO-MgO-FeO Pyroxene Compositions of the Duffield Sill with the South Pennine Basalts	76
7.10	A Comparison of the MnO-TiO ₂ -Na ₂ O Pyroxene Compositions of the Duffield Sill with the South Pennine Basalts	76
7.11	A Comparison of the Major Element Geochemical Variations versus Solidification Index of the Duffield Sill and South Pennine Basalts	77
7.12	Ni and Cr Variations in the Duffield Sill and South Pennine Basalts	78
8.1	Zr versus P ₂ O ₅ and TiO ₂ versus Zr/P ₂ O ₅ Discriminant Magma Type Plots for the South Pennine Basalts	83
9.1	Geochemical Variations - Hallicar Wood Adit	91
9.2	Geochemical Variations - Conksbury No.5 Borehole	93
9.3	Geochemical Variations - Maury Adit	95
9.4	Geochemical Variations - Mogshaw No. 3 Borehole	97
9.5	Diagrammatic Representation of the Relationship between Hydrothermal Diffusion Gradient and Wall Rock Alteration Magnesium Concentrations	110
9.6	Relationships between Wall Rock Zoned Alteration and Hydrothermal Diffusion Equilibrium	110
9.7	Geological Sketch Map of the Ible Sill, Via Gellia	113
10.1	Geochemical Variations - Lower Toadstone Clay Sequence of the Millers Dale Lower Lava, Tunstead No.21 Borehole	120
10.2	Geochemical Variations - Upper Toadstone Clay Sequence of the Conksbury Bridge Lava, Haddonfield No. 11 Borehole	121

10.3	Geochemical Variations - Upper Toadstone Clay Sequence of the Millers Dale Lower Lava, White Rake Opencast	121
10.4	Geochemical Variations - Toadstone Clay Alteration of the Matlock Lower Lava, Hoptonwood Quarries	122
11.1	Distribution Patterns of Recent Volcanic Ash Fall Deposits	133
11.2	Trace Element Location and Postulated Behaviour during Diagenetic Alteration, Supra-Wyrley Yard Tonstein	143
11.3	TiO ₂ -Zr-Al ₂ O ₃ Geochemistry of Wayboards, Lavas, Tuffs and Sediments	145
11.4	TiO ₂ -Al ₂ O ₃ -K ₂ O Geochemistry of Wayboards, Lavas, Tuffs and Sediments	145
11.5	TiO ₂ -Y-Zr Geochemistry of Wayboards, Lavas, Tuffs and Sediments	145
11.6	TiO ₂ -Al ₂ O ₃ -P ₂ O ₅ Geochemistry of Wayboards, Lavas, Tuffs and Sediments	145
11.7	TiO ₂ -V-Zr Geochemistry of Wayboards, Lavas, Tuffs and Sediments	145
12.1	Whole Rock K ₂ O% versus K-Ar Age	155
12.2	Theoretical K-Ar Age Profiles	157
12.3	A Comparison of Theoretical and Observed K-Ar Age Profiles	157

LIST OF TABLES

		<u>Facing Page</u>
2.1	XRF Instrumental Settings	6
2.2	Operating Conditions for Rb, Sr, Y and Zr	6
2.3	Operating Conditions for Pb and Ba	6
2.4	Operating Conditions for Zn, Cu, Ni, Co, Mn, Cr and V	6
2.5	Replicate XRF Analyses	6
2.6	Replicate Microprobe Analyses	6
2.7	Operating Conditions for Atomic Absorption	8
2.8	Atomic Absorption Major Element Results	10
2.9	Atomic Absorption Minor and Trace Element Results	10
2.10	Recommended Values for International Standards	10
2.11	XRD Operating Conditions	11
4.1	XRD Results of Clay Alteration Products	35
4.2	Chemical Analyses of Smectite Alteration Products in Basalts	35
4.3	Analyses of Vesicle and Vein Infilling Alteration Phases in Basalts	37
6.1	The Effect of Oxidation State on Normative Values	55
6.2	Weathering Index Values for 'Fresh' Derbyshire Basalts	56
7.1	'Average' Corrected Trace and Minor Element Concentrations	70
7.2	Geochemistry and petrology of the Duffield Sill	74

Facing Page

9.1	Comparisons of Actual and Recalculated Immobile Element Concentrations Relative to Constant TiO_2	86
9.2	Clay Mineralogy of Hydrothermally Altered Basalts	97
9.3	Geochemistry of Alteration, Ible Sill	115
11.1	XRD Analysis of Clay Wayboards	138
12.1	K-Ar Dating Results	153
12.2	K-Ar Dating Results for Whole Rock Chips and Tema Ground Samples	153

LIST OF PLATES

- 1.1 Waterswallows Sill. Lower Horizon - Waterswallows Quarry.
- 1.2 Millers Dale Upper Lava. Wham Sough Dig - Taddington.
- 1.3 Tunstead North Dyke. Buxton Bridge, Great Rocks Dale.
- 1.4 Basalt Petrographic Types.
- 1.5 Basalt Petrographic Types.
- 1.6 Petrographic Variations in Intrusive Dolerites.
- 1.7 Textural Variations, Waterswallows Sill - Waterswallows Quarry.
- 1.8 Tuffs, Agglomerates and Autobreccias.
- 1.9 Pyroclastic Photomicrographs.
- 1.10 Pyroclastic Photomicrographs.

- 2.1 Interstitial Phases and Secondary Alteration Products.
- 2.2 Interstitial Phases and Olivine Alteration Products.
- 2.3 Ilmenite and Titanomagnetite Opaque Phases.

- 3.1 Sulphide Textures, Altered Shacklow Wood Lava - Mogshaw No. 3 Borehole.
- 3.2 Opaque Phases - Hydrothermally Altered Lavas.
- 3.3 Hydrothermal Alteration of Fe-Ti Oxides.
- 3.4 Hydrothermal Alteration, Shacklow Wood Lava - Mogshaw No. 3 Borehole and Conksbury Bridge Lava - Conksbury No. 5 Borehole.
- 3.5 Altered Potluck Sill Dolerite, Black Hillock Mine Dump and Millers Dale Upper Lava, Maury Mine Dumps.
- 3.6 Alteration of the Ible Sill, Ible Quarry.

FRONTISPIECES

Outcrop distribution of the igneous horizons of the south Pennine Orefield.

Watts Shaft - 'Old' Millclose Mine about 1874. The southernmost workings of Millclose Mine penetrated the Matlock Upper Lava (18 m thick in Watts Shaft).

Sample Preparation techniques - a composite of all stages from crushing to fused discs for XRF.

Massive limestones of the Upper Asbian Millers Dale Beds with dark staining overlying the Millers Dale Lower Lava, Ravenstor in Millers Dale.

Spectacular columnar structure in the 'lower horizon' of the Waterswallows Sill, Waterswallows Quarry.

Photomicrograph of the Waterswallows dolerite, Waterswallows Quarry - see explanation to Plate 1.1 for further details.

Large block of the Millers Dale Lower Lava, Waterswallows Quarry. The veined and partly amygdaloidal basalt represents material 'unsuitable' for analysis.

River Wye, flowing over the Millers Dale Lower Lava in Millers Dale. Scattered outcrops of basalt occur in the banks with more extensive exposures located in road cuttings above the bank to the right.

Lathkill Dale above Conksbury Bridge, numerous exposures of the Conksbury Bridge Lava are located in the steep bank side left of centre.

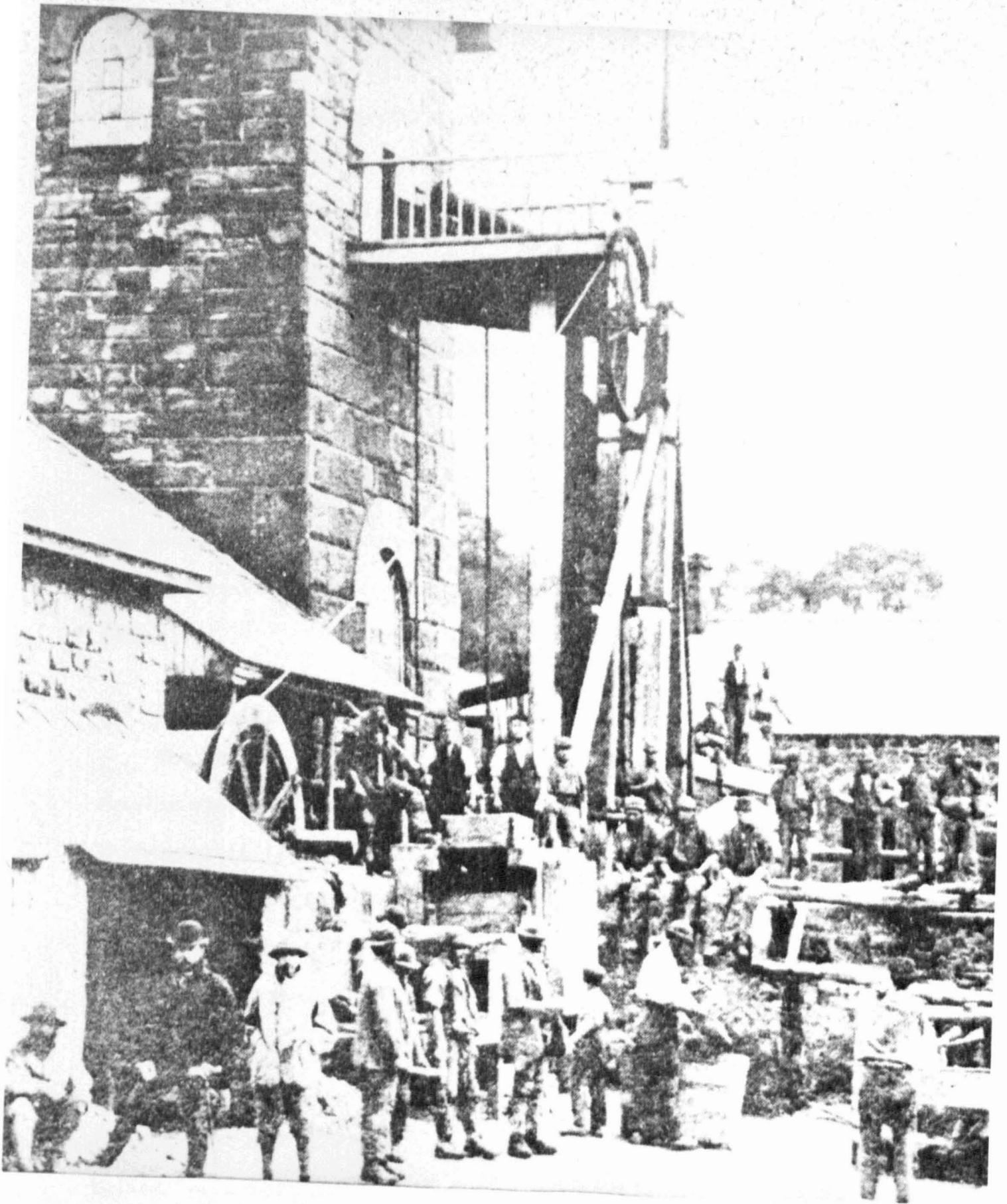
The present-day remains of Watts Shaft Engine House, Old Millclose Mine.

Millers Dale Lower Lava, upper toadstone clay sequence - White Rake Opencast on Tideswell Moor. Typical example of the overgrown and weathered nature of the majority of basalt exposures. Bleached toadstone clay is visible in excavated section right of centre.

Prominent clay-wayboard horizons in massive Lower Asbian Hoptonwood Limestones, Ben Bennet's Quarry - Via Gellia.

Columnar structure in the Waterswallows Sill 'Lower Horizon', Waterswallows Quarry.

CHAPTER ONE



Chapter One

Historical Review and Scope of Proposed Research

1:1 Introduction

The most comprehensive study of the igneous rocks of the south Pennine orefield was published by Bemrose (1894,1907). Subsequently; and despite advances in stratigraphic correlation, new information concerning the distribution of the Lava, Tuffs and Sills and the development of sophisticated analytical techniques; no complete synthesis of their distribution, petrography or geochemistry has been forthcoming.

Recent contributions (e.g. Ixer, 1972) have been restricted in scope in that they concentrated on petrographic aspects of a limited number of lavas or dolerites. It is proposed that the majority of the previously available geochemical analyses are invalid as these were undertaken on material which had been subjected to complex alterations.

1:2 Historical Review

The basaltic horizons within the Dinantian limestones of the south Pennine orefield were noted by a number of 18th and 19th century geologists: Whitehurst (1778), Pilkington (1789), Watson (1811) and Farey (1811), amongst others. Bemrose's accounts (1894, 1899, 1907, 1910) under the stimulus of Geikie (1897), have remained the most authoritative account of the petrography and field relationships of the lavas, tuffs and sills.

The geochemistry of the basalts was first noted by Sargent (1917) who proposed a 'primary spilitic' magma type to account for the unusual, alkali-rich, nature shown by certain basalts. The complex relationships between extrusive basalts, tuffs and intrusive dolerite, at Calton Hill

Quarry, were described by Tomkeieff (1928) who included petrographic descriptions and chemical analyses of the various rock types. Cope (1933) noted an olivine-dolerite dyke at Buxton Bridge as 'tholeiitic' with olivine and augite phenocrysts.

The extensive workings of Millclose Mine (Traill, 1939, 1940; Shirley, 1950) indicated a greater complexity of volcanic stratigraphy than previously thought, and intersected seven major lava horizons, five unrepresented at outcrop. Boreholes in the Ashover area (Ramsbottom et al., 1962) proved a thick and variable sequence of tuffs, lavas and breccias with limestone intercalations. Detailed petrographic descriptions and geochemical analyses were given but unfortunately all material was highly altered. More recent geochemical and outcrop details of the Ashover Tuff were reported by Kelman (1980).

The Millers Dale Upper and Lower Lavas were examined by Malki (1967) who included petrographic descriptions and major element analyses of nine samples. Five of these, representing the Lower Lava, were of vesicular and altered basalts. The remaining samples, from the Upper Lava, represent unaltered material. Mantle derived, lherzolitic, nodules associated with the intrusive dolerite at Calton Hill were described by Hamad (1963) and Donaldson (1978).

The distribution and stratigraphy of igneous horizons within the northern area of the Orefield were described by Stevenson and Gaunt (1971) in which the extensive subsurface development of the Cressbrook Dale Lava was recognised. Petrographic descriptions and chemical analyses of the Waterswallows Sill and a further dyke south of Buxton Bridge were also included. In the Castleton area, the disputed Speedwell 'vent' (Wilkinson, 1967), was re-interpreted as a littoral cone by Chesire and Bell (1977).

Smith et al. (1967) reviewed the petrography and distribution of lavas and sills in the Matlock area. In a detailed geochemical study of the mineralisation at Masson Hill, Ixer (1972) included six major and trace element analyses of the altered Matlock Upper Lava and two analyses of unaltered dolerite from the Bonsall Sill. The altered, tuffaceous, top of the Matlock Upper Lava intersected in the Tansley borehole was described by Amin (1980).

K-Ar dating of the basalts and dolerites (Fitch et al., 1970) indicated that they had undergone complex post-crystallisation hydrothermal events. The attendant alteration phases were used to date the mineralising episodes by Ineson and Mitchell (1973).

The influence of the igneous horizons in the 'channelling' of mineralising fluids and the localisation of orebodies was noted by Traill (1940), Shirley (1950) and Ford (1977) amongst others. The interaction between hydrothermal fluids and the basalts resulted in clay-rich wall rock alteration aureoles. Although these were noted by Garnett (1923), Walkden (1972) and Ixer (1972), they have received minimal geochemical attention.

Thus, prior to this study, there was no synthesis available of the stratigraphy and distribution of the igneous horizon, their geochemical interaction with mineralisation had not been studied in detail and although the petrography of the lavas had been described by numerous authors the geochemistry of the basalts had received minimal attention. Forty-one major element analyses were available, representing twenty lavas, seven dolerites, two dykes, two basaltic breccias and ten tuffs. Of the twenty lava analyses, only four - all from the Millers Dale Upper Lava - can be regarded as representing 'unaltered' material. Of the eighteen trace element analyses available six were from tuffs or breccias, four from dolerite sills and dykes and eight from lavas. There were no

trace element analyses for 'unaltered' lavas. The majority of attention had been concentrated on the Ashover volcanics, and the Millers Dale and Matlock Upper and Lower Lavas. The less well exposed, but equally as extensive, horizons such as the Cressbrook Dale Lava or the Shacklow Wood Lava had received either minimal attention or none at all.

1:3 Aims of the Present Research

The research project had a threefold primary objective:

- (1) To produce a thorough compilation of the stratigraphy and distribution of the igneous horizons and to reconstruct the palaeogeographical environment of vulcanicity. This would incorporate information from numerous unpublished exploration boreholes, obtained by close collaboration with the mineral extractive companies active in the Orefield.
- (2) To study the petrography, petrology and geochemistry of the major lava horizons and sills. It was anticipated that by sampling from borehole cores and developing strict selection criteria, the complex alterations which invalidated the majority of previously available analyses could be overcome. It was also intended to classify the magmatic affinities of the basalts in terms of either a tholeiitic or alkali-olivine parentage.
- (3) To characterise the mineralogy and geochemistry of wall-rock alteration aureoles. Sampling from underground exposures and borehole cores would enable variations in geochemistry and mineralogy to be spatially related to mineralisation.

It was anticipated that resulting from the detailed studies of 'fresh' basalts and their various alterations, a programme of K-Ar dating would further elucidate the relationships of the varied alteration types and their associated phases.

CHAPTER TWO



Chapter Two

Analytical Techniques

2:1 Grinding

Samples selected for analysis were crushed in a roll-jaw crusher, if weathering rinds were observed these were initially removed with a rock-splitting vice. The selection of 'unveined' chips was undertaken between the crushing and the grinding stages in the case of 'fresh' basalts, but no attempt was made at this stage to separate the strongly veined, mineralised samples. The chips were coned and quartered and subsequently fine ground in a TemaDisc Mill. Samples for XRF trace element analysis were further ground, until the resultant material had a grain size of approximately 20 μ . The powders were coned and quartered to give a sample of approximately 100 grms which was stored in airtight polythene bottles.

2:2 'Wet Chemistry'

FeO, H₂O⁺, H₂O⁻, CO₂ and Na₂O were analysed by wet-chemical methods as a precursor to both XRF and Atomic Absorption analysis. H₂O⁻ was determined by weight loss after drying at 110°C for four hours. H₂O⁺ was calculated as the difference between the 'total water' value obtained by the 'Penfield Tube Method' and %H₂O⁻. Na₂O was analysed using atomic absorption spectrophotometric techniques after H₂SO₄/HF decomposition, FeO% analyses used an H₂SO₄/HF decomposition followed by solution in boric acid and titration with potassium dichromate. Acidified sodium diphenylamine sulphonate was used as the indicator. CO₂ was calculated by the weight absorbed on 'soda-asbestos' after being evolved with hot phosphoric acid.

Table 2.1

TABLE 2.1
XRF Instrumental Settings

Element	Angle 2 θ ^o	Crystal	Collimeter	Counter Employed	Counting Time (Seconds)	Kv mA
K	50.60	PE*	Fine	Flow	10	60 24
Fe	57.46	LiF**	Fine	Flow	10	60 24
Mn	62.95	LiF	Fine	Scintillation	100	60 32
S	75.80	PE	Coarse	Flow	100	60 32
Ti	86.13	LiF	Fine	Flow	10	40 24
P	89.51	PE	Coarse	Flow	100	60 32
Si	109.17	PE	Coarse	Flow	40	60 32
Ca	113.13	LiF	Fine	Flow	10	40 16
Mg	136.60	ADP**	Coarse	Flow	100	60 32
Al	145.20	PE	Coarse	Flow	40	60 32

*PE = Pentaerythritol $2d = 8.742 \text{ \AA}$, reflection plane (002)

**Lif = Lithium fluoride $2d = 4.028 \text{ \AA}$, reflection plane (200)

**ADP = Ammonium dihydrogen phosphate $2d = 10.648 \text{ \AA}$, reflection plane (1

TABLE 2.2

Operating Conditions for Rb, Sr, Y and Zr

Common Conditions:		W tube - 60 kV 32 mA, fine collimator, spinner, vacuum EXT window, LiF (220) - (1,1), Scintillation counter									
$2\theta^{\circ}$		31.00	32.10	33.20	33.91	34.62	34.90	35.85	36.80	37.97	39.14
Line		Bgd.	Zrk $_{\alpha}$	Bgd.	Yk $_{\alpha}$	Bdg.	Bdg.	Srk $_{\alpha}$	Bgd.	Rbk $_{\alpha}$	Bgd.
Counting Time (seconds)		20	100	20	100	20	20	100	20	100	20
Standard Total Counts		47.00	56.00	38.00	515.00	32.00	30.00	450.00	23.00	370.00	17.00

Table 2.2

TABLE 2.3

Operating Condition for Pb and Ba

Common Conditions:	W tube - 60 kV 32 mA, fine collimator, spinner, vacuum					
$2\theta^\circ$	33.00	33.92	34.50	126.82	128.82	130.82
Line	Bgd	PbL $_{\alpha}$	Bgd.	Bgd.	BaL β_1	Bgd.
Counting Time (seconds)	20	100	20	20	100	20
	Flow + Scint.			Flow		
	3.5 LL	3.00W			EXT Window	
	LiF (200) - (3-1)			LiF (220) - (1-1)		
Standard Total Counts	160.00	1080.00	105.00	4.00	98.00	4.00

TABLE 2.4

Operating Conditions for Zn and Cu

Common Conditions:	W tube - 60 kV 32 mA, fine collimator, spinner, vacuum EXT window, LiF (220) - (1,1), Flow Counter			
$2\theta^\circ$	59.20	60.53	65.50	68.75
Line	Bgd.	Znk α	Cuk α	Bgd.
Counting Time (seconds)	20	100	100	20
Standard Total Counts	48.00	1650.00	925.00	35.00

TABLE 2.4 (cont)
Operating Condition for Ni, Co, Mn, Cr and V

Common Conditions: W tube - 60 kV 32 mA, fine collimator, spinner, vacuum
 EXT window, LiF (220), Flow counter

$2\theta^\circ$	70.00	71.20	75.18	77.85	93.00	95.11	105.50	107.10	120.50	123.23	124.00
Line	Bgd.	Ni α	Bgd	Co α	Bgd	Mn α	Bgd	Cr α	Bgd	V α	Ti β
Counting Time (seconds)	20	100	20	100	20	20	20	100	20	100	20
Standard Total Counts	32.00	1025.00	25.00	930.00	12.00	108.00	8.00	520.00	4.00	360.00	15.00

Table 2.4

Table 2.5

TABLE 2.5: Replicate XRF Analyses

Sample 32-ED3				
	1	2	3	
SiO ₂	45.63	45.62	45.60	
TiO ₂	1.74	1.74	1.74	
Al ₂ O ₃	14.00	14.00	13.99	
Fe ₂ O ₃ (total Fe)	11.34	11.30	11.28	
MnO	0.10	0.10	0.08	
MgO	10.11	10.20	10.26	
CaO	7.11	7.10	7.10	
Na ₂ O	2.11	2.11	2.11*	
K ₂ O	0.85	0.84	0.84	
H ₂ O [±]	7.02	7.02	7.02*	
CO ₂	B.D.	B.D.	B.D.	
SO ₃	0.10	0.07	0.07	
P ₂ O ₅	0.30	0.30	0.29	
Total	100.41	100.40	100.37	4
Ba	237	240	254	
Co	85	80	77	
Cr	384	386	383	
Cu	40	43	43	
Ni	210	209	210	
Pb	5	B.D.	B.D.	6
Rb	16	16	13	17
Sr	340	340	336	336
V	189	191	189	
Y	23	25	26	19
Zn	115	112	112	116
Zr	120	121	124	124

*Average wet-chemical determination

Analysis 4 average duplicate determination provided by the University of Leicester Geology Dept.

TABLE 2.6: Replicate Microprobe Analyses

Synthetic Anorthite (An 90)				
	Recommended Value*		Observed Values	
SiO ₂	45.6	46.4	45.6	45.8
Al ₂ O ₃	35.0	35.0	34.8	34.9
FeO	-	0.1	0.1	0.1
CaO	18.3	18.2	18.6	18.2
Na ₂ O	1.1	1.1	1.1	1.1
K ₂ O	-	-	-	-
% An.	90	90	90	90
Standard Augite				
	Recommended Ranges*		Observed Values	
Na ₂ O	1.27- 1.32		1.36	1.34
MgO	16.0 -16.6		15.8	15.7
Al ₂ O ₃	7.9 - 8.7		8.3	8.4
SiO ₂	50.1 -50.7		50.6	50.6
CaO	15.8 -16.3		16.3	16.3
TiO ₂	0.8 - 0.9		0.8	0.8
Cr ₂ O ₃	0.14		0.17	0.17
MnO	0.13		0.14	0.11
FeO	6.3 - 6.8		6.5	6.5

*Gibb - pers. comm.

2:3 X-Ray Fluorescence Spectrometry (XRF)

Sample preparation, prior to XRF analysis, followed the methods of Norrish and Hutton (1969). Major element analyses were performed on fused glass discs using lithium metaborate flux and sodium nitrate as the oxidising agent. The International Geochemical Standard BCR-1 (Columbian River Basalt) was used as the internal standard for calibration. Trace elements were determined using the fine-ground powder (20 μ) pressed onto a boric acid backing. Major element, mass absorption corrections were performed using a computer program developed within the Department. Operating conditions for major and minor element analyses programs and details of replicate analyses are given in Tables 2.1, 2.2, 2.3, 2.4 and 2.5.

2:4 Electron Microprobe Analyses

Major element compositions of pyroxenes, plagioclase, olivine and olivine pseudomorphs were studied using a Cambridge Instruments Microscan 9 electron microprobe. Samples were prepared as graphite coated, polished thin sections approximately 40 microns thick. The results of replicate analyses of standard materials is given in Table 2.6.

2:5 Atomic Absorption Spectrophotometry (AA)

The strongly altered and mineralised samples representing alteration aureoles adjacent to mineral veins, presented special analytical difficulties. The routine XRF procedures outlined earlier could not be utilised for the analyses of these specimens due to a number of factors. These were highlighted during a pilot XRF study of five altered samples:

- (a) High carbonate and water contents produced erratic fusion losses due to rapid degassing, often involving some actual sample loss.

- (b) High contents of sulphides (especially pyrite) resulted in the failure of the oxidising agent to fully decompose the material, the weight of the oxidising agent was 'fixed' and incorporated into the computer correction programs. The presence of reduced iron, together with high Zn and Pb contents also resulted in severe Platinum alloy crucible etching.
- (c) Assuming no sample losses during fusion, low totals may also be attributed to the presence of fluorite not detected by XRF analysis.

The only practical method to achieve reliable 'totals' would be to undertake duplicate or triplicate analyses on these samples, involving a considerable waste of analytical time and money. It was decided, therefore to develop a rapid AA technique for the partial analyses of these samples.

Fusion techniques, employing a lithium metaborate flux followed by dissolution of the fused material, have been reported to be an efficient and accurate method of decomposition for a wide range of silicates (see Shapiro, 1967; Van Loon and Parissis, 1969; Boar and Ingram, 1970). However, there is no consensus as to the optimum condition of fusion and analysis, such as flux-sample ratios, duration of fusion, method of dissolution and AA analytical procedures. Hence, all variables were determined experimentally to establish optimum conditions for the particular samples intended for analysis.

The fusion technique arrived at was similar to that outlined by Shapiro (1967) and Swanson (1969), in using a sample:flux ratio of 6:1. This value is also in the range recommended by Ingamells (1970) of between 5:2-7:1. As platinum attack may take place by reduced iron, as experienced in XRF fusion procedures and also reported by Butler and Kokot (1969) an excess of oxidising agent (ammonium metavanadate) was added.

0.200 grms of sample, 1.200 grms of flux and 0.040 grms of oxidising agent were thoroughly mixed with a platinum rod in a platinum crucible prior to fusion in a muffle furnace at 950°C. Reported fusion times vary widely, however, 15 mins. was found to be sufficient. The crucible and melt were removed from the furnace, reheated over a 'meeker' burner to 'white heat' and the melt quenched in distilled water. The use of platinum-rhodium-iridium alloy crucibles minimised melt retention which occurred if pure platinum crucibles were employed.

To ensure a minimal sample loss, all the crucibles were quenched (together with the fusion) in a beaker containing approximately 100 ml of distilled water acidified with 10 ml. of conc. HCl. Dissolution times were directly related to the efficiency of stirring and varied from 45 mins. to 2 hours. The resulting clear solution (with a pale yellow tinge) was made up to 200 ml, transferred to polypropylene bottles and stored in a cool, dark area.*

A series of 'stock solutions' were prepared by dilution methods to produce element concentrations within the optimum working range of the AA (see Table 2.7). A 1:10 dilution for K, Na and Mg and a 1:50 dilution for Ca and Fe were selected.

The formation of non-ionizing, stable, compounds in the AA flame, particularly Mg and Ca, have been reported, e.g. Butler and Kokot (1969), Medlin and Suhr (1969), Van Loon and Parassis (1969). This interference can be overcome by the addition of releasing agents such as lanthanum or 'E.D.T.A.'. By experimentation it was found that an aspirated solution with a concentration of 0.4% lanthanum in the form of lanthanum chloride solution minimised complexing effects.

*Note: Solutions should be run as soon after fusion as possible.

TABLE 2.7: Operating Conditions for Atomic Absorption

Element	Wavelength (nm)	Slit (nm)	Light Source	Operating Current	Flame	Linear Range (µg/ml)
Ca	422.7	0.7	Int.Al, Ca, Mg*	20 mA	A/A	0.08- 6.0
Mg	285.2	0.7	Int.Al, Ca, Mg*	20 mA	A/A	0.01- 1.0
K	766.5	2.0	Int. K, Na	12 mA	A/A	0.04- 3.0
Na	589.2	0.7	Int. K, Na	12 mA	A/A	0.02- 1.0
Fe	248.3	0.2	Int.Cu, Co, Cr, Fe, Mn, Ni	30 mA	A/A	0.12- 5.0
Cu	324.8	0.7	Int.Cu, Co, Cr, Fe, Mn, Ni	30 mA	A/A	0.09- 5.0
Ni	232.0	0.2	Int.Cu, Co, Cr, Fe, Mn, Ni	30 mA	A/A	0.15- 7.0
Zn	213.9	0.7	Int.Zn	15 mA	A/A	0.02- 1.0
Ti	365.3	0.2	S & J, Ti	15 mA	N/A	1.9 -200

*Int - Perkin-Elmer 'Intensitron' Hollow-Cathode Lamps

S & J- S & J 'Juniper' Hollow-Cathode Lamp

A/A - Air/Acetylene (40/32 p.s.i.)

N/A - Nitrous Oxide/Acetylene (35/55 p.s.i.)

Scale Expansions: Cu x 100; Ni x 10; Zn x 30; Ti x 10

Integration Time: 3 secs. for all

An acute problem in major element analyses of silicate rocks are 'matrix effects', particularly that of Mg and Ca by Al, Si and Ti. However, these can be minimised by matching the matrix of the standards with that of the samples. To achieve this International Igneous Rock Standards G1, G2, BCR-1, W1, DRN and T-1 were prepared in an identical manner to the altered samples and used to calibrate the AA, as recommended by Medlin and Suhr (1969) and Buckley and Cranston (1971). Combinations of three standards were used for calibration whilst those remaining were run as 'unknowns' to check accuracy. Due to the nature of the altered samples, the 'international standards' failed to cover the concentration ranges for certain elements, particularly Fe and Ca. In these instances a series of spiked standards were prepared.

Solutions were run on a Perkin-Elmer Model No.460 AA. An automatic calibration and direct readout unit enabled major element analyses to be reported as oxide weight %. Samples were run in batches of twelve, followed by a routine check to ensure that 'machine drift' was either absent or minimal. Standards were recalibrated between batches, and all major element analyses were repeated in triplicate. The full list of operating conditions are given in Table 2.7*.

TiO₂, Cu, Ni and Zn were determined using standard flame techniques as opposed to the heated graphite furnace. A range of spiked method blanks and international standards were used to construct calibrations. Cu, Ni and Zn content in the lithium metaborate reagent had the effect of a 'standard addition' to all samples. Calibrations were linear at low concentrations, and detection limits were drawn at 5 ppm. Due to low concentrations of Cu, Ni and Zn, high scale expansions were necessary to obtain accuracy and the validity of these trace element results is discussed in Section 2.6

*Note: As Medlin et al. (1969) reported, low fuel cylinder pressure can create erratic results and should be maintained above 75 p.s.i.

2.6 Accuracy and Precision of AA Techniques

The use of international standards for calibration involved the allocation of definite values for each element. Although many of these standards have been in use for over ten years, disputes have arisen as to the 'correct' numerical values. Any technique which involves calibration on these standards must include an assessment as to the reliability and derivation of published 'recommended' analyses. In the use of published compilations it is natural to place emphasis on the more recent results, reflecting advances in analytical techniques. However, the methods behind these compilations and their possible short-comings must always be remembered. Abbey (1977, 1978) and Abbey et al (1979) give a resume of the problems involved, including sample inhomogeneity, inter and intra laboratory variations, and the use of subjective criteria such as the selection of 'reliable' laboratories. The majority of standards used in the present study belonged to the United States Geological Survey's Series 1 and 2. Certain standards (DRN and T1) are the product of smaller institutions implying a lower reliability and were not used in calibrations. Actual values used for calibrations were taken from Abbey (1977, 1978). Although, as Table 2.10 indicates, the results of the major compilations are often in close agreement, it must be remembered that these values are averages of available data. To indicate the spread of analyses involved, Table 2.10 also indicates the spread of analytical values used in the compilations of Flannagan (1972, 1976). The statistical approaches to producing 'means' or 'recommended' values from such spreads are discussed by Abbey et al (1979).

The results obtained during the present study, when standards were run as unknowns, are presented in Table 2.8 and 2.9. The major element results indicate acceptable levels of precision and accuracy. Some values, e.g. total Fe for BCR, fall noticeably outside the recommended ranges but

Table 2.8

TABLE 2.8: Atomic Absorption Major Element Results

Sample	Observed Values			Mean	Recommended Values		
MgO (wt.%)							
G2	0.77	0.78	0.78	0.78	(3) * 0.77	(2) * 0.76	(4)* 0.75
BCR-1	3.60	3.60	3.60	3.60	3.49	3.46	3.48
TB19	1.26	1.27	1.27	1.27	1.58		
HF18B	2.46	2.49	2.47	2.47	3.01		
GT23	5.08	5.10	5.09	5.09	5.68		
BH16	0.31	0.32	0.32	0.32	0.52		
Total Fe as Fe ₂ O ₃ (wt.%)							
DRN	9.78	9.97	9.87	9.87	(5) 9.72	(2) 9.91	(3) 9.69
BCR-1	12.66	13.16	12.77	12.86	(3) 13.54	(2) 13.47	(4) 13.44
TB19	3.22	2.99	3.31	3.17	3.04		
HF18B	4.74	4.44	4.65	4.61	4.38		
GT23	10.58	10.84	10.62	10.58	10.71		
BH16	0.75	1.00	0.99	0.91	1.06		
MG17A	9.90	9.98	9.92	9.93	9.69		
K ₂ O (wt. %)							
T1	1.20	1.21	1.20	1.20	(7) 1.23	(3) 1.23	
G2	4.58	4.62	4.60	4.60	(3) 4.52	(2) 4.51	(4) 4.46
Mg17A	2.22	2.23	2.20	2.22	2.26		
GT23	0.55	0.55	0.55	0.55	0.60		
BH16	0.87	0.88	0.85	0.87	0.89		
TB19	1.85	1.81	1.87	1.84	1.94		
HF18B	4.02	4.01	4.00	4.01	4.09		
Na ₂ O (wt. %)							
G1	3.37	3.37	3.39	3.38	(2) 3.32		
DRN	2.96	2.97	2.97	2.97	(5) 2.90	(2) 3.00	(3) 3.00
G2	4.07	4.16	4.15	4.13	(3) 4.06	(2) 4.07	(4) 4.06
Mg17A	2.48	2.51	2.53	2.51	2.34		
GT23	2.52	2.56	2.55	2.54	2.42		
BH16	0.76	0.75	0.72	0.74	0.52		
TB19	0.47	0.53	0.45	0.48	0.38		
CaO (wt. %)							
W1	10.51	10.61	10.54	10.55	(1) 10.80	(2) 10.96	(3) 10.96
DRN	6.93	6.92	6.91	6.92	(5) 7.10	(2) 7.08	(3) 7.08
T1	5.03	5.09	5.10	5.07	(7) 5.18	(3) 5.19	
G1	1.47	1.43	1.46	1.45	(2) 1.39		
MG17A	4.46	4.47	4.44	4.46	4.58		
GT23	7.16	7.25	7.18	7.20	7.85		
BH16	20.26	20.14	20.15	20.18	22.96		
HF18B	12.59	12.43	12.44	12.49	13.89		
TB19	13.83	13.80	13.86	13.83	14.80		

* reference numbers Table 2.10

TABLE 2.9: Atomic Absorption Minor and Trace Element Results

Table 2.9

Sample	Observed Values				Mean	Recommended Values		
TiO₂ (wt.%)								
G1	0.21	0.24	0.30	0.35	0.27	(2)* ⁺ 0.27		
G2	0.43	0.45	0.41	0.44	0.43	(3)* 0.50	(2) 0.55	(4) 0.48
T1	0.60	0.52	0.50	0.60	0.56	(7) 0.60	(3) 0.59	
DRN	1.08	1.07	1.07	1.09	1.08	(5) 1.05	(2) 1.11	(3) 1.10
BCR	2.35	2.30	2.15	2.26	2.26	(3) 2.22	(2) 2.20	(4) 2.26
W1	1.12	1.07	1.04	1.05	1.07	(1) 1.07	(2) 1.07	(3) 1.07
G2	1.43	0.45	0.41	0.44	0.43	(3) 0.50	(2) 0.55	(4) 0.48
BH16	1.38	1.32	1.28	1.25	1.31	1.43		
TB19	1.67	1.63	1.57	1.61	1.62	1.80		
HF18B	1.80	1.77	1.78	1.80	1.79	1.96		
MG17A	1.92	1.92	1.90	1.95	1.92	1.87		
Cu (p.p.m.)								
BCR	22	22	26	24	23	(3) 19	(2) 18	(4) 16
W1	92	102	94	104	98	(1) 100	(2) 110	(3) 110
G1	6	<5	9	9	7	(2) 13		
G2	15	9	11	12	12	(3) 11	(2) 117	(4) 10
DRN	41	45	42	46	44	(2) 52	(3) 52	
T1	35	39	30	44	37	(7) 47	(3) 45	
BH16	28	23	11	13	19	15		
HF18B	89	81	81	90	85	79		
MG17A	54	53	60	57	56	54		
GT23	56	49	51	45	60	63		
TB19	10	8	<5	8	8	12		
Ni (p.p.m.)								
T1	<5	7	18	<5	9	(3) 10	(7) 13	
DRN	10	22	8	12	13	(2) 16	(3) 22	
BCR	36	41	6	10	23	(2) 16	(3) 13	(4) 10
W1	39	34	35	49	40	(1) 76	(2) 76	(3) 78
G2	5	<5	11	10	8	(3) 6	(2) 5	(4) 4
BH16	12	8	14	11	11	50		
TB19	97	75	96	98	91	79		
HF	36	40	70	65	53	144		
MG17A	192	171	164	145	168	167		
Zn (p.p.m.)								
G1	30	43	42	35	38	(2) 45		
G2	127	130	161	134	127	(3) 85	(2) 85	(4) 84
W1	72	90	86	85	83	(1) 86	(2) 86	(3) 86
BCR-1	122	119	115	117	118	(3) 120	(2) 120	(4) 125
DRN	138	134	145	142	140	(2) 150		
BH16	15	15	29	16	19	6		
HF18B	42	48	43	39	43	37		
MG17A	135	140	147	136	140	138		
TB19	54	69	55	60	60	13		

TABLE 2.10: Recommended Values for International Standards

Table 2.10

Sample - W1 (Basalt)						
	(1)	(2)	(3)	Range in (2)		
Fe ₂ O ₃ *	11.09	11.09	11.10	10.38-13.98		
MgO	6.62	6.62	6.62	6.17- 6.84		
CaO	10.80	10.96	10.96	10.41-11.25		
Na ₂ O	2.15	2.15	2.15	2.00- 2.37		
K ₂ O	0.64	0.64	0.64	0.54- 0.72		
TiO ₂	1.07	1.07	1.07	0.89- 1.12		
Cu (ppm)	100	110	110	72.5 -162		
Ni	76	76	78	56 - 91		
Zn	86	86	86	69 -110		
Sample - BCR (Basalt)						
	(2)	(3)	(4)	Range in (2)		
Fe ₂ O ₃ *	13.54	13.47	13.44	12.49-14.17		
MgO	3.49	3.46	3.48	3.33- 3.50		
CaO	6.98	6.92	6.97	6.66- 7.10		
Na ₂ O	3.29	3.27	3.30	2.78- 3.44		
K ₂ O	1.68	1.77	1.70	1.45- 1.75		
TiO ₂	2.22	2.20	2.26	2.00- 2.27		
Cu (ppm)	19	18	16	8 - 28		
Ni	13	16	10	7 - 38		
Zn	120	120	125	96 -190		
Sample - G1 (Granite)			Sample - G2 (Granite)			
	(2)	(2)	(2)	(3)	(4)	Range in (2)
Fe ₂ O ₃ *	1.90	1.65-2.22	2.62	2.69	2.67	2.35- 2.90
MgO	0.38	0.24-0.50	0.77	0.76	0.75	0.64- 0.92
CaO	1.39	1.28-1.51	1.98	1.94	1.96	1.73- 2.18
Na ₂ O	3.32	3.10-3.67	4.06	4.07	4.06	3.56- 4.56
K ₂ O	5.48	5.18-6.30	4.52	4.51	4.46	4.16- 4.87
TiO ₂	0.26	0.24-0.28	0.50	0.55	0.48	0.45- 0.57
Cu (ppm)	13	9 -16	11	11.7	10	5 -21
Ni	1	1 -6.4	6	5.1	3.5	1.5-20
Zn	45	38 -54	85	85	84	58 -113
Sample - DRN (Diorite)			Sample - T1 (Tonalite)			
	(5)	(2)	(3)	(6)	(3)	
Fe ₂ O ₃ *	9.72	9.91	9.69	5.99	6.03	
MgO	4.40	4.50	4.47	1.90	1.89	
CaO	7.10	7.08	7.09	5.18	5.19	
Na ₂ O	2.90	3.00	3.00	4.40	4.39	
K ₂ O	1.70	1.70	1.73	1.23	1.23	
TiO ₂	1.05	1.11	1.10	0.60	0.59	
Cu (ppm)	-	52	52	47	45	
Ni	-	16	22	13	10	
Zn	-	150	-	190	200	

*Total Fe as Fe₂O₃

References: (1) Flannagan (1969); (2) Flannagan (1972a, 1976 - ranges taken from 1976);
 (3) Abbey (1977); (4) Abbey (1978); (5) La Roche & Govindaraju (1973);
 (6) Thomas & Kempe (1963).

as the remaining elements for BCR all show close agreements with recommended values the reason for these sporadic variations are unclear and may be the result of sample inhomogeneity. Trace element results indicate a lower degree of precision than the major elements. This is a direct function of the analytical technique, in which 'lamp noise' was accentuated by the high scale expansions employed. These are random variations within set limits and can be overcome by averaging a larger set of results. Thus, although the precision is low the accuracy of the averaged results is satisfactory.

Tables 2.8 and 2.9 as well as indicating recommended ranges for the international standards, also report the AA analyses of the five altered samples run on the XRF. These are included more for an indication of the precision of the AA results rather than accuracy. Although XRF and AA results are often in close agreement some large variations are present. In these instances it must be remembered that the XRF analyses are the result of a single determination that was obtained with difficulty and therefore must be treated with caution.

2:7 X-Ray Diffraction (XRD)

Both whole rock and clay separates were prepared for XRD analyses. Whole rock smear samples were prepared by disaggregation in distilled water using a mortar and pestle and a thick suspension allowed to dry on a glass slide. The resolution of the XRD traces, however, were considerably improved by using the -2μ clay fractions. This was most noticeable for the highly calcitised specimens. Samples for clay separation were mechanically disaggregated in distilled water, using an anti-flocculating agent, and the suspension allowed to settle for six hours. The material remaining in suspension after this time was sedimented onto a glass slide and dried. No significant variations were observed in the clay mineralogy of specimens prepared as whole rock smears and sedimented mounts. In

TABLE 2.11: XRD Operating Conditions

Phillips 1130-90 Generator

Standard Vertical Goniometer

Cu X-ray tube operated at 35 kV and 60 mA

Ni Filter (secondary)

Scan Range* - $1^{\circ}/\text{min}$

Chart Speed* - 2 cm/min

Pulse Height Analyser - Lower Level - 180 divisions

Window - 220 divisions x 10-100%

Gain - 64

Ratemeter Range* - $10^3 \times 4$

Time Constant - 1 sec.

Mode - c/s

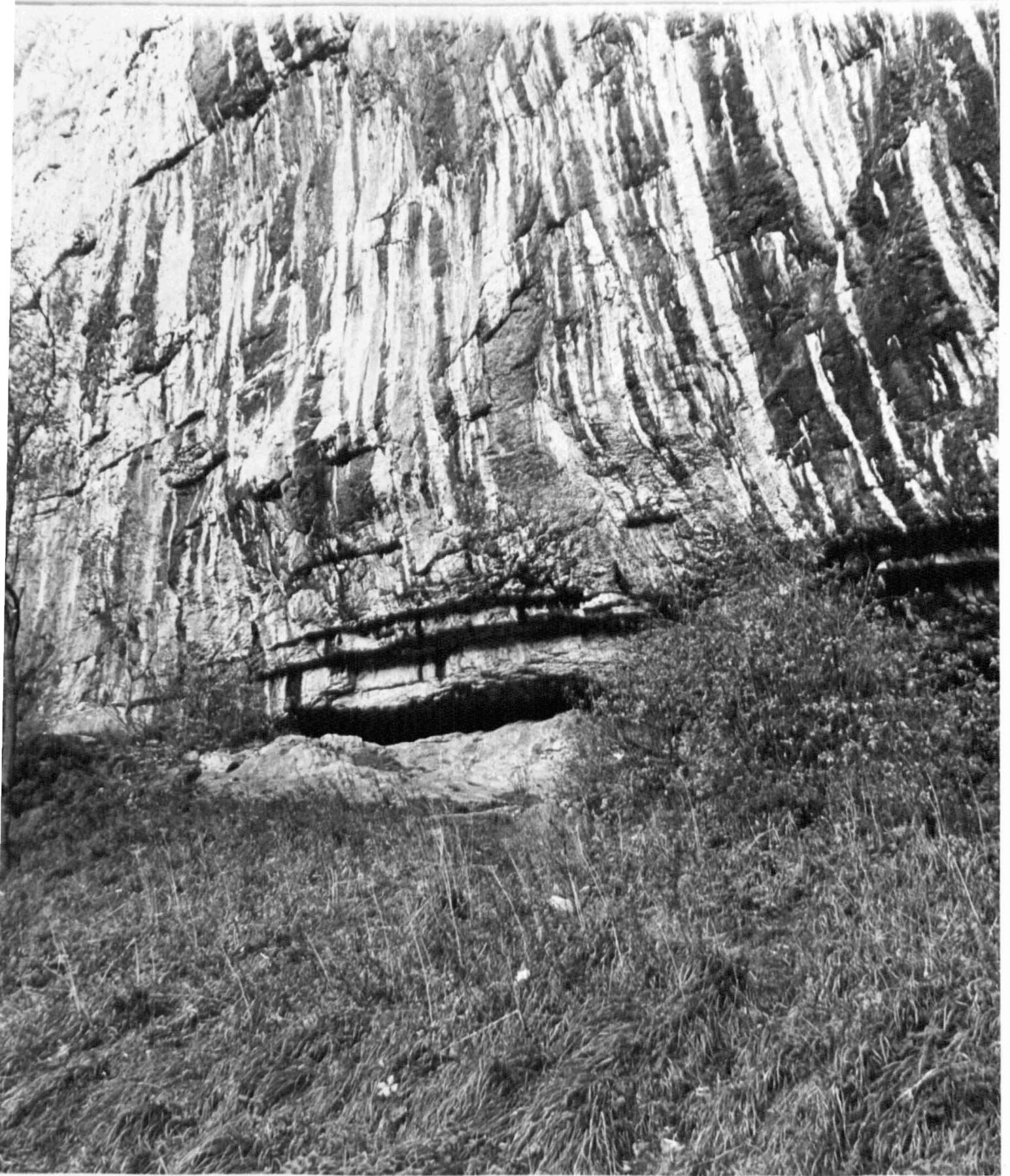
(*Conditions varied to suit samples, parameters quoted used in the majority of runs)

addition, a small number of unorientated, whole rock samples were prepared using the 'cavity mount' technique. Samples were analysed according to the conditions summarised in Table 2.11.

2:8 Petrological Techniques

Over three-hundred thin sections, polished thin sections and polished blocks were examined. Modal analyses were obtained using a Swift Automatic Point Counter, using one-thousand counts per slide. The presence of 'abundant orthoclase' (Sargent, 1917) had been alluded to in the Derbyshire basalts. Initially, areas of untwinned feldspar, apparently of a 'late stage' interstitial nature (see Chapter 4) were suspected of being potassic feldspar. A number of thin sections were stained to investigate this possibility. The method used was similar to that described by Hutchinson (1974, p.21). Uncovered thin sections were etched over fuming hydrofluoric acid for 20 secs., immersed in a solution of sodium cobaltinitrite (20 secs.) rinsed and dried. The slides were further etched over fuming HF (10 secs.) immersed in a solution of 5% by weight barium chloride, rinsed in distilled water and dried. This was followed by immersion in a solution of amaranth red (20 secs.) and washing to give the required staining density. This method stains K-feldspar yellow, plagioclase red and leaves quartz unaffected.

CHAPTER THREE



Chapter Three
Stratigraphy, Distribution and Styles of
Igneous Activity

3:1 Stratigraphy and Distribution

Information from archives, field mapping, underground exploration, borehole cores and logs as well as the 1:10,000 Institute of Geological Sciences maps have enabled a synthesis of the stratigraphy and distribution of igneous horizons in the south Pennine orefield to be compiled. The results have been published by Walters and Ineson (1981) a copy of which is included as Appendix 12.

Over forty Lava and Tuff horizons have been recognised, a third of which have no surface expressions. Figures 3.1, 3.2, 3.3 and 3.4 indicate the outcrop distributions of the Lavas, Tuffs and Sills whilst Figure 3.5 summarises the volcanic stratigraphy of the orefield.

3:2 Styles of Extrusive Igneous Activity

The term 'Lava' is used to refer to a mappable stratigraphic unit e.g. the Conksbury Bridge Lava. Individual Lavas may be comprised of a number of separate lava flows, pyroclastic horizons or limestone intercalations. The term lava signifies a single event of basalt extrusion.

The distributional maps of Walters and Ineson (op.cit.) indicate the broadly circular to ovate limits of individual Lavas. The most extensive units have diameters between 10-12 km with a maximum thickness around 100 m in the central vent area.

Borehole evidence indicates low angle effusive slopes of between 0.5° - 2° and a gradual thinning with increasing distance from source. In profile the Lavas are comparable with the small basaltic shield volcanoes described by MacDonald (1972, p.195). The extent and volume

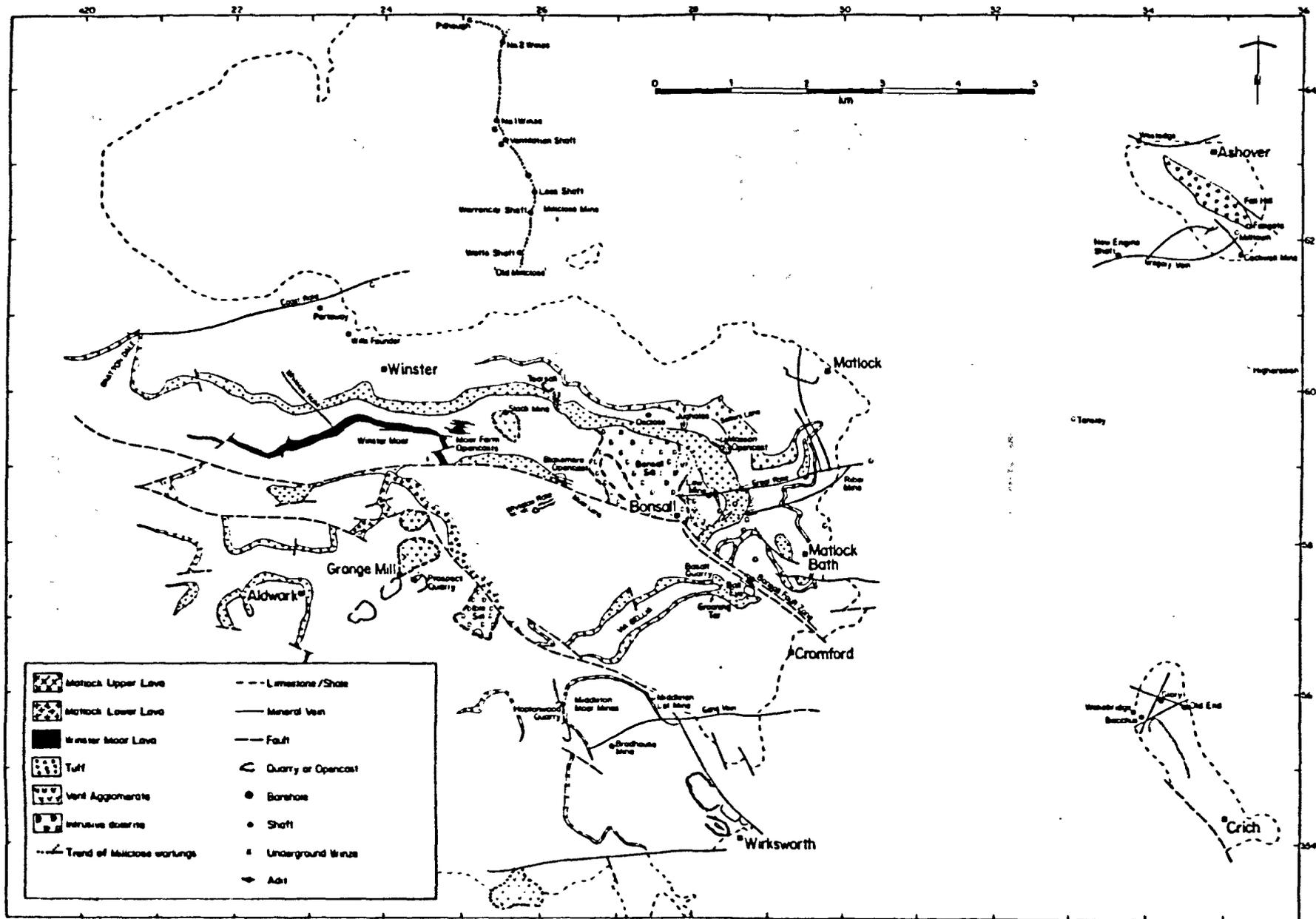


FIG. 3.1 GENERAL MAP OF THE IGNEOUS HORIZONS IN THE MATLOCK-WIRKSWORTH-ASHOVER-CRICH AREA
 (Figs. 3.1-3.4 from Walters and Ineson, 1981.)

Fig 3.2

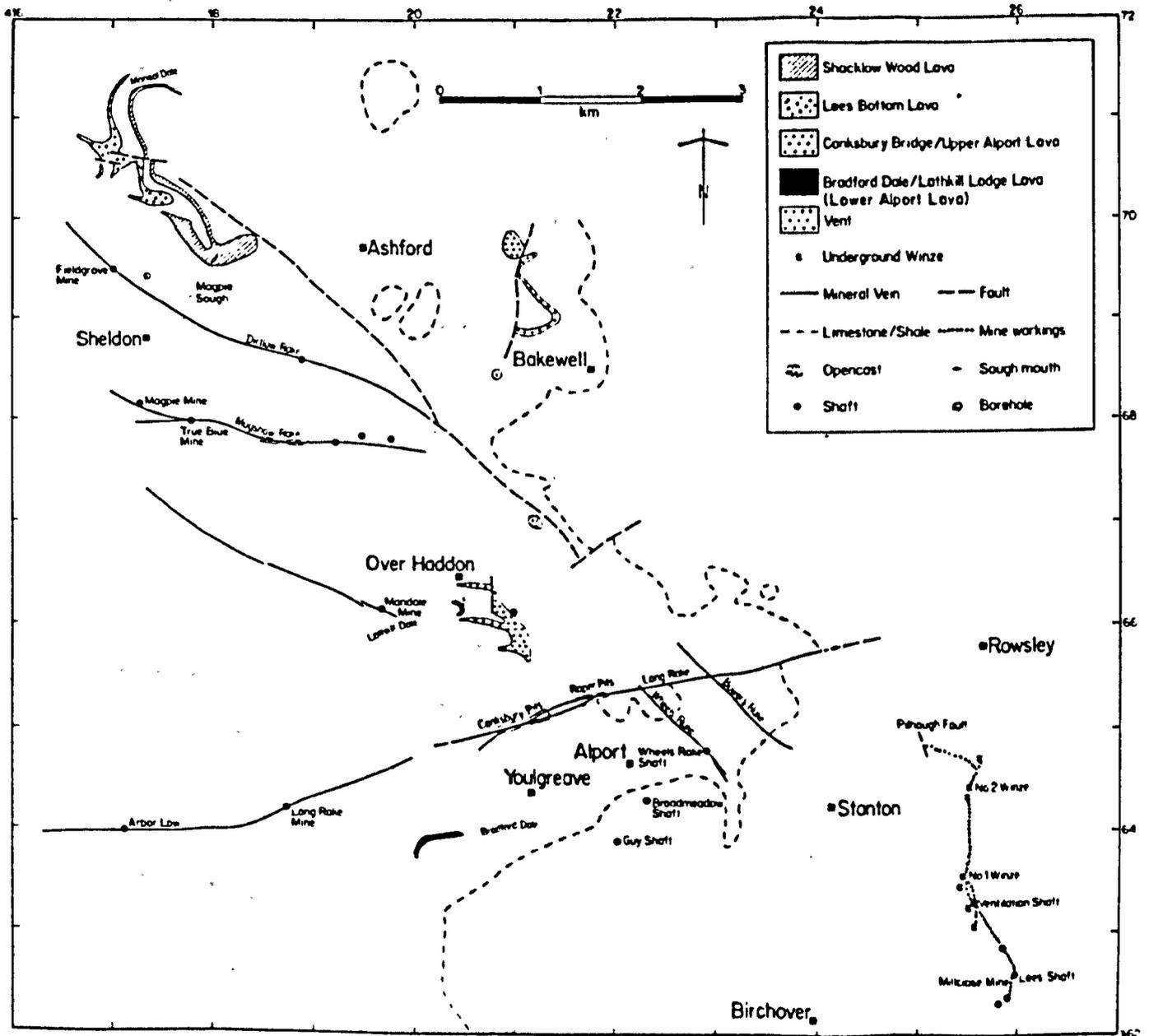


FIG. 3.2 GENERAL MAP OF THE IGNEOUS HORIZONS IN THE ALPORT-BAKEWELL TADDINGTON DALE AREA

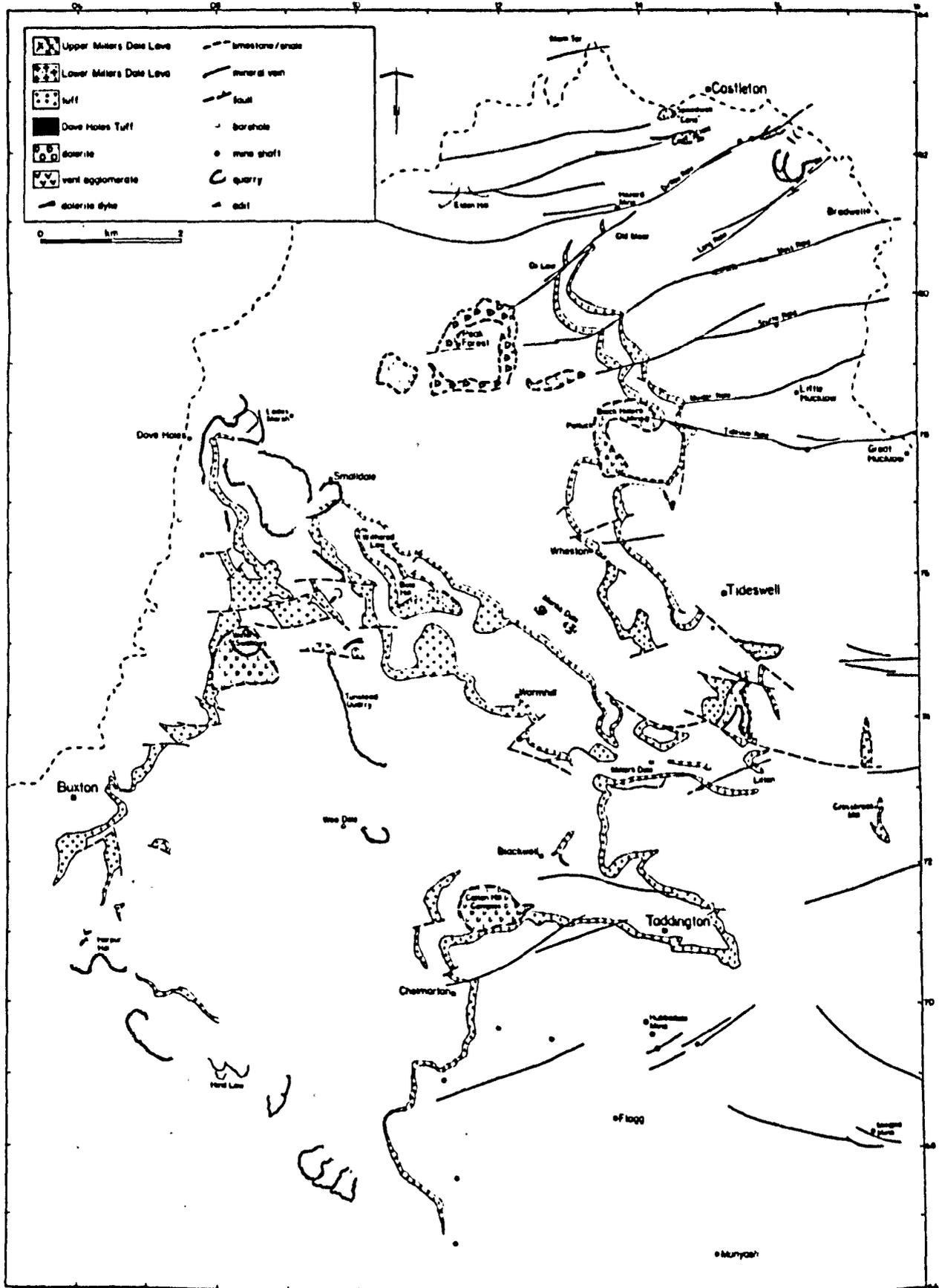


FIG. 3.3 GENERAL MAP OF THE IGNEOUS HORIZONS IN THE BUXTON-TIDESWELL-CASTLETON AREA

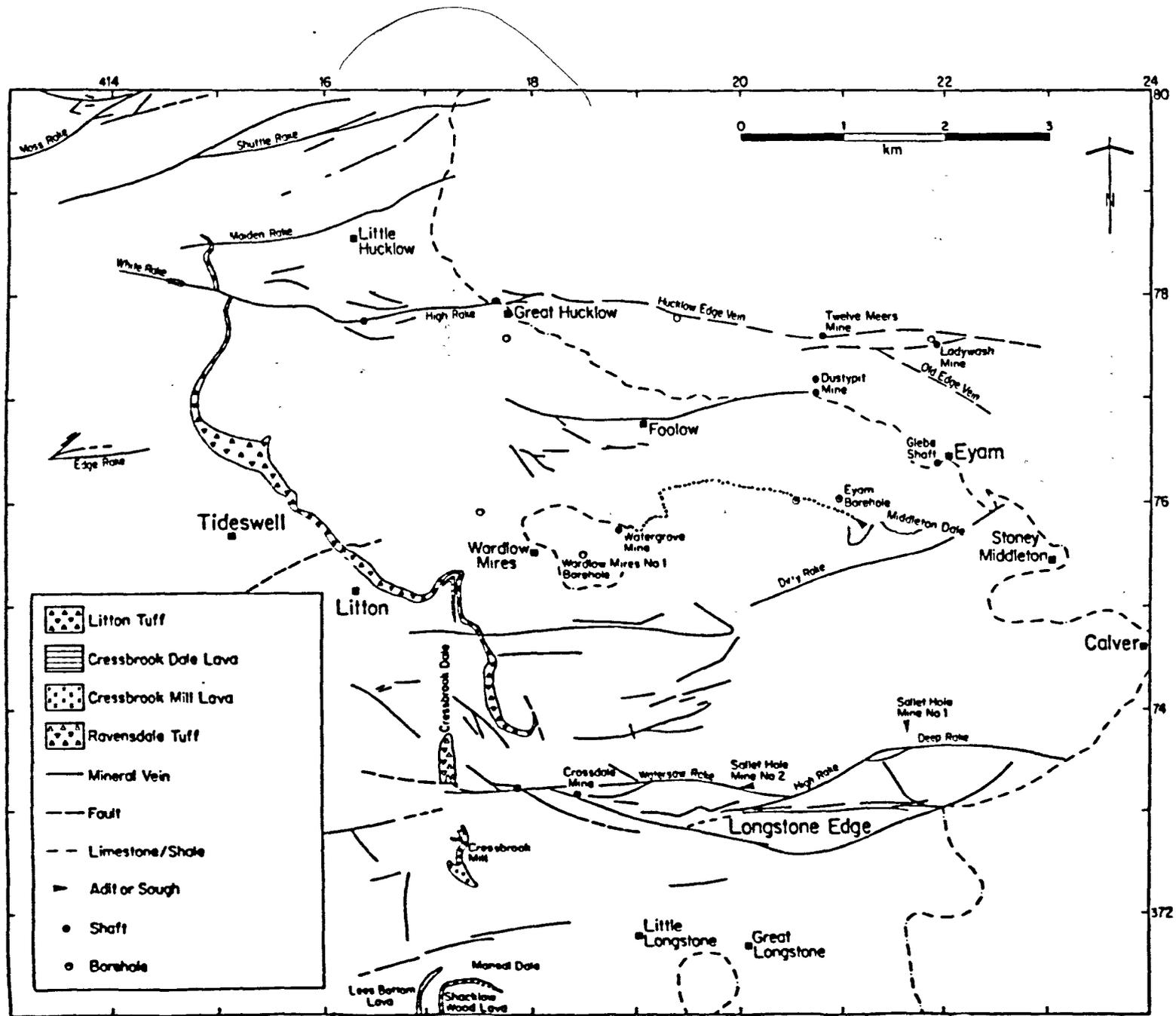


FIG. 3.4 GENERAL MAP OF THE IGNEOUS HORIZONS IN THE EYAM-LONGSTONE-LITTON AREA

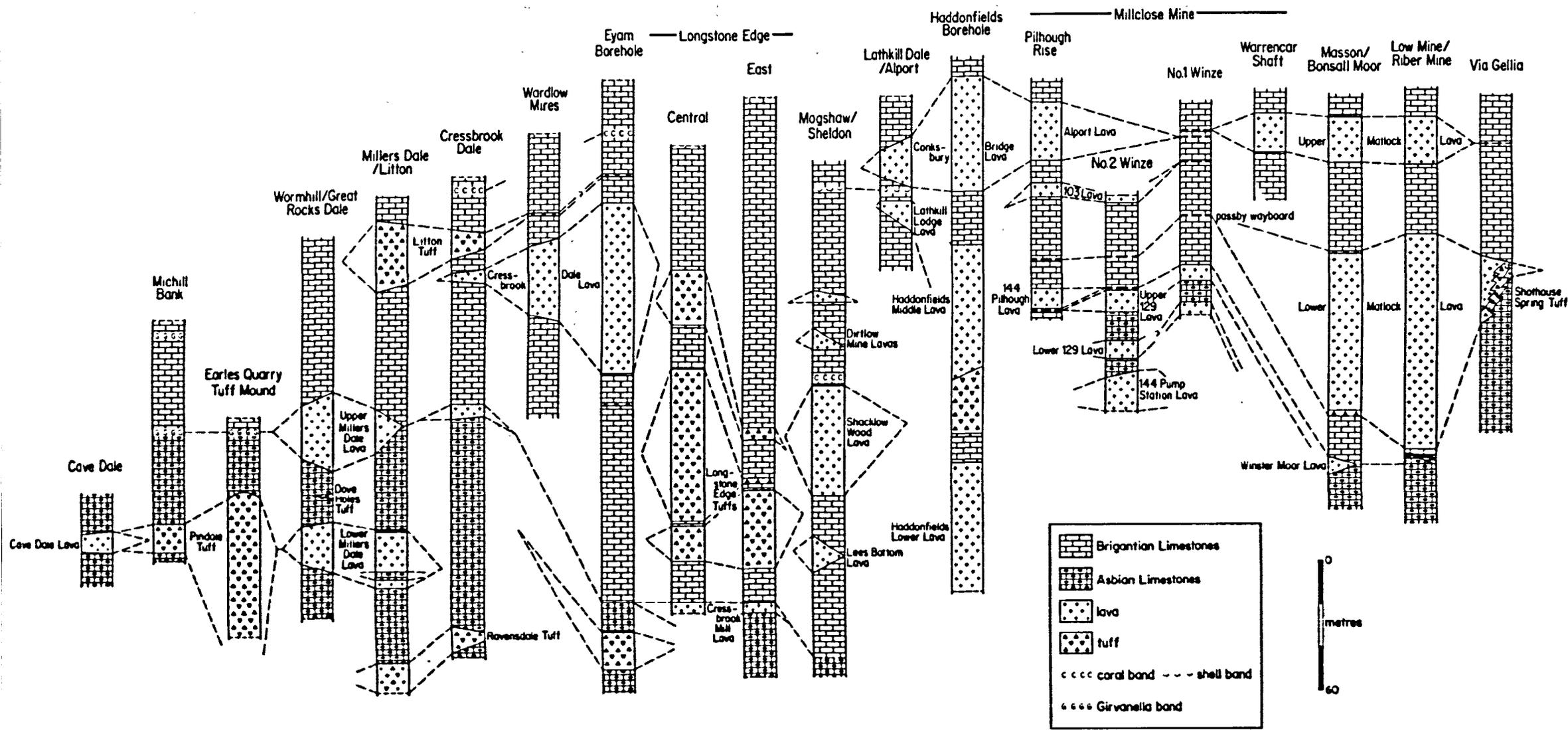


FIG. 3.5 SIMPLIFIED SUMMARY OF THE VOLCANIC STRATIGRAPHY OF THE SOUTH PENNINE OREFIELD

of the Lavas are an order of magnitude less than, for example, the classic Icelandic occurrences, being more comparable with the small shield volcanoes designated as 'scutulum type' by Nygard (1968). The divisions between shields and scutulum volcanoes are illustrated in Figure 3.6.

Nichols (1936) and Walker (1970) classified lava flows on the basis of their internal structures and relationships into composite, simple, compound, and multiple types. A composite 'lava' is capable of subdivision into a number of distinct flows, or sets of flow units, each separated by an appreciable time interval which was sufficient for the onset of weathering, sedimentation or pyroclastic activity. Simple lava flows occur as extensive flood-like extrusions each flow divisible into an upper and a lower vesicular margin with a massive interior. An assemblage of simple flows constitutes a composite Lava. Compound lavas have 'flow units' comparable to simple flows but the individual units are not laterally extensive. Typical examples of this type are pahoehoe lavas which have a tabular or 'bun'shaped cross-section and the flow units produced by the advancing lava constantly over-riding itself result in a series of tongues. The controlling factor in differentiating simple and compound lavas is the effusion rate (Walker, 1970) where simple flows result from the more rapid effusion of material, while in compound lavas the time interval between successive units is only sufficient for a skin to form on the lower unit before it is inundated. Multiple flows are a variant of compound flows in which the time interval is such that no physical divisions are evident. Individual flows are recognised by variations in the concentration, shape and size of the vesicular horizon.

Logs of the Cressbrook Dale Lava (Figure 3.7) and the Lower Millers Dale Lava (Figure 3.8) illustrate the above characteristics. Variations in the vesicularity of the Cressbrook Dale Lava indicate that it is

Fig 3.6

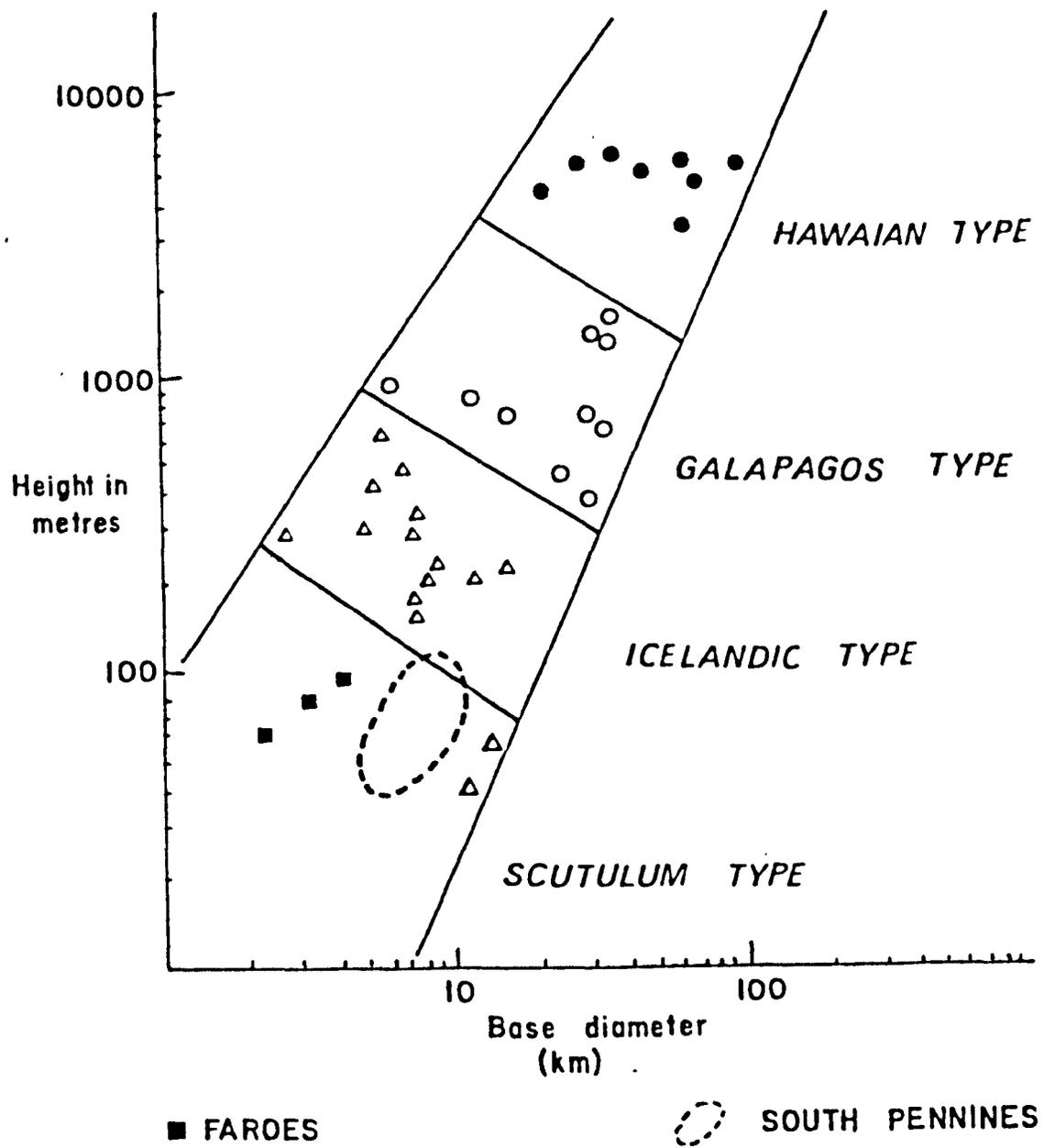
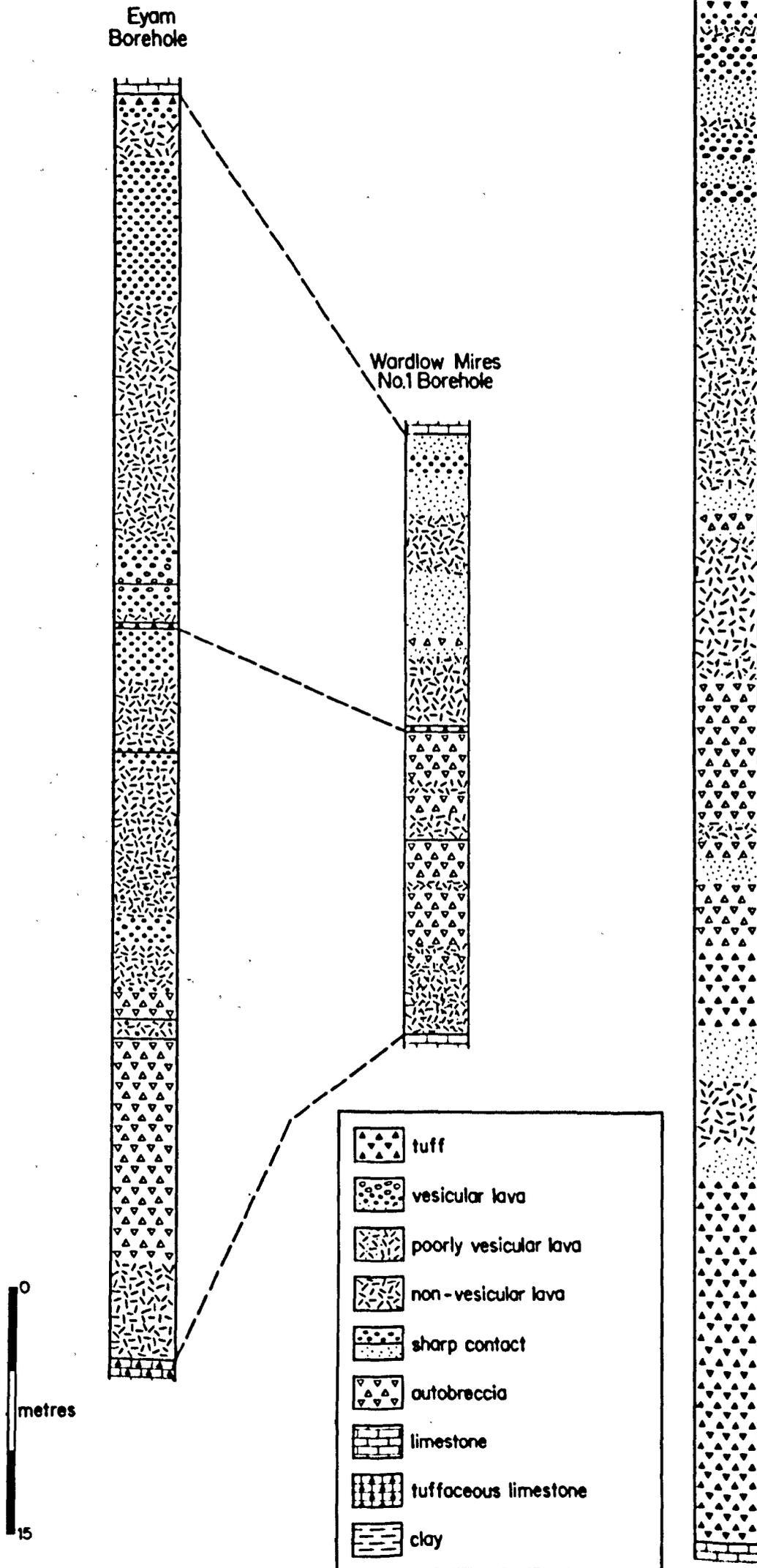


FIG 3.6 HEIGHT-DIAMETER RELATIONSHIPS OF BASALTIC SHIELDS
(adapted from Fielder & Wilson, 1975.)

FIG. 3.7 INTERNAL STRUCTURES OF THE CRESSBROOK DALE
AND HADDONFIELDS LOWER LAVAS

Haddonfields
Borehole

Fig
3.7



predominantly of compound type. However, the sharp contacts (for example at a depth of 90 m in the Eyam Borehole) between highly vesicular (hematised) lava, marked by a 0.1 m thick tuff, divides the Lava into two distinct effusive phases. In contrast the Lower Millers Dale Lava consists of individual flow units separated by tuff intercalations indicating a composite Lava with three effusive episodes followed by pyroclastic activity. Thin limestone intercalations are occasionally observed between flow units, e.g. in the Litton Dale borehole (SK 160750) and in White Rake Opencast (SK 146782). The Matlock Lower Lava is another example of a 'composite flow', exposures in the Bonsall Basalt Quarry and in Groaning Tor Adit, Via Gellia (SK 284574 and SK 283572) of a flow unit approximately 12 m thick indicate proximity to source. The individual flows of simple type rarely exceed 9 m in thickness and gradually attenuate with distance from the central vent areas. The Upper Millers Dale Lava is also a composite Lava, limestone intercalations are evident at Bole Hill (SK 108757) while Bemrose's (1894) section in the old Millers Dale Lime Works reported coarse ash layers within the 'Lava' and a subdivision into at least two units. The Shacklow Wood Lava (Appendix 7) is an example of multiple lavas divisible into a limited number of effusive episodes by pyroclastic intercalations. The multiple flows exhibit large variations in apparent thickness. In the thinner flows, more rapid cooling preserves a vesicular central zone, while in the thicker flows (up to 25 m) the slower cooling gives rise to coarse holocrystalline central areas characterised by augite approaching a subophitic texture.

Volcanic 'breccias' have been recorded from the Ashover borehole (Ramsbottom et al., 1962) and the Eyam and Wardlow Mires No.1 Boreholes (Walters and Ineson, 1981) as well as from the east end of Long Rake (Appendix 7). The breccias appear to be related to areas of maximum

development of lava in proximity to cone structures. However they are not invariably present, for example breccias are not developed adjacent to the 'central vent' of the Lower Matlock Lava in the Masson Hill area (Walters and Ineson, 1981). The lateral extent of brecciation are not known in detail, the breccias associated with the Cressbrook Dale Lava persist from the envisaged source area near Eyam, thinning towards the edge of the Lava near Wardlow Mires - a distance of 3 km. The petrology of the breccias is described in Chapter 5 and they show characteristics suggesting subaerial auto-brecciation (Parsons, 1969).

The 0.5° - 2° profiles calculated for the Lavas assumes gradual thinning. Although in the majority of instances this is based on borehole evidence, more abrupt localised terminations of lava flows have been recorded. Flow fronts with inclinations as high as 40° being noted from Millclose Mine (Traill, 1940), at Taddington (Cope, 1937), and near Middleton Limestone Mine (Smith et al., 1967). The only currently accessible exposures of a flow front is that of the Upper Millers Dale Lava located in the disused railway cuttings above Litton Mill (SK 157729). The Litton Mill flow front (Walkden, 1977) and that reported by Traill (op.cit.), the 144 Pump Station flow front in Millclose Mine, show a number of features which suggest the interaction of lava and water. Traill noted that pillow structures and a 'slaggy' appearance were evident, while Walkden (op.cit.) described the flow front at Litton as having brecciated fragments in a glassy groundmass. The main body of the lava behind the Litton flow front is unbrecciated and illustrates simple flow type structures. The flow front breccias arise from the entry of subaerial lava into shallow water (Jones and Nelson, 1970). The chilling and brecciation was sufficient to halt

the flow of lava and give rise to local abrupt terminations at steep flow fronts, a feature absent from totally subaerial flows.

3:3 Styles of Pyroclastic Activity

Individual lavas contain minor components of pyroclastic material. This is most noticeable in proximity to vents where pyroclastics formed a central 'boss' to the shield. The central cones exhibit high angle graded tuff bedding in the region of 30° . Thick tuff sequences representing such structures have been noted at Ashover, Low Mine near Matlock, and at Rowsley (see Walters and Ineson, 1981; and Appendix 7). Pyroclastic activity commonly precedes the main phase of basalt extrusion or marks its impending cessation. Proximal explosive activity precedes the effusive phase at Low Mine and Rowsley while at Ashover it overlies a series of basalt flows and breccias.

The fragmented nature of the tuffs (see Plates 1.8 to 1.10) is in contrast with the predominantly quiet effusive nature of lava extrusion. The tuffs often extend over larger areas than their associated lavas enabling the extended correlation of the volcanic events. Employing the criteria of Walker and Croasdale (1970) for distinguishing subaerial Strombolian/Hawaiian from shallow marine Surtseyan type pyroclastic activity, the tuffs exhibit conflicting characteristics. Achnelithic lapilli typically associated with Strombolian vulcanicity are rare, however the lack of accretionary lapilli and the presence of large scale graded tuff bedding are not typical of Surtseyan type pyroclastics. The paleoenvironment of vulcanicity discussed in the following section, indicates that the pyroclastic activity with its violent fragmentation probably represents phreatomagmatic interactions between magma in the vent and groundwater.

A number of cone structures are characterised by the total absence or the restricted occurrence of lavas. Typical examples are the Shothouse Spring Tuff/Grangemill Vents, Dove Holes Tuff, Litton Tuff, Brook Bottom Tuff, Ravensdale Tuff, Pindale/Cavedale Tuff-Lava and the Longstone Edge Tuffs. These cones and their ejecta either occurred independently of a major extrusive episode or formed positive areas around which the lava flowed (Walters and Ineson, 1981). In volume they are subordinate to the main Lavas.

The Grangemill vents are perhaps the most well-known and are spatially related to the Shothouse Spring Tuff. The Tuff, at the horizon of the Matlock Lower Lava (Smith et al., 1967) dilates at the expense of the latter which envelopes the 'positive' area formed by the vents. A similar relationship can be inferred for the poorly exposed Brook Bottom Tuff where the Upper Millers Dale Lava thinned to the north of Tideswell.

The Litton Tuff represents one of the largest cone structures in the area with diameter of 6 km and a maximum thickness in excess of 30 m. In profile it resembles a typical low angle basaltic tuff cone produced by high level phreatomagmatic activity. The tuff unfortunately is poorly exposed, however Stevenson et al. (1971) noted that in the vicinity of the inferred vent (i.e. near Litton) a greater proportion of coarse ejecta, cinder and bombs occur. The extremities of the cone intersected in the Wardlow Mires Borehole are represented by a sequence of silty horizons deposited in shallow water. The Pindale Tuff has been outlined by exploratory drilling which indicates the presence of an elongate cone attaining a height of at least 30 m. Peripheral to the vents, coarse unsorted tuff with angular limestone blocks pass into graded tuff on the flanks while to the north of the cone a flank eruption emitted the Cave Dale Lava.

The steep profile of the cone suggests that phreatomagmatic interaction were not as important as in, for example, the Litton Tuff cone, and this hypothesis could be consistent with the emergent episode envisaged by Chesire and Bell (op.cit.).

3:4 The Paleoenvironment of Vulcanicity

Ford (1977, p.61), Stevenson (In: Cheshire and Bell, 1977) and Walkden (in Discussion, 1977) have alluded to the possibilities of subaerial or submarine extrusion. As Walkden (op.cit.) notes the evidence indicates that the bulk of activity occurred on periodic emergent platforms. Pillow lava structures are absent except where additional evidence indicates a localised flow into an area of shallow water. Marginal to the platform, true pillow structures are noted, and here deep water facies are evident (Fearnside and Templemann, 1932). Numerous emergences of the platform, not associated with extrusive activity, have been demonstrated by Walkden (1974, 1977) as being marked by potholed surfaces, characteristic crustiform textures and wayboard clays (see Chapter 11). In a number of instances (e.g. Traill, 1940, p.204) lava directly overlies one of these surfaces. The erosional surface beneath the Upper Millers Dale Lava in Millers Dale is well developed (Cope, 1937; Walkden, 1977) and relates to an extensive emergent period (basal Brigantian) which was accompanied by volcanism emanating over a wide area. The Lower Millers Dale Lava in the Great Rocks Dale area similarly overlies a strongly potholed surface infilled with wayboard clay. Further support for the proposition that extrusion occurred on an emergent fully lithified carbonate platform is the absence of calcareous 'injection breccias' at the base of the individual flows. Injection breccias have been described by Strogon (1973) in Ireland, where the Carboniferous Lavas have been extruded into shallow littoral environments. The flow of lava onto an unlithified carbonate base

creates steam generation and baking which results in the injection of the lime muds and the attendant brecciation of the lava. In a number of instances, for example the section of the Cressbrook Dale Lava in the Eyam Borehole, the base of the Lava resting on limestone does not show any of the characteristic features typical of such an environment, in this instance the lava is devoid of vesicles in the basal section. The presence of 'pipe-vesicles', characteristic of the flow of lava over a 'wet surface' (i.e. extremely shallow water) have only been observed in the basal Conksbury Bridge Lava at Conksbury Bridge (Appendix 7).

Although extrusion may be coincidental with widespread emergence, on a local scale the interplay between sedimentation, emergence and volcanicity was finely balanced. Episodes of major lava outpourings were associated with local uplift which is more evident adjacent to central vent areas and appear to be independent of the widespread, cyclic, emergences noted earlier. The transitions from sedimentation to emergence are marked by tuff sequences showing strong evidence of the phreatomagmatic, or possibly shallow marine interactions outlined earlier. Tuff sequences at Low Mine (Walters and Ineson, 1981) and at Ashover, (Ramsbottom et al., 1962) have thin limestone intercalations which demonstrate this fine volcanic/sedimentological interplay. Emergence in the central vent areas with peripheral periodic inundations of a lava sequence is illustrated by the Lower Millers Dale Lava in the Wormhill/Great Rocks Dale area. Walters and Ineson (in prep., Appendix 13) have demonstrated that the Lower Millers Dale Lava was extruded in this general area and the Lava in this vicinity although capable of being separated into distinct extrusive episodes (Figure 3.8) does not contain limestone intercalations nor does it exhibit the development of weathered 'boles'. Towards the periphery of the flow,

however, limestone intercalations between 3-4 m thick are present between individual flow and are located in the Litton Dale Borehole and in White Rake Opencast.

The cessation of an episode of extrusive activity, usually marked by pyroclastic activity, was followed by rapid subsidence, inundation and renewal of carbonate sedimentation. Contacts between limestone/tuff or limestone/lava are clearly defined and show no weathering or erosional features. Overlying limestones occasionally exhibit thin transitional lithologies of tuffaceous limestone where the preceding pyroclastic activity is well developed and these horizons probably indicate a more gradual subsidence and inundation.

3:5 Igneous Activity of the South Pennine Orefield in its Regional Context

The present study and the compilation of Walters and Ineson (1981) concentrates on igneous activity within the Orefield of the Southern Pennines. This reflects the importance of the igneous horizons in their control on the location of mineralisation, the increased exploration drilling within this area and consequent availability of borehole material for examination. However, as Walters and Ineson (op.cit.) stress, the igneous activity represents the western portion of a Lower Carboniferous igneous province extending to the east of the limestone outcrop.

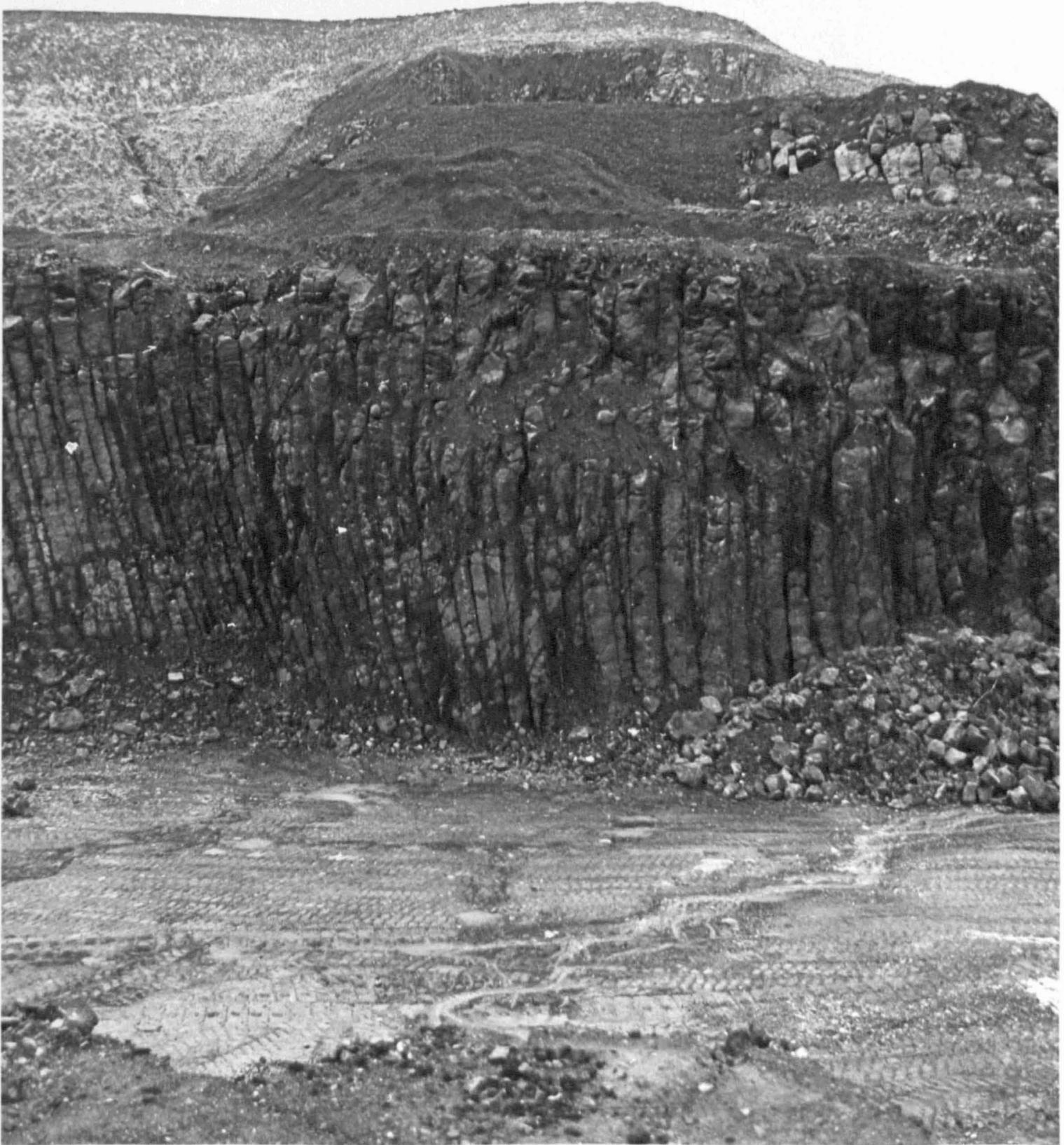
To the west of the Orefield, the Millers Dale Lower Lava extends beneath the Namurian cover (Walters and Ineson, 1981). There is minimal information regarding the Lower Carboniferous in this area, but in the Astbury inlier adjacent to the Red Rock Fault, the occurrence of a coarse and poorly consolidated tuff suggestive of proximal activity (of Middle Brigantian age) was described by Bemrose, In: Gibson and Hind (1899).

Igneous horizons do not outcrop to the south-west of the ore-field, around Hartington and Dovedale, in strata ranging from Chadian to Brigantian in age (George et al., 1976). The Gun Hill Borehole further west, however, intersected pyroclastic horizons of Lower Asbian and basal Holkerian age (Hudson and Cotton, 1945). East of Dovedale, Brigantian pyroclastics around Tissington were described by Bemrose (1899, 1903). This pyroclastic activity of Upper Brigantian age can be traced southwards in the Duffield Borehole (Frost and Smart, 1979).

To the east of the Orefield igneous horizons have been intersected in a number of exploration boreholes. Minimal strata recovery due to the drilling techniques employed has caused confusion as to the intrusive or extrusive nature of the basalts. Igneous activity is reminiscent of the exposed volcanics with variable and localised flows of basalts and pyroclastics that render correlations between widely spaced boreholes speculative. Volcanic activity in the Ironville 1, 2 and 3 Boreholes was tentatively assigned to a Brigantian age with minor Lower Asbian activity (Frost and Smart, 1979). To the north-east of Ashover volcanic sequences of probable Brigantian age, were intersected in the Brimington and Calow No.1 Boreholes (Smith et al., 1967). Further east vulcanicity appears to die out in the Bothamsall and Eakring areas, (Smith et al., 1973). Minor activity is concentrated in strata of Arundian age (George et al., 1976).

To the north of the Orefield, pillow lavas associated with Brigantian basinal facies are present beneath the Namurian cover at Castleton (Fearnside and Templeman, 1923) and pyroclastic activity of a similar age can be traced in the Alport and Edale Boreholes (Hudson and Cotton, 1945).

CHAPTER FOUR



Chapter Four

Mineralogy of the Basalts and Dolerites

4:1 Introduction

The basalts and dolerites exhibit a uniform mineralogy. Labradorite and granular augite dominate the groundmass with subordinate magnetite, ilmenite, and apatite. Microphenocrysts are ubiquitous and may comprise over 25% of the rock. Phenocryst phases are dominated by olivine, often with small spinel inclusions, but both plagioclase and clinopyroxene also occur. Many basalts show a 3-phase phenocryst assemblage with olivine-plagioclase-clinopyroxene in order of abundance. Olivine is commonly pseudomorphed by phyllosilicate phases and similar material occupies an intersertal position in the groundmass. The latter represents a pseudomorphous replacement after primary palagonitic glass or, in some instance, analcite. A wide range of secondary replacements are present in vesicular and altered basalts, these include silica, carbonates and sulphides. Petrographic variations are discussed in Chapter 5, and modal analyses are presented in Appendix 4.

4:2 Plagioclase Feldspars

The lavas and dolerites contain between 40 and 60% plagioclase. Two distinct generations occur as noted by Bemrose (1894), however no detailed study of their relationships had been previously undertaken. In addition to optical investigations thirty-eight microprobe analyses of phenocryst and groundmass phases were undertaken and the results are presented in Appendix 6.

Phenocrysts are up to 5 mm in length and are visually distinct from groundmass plagioclase in having lozenge-shaped, euhedral sections in addition to more normal elongate lath-shaped outlines. They are

also distinct in exhibiting simple twinning or an absence of twinning. Strong zoning is common and takes the form of fine-scale oscillations, up to twenty zones being present in individual phenocrysts, parallel to their euhedral outlines. There is no indication (Figure 4.1) of a uniform trend towards more sodic rims and 'normal' reversed and oscillatory trends are all present. As is typical in cases of oscillatory zoning (Smith, 1974), compositional differences between adjacent zones are in the order of 2% anorthite molecule (An). Petrographic and microprobe data indicates that 95% of the phenocrysts examined fall in the range of calcic labradorites (An% 60-70) and are of a more calcic nature than the groundmass phases (Figure 4.1).

Phenocrysts in dolerites and coarse-grained holocrystalline basalts show strong resorption. Euhedral outlines become rounded or irregular, in extreme cases resulting in a 'pseudo intersertal' texture with partial alteration proceeding along internal cracks. Their untwinned nature and apparently 'late' crystallisation and partial alteration suggested, on initial inspection, areas of orthoclase. However, thin section staining (see Section 2.8) refuted this proposal and microprobe analyses confirmed a resorbed phenocryst origin. A similar relationship was noted by Dunham and Kaye (1965) from the Little Whin Sill, Co. Durham. Resorbed phenocrysts would appear to account for the unsubstantiated observation by Ixer (1972) that apparently "... a more sodic interstitial (plagioclase) phase, with strong zoning" was present in the Matlock Upper Lava.

Many basalts, on close examination, reveal the presence of a small percentage (approximately 5%) of plagioclase phenocrysts or microphenocrysts. The relationship in sills is often masked by their coarse textures. Further evidence for the occurrence of early phase euhedral phenocrysts arises from the examination of pyroclastic and autobrecciated

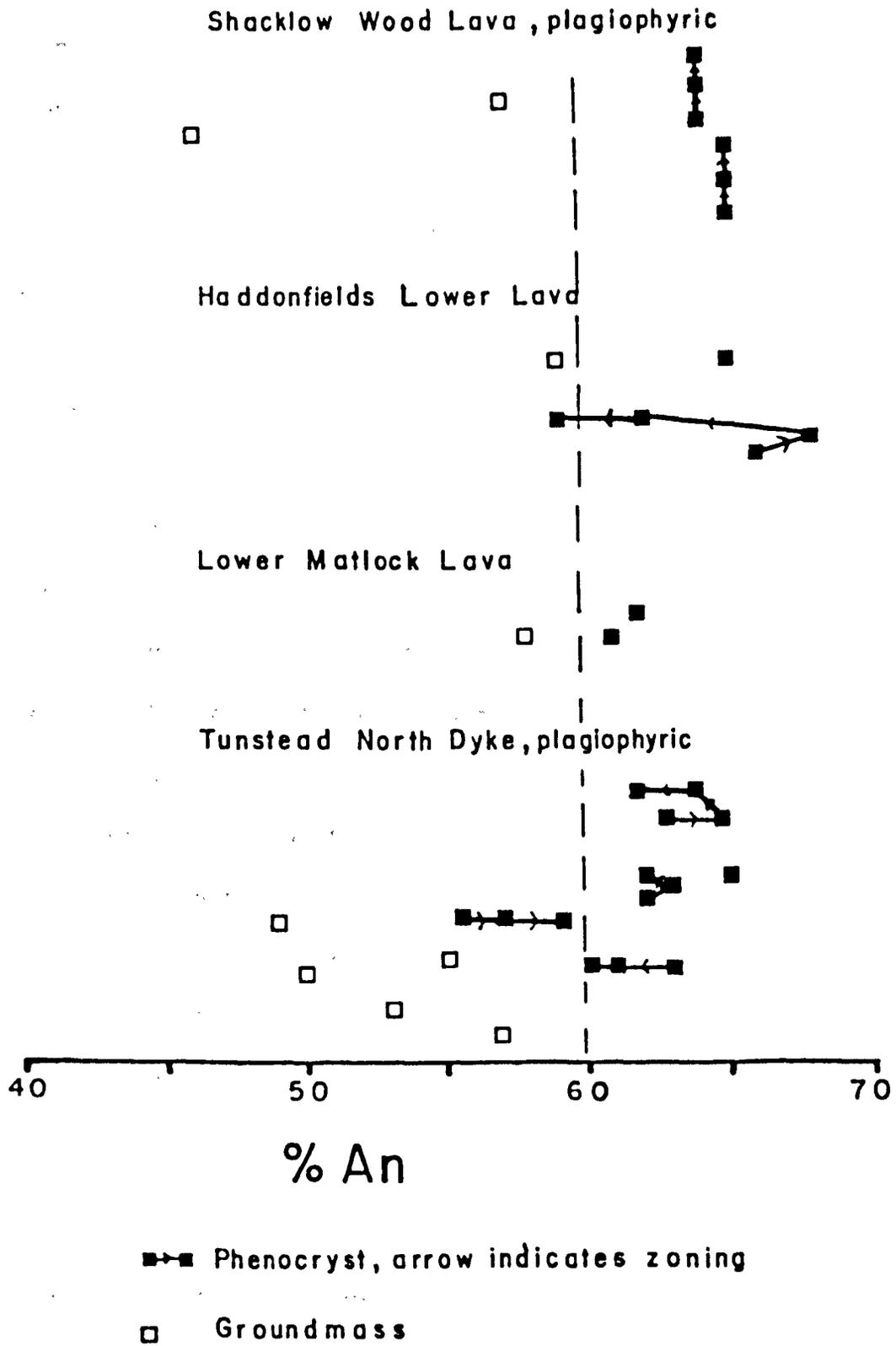


FIG. 4.1 COMPOSITIONAL VARIATIONS OF ZONED PHENOCRYST AND GROUNDMASS PLAGIOCLASES

material. Phenocrystal plagioclase, together with pseudomorphed olivine and pyroxene, is invariably present in a devitrified glassy groundmass. The present study however, has indicated the occurrence of distinct plagiophyric and plagiophyric flows. The former contain over 20% of euhedral, zoned labradorite phenocrysts with subordinate amounts of olivine pseudomorphs, set in a fine-grained groundmass. Examples are noted from the Tunstead Dykes, the Shacklow Wood Lava and the Cressbrook Dale Lava. Within these Lavas, plagiophyric flows developed towards the end of the extrusive phase and were preceded by aphyric types. In plagiophyric flows, groundmass feldspar exhibits strong fluxioning to give a 'trachytic' texture.

Groundmass plagioclase is distinct from phenocrysts in exhibiting lath shaped sections, strong albite twinning and their size (<0.1 mm). Zoning is occasionally observed but oscillatory zoning is very rare. Microprobe data (Figure 4.1) indicates that the groundmass phase is less calcic than the phenocrysts. Compositions range between An% 45-60 (calcic andesites and sodic labradorites). This is in agreement with petrographic observations and with the petrographic data of Ixer (1972) who noted average groundmass compositions of An⁵² from the Matlock Upper Lava and An⁵⁰ from the Bonsall Sill with phenocrysts of An⁵⁹. Normative feldspar compositions (Appendix 3) range from An³⁸ to An⁶⁰ with the majority between An⁵⁰⁻⁶⁰.

4:3 Pyroxenes

Pyroxenes constitute between 20 and 25% of the basalt lavas and dolerites. Clinopyroxene occurs as a microphenocryst and groundmass phase with an absence of co-existing orthopyroxene or pigeonite. The nature and differentiation trends of pyroxenes have been used as reliable indicators of host magma type even in highly altered basalts, e.g. Le Bas

(1962), Coombs (1963), Brown (1967), Nisbet and Pearce (1977). As geochemical analyses of the basalts indicated a transitional alkaline/tholeiitic nature a microprobe investigation of the clinopyroxene geochemistry was undertaken. Twenty-seven microprobe analyses are presented in Appendix 6.

Previously available pyroxene analyses were limited in number. Malki (1967) presented three analyses from the Millers Dale Upper Lava whilst Donaldson (1978) briefly noted the composition of pyroxenes from the Calton Hill dolerite. Malki's results, obtained from electromagnetic concentrations of 'approximately 98% purity' indicate abnormally high levels of TiO_2 and FeO. These have not been confirmed by the present study and it appears probable that the concentrates were contaminated by ilmenite. Harrison (in Smith et al., 1967) and Ixer (1972) referred to the pyroxenes as titanaugites but did not provide supporting geochemical data.

In thin section the clinopyroxene is typically colourless or pale yellow. A pale-pink colour with weak pleochroism is noted from dolerites and coarse holocrystalline basalt flows. Microphenocryst and groundmass phase pyroxenes occur in all the basalts. Groundmass pyroxenes in basalt lavas typically exhibit a granular texture (< 0.1 mm) intersertal to the plagioclase. In the more slowly cooled holocrystalline centres of thick flow units there is a tendency towards a sub-ophitic texture. The true ophitic texture, with plagioclase laths enclosed by pyroxene, only occurs as a facies of large dolerite intrusions with pyroxene plates up to 4 mm across. A number of dolerite intrusions, for example the Waterswallows Sill, do not exhibit the ophitic texture.

Basalts with a high proportion of clinopyroxene microphenocrysts are uncommon, but have been recorded from the Matlock Lower Lava (loc. 17-19, see Appendix 5), Millers Dale Upper Lava (loc. 24-25), Buxton Bridge Dykes (loc. 59, 84, 85) and the Calton Hill dolerite (anal.

86-87). The majority of the basalts contain occasional microphenocrysts.

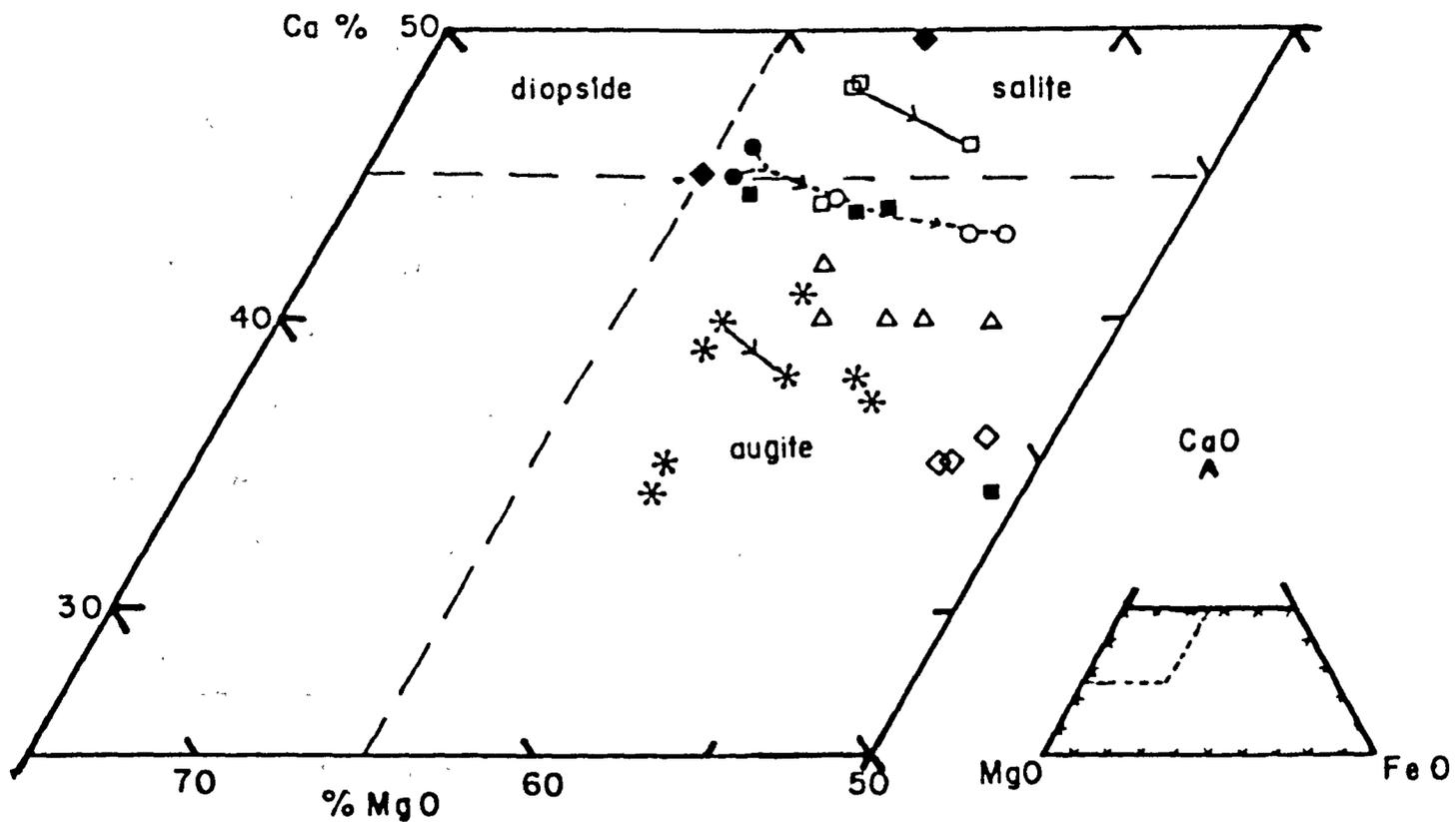
Microphenocrysts are 1-2 mm in diameter and commonly occur in glomeroporphyritic aggregates in excess of 3 mm. The majority of phenocrysts have rounded outlines, but euhedral phenocrysts have been noted from the Millers Dale Upper Lava (loc.24) and the Calton Hill dolerite. Zoning is rare and takes the form of either a faint oscillatory type parallel to euhedral outlines or as distinct overgrowth rims in optical continuity. The occurrence of pyroxene phenocrysts was first recorded by Bemrose (1894).

Analyses indicate that the pyroxenes are Ca-rich augites and salites (Figure 4.2). Using the criteria of Deer et al. (1978) the majority are titaniferous salites and augites (1-2% TiO_2) rather than titanaugites (> 2% TiO_2). The high chrome content of a number of analyses allows a further classification into Cr-salites and Cr-augites.

Ca-rich, titaniferous pyroxene phases, exhibiting limited iron enrichment and limited Ca-depletion during differentiation with an absence of either orthopyroxenes or Ca-poor phases have been regarded as an indicator of alkali-olivine basalt parentage (Wilkinson, 1967). However, as Barberi et al. (1971) indicate, the classic two-pyroxene 'tholeiitic' trend is rarely observed in volcanic rocks. This is a function of rapid cooling and the production of metastable pyroxene assemblages that lie in the 'immiscibility' field of tholeiitic pyroxenes crystallising in equilibrium. Thus volcanic tholeiites may contain a single augitic pyroxene phase but this will show a more pronounced iron enrichment than the augite of a 2-phase assemblage in equilibrium.

The pyroxene data for the Derbyshire basalts are plotted on the 'pyroxene quadrilateral' in Figure 4.2. Although all the analyses indicate a single Ca-rich augite or salite phase a number of conflicting trends

FIG. 4.2 CaO-MgO-FeO PLOT OF CLINOPYROXENE ANALYSES

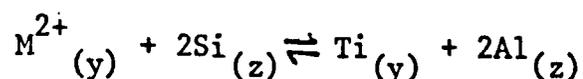


KEY

- * Tunstead North Dyke
- △ Haddonfields Lower Lava
- Matlock Lower Lava -phenocrysts
- Matlock Lower Lava -groundmass
- Millers Dale Upper Lava -phenocrysts
- Potluck Sill
- ◆ Calton Hill dolerite (Donaldson,1978.)
- ◇ Millers Dale Upper Lava (Malki,1967.)

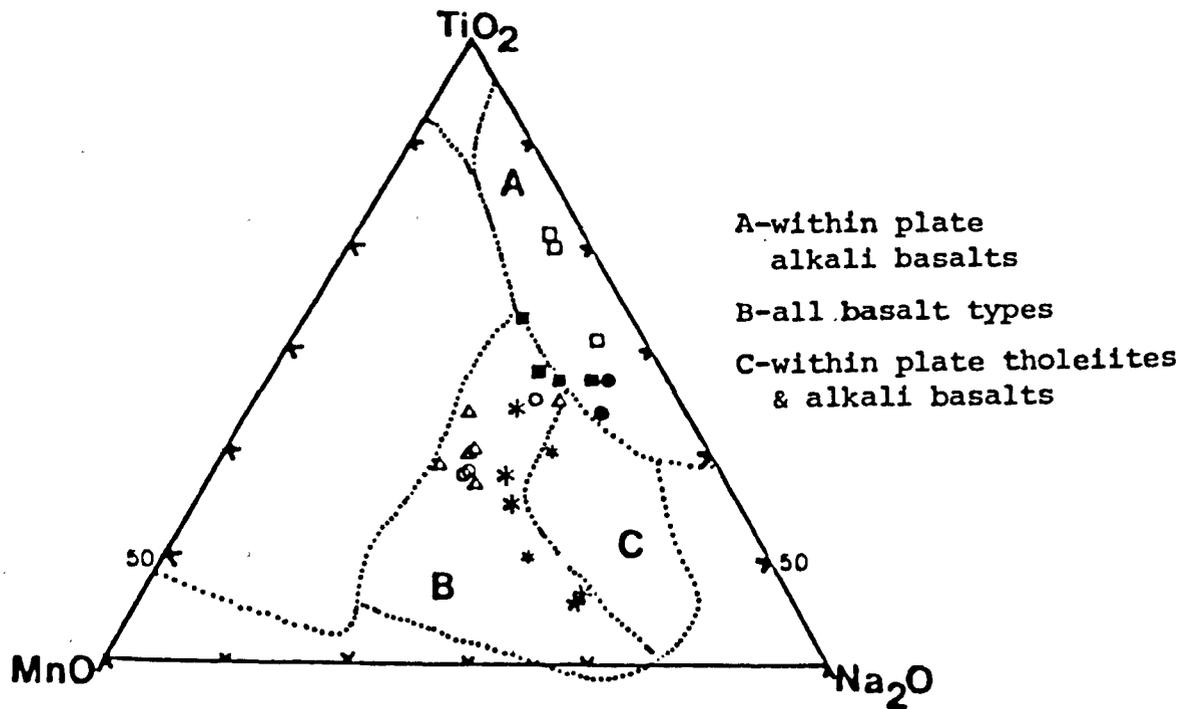
are present. Analyses of co-existing pyroxenes from the Haddonfields Lower Lava, the Matlock Lower Lava and the Calton Hill dolerite show trends of restricted Fe-enrichment with limited Ca depletion and are typical of alkali-basalts. A number however, show trends of Ca-depletion, particularly in the case of the Buxton Bridge North dyke. The majority of analyses are not enriched in titanium (1-2% TiO₂) unlike typical pyroxenes from alkali-basalts.

As Barberi et al. (1971) and Gibb (1973) recognised, clinopyroxene fractionation trends are controlled by both the initial magma composition and the environment of crystallisation. Thus p_{H₂O}, f_{O₂} and T^oc have direct effects on the nature of iron and titanium enrichments. Le Bas (1962) related the TiO₂ and Al₂O₃ contents of pyroxenes to silica activity and hence magma type. The use of these as discriminants was criticised by Gibb (1971) but still has validity at low temperature/pressures (T/P) i.e. - groundmass phases. A plot of Al₂O₃ v SiO₂ for the pyroxenes of the Derbyshire basalts is presented in Figure 4.3. The majority of analyses fall within the tholeiitic field, but close to the alkaline boundary. Analyses falling within the alkaline field all represent microphenocryst phases and this relationship can be explained by the sympathetic behaviour between Si, Al and Ti (Gibb, 1973). Their incorporation into pyroxene phases can be related by the equation:



High T/P favours olivine and pyroxene phenocryst crystallisation leading to relative enrichment of the melt in Al. This drives the equation to the right resulting in a more aluminous and titaniferous pyroxene. Under similar T/P conditions but low p_{H₂O} plagioclase phenocryst crystallisation is favoured resulting in a depletion of the melt in Al leading to the crystallisation of low-alumina, and low titanium, pyroxenes of 'tholeiitic'

FIG. 4.4 TRIANGULAR PLOT OF TiO_2 - MnO - Na_2O FOR DISCRIMINATING BETWEEN PYROXENES FROM DIFFERENT MAGMA TYPES



A-within plate
alkali basalts
B-all basalt types
C-within plate tholeiites
& alkali basalts

(field boundaries from Nisbet & Pearce, 1977)

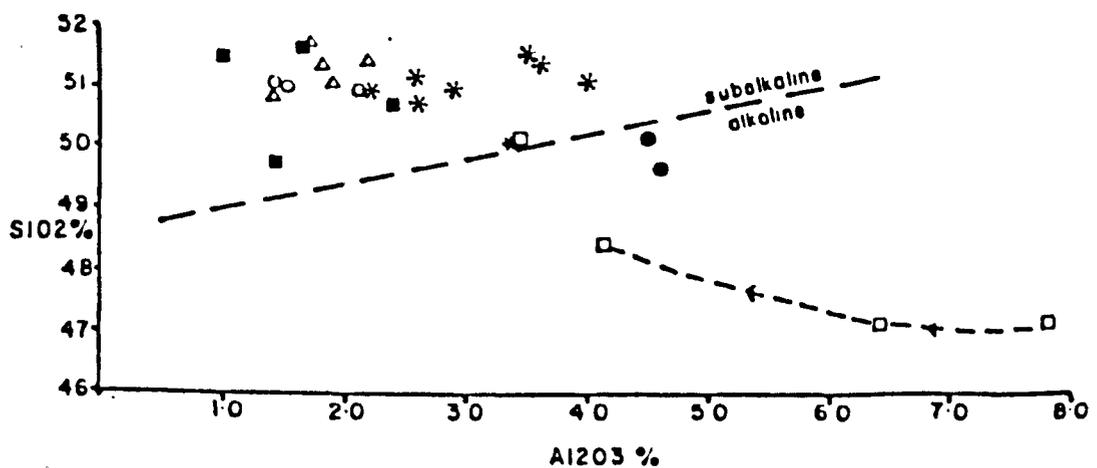


FIG. 4.3 SiO_2 versus Al_2O_3 DISCRIMINANT DIAGRAM FOR PYROXENE MAGMA TYPES

Key as Fig. 4.2

affinities. Thus, the effect of pH_2O can negate the effect of silica activity and control the crystallisation of 'tholeiitic' pyroxenes even from alkaline or mildly alkaline magmas (Barberi et al., 1971). These inter-relationships can be invoked to explain the apparent contrasting trends shown by the augite phenocrysts of the Buxton Bridge North dyke.

These show a trend of Ca-depletion, are less calcic and have lower concentrations of alumina than phenocrysts from other basalts. The dyke is plagiophyric with zoned, euhedral calcic labradorite phenocrysts, (see Chapter 5), suggesting that conditions of low pH_2O were responsible for the variation in geochemistry. It is noted that the pyroxene phenocrysts which exhibit the highest concentrations of Al_2O_3 and TiO_2 (locs. 24-25) are associated with lavas devoid of plagioclase phenocrysts.

There is a constant relationship between the chromium content of the phenocryst and the groundmass phases. The phenocrysts are chrome-rich, 0.6 to 1.0% Cr_2O_5 , whereas groundmass pyroxenes have $\ll 0.3\%$. This is a typical trend associated with salitic and augitic pyroxenes (Deer et al., 1978). Similar relationships were noted from the Shiant Isles Sill by Gibb (1973). Early formed pyroxenes exhibited strong Cr-enrichment, up to 0.3 atoms per formula unit, where $\text{Mg}/\text{Mg}+\text{Fe}$ exceeded 0.75. This was attributed (Gibb, op.cit.) to the strong partitioning of Cr from the melt into the early clinopyroxene phase (see also page 65). This resulted in a subsequent depletion in Cr which was enhanced by the early crystallisation of Cr-spinel. A similar mechanism can be invoked for the pyroxenes of the Derbyshire basalts, also enhanced by the presence of an early Cr-spinel phase as inclusions in olivine phenocrysts.

Zoning within pyroxene phenocrysts is uncommon. Occasional phenocrysts from the Buxton Bridge North dyke exhibited thin overgrowth rims and microprobe analyses (anal. 41 and 42) illustrate limited Fe-enrichment and slight depletion in Cr and Al from core to rim. More pronounced zoning

was observed in material from the Millers Dale Upper Lava (loc. 24). Microprobe analyses of a pyroxene phenocryst from this locality exhibiting a dark green core overlain by a pale brown coloured outer region with a partly rounded outline (anal. 47-49), indicates iron enrichment with no Ca-depletion, a depletion in Cr and Al and an enrichment in Ti from core to rim in the field occupied by titansalites (Figure 4.2).

The Na_2O v TiO_2 v MnO ratios of pyroxenes have been used by Nisbet and Pearce (1977) as indicators of basalt parentage. When analysis of pyroxenes from the Derbyshire basalts are plotted on the discriminant diagram of Nisbet and Pearce (op.cit.) the results are not conclusive (Figure 4.4). The majority of analyses fall in the field occupied by both within-plate alkali and tholeiitic basalts, with a number lying on the boundary with the field occupied solely by alkali-basalts. All analyses falling in the alkali-field represent phenocrysts and this can be explained as a function of inter-relationships between TiO_2 and SiO_2 outlined earlier.

Thus, the geochemistry of clinopyroxenes from the Derbyshire basalts show conflicting trends. On a number of discriminant diagrams the majority of the analyses fall in the field of tholeiitic pyroxenes, close to the boundary with alkali-olivine types. Trends exhibited on the pyroxene quadrilateral can be assigned to both alkali and tholeiitic types, but the relationship is probably a function of varying pH_2O . They are comparable with the pyroxenes of the Kap Edvard Holm intrusion in Greenland (Elsdon, 1971) described as transitional between alkali and tholeiitic types.

4:4 Olivines

Fresh olivine has not been detected in the extrusive basalts, although pseudomorphs after olivine are a ubiquitous feature and in

certain examples occur in excess of 25%. Primary olivine is noted however, from a number of dolerite sills where it exhibits a degree of incipient alteration along external surfaces and internal cracks. Olivine occurs in the form of microphenocrysts rarely exceeding 2 mm in length, larger 'phenocrysts' are the result of glomeroporphyritic aggregations. In coarse holocrystalline lavas and dolerites, the microphenocrysts exhibit a rounded, lobate, outline indicative of partial resorption - although reaction rims are not present. Euhedral pseudomorphs are more common amongst rapidly cooled lavas.

The possible status of olivine as a groundmass phase in addition to a phenocryst phase has not been recognised by previous authors (e.g. Bemrose, 1894; Smith et al., 1967; Ixer, 1972). The detection of pseudomorphed groundmass olivine of similar dimensions and with similar pseudomorphing phases to interstitial areas present difficulties. However, there are sufficient distinguishing criteria to strongly suggest that a proportion of this 'groundmass clay' does represent degraded olivine. In the case of dolerite sills the situation is less ambiguous. The majority of the olivine is present as microphenocrysts in the size range 1-2 mm, however, there is an undoubted gradation of subordinate olivine to dimensions of less than 0.1 mm but below this size even incipient marginal alteration results in a complete pseudomorphism. It is possible that the fine grained olivine represents relict, 'fragmented', microphenocrysts arising from the resorption noted earlier. However, many of these fine-grained olivine crystals have euhedral outlines when compared with the rounded outlines of the phenocryst phase. It is evident that the olivine in the Derbyshire basalts represents both initial crystallisation as phenocrysts in the sub-volcanic magma chamber and during ascent to the surface as well as rapid crystallisation on extrusion. The result is a dominance of microphenocrysts which have a

complete gradation in size towards a euhedral groundmass phase. The groundmass olivines crystallised prior to the formation of augite.

Optical determinations of relict olivine from the Bonsall Sill (Smith et al., 1967) indicated a magnesium rich composition in the region of Fo⁸⁵. The average composition of five microprobe analyses of olivines from the Potluck Sill (Appendix 6) indicated a more iron rich composition, with an average of Fo⁶⁸ (range Fo⁶³⁻⁷²).

4:5 Olivine Alteration

Olivine phenocrysts in holocrystalline basalts show a ubiquitous total replacement by phyllosilicate aggregates. The pseudomorphed olivines often constitute in excess of 15% by volume and the chemistry of alteration, with possible selective leachings, will have an important influence on 'primary' geochemical trends in the basalts.

Initial alteration proceeds along external surfaces and internal cracks, in its intermediate stages isolated relics of olivine in optical continuity occur as 'islands' surrounded by alteration products. This initial alteration is ubiquitous in dolerites and lavas and can be distinguished from the pseudomorphing phases constituting the remainder of the phenocryst by slight variations in colour, pleochroism and optical orientation. Red and green phyllosilicates are the predominant pseudomorphing phases occurring either as a homogeneous replacement of a single phenocryst or with a variety of fibrous and patchy textures. Homogeneous replacement phases behave as if a discrete mineral species, exhibiting pleochroism and extinction features. Low second order birefringence colours, often partially masked by body colour, are common. Red alteration phases are pleochroic in the range maroon-red-pink whilst the more widespread green alteration phases are pleochroic in the range dark green to colourless. In examples of well developed fibrous

or platy textures maximum pleochroism occurs when the fibres are elongated north-south. Where relict olivine is present the optical orientation of the homogeneous alteration phase can be seen to be inherited from the primary olivine. Both red and green alteration phases can occur within an individual pseudomorph but more commonly are observed in discrete areas. The 'swelling characteristics' of these alteration phases was noted during microscopic preparation and it is probable that open partings and distorted fibrous textures observed in thin section were related to swelling and distortion during preparation.

The selective replacement of olivine is a typical feature of basalts, in particular alkali-olivine basalts (e.g. Kuno, 1967; Scheidegger and Stakes, 1977). The processes of replacement are usually referred to as deuteric, i.e. taking place in direct continuation of the consolidation of the magma (Wilshire, 1958). The mineralogy and geochemistry of 'deuteric' alterations have been investigated by numerous authors (see Wilshire op.cit.). The alteration phases were initially regarded as discrete mineral species and allocated a specific nomenclature. Red pleochroic products after olivine were termed iddingsite by Ross and Shannon (1925), green alteration products are usually termed bowlingite whilst chlorophaeite has had a rather indiscriminate usage (Wilshire, 1958). However the status of 'iddingsite', 'bowlingite' and 'chlorophaeite' as discrete mineral species has been discredited. Wilshire (1958), Smith (1959) and Baker and Haggerty (1967) have all demonstrated that these alteration products represent complex mixtures of both clay and non-clay components. Their apparent behaviour as optically homogeneous 'minerals' has been related to the orientation of sub-microscopic goethite rods inherited from the orientation of the primary olivine (Ming-Shan Sun, 1957; Brown and Stephen, 1959; Baker and Haggerty, 1967). The relationships between the various colours is essentially a function of

oxidation state, the retention of iron in the replacing phases and the iron content of the primary olivine (Fawcett, 1965; Wilshire, 1958). Although deuteritic activity sensu stricto involves volatile rich fluids generated within a cooling basalt, identical phases can arise from low temperature basalt/seawater interactions and this may even continue into the weathering cycle (Wilshire, 1958; Scheidegger and Stakes, 1977).

Ming-Shan Sun (1957), Wilshire (1958), Baker and Haggerty (1967), Melson and Thompson (1973), Scheidegger and Stakes (1977) and Seyfried et al. (1978) have investigated the geochemistry and mineralogy of deuteritic alterations. The main trends associated with 'iddingsite' are strong oxidation of iron, but no net losses, a uniformity of Al_2O_3 concentrations, a marked loss of MgO and SiO_2 with an increase in total H_2O . In 'bowl-ingite' alteration SiO_2 is retained, H_2O and Al_2O_3 increase while $Fe_{(total)}$ and MgO show variable relationships. Although illite, calcite, celadonite, talc, serpentine and chlorite have all been noted as components of deuteritic alteration, detailed XRD investigations have indicated that Fe-rich smectites (nontronites and saponites) are the dominant phases occurring not only as olivine pseudomorphs but also as vesicle and fracture infills and as interstitial replacements. (Melson and Thompson, 1973; Scheidegger and Stakes, 1977; Seyfried et al, 1978; Fall, 1980).

Olivine alteration products in the Derbyshire basalts were noted by Bemrose (1894) who distinguished two 'types' of alteration. 'Potluck pseudomorph' types included red and green alteration products that were optically homogeneous and pleochroic. 'Peak Forest' types were not homogeneous, commonly yellow in colour with a fibrous texture. Both types could occur in the same specimen according to Bemrose (op.cit.) the material was 'mica-like' but 'probably not iddingsite'. Subsequently the use of the term 'chlorite' has been widely and indiscriminantly applied to a variety of alteration products in the Derbyshire basalts

and has become entrenched in the literature (Sargent, 1917; Garnett, 1920; Tomkeieff, 1926, 1928; Cope, 1933; Hamad, 1963; Ford and Sarjeant, 1964; Sarjeant, 1967; Wilkinson, 1967; Smith et al., 1967; Stevenson et al. 1971; Ford, 1977). Tomkeieff (1926) subdivided the 'chlorites' into three groups: primary chlorite, post-volcanic (vesicle infilling) chlorite and secondary chlorite produced during weathering. The identification of fine-grained alteration phases on the basis of optical properties alone is unsatisfactory. This was emphasised by Melson and Thompson (1973) who noted smectite alteration aggregations in basalts as exhibiting low birefringences typical of that normally associated with chlorites.

XRD investigations of alteration phases in the Derbyshire basalts has thrown doubt on the dominance of 'chlorite'. Walkden (1972) demonstrated that mixed layer illite-smectites were the dominant clay phases of green 'toadstone clays' and that chlorite components were either minimal or absent. Smith et al. (1967) and Ixer (1972) noted mixed layer smectite-chlorites as the alteration phases after olivine in the Bonsall Sill. Veins and replacement areas in the Calton Hill complex were shown to be iron-rich smectites by Curtis (1976).

A more detailed investigation of the mineralogy and geochemistry of olivine alteration phases was undertaken using XRD and microprobe techniques. Olivine pseudomorphs were carefully extracted from cut faces and prepared for XRD as smear mounts. Results were compared with whole rock smears and clay fraction mounts and are presented in Table 4.1. Two microprobe analyses of red pleochroic ('iddingsitic') alteration products from the Potluck Sill were undertaken (Table 4.2). Special problems are encountered with microprobe analyses of clays (see Melson and Thompson, 1973). However, the close agreement of these

TABLE 4.1: XRD Results of Clay Alteration Products

Sample	Type of Preparation	Air Dried, 4-30°2θ	Glycol, 4-10°	450°C, 4-10°
Cressbrook Dale Lava (Analysis No.34)	Olivine pseudomorphs	15.1Å (vs)*, 7.4 (wb), 3.04 (ws)	16.83 (vs)	9.83 (mb)
Shacklow Wood Lava (Analysis No.16)	Olivine pseudomorphs	15.2 (vs), c 7.5 (mb)	16.8 (vs)	10.0 (mb)
Shacklow Wood Lava (Analysis No.15)	Whole rock smear	14.6 (ms) not done	16.7 (ms)	10.0 (mb)
Matlock Upper Lava (Analysis No.21)	Whole rock smear	14.5 (ms) not done	16.5 (ms)	9.95 (mb)
Ible Sill (Analysis No.37)	Olivine pseudomorph	15.0 (vs), 7.4 (mb)	16.2 (mb)	10.0 (mb)
Waterswallows Sill ('gabbroic')	Olivine pseudomorph	14.8 (vs) not done	16.3 (vs)	9.8 (sb)
Waterswallows Sill (dolerite)	Whole rock smear	15.1 (vs), 7.5 (wb)	16.8 (vs)	9.83 (mb)
Waterswallows Sill (dolerite)	Clay fraction sedimented mount	15.1 (vs), 7.4 (mb)	16.7 (vs)	9.77 (mb)

*vs - strong, sharp peak; mb - medium, broad peak;
ms - medium, strong peak; ws - weak, sharp peak

Table 4.2

TABLE 4.2: Chemical Analyses of Smectite Alteration
Products in Basalts

	1	2	3	4	5	6	7
SiO ₂	42.8	45.7	43.05	39.11	46.83	43.98	45.12
TiO ₂			-	0.18	0.64	0.16	0.23
Al ₂ O ₃	4.1	4.0	6.40	3.29	8.95	10.15	5.13
Fe ₂ O ₃			17.86	31.49	7.87	7.85	11.14
FeO	28.9*	28.3*	0.10	0.96	4.88	5.32	4.77
MgO	7.9	8.3	4.46	8.05	11.08	18.02	17.06
CaO	2.0	1.9	2.92	2.28	2.78	2.78	0.21
Na ₂ O	0.1	0.1			1.71		2.68
K ₂ O					1.93		0.85
H ₂ O ⁺	14.2**	11.7**	23.93	16.27	5.39	9.24	13.60
H ₂ O ⁻					6.81	6.24	
Total	100.0**	100.0**	98.72	101.63	98.87	103.74	100.83

1 & 2 Microprobe analyses, red pleochroic alteration of olivine - Potluck Sill.

3 Fe-rich nontronite in altered basalt (Weaver and Pollard, 1973).

4. Average of five 'iddingsite' analyses . (Ross and Shannon, 1925).

5. Mixed nontronite/saponite infilling vesicle in basalt. (Scheidegger and Stakes, 1977).

6. Saponite in altered basalt (Weaver and Pollard, 1973).

7. Saponite in altered basalt (Seyfried et al., 1978).

*Total iron as FeO

**Total H₂O calculated by subtraction of other oxides from 100%, may include small but significant values of TiO₂ and K₂O.

analyses obtained from different pseudomorphs is the strongest indication that the results are reliable.

The XRD results indicate that smectites are the predominant alteration phases after olivine. Microprobe analyses indicate an iron-rich, low-alumina variety. Comparisons with published nontronite and saponite analyses (Table 4.2) suggests that Fe-rich nontronite is the dominant phase in a nontronite/saponite aggregate. Melson and Thompson (1973) and Scheidegger and Stakes (1977) have indicated that nontronite and saponite occur as intimate admixtures in deuteric pseudomorphs, further studies to attempt to characterise the di- or tri-octahedral nature of smectites in the Derbyshire basalts were not pursued.

Compared with primary olivine compositions (Appendix 6), the smectite pseudomorphs in the Potluck Sill exhibit a slight increase in SiO_2 and Al_2O_3 concentrations, no change in total FeO and a strong depletion in the MgO content. The high concentration of iron is likely to be present in the Fe^{3+} form both in the smectite lattice and as a discrete goethite phase. The low MgO contents may not be typical of pseudomorphing phases as a whole. As Scheidegger and Stakes (op.cit.) noted, the more highly coloured, red 'iddingsitic' alteration phases tend to be nontronite rich compared with the green or brown saponite rich aggregates. Analyses were not obtained for the more widespread green pseudomorphs which would be expected to exhibit minimal MgO depletion. This is supported by comparisons with green alteration products not associated with olivine pseudomorphs (section 4.6) and the observations outlined in Chapter 7 that there is no net loss of MgO from the basalts.

The absence of macroscopic oxide phases (such as the haematite stringers noted by Fall, 1980) and the dominance of smectites is typical of a 'low oxidative' environment (Seyfried et al, 1978) with the low diffusion

rate of O_2 allowing the incorporation of most of the Fe^{2+} and Fe^{3+} within the clay-phase lattice. Scheidegger and Stakes (1977) noted that smectite-calcite phases as opposed to chlorite-zeolite alteration phases were favoured by conditions of high pCO_2 , H_2O and low temperature (1-300°C). High pCO_2 was attributed to the influence of interbedded calcareous sediments.

Smectite pseudomorphs in the Derbyshire basalts show further secondary replacements by calcite and/or silica. Carbonate replacements are associated with iron oxide rims representing the iron content of the previous smectite phase. Both carbonate and silica replacements involve large scale leaching and mobilisation effects and were thus avoided in the selection of 'fresh' basalts as outlined in Chapter 6.

4:6 Interstitial Alteration Phases

Areas of clay-rich alteration which do not appear to pseudomorph primary mineral phases can constitute over 20% by volume of the basalts. These typically occur as intersertal areas bounded by groundmass pyroxenes and augite suggesting an origin either as a primary, late stage residual product, or as an alteration after such a product.

The interstitial clays are similar in optical characteristics to the green smectite pseudomorphs after olivine described in Section 4:5. Pleochroism however is less well pronounced or absent. Zonation is a common feature in the interstitial replacement, peripheral zones are commonly dark-brown and non-pleochroic contrasting with the pale green central areas. Radiating fibrous textures project inwards from the periphery with central regions exhibiting spherulitic textures.

The close similarity with olivine pseudomorph phases suggest a smectite rich nature. This is confirmed by the XRD results of whole rock smears (Table 4.1) which indicate that smectites are the only alteration phases within the basalts and dolerites. Although the

TABLE 4.3: Analyses of Vesicle and Vein Infilling
Alteration Phases in Basalts

	1	2	3	4	5	6	7
SiO ₂	35.92	42.58	41.70	36.24	43.98	40.44	43.00
TiO ₂	0.00	0.01	0.00	-	0.16	-	-
Al ₂ O ₃	12.20	7.69	6.09	13.10	10.15	14.52	7.20
Fe ₂ O ₃	7.59	9.50	5.55		7.85	1.85	7.79
FeO	4.66	1.95	5.05	21.06*	5.32	2.37	2.53
MgO	21.82	17.52	20.36	17.18	18.02	21.11	21.00
CaO	1.82	1.74	2.10	trace	2.78	2.32	0.4
Na ₂ O	-	0.03	0.01		-	0.42	3.3
K ₂ O	-	0.01	0.05		-	-	0.4
H ₂ O ⁺	9.20	18.44	19.04	11.68	9.24	6.31	18.9
H ₂ O ⁻	6.50				6.24	10.65	
Total	99.71	99.59	99.95	99.26	103.74	99.99	104.52

*Total iron as FeO

1. 'chlorite var. delessite' - infilling vesicles in decomposed basalt, Calton Hill. (Tomkeieff, 1928).
2. 'chlorite var. delessite' 'weathering to clay minerals', fibrous vein infills in dolerite, Calton Hill. (Sarjeant, 1967).
3. Saponite, fibrous vein infills in dolerite, Calton Hill. (Curtis, 1976).
4. 'chlorite var. diabantite', infilling vesicles in Matlock Upper Lava, Mill Close Mine. (Garnett, 1923).
5. Saponite in altered basalt. (Weaver and Pollard, 1973).
6. Saponite, hydrothermally altered breccia (Weaver and Pollard, 1973).
7. Fe-rich saponite in basalt (Seyfried et al, 1978).

majority of basalts show smectites as the interstitial phase some contain relict interstitial areas of either primary glass or analcite indicating that the smectite is a secondary, replacement phase. Primary glass is pale-brown in colour and clouded by opaque inclusions, relict analcite is less common only being noted from the Matlock Upper Lava, tuff associated with the Haddonfields Middle Lava and the Calton Hill dolerite. Analcite can be distinguished from glass by its lack of opaque inclusions. All stages in the replacement of glass and analcite by smectites can be found. Selective smectite alteration of primary interstitial glass is a common feature of basalts and has been noted by Melson and Thompson (1973), Scheidegger and Stakes (1977) and Wood et al. (1978).

Estimates of the composition of the smectite can be made by comparison with analyses of similar material occurring as vein and vesicle infills in the Derbyshire basalts (Table 4.3). Compared with olivine pseudomorphs the interstitial and vesicle infilling smectites appear to be more enriched in the saponite components, with lower Fe(total) and higher MgO concentrations. Total iron concentrations are slightly higher than calculated whole rock (groundmass) values, a feature in keeping with observed geochemical trends and implying no selective leaching or enrichment of Fe. The higher MgO values balances any selective leaching from olivine pseudomorphs. The brown, peripheral, zones of the interstitial areas may represent an iron-rich nontronite, early deuteric phase similar to the observations of Scheidegger and Stakes (1977).

4:7 Opaque and Minor Phases

The opaque mineralogy of the 'fresh' holocrystalline basalts are dominated by Fe-Ti oxides which on average constitute some 5% by volume

(see Appendix 4). Titanomagnetite is the dominant phase with subordinate ilmenite, although in a small number of samples this relationship is reversed. The titanomagnetite and ilmenite occur as equant and lath shaped grains with complex lobate outlines. The anhedral nature of the Fe-Ti oxides is indicative of late-stage crystallisation contemporaneous with augite crystallisation. Accordingly the grain-size varies with the overall grain size of the basalt. In coarse, holocrystalline lavas and dolerites, the Fe-Ti oxides may exceed 0.5 mm in length, whilst in fine-grained basalts average dimensions are in the order of 0.1 to 0.2 mm. 'Pseudoplagiophytic' basalts (see Chapter 5) exhibit features related to more rapid cooling including the development of complex, skeletal magnetites. Fe-Ti oxide phenocrysts have only been noted from a single basalt sample of unusual mineralogy from the Cressbrook Dale Lava where they constitute over 15% and occur as elongate laths up to 3 mm in length.

Titanomagnetites and ilmenites in the 'fresh' basalts exhibit a high degree of homogeneity. The restricted development of thin, sharply defined and well orientated ilmenite lamellae in the titanomagnetite phase is ubiquitous and represents sub-solidus oxidation consistent with a limited degree of high temperature (deuteric) oxidation. A comparison of the textures with the six-point oxidation scales proposed by Watkins and Haggerty (1967) and Ade-Hall and Lawley (1970) indicate that the majority can be placed within class 2. This is in accord with the 'low oxidative' nature of the deuteric olivine alteration products proposed in Section 4:5.

Discrete sulphides occur as minor phase disseminations in many basalts. Chalcopyrite is dominant with subordinate pyrite and bornite. Sulphide phases are extremely fine grained (c. 0.01 mm) and it is not possible to ascertain their primary or 'secondary' deuteric origin.

Larger pyrite inclusions of a probable secondary nature are common in calcic labradorite phenocrysts in plagiophyric basalts.

Euhedral spinel inclusions (c. 0.02 mm) occur in olivine phenocrysts and can be recognised within deuteric pseudomorphs as a non-reactive phase. Apatite occurs as fine grained needles concentrated in areas of late-stage crystallisation.

4:8 The Status of 'Chlorites'

As sections 4:5 and 4:6 have indicated, deuteric alteration products in the lavas and dolerites are dominated by smectites. Previous records of 'chlorite' without supporting XRD analyses must be regarded as dubious. Likewise a detailed investigation of hydrothermal alteration phases (Chapter 9) indicates an absence of 'chlorites'.

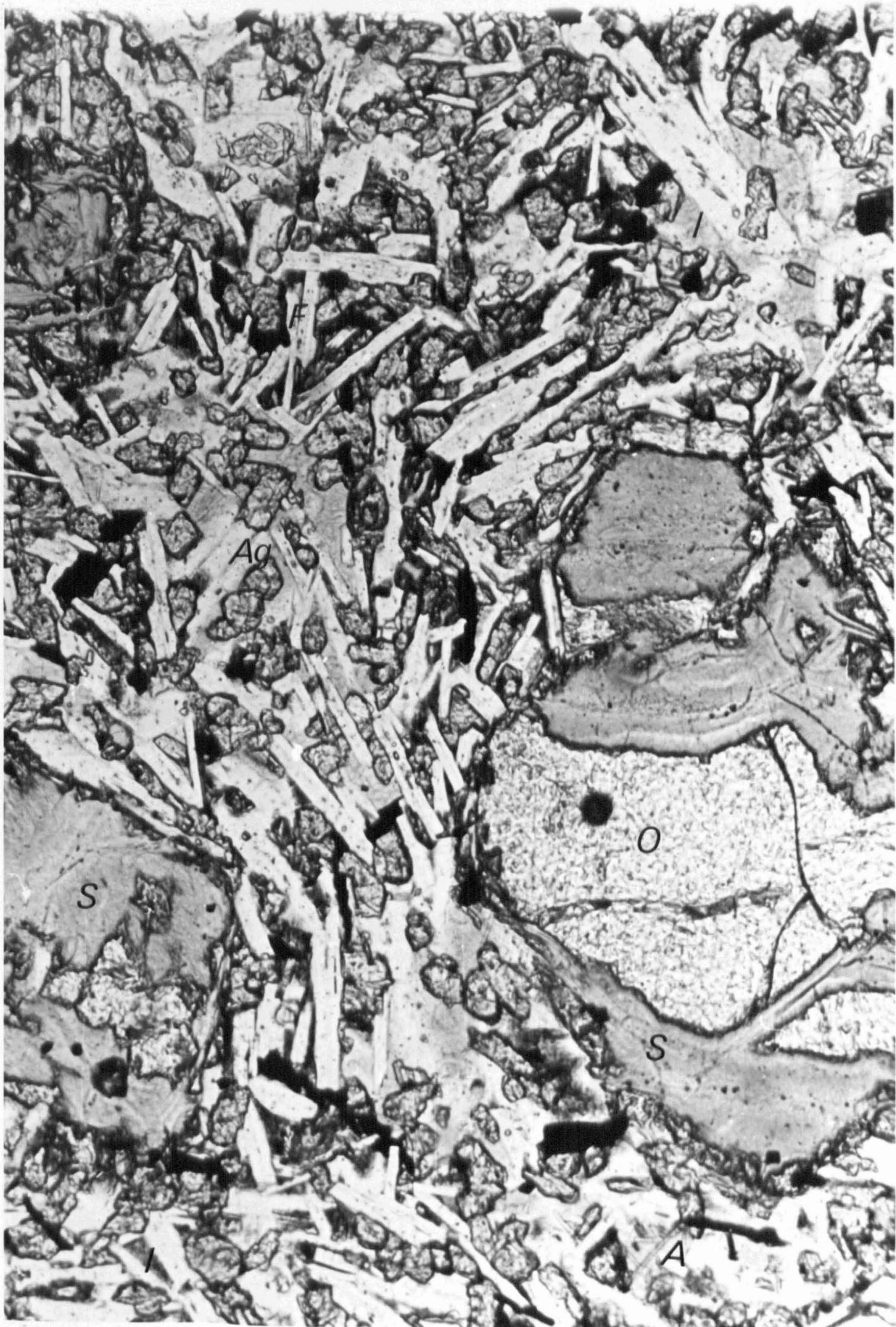
Although the status of 'chlorite' occurrences has been questioned, it is incorrect to suggest the total absence of 'chlorites' from the basalts of the Southern Pennines for undoubted chlorite occurrences were noted from three localities and are considered to represent atypical situations. Chlorite was confirmed by XRD as the pseudomorphing phase of highly fragmented shards representing a phraeatomagmatic tuff from the Cressbrookdale Lava, Hucklow Edge (see Chapter 5) while Spherulitic chlorite intergrown with silica constitutes the 'matrix' of autobrecciated lavas from the Eyam Borehole. In both these instances the environment of formation represents a degree of rapid cooling and high temperature interaction with water. By comparison, coarse tuffs associated with the phraeatomagmatic tuff above the Cressbrookdale Lava show a more 'typical' mineralogy, dominated by smectites. The third occurrence is from the Ible Quarry, Via Gellia. Chloritised dolerite occurs as a vertical 'stratum' within 'fresh' dolerite with smectite pseudomorphs. The locality exhibits a number of unusual features which are described in Chapter 9:11

4:9 Mineralogical Evidence for the Magmatic Affinities of the Derbyshire Basalts

As Wilkinson (1967) noted, the basalts appear to range in petrological type from tholeiitic to alkaline. Mineralogical distinctions between the two series have been outlined in Hess (1967), Carmichael et al. (1974) and Sorenson (1972). Tholeiitic basalts typically exhibit a more complex pyroxene assemblage with co-existing Ca-rich and Ca-poor clinopyroxene phases and orthopyroxenes. Olivine in tholeiites is not an essential constituent, occurring only as phenocrysts usually with pyroxene mantled reaction rims. Intersertal residues are dominated by siliceous glass. Typical alkali-basalts contain a single, titaniferous, clinopyroxene phase with intersertal residues of alkali-feldspar or analcite. Olivine occurs as both a phenocryst and groundmass phase.

The mineralogy of the Derbyshire basalts is not representative of either 'typical' alkali or tholeiitic types. Weakly titaniferous augites and salites constitute a single clinopyroxene phase, olivine occurs mainly as phenocrysts with a subordinate groundmass phase. Alkali-feldspars are not present. Primary intersertal phases are commonly pseudomorphed although relict areas indicate that both glass residuum and analcite can occur.

The mineralogy is of a 'transitional' nature rather than representing a continuous range from alkali to tholeiitic types. As MacDonald and Katsura (1964) noted, the use of mineralogical criteria alone in ascertaining the tholeiitic or alkaline affinities of basalts can only be applied with 'great care' and this is particularly relevant to a study of the Derbyshire basalts.



Chapter Five

Petrography of the Basalts

5:1 Introduction

Eight petrographic groups of basaltic lavas and dolerites are recognised based on phenocryst assemblages and textural variations. Individual lava flows show a uniformity of petrographic type, with only minor textural variations between vesicular margins and the holocrystal-line cores. The only consistent difference is in the greater degree of alteration associated with vesicular units. Single Lavas, e.g. the Cressbrook Dale Lava, however, may be composed of individual flows of different petrographic type. Variations in petrographic types can often be correlated between outcrops and/or boreholes. For example plagiophyric types only occur as a late stage component of thick, extrusive sequences and suggest an origin from a zoned magma chamber.

There is no direct relationship between petrographic type and stratigraphic horizon. Neither is it possible to make definitive statements relating petrographic types to variations in geochemistry and hence nomenclature, as was demonstrated for the Dinantian lavas of Scotland by MacDonald (1974). This results from a paucity of analytical data for certain types as well as difficulties of nomenclature within a 'transitional' basalt series (see Chapter 8).

5:2 Petrographic Types

Under a textural terminology 'fine grained' refers to an average groundmass size of less than 1 mm and 'medium grained' averages between 1 and 3 mm. The term 'basalt lava' and 'dolerite' imply no textural connotations and their use is restricted to a differentiation between extrusive and intrusive products. 'Basalts' encompasses a range of geochemistry which includes both the basalt lavas and dolerites. The majority

of the basalt lavas and dolerites are microphyric with average phenocrysts between 1 and 2 mm, occasional macrophyric types occur and these have phenocrysts greater than 2 mm. Truly aphyric types have not been observed.

Eight petrographic types based on phenocryst assemblages and textural variations are defined. These are illustrated by Plates 1.1 to 1.7 and the petrography of the pyroclastic horizons are illustrated by Plates 1.8 to 1.10.

1. Olivine-Plagioclase Phyric Basalts

These are medium grained basalts with between 20 and 30% of olivine and plagioclase microphenocrysts, with olivine dominant. Rare clinopyroxene microphenocrysts also occur. The groundmass consists of randomly orientated plagioclase laths and granular to subophitic augite (up to 1 mm) with intersertal clays. Ilmenite and magnetite occur as euhedral rods and grains. A common feature of the calcic labradorite microphenocrysts is their strong zoning and resorption. This constitutes the predominant sub-group amongst the Derbyshire basalts.

2. Plagiophyric Basalts

These constitute a distinct type characterised by an excess of plagioclase phenocrysts (up to 15%) with respect to olivine. Phenocrystal plagioclase exhibit either simple twinning or are untwinned with euhedral lath-shaped or rhombic sections and show strong oscillatory zoning. Silicification of olivine, and possibly clinopyroxene, is a ubiquitous feature. The phenocrysts are set in a fine-grained matrix of granular augite, plagioclase laths and granular iron-titanium oxides which often exhibit skeletal textures.

3. Olivine-Phyric Basalts

Olivine constitutes the dominant phenocryst phase, which can exceed 25%, with rare clinopyroxene microphenocrysts. The euhedral olivine phenocrysts are set in a fine grained matrix of granular augite, euhedral to granular iron-titanium oxides and plagioclase laths. The latter often exhibit a strong fluxioning to produce a 'trachytic' texture.

4. Clinopyroxene-Olivine Phyric Basalts

Clinopyroxene and olivine phenocrysts (20-30%) occur in equal proportions with rare plagioclase phenocrysts. Pyroxene phenocrysts are euhedral and exhibit strong zoning. The groundmass is fine grained with granular augite, plagioclase laths and areas of interstitial analcite. This type has only been noted as a facies of the intrusive dolerite at Calton Hill. It is nepheline-normative and can be designated as a typical alkali-olivine basalt.

5. 'Pseudo-Plagiophyric' Basalts

Fine-grained plagioclase laths with granular augite are set in a dark glassy mesostasis charged with opaque oxides which 'outlines' the plagioclase producing a 'pseudo-plagiophyric' texture. True microphyric plagioclase is rare and olivine dominates the sparse phenocryst assemblages. Fe-Ti oxides have a characteristic 'dendritic' or skeletal form while the plagioclase laths have a corroded appearance.

6. Olivine-Phyric, Ophitic Dolerites

This is predominantly a textural sub-division and is confined to facies of doleritic intrusions. Olivine, often macrophyric, is the dominant phenocryst phase (20-30%). The groundmass is medium to coarse

grained with a characteristic ophitic texture of augites enclosing labradorite laths. The amount of interstitial material is less than in the other subdivisions.

7. Plagioclase-Clinopyroxene Phyric Basalts

Plagioclase and clinopyroxene are the dominant phenocrysts with olivine wholly subordinate or absent. Fe-Ti oxides occur in the skeletal form and can occur as phenocrysts. This is a rare petrographic type, probably capable of further subdivision, and has only been noted from the Buxton Bridge dykes and as a late flow within the Cressbrook Dale Lava. The geochemistry of these basalts is more 'evolved' than the previous types.

8. Auto-brecciated Basalts

Auto-breccias visually resemble 'block lavas' and commonly form a component of Lavas in close proximity to central vent cones. The individual 'blocks' are on average less than 5 cm in diameter but can attain sizes of up to 1 m and in such instances these large blocks illustrate a rounding which may lend to their misinterpretation as 'pillows'. The blocks are polyhedral with angular to subangular outlines with rare spinose projections. A fine-grained clastic matrix is absent and the voids between blocks have an infill of secondary spherulitic silica and chlorite.

The petrography of individual blocks is dominated by dark brown, palagonitic glass with abundant, usually pseudomorphed, microphenocrysts of plagioclase with lesser amounts of olivine and pyroxene. Large plagioclase phenocrysts at the periphery of blocks show truncation, indicating that the lavas were consolidated prior to brecciation. 'Reaction rims' between clasts and the siliceous matrix have been noted by Elliot, (in Ramsbottom et al., 1963). However, during the present study it was noted

that devitrification of the primary palagonite and replacement by green phyllosilicates is a common feature and as this proceeds in many instances from the periphery it can give the impression of a 'reaction rim'.

A feature of auto-breccias is their interdigitation with more 'normal' massive, non-vesicular, basalt flows. Blocks within the auto-breccias are either poorly vesicular or non-vesicular and vesicles do not exhibit the deformation common to molten pyroclastic ejecta. Apart from their finer clast size, the auto-breccias compare favourably with block lavas described by MacDonald (1972). The mode of formation of block lavas is uncertain, but as MacDonald (op. cit.) notes, they seem to advance by sliding rather than flow tending to internal disruption. This would be expected to be more common on the flanks of steep ash cones developed adjacent to central vents. The auto-breccias appear to represent volatile depleted, highly fluid flows which have been disrupted by such a mechanism.

5:3 Petrographic Variations within Lavas

The examination of borehole core material from the major Lava horizons of the Orefield has enabled their internal structures and petrographic variations to be examined. Detailed 'lithologs' and the location of the samples are given in Appendix 7. The internal structures of Lavas - pyroclastic components, flow unit thickness etc. were outlined in Chapter 3. Petrographic variations within Lavas are discussed in relation to the terminology of Section 5:2.

a. The Cressbrook Dale Lava

The full thickness of the lava was intersected in the Eyam Borehole (76.6 m) and the Wardlow Mires No. 1 Borehole (33.8 m) and both show a number of common features. The Lava is capable of a two-fold division into a sequence dominated by auto-breccias overlain by a sequence of

thick flow units with minimal pyroclastic components.

The auto-breccias are interdigitated with more 'normal', non-vesicular, thin basalt flows. The lower contact of the Lava in both boreholes is non-vesicular basalt which rests on a thin sequence of tuffaceous limestone. The basal lava sequence in the Wardlow Mires No.1 Borehole is a pseudo-plagiophyric type whilst that of the Eyam Borehole is slightly coarser grained and gradational towards an olivine-plagiophyric type. The auto-breccias exhibit the typical petrographic features outlined earlier with random blocks and variations in clast size, interdigitated with thin flows of pseudo-plagiophyric type. In the Wardlow Mires Borehole, the auto-breccias are overlain by a thin tuff whilst in the Eyam Borehole a transitional sequence of basalt occurs between the auto-breccias and a thin tuff. These are fine-grained, olivine-phyric basalts with euhedral olivine pseudomorphs and fluxioned plagioclase.

The upper sequence in both boreholes is characterised by thick flow units with holocrystalline, medium grained central regions. The basalts are plagiophyric with resorbed, zoned phenocrysts. An unusual, coarse variant is recognised from a sample at a depth of 77 m in the Eyam Borehole. Average grain size is in excess of 3 mm with pale-pink, sub-ophitic pyroxene and phenocrystal iron-titanium oxides 3 mm in length and associated interstitial areas with abundant iron-titanium oxides of smaller size. A notable feature is the apparent absence of pseudomorphs after olivine. The unusual petrography of the basalt is matched by its geochemistry (see Chapter 7) which indicates that it is more highly evolved when compared with the majority of the basalts. The upper sequence in the Wardlow Mires Borehole exhibits ubiquitous albitisation and clay replacement in contrast to the basalts in the Eyam Borehole.

b. The Shacklow Wood Lava

The Lava was intersected in the Mogshaw No. 3 Borehole, but its base was not penetrated. The lower 10 m of the borehole intersected highly vesicular, altered lava. Variations in vesicularity suggest a number of rapidly erupted thin flows. Although altered the lavas show a uniformity of relict texture indicating a medium-grained, olivine-phyric type. There is a distinct transition from vesicular to non-vesicular basalt at 113.6 m. Vesicular, iron-stained, lava is overlain by a thick (> 25 m) non-vesicular, holocrystalline basalt. Above the abrupt transition the basal sequence of non-vesicular lava exhibits a degree of 'chilling' with euhedral olivine pseudomorphs set in an extremely fine-grained groundmass. The 'chilled' facies grades upwards into a thick sequence of coarse feldspar-olivine phyric basalt over a 3 m transitional zone. In this transitional zone the basalt is a medium to fine-grained olivine-phyric type with fluxioned plagioclase laths, granular augite and sporadic clinopyroxene microphenocrysts. The majority of the flow unit is composed of a medium to coarse grained olivine-plagiophyric basalt. Plagioclase phenocrysts exhibit oscillatory zoning and resorbed outlines. At a depth of 118 m the texture displays its coarsest development with subophitic groundmass augite and sporadic clinopyroxene phenocrysts. The upper sequence of this unit grades into vesicular lava where primary textures have been destroyed by subsequent hydrothermal alterations. The flow is overlain by 4 m of tuff and by a further thin flow (4 m) of plagiophyric basalt with euhedral phenocrysts in a fine-grained groundmass. The final volcanic activity is represented by a 1.5 m thick pyritous tuff.

c. The Conksbury Bridge Lava

The Conksbury Bridge Lava was intersected by the Conksbury East No. 1 and 5 Boreholes and the Haddonfields No.11 Borehole (Walters and

Ineson, 1981). The 35 m thickness indicated by the Conksbury East No. 5 Borehole is considered to be an expanded sequence due to fault repetition when compared with the 25 m thickness intersected by the nearby No.1 Borehole. The uppermost 20 m of the No.5 Borehole core was not available for relogging and much of the remaining core exhibited the effects of hydrothermal alterations. The least altered material from a depth of 50 to 55 m, is an olivine-phyric basalt with in excess of 20% olivine pseudomorphs set in a fine-grained groundmass lacking phenocrystal plagioclase. This distinctive type can be recognized from relict textures as persisting throughout the lower horizons. The basal sequence exhibits large 'pipe-vesicles' up to 5 cm wide and in excess of 20 cm in length. Pyroclastic components within the Lava are minimal.

The upper sequence of the Lava is exposed to the west of Conksbury Bridge in Lathkill Dale. A number of thin flows with vesicular margins are evident in contrast to the thick flow units in the lower parts of the Conksbury East boreholes. The basalt, whilst still of olivine-phyric type, has a medium-grained groundmass despite the minimal thickness of individual flows.

The 'Upper Lava' of the Haddonfields No.11 Borehole has been correlated with the Conksbury Bridge Lava by Walters and Ineson (1981) and it exhibits similar features in the Conksbury East/Lathkill Dale sections. An upper sequence of thin flow units grades into fine-grained, olivine-phyric basalts identical to the lower sequence of the Conksbury East No. 5 Borehole.

d. The Haddonfields 'Lower' Lava

Haddonfields No.11 Borehole intersected 58 m of the Lower Lava without penetrating its base. The upper sequence (25 m) represents a

single flow unit characterised by olivine-phyric, medium-grained basalts with rare clinopyroxene and plagioclase microphenocrysts. Relict glass, clouded with opaques, produces a marked interstitial texture and exhibits a high degree of clay replacement. Beneath this thick flow unit are a series of thinner-vesicular lava flows. The Lower Lava contains no pyroclastic components.

e. The Lower Millers Dale Lava

ICI's TB-21 Borehole, located north-east of Buxton Bridge intersected the Lower Millers Dale Lava and proved a thickness of 30 m (Walters and Ineson, 1981). The lava can be subdivided into four extrusive events, the final event dominated by pyroclastic activity. The lower three flows exhibit a uniformity of petrographic type both amongst vesicular and non-vesicular basalts. Pseudomorphed olivine microphenocrysts are set in a medium-grained groundmass with occasional resorbed plagioclase phenocrysts and rare clinopyroxene microphenocrysts. A high percentage of interstitial relict glass altering to clay aggregates occur and result in a texture similar to that shown by the Haddonfield Lower Lava.

Explanation to Plates

PLATE 1.1 WATERSWALLOWS SILL. LOWER HORIZON-WATERSWALLOWS QUARRY.
(55/Type 3)^{*} -Frontispiece to Chapter 4.

Fine grained intrusive basalt with partly altered olivine microphenocrysts in a groundmass of plagioclase laths, granular augite, lobate Fe-Ti oxides, smectite intersertal areas associated with acicular apatite. O-relict olivine, S-smectite alteration of olivine, A-apatite, Ag-augite, I-interstitial secondary smectites, F-lobate Fe-Ti oxides crystallizing after augite. (4.5mm, ppl)⁺

PLATE 1.2 MILLERS DALE UPPER LAVA. WHAM SOUGH DIG-TADDINGTON.
(24, 25/Type 3)^{*}

A). Fine grained, non vesicular olivine microphyric basalt. Smectite pseudomorphs after euhedral olivine microphenocrysts exhibit a degree of secondary silica replacement (clear areas) Groundmass of fluxioned plagioclase laths, granular augite and Fe-Ti oxides with a low concentration of interstitial smectite. (4.5mm, ppl)⁺

B). Fine grained, olivine microphyric basalt similar to (A) but with slightly coarser groundmass and more evenly distributed and finer grained olivine microphenocrysts. (4.5mm, ppl)

C). Glomeroporphyritic aggregate of three, rounded titaniferous sillite microphenocrysts. (2.0mm, pxpl)

D). Euhedral sillite microphenocryst in a fine-grained groundmass with fluxioned labradorite laths and aggregates of granular clinopyroxene. (4.5mm, ppl)

E). Higher magnification view of the euhedral microphenocryst in (D) illustrating faint oscillatory zoning parallel to euhedral outline. (0.8mm,pxpl)

F). Additional view of the euhedral microphenocryst illustrating the strongly sieved core and faint body colour indications of zoning. (2.0mm,ppl)

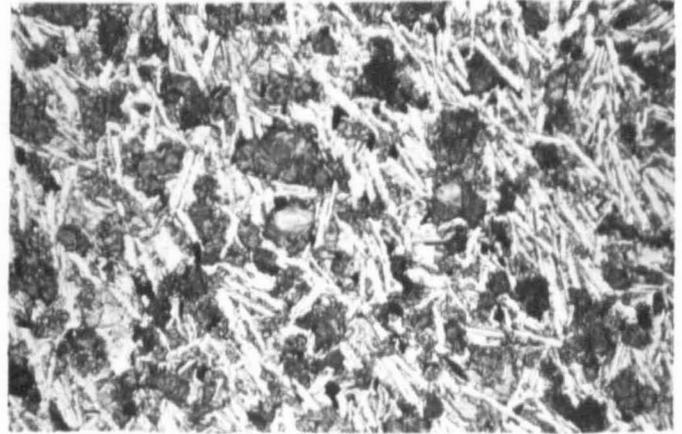
*-The initial number indicates the "analysis number" of the specimen concerned and this can be cross referenced to geochemical, modal and more detailed location information contained in Appendices 1 to 6. "Type" number refers to the petrographic types defined in Chapter 5.2.

+ Dimensions refer to the longest side of the rectangular field of view. A limited number of magnifications are represented, the majority are 4.5mm enabling rapid comparisons of textural variations. Ppl = plane polarised light, Xpl =crossed polars, Pxpl =partly crossed polars.

Plate 1·2



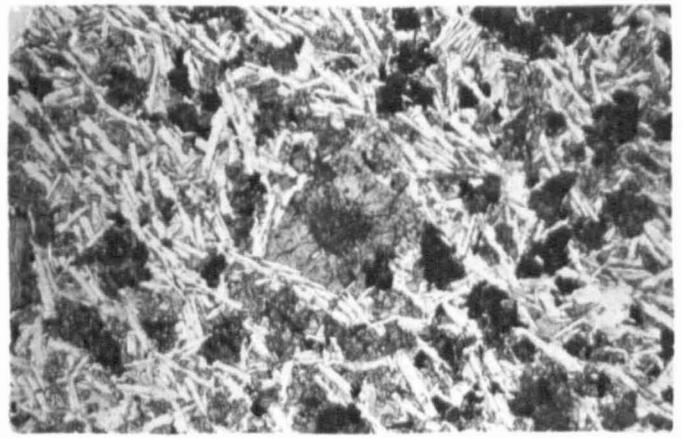
A



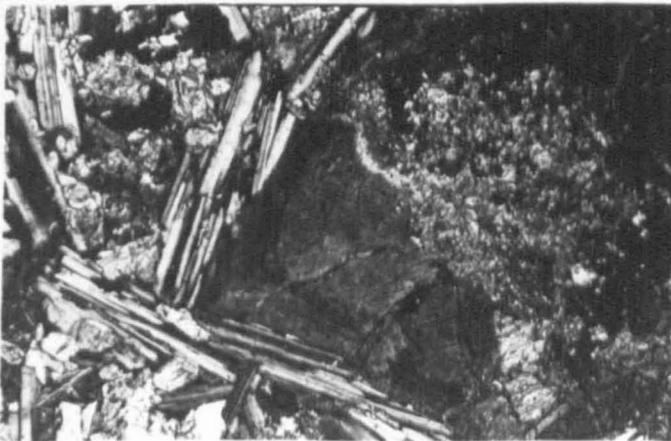
B



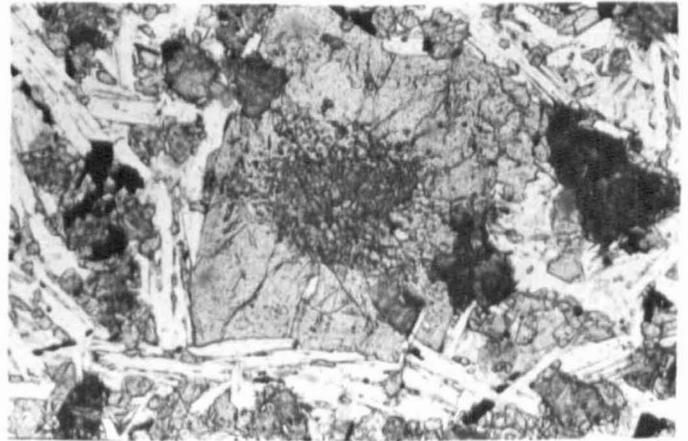
C



D



E



F

PLATE 1.3 TUNSTEAD NORTH DYKE. BUXTON BRIDGE, GREAT ROCKS DALE.

(59/Type 7)

A) & B). Typical plagiophyric texture with euhedral calcic labradorite phenocrysts illustrating simple twinning and faint oscillatory zoning, with scattered augite microphenocrysts. Groundmass of labradorite laths, granular augite, skeletal Fe-Ti oxides and a high proportion of turbid devitrified glass and secondary red and green smectites. (4.5mm, ppl)

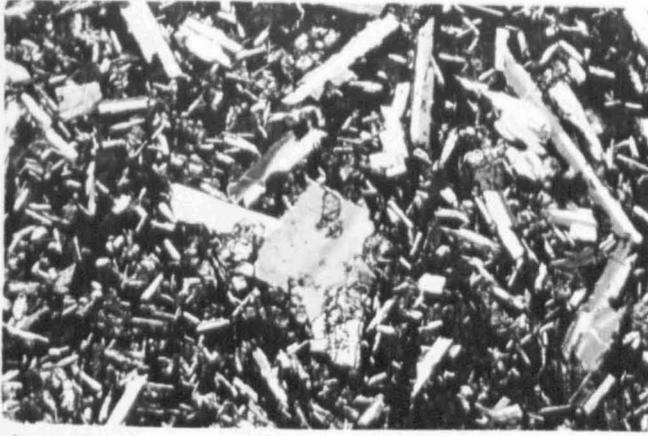
C). Lozenge shaped calcic labradorite microphenocryst illustrating fine-scale oscillatory zoning parallel to euhedral outline. (2.0mm, pxpl)

D). General view of microphenocryst in (C) (4.5, ppl)

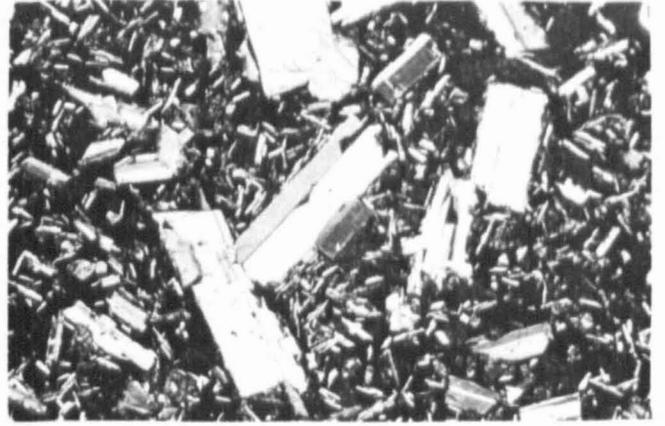
E). Typical sub-rounded augite microphenocryst (upper centre) with faint overgrowth rim of similar composition. (4.5mm, ppl)

F). Oscillatory zoned calcic labradorite phenocryst associated with a rare clay filled vesicle and areas of calcite replacements (lower centre) probably representing preferential replacement of augite microphenocrysts. (4.5mm, xpl)

Plate 1-3



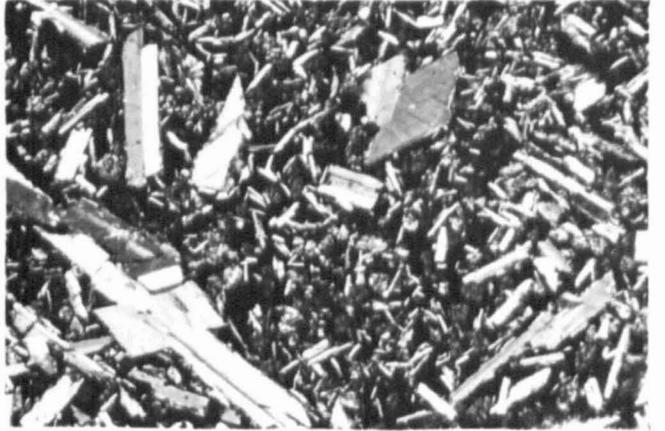
A



B



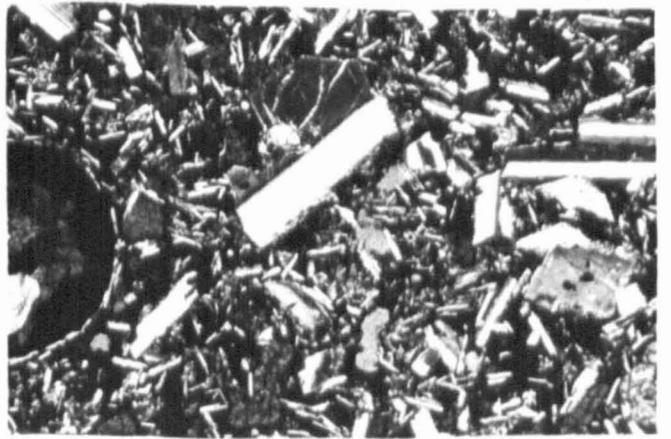
C



D



E



F

PLATE 1.4 BASALT PETROGRAPHIC TYPES.

A). AUTOBRECCIA, CRESSBROOK DALE LAVA-EYAM BOREHOLE, 119m. (-/Type 8). Partly rounded, fine grained clasts of chilled basalt with devitrified, turbid glass and recognizable pseudomorphs of plagioclase (some truncated at edge of clast) in a matrix of silica and chlorites which exhibit striking spherulitic and radial textures. (4.5mm, pxpl)

B). MATLOCK UPPER LAVA, PSALTERS LANE. (21/Type 1) Coarse groundmass of plagioclase, augite and opaques with a typical example of a partly resorbed microphenocryst of plagioclase. Lozenge shaped calcic labradorite (upper centre) exhibits a rounded and irregular outline. (2.0mm, ppl)

C). CRESSBROOK DALE LAVA, EYAM BOREHOLE-125m (-/Type 5). Pseudo plagiophyric basalt with ragged plagioclase laths outlined by concentrations of fine-grained magnetites illustrating complex skeletal growth textures. (0.8mm, ppl)

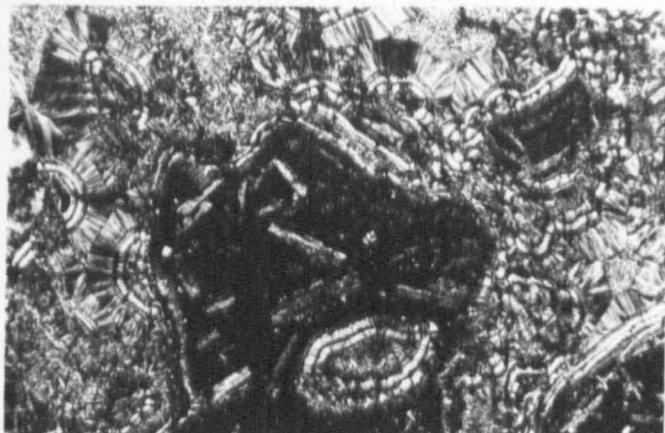
D). HADDONFIELDS LOWER LAVA, HADDONFIELDS No. 11 BOREHOLE. (9/Type 3). Typical coarse "holocrystalline" lava from the central region of a thick flow unit. Randomly orientated plagioclase laths are accompanied by coarse, granular augite becoming sub-ophitic, laths of ilmenite and equant grains of magnetite with a high proportion of interstitial turbid glass and secondary dueteric smectites. The nature of the interstitial smectite areas introduces difficulties in modal distinction of similarly pseudomorphed olivine microphenocrsts. (4.5mm, ppl).

PLATE 1.4 BASALT PETROGRAPHIC TYPES--(CONTINUED)

E). "CHILLED" SHACKLOW WOOD LAVA, MOGSHAW No. 3 BOREHOLE-131.5m. (-/Type 3). Euhedral pseudomorphs after olivine in an extremely fine-grained groundmass from the lower contact of a thick flow unit. (4.5mm, ppl)

F). CONKS BURY BRIDGE LAVA, CONKS BURY No. 5 BOREHOLE. (1/Type 3). Euhedral smectite pseudomorphs after olivine illustrating a complete gradation in size, in a fine grained groundmass of plagioclase laths, granular augite and interstitial green smectite. Basalt from the central region of a thick flow unit. (4.5mm, ppl)

Plate 1·4



A



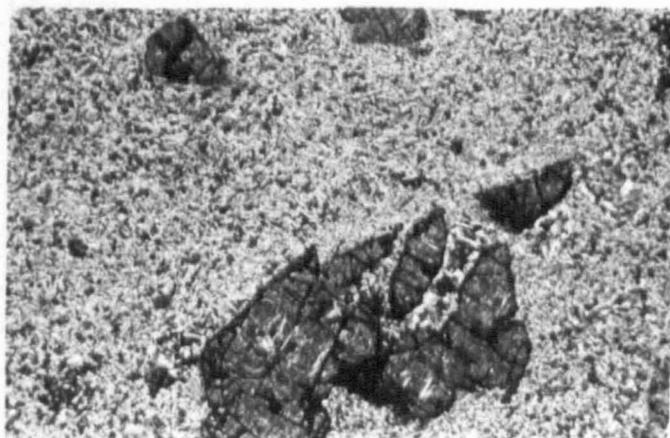
B



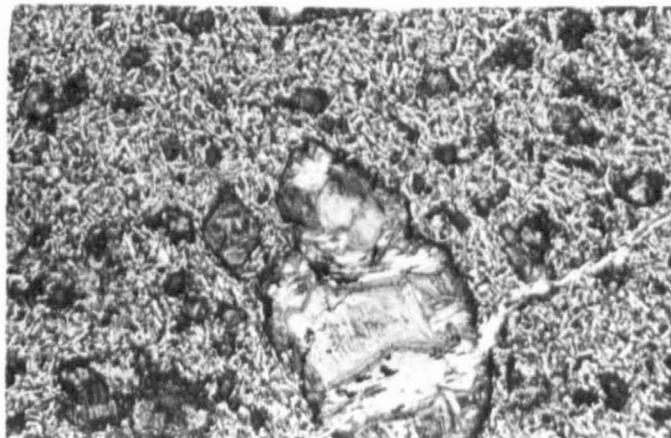
C



D



E

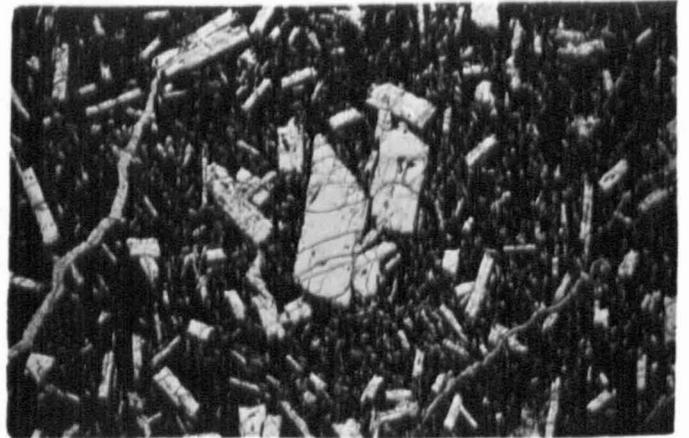


F

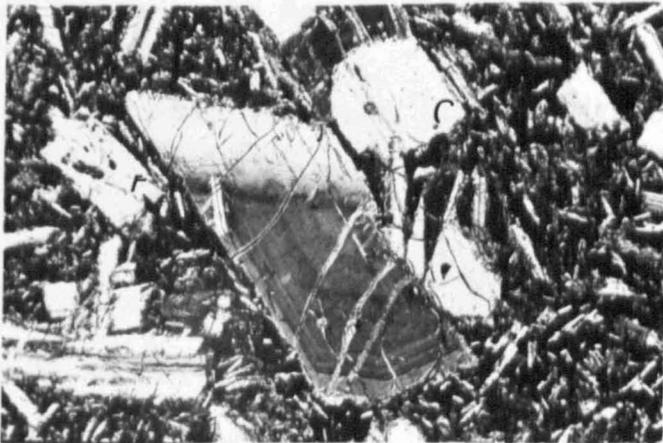
Plate 1.5



A



B



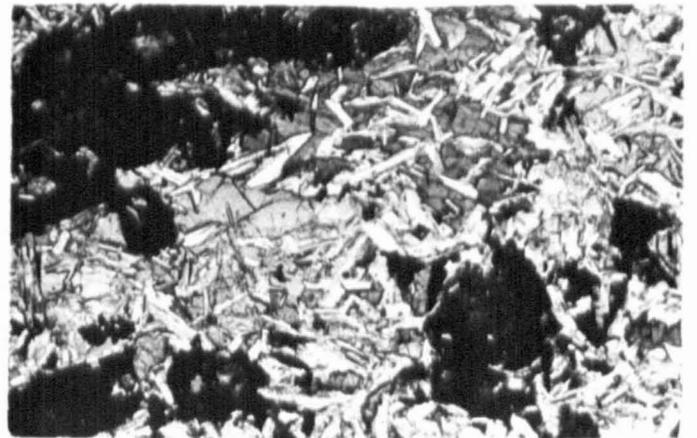
C



D

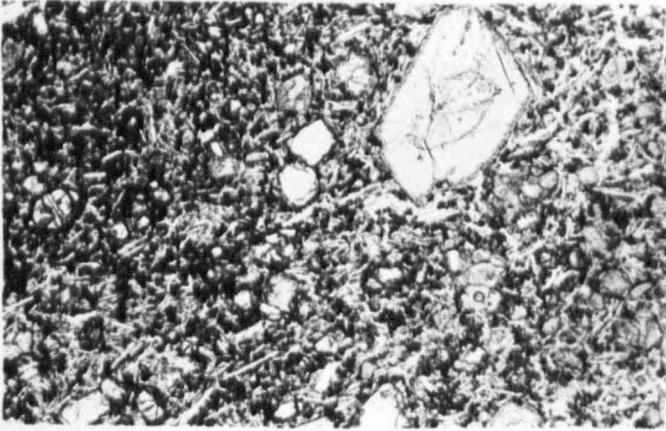


E

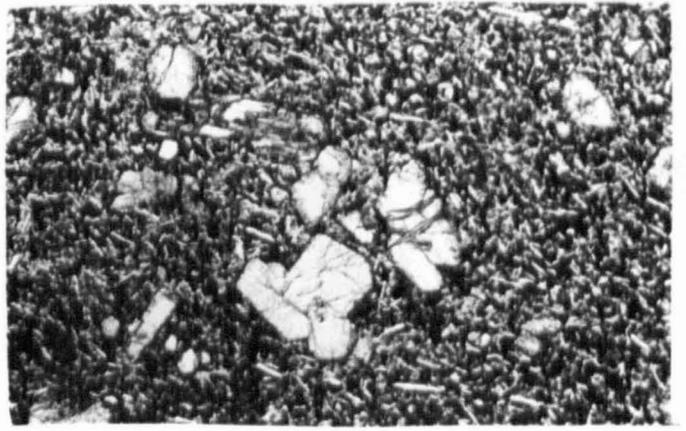


F

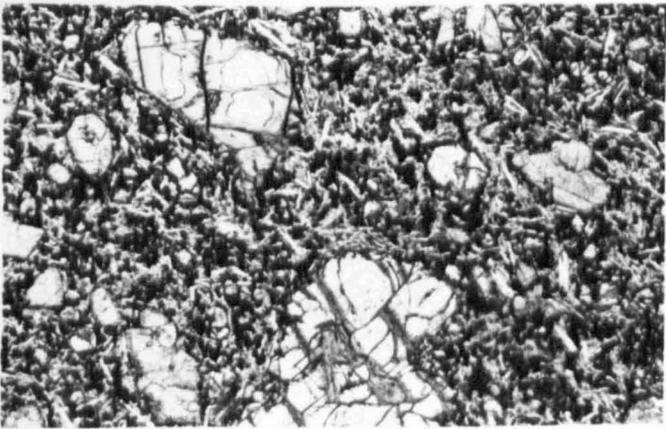
Plate 1·6



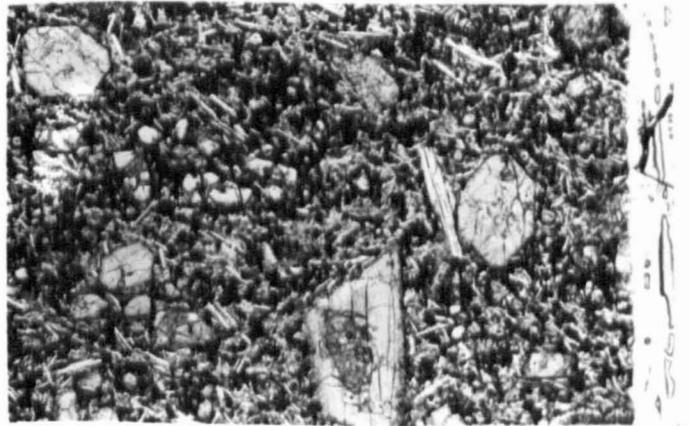
A



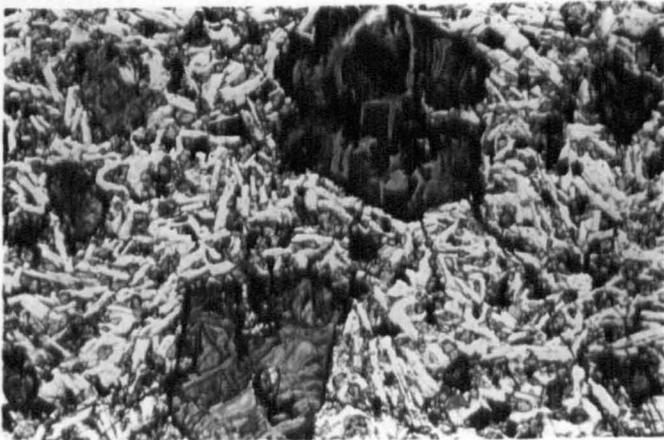
B



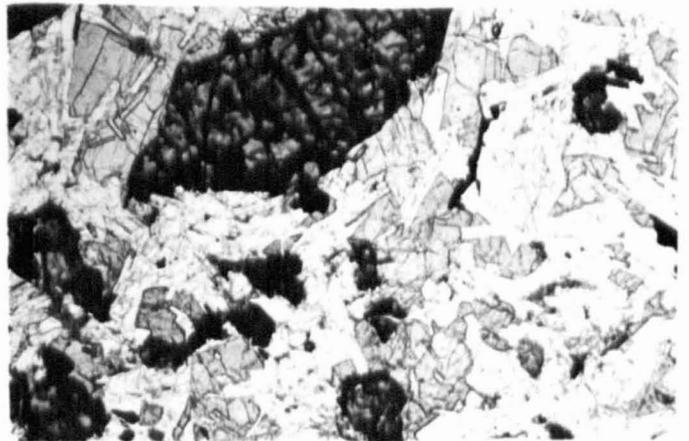
C



D

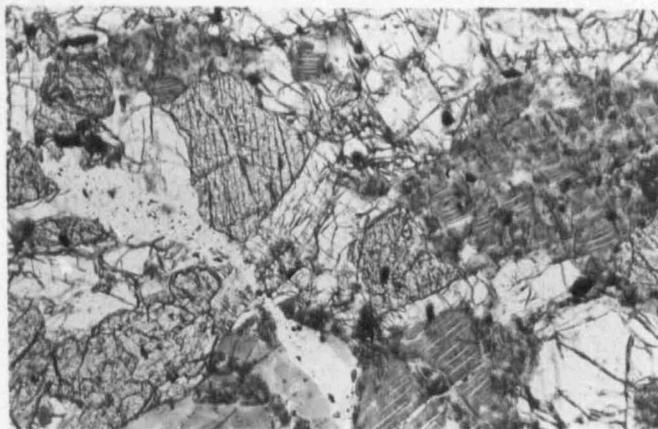


E



F

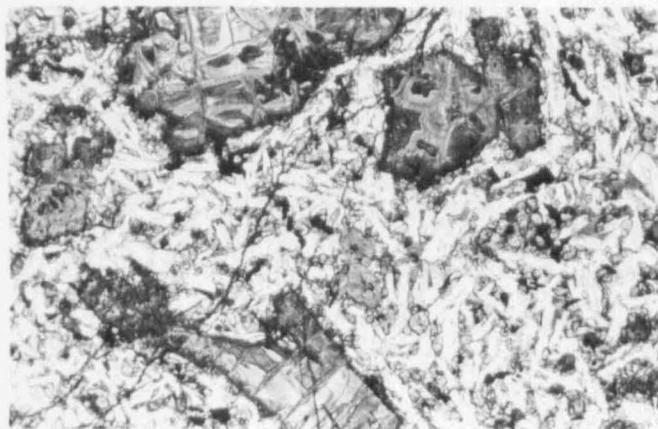
Plate 1·7



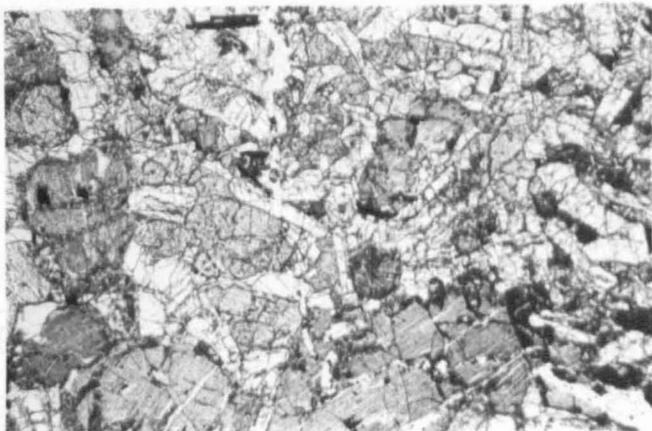
A



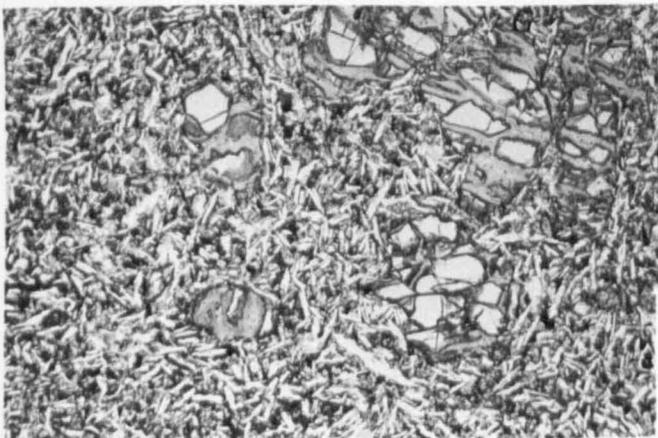
B



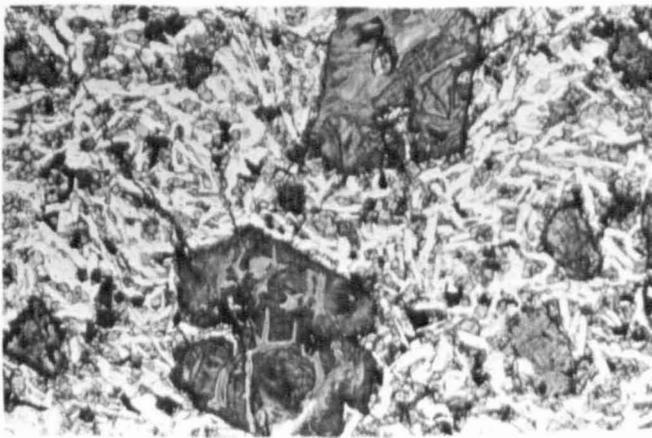
C



D



E



F

PLATE 1.8 TUFFS, AGGLOMERATES AND AUTOBRECCIAS.

A). TUFF-TOP OF CRESSBROOKDALE LAVA, Hucklow Edge No.9 Borehole 165 m. Coarse, lapilli tuffs poorly sorted with rounded limestone clasts.

B). TUFF-TOP OF CRESSBROOKDALE LAVA, Hucklow Edge No.9 Borehole 188.7m and 170m. Left-pale-green extremely fine-grained tuff with no discernable macroscopic textures (but see Plate 1.9f). This illustrates the caution necessary in the interpretation of all borehole logs of igneous horizons, the superficial resemblance to partly altered non-vesicular lava is striking. Right-graded tuff bedding with sharply defined alternations of coarse and fine-grained horizons.

C). AGGLOMERATE-MILLERS DALE LOWER LAVA, lower level of Waterswallows Quarry. Coarse agglomerate with abundant rounded and recrystallized limestone clasts, with occasional lava fragments in an iron-stained, fine grained calcitized tuffaceous matrix.

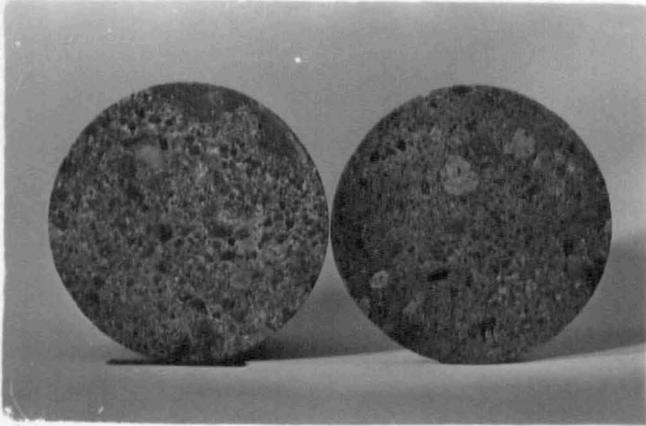
D). PINDALE TUFF-borehole in Hope Cement Works Quarry. Coarse tuff with poorly sorted devitrified lapilli in a dark green smectite rich matrix.

E). "PSEUDOTUFF"-PEAK FOREST SILL, near Blacklane Farm (102 783). Fine scale, net-like veining, brecciation and alteration of dolerite adjacent to mineralisation results in a rock superficially very similar to a coarse tuff, field relationships and transitional types indicate its true origin.

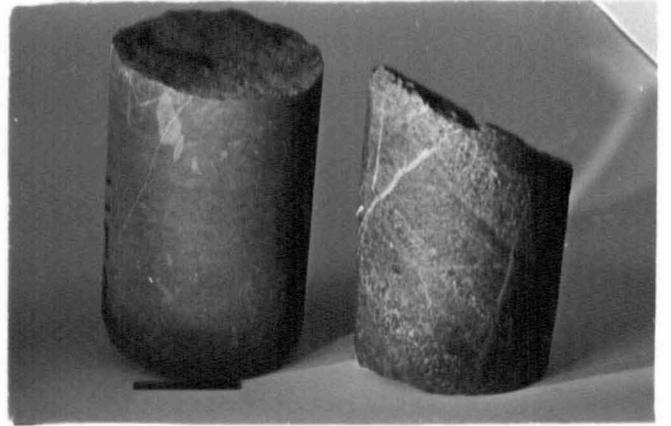
F). AUTOBRECCIAS-Wardlow Mires No.1 Borehole. Poorly sorted angular and spinose clasts of chilled devitrified lava in matrix of chlorite and silica. (see Plate 1.4a) Sample on right contains a typical large rounded block of coarser basalt.

BAR SCALE =3cm

Plate 1-8



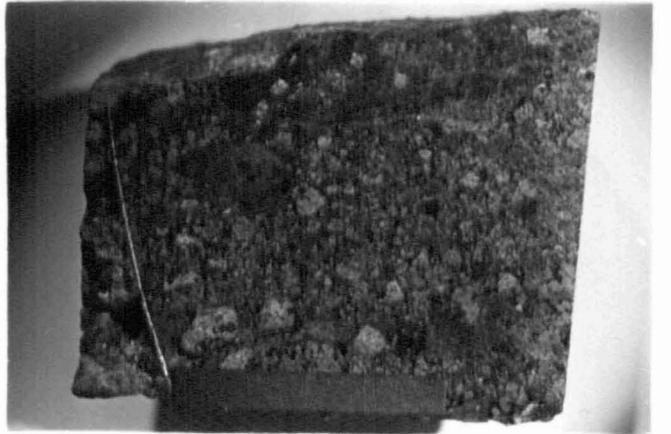
A



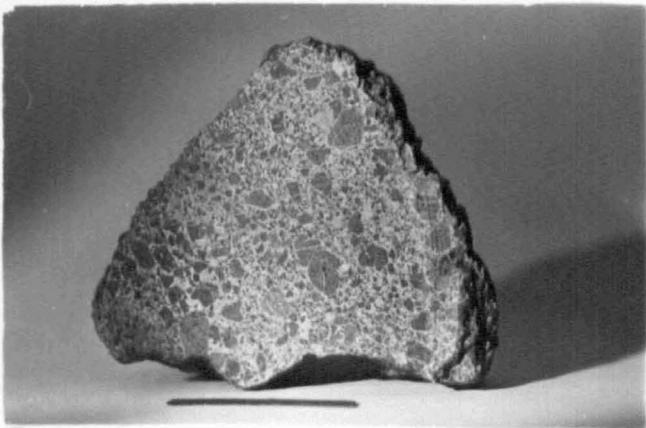
B



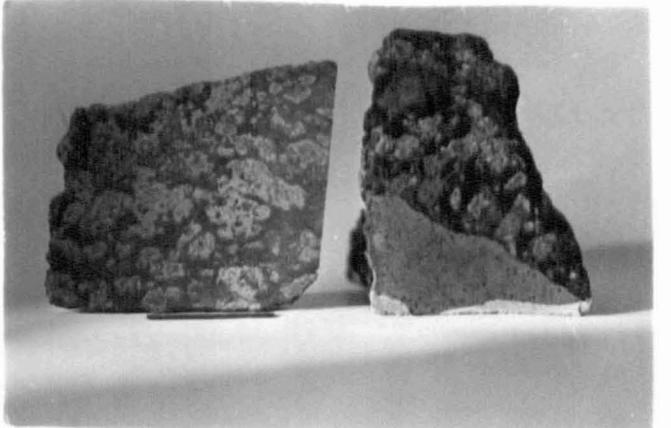
C



D



E



F

PLATE 1.9 PYROCLASTIC PHOTOMICROGRAPHS.

A). TUFF-HADDON FIELDS MIDDLE LAVA, Haddonfields
No. 11 Borehole-206m. Medium grained tuff from sequence
of graded tuff bedding. Angular and cusped shreds are
indicative of violent, explosive activity. (4.5mm, ppl)

B). TUFF-TOP OF CRESSBROOKDALE LAVA, Hucklow Edge
No. 9 Borehole-165m. Coarse, poorly sorted tuff with large
cinder fragment illustrating rounded but irregular
outline bounded by vesicle fractures, in a matrix of
cusped shreds. Primary palagonite replaced by smectites
with silica and carbonate replacement of groundmass.
Analcite occurs as vesicle infills and associated with
areas of coarse carbonate. (4.5mm, ppl)

C). TUFF-HADDONFIELDS MIDDLE LAVA, Haddonfields
No. 11 Borehole-206m. Highly vesicular, pumice fragments
with regular outlines in a matrix of primary turbid
analcite (dark grey) altering to fibrous smectites
in peripheral areas. (4.5mm, ppl)

D). TUFF-TOP OF MATLOCK LOWER LAVA, Hallicar
Wood Adit. Typical recrystallized, rounded limestone
fragment in fine grained tuff matrix. (4.5mm, ppl)

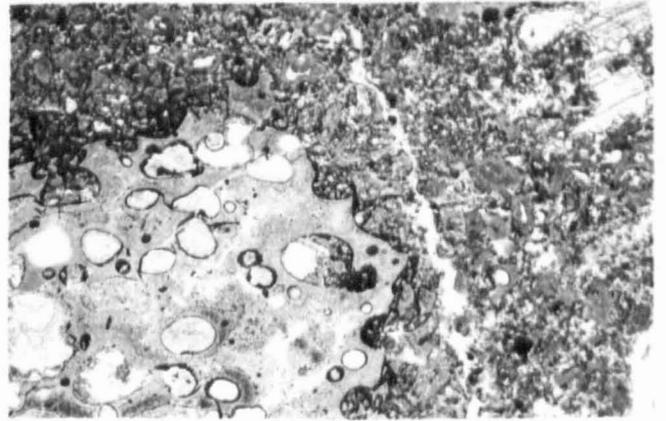
E). TUFF-TOP OF CRESSBROOK DALE LAVA, Hucklow
Edge No. 11 Borehole-170m. Dark, isotropic areas of
secondary analcite in coarse tuff. Analcite occurs as
euhedral crystals in areas of coarse carbonate (right
centre), as components of vesicle infills and as an
alteration phase of the matrix. (4.5mm, xpl)

F). TUFF-TOP OF CRESSBROOKDALE LAVA, Hucklow Edge
No. 11 Borehole-188.7m. Extremely fine grained, fragmented
tuff with devitrified cusped shreds and an absence of
lapilli indicating explosive eruption probably the
result of phreatomagmatic interactions. Matrix is replaced
by aggregates of silica, carbonate and analcite, shreds
replaced by chlorites. (2.0mm, ppl)

Plate 1·9



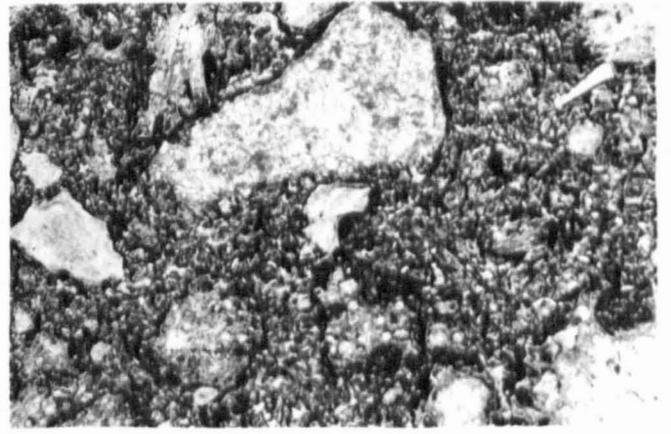
A



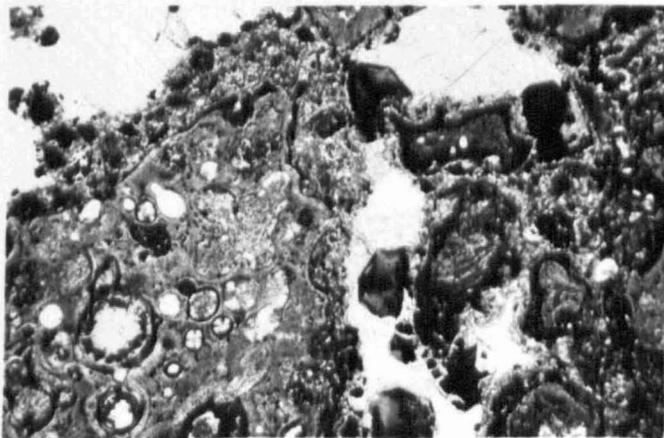
B



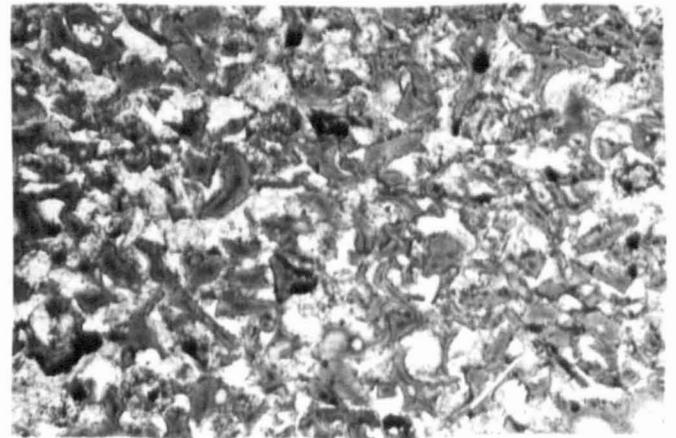
C



D



E



F

PLATE 1.10 PYROCLASTIC PHOTOMICROGRAPHS.

A). TUFF-HADDONFIELDS MIDDLE LAVA, Haddonfields
No. 11 Borehole-206m. Coarse tuff with pumice -note
regular outlines and deformed vesicles. (4.5, ppl)

B). PINDALE TUFF, Borehole in Hope Cement Works
Quarry. Coarse tuff with lapilli containing abundant
pseudomorphed microphenocrysts of plagioclase, olivine
and/or augite. The relict textures in the lapilli contrast
for example with (A) and suggest minimal phreatomagmatic
interactions a proposal supported by the steep profile
of the associated tuff cone in the quarry. (4.5mm, ppl)

C). ASHOVER TUFF, Fallgate Borehole. Coarse tuff
with vesicular lapilli illustrating regular outlines.
Fine grained matrix is replaced by carbonates. (4.5mm, ppl)

D). "PALAGONITE" TUFF, Alport Borehole-457m. In
hand specimen there are no macroscopic indications of
a pyroclastic texture. The photomicrograph, however,
illustrates a fine grained highly fragmented tuff with
shards and cusped fragments. Primary palagonite is
largely replaced by silica and carbonates. (4.5mm, ppl)

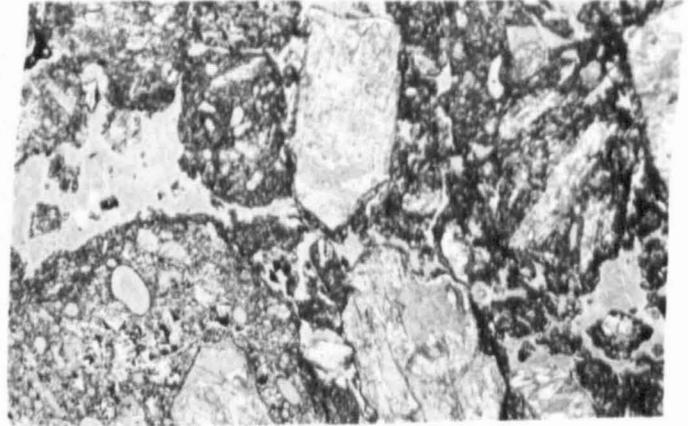
E). TUFF-HADDONFIELDS MIDDLE LAVA, Haddonfields
No. 11 Borehole. Coarse tuff with pumice lapilli containing
pseudomorphed microphenocrysts, probably representing
olivine. (4.5mm, ppl)

F). TUFF-TOP OF CRESSBROOKDALE LAVA, Hucklow
Edge No. 11 Borehole-165m. Very coarse tuff with achnelithic
lapilli-smooth external outline controlled by surface
tension and typical of Strombolian activity. Also note
the occurrence of clear, euhedral analcite associated with
areas of coarse carbonate. (4.5mm, ppl)

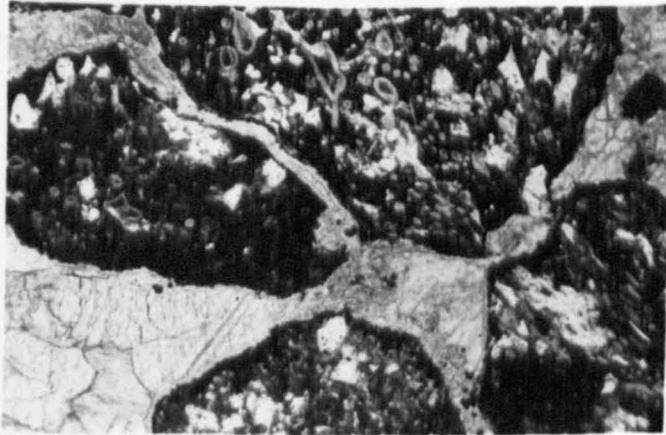
Plate 1·10



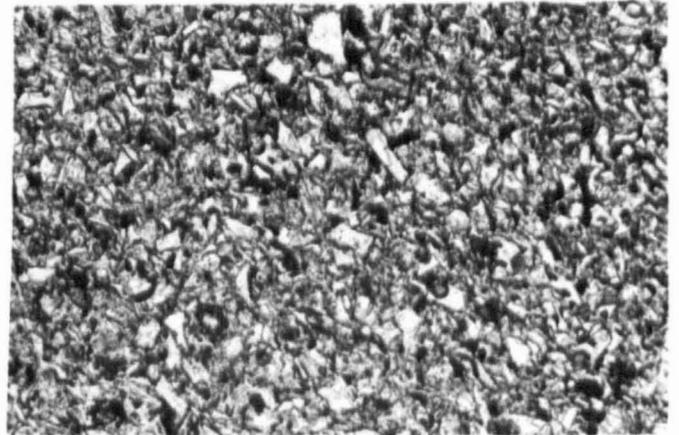
A



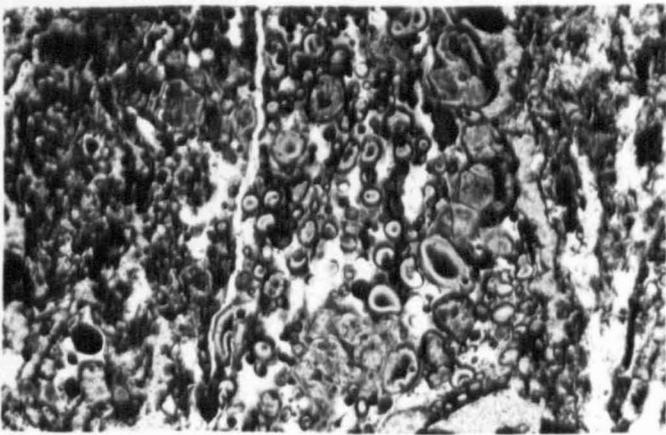
B



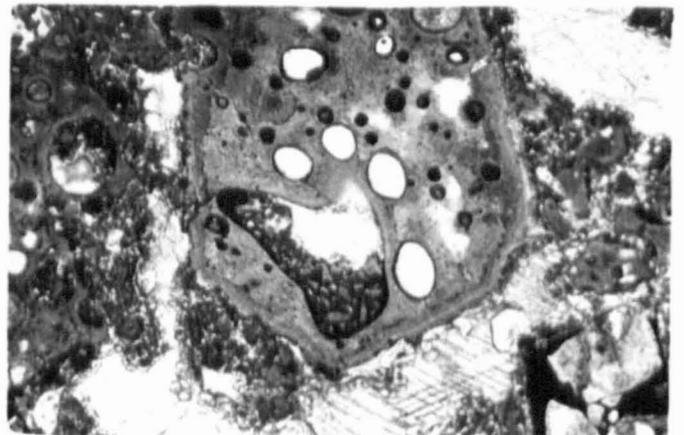
C



D



E



F

PLATE 2.1 INTERSTITIAL PHASES AND SECONDARY ALTERATION PRODUCTS.

A). TUFF, HADDONFIELDS MIDDLE LAVA-HADDON-FIELDS No. 11 BOREHOLE, 206m. Primary analcite (lower centre) exhibits secondary smectite replacement. Pale pink analcite grades out into a transitional, non-isotropic, colourless zone and into a peripheral zone of green, fibrous smectite with inclusions of opaque anatase. Area to right of centre exhibits a more advanced state of alteration with abundant inclusions of anatase. (2.0mm, ppl)

(B) to (D) - HADDONFIELDS LOWER LAVA, HADDONFIELDS No. 11 Borehole. (9/Type 3)

B). Prominent areas of intersertal, dark turbid glass clouded with opaque inclusions. (2mm, ppl)

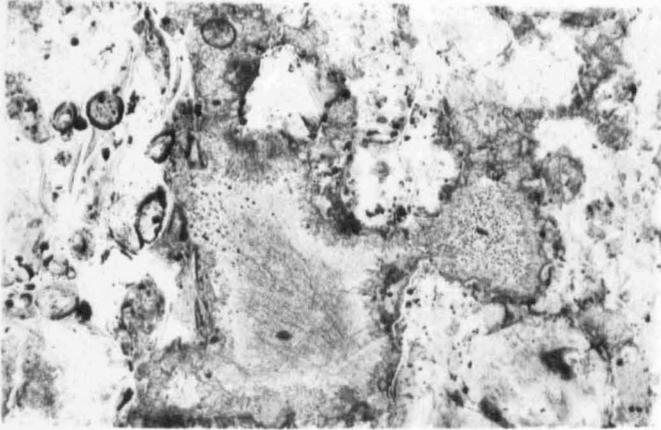
C). All relict glass has been replaced by deuteritic smectites with a dark brown fibrous rim and a green spherulitic central region. (2.0mm, ppl)

D). Transitional stages of deuteritic smectite replacement. Relict glass is present (lower centre) together with areas of zoned smectite replacements (top left) and areas of intermediate replacement type. (2.0mm, ppl)

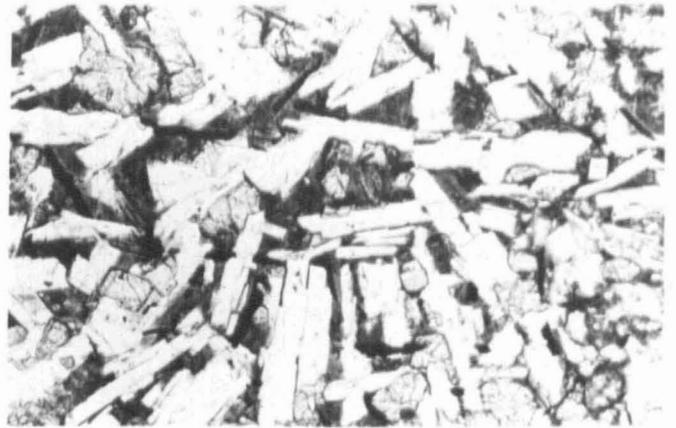
E). WATERSWALLOWS SILL-MIDDLE HORIZON WATERSWALLOWS QUARRY. (57/Type 3) Dark intersertal areas of green deuteritic smectite with some patches of partly devitrified glass with opaque inclusions (e.g. top left). Also note spinel inclusions in pseudomorph after olivine. (0.8mm, ppl)

F). WATERSWALLOWS SILL-LOWER HORIZON WATERSWALLOWS QUARRY. (55/Type 3) Higher proportion relict interstitial glass in comparison with (E). Unaltered glass detectable by intersertal position and slight concentrations of apatite and opaque inclusions. Partial devitrification and a degree of smectite replacement are present in some areas (e.g. lower centre). (0.8mm, ppl)

Plate 2·1



A



B



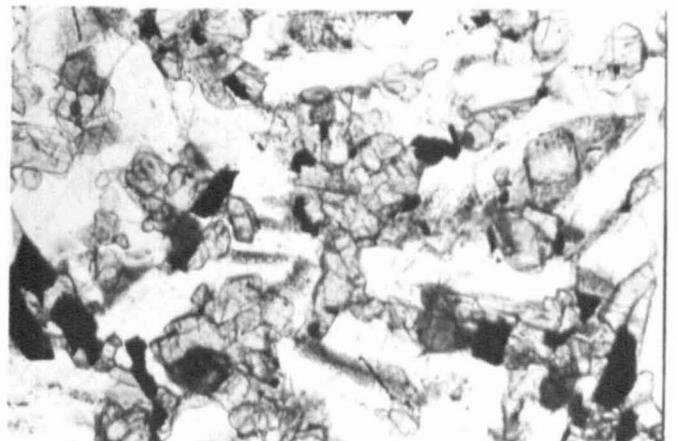
C



D



E



F

PLATE 2.2 INTERSTITIAL PHASES AND OLIVINE ALTERATION PRODUCTS.

A). MATLOCK UPPER LAVA-PSALTERS LANE. (22/Type 1)
Coarse areas of green interstitial smectites pseudo-
morphing primary analcite, all stages in the replacement
of analcite by smectite can be observed in the specimen
(0.8mm, ppl)

B). MATLOCK UPPER LAVA, PSALTERS LANE. (21/Type 1)
Primary pale pink, isotropic interstitial analcite
(lower centre). (0.8mm, ppl)

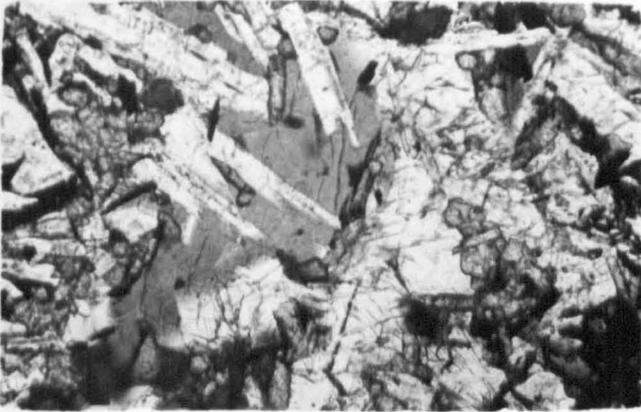
C). POTLUCK SILL, BLACK HILLOCK MINE DUMP.
(40,41/Type 6) Smectite replacement of olivine
pseudomorph. Ragged areas of relict olivine are present
in the core region and the optically homogeneous
behaviour of the smectite/goethite aggregate can be
related to the optical orientation of the relict
olivine. (4.5mm, ppl)

D). WATERSWALLOWS SILL-LOWER HORIZON, WATER-
SWALLOWS QUARRY. (55/Type 3) Incipient smectite
alteration of olivine along external surfaces and
internal cracks. This initial smectite alteration
commonly differs in pleochroic and optical orientation
from the smectite constituting the remaining bulk
of completely pseudomorphed olivines and can be
detected as "relict" or "ghost" textures. (4.5mm, pxpl)

E). WATERSWALLOWS SILL-UPPER "GABBROIC"
HORIZON, WATERSWALLOWS QUARRY. (58/Type 3) Smectite
pseudomorph after olivine phenocryst. Strong development
of an orientated open parting with maximum pleochroic
absorption (dark green) occurring when the fibres
are elongated E-W. (4.5mm, ppl)

F). IBLE SILL, IBLE QUARRY-VIA GELLIA. (37/Type 6)
Smectite pseudomorph after olivine phenocryst. Note
the preservation of internal cracks as "relict" or
"ghost" textures indicated by areas of darker smectite.
(2.0mm, ppl)

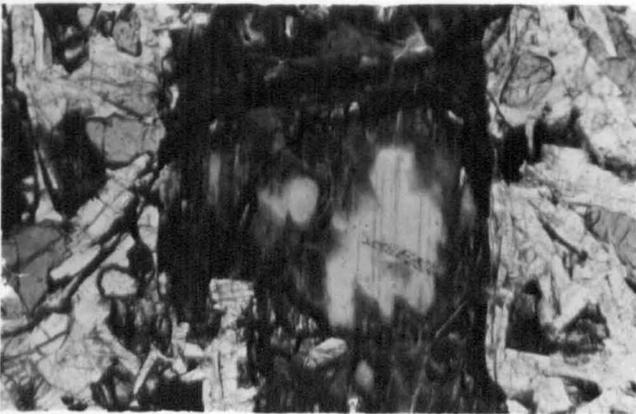
Plate 2·2



A



B



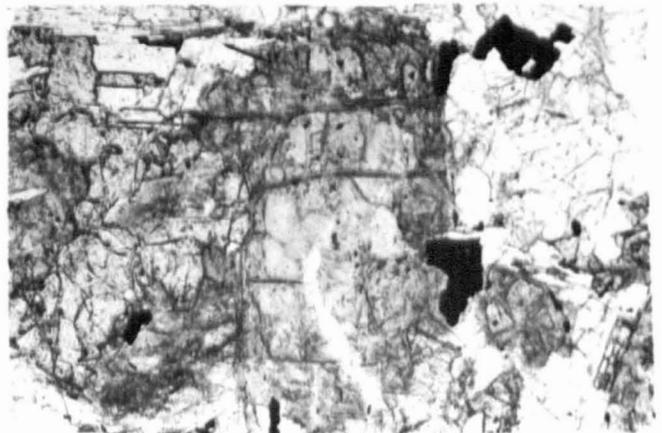
C



D



E



F

PLATE 2.3 ILMENITE AND TITANOMAGNETITE OPAQUE PHASES

A) and B). POTLUCK SILL, BLACK HILLOCK MINE DUMP. (41/Type 6)

A). Homogeneous titanomagnetite, note anhedral lobate outline reflecting late stage-post augite and plagioclase-crystallization. (0.8mm, ppl)*

B). Homogeneous ilmenite also illustrating anhedral lobate outline. (0.8mm, ppl)

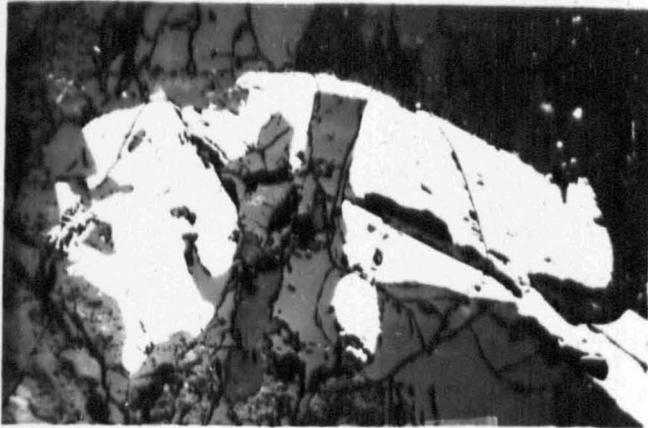
C). MATLOCK LOWER LAVA, BONSALL BASALT QUARRY-VIA GELLIA. (17/Type 1-4). Oxidation of titanomagnetite associated with pyroxene replacement. Patchy exsolution of coarse ilmenite lamellae in titanomagnetite, altered pyroxenes can be detected by concentrations of anatase grains (white with internal reflections) at relict grain boundaries. (0.4mm, pxpl)

D). MATLOCK UPPER LAVA, WHAM SOUGH DIG. (24/Type 3)
Lobate and partly skeletal, fine grained titanomagnetite light grey areas are augite. (0.4mm, ppl)

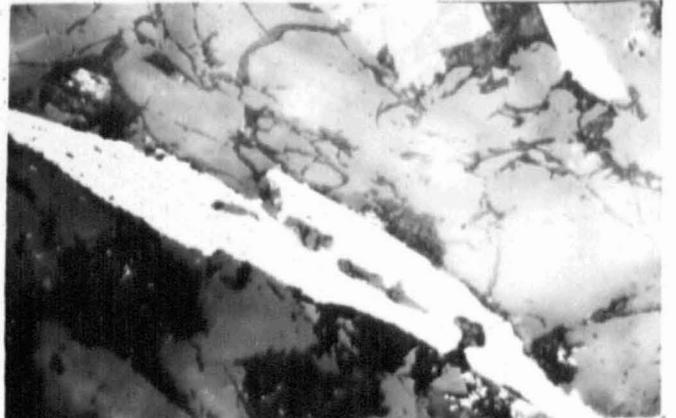
E) and F). MATLOCK LOWER LAVA, HALLICAR WOOD ADIT-VIA GELLIA. (20-101/Type 1). Patchy exsolution textures in titanomagnetite associated with pyroxene replacement. (0.4mm, pxpl and ppl)

(* All photomicrographs in reflected light.)

Plate 2·3



A



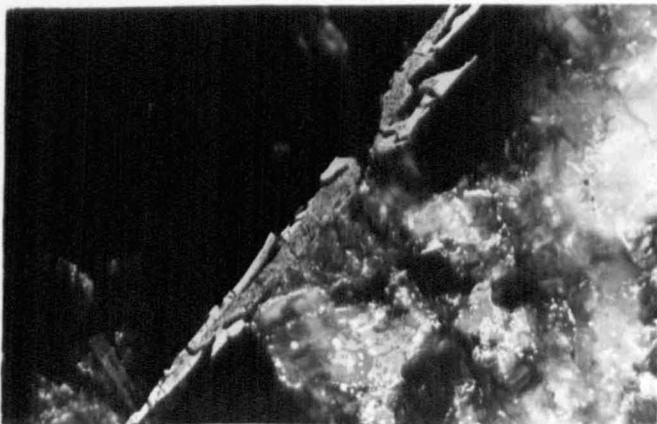
B



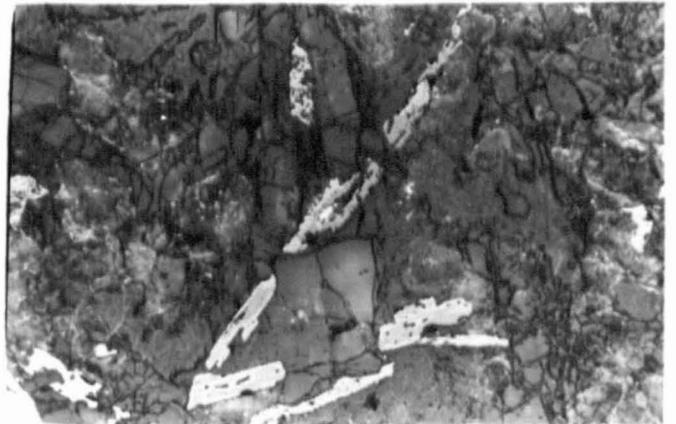
C



D



E



F

CHAPTER SIX



Chapter Six

Selection of Unaltered Basalts - Petrographic Selection Criteria

6:1 Sampling Criteria

The Derbyshire basalts have a reputation for illustrating excessive hydrothermal alterations and weathering, as Wilkinson (1967) comments "considerable difficulty attaches to the mineralogical and chemical study of these rocks, particularly the lavas, because of the alteration which many have undergone". Any attempt to present 'primary' geochemical trends obtained from 'unaltered' or 'fresh' material must first establish the validity of these statements.

The majority of samples for major and trace element analysis were obtained from borehole cores. Sampling was biased towards non-vesicular, holocrystalline basalts from the central regions of thick flow units. This was designed to minimise the effects of weathering and deuteric alterations which are most pronounced in the vesicular margins of flow units. The majority of analyses available prior to the present study were of this vesicular, altered, lava type.

In addition to the programme of core sampling, extensive fieldwork was directed towards the examination and sampling of all significant outcrops and accessible underground exposures. Collecting was biased towards either mine or quarried localities to minimise possible weathering effects. Where the basalts exhibited spheroidal weathering structures only the central portions of large spheroids were selected for analysis.

6:2 Petrographic Criteria

Over three-hundred thin sections and polished blocks of lavas and dolerites were examined. This enabled the development of a number of

petrographic criteria to assist in the selection of the 'freshest' material available. However, despite the extensive sampling programme all the lavas examined contained pseudomorphed olivines and areas of interstitial clay replacing primary glass. Although many of the dolerites contained relict olivine these also contained high percentages of secondary clays. Thus the term 'fresh' or 'unaltered' as used in the context of the present study is a relative term and must be taken to indicate the 'least altered' material available.

The following petrographic criteria were used in the selection of this 'least altered' or 'fresh' material for analysis:

- (1) Plagioclase and clinopyroxene were free from alteration phases.
- (2) Although no primary olivine remained in the lavas the pseudomorphing phase was a clay aggregate rather than carbonate or silica.
- (3) Microveining was absent or could be discarded during crushing.
- (4) The basalts were non-vesicular.

Samples selected using these petrographic criteria could be further screened by 'wet-chemical' analysis before a more time-consuming XRF analysis. Only those samples with low $\text{CO}_2\%$ were selected, the majority contained $< 0.5\% \text{CO}_2$ with an upper limit of 1.5%. In addition low $\text{Na}_2\text{O}\%$, < 2.0 , was considered to be an indication of hydrothermal alteration.

The use of 'selection criteria' however, has one disadvantage, i.e. the possible rejection of material whose alterations are a direct function of some atypical primary magma type. This particularly applied to plagiophyric-rich flows characterised by siliceous replacements of olivine pseudomorphs. In order to avoid any possible bias and also to test the efficiency of the selection criteria, a number of 'petrographic types' were included which failed to satisfy all these criteria.

In all forty three major and trace element analyses for 'fresh' basaltic lavas and sills were undertaken by XRF.

6:3 Constraints on the Validity of the Geochemical Data

Despite the above mentioned petrographic and wet-chemical selection criteria for 'fresh' material, all samples have undergone some degree of alteration. This is shown by the olivine pseudomorphs, the interstitial clay areas after glass or zeolites, high total water contents up to 6% and high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios approaching 1:1. These are typical deuteric effects of alkali-olivine basalts, (Kuno, 1967, p.663) but the possibility remains that this alteration may in part be due to atmospheric weathering or hydro-thermal alterations. The remainder of this chapter will be devoted to establishing that 'weathering' was not a factor, that deuteric activity can be confined in a 'closed system' and that variations in geochemistry, differentiation trends and normative data presented in the succeeding chapters reflect primary variations.

6:4 Iron Oxidation Ratios

The high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios can be attributed to deuteric rather than weathering processes and involved selective alteration of primary olivine. Smectite/iron oxide pseudomorphs after olivine constitute up to 20% of lavas and dolerites. Probe data from unaltered olivines in dolerites indicate an average composition of FO^{68} with 30% total iron. The iron content of olivines is almost wholly in the form Fe^{2+} ; given an average phenocryst content of 15% some 4.5% FeO of the whole rock is accommodated in the olivine. Probe data on pseudomorphs indicate that the total iron content remains unchanged but this is present in the form of goethite rods and Fe^{3+} (see Chapter 4). Thus, during deuteric alteration of a basalt with 15% phenocrystal olivine 4.5% FeO, is oxidised to 4.5% Fe_2O_3 . Given total iron contents of 9-11% the predicted net effect would be $\text{Fe}^{3+}/\text{Fe}^{2+}$

ratios of roughly 1:1. This is the relationship observed and is further confirmed by the lower ratios shown by dolerites containing relict olivine.

There is no net loss of total iron during deuteric alteration and readjustments towards estimated primary oxidation ratios can be calculated. The hydration state of the basalts can be related to the high smectite contents, (20-30%). Microprobe analyses indicate 12-13% total H_2O for smectite pseudomorphs, which is in reasonable agreement with Weaver and Pollard (1973), Fall (1980). 'Projecting' this value for 30% smectite gives a whole rock total H_2O of 3.75. This compares with observed H_2O^+ content of between 2.5-4% and H_2O^- between 0.5-2.5%. The maximum smectite contents are in excess of 40%.

Both the oxidation ratios and hydration states of the basalts can be attributed to deuteric alteration and not weathering. This is supported by the homogeneous nature of the iron-titanium oxides (Chapter 4) which likewise indicate minimal weathering.

A common feature of otherwise 'fresh' basalts is a secondary replacement of smectite pseudomorphs by carbonates or silica. Samples showing such replacements were rejected for analysis. The replacement of 20% smectite by carbonate, for example, involves strong mobilisation of SiO_2 , Al_2O_3 , Fe_2O_3 and MgO with resulting net losses. This secondary replacement is associated with hydrothermal/metasomatic alteration rather than deuteric activity, exceptions being the silica pseudomorphs associated with plagiophyric lavas which are deuteric features.

Confirmation that deuteric activity in the holocrystalline basalts did in fact take place within a 'closed system' is further given by the low degree of scatter and well defined trends shown by MgO and FeO against various indices which will be demonstrated in Chapter 7.

6:5 CIPW Norm Calculations and Readjustments

Although deuteric activity is considered to represent a 'closed system' addition of volatiles, H₂O and CO₂, and oxidation undoubtedly took place. These must be compensated for before carrying out normative calculations. It is conventional to recalculate analyses on an anhydrous CO₂ free basis, e.g. Cox and Bell (1979). However, readjustment of oxidation ratios has a critical effect on certain normative values. A number of schemes have been proposed for such readjustments. Irvine and Barranger (1974) suggested recalculation of Fe₂O₃ according to the equation:

$$\text{Fe}_2\text{O}_3 \text{ (normative)} = \text{TiO}_2\% + 1.5$$

Using this scheme for the Derbyshire basalts would produce 'standard' Fe₂O₃% values in excess of those actually observed in dolerites with relict olivine and is therefore rejected. An alternative scheme, and the one adopted throughout this study, was proposed by Thompson et al. (1972) and MacDonald (1974) in which Fe₂O₃% is standardised at 1.5% if total alkalis are <4%.

The effect of this adjustment is to produce large variations in the normative values of pyroxene, olivines and quartz, but does not affect felsic constituents, compared with norms calculated with observed oxidation ratios. The high quartz values in uncorrected norms is due to the allocation of Fe₂O₃ to normative magnetite. This has a dual effect, magnetite is a non-silicate and this increases the SiO₂ available for other normative minerals but the low FeO remaining is insufficient to form enough olivine or pyroxene to accommodate this SiO₂ and in itself produces more residual SiO₂ expressed as normative quartz. This is shown in Table 6.1, by comparing normative values of selected Derbyshire basalts before and after oxidation ratio readjustments. Previously available analyses

Table 6.1

TABLE 6.1 The Effect of Oxidation State
on Normative Values

		1		2	
		Uncorrected	Fe ³⁺ Corrected	Uncorrected	Fe ³⁺ Corrected
Q		1.47	0.00	1.66	0.00
Or		4.79	4.79	2.90	2.90
Ab		22.68	22.68	21.32	21.32
An		26.54	26.54	29.32	29.32
Di	Wo	7.27	7.27	5.15	5.15
	En	5.45	4.37	3.86	3.20
	Fs	1.09	2.51	0.78	1.65
Hy	En	15.94	11.95	20.01	16.49
	Fs	3.17	6.85	4.06	8.51
Ol	Fo	0.00	3.56	0.00	2.93
	Fa	0.00	2.25	0.00	1.66
M+		6.86	2.18	6.55	2.18
Il		3.63	3.63	3.36	3.36
Ap		0.91	0.91	0.70	0.70
Py		0.11	0.11	0.13	0.13

1 - Analysis 37, Ible Sill dolerite

2 - Analysis 10, Haddonfields Lower Lava

of fresh material quoted as quartz-normative, e.g. Malki (1967), all show no normative quartz after readjustment.

The readjustment of oxidation ratios produces a hypersthene-olivine norm without quartz. It does not give rise to nepheline normative types if nepheline was not present in the norm before adjustment. The selection of oxidation-ratios is a critical factor and it would be unwise to accept any conclusions based solely on normative data. The concurrence of results based on a number of different techniques, re: norm data, stable trace element data and microprobe studies, must provide the strongest indication possible that the results are meaningful.

6:6 A Weathering Index

A number of chemical indices to assess the degree of weathering undergone by igneous rocks have been proposed by Ruxton (1968) and Parker (1970). The index suggested by Parker (op.cit.) was used to further assess the possibility that material selected for analysis may have undergone weathering. The index can be defined as:

$$\left[\frac{(Na)a}{(Na-O)b} + \frac{(Mg)a}{(Mg-O)b} + \frac{(K)a}{(K-O)b} + \frac{(Ca)a}{(Ca-O)b} \right] \times 100$$

(* X=Na,Ca,K or Mg)

where (X)a indicates the atomic proportion of element X and (X-O)b is the bond strength of element X with oxygen.

Weathering Index (WI) values for the Derbyshire basalts are given in Table 6.2. It must be remembered that results are not strictly comparable between lavas due to differing initial compositions, e.g. Anal 60,61,86 and 87 appear higher because of their higher alkali content and normative nepheline nature compared with other basalts.

However, the results do show a general trend in that 80% show WI > 70 with 55% between WI = 70-76. All the lower values show normative quartz

Table 6.2

TABLE 6 :2 Weathering Index Values for 'Fresh'
Derbyshire Basalts

Analysis Number	WI	Analysis Number	WI
1	74.8	26	70.3
2	71.2	27	68.9*
4	76.8	28	71.1
5	69.9*	31	64.3o
6	74.5	32	72.8
7	63.5*	33	75.2
8	80.5	34	72.9
9	76.1	37	77.3
10	71.6	40	76.7
11	66.0x	41	78.1
12	78.0+	60	86.5
13	68.0x	61	82.3
14	61.7x	71	66.0
15	70.4	72	73.0
16	70.0x	73	80.0
17	74.6	74	72.0
18	72.7	83	72.7
19	74.2	86	80.0
20	63.2+	87	91.0
21	75.8	88	75.6
22	76.6		
23	75.2		
24	75.7		
25	72.1		

- * Petrographically 'fresh' basalts but all show some normative quartz.
x Plagiophyric basalts with siliceous pseudomorphs and normative quartz.
+ Show some alteration attributable to hydrothermal processes.
o Unusual 'gabbroic' petrographic type.

and include plagiophyric types whilst the rest probably indicate a degree of smectite secondary replacement. In the basaltic weathering profiles compiled by Parker (1970) unaltered basalts exhibit a WI in the range 70-90 with weathered values of 2-20.

Thus the weathering index provides a further line of evidence that the analysed samples had undergone minimal weathering. It is of interest to note that the WI is not a suitable indicator for hydrothermal alteration due to the inverse relationships between MgO/CaO and Na_2O/K_2O , e.g. Anal.12, this will be discussed in more detail in Chapter 9.

CHAPTER SEVEN



Chapter Seven

Geochemistry of the Basalts

7:1 Readjustments and Fractionation Indices

The petrological uniformity of basalts from the south Pennine ore-field is reflected in the uniformity of major-element geochemistry. However, there are significant trends, particularly amongst the incompatible trace elements, that can be related to petrogenetic and stratigraphic factors. The results must be examined in order to:

- i. detect and interpret 'primary' igneous trends
- ii. Substantiate the criteria outlined in Chapter 6 that weathering and/or deuteric processes have not modified the geochemistry of the 'fresh' basalts.

All geochemical variation diagrams were plotted using data adjusted for post-crystallisation effects. Analyses were recalculated on an anhydrous, CO₂ free basis and with Fe₂O₃ standardised to 1.5%. The uncorrected data is presented in Appendices 1 and 2. In the presentation of igneous geochemical trends the choice of a particular parameter as an index of relative 'evolution' or 'fractionation' is of the greatest importance. Major elements were plotted against the Solidification Index (SI) which is expressed as:

$$SI = \frac{100 \text{ MgO}}{\text{MgO} + \text{FeO} + \text{Fe}_2\text{O}_3 + \text{Na}_2\text{O} + \text{K}_2\text{O}}$$

In basaltic rocks the low concentrations of Na₂O and K₂O result in a similarity of this index to those employing Fe/Fe+Mg, e.g. Thompson et al. (1972, 1980). The SI has a number of advantages which are relevant to this study. The adjustment of oxidation ratios has minimal effect on its values and the use of non-normative parameters also negates the

critical effect of oxidation ratios on the normative Z of ferromagnesian minerals and quartz. This particularly applies to the Differentiation Index (DI) of Thornton and Tuttle (1960), used by MacDonald (1974) in his study of the Scottish Dinantian Lava. The DI is defined as:

$$DI = \text{normative quartz} + \text{orthoclase} + \text{albite}$$

Despite these advantages, the use of a parameter which has been calculated using major elements known to have been mobilised during late-stage, deuteric, activity but within a 'closed system' must be treated with caution. The resultant plots gain credence when they concur with immobile trace element trends.

Trace elements and minor element variations were plotted using Zr as an index of fractionation, (see for example Beckinsale et al. 1978). This is considered to be a valid index given that Zr behaved as a truly incompatible element and was not incorporated into the fractionating phases. This assumption is supported by plots of Zr/Y or Zr/P₂O₅ (Figures 7.3, 7.4) which show well defined trends similar to those described by Wood et al. (1976) for Icelandic lavas. There are no indications of selective fractionating, such as that demonstrated by Thompson et al. (1980) for the lavas of Skye, which would invalidate the use of Zr as a fractionation index. SI falls with progressive fractional evolution of a melt and the Zr concentration increases.

7:2 Major Element Variations

Major element variations against SI are indicated in Figure 7.1. Concentrations of MgO, Na₂O, TiO₂ and FeO for both lavas and dolerite intrusions fall on a well defined 'liquid line of descent' indicating that sills and lavas were consanguineous or 'cogenetic'. SI varies from 49 to 31, a slight gap between SI 39 to 41.5, is considered to be fortuitous and is not substantiated by trace element data. Forty-seven

major element analyses were used in the compilations, the extreme compositions are represented by a minimal number of samples.

The major element variations illustrate differentiation trends that can be attributed to 'low pressure' fractional crystallisation. MgO ranges from 12 to 7%, Na₂O from 2 to 3.5%, Al₂O₃ increases from 13 to 17% prior to an inflection to 13% at SI < 33 and FeO (adjusted) is uniform in concentration from SI 45 to 33 before increasing from 10.5 to 12%. All the above mentioned major elements exhibit well defined trends of differentiation. This is somewhat surprising given the porphyritic nature of the samples, as variations in the relative proportions of phenocryst phases would normally tend to obscure such trends. However, porphyritic lavas whose major element compositions do not depart from a 'liquid line of descent' are "reasonably common" (Cox and Bell, 1979). The most plausible explanations are that the phenocrysts have either undergone minimal fractionation or have been added to the melt at the same rate that they have been fractionated - i.e. compensated crystal settling.

This adherence to a trend is most noticeable for the plagiophyric basalts (> 20% phenocrysts) within the Shacklow Wood Lava. If the phenocrysts resulted from cumulus enrichment or selective crystal fractionation the geochemistry would exhibit increased Al₂O₃ and CaO with decreased FeO concentrations in comparison with the general trends of the olivine-phyric lavas, e.g. Gass et al. (1973). The plagiophyric lavas show no significant increase in either Al₂O₃ or CaO. Slight decrease in FeO% is due to the silicification of olivine pseudomorphs (Chapter 4), a proposal supported by a concomittant decrease in MgO concentration.

Fig 7.1

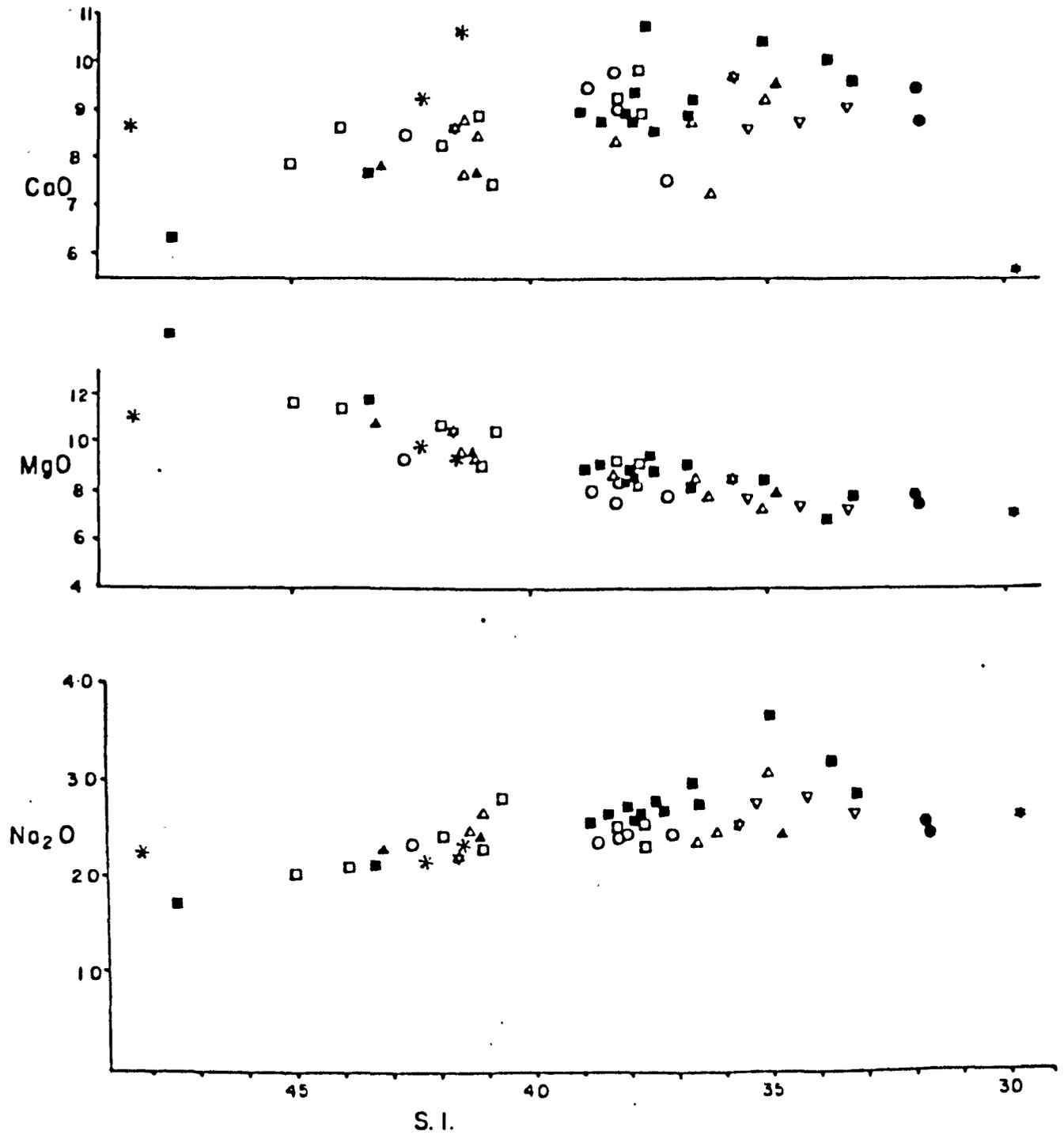


FIG. 7.1 MAJOR ELEMENT GEOCHEMICAL VARIATIONS VERSUS SOLIDIFICATION INDEX

(all analyses plotted using data recalculated on an anhydrous, calcite free basis with normalized FeO)

FOR KEY SEE FIG. 7.6

Fig 7.1
(cont)

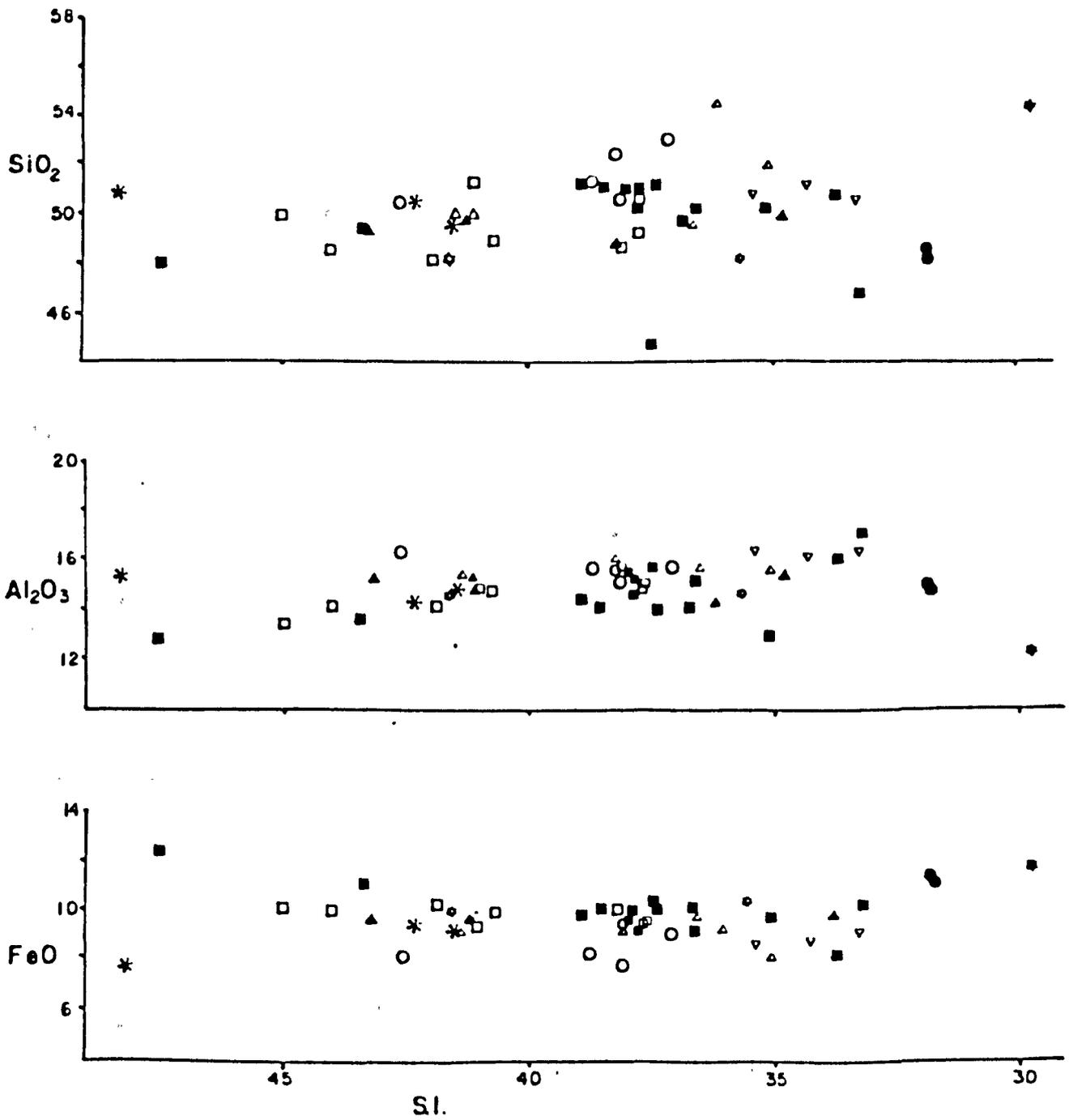


FIG 7.1 MAJOR ELEMENT GEOCHEMICAL VARIATIONS VERSUS SOLIDIFICATION INDEX
(CONT.)

Fig 7.1
(cont)

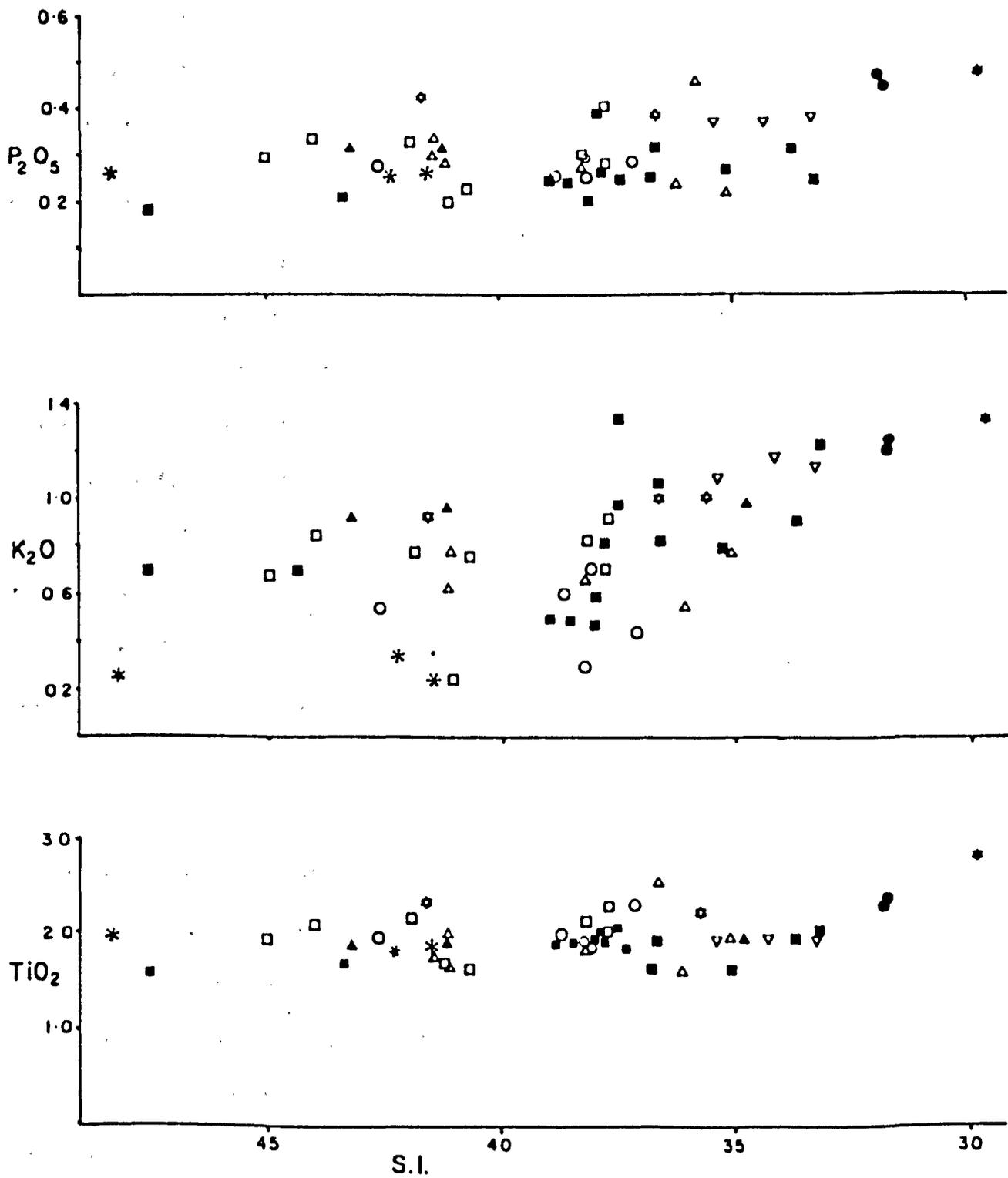


FIG 7.1 MAJOR ELEMENT GEOCHEMICAL VARIATIONS VERSUS SOLIDIFICATION INDEX (CONT.)

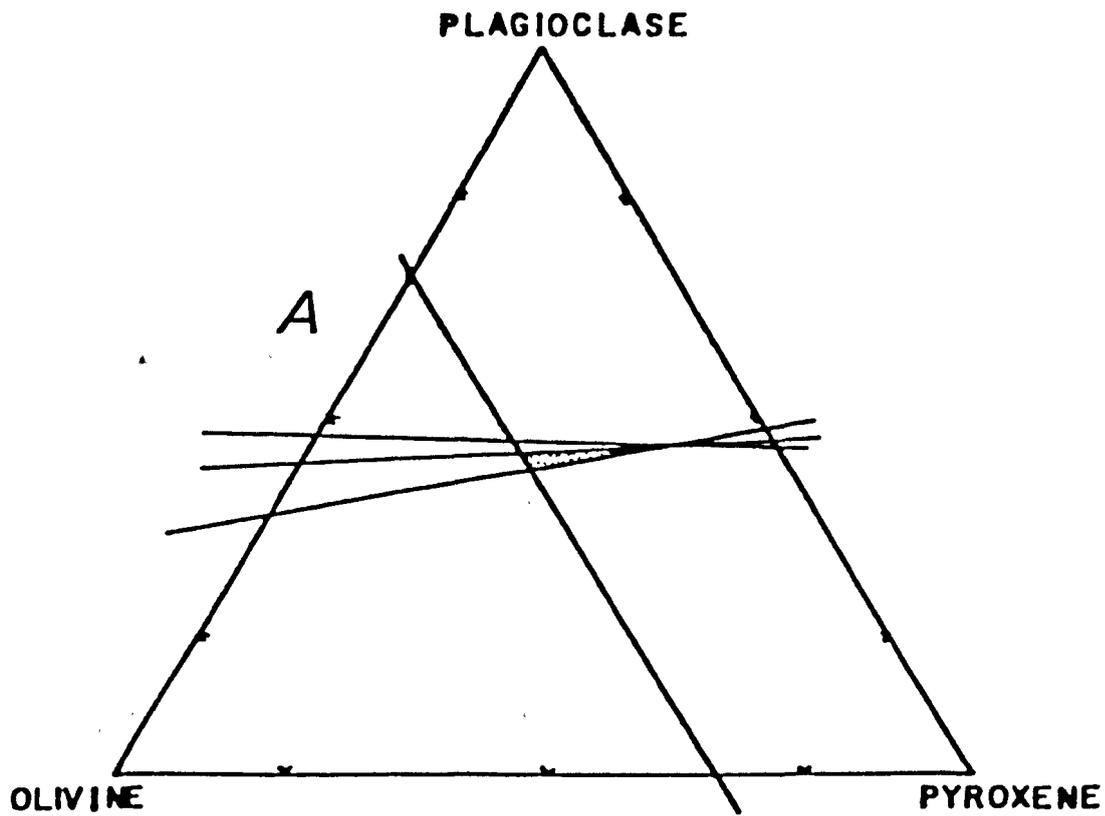
For Key to Lava symbols see Fig. 7.6
■ -Dolerite sills

CaO and SiO₂ against SI (Fig. 7.1) show a high degree of scatter with an overall tendency towards higher concentrations with differentiation. This diffuse pattern may be partly due to incipient silicification or calcitization in the crushed sample. P₂O₅, K₂O and TiO₂ likewise illustrate a scattered distribution when plotted against SI (Figure 7.1). However, when these are plotted against Zr, (Figures 7.3, 7.4) a much more defined trend with strong enrichments is apparent.

7:3 Low Pressure Fractionation

The ubiquitous presence of olivine, plagioclase and clinopyroxene phenocrysts would imply that the geochemical variations are the result of low pressure fractionation. The predominance of olivine phenocrysts might further suggest that these variations could have been controlled by olivine fractionation. Basalts exhibiting such control show marked depletion of Ni due to its selective partitioning into olivine (Gunn, 1971; Wood, 1978; Llyle, 1978). The Derbyshire basalts do not exhibit such a trend (Figure 7.3) and the conclusion must be that olivine fractionation alone was not the dominant process.

A more complex situation is suggested by the availability of olivine and plagioclase and clinopyroxene phenocrysts. The involvement of all three can be demonstrated using the graphical methods of Cox and Bell (1979, p.151). 'Average' phenocryst compositions were compiled from microprobe data and a number of 'extract triangles' were constructed for those major elements that exhibited well defined 'lines of liquid descent', i.e. MgO, FeO, Al₂O₃ and Na₂O. Compositional trends calculated from the average results of major lava flows and sills were projected onto the extracts and the indicated ratios of fractionated phenocryst phases required to produce the observed major element variations calculated. The ratios were superimposed on an equilateral triangle (Figure 7.2) to



For explanation see text.

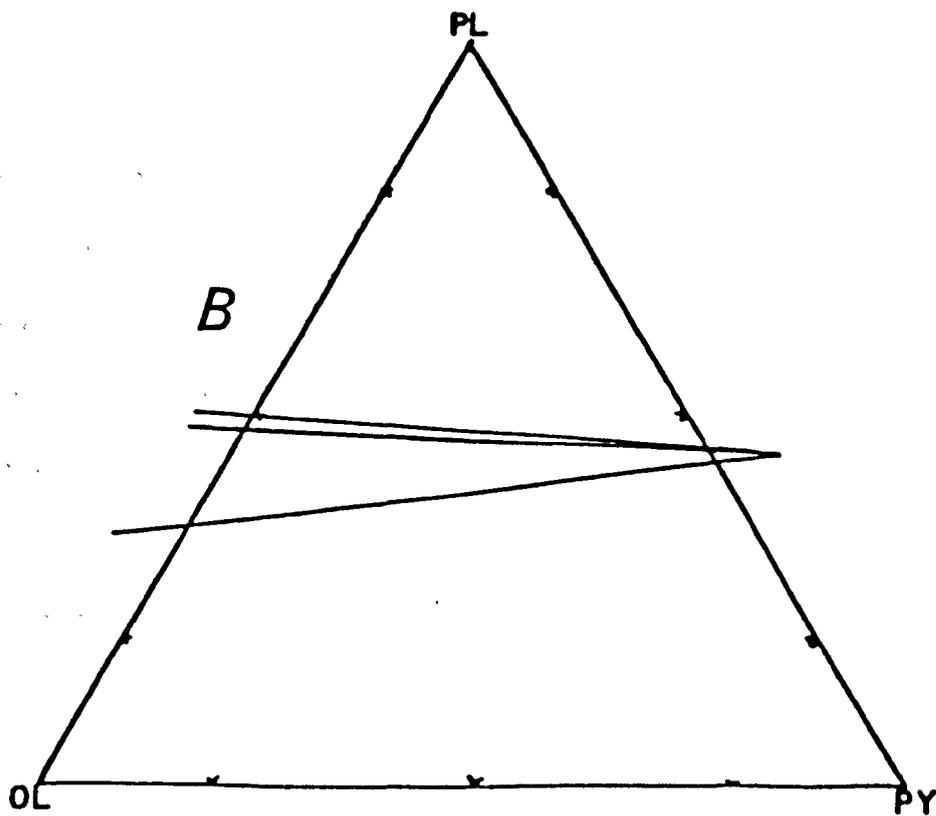


FIG. 7.2 THREE PHASE PHENOCRYST EXTRACT TRIANGLES

- a). General trend, all analyses.
- b). "Evolved Cressbrook Dale Lava.

determine the degree of concordance of the various plots. The resultant 'triangle of error' indicates required phenocryst extracts in the ratios plagioclase:olivine:clinopyroxene of $45 \pm 2\%:25 \pm 7\%:30 \pm 7\%$. Additional confirmation is provided by calculated ratios from Na_2O v Al_2O_3 , which cannot be accommodated on a triangular diagram. This extract indicates fractionation of plagioclase:olivine + pyroxene in the ratio 45:55. Those calculations confirm that the observed phenocryst phases are capable of fractionation to produce the major element variations, with respect to Na_2O , CaO , Al_2O_3 and MgO .

This method is only regarded as a semi-quantitative approach (Cox and Bell, 1979). The predicted results gain credence by:

- (a) their degree of concordancy
- (b) the cogenetic relationships of the basalts
- (c) variation can be explained in terms of observed phenocrysts

Although the relative proportions of the fractionating phases are indicated the actual amount of fractionation is not. It is not possible to calculate this given the absence of aphyric or 'primitive' lavas necessary to establish 'pre-fractionation' compositions. The fractionation ratios could be refined by the use of computer 'mixing' calculations as described by Wright and Doherty (1970).

Although the majority of the basalts show well defined major element trends capable of interpretation using the calculated three-phase extracts a minimal number are apparently 'more evolved' and show strong inflections with respect to CaO , Al_2O_3 and FeO (Figure 7.1). These represent the youngest lava flow in the Orefield, i.e. the Cressbrook Dale Lavas, the Matlock Upper Lava and the Conksbury Bridge Lava (Figure 7.6). The 'evolved' basalt associated with the Cressbrook Dale Lava is atypical

of the Lava as a whole and only occurs as part of the ultimate flow. It is coarse grained with no olivine and contains phenocrystal Fe-Ti oxides, (See Chapter 4). Phenocryst extract calculations indicate that fractionation was produced by equal proportions of plagioclase and clinopyroxene and did not require olivine (Figure 7.2) a proposal in accordance with the observed phases. The degree of fractionation was greater than for other basalts resulting in marked depletion in CaO and Al_2O_3 with enrichment in FeO, SiO_2 and TiO_2 . The increase in FeO was buffered to an extent by the fractionation of Fe-Ti oxides. It will be demonstrated in section 7:4 that the trace-element variations are in accordance with this model. The other 'evolved' lavas show less extreme trends compared to the Cressbrook Dale basalt. Variations can be ascribed to higher degrees of fractionation compared to the other basalts but still involving a three-phase extract.

The behaviour noted above is typical of that described by Cox (1980) for apparently 'monotonous' flood basalt sequences. Low levels of major element variations are a product of the 'mutual buffering' effect of the fractional crystallisation of olivine and clinopyroxene and plagioclase on oxides such as Al_2O_3 , MgO, CaO, SiO_2 and FeO. Even large variations in the relative proportions of the three phenocryst phases can result in minimal bulk geochemical variations in the remaining melt. Only when there is a change in the phenocryst phases involved, i.e. one or more phases ceases to fractionate or a new phase is added, will marked variation in geochemistry result.

The phenocryst/melt relationships proposed for the Derbyshire basalts can be compared to those demonstrated for the lavas of Kilauea, Hawaii by MacDonald and Katsura (1964), and Thompson and Tilley (1969). This involves a relatively simple system operating at a pressure of 1 atmosphere. A large crystallisation interval of olivine is rapidly joined, over a limited

temperature range but wide Fe/Mg ranges, by clinopyroxene and then plagioclase. Simultaneous entry of all three phases was observed in some samples. In the more evolved basalts olivine is no longer on the liquidus and fractionation is controlled by plagioclase and pyroxene.

7:4 Trace and Minor Element Variations

Trace and minor elements are sensitive indicators to the crystallisation histories of igneous rocks. Hypotheses based on major element trends may be tested and refined using trace element data. The 'immobile' nature of a number of trace elements makes them insensitive to either deuteric or hydrothermal alterations which may have influenced major element variations.

The 'incompatible' or large ion lithophile elements (e.g. K, Rb, Zr, Y) are often excluded from the lattices of the common rock forming minerals and concentrated during fractionation. Using Zr as the fractionation index (Figures 7.3, 7.4) Y and P_2O_5 show well defined trends of enrichment. K_2O v. Zr shows a degree of scatter but with a strong trend towards enrichment. TiO_2 v. Zr results in a well-defined positive trend linear up to 2.3% TiO_2 before falling off. The behaviour of TiO_2 can be attributed to the proposed Fe-Ti oxide fractionation in the more evolved basalts. This is supported by the parallel behaviour of vanadium (Figure 7.3) which is partitioned into lattices of iron titanium oxides (Carmichael, 1964) Rb exhibits a diffuse trend of enrichment, much of its scatter can be attributed to low concentration levels and the 'noise' resulting from analytical techniques. Enrichments of 200 to 600% in the concentration of some 'incompatible' elements is in direct contrast to the overall uniformity of the major element trends.

Sr substitutes for Ca in plagioclase, especially at lower temperatures and more albite rich compositions (Wood, 1978). Strontium is enriched during fractionation of a melt, unless plagioclase is undergoing substantial

Fig 7.3

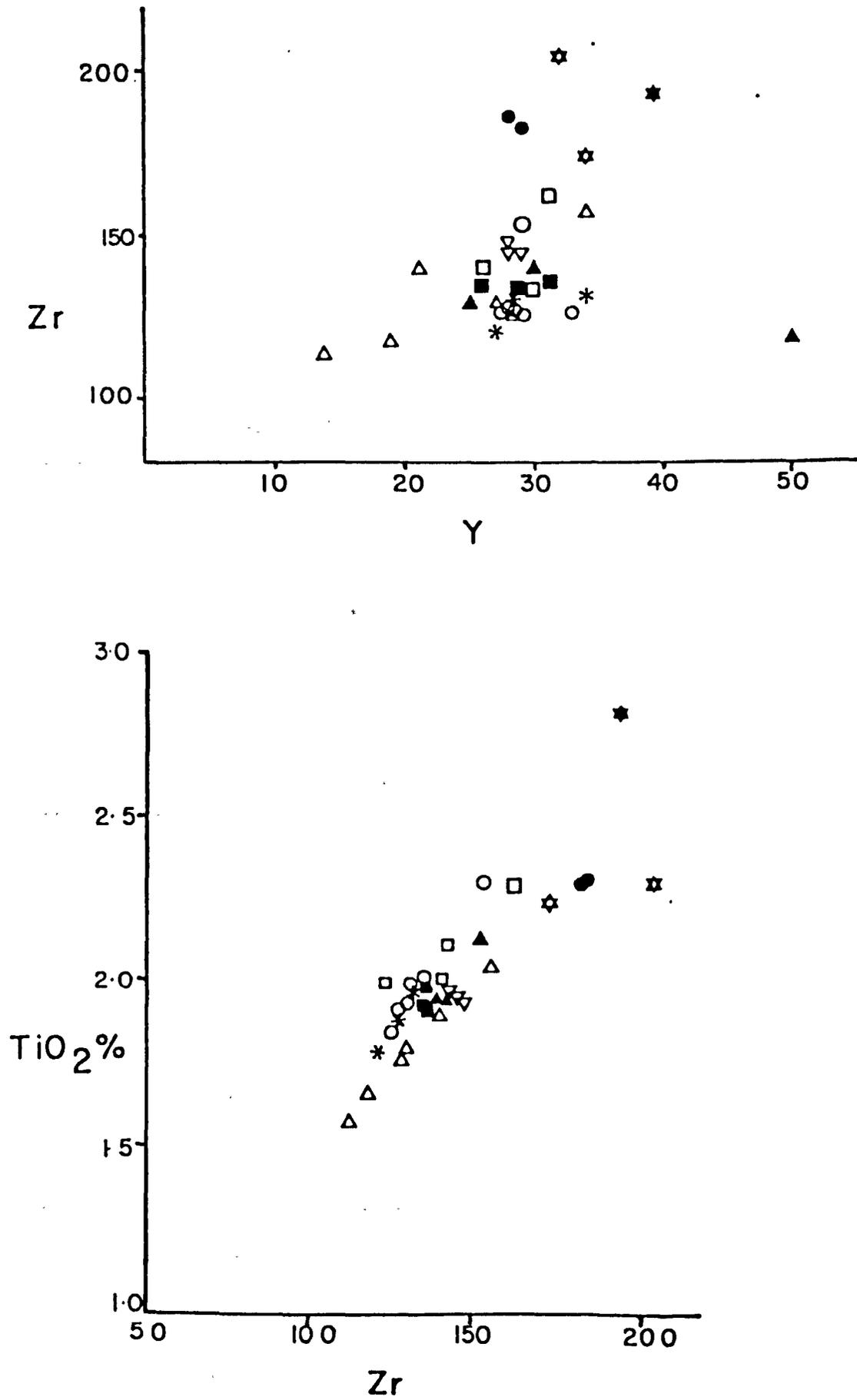


FIG. 7.3 TiO₂ & Y VERSUS Zr (symbols as Fig. 7.1)

Fig 7.4

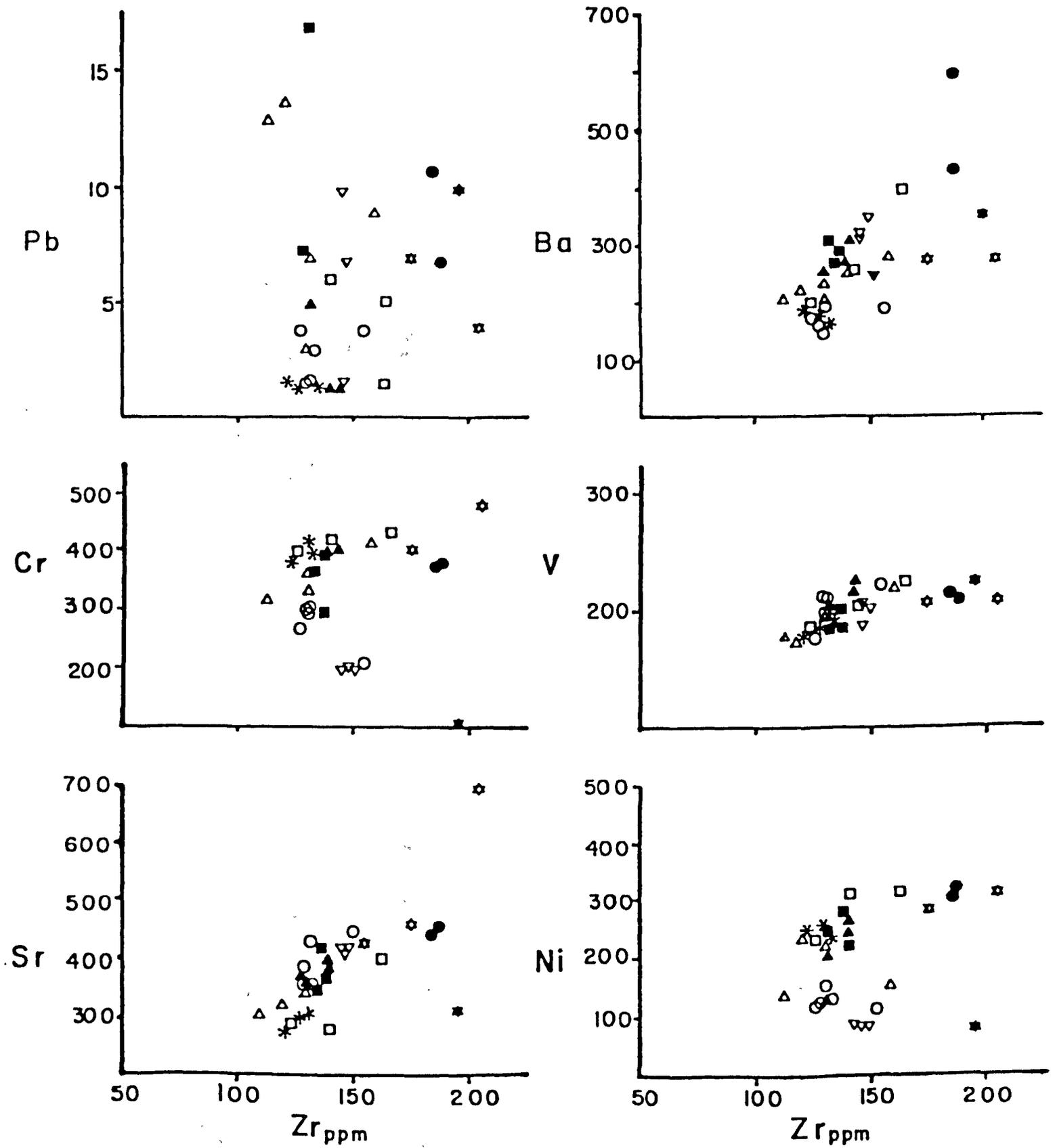


FIG. 7.4 TRACE ELEMENT GEOCHEMICAL VARIATIONS VERSUS ZIRCONIUM

(symbols as Fig. 7.6)

Fig 7.4
(cont)

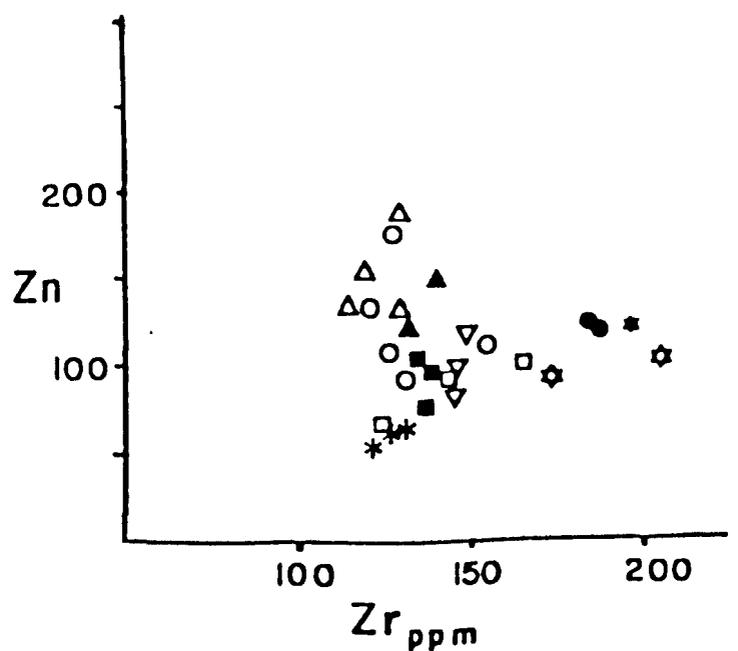
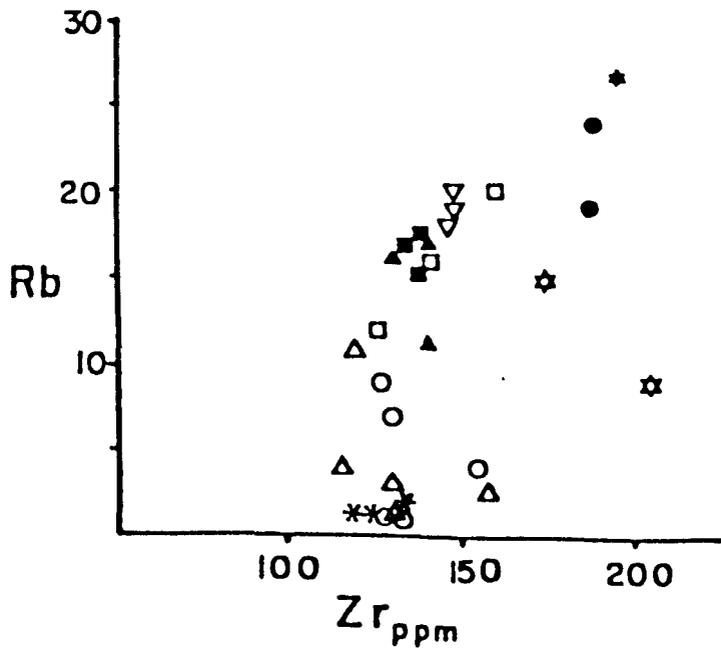
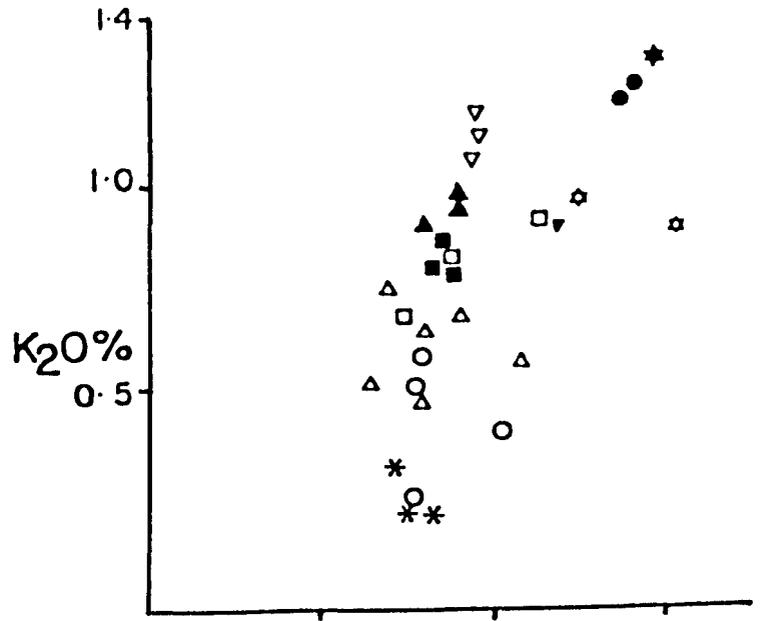
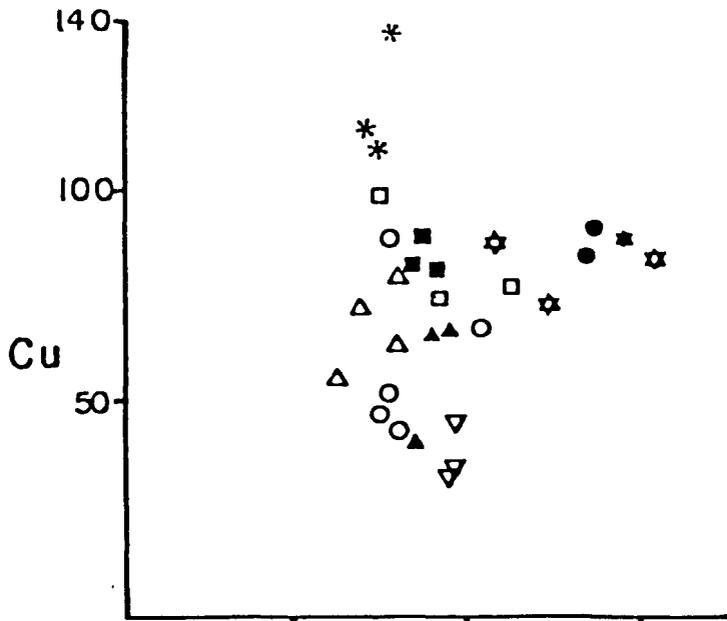
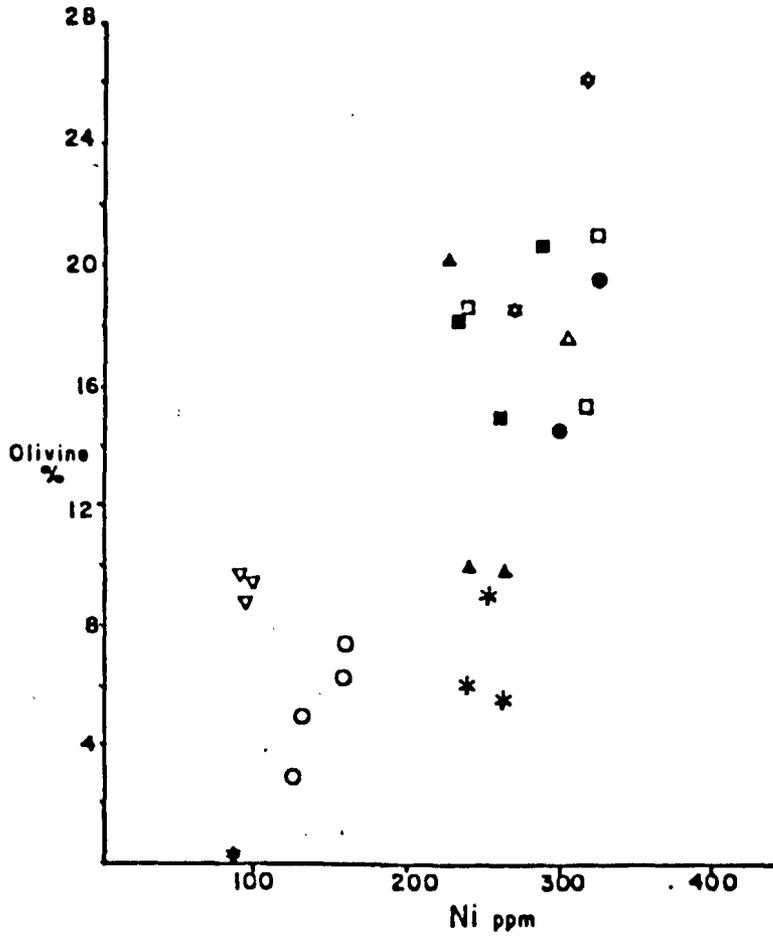


FIG. 7.4 TRACE ELEMENT GEOCHEMICAL VARIATIONS VERSUS ZIRCONIUM
(CONT.)

fractionation which acts as a 'buffer' to enrichment. A high degree of plagioclase fractionation was advocated by Wood (op.cit.) from a study of Icelandic basalts. These exhibited a broader compositional range compared with the Derbyshire basalts, but with an Sr enrichment of only 230 to 310 ppm compared with 260 to 460 ppm. Furthermore, the plagiophyric basalts of the Orefield, which contain over 20% phenocrystal labradorite, are not enriched in Sr and fall within a well defined trend of Zr v. Sr (Figure 7.4). Although plagioclase was a fractionating phase, it is concluded that the relative degree of fractionation was minimal. The evolved Cressbrook Dale basalt departs from this trend, showing strong Sr depletion. This is in accordance with the model proposed for its major element variations involving a high degree of plagioclase fractionation compared to the majority of the basalts.

Cr and Ni are partitioned into olivine and clinopyroxene (Gunn, 1971; Hart and Davis, 1978; Krishnamurthy and Cox, 1977). Cr/Ni ratios are higher in augites than in olivines, but this is buffered by the common association of Cr-spinel inclusions in olivine phenocrysts (Chapter 4). A related series of lavas resulting from olivine fractionation exhibit very marked depletion in Ni and Cr (Flower, 1973; Wood, 1978; Llyle, 1980). The Derbyshire basalts show no such depletion (Figure 7.4) and this is taken to indicate that olivine or pyroxene fractionation were not major factors. The majority of samples indicate Ni and Cr enrichment, however, both Ni and Cr show parallel behaviour with a consistent dichotomy with a small number of basalts showing a trend of Ni and Cr depletion. When Cr and Ni concentrations are plotted against % phenocryst olivine (Figure 7.5) the resulting correlations indicate that those samples with high Cr and Ni have a high % of phenocryst olivine and vice versa. Certain samples, particularly the clinopyroxene-phyric basalts from the Matlock Lower Lava, are located above this trend indicating that both olivine



FOR KEY SEE FIG. 7.6

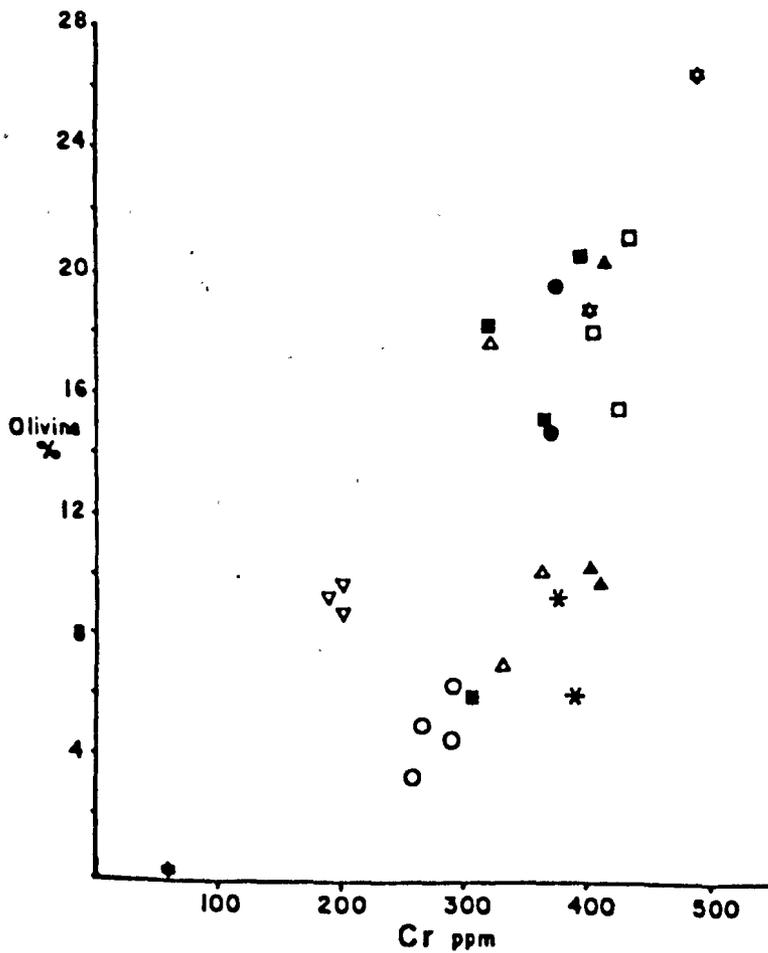


FIG. 7.5 NICKEL AND CHROME VARIATIONS VERSUS MODAL OLIVINE%

and pyroxene are responsible for variations in Ni and Cr concentrations. The evolved Cressbrook Dale basalt is once more at variance with the general trends. It exhibits a more pronounced depletion of Cr relative to Ni than the other basalts, further confirming the proposal that pyroxene rather than olivine was the fractionating phase.

The reason for selective fractionation of olivine in a limited number of samples is difficult to deduce. There is no correlation with the stratigraphical locations of the samples or with their overall chemical evolution. It may be a fortuitous relationship that the samples involved are from the central part of thick flow units. Variations in the percentage of ferromagnesian phenocrysts have been observed within such flow units and may imply a degree of post-extrusive crystal settling.

The crux of these observations is that although a small degree of selective crystal fractionation has taken place it is not reflected in either the major element or incompatible element trends. Under normal circumstances such wide variations in the relative percentages of fractionating phenocryst phases would result in a broad scatter amongst major element concentrations. The absence of such a feature amongst the Derbyshire basalts strongly supports the proposal of 'mutual buffering' in three-phase extracts involving olivine, plagioclase and pyroxene (Section 7:3).

Variations in the concentrations of Cu and Zn show less well defined trends. Cu may be partitioned in sulphide phases, titanomagnetite or olivine, as reported by Flower (1973) and Fall (1980). The behaviour of Cu in the Derbyshire basalts is broadly parallel to that shown by Cr and Ni suggesting the major partitioning phase was olivine. The evolved Cressbrook Dale basalt has a high Cu concentration relative to the basalts depleted in olivine further supporting this proposal. The behaviour of Zn is less predictable and can be partitioned in a number

of phases, e.g. magnetite as suggested by Dissanayake and Vincent (1972). This variability is reflected in the broader scatter of Zn v. Zr (Figure 7:4).

7:5 A Model for the Magmatic Evolution of the Basalts

Any proposed model must account for the following observations:

- (a) The Derbyshire basalts are all highly phyric, usually with olivine, plagioclase and clinopyroxene phases.
- (b) They exhibit a restricted range of major-element compositions.
- (c) Despite their phyric nature the degree of fractional crystallisation appears minimal.
- (d) Incompatible and even some compatible trace elements show strong enrichments compared to the major element trends.
- (e) The consanguineous nature, yet relatively small volumes, of extrusive lavas and intrusive sills.
- (f) The lavas exhibit a geochemical trend of evolution that can be related to their stratigraphical horizon.

Despite a hiatus between extrusive and intrusive phases, the sills fall within the geochemical trends defined by the lavas.

An explanation encompassing all the above features can be proposed based on the model of O'Hara (1977,1981). This involves low-pressure fractionation within a periodically refilled magma chamber. In a closed system, fractionation would result in substantial variations in major element concentrations. With O'Hara's model, magma within the chamber undergoes a period of fractional crystallisation to be followed by an influx of unfractionated magma from a parental source. The new magma batch mixes with the more evolved, fractionated, magma in the chamber and the influx of new magma results in an extrusion. The process is repeated with new

magma batches supplied to the chamber, at irregular intervals, giving rise to eruptions or intrusions. The resulting lavas according to O'Hara (op.cit.) would have the following characteristics:

1. Given the assumption that new magma batches were from the same source, the lavas would show a uniformity of major element compositions but strong enrichments of incompatible elements. Furthermore, enrichment factors would be more enhanced in the ultimate products of effusive phases.
2. Variations in major element compositions will be controlled by low pressure phase equilibria; and due to the high degree of 'steady-state' melt composition resulting from periodic influxes of unfractionated magma crystalliation will be maintained at low pressure cotectics with two or more phenocryst phases close to saturation.
3. Significant variations in the ratios of some incompatible elements will occur due to the enhancement of slight differences in partition coefficients during the repeated mixing and fractionations within the magma chamber.
4. Certain compatible elements (e.g. Cr and Ni) may be enriched even though fractional crystallisation occurs because this is not the dominant process.
5. Although the actual magma chamber need not be large, the volume of new magma batches will be such that the composition of the melt within the magma chamber is insensitive to the increasingly contrasting composition of the 'parental' magma influxes. The result would be a gradual chemical evolution of erupted products away from the composition of the 'parental' or 'primary' magma type.

All of the above aspects are valid when applied to variations shown by the Derbyshire basalts. For example, point 3 is illustrated by the greater enrichment of Rb (<3 to 27 ppm) compared with Ba (150 to 600) or Sr (270 to 700 ppm). Successive Lavas exhibit gradual chemical evolution with regard to both major and trace elements, the latter more pronounced. However, this 'overall' trend is in fact composed of a superimposition of slightly overlapping lineages. The final product of a Lava is often more 'evolved' than the initial product of the subsequent Lava. The cessation in the supply of new magma batches to the chambers towards the end of the Dinantian resulted in the culmination of geochemical evolution in the final extrusive phases: the Cressbrook Dale Lava, the Matlock Upper Lava and the Conksbury Bridge Lava (re. points 1 & 5).

Although there was a hiatus between extrusive and intrusive activity (see Chapter 12) the intrusive magma utilised the same magma chambers and conduits responsible for the extrusive activity as is witnessed by the close spatial association of sills with the central vent areas of the lavas (Walters and Ineson, 1981). The greater volume of this magma influx compared to any residuum within the chamber resulted in a reversal of the chemical evolution trend defined by the lavas (re. point 5). Thus, the sills are less 'evolved' than the ultimate Lavas (Figure 7.7). The intrusive magma did not return to the most 'primitive' chemistry shown by the oldest Lavas, no doubt due to mixing with the smaller volume of evolved residuum in the chamber. Once the supply of new magma batches had recommenced the trends of gradual major element evolution/enrichment in incompatible elements also resumed and the compositional variations shown by the sills fall within the trends defined by the Lavas.

Mechanisms for the localisation of extrusive vents, and hence intrusive sills, is difficult to envisage. There is evidence for the association of igneous centres with some of the major mineralised faults in the Orefield, but this may be a function of more detailed local knowledge due to increased exploratory drilling in their vicinity. Likewise there is evidence for an easterly migration of extrusive centres with time. This again may be a fortuitous relationship due to the lack of deep boreholes penetrating older strata on the eastern edge of the Orefield.

7:6 Relationships between Geochemistry and Stratigraphy

The proposed model of magmatic evolution explains the cogenetic nature of the lavas and sills. However, the model also requires progressive chemical evolution of Lavas related to stratigraphy. Chemical variation on an intra-Lava basis, i.e. initial extrusive activity less evolved than ultimate activity, and on an inter-Lava basis, with subsequent Lavas more evolved, would be expected to be present. Therefore, the Lavas should exhibit a correlation between chemical evolution and stratigraphy.

This proposal can be tested by examining the stratigraphical relationships of the Lavas (Figure 7.6) and correlations with the variation shown by minor and incompatible elements (Figure 7.7). Average compositions for individual Lavas are plotted on Figure 7.7, to clarify the relationships. However, it must be remembered that subsequent Lavas fall on trends defined by slightly overlapping lineages (see page 69). Incompatible elements are most sensitive to 'evolution' and average values using various indices are presented in Table 7.1, and Figure 7.6. The conclusions are identical despite the use of various indices, TiO_2 , Zr, SI, etc. and indicate that the relationships are not fortuitous. The only samples to exhibit variance with the whole data set are from the Conksbury Bridge Lava. The flow is

SYMBOLS INDICATE KEY FOR FIGS. 7.1-7.5

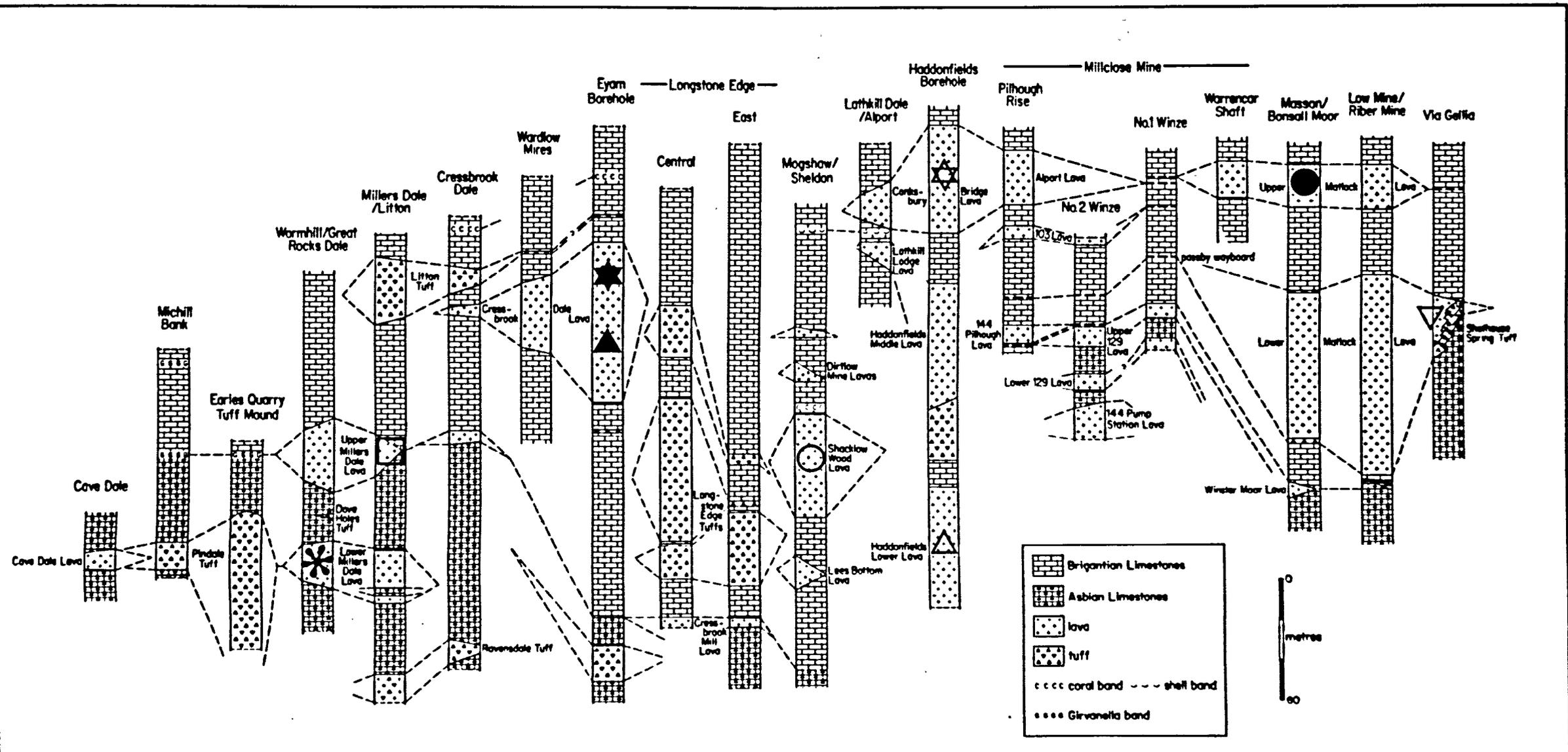


FIG. 7.6 VOLCANIC STRATIGRAPHY OF THE SOUTH PENNINE OREFIELD INDICATING THE RELATIONSHIPS BETWEEN THE MAIN SAMPLED LAVA HORIZONS

Fig 7.6

Table 7.1

TABLE 7.1: 'Average' Corrected Trace and Minor
Element Concentrations

Lava/Sill	S.I	TiO ₂	K ₂ O	P ₂ O ₅	Zr	Y	Ba	Rb
Upper Haddonfields Lava/ Conksbury Bridge Lava	38.7	2.28	0.98	0.45	191	33	277	12
Upper Matlock Lava	31.8	2.30	1.24	0.47	186	29	521	22
Cressbrook Dale Lava	39.7	1.92	0.96	0.34	136	39	356	14
Cressbrook Dale Lava - 'evolved basalt'	29.8	2.82	1.32	0.48	196	27	280	27
Shacklow Wood Lava	38.9	2.00	0.51	0.27	133	29	174	5
Matlock Lower Lava	34.3	1.95	1.13	0.37	146	27	333	19
Millers Dale Upper Lava	39.8	2.17	0.82	0.34	142	29	283	16
Millers Dale Lower Lava	44.0	1.86	0.24	0.26	127	30	169	<BD
Ible Sill	37.8	1.91	0.81	0.39	132	28	310	17
Potluck Sill	35.2	1.94	0.86	0.31	137	29	282	16

unusual in containing only olivine phenocrysts (25%) which is reflected in a high MgO% in turn producing an anomalously high SI.

As Figure 7.7 indicates, the Millers Dale Lower Lava and the Haddonfields Lower Lava exhibit the more 'primitive' compositions. Although in close juxtaposition on many plots the Millers Dale Lower Lava is the lesser evolved of the two when K_2O and Rb concentrations are examined. The Millers Dale Lower Lava is the lowest stratigraphical major volcanic horizon yet recorded from the Orefield (i.e. Middle Asbian), whilst the relative age of Haddonfields Lower Lava is uncertain it is of a probable Upper Asbian age (Walters and Ineson, 1981).

The Millers Dale Upper Lava, the Shacklow Wood Lava and the Cressbrook Dale Lava plot in close juxtaposition. All were extruded during the Lower Brigantian, but although the Millers Dale Upper Lava occurs at a distinct lower stratigraphic horizon (Figure 7.6) the Shacklow Wood Lava is the least evolved. The Millers Dale Upper Lava plots close to the Matlock Lower Lava and as these are identical in age it would imply that the Shacklow Wood Lava, and to a lesser degree the Cressbrook Dale Lava, are 'under evolved' rather than vice versa. A possible explanation for this relationship could be the large volumes of basalt associated with the Cressbrook Dale and Shacklow Wood Lava in comparison with the Matlock or Millers Dale Lavas. This implies a large influx of new magma into the magma chamber resulting in a greater degree of 'dilution' (see point 5 of Section 7:5). In the case of the Cressbrook Dale Lava once this 'dilution' had been overcome the hiatus in the supply of new magma allowed the magma chamber to undergo more extreme fractional crystallisation leading to the ultimate eruption of the evolved basalt. The Matlock Upper Lava and the Conksbury Bridge Lava are stratigraphically the most recent and as such exhibit the highest degrees of evolution.

Fig 7.7

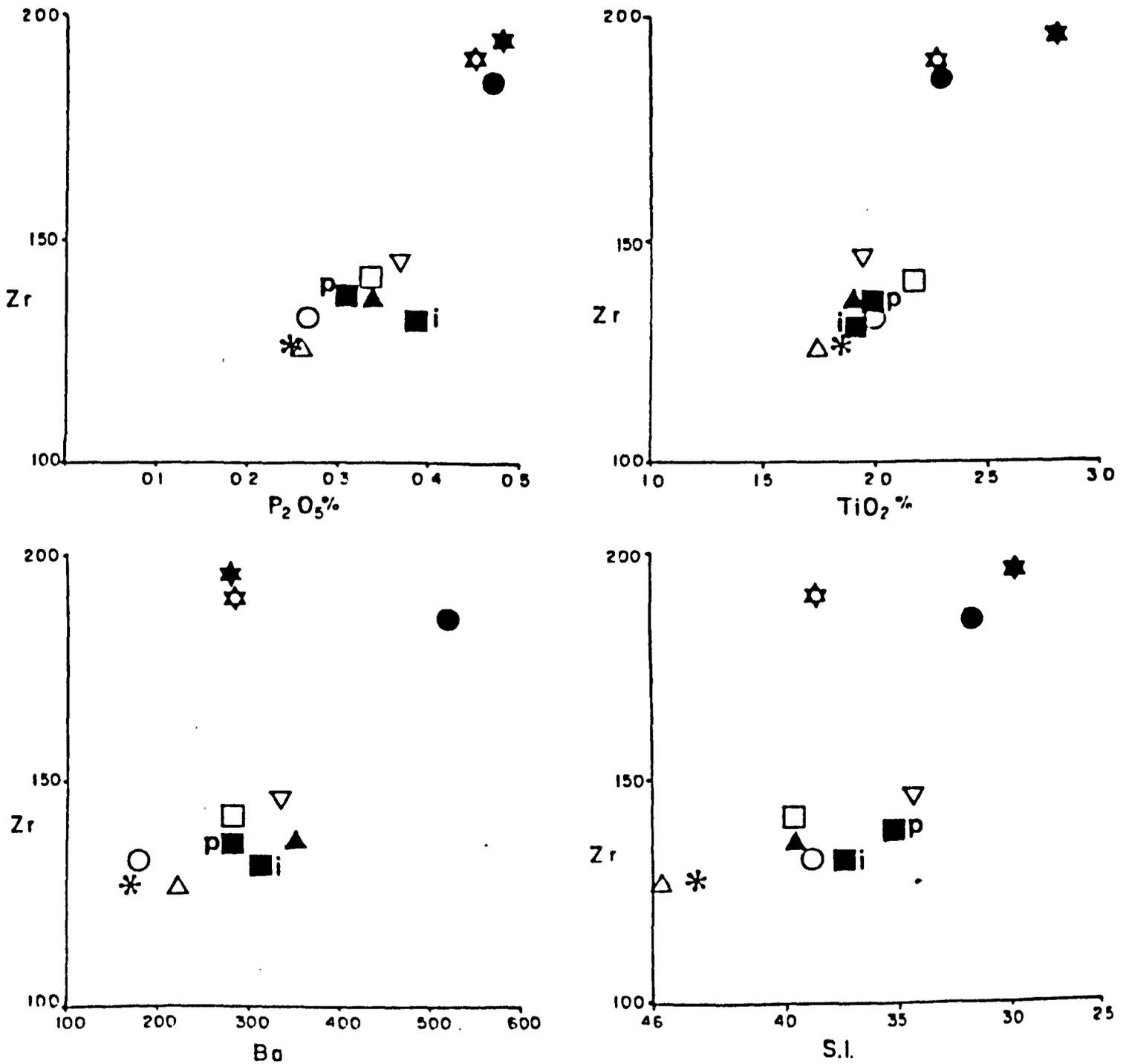


FIG. 7.7 "AVERAGE" TRACE AND MINOR ELEMENT GEOCHEMICAL VARIATIONS

I-Ible Sill P-Potluck Sill. Other symbols as Fig. 7.6
 B-Bonsall Sill C-Calton Hill Sill

Fig 7.7
(cont)

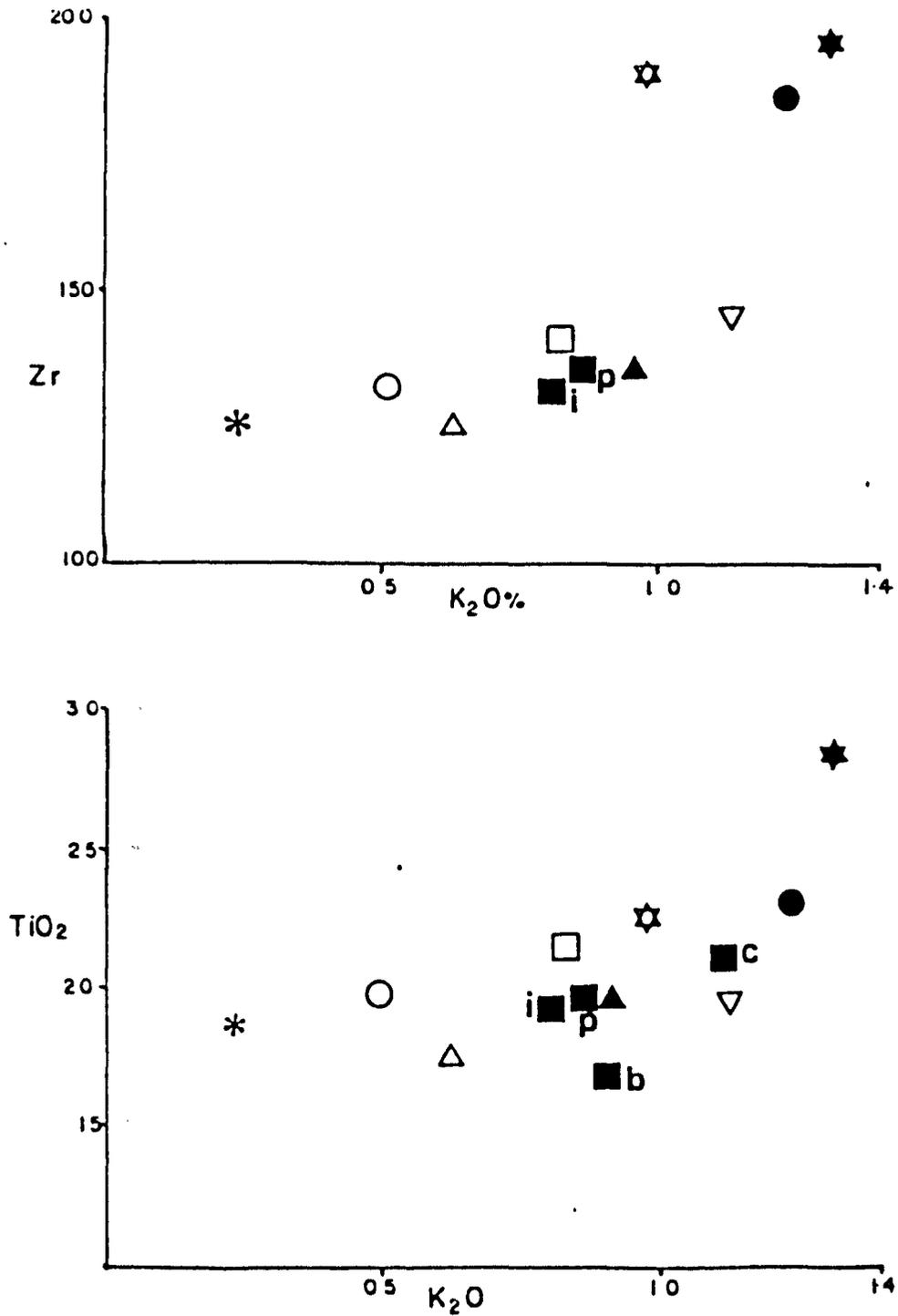


FIG. 7.7 "AVERAGE" TRACE AND MINOR ELEMENT GEOCHEMICAL VARIATIONS (CONT.)

Fig 7.7
(cont)

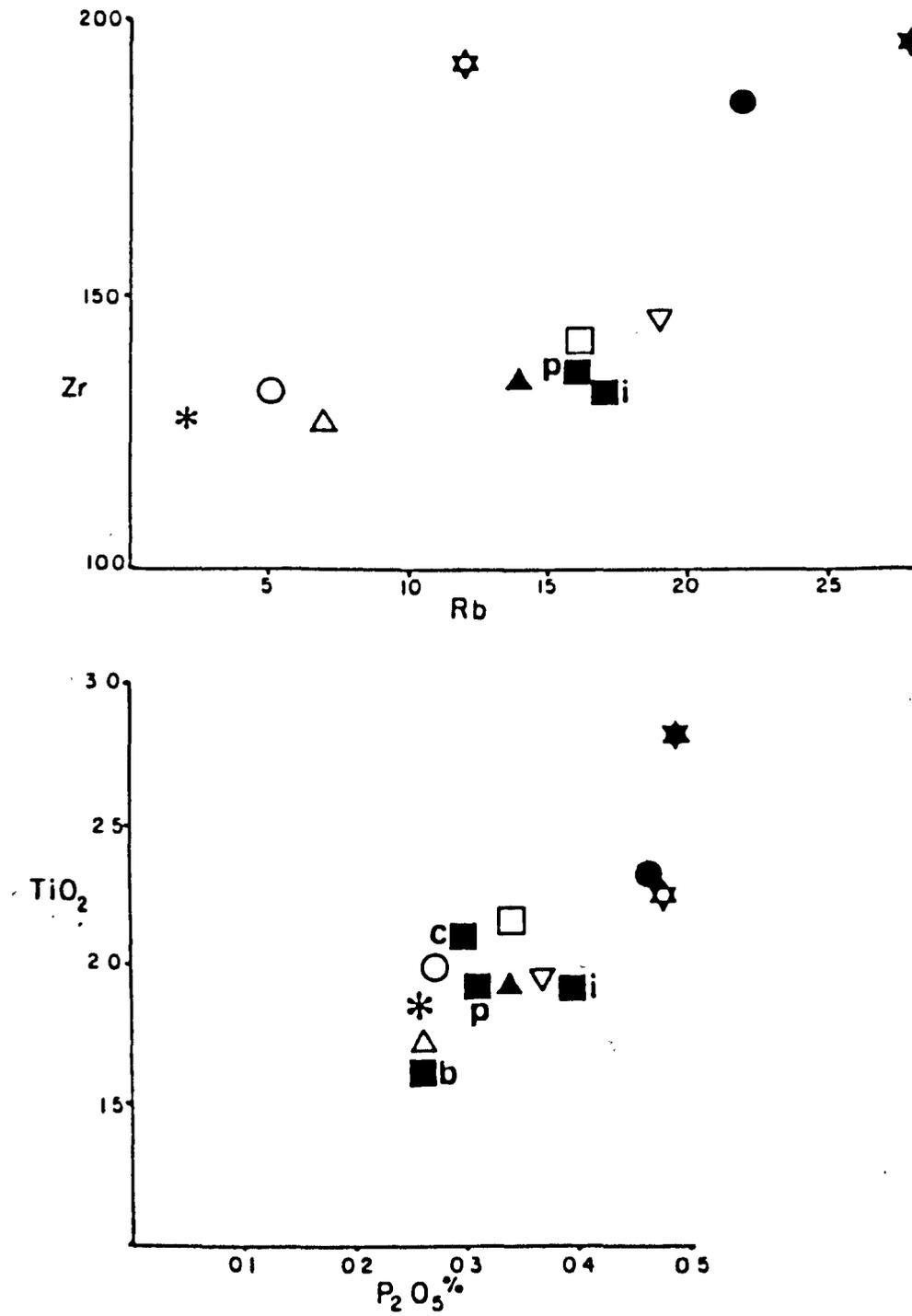


FIG. 7.7 "AVERAGE" TRACE AND MINOR ELEMENT GEOCHEMICAL VARIATIONS (CONT.)

Fig 7.7
(cont)

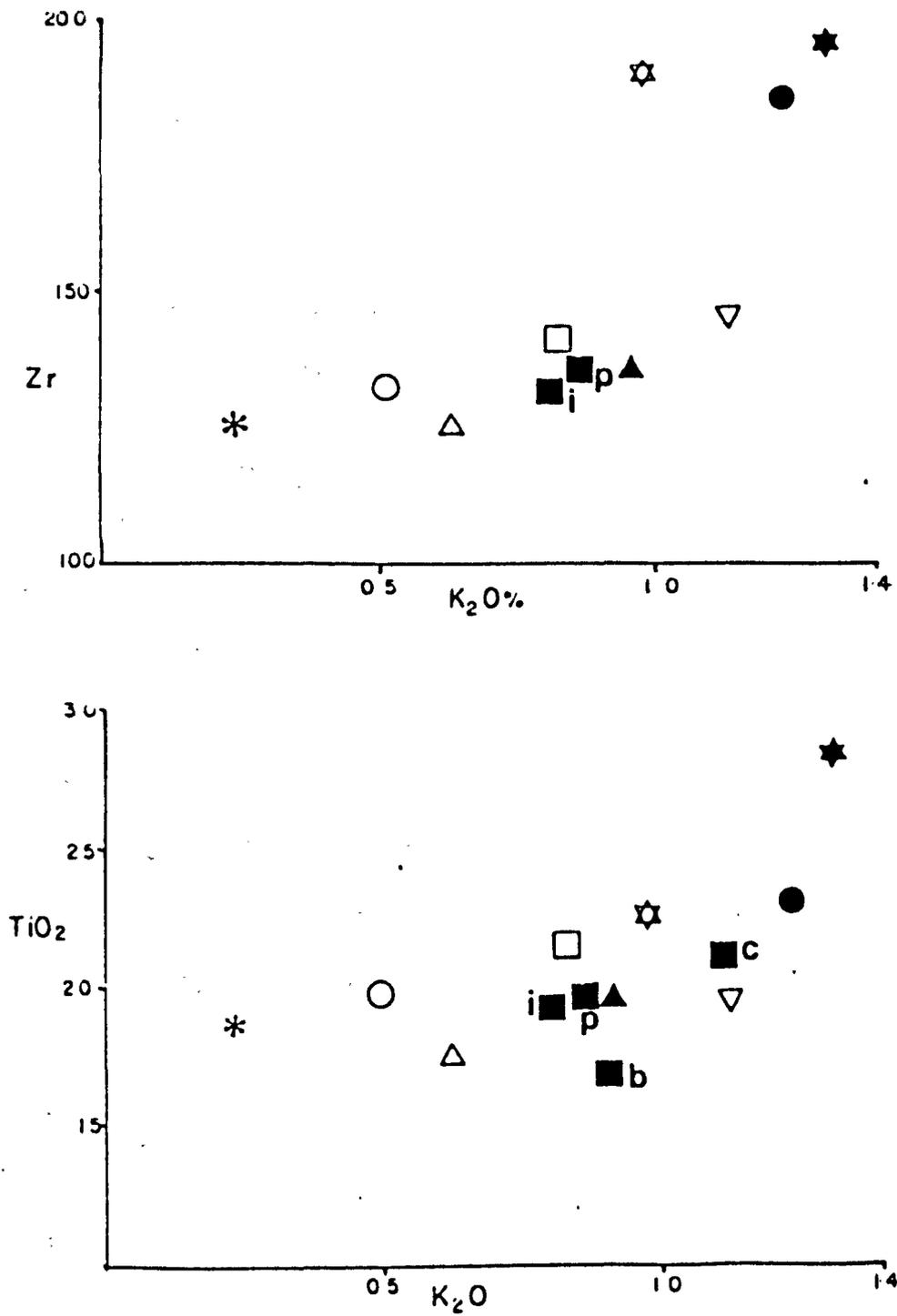


FIG. 7.7 "AVERAGE" TRACE AND MINOR ELEMENT GEOCHEMICAL VARIATIONS (CONT.)

As outlined in Section 7.5, the sills returned to an intermediate geochemical position on the evolutionary trends defined by the lavas. This corresponds to the fields occupied by the Millers Dale Upper/Matlock Lower/Cressbrook Dale Lavas. Unfortunately, there is no reliable trace element data for the Calton Hill or Bonsall Sills. They can, however, be incorporated on a P_2O_5/TiO_2 diagram (Figure 7.7) from which it is tentatively concluded that the Bonsall Sill, the most voluminous, exhibits a more 'primitive' geochemistry with regard to P_2O_5 and TiO_2 . Further details regarding the Waterswallows Sill are contained in Walters and Ineson (in prep.) (see Appendix 13).

7:7 Geochemical Evidence for the Validity of the Major and Trace Element Results

The petrographic sampling criteria outlined in Chapter 6 would appear to be validated by the definitive trends shown by the majority of the major and trace elements. In particular, the correlations exhibited by MgO and FeO support the proposal that deuteric activity in non-vesicular, holocrystalline basalts could take place in a 'closed system'. However, certain oxides i.e. K_2O , SiO_2 and to a lesser degree CaO show less well defined, 'scattered', distributions which may be the result of selective alterations.

Although a number of minor and trace elements are regarded as 'immobile' during alterations, (Winchester and Floyd, 1975) there is abundant evidence of low and high temperature basalt/sea water interactions resulting in migration of certain elements, particularly SiO_2 , MgO, K_2O , Rb and Sr (see the review of Fall, 1980). There is no evidence that the sampled lavas were erupted in a subaqueous environment (see Chapter 3), inferring that any possible interactions would have been of a low-temperature nature.

Hart (1971), Wood et al. (1976) and Fall (1980) have shown that K_2O and Rb in basalts are most sensitive to low temperature sea water and zeolitic alterations. A correlation between increasing H_2O^+ as an index of alteration and K_2O and Rb was demonstrated by Fall (1980), for Jurassic basalts from the North Sea. A similar plot for the 'fresh' Derbyshire basalts (Figure 7.8) exhibits no such correlations (Note: $K_2O\%$ and Rb ppm are plotted using adjusted anhydrous, values to eliminate possible 'dilution' effects with varying % H_2O^+). MgO and Sr are also sensitive to alterations and the correlation of MgO v SI (Figure 7.1) and Sr v. Zr (Figure 7.3) confirms that there is no geochemical evidence for alteration.

In addition to deuteric and low temperature seawater interactions, many basalts illustrate the effects of prolonged contact with hydrothermal mineralising brines. In order to assess the geochemical effects of the various alterations a number of altered samples were included in the study. Analysis 12 represents a vesicular lava in which the ferromagnesian minerals have been replaced by clay aggregates, plagioclase is albitised and the vesicles have an infill of clays rather than calcite. Anal. 20, a holocrystalline basalt less altered than Anal. 12, exhibits clay alteration of ferromagnesian minerals and areas of incipient calcitisation whereas the plagioclase is unaltered. Anal. 36, 38, 39, represent degraded dolerite with chloritisation and albitisation. Anal. 42 is from a hydrothermally altered dolerite with intense calcitisation and relict albite with kaolinite. Vesicular alterations are represented by Anal. 63 to 67 and 75 to 82.

The common geochemical indications of alteration are a high concentration of H_2O^+ and CO_2 with low $MgO\%$. Sr and Ba decrease during albitisation, whereas Rb increases. Although the vesicular and hydrothermally altered basalts clearly display these trends, samples with only incipient alteration,

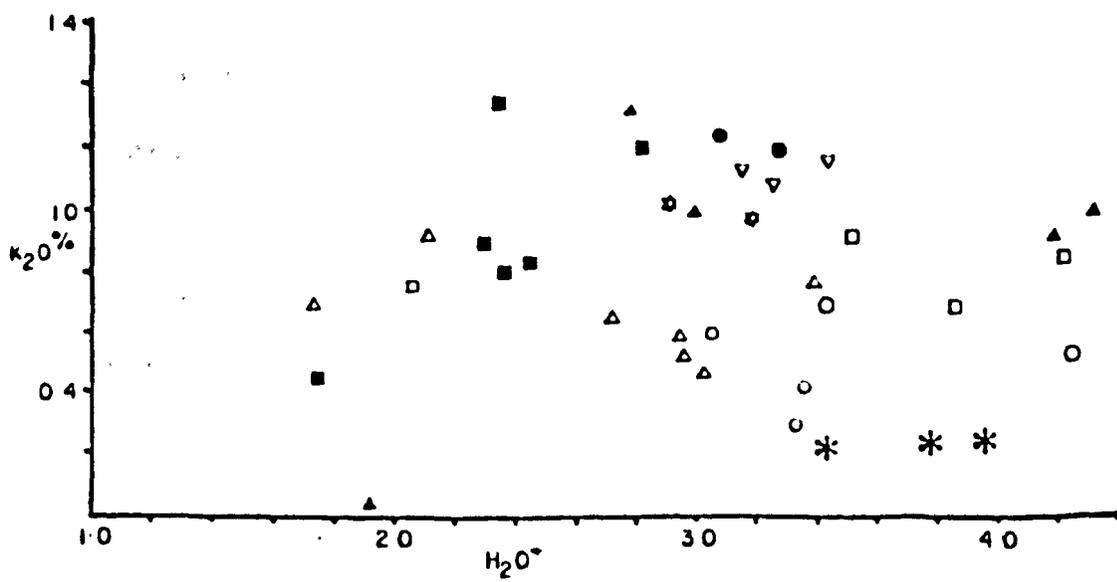
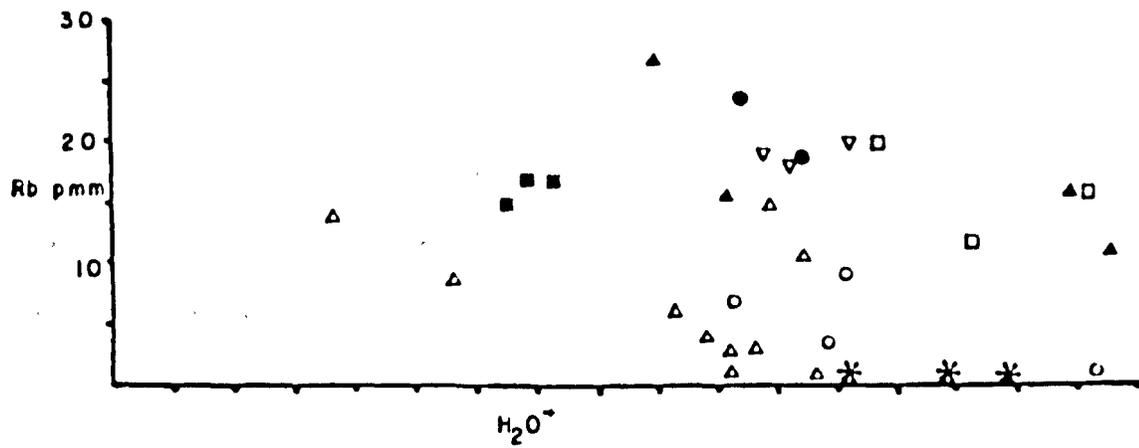


FIG. 7.8 Rb AND K₂O VARIATIONS VERSUS H₂O⁺

SYMBOLS AS IN FIG 7.6

e.g. Anal. 20, display only minimal indications. In these instances petrographic features are the main indicators of alteration.

Thus, the validity of the geochemical variations as representative of 'unaltered' material has been vindicated. The most sensitive selection criteria are based on petrographic examinations rather than geochemistry.

7:8 Comparisons with the Duffield Sill

The Duffield Borehole (SK 3428 4217) proved 642 m of Asbian and Brigantian mudstones and distal turbidites with thin pyroclastic horizons of Upper Brigantian age (George et al., 1976; Harrison, 1977; Frost and Smart, 1979). Two analcite-dolerite sills were intersected, an upper sill (8.5 m thick) intruded in Upper Brigantian mudstones and pyroclastics and a much thicker (65.8 m) lower sill intruded in Upper Asbian strata. Detailed petrological and geochemical variations within the lower or 'Duffield' sill were described by Harrison (1977).

The Duffield Sill exhibits marked differentiation with chilled margins of dolerite, a lower picritic unit (21 m thick) containing some 35% pseudomorphed olivines and an upper analcite dolerite/gabbro unit (43 m thick) with random areas of later-stage interstitial analcite. The picrite and gabbro are separated by a thin (0.8 m) band of pyroxenite which contains >50% clinopyroxene with subordinate olivine and plagioclase (Table 7.2) in a fine grained altered matrix. The analcite gabbro exhibits progressive hybridisation with veining and late stage injections of pale pink microsyenite. Modal analyses (Table 7.2) indicate an enrichment of apatite, Fe-Ti oxides and analcite with depletion of olivine and clinopyroxene within the upper gabbroic sequence.

Although pyroxene is unaltered, oxidation of Fe-Ti oxides, pseudomorphs after olivine, albitisation and extensive alteration of interstitial areas are ubiquitous. Harrison (op.cit.) considered the alteration to be the result of deuteric activity enhanced by high p_{H_2O} associated with

TABLE 7.2: Geochemistry and Petrology of the Duffield Sill

Geochemistry (oxide wgt%)	Picrite	Pyroxenite	Dolerite	Hybridized Analcite- Gabbro	Micro- Syenite	Bulk Average ⁺
SiO ₂ *	44.97	48.46	50.05	49.49	61.04	48.8
Al ₂ O ₃	8.89	10.54	14.35	16.50	19.00	13.9
Fe ₂ O ₃	5.75	2.98	1.99	3.63	0.96	3.0
FeO	8.81	6.60	7.21	7.40	2.48	7.5
MgO	21.59	14.35	9.38	4.93	1.16	10.9
CaO	5.29	11.64	9.06	6.76	0.86	6.4
Na ₂ O	1.37	2.19	3.93	5.31	6.26	3.8
K ₂ O	0.68	0.51	1.40	2.08	6.93	1.5
TiO ₂	1.31	1.70	1.75	2.61	0.66	1.6
P ₂ O ₅	0.27	0.29	0.28	0.46	0.13	-
MnO	0.25	0.18	0.19	0.17	0.05	-
CO ₂	0.22	0.08	0.07	0.07	0.06	-
SI	49.6	53.9	39.2	21.1	6.6	40.8

* All elements recalculated on an anhydrous basis

+ Average of 40 partial analysis. Fe₂O₃, Al₂O₃ and TiO₂ calculated as average of 5 preceding analyses

TABLE 7.2 (Cont.): Geochemistry and Petrology of the Duffield Sill

Modal Analyses (Volume %)	Picrite	Pyroxenite	Dolerite	Analcite- Gabbro	Micro- Syenite
Olivine Pseudomorphs	34.8	3.8	0.7	0.1	-
Clinopyroxene	8.0	53.0	30.5	16.3	-
Plagioclase (albitised)	0.5	4.4	47.4	43.7	50.7
Orthoclase	-	-	-	0.5	37.1
Apatite	trace	trace	0.1	1.0	0.8
Biotite	2.1	2.2	2.0	1.5	3.9
Opaques	3.4	0.9	2.7	11.2	1.2
Interstitial ground- mass (clays)	26.4	19.4	2.0	1.6	1.9
Chlorite	24.8	16.3	13.4	7.7	2.7
Carbonate	-	-	-	0.3	-
Analcite	-	-	1.2	16.1	1.6

intrusion in thick sequences of 'wet' sediments. XRD analysis indicates that chlorite "... possibly a swelling variety ..." and/or smectite and illite-smectite constitute the areas of interstitial alteration while pseudomorphs after olivine in the picrite consists of "... an expanding mineral (probably bowlingite) ..." associated with interlayered minerals.

The differentiation of the Duffield Sill contrasts with the Viséan intrusions in the south Pennines and the Westphalian intrusions in the east Midlands, and was attributed by Harrison (op.cit.) as partly due to the thickness of the sill and the influence of analcite in lowering the viscosity of the magma. Differentiation represents a density stratification arising from gravity settling either in the pre-intrusive magma chamber or after intrusion of the sill, or alternatively by a process of elutriation in the conduit during magma ascent. The occurrence of analcite in the gabbroic unit is essentially random with variations of between 1.85% and 3.66% Na₂O noted from adjacent samples. Consanguineous analcite-bearing and analcite-free intrusive dolerite suites in the Upper Carboniferous of the east Midlands were noted by Francis (1970) and Harrison (1977) while in the south Pennines analcite is restricted to the more 'evolved' Lavas and Sills of alkali-transitional rather than tholeiitic nature.

Harrison (op.cit.) concluded that comparisons of the Duffield Sill with intrusive activity in the south Pennines, over a distance of only 20 km, was 'problematical'. However, a number of geochemical and petrographic similarities between these areas can be demonstrated which suggest consanguineous activity. Microprobe analyses of pyroxenes from the Duffield Sill (Harrison, op.cit.) indicate minimal variations within the compositional field of salites (Figure 7.9). The MgO-FeO-CaO concentrations are typical of pyroxenes associated with alkali-

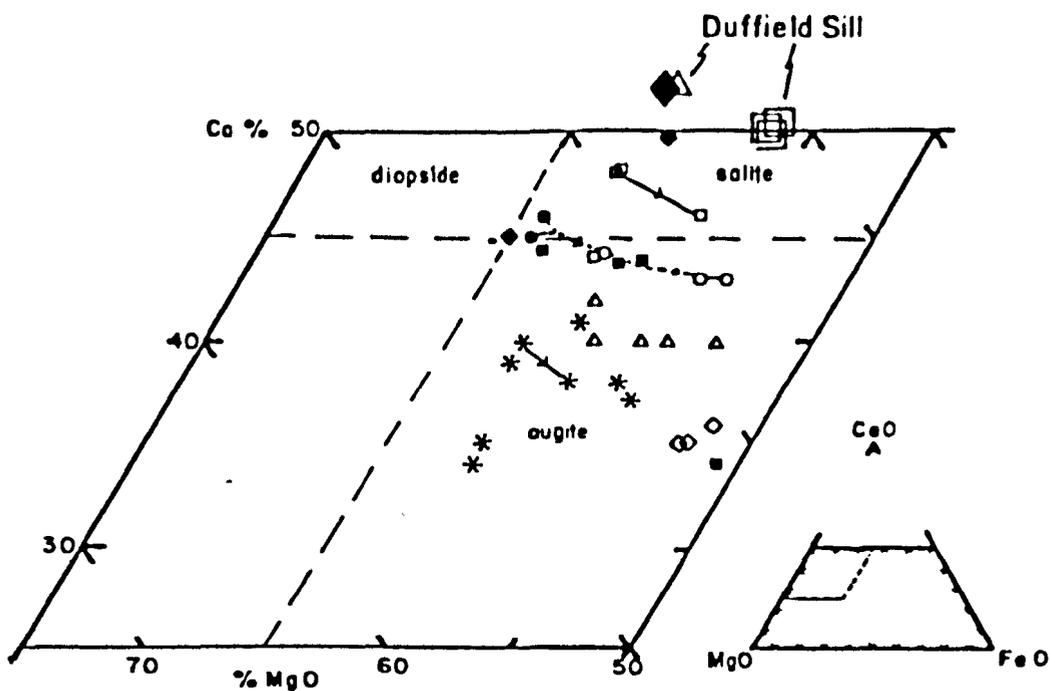


FIG. 7.9 A COMPARISON OF THE CaO-MgO-FeO PYROXENE COMPOSITIONS OF THE DUFFIELD SILL WITH THE SOUTH PENNINE BASALTS

(for key to South Pennine analyses see Fig 4.2)

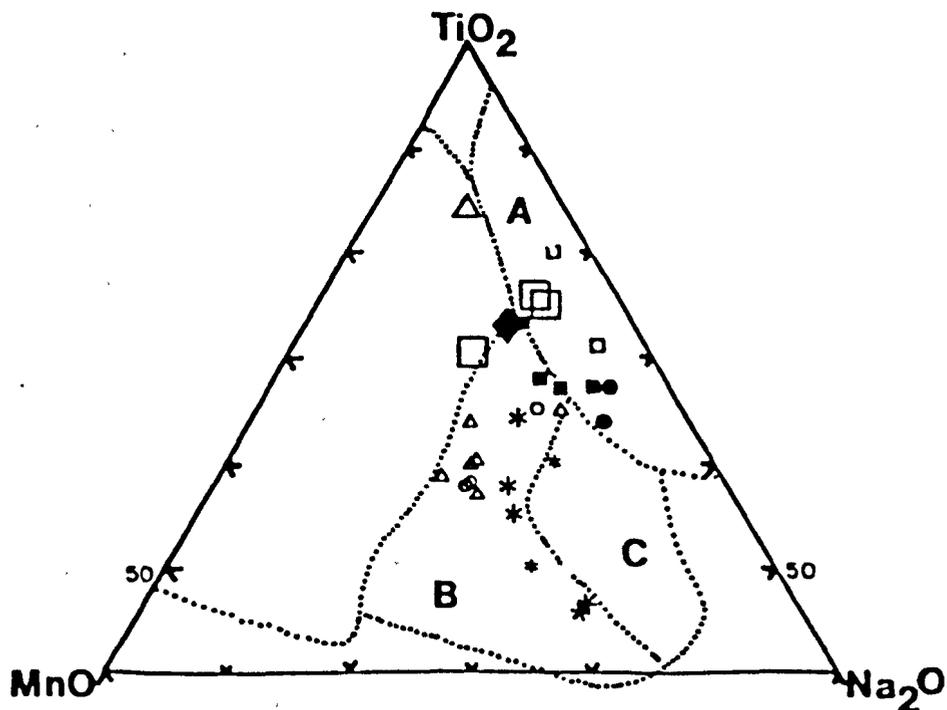


FIG. 7.10 A COMPARISON OF THE MnO-TiO₂-Na₂O PYROXENE COMPOSITIONS OF THE DUFFIELD SILL WITH THE SOUTH PENNINE BASALTS

olivine basalts and are comparable with the groundmass pyroxene compositions noted from the intrusive analcite dolerite at Calton Hill. However, the low $\text{TiO}_2\%$ of the Duffield Sill pyroxenes is directly comparable with the 'transitional' nature of pyroxenes in the south Pennine basalts (Figure 7.10). The minimal variations in pyroxene composition suggests that differentiation is the result of gravity settling or elutriation after the bulk of crystallisation had occurred.

The geochemistry of differentiation is a function of relative proportions of the individual phases rather than geochemical variations accommodated within individual phases, associated with the progressive concentration of alkali-enriched residual melt culminating in the micro-syenitic segregations. Major element analyses (recalculated on an anhydrous, CO_2 free basis) are included in Table 7.2 together with the 'bulk' composition of the sill compiled from the average of forty analyses. Geochemical variations versus Solidification Index (Figure 7.11) indicate a close correspondence between the bulk sill composition and the analcite-dolerite which suggests an attainment of 'equilibrium' between crystal settling and residual enrichment towards the centre of the sill. A comparison of the analcite-dolerite and 'bulk' compositions of the Duffield Sill with the south Pennine basalts (Figure 7.11) indicate a pre-fractionation major-element geochemistry comparable with the Ible or Waterswallows Sills. Relative reduction of CaO associated with the 'bulk' composition can be attributed to the effects of widespread albitisation and lack of calcitisation, features more pronounced in the lower picritic unit. Enhanced K_2O and Na_2O levels in the Duffield Sill may be a primary feature of the magma or alternatively represent a derivation of microsyenitic and analcite residues from the deeper, parental, magma chamber (Harrison, op.cit.). Although enhanced in comparison with the majority of the south Pennine basalts,

alkali concentrations in the Duffield Sill are similar to 'anomalous' enrichments noted from the Calton Hill and Bonsall Sills which also contain analcite.

The geochemical variations of the differentiated units (Figure 7.11) are compatible with a mechanism of gravity settling involving a restricted number of phases from a pre-differentiation composition corresponding to the 'bulk' analyses and the analcite-dolerite. Accumulation of olivine in preference to plagioclase in the picrite unit involves a relative enrichment in MgO and FeO together with a reduction in SiO₂, Al₂O₃ and K₂O. Enrichment of titaniferous salite in the pyroxenite would be expected to result in enrichment of CaO and MgO, minor variations in SiO₂ and TiO₂ with reduction of FeO, Na₂O, Al₂O₃ and K₂O. The geochemistry of the hybridised analcite-gabbro is compatible with olivine and pyroxene depletion accompanied by enrichment in plagioclase, apatite, Fe-Ti oxides and alkali-rich residues.

Variations in geochemical trends between the Duffield Sill analcite-gabbro and the more 'evolved' south Pennine basalts (in particular the Cressbrook Dale lava) are related to fundamental differences in the proposed mechanisms of differentiation. Gravity settling of olivine and pyroxene in the analcite-gabbro contrasts with plagioclase and pyroxene differentiation in the magma chamber associated with the 'evolved' basalts. The dominance of plagioclase in preference to olivine involves relative reduction in Al₂O₃ and CaO with enrichment of SiO₂ (Figure 7.11). Reduction of Na₂O and FeO in the evolved south Pennine basalts is offset in the Duffield Sill by alkali-rich residue and greater Fe-Ti oxide concentrations in the final products of crystallisation which culminates in the microsyenite segregation depleted in all major and trace elements associated with the crystallised phases.

Fig 7.11

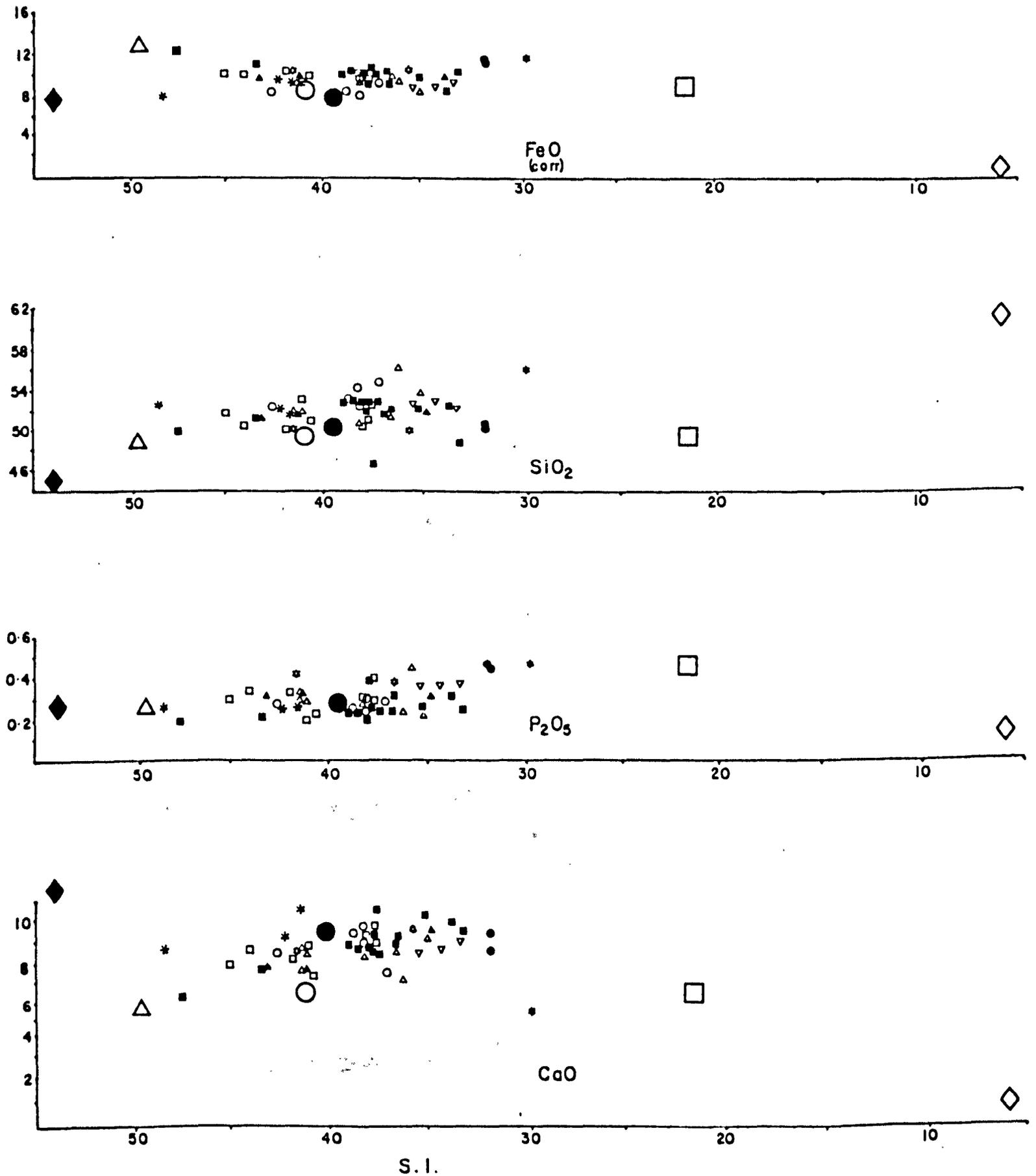
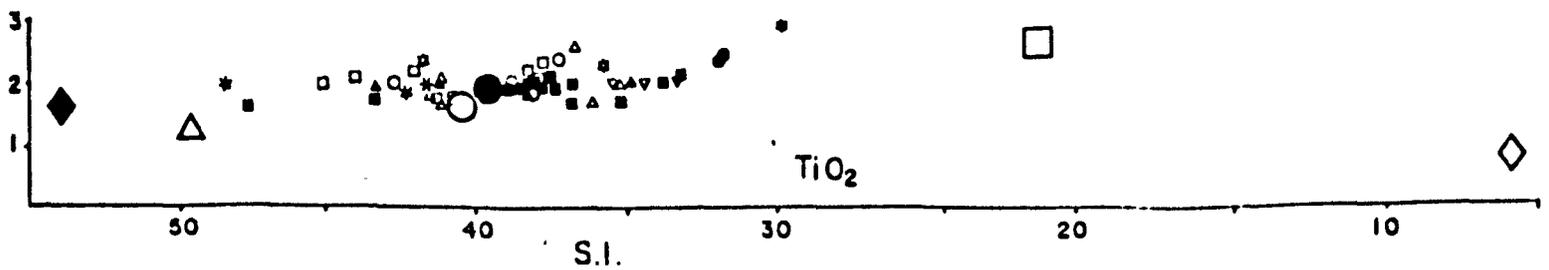
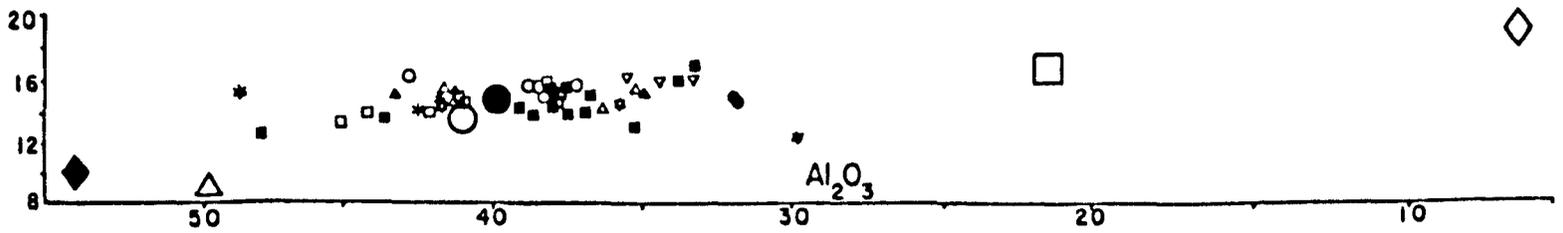
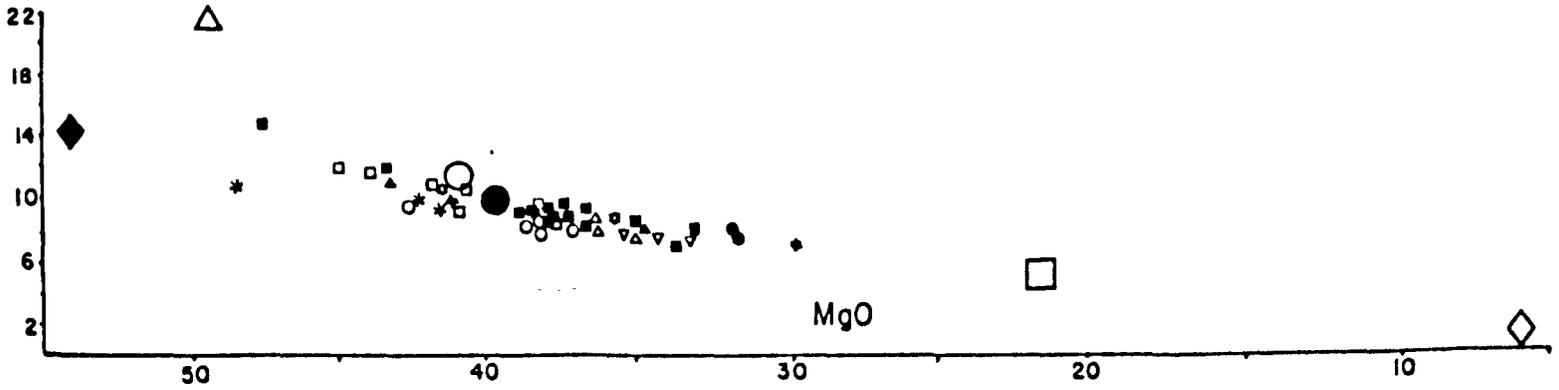
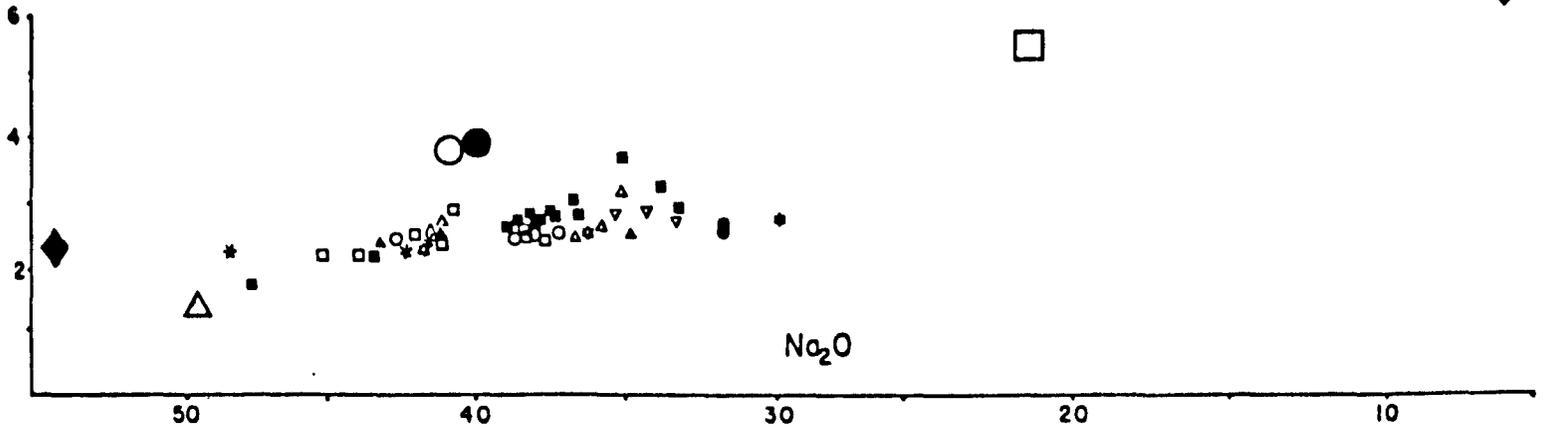


FIG. 7.11 A COMPARISON OF THE MAJOR ELEMENT GEOCHEMICAL VARIATIONS VERSUS SOLIDIFICATION INDEX OF THE DUFFIELD SILL AND SOUTH PENNINE BASALTS

For key to small symbols see Fig. 7.6

FIG 7.11 (CONT.)



- ◆ Pyroxenite
- △ Picrite
- Average bulk comp.
- Dolerite
- Hybrid analcite-gabbro
- ◇ Syenitic segregation

The interpretation of trace element variations in the Duffield Sill is complicated by the erratic nature of the reported Zr concentrations (Harrison, *op.cit.*). Extreme, random, variations are noted for adjacent samples and those samples selected for full geochemical analysis (Table 7.2) all exhibit reduced Zr levels in comparison with average concentrations. Minimal details regarding the 'spectrochemical' analytical techniques employed in the determination of trace elements are given in Harrison (*op.cit.*) and it is not therefore feasible to compare the trace element versus Zr trends of the south Pennine basalts with the Duffield Sill trends. Variations in Ba and Sr are also of limited significance due to ubiquitous albitisation and alteration. Ni and Cr variations in the Duffield Sill can be related to partition coefficients between olivine and pyroxene (see Section 7.4). Figure 7.12 indicates a comparison of Ni and Cr against % olivine with the south Pennine basalts. Reduction of olivine and pyroxene in the syenite and analcite gabbro is reflected in the depletion of Ni and Cr. The accumulation of olivine in the picrite is indicated by enrichment of Ni and Cr, with Ni > Cr. Pyroxene accumulation in the dolerite and especially the pyroxenite is also indicated by enrichment of Ni and Cr but in accordance with the predicted partition-coefficient behaviour Cr >> Ni.

In conclusion the pre-differentiation geochemistry of the Duffield Sill magma can be compared with that of a number of intrusions in the south Pennines except for a greater degree of alkali enrichment. The differentiated units represent the result of gravity settling of pyroxene and olivine probably within the cooling sill. The geochemical trends shown by the south Pennine Lavas are attributable to a process of minimal fractionation involving 3-phase, eutectic, crystallisation in a periodically replenished magma chamber while the more evolved basalts

Δ Fig 7.12

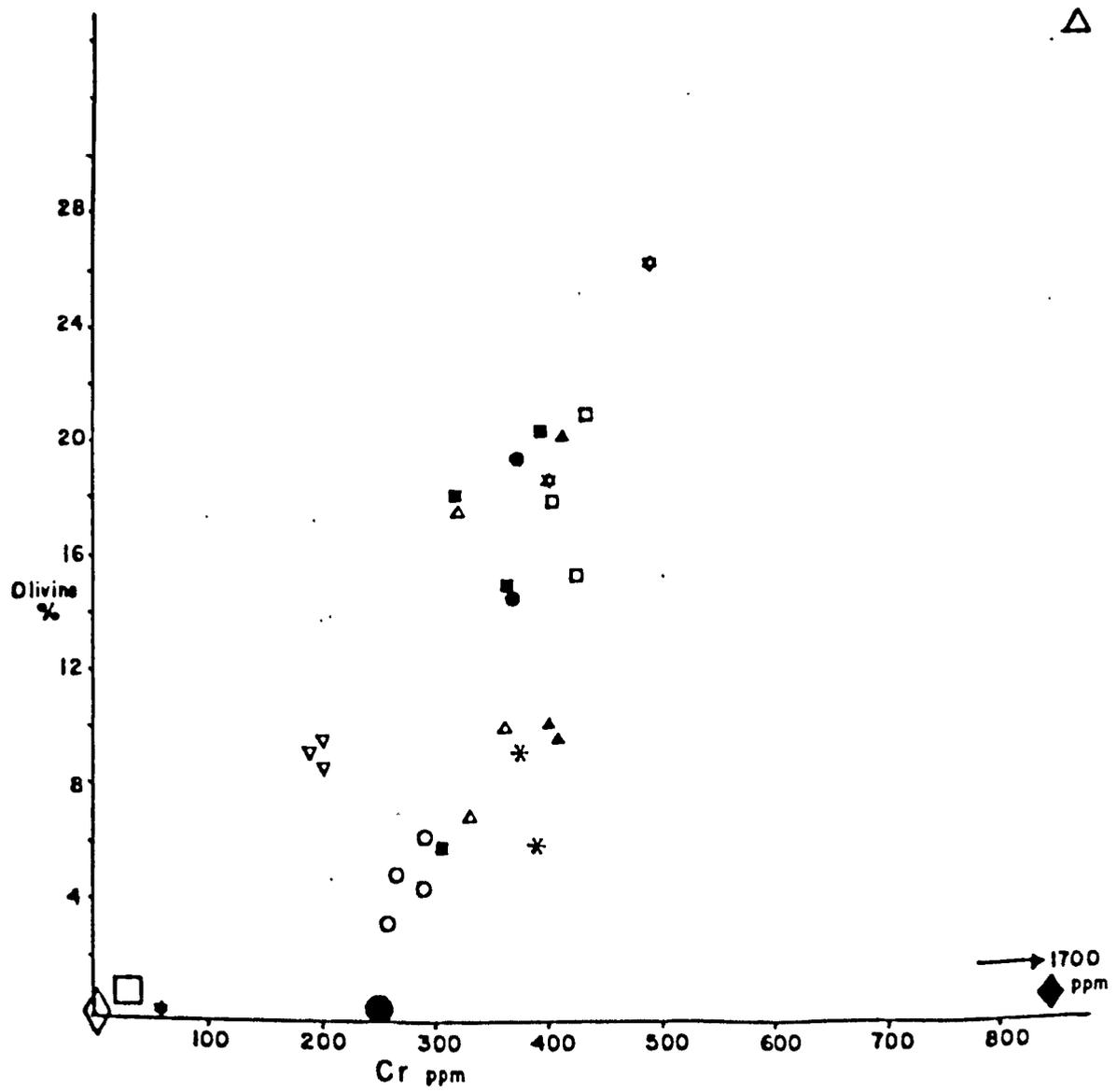
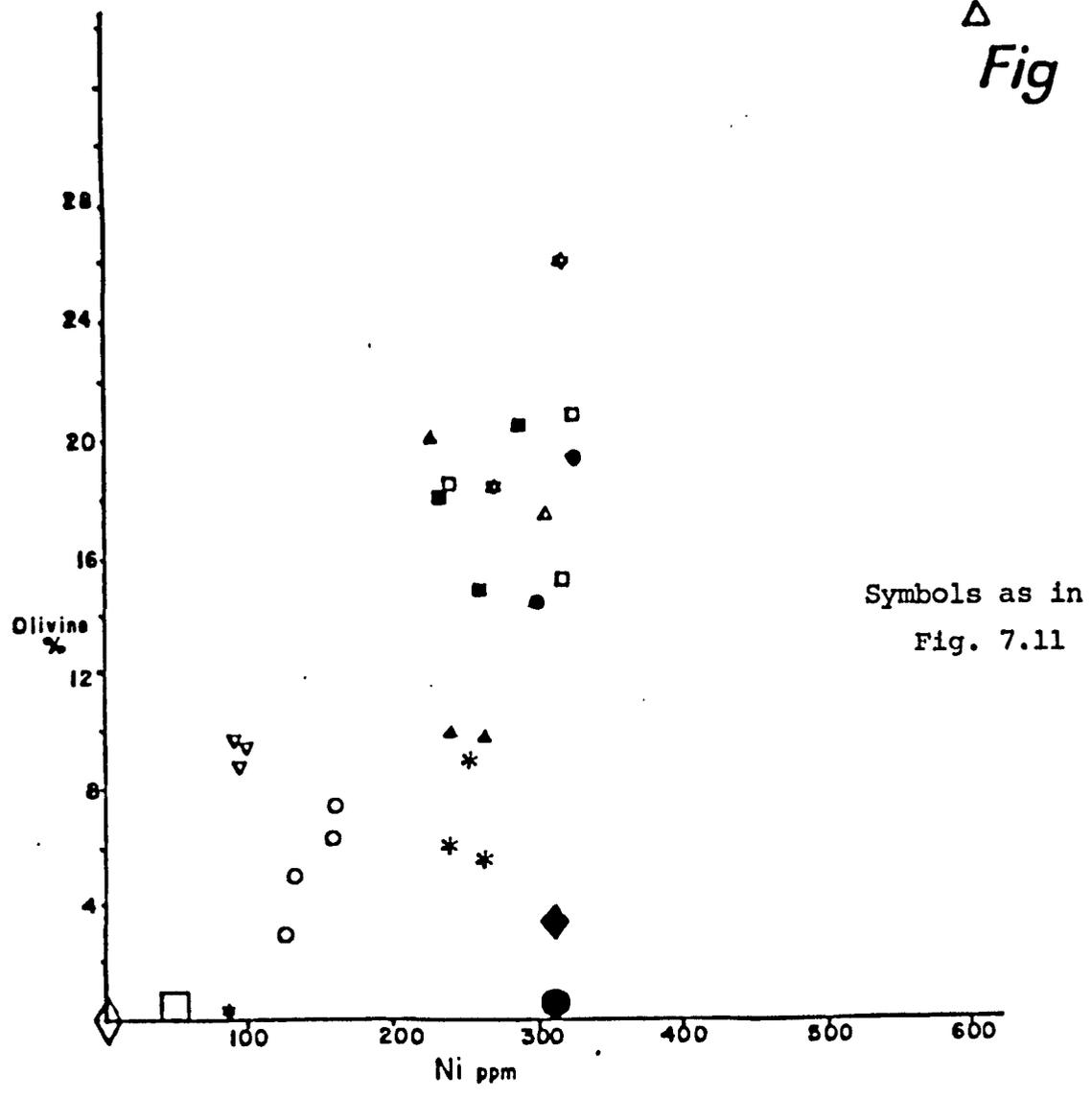


FIG 7.12 Ni AND Cr VARIATIONS IN THE DUFFIELD SILL AND SOUTH PENNINE BASALTS

were controlled by 2-phase (plagioclase + pyroxene) fractionation. Comparable trends of gravity differentiation have not at present been fully documented from the major intrusions on the south Pennines. The olivine enriched 'gabbroic' horizon in the Waterswallows Sill (Appendix 13) exhibits trends comparable with the picrite unit in the Duffield Sill and suggests a degree of gravity differentiation with probable erosion of the alkali enriched units at higher levels.

CHAPTER EIGHT



Chapter Eight

Nomenclature and Magmatic Affinities of the Derbyshire Basalts

8:1 Introduction

Confusion has arisen as to the magmatic affinities and nomenclature of the basalts. The Buxton Bridge Dyke was described as tholeiitic by Cope (1933) while the Millers Dale Upper and Lower Lavas and the Cave Dale Lava were designated as tholeiitic types on geochemical and normative criteria by Malki (1967). Wilkinson (1967), however, considered that on the basis of petrography, the basalts and dolerites exhibited a range from tholeiitic to alkaline types. Harrison (in Stevenson et al., 1971) designated the Waterswallows dolerite and the dyke south of Buxton Bridge as tholeiitic as was the Cave Dale Lava by Cheshire and Bell (1978). Cheshire and Bell (op.cit.) interpreted Wilkinson's (1967) evidence as indicating the co-existence of two separate magmas - tholeiitic and an alkaline magma. Donaldson (1978) described the intrusive dolerite at Calton Hill as an ankaramitic alkali-olivine basalt.

8:2 The Concept of Magma Series

The concept of a volcanic magma series traditionally divides the basalts into tholeiitic or alkali-olivine lineages, (Tilley, 1950). This division was initially based on petrographic criteria and the concept of silica saturation v. alkali content. Yoder and Tilley (1962) re-defined tholeiites as hypersthene normative and alkali-basalts as a nepheline normative. In recognising hypersthene-normative basalts with alkali-olivine petrographic features they considered this to be an effect of alteration. In a re-examination of the Hebridean Plateau Magma Type. Tilley and Muir (1962) concluded that: "... hydration, oxidation and serpentinisation in the form of pseudomorphous replacement of olivine, processes often accom-

panied by selective leaching are, without doubt, mainly responsible for the appearance of significant hypersthene in the norms (of alkali-basalts)" This was disputed by Poldervaart (1964) who concluded that hypersthene normative, unaltered, basalts in which quartz + nepheline = 0 did occur and were not accommodated by the classification of Yoder and Tilley. Poldervaart (op.cit.) derived a normative equation which allotted hypersthene-normative types into the tholeiite/alkali-olivine groupings. The use of discriminant functions was pursued further by Chayes (1966). He observed, however, that although primary hypersthene normative (quartz + nepheline = 0) basalts existed it could also arise due to alterations, as suggested by Tilley and Muir (1962). Chayes (op.cit.) developed selective criteria based on $\%H_2O^+$ /oxidation ratios to avoid 'altered samples'. Irvine and Barrager (1971), in their review of the chemical classification of volcanic rocks, continued the practice of assigning basalts with normative hypersthene and $Q + Ne = 0$ into either the tholeiitic or alkali series.

Although the alkaline and the tholeiitic (or sub-alkaline) series are undoubtedly the dominant volcanic associations it is now realised there is a continuum of basalt types between the series, e.g. Carmichael et al (1974). The status of hypersthene normative basalts as a primary type has gained acceptance amongst the basalts of the British Tertiary Volcanic Province (Ridley, 1971; Thompson et al., 1972; Holland and Brown, 1972; Beckinsale et al., 1978; Llyle, 1980). In particular, Thompson et al. (1972) demonstrated that the hypersthene normative basalts of Skye were the result of primary geochemistry in a parental magma rather than a product of post or syn-consolidation alterations. Such basalts have been termed 'transitional' or 'hypersthene-normative'. Transitional types have been noted from elsewhere, e.g. as a component of the 'mildly alkaline' Dinantian lavas of Southern Scotland (MacDonald, 1975) and from the Somali

Trap Series of Ethiopia by Brotzu et al. (1974). Flower (1973) proposed a primary transitional basalt-hawaiite series in volcanics from the western Indian Ocean.

Within this transitional range, Llyle (1980) and Brotzu et al. (1974) have used the alkali/silica plot in an attempt to subdivide transitional basalts into those with tholeiitic or alkaline 'affinities'. Whilst this approach may have limited applications for indicating different types of transitional basalts with the same series, e.g. Brotzu et al. (op. cit.) the use of such criteria is dependent on the choice of the discriminatory division. Schwarzer and Rodgers (1974) reviewed the use of the alkali/silica plot and proposed four dividing curves. Although the majority of alkali-basalts plot in the relevant field they noted that there was: "a continuum in compositions between all basalt types rather than discrete groupings". Therefore, some basalts that lie close to the boundary curves have properties intermediate between alkaline and subalkaline rocks.

8:3 A Normative Classification of the Derbyshire Basalts

The computation of norms on vesicular or altered basalts has produced misleading results, e.g. Malki (1967) and Cheshire and Bell (1978). As demonstrated in Chapter 6, late magmatic or deuteric alterations are ubiquitous amongst the Derbyshire basalts and are typical of alkali-olivine basalts as a whole. The attendant hydration and oxidation must be compensated before normative calculations are undertaken (see Section 6:4) as these adjustments have critical effects on normative values for quartz and the ferromagnesian minerals. As Table 6:2 indicated adjustment of oxidation ratios, produces hypersthene-olivine norms from

analyses which would otherwise be classed as quartz-normative. Previously available analyses of unaltered 'tholeiitic' or 'quartz-normative' basalts, e.g. Malki (1967) and Stevenson et al. (1971) become hypersthene-normative or 'transitional' when adjusted oxidation ratios are employed. Of the basalts analysed during this study 90% show transitional norms after re-adjustment while 8% are quartz-hypersthene normative and can be directly attributed to secondary silicification (common in plagiophytic lavas) or a greater degree of alteration. There is a direct relationship between % normative quartz and alteration, e.g. Anal. 20. A small number of dolerite sill analyses (Hamad, 1963; Ixer, 1972) show normative nepheline before and after adjustments and indicate a possible trend to more typical alkali-olivine basalts (see Appendix 3).

The normative data indicates that the basalts are of transitional nature. However, given the critical effects of re-adjustment, particularly of oxidation ratios, conclusions based solely on normative data must be interpreted with caution.

8:4 Discrimination Based on 'Immobile' Trace Elements

The 'immobile' nature of a number of trace and minor element during alteration has been demonstrated by Pearce and Cann (1973), Winchester and Floyd (1975) and Floyd and Winchester (1975) amongst others. The relative concentrations of these elements and in particular Zr, Nb, Y, TiO_2 and P_2O_5 have been used as discriminant functions to distinguish tholeiitic or alkaline basalts in metamorphosed or splitised terrains. This approach is applicable to the Derbyshire basalts which have only undergone deuteric alteration.

Plots of TiO_2 v. Zr/P_2O_5 and Zr v. P_2O_5 are presented in Figure 8.1, with field boundaries taken from Floyd and Winchester (1975). The diagrams substantiate the normative conclusions and indicate that the

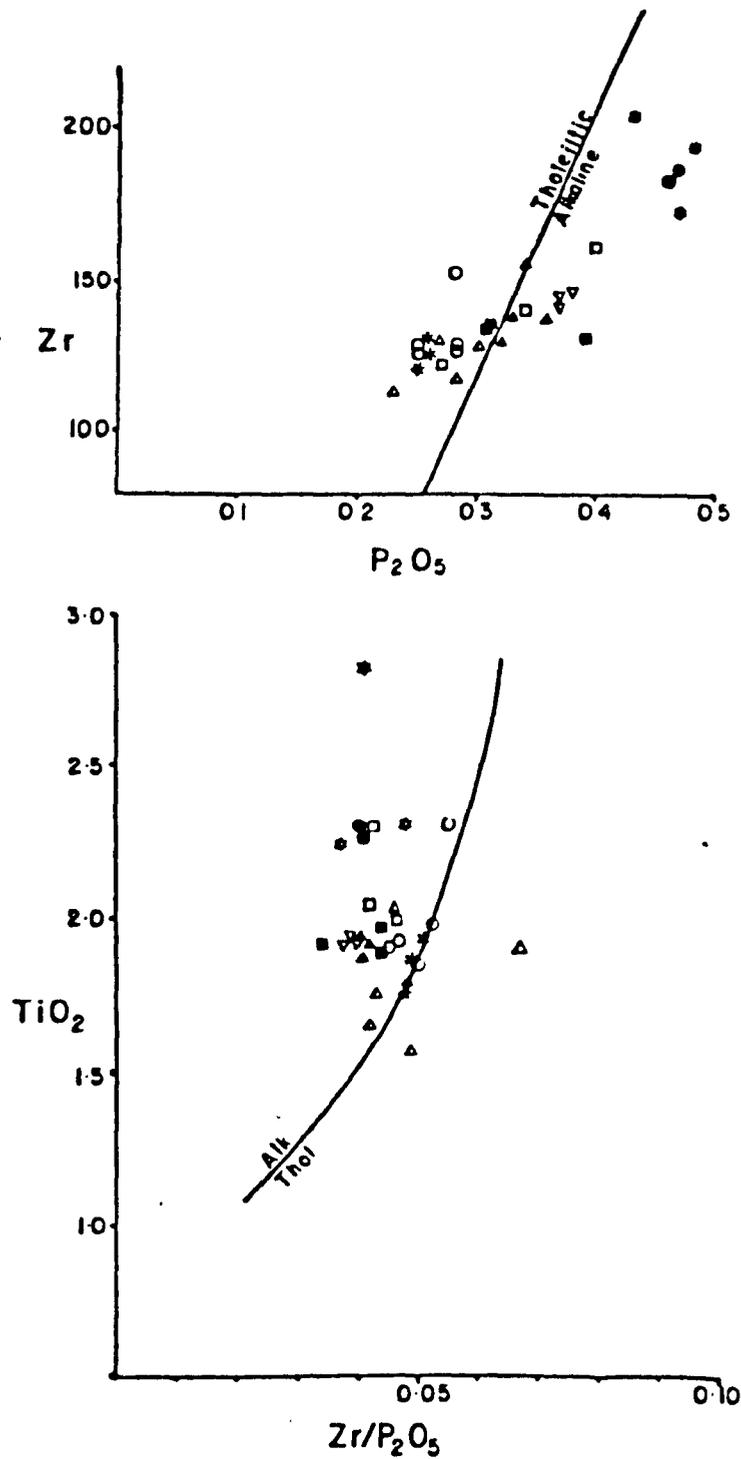


FIG. 8.1 Zr VERSUS P₂O₅ and TiO₂ VERSUS Zr/P₂O₅ DISCRIMINANT
MAGMA TYPE PLOTS FOR THE SOUTH PENNINE BASALTS

(SYMBOLS AS IN FIG. 7.6)

Derbyshire basalts are transitional in nature. On a plot of TiO_2 v. $\text{Zr}/\text{P}_2\text{O}_5$ the majority of analyses plot close to the dividing line but within the alkaline field. On a plot of Zr v. P_2O_5 the basalts fall on a well defined trend with the stratigraphically oldest at the tholeiitic end of this trend and the youngest falling in the alkaline field. Unfortunately, stable trace element data is not available for the nepheline-normative dolerites.

There is concordance between classification and magmatic affinities based on petrography, pyroxene compositions, adjusted norms and immobile trace element data. The Derbyshire basalts are of transitional type, intermediate between alkaline-olivine and tholeiitic basalts in all respects. Previous suggestions that two contrasting magmas were simultaneously available (Cheshire and Bell, 1978) can be discarded. The 'quartz-normative' nature of previously available analyses was, it is suggested, due to the inappropriate use of normative calculations or the selection of altered material.

CHAPTER NINE



Chapter Nine

Geochemistry, Mineralogy and Origin of Wall-Rock Alteration in Basalts

9:1 Introduction

The basalts of the south Pennine orefield have been regarded as 'unproductive' or 'barren' with respect to economic mineralisation. This is a misleading over-generalisation and a number of examples can be cited of exploitation in Lavas, e.g. Ladywash Mine, Sallet Hole Mine and White Rake Opencast on Tideslow Moor. Historical records also indicate the extraction of galena-rich veins within basalts, e.g. High Rake Mine at Hucklow, and Wakebridge Mine at Crich. A compilation of over forty such occurrences, with brief geological and historical notes, have been reported by Walters and Ineson (1980a - a copy of which is included as Appendix 9).

9:2 Mineralisation and Wall-Rock Alteration in Basalts

Mineralisation in the basalts contrasts strongly with carbonate hosted veins. 'Squinting' or vein refraction, differences in mineral assemblages and the occurrence of swarms of interconnecting veinlets rather than a single well-defined fissure, have been noted by Walters and Ineson (op. cit.). Veinlet swarms are associated with broadly symmetrical zones of wall-rock alteration involving bleaching, argillisation, calcitisation, etc.

The clear spatial relationships of alteration to mineralisation indicate a hydrothermal origin. It is envisaged that the veinlets were 'sealed' during the early stages of a hydrothermal episode and remained 'impervious' to subsequent influxes, with the resultant clay-rich alteration aureoles inhibiting further propagation of open fractures. This impermeability and the absence of interconnecting vugs from the

'sealed' veinlets also inhibits the infiltration of groundwaters through these zones.

9:3 Selection of Sampling Localities and Presentation of Geochemical Data

The majority of the wall-rock alteration aureoles selected for analysis were selected from borehole or underground localities in an attempt to minimise the possible effects of weathering. Pre-hydrothermal, deuteric, alterations were avoided by selecting alteration aureoles developed in non-vesicular, coarse basalts or dolerites. Six localities were chosen for detailed geochemical, mineralogical and isotopic investigations, four representing mineralisation within Lavas and two within Sills.

Some seventy samples were analysed by A.A. Spectrophotometry and wet-chemical methods for TiO_2 , CaO , FeO , Fe_2O_3 , MgO , Na_2O , K_2O , H_2O^+ , Cu , Ni and Zn (Appendix 1a). In addition, a small number of samples were analysed for a wider range of elements by XRF (Appendix 1a and b). Mineralogical variations were investigated by XRD, transmitted and reflected light techniques.

The presentation and interpretation of the geochemical variations is complicated by a number of factors. Fine-scale calcite and silica veining is a dominant feature of the alteration aureoles culminating in the central veinlet swarms and in addition calcite amygdales are common at certain localities. Selection of unveined material during sample preparation was not feasible and any attempt may have introduced sampling bias. The effect of veining is a 'dilution' in the analysed sample of constituents associated with the altered wall-rock. This has been compensated for by recalculating the analytical element concentrations relative to an 'immobile' constituent. The immobile nature of TiO_2 , P_2O_5 , Zr and to a lesser degree Y , Cr and V were outlined in the previous chapter. Geochemical variation diagrams (Figures 9.1 to 9.4) represent

TABLE 9.1: Comparisons of Actual and Recalculated Immobile Element Concentrations Relative to Constant TiO₂

a. Potluck Sill - TiO ₂ Correction Factor = 1.32		
	Analysis 42 (Altered)	Analysis 41 (Unaltered)
Cr (ppm)	387	379
V	205	196
Y	25	25
Zr	116	130
P ₂ O ₅ %	0.28	0.30
b. Conksbury Bridge Lava - TiO ₂ Correction Factor = 1.10		
	Analysis 3 (Altered)	Analysis 4 (Unaltered)
V	205	208
Y	33	32
Zr	174	167

concentrations normalised to a constant $\text{TiO}_2\%$. Altered samples with minimal veining exhibit minor TiO_2 variations, and implies equal volume replacement in accord with the preservation of relict textures in altered basalts as well as the minor variations in Specific Gravity noted by Ixer (1972) between altered and unaltered basalts.

The validity of this method can be assessed by comparing the recalculated ' $\text{TiO}_2\%$ equivalent' concentrations of other immobile elements in the altered basalts with their unaltered counterparts. Table 9.1 indicates acceptable levels of concordance, within normal inter-sample variations, between recalculated and actual concentrations of immobile elements from altered and unaltered samples of the Conksbury Bridge Lava and the Potluck Sill.

Although calcite is the dominant 'diluting' phase, veinlet occurrences of sulphides are also noted. Correlation of high Fe_2O_3 with Cu, Ni and Zn and large ' TiO_2 correction' factors may indicate the presence of vein sulphides. In these instances the location of sulphide phases must be petrographically determined.

9.4 Locality and Sampling Details

a. Hallicar Wood Adit, Via Gellia (4)*

Recent excavations have allowed access to a section in the Matlock Lower Lava (Walters and Ineson 1980b - Appendix 10). The coarse, non-vesicular basalt is traversed by a number of vertical and sub-vertical zones of bleached and altered material. The bleached zones, up to 2 m in thickness, are associated with swarms of interconnecting calcite veinlets with pyrite and traces of baryte. Thicker 'central feeder' veins may be present within the veinlet swarms and a minimum displacement

* Numbers refer to the list in Walters and Ineson (1980a)

of 0.4 m has been recorded across one central feeder (Walters and Ineson, op.cit.).

Sampling was undertaken adjacent to a 1.5 m wide bleached zone some 31 m from the excavated winze. The abrupt visual termination of bleaching across a thick calcite veinlet was utilised as the datum for a horizontal sampling traverse in non-vesicular lava. Sampling from the interval +0.1 to +2.5 m from datum was dictated by the availability of material. Channel samples 10 cm wide were collected in the bleached zone to a limit of -0.5 m.

b. Conksbury East No.5 Borehole (29)

No. 5 borehole intersected Long Rake in the Conksbury Bridge Lava. Long Rake is a plexus of mineralised faults with evidence of polyphase mineralisation (Butcher, 1976) and this is evident in the nature and disposition of veining and alteration in the Lava. Two zones of intense bleaching occur at 56.5 to 57.4 m and 60.5 to 61.8 m and numerous, ramifying veinlets are noted between 56.5 m and 62 m (Plate 3.4-B). Within this interval veinlet concentrations around 57.3 m and 60.5 m exhibit close but not perfect symmetrical relationships with the zones of maximum bleaching. Fault gouge and strong shearing is evident in the altered zone around 61.5 m indicating polyphase movements (Plate 3.4-B4). Fault displacement along this shear zone accounts for the apparent thickness of 35 m for the Lava intersected in the No. 5 Borehole compared with the 25 m noted from boreholes located away from the fault belt.

Samples were collected as split half-cores 5 cm in length, the position of which are indicated in Appendix 7.

c. Maury Adit, Millers Dale (41)

The exploitation of Maury Rake in the Millers Dale Upper Lava at Maury Mine was noted by Farey (1811). Some 50 m of adit workings are

currently accessible exposing the continuation of the Rake in the lava. Mineralisation is present as a concentration of thin, interconnecting veinlets associated with alteration and bleaching in a zone up to 1.2 m wide. An abrupt transition from bleached and veined lava to iron-stained, non-vesicular lava with only scattered veinlets is noted. A gradation into unaltered wall-rock is not present. Dump material includes abundant blocks of bleached and altered basalt hosting sulphide mineralisation. Thin interconnecting veinlets of sphalerite (Plate 3.5-B) are dominant, with subordinate galena and bravoitic pyrite and secondary smithsonite, cerussite, goethite and pyromorphite. Sulphide mineralisation is not conspicuous in the section of veining currently exposed in the adit.

Sampling was undertaken 20 m from the entrance across a 0.6 m wide bleached and veined zone. Channel samples were collected in continuous 10 cm intervals across the width of the adit, including the full width of bleaching. An abrupt transition from bleached and veined lava to iron-stained lava was noted at 0.7 m in the sampling traverse.

d. Mogshaw No. 3 Borehole, Nr. Sheldon (35)

No. 3 Borehole intersected the probable continuation of Mogshaw Rake in the Shacklow Wood Lava. Alteration and bleaching are present between 102 and 105 m, with veinlet concentrations noted from 102.5 m to 103 m and at 105 m. The locality is unusual in the occurrence of small open vugs in the thicker veinlets, with green euhedral fluorite overgrowths on dog-tooth calcite. Disseminated marcasite and pyrite are abundant, constituting up to 50% of the altered basalt associated with the veining at 105 m (Plate 3.4-A). Alteration is developed at the contact of the two flow units resulting in a concentration of calcite amygdales within the zone of bleaching.

Samples were collected as split half cores 10 cm in length, the location of which is indicated in Appendix 7.

e. Black Hillock Mine, Tideslow Moor (50)

The continuation of White Rake in the Potluck Sill and its exploitation for galena have been documented by Walters (1980 - Appendix 8). The mine workings are no longer accessible and samples of bleached and veined dolerite together with unaltered dolerite were collected from the dumps.

f. Great Rake, West of Low Mine (8)

Recent fluorspar opencast operations have exploited the western end of Great Rake from a shallow opencast in the Bonsall Sill. A sample of altered dolerite adjacent to mineralisation was collected from the opencast.

9.5 Geochemistry and Mineralogy of Hydrothermal Alteration

a. Hallicar Wood Adit

The wall-rock at +2.5 m from datum is a coarse, non-vesicular basalt. In thin-section, smectite pseudomorphs of olivine exhibit incipient secondary replacement by calcite and silica. Primary clinopyroxene is replaced by spherulitic smectite with anatase concentrations at relict grain boundaries (Plate 3.3c). Plagioclase is unaffected apart from the occurrence of thin carbonate veinlets along cleavage directions. Interstitial turbid glass partly altered to smectites is also present.

In comparison with analyses of unaltered, olivine-phyric samples of the Matlock Lower Lava from the nearby Bonsall Basalt Quarry (Analyses 17 to 19), minimal variations in SiO_2 , TiO_2 , Al_2O_3 , K_2O and Na_2O are noted. Reduction of MgO and CaO with an increase in CO_2 correspond with the smectite and secondary carbonate alteration of primary ferromagnesian minerals. Trace element variations are likewise minimal in

extent the reduction of Ba is probably a result of incipient alteration of plagioclase.

Calcitisation increases towards the zone of bleaching but interstitial smectite and primary glass remain unaffected up to +0.4m. Abundant fine-grained haematite 'dust' is concentrated at grain boundaries particularly in calcitised olivine pseudomorphs. Primary titanomagnetites and ilmenite exhibit patchy exsolution textures, more pronounced in the titanomagnetites (Plate 3.3). At a distance of +0.8 m all primary Fe-Ti oxides are pseudomorphed, titanomagnetites by orientated haematite laths and anatase and ilmenites by aggregates of anatase.

Veinlets at +0.8 m are associated with a local increase in calcitisation and chalcopryrite disseminations with minor pyrite, bornite and chalcocite. Increasing carbonate replacement of smectites and plagioclase between +0.8 to +0.3 m is noted. An abrupt petrographic change occurs around +0.2 m involving calcitisation of relict smectite pseudomorphs, albitisation and calcitisation of plagioclase and irregular areas of replacive pyrite. The onset of bleaching at 0.0 m coincides with the transition from disseminated haematite to pyrite.

Veining and sulphide impregnations increase in the interval -0.2 to -0.5 m associated with intense bleaching and clay-rich alteration which rendered the samples unsuitable for petrographic preparation. XRD analyses (Table 9.2) indicate that mixed layer illite-smectites with a high proportion of smectite constitute the dominant clay phase with minor kaolinite.

Geochemical trends correspond with observed mineralogical variations (Figure 9.1). Minimal major-element variations occur between +2.5 and +0.9 m. Veining at +0.8 m is represented by the localised reductions of FeO and MgO, and enrichment of K_2O . Between +0.8 m and +0.2 m Fe_2O_3 and Na_2O are reduced while H_2O^+ and K_2O are enriched. The abrupt petro-

Fig 9.1

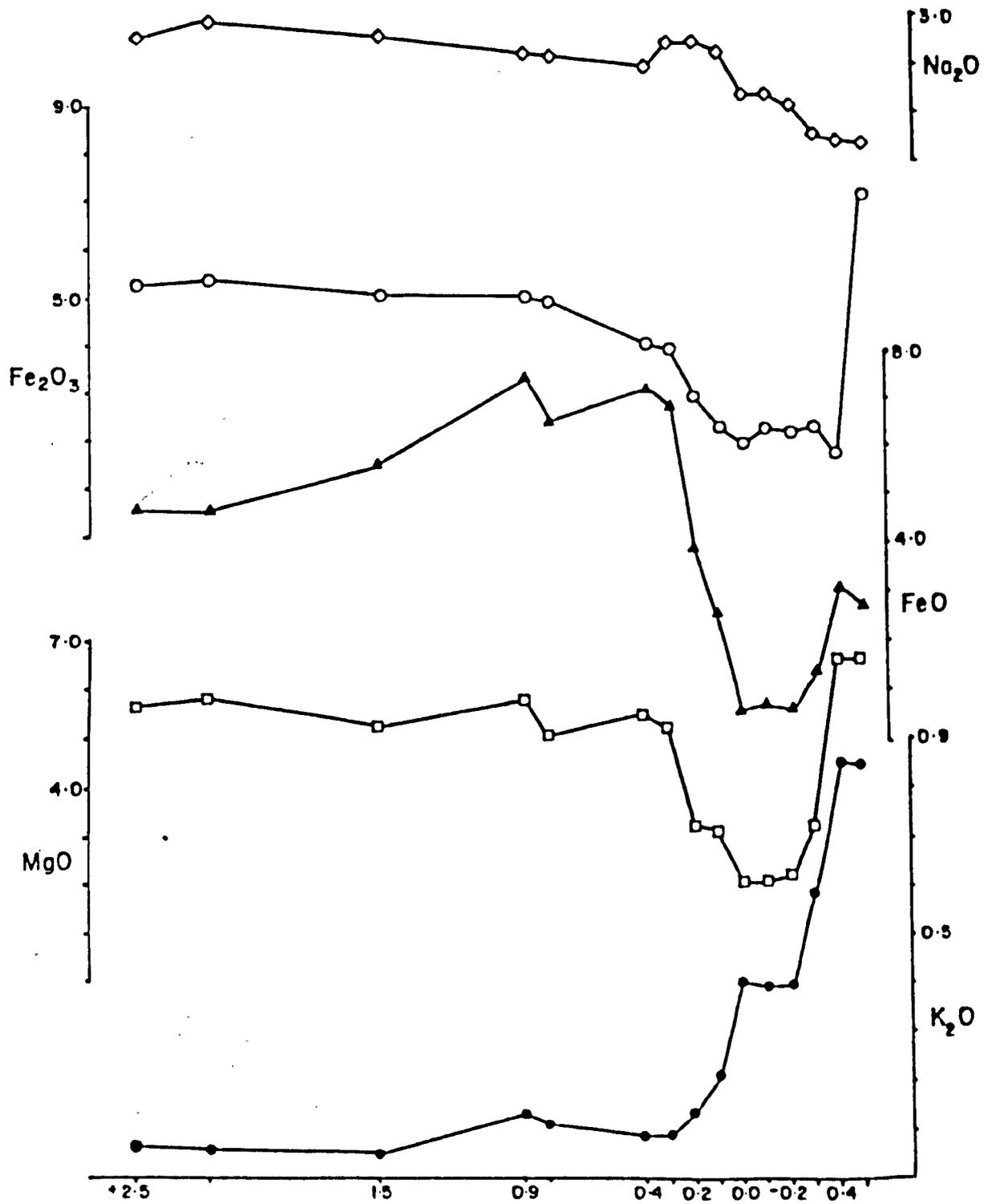


FIG. 9.1 GEOCHEMICAL VARIATIONS- HALLICAR WOOD ADIT

Fig 9.1

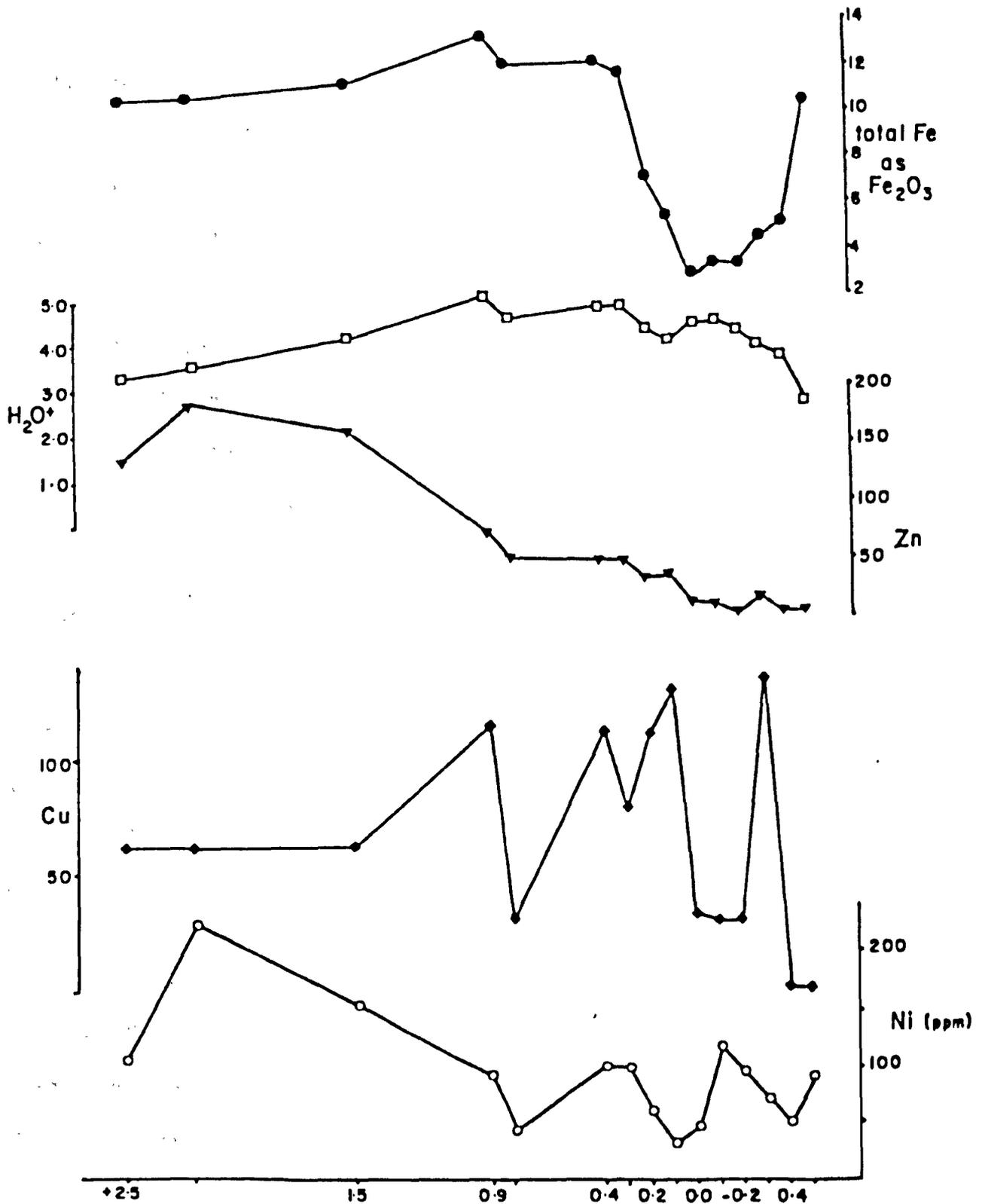


FIG. 9.1 GEOCHEMICAL VARIATIONS -HALLICAR WOOD ADIT (CONT.)

graphic variations at +0.2 m is likewise reflected in the major-element trends, MgO, FeO and Fe₂O₃ are depleted and K₂O increased. Na₂O is enhanced between +0.3 m to +0.1 m related to the dominance of albite but with increasing proximity to mineralisation argillic alteration of albite results in a reduction of Na₂O.

Metasomatic calcitisation and albitisation are the dominant alterations in the interval +0.3 to -0.2 m. Within the bleached zone clay-rich alteration with calcite veining increases. Enhancement of illite-smectite clay and pyrite concentrations result in increased MgO, FeO, Fe₂O₃ and K₂O levels.

The behaviour of Cu and Ni are more erratic. Reduction of Cu associated with minor veining at +0.8 m is accompanied by a symmetric pattern of enrichment adjacent to the veining related to the occurrence of disseminated chalcopyrite. In proximity to the zone of bleaching Cu is depleted with localised enrichments representing veinlet occurrences of sulphides. The variations of Ni are not readily attributable to sulphide occurrences. There are indications of a broad enrichment pattern around +2.0 m which is not related to petrographic variations or veining. Zn depletion in the bleached zone exhibits a less erratic profile with a broad pattern of enrichment around +2.0 m, similar to but more pronounced than the variations in Ni.

b. Conksbury Edge No. 5 Borehole

Alteration occurs in a sequence of fine-grained, non-vesicular to poorly vesicular olivine-phyric basalt. The basalt is unaltered at 55.7 m and contains granular augite, unaltered plagioclase, interstitial green smectite and smectite pseudomorphs after olivine (Plate 1.4 f). An abrupt transition is noted at 56 m which involves the selective calcitisation of olivine pseudomorphs, albitisation and smectite-carbonate

replacement of clinopyroxene. Smectite phases persist up to 56.5 m, adjacent to a zone of intense bleaching and veining at 57 m (Plate 3.4-B2). Within this zone, smectite, and to a lesser degree albite, are replaced by silica-carbonate aggregates preserving relict textures (Plate 3.2-a and b). Minor amounts of pyrite occur in veinlets and as disseminations restricted to calcitised interstitial areas.

Between 57.5 and 59.5 m the lava exhibits pale bleaching with scattered veinlets (Plate 3.4-B3). Interstitial smectite is unaffected but pyroxene is pseudomorphed by smectite, feldspar is albitised and secondary carbonate replacements of olivine pseudomorphs occur. Selvages of a bright green pleochroic clay are associated with veining. The optical properties and mode of occurrence are unlike typical smectites and XRD analyses indicates a sharp peak at 10.0\AA which is unaffected by glycolation or heating to 450°C indicative of an illitic clay.

The core between 60.5 and 61.8 m is bleached, veined and sheared (Plate 3.4-B4). Calcitisation of smectite, partial siliceous-carbonate replacements of albite and calcite veining are the main features. The clay component is dominated by kaolinite (Table 9.2). Shearing and brecciation accompanied by fault gouge are present between 61.0 to 61.8 m and within the bleached zone intense veining occurs at 60.6 m.

Between 62.0 and 64.5 m the lava exhibits pale bleaching with scattered pyrite-bearing calcite veinlets. Feldspar is albitised but interstitial smectite is not affected by strong calcitisation. Increasing vesicularity is encountered in the samples from 64 m indicating proximity to the lower vesicular margin of the flow unit.

Geochemical trends correspond with observed petrographic variations (Figure 9.2). Reduction of MgO , FeO , Fe_2O_3 and enrichment of K_2O and H_2O^+ adjacent to the bleached zone at 57 m correspond with alteration of pyroxene and secondary carbonate replacement of olivine pseudomorphs.

Fig 9.2

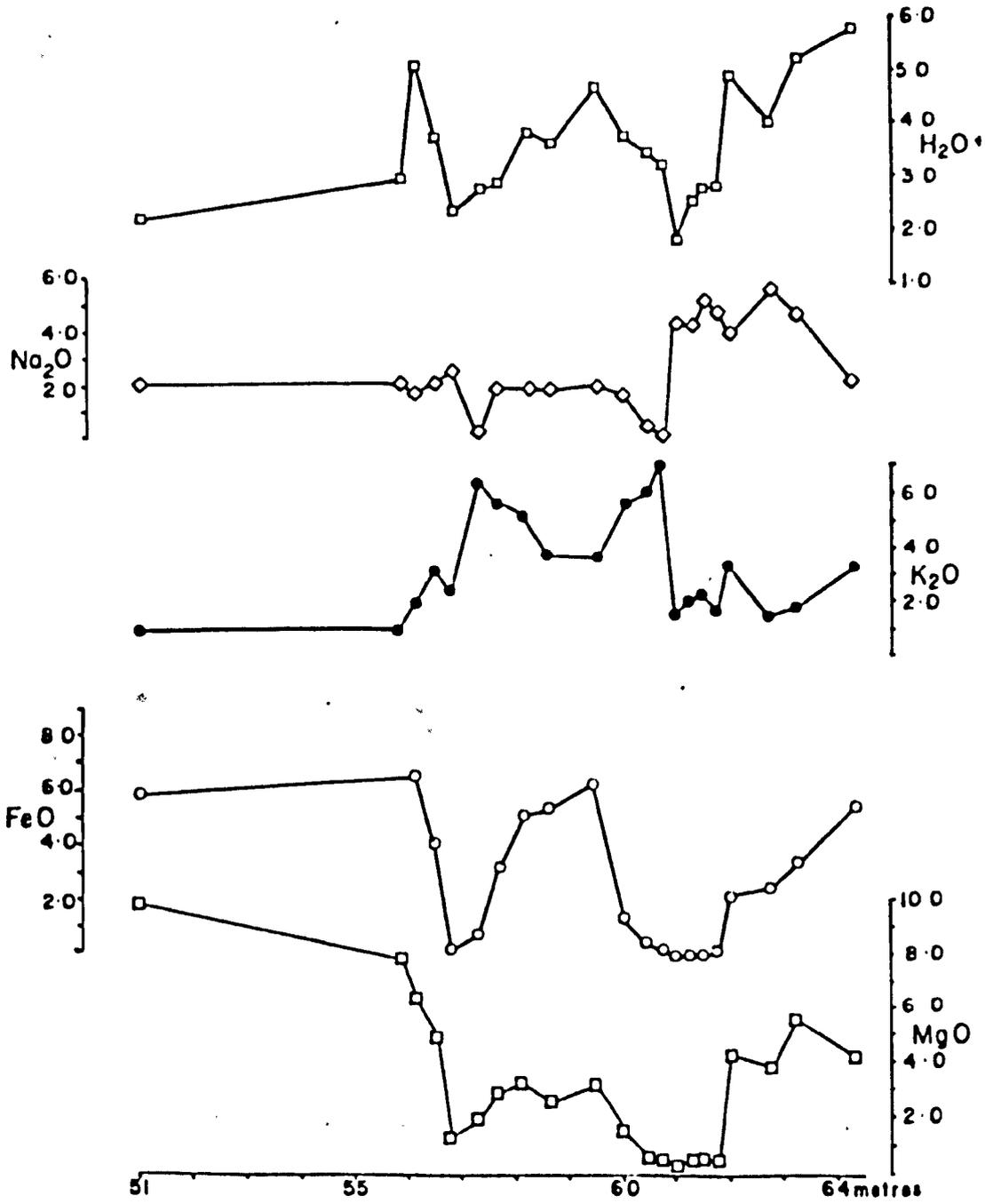


FIG. 9.2 GEOCHEMICAL VARIATIONS -CONKSURRY No.5 BOREHOLE

Fig 9.2

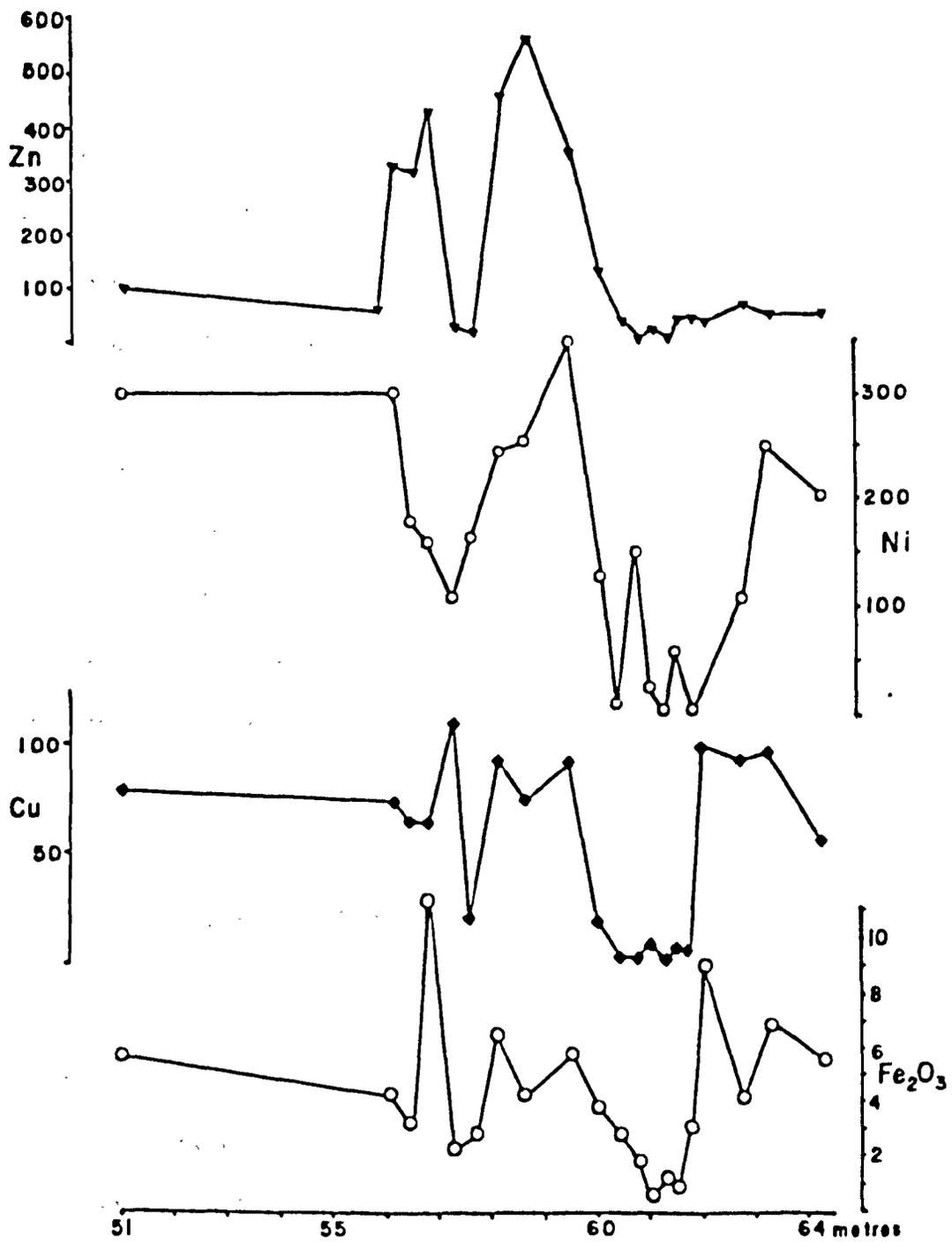


FIG.9.2 GEOCHEMICAL VARIATIONS - CONKSBUY No. 5 BOREHOLE (CONT.)

Within the bleached zone further depletion of MgO, FeO and enrichment of K_2O occur. Pyrite concentrations result in enhanced Fe_2O_3 levels. Na_2O is unaffected adjacent to the bleached zone due to its incorporation in albite, while within the zone secondary albite replacement results in Na_2O depletion.

The partly altered nature of the basalt between 57.5 and 59.5 m is indicated by the reduction of MgO and enrichment of K_2O and H_2O^+ in comparison with background concentrations. Strong enrichment of K_2O correlates with the occurrence of illite selvages associated with veining.

Geochemical trends associated with the bleached zone between 60.5 and 61.8 m are similar to those noted around 57 m. The position of maximum Na_2O reduction and K_2O enrichment corresponds with the concentration of veinlets noted at 60.5 m.

Cu, Ni and Zn are depleted in the zones of maximum alteration. Symmetrical Zn enrichment patterns involving a five-fold increase relative to background concentrations are associated with the alteration at 57.3 m and a similar, but less pronounced, enrichment trend for Cu is also noted.

c. Maury Adit

The wall-rock at 1.6 m is an iron stained, calcitised, non-vesicular basalt. Albitisation, haematite/anatase pseudomorphs after primary skeletal Fe-Ti oxides, calcitised interstitial areas, disseminated anatase and haematite partly altered to goethite and carbonate pseudomorphs after olivine are noted between 1.6 and 1.3 m with a minor concentration of veinlets at 1.3 m. In the interval 1.3 to 0.8 m iron staining is present, calcite pseudomorphs exhibit secondary replacement by silica and albite is 'clouded' with secondary clay aggregates. An

abrupt transition occurs at 0.7 m resulting in intense bleaching and veining of the lava between 0.7 and 0.1 m with a concentration of pyrite bearing calcite-silica veinlets around 0.5 m.

X.R.D. analysis indicates that calcite and albite are the dominant phases between 1.6 and 1.3 m. Secondary replacement of albite resulting in increasing concentrations of smectite with minor illite-smectite and kaolinite are noted between 1.2 and 0.8 m. The bleached and veined zone at 0.7 to 0.5 m correlates with the dominance of kaolinite. Between 0.5 and 0.1 m subordinate illite-smectite is noted in addition to kaolinite.

Geochemical variations (Fig. 9.3) reflect the absence of a transition into unaltered wall-rock with reduction of FeO and enrichment of K_2O noted in all the analysed material. The maximum development of calcitisation and albitisation (1.6 to 1.3 m) corresponds with the depletion of FeO, MgO and H_2O^+ and enrichment of Na_2O and K_2O . The veinlet occurrence at 1.3 m is represented by localised enrichment of MgO, FeO, K_2O , H_2O^+ and depletion of Na_2O . Similar trends are noted adjacent to the zone of bleaching. Enrichment of MgO, FeO and H_2O^+ reflects the secondary argillisation of albite and interstitial areas, depletion of Na_2O , correlating with the alteration of albite. Despite the red colouration of the lava, pigmentation is the result of finely dispersed Fe_2O_3 rather than a strong enrichment. Within the bleached zone the disseminated goethite is not present and Fe_2O_3 is depleted. The predominance of kaolinite results in the depletion of MgO, FeO and H_2O^+ . Maximum K_2O enrichment corresponds with maximum veining at 0.5 m.

Variations in Ni and Cu concentrations between 1.6 and 0.8 m correlate with Fe_2O_3 and imply an association of nickeliferous pyrite or bravoite and chalcopyrite with pyrite. Ni and Cu are depleted within

Fig 9.3

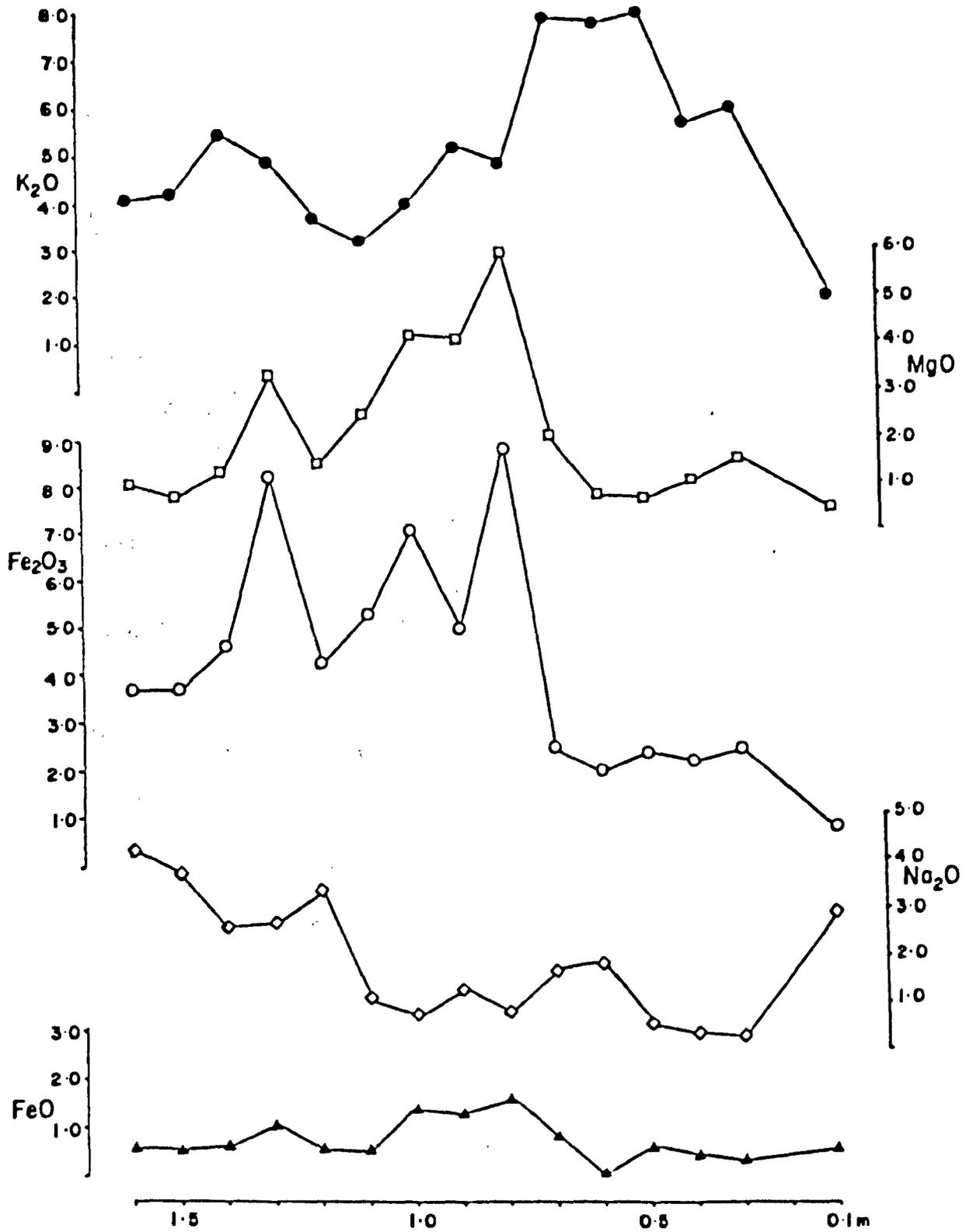


FIG. 9.3 GEOCHEMICAL VARIATIONS - MAURY ADIT

Fig 9.3

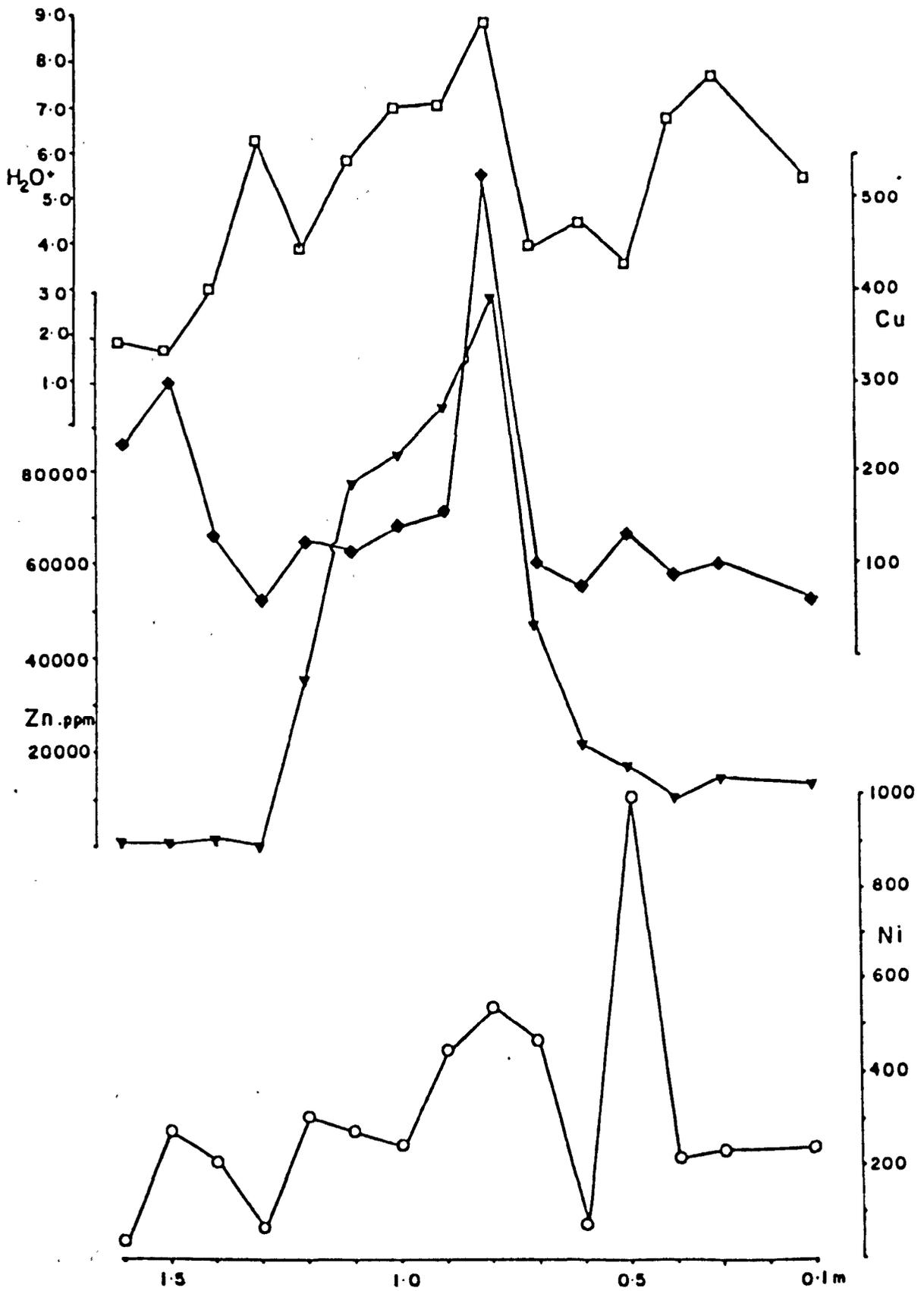


FIG 9.3 GEOCHEMICAL VARIATIONS - MAURY ADIT (CONT.)

the bleached zone, the localised enrichment of Ni at 0.4 m related to the occurrence of bravoite. Adjacent to this zone Ni exhibits a broad enrichment profile. Enhancement of Zn is noted in all the analysed material, with maximum values ($> 120,000$ ppm) occurring between 1.2 and 0.8 m. Sphalerite was not detected in these samples, however a concentration of a low reflectivity, octahedral phase resembling spinels and occurring as euhedral inclusions in pseudomorphed olivines associated with areas of silicification is noted (Plate 3.2 c to f). Although similar to the Cr-spinels occurring as primary inclusions in olivines (Chapter 4), the abundance and disposition of the spinel phases in the altered basalt is atypical of such primary inclusions. The possibility remains of a hydrothermal, Zn-rich spinel phase. In this context Cu and Ni-rich spinels as minor components of the Mississippi Valley Type orebodies of south-east Missouri were recorded by Craig and Carpenter (1977).

d. Mogshaw No.3 Borehole

Alteration and bleaching occurs between 102.5 m and 104.5 m. The 'unaltered' wall-rock at 102 m is an iron-stained, albitised vesicular lava with calcite amygdales (Plate 3.4-A2). Interstitial smectite and smectite pseudomorphs after olivine exhibit minimal secondary replacements and this is reflected in the minor variations noted for MgO, FeO and Na₂O, in comparison to background concentrations (Figure 9.4). Enrichment of K₂O is the only indication of proximity to mineralisation.

Veining in the altered section of core is not visually as intense as on the previous examples. A concentration of thick veinlets is noted around 103 m, some containing open vugs with overgrowths of fluorite on calcite and marcasite, minor veining at 104.9 m is associated with disseminations of marcasite. Areas of maximum veining correspond

with bleaching, calcitisation of interstitial areas, and secondary siliceous replacements. Adjacent to the areas of intense bleaching and veining relict interstitial smectites are noted in addition to albite and calcite replacements.

Marcasite is abundant throughout the altered basalt (Plate 3.1). Anhedral, replacive marcasite is associated with calcitised interstitial areas whilst coarse, euhedral marcasite with pyrite overgrowths occurs in areas of coarse carbonate replacements and veins. A degree of poly-phase movement associated with veining at 104.9 m is indicated by the brecciated textures in euhedral marcasite (Plate 3.1-e and f). An abrupt visual transition from bleached to dark, non-vesicular lava is noted at 105.1 m (Plate 3.4 - A4). Smectite is the dominant clay phase in the altered and partly altered lava (Table 9.2). Localised enrichment of kaolinite corresponds with the veining between 103 and 104.5 m.

Geochemical trends (Figure 9.4) correlate with petrographic variations and the occurrence of veining. Maximum MgO and FeO reduction corresponds with the calcite-fluorite veining at 103.2 m, however the relative decrease is less than in previous examples. The behaviour of Na₂O is also at variance with previously noted trends. Maximum enrichment corresponds with the area of maximum vesicularity in the core and suggests a probable deuteric relationship with a partial hydrothermal overprint. Enhanced Fe₂O₃ concentrations reflect the abundance of marcasite. The visual transition at 105.1 m does not correspond with marked variations in Na₂O, K₂O, FeO or MgO.

Zn, Ni and Co exhibit depletion associated with veining at 103.2 m with limited enrichment aureoles. The minor veining at 105 m is associated with the reduction of Cu, minimal Zn variations and enrichment of Ni probably related to nickeliferous marcasite.

Fig 9.4

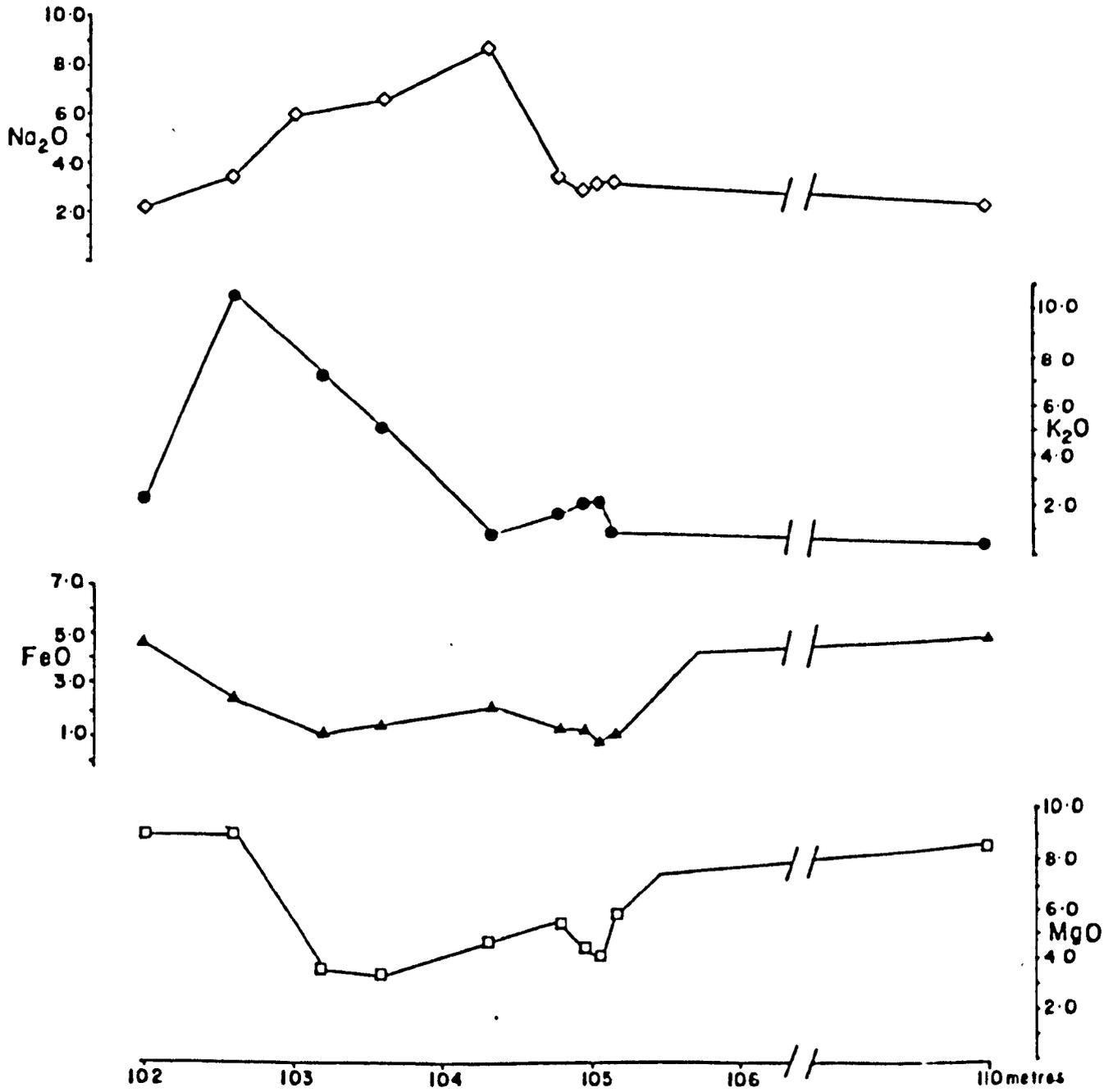


FIG. 9.4 GEOCHEMICAL VARIATIONS - MOGSHAW No.3 BOREHOLE

Fig 9.4

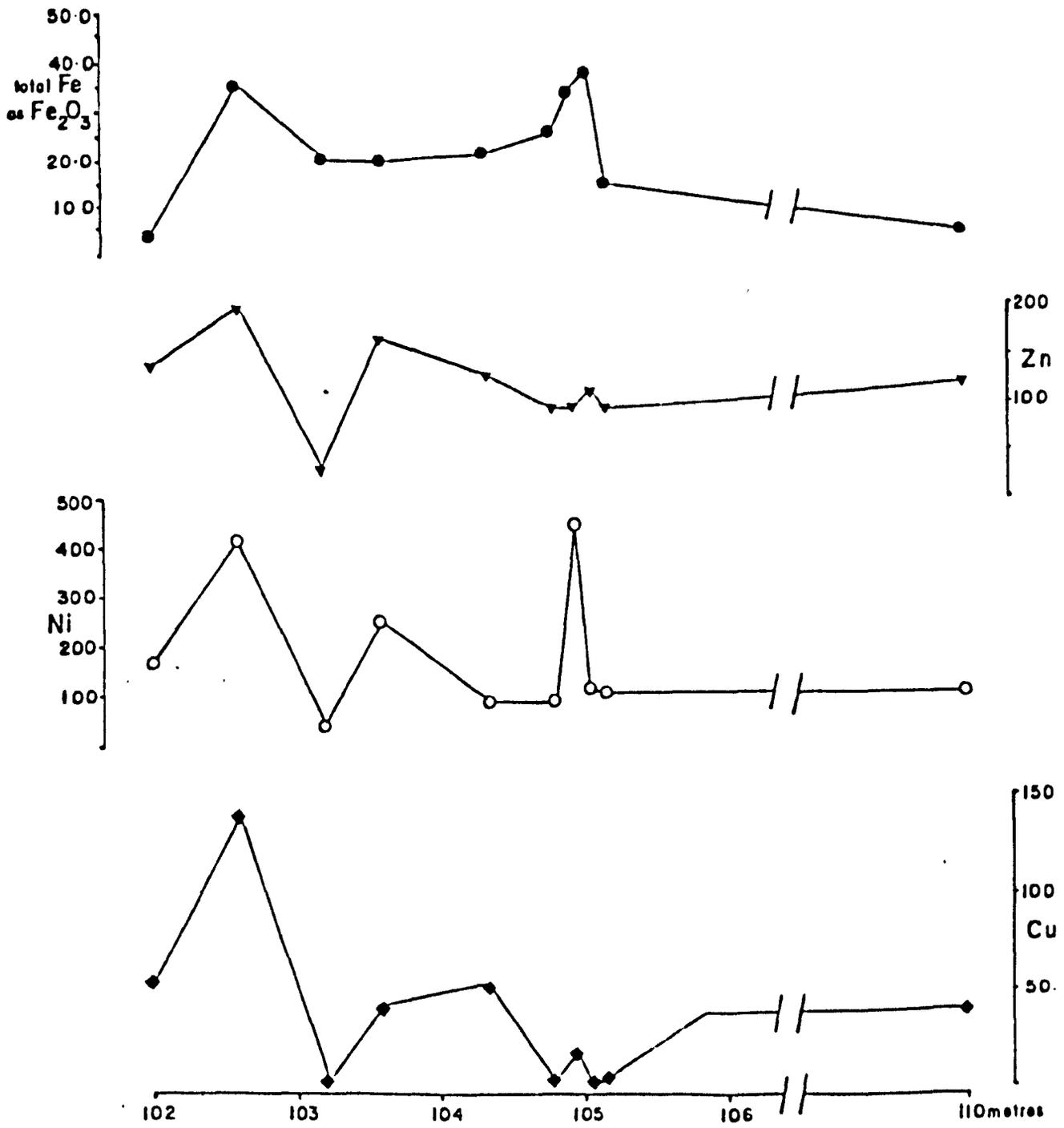


FIG. 9.4 GEOCHEMICAL VARIATIONS - MOGSHAW No.3 BOREHOLE (CONT.)

Table 9.2

TABLE 9.2: Clay Mineralogy of Hydrothermally Altered Basalts

Analysis Number	Location	Smectite	Illite	Kaolinite	Mixed-Layer Illite-Smectites
Hallicar Wood Adit					
108	+ 0.1 m	minor clay component		t	t ^x
109	0.0	-	-	m ^x	m - 11.91Å*
111	- 0.2	-	-	m	m - 11.33Å
112	- 0.3	-	-	m	m - very broad
113	- 0.4	-	-	t	m - 10.92Å
114	- 0.5	-	-	t	m - 11.71Å
Maury Adit					
116	1.6 m	minor clay component		t	t
118	1.4	minor clay component		-	-
119	1.3	minor clay component		-	t
120	1.2	-	-	-	w - illite rich
121	1.1	w	-	w	w - illite rich
122	1.0	s	-	w	w - illite rich
123	0.9	m	-	w	-
124	0.8	m	-	m	-
125	0.7	-	-	m	-
126	0.6	-	-	m	-
127	0.5	-	-	m	m - 10.4Å
129	0.4	-	-	vs	m - 10.78Å
130	0.3	-	-	s to m	m - 10.9Å
134	0.2	-	-	vs	w to m - 10.5Å
132	0.1	-	-	s	t

Table 9.2

TABLE 9.2 (Cont.): Clay Mineralogy of Hydrothermally Altered Basalts

Analysis Number	Location	Smectite	Illite	Kaolinite	Mixed-Layer Illite-Smectite
Conksbury No.5 Borehole					
138	56.5 m	m	m	m	t
139	56.8	m	-	-	-
140	57.3	-	m	t	slightly asymmetric illite peak
141	57.7	m	m to s	m	-
142	58.1	m to w	s	m	-
143	58.7	m to w	s	m	-
144	59.5	w	w	m	-
146	60.4	-	t	s	m - 10.3Å
147	60.7	-	-	s	w - illite rich
148	61.0	-	-	m	-
149	61.3	-	-	m	-
150	61.5	-	-	m	t
151	61.7	-	-	s	t
152	62.0	w	-	w	w - 10.4Å
153	62.7	s	-	s	t
Mogshaw No.3 Borehole					
156	102.0 m	s	-	s	-
157	102.6	m	minor clay component		-
158	103.2	minor clay component		t	-
160	104.3	m	-	m	t
161	104.8	s	-	-	-
163	105.1	m	-	-	t
164	105.2	m	-	-	t

x t - trace, w - weak, m - medium, s - strong, vs - very strong.

This gives an indication of the strength of the major peaks and enables broad comparisons of relative concentrations of individual phases between samples.

* Mixed-layer illite-smectite peaks are broad, where possible an estimation of the central peak position is given as an indication of the ratio of mixed-layering.

e. Black Hillock Mine

The analysed material exhibits calcitisation and albitisation with the preservation of relict textures (Plate 3.5-A). Veining and sulphide impregnation were not dominant features and kaolinite constituted the minor clay phase.

Geochemical variations (Analyses 42 and 173) indicate enrichment of CaO, CO₂ and K₂O with depletion of FeO, MgO and Fe₂O₃ relative to analyses of unaltered dolerite (Analyses 40 and 41). Minor reduction of Al₂O₃ and enrichment of SiO₂ are also noted.

Depletion of FeO, MgO, Fe₂O₃ and enrichment of K₂O is more pronounced in sample 173 indicating a more advanced alteration in comparison with sample 42. Trace and minor element trends exhibit reduction in Ba, Co, Sr and Zn with minimal variation in Pb, Rb, Y, Zr, V, Cr, TiO₂ and P₂O₅ (see Table 9.1). Minimal Zn reduction is noted in sample 173, although highly altered and probably reflects a Zn enrichment aureole.

f. Great Rake, West of Low Mine

The material exhibits calcitisation and albitisation with minor kaolinite and is similar to samples from Black Hillock Mine. Geochemical variations (Analysis 175) in relation to the unaltered Bonsall Sill (Ixer, 1972) exhibit enrichment of CaO, CO₂, H₂O⁺ and K₂O with reduction of Fe₂O₃, FeO, MgO, Na₂O, Cu, Ni and Zn.

9.6 Previous Geochemical Research

The geochemical variations resulting from the hydrothermal alteration of basalts in the south Pennines were briefly noted by Ixer (1972), who presented six major and eight trace element analyses for random samples of the Matlock Upper Lava. Overall trends reported are enrichment of K₂O, Fe₂O₃, CO₂ and reduction of MgO, Na₂O, FeO, MnO

with minor variations of SiO_2 , Al_2O_3 , total Fe and CaO. Considering analyses of the Bonsall Sill to be representative of the pre-alteration geochemistry of the Matlock Upper Lava involves a 'gross approximation' (Ixer, op.cit.). A more realistic comparison with analyses of non-vesicular, unaltered Matlock Lower Lava (Appendix 1) indicate minimal variations of TiO_2 and P_2O_5 with alteration and not enrichment as previously reported.

Failure to compensate for the 'dilution' effect of veining in the highly altered material also resulted in misleading interpretations of trace-element variations. Utilising a ' TiO_2 correction' factor (see Table 9.1) V, Cr and Y concentrations remain constant. Ni and Sr are reduced, Cu concentrations are erratic with an overall trend of depletion with enrichment of Zn and Pb in the most altered material, with Zn enrichment exceeding that of Pb. Samples of the 'Sallet Hole Tuff' in proximity to mineralisation exhibited a similar enrichment of Zn and Pb (Ineson, 1970).

Alteration of the Whin Sill adjacent to Pb-Zn-F-Ca mineralisation in the north Pennine orefield was investigated by Wager (1924) and Ineson (1967, 1968 and 1972). The bleached dolerite is known locally as White Whin and relict texture is preserved by aggregates of carbonates, anatase, albite, potassium-rich clays, quartz and apatite. The clay minerals were identified as illite and kaolinite by Ineson (1968) whilst Smith (1974) recorded illite and illite rich mixed layer illite-smectite with minor kaolinite. Reduction of CaO, MgO, Na_2O , total Fe and enrichment of CO_2 , K_2O and H_2O associated with minor variations in SiO_2 , Al_2O_3 , TiO_2 and P_2O_5 were noted (Ineson, 1967).

Trace-element variations in White Whin adjacent to the mineralised Closehouse Fault (Ineson, 1968) indicated depletion of Cu, Ni, Sr and enrichment of Zn, Rb and Ba with erratic enrichment of Pb in proximity

to mineralisation. Minor reduction of Zr, V and Cr are not substantiated from other localities (Ineson, 1967 and 1972) and in the absence of density/veining corrections these can be regarded as immobile.

More erratic trace-element variations were noted from sampling traverses at Cow Green, Force Burn, Wynch Bridge and Settlingstones Mine (Ineson, 1967 and 1972). At Cow Green Ni and Cu were reduced adjacent to mineralisation whereas Zn was enriched. Similar relationships for Zn and Cu were noted from Force Burn but at Wynch Bridge Zn was depleted adjacent to veining but enriched at greater distances. Erratic relationships between reduction and enrichment of Zn, Cu and Pb were noted from Settlingstones Mine.

The hydrothermal alteration of the White Whin exhibits similarities to the alteration in the south Pennines. Petrographic variations are comparable apart from the dominance of smectites in the south Pennines as opposed to illite in the north Pennines. This is considered to be a reflection of the occurrence of interstitial orthoclase as opposed to smectite in the unaltered Whin Sill (Dunham and Kaye, 1967). Major and trace element trends are also in broad agreement, although variations of CaO, CO₂ and Na₂O in the south Pennines exhibit more complex relationships than previously noted from White Whin alteration. Depletion of Cu, Ni, Sr and minimal variations of TiO₂, P₂O₅, V, Y, Zr and Cr are ubiquitous. Enrichment profiles of Zn and Pb both coincident with veining and displaced are also noted.

9.7 Geochemical Variation and Hydrothermal Zonation

The petrographic and geochemical trends described in section 9.5 relate to a sequence of zoned hydrothermal alteration. There are constant relationships between adjacent zones and the proximity

of mineralisation. Alteration adjacent to a major occurrence of mineralisation in a non-vesicular lava, illustrates four distinct zones:

1. Incipient Alteration

The effects of incipient alteration are comparable with those of advanced deuteric alterations (see section 9.10). Pyroxene is pseudomorphed by smectite and anatase, partial oxidation of Fe-Ti oxides (particularly titanomagnetite) occurs with incipient alteration of plagioclase along cleavages. Interstitial smectite is unaffected but smectite pseudomorphs after olivine exhibit increasing secondary replacement by calcite and silica. Iron is dispersed as fine-grained haematite/goethite. Veining and bleaching are not conspicuous in the initial stages but with increasing alteration pale bleaching is noted.

The main geochemical trends are minor reductions of MgO and FeO related to secondary replacement of smectite. Incipient alteration of plagioclase results in reduction of CaO, Na₂O and Ba with enrichment of CO₂.

2. Calcitisation and Albitisation

An abrupt transition is often noted with incipient alteration. Silica and carbonate replacement of olivine pseudomorphs and interstitial smectite together with albitisation of feldspar are noted. Haematite and anatase pseudomorphs after primary Fe-Ti oxides occur, while smectite, illite-smectites and subordinate kaolinite comprise the small concentration of clay components. With increasing alteration strong bleaching of the lava and depletion of disseminated haematite occur. Albite is 'clouded' with secondary alteration phases and mixed layer illite-smectites and kaolinite increase in concentration.

Geochemical trends involve depletion of MgO, FeO, Fe₂O₃, H₂O⁺ and enrichment of K₂O, CaO and CO₂ with minimal variations of TiO₂, Al₂O₃, SiO₂ and P₂O₅. Na₂O is enriched in initial alteration but with increasing secondary replacement of albite depletion occurs. Trace element variation involves depletion of Ba, Co, Sr, Cu, Ni and Zn with minimal variations of Y, Zr, V and Cr. Metasomatic enrichment aureoles involving Cu, Ni, Zn and Pb are related to the proximity of mineralisation and occur independent of the intensity of alteration.

3. Argillic Alteration

With increasing alteration Zone (2) grades into argillic-rich alteration which can be further subdivided into illite-smectite rich and kaolinite rich types related to the intensity of the adjacent mineralisation.

a. Illite-Smectite-Rich Argillic Alteration: Secondary clay alteration of albite and areas of fine-grained carbonate occur associated with bleaching and veining. Increasing concentrations of smectite and illite-smectite clay phases results in enrichment of FeO, MgO, H₂O⁺ and K₂O, whilst the secondary replacement of albite results in Na₂O depletion. Depletion of Cu, Ni and Zn are noted but localised enrichments related to the presence of disseminated and vein sulphides occur. Kaolinite is present as a minor component, with increasing concentrations grading into kaolinite-rich argillic alteration.

b. Kaolinite-Rich Argillic Alteration: Kaolinite-rich alteration is associated with intense bleaching, veining, silicification accompanied by subordinate calcitisation with minor anatase and relict albite. Depletion of MgO, total Fe, Cu, Ni, Zn, reduction of CaO and H₂O and enrichment of K₂O occur relative to less advanced argillic alteration. Its

development is restricted to zones adjacent to major, mineralised channelways within Lavas and Sills.

The full sequence of zoned alteration is present adjacent to Maury Rake in the Millers Dale Upper Lava. Maximum alteration at Hallicar Wood Adit is of an illite-smectite rich argillic type while the Conksbury No. 5 Borehole and the dump samples from Black Hillock Mine and Great Rake exhibit advanced calcitisation and albitisation. The alteration encountered in the Mogshaw No. 3 Borehole is of an intermediate calcitisation and albitisation type.

Basalt alteration in the south Pennines corresponds with the Propylitic and Intermediate Argillic Alteration types designated by Burnham (1952), Hemley and Jones (1964) and Meyer and Hemley (1967). The argillic (type 3) alteration described previously corresponds with the Intermediate Argillic type with the division into smectite-rich and kaolinite-rich sub-types typical of argillic alteration of silicate wall rocks dominated by plagioclase (Meyer and Hemley, 1967). Calcitisation and albitisation (type 2) alteration corresponds with the advanced Propylitic type while incipient (type 1) alteration can be equated with the weak Propylitic type grading into unaltered wall-rock.

Intermediate Argillic alteration developed in a granodiorite host adjacent to copper mineralisation at Butte Montana was described by Lovering (1950). The geochemistry of alteration exhibits similar trends to variations described from the south Pennines. These include the enrichment of Fe_2O_3 , FeO and H_2O with increasing smectite-rich alteration followed by a reduction in the kaolinite-rich subzone.

9:8 Geochemical Interactions between Hydrothermal Fluids and Wall-Rock Alteration

The importance of hydrogen metasomatism (hydrolysis) in wall-rock alteration of silicate rocks was indicated by Hemley and Jones (1964).

- a. Base cation exchanges other than H^+ metasomatism which occur if the hydrothermal fluid is enriched in components such as K^+ or Na^+ relative to the wall-rock.
- b. Diffusion gradients will vary adjacent to different mineral phases, e.g. the K^+ diffusion gradient between a K-rich hydrothermal fluid and orthoclase would be less than that with pyroxene. The resulting alteration phases may undergo equilibration with the hydrothermal diffusion gradient at different rates.
- c. Progressive geochemical variations related to diffusion gradient equilibration will occur if capable of incorporation into a specific phase. However, when this is replaced by a new phase incapable of accommodating specific elements incorporated into the previous phase pronounced geochemical variations will result, e.g. the transition from smectite to kaolinite.
- d. Variations in the geochemistry of the hydrothermal fluid with time may be a significant factor in episodic mineralisation resulting in geochemical 'overprints'.
- e. Specific mineral phases may remain in a state of disequilibrium with hydrothermal diffusion gradients. In addition to the development of gradients, diffusion is also a function of the activity coefficient and equilibrium constant of the phase involved (Hemley and Jones, 1964). Thus specific phases may remain 'immobile' during alteration, e.g. TiO_2 in the form of anatase.

9.9 Geochemistry of Mississippi Valley Type Hydrothermal Brines and Specific Wall-Rock Interactions

There is a consensus of opinion regarding the origin of the Mississippi Valley Type orebodies, of which the Pennine orefields are an example. Modified connate fluids of basinal origin are driven towards 'basement' highs associated with carbonates. The hydrothermal fluids are low-temperature brines with high salinities of NaCl, KCl and CaCl₂ and low concentrations of soluble metal chloride complexes. Intermixing of reduced sulphur generated and trapped in the carbonate host with the brines is a major factor in ore deposition (Dunham, 1970; Dozy, 1970; Nriagu and Anderson, 1970; Anderson, 1973 and 1975; Dunsmore, 1973; Beales, 1975).

Fluid inclusion studies from the Askrigg Block and south Pennine orefields (Rodgers 1977 and 1978) indicate hydrothermal brines enriched in NaCl, KCl and CaCl₂ with total salinities in the range 18 to 25% equivalent weight NaCl, K/Na ratios of 0.035 to 0.008 for the south Pennines and temperatures in the region of 100 to 165°C. Potassium enrichment in comparison with normal connate fluids (Dunham, 1970) suggests a contribution from Lower Carboniferous evaporite sequences known to be present to the east of the orefield (Llewellyn and Stabbins, 1968).

The stability of co-precipitated calcite + pyrite + calcopyrite given the range of conditions indicated by fluid inclusion data is indicative of ore deposition within one pH unit either side of neutrality resulting from localised supply of reduced sulphur (Anderson, 1973, p.487). This is in agreement with the observed geological evidence that concurrent carbonate host dissolution and ore deposition were not important processes. The association of intermediate argillic alteration and fringe propylitic alteration with pyrite, chalcopyrite and minor

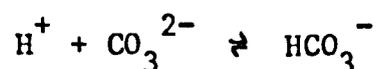
chalcocite, bornite in the altered basalts of the south Pennines is also indicative of ore deposition from hydrothermal fluids enriched in reduced sulphur and marginally on the acid side of neutral (Meyer and Hemley, 1967, p.222). High sulphur and oxygen fugacity and low temperatures favour extensive hydrogen metasomatism.

Geochemical evidence from fluid inclusion studies indicate that in addition to H^+ metasomatism, base cation exchanges involving Na, K and Ca must be considered. Alteration involves the establishment of hydrothermal diffusion gradients involving H^+ , Na, Ca and K and the attainment of wall-rock equilibration under the limiting factors A to E described in Section 9.8. The ratio of the volume of hydrothermal fluid/volume of wall-rock alteration is sufficiently large to discount the possibility of bulk geochemical modification of the hydrothermal brine during basalt alteration.

Variation of Mg in wall-rock alteration can be explained in terms of the operation of diffusion gradients. Incipient propylitic alteration is associated with Mg reduction accompanied by hydrolysis and introduction of CO_2 . Low concentrations of Mg in the hydrothermal brines establishes 'negative' diffusion gradients adjacent to smectites and pyroxenes - the Mg-bearing phases of the incipient propylitic zone ('negative' used in this context denotes the potential for diffusion migration out of a wall-rock phase). The preferential replacement of smectite pseudomorphs after olivine as opposed to interstitial smectite is probably related to the higher MgO% of the olivine pseudomorphs (see Chapter 4) which results in more pronounced (negative) diffusion gradients (i.e. point B, Section 9.8). Within the zone of calcitisation and albitisation, more extensive base cation exchanges and hydrolysis result in Mg depletion. In the transition to argillic alteration, secondary smectites result from albite breakdown. The increased Mg diffusion

gradient in proximity to the central channel way establishes a 'positive' gradient adjacent to the secondary smectite phase and results in degree of MgO enrichment. However, with the transition to kaolinite-rich argillic alteration the Mg formerly concentrated in smectite is not capable of accommodation into the kaolinite lattice and net MgO reduction occurs, even in the presence of 'positive' gradients (i.e. point c, Section 9.8). The relationships between diffusion gradients and Mg concentration are summarised in Figure 9.5. This indicates that between points B and C the operation of a 'negative' diffusion gradient results in MgO depletion attaining equilibrium with the hydrothermal diffusion gradient at D. Equilibrium is maintained between D and E, the increasing hydrothermal diffusion gradient (A-A') resulting in a degree of Mg enrichment incorporated into secondary smectite phases. Between point E-F alteration is dominated by kaolinite resulting in Mg depletion irrespective of positive diffusion gradients.

The concentration of Ca in the hydrothermal brines is intermediate between Mg and K. Incipient propylitic alteration is associated with reduction of Ca from plagioclase and enrichment of Ca resulting from calcitisation of smectite but with a net overall reduction. Calcitisation and albitisation involves strong Ca enrichment in the form of carbonates. Adjacent to the central channelway calcitisation is not the dominant feature. This is probably a function of the reaction:



This 'buffers' the hydrothermal fluid at a point near neutrality while retaining the potential for hydrolysis. Extensive base cation exchanges and hydrolysis in the zone of calcitisation and albitisation results in H^+ depletion driving the reaction to the left. The enhancement of CO_3^{2-} and the availability of Ca^{2+} rather than Mg^{2+} results in

FIG. 9.5 DIAGRAMMATIC REPRESENTATION OF THE RELATIONSHIP BETWEEN HYDROTHERMAL DIFFUSION GRADIENT AND WALL ROCK ALTERATION MAGNESIUM CONCENTRATIONS

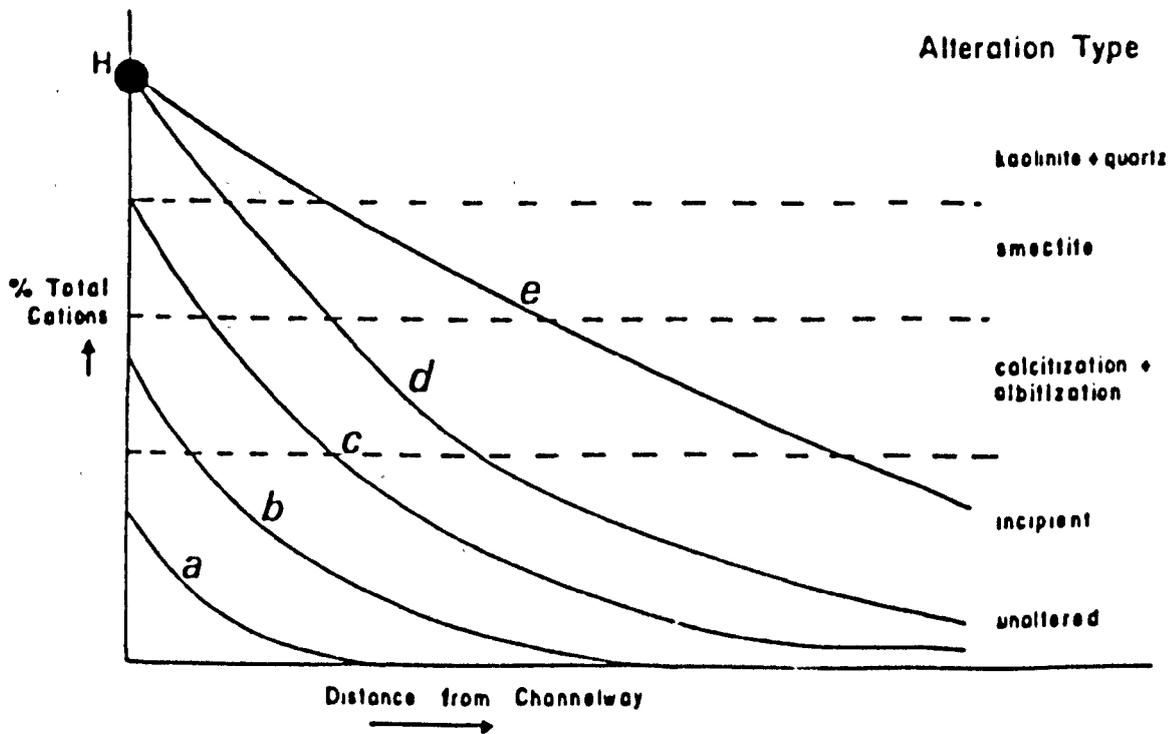
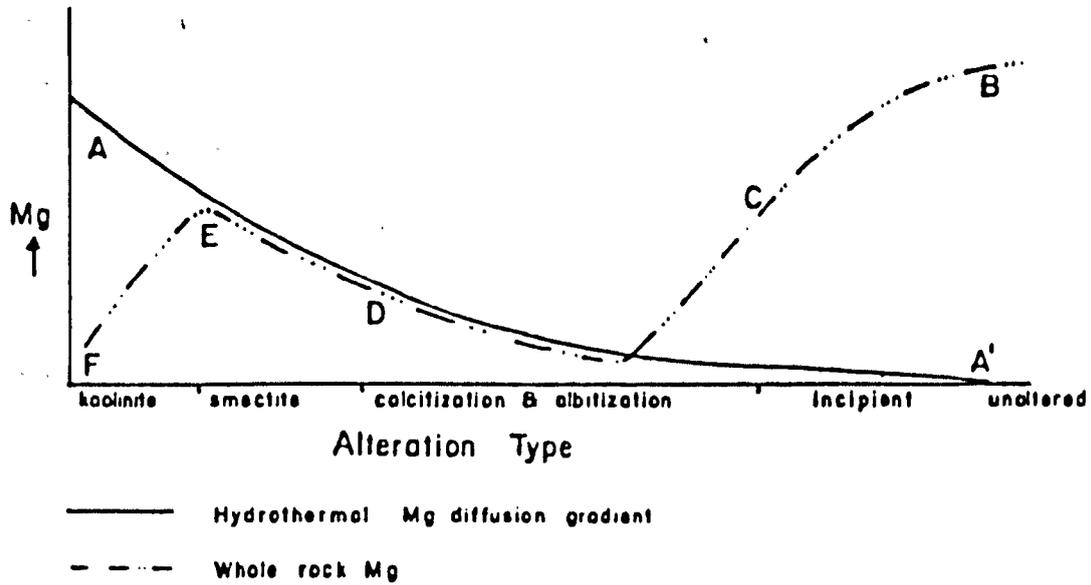


FIG. 9.6 RELATIONSHIPS BETWEEN WALL ROCK ZONED ALTERATION AND HYDROTHERMAL DIFFUSION EQUILIBRIUM

For explanation see text.

calcite formation (Holland, 1967). Adjacent to the channelway this effect is less important and with the increasing activity of Na and K chlorides, calcite solubility increases resulting in reduction of CaO and CO₂ (Holland, op.cit., p.407).

Na enrichment and albitisation are functions of high brine concentration of NaCl (Rodgers, 1977, 1978). Secondary argillisation of albite results in Na reduction, indicating that Na was not incorporated into the secondary smectite phase despite strong 'positive' gradients.

K enrichment is noted during incipient alteration associated with minimal Na variations. This is probably a function of lower whole rock K₂O concentrations in the unaltered basalt relative to Na₂O and the fixation of K into illite-smectite clay phases. With increasing clay-rich alteration further K-enrichment occurs. Although K-enrichment is a dominant feature of alteration it is noted that K⁺/H⁺ ratios were insufficient to introduce orthoclase as a stable alteration phase (e.g. Hemley and Jones, 1964, p.559).

The transition from bleached to unbleached wall-rock during alteration is often visually abrupt but not coincident with the region of maximum geochemical and petrographic variations. The colour change represents the transition from the stability field of haematite to sulphides. Anderson (1973, 1975) demonstrated the sensitivity of this transition, controlled for example by an increase in reduced sulphur, minimal pH or Eh variations, etc., which may not be reflected by bulk geochemical variations in the altered wall-rock.

The geochemical and mineralogical zoned wall-rock alteration in the basalts of the south Pennines can be related to the geochemistry of the hydrothermal brines and the operation of complex, interacting diffusion gradients. Partial development of the 'complete' alteration sequence is noted at a number of localities. This does not infer

variations in the total salinities of the brines and can be related to the duration and temperature of hydrothermal flow through the central channelways before 'sealing'. Given a limited flow duration of low-temperature mineralising fluids, the diffusion gradients in the adjacent wall-rock would not reach equilibrium with either the hydrothermal fluid or the alteration phases.

The effect of a short 'pulse' of hydrothermal flow would result in propylitic alteration adjacent to the central channelway, while prolonged flow duration of identical brine composition results in the development of the full sequence of alteration. This concept is represented in Figure 9.6, where the sequence and relative widths of the alteration zones are defined by the intersection of the horizontal boundary lines and the series of hydrothermal diffusion profiles, A to E. The horizontal boundaries represent the 'stability' limits of each alteration assemblage with varying hydrothermal fluid/basalt host cation ratios and the profiles A to E represent varying degrees of wall-rock diffusion equilibrium with the total cation content (H) of the hydrothermal fluid. Profile A results from a limited flow duration and E represents prolonged flow.

Components of the 'ore-suite' i.e. Pb, Zn, Ni, Cu, Fe, display variations that are not accountable in terms of the simple operation of a constant diffusion gradient. The localities described in Section 9.5 exhibit depletion of Pb, Zn, Ni and Cu adjacent to the central channelway but enrichment at greater distances which is most pronounced for Zn and Pb. The point of maximum enrichment is independent of the zone of alteration and the degree of enrichment corresponds with the size of the central feeder channelways. These variations can be interpreted in terms of 'short-lived metal enrichments' in the hydrothermal brine. A distinct 'pulse' of metal enriched brine resulted in wall-rock

enrichment followed by the flow of metal-deficient brine resulting in depletion adjacent to the central channelway. This interpretation is given credence by the banded (crustification) occurrences of sulphides in paragenetic sequences. Similar enrichment patterns have been detected adjacent to mineralisation in carbonate hosts (Ineson, 1969, Figures 8 (a), (b)).

9.10 Hydrothermal Versus Deuteric Alteration

Basalts exhibiting excessive deuteric alterations, and in particular vesicular lavas, were excluded from detailed analysis (see Chapter 6) However, by fulfilling the objectives of geochemically and petrographically defining the primary variations in 'unaltered' basalts and the variations resulting from the interaction with hydrothermal fluids, the effects of deuteric alterations are capable of isolation.

Previously available analyses of vesicular, altered basalts are presented in Appendix 1 (Analyses 12, 62-67, 75-78, 82). Petrographically, deuteric alteration is similar to incipient hydrothermal alteration. The pyroxenes are replaced by smectite and anatase Fe-Ti oxides exhibit exsolution and oxidation textures and secondary calcite replacements of smectite pseudomorphs after olivine occur. The main distinction is in the albitisation and further secondary replacement of plagioclase which is not accompanied by extensive interstitial calcitisation. Vesicles exhibit dominant calcitic infills but silica, clays and rare analcite are also noted.

Geochemical trends associated with vesicular lavas involve enrichment of CO_2 and H_2O , reduction of Mg and minor variations in total Fe. Enrichment of CaO occurs in association with concentrations of calcite amygdalae while poorly vesicular basalts exhibit CaO reduction. The implication is that CaO variations are a function of redistribution resulting from Ca liberation from albitised feldspar rather than a

primary CaO enriched deuteritic fluid. Na₂O and K₂O concentrations are unaffected.

Analyses 12 (Shacklow Wood Lava) represents a vesicular lava in proximity to mineralisation which has been affected by incipient hydrothermal and deuteritic alterations. Minimal reduction of MgO, strong reduction of CaO and low concentrations of CO₂ are noted, associated with deuteritic type albitisation. Na₂O is unaffected, but K₂O is enriched and can be attributed to hydrothermal interactions. Similar relationships are noted from analyses of altered, vesicular samples of the Matlock Upper Lava (Analyses 63-67), enrichment of K₂O and reduction in Na₂O resulting from hydrothermal alteration with reduction of MgO, enrichment of CaO and strong albitisation related to deuteritic interactions.

Trace-element variations associated with deuteritic alterations are not fully documented. Analysis 12 represents deuteritic and incipient hydrothermal alteration and illustrates minor trace-element variations. Cu, Ni and Zn, normally sensitive indicators of hydrothermal interactions are not affected as are the normally 'immobile' elements - V, Cr, Y, Zr. Albitisation and secondary calcite replacements are reflected by depletion of Sr and enrichment of Rb. The major element analyses of the Matlock Upper Lava, in particular the Na/K ratios, indicate a greater extent of 'hydrothermal' overprinting, than in sample 12, resulting in depletion of Cu and Zn while Ni is unaffected, Rb is enriched and Sr depleted.

A degree of deuteritic alteration is noted in all basalt samples from the south Pennines (Chapter 6). In the case of non-vesicular basalts, hydration is the dominant process resulting in smectite pseudomorphs after olivine and primary glass accompanied by subordinate introduction of CO₂. In the vesicular margins of flow units, concentrations of deuteritic

FIG. 9.7 GEOLOGICAL SKETCH MAP OF THE IBLE SILL, VIA GELLIA

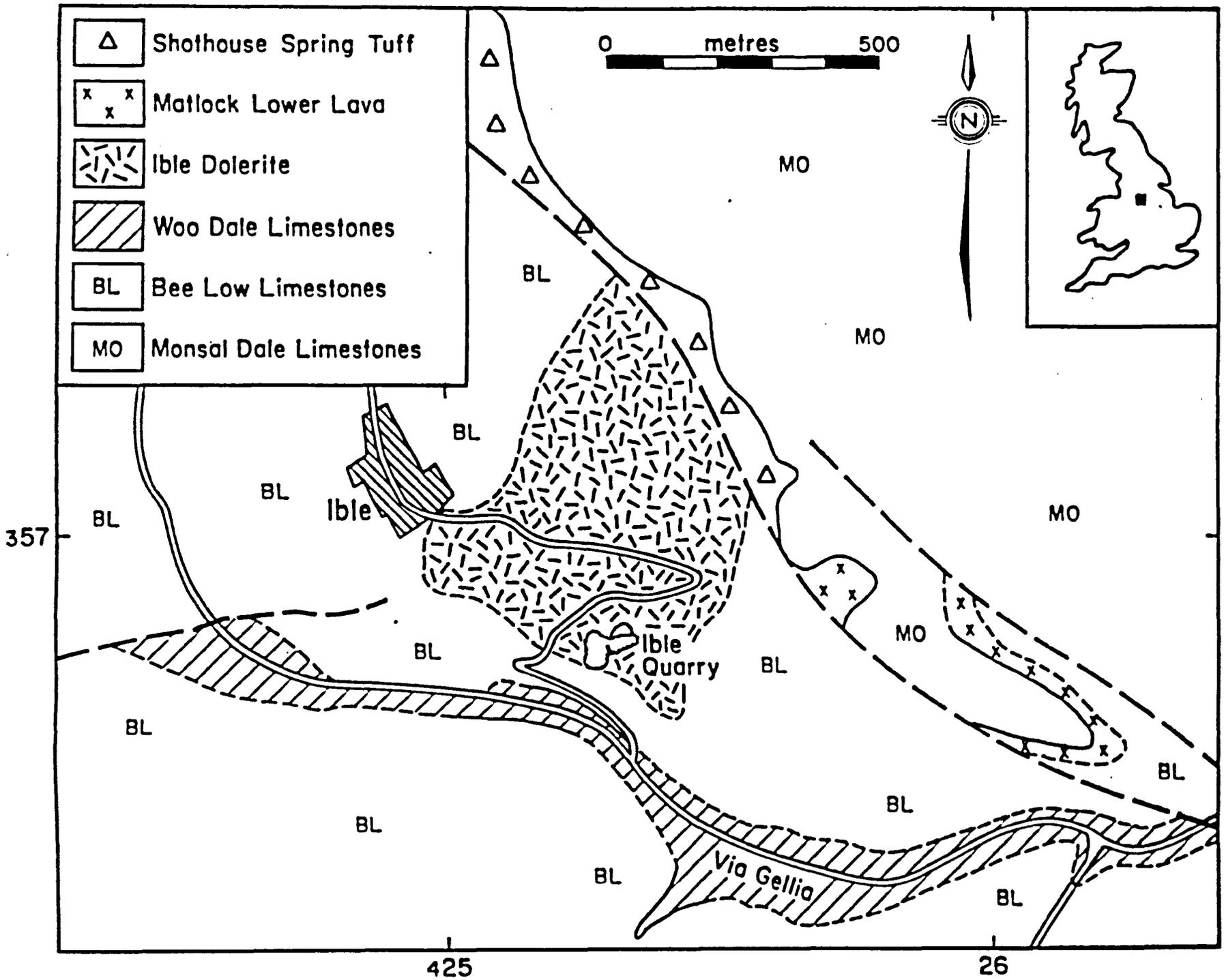


Fig 9.7

fluid enriched in CO_2 and other volatiles result in albitisation of plagioclase and calcite formation, but has minimal effect on the trace-elements other than Rb and Sr which are associated with plagioclase alteration. These observations agree with Carmichael et al.'s (1974) data indicating that water (>90%) and carbon dioxide are the principal components of volcanic gasses together with a range of subordinate volatile constituents such as halogens and sulphur. It is concluded that K_2O enrichment is a sensitive indicator of hydrothermal interactions, which can be detected even as an overprint on deuteric alteration.

9.11 Alteration of the Ible Sill

An unusual type of alteration was reported by Garnett (1923) from the disused roadstone quarry in the Ible Sill (Figure 9.7). Within the quarry the dolerite is traversed by numerous, disorientated veinlets up to 10 cm in width. These veinlets have an infill of fibrous calcite, quartz and a resinous olive-green mineral considered by Garnett (op.cit.) to be chrysotile-asbestos, however an XRD investigation by Sarjeant (1967) indicated a chlorite-smectite. There is no visual wall-rock alteration associated with these veinlets. A sub-vertical zone of pale-bleaching and alteration, up to 1.5 m in width, is present in the quarry. This altered zone trends E-W and can be observed on the lip of the upper bench in the quarry. The margin of the zone are indistinct but there is a rapid gradation into unbleached dolerite. In hand specimen the altered dolerite is pale green with diffuse areas of darker alteration up to 4 mm in diameter giving rise to a 'spotted' texture. Alteration is associated with an open fissure occurring in the centre of the zone.

The altered dolerite was described by Garnet (op. cit.) as a 'chlorite-rock'. In view of the dubious status of these early records of 'chlorite' (see Section 4.8) and the unusual mode of occurrence of the alteration the locality was re-investigated. Four samples of dolerite representing the transition from unaltered to altered dolerite were subjected to XRF, XRD, K-Ar isotopic age determinations and petrographic examination.

The unaltered material is a typical coarse, ophitic olivine-dolerite. Ophitic-augite up to 4 mm in diameter encloses unaltered labradorite with subordinate ilmenite, magnetite and apatite (Plate 1.6c). Olivine phenocrysts are pseudomorphed by aggregates of olive-green and red pleochroic clays with preservation of relict internal cracks (Plate 2.2f). XRD analysis of extracted material indicates that the pseudomorphing phase is a smectite (Table 4.1).

In the altered dolerite primary pyroxene is pseudomorphed by a homogeneous, apple-green phase exhibiting weak pleochroism and lower birefringence compared with the smectite pseudomorphs in the unaltered dolerite. Relict ophitic texture is discernible by the concentration of fine-grained anatase at original grain boundaries. The smectite pseudomorphs after olivine are similarly replaced. Feldspar laths are albitised and ilmenite and magnetite are partly altered to aggregates of euhedral anatase (Plate 4.1 a,b). With increasing alteration albite is replaced by the apple-green phase, initially along cracks and showing preference for albite cores leading to complete pseudomorphism in many instances. Relict ilmenite or magnetite is no longer present, and only minor areas of carbonate replacements are noted.

XRD analysis of the altered dolerite indicates that the apple-green mineral is a chlorite with sharp peaks (in order of intensity) at 7.2\AA , 14.5\AA and 3.6\AA which are unaffected by glycolation but on

heating to 550°C for 1 hour the 7.2Å peak is destroyed and the 14.5Å peak migrates to 14.0Å. The dominance of chlorite is in direct variance with the petrology of alteration from other localities in the south Pennines and in this instance supports the description of Garnett (op.cit.) of the altered dolerite as 'chlorite-rock'.

The geochemistry of alteration is also at variance (Table 9.3). Minimal depletion of MgO and SiO₂, and enrichment of Al₂O₃ occurs in the zone of alteration. Strong depletion of CaO and low concentrations of CO₂ reflect the alteration of the feldspar and lack of carbonates. FeO and Fe₂O₃ are both enriched with minor variations in the oxidation ratios while enrichment of H₂O⁺ occurs. The alkali variations are typical of hydrothermal alteration in that Na₂O increases with albitisation followed by depletion during chlorite replacement of albite and K₂O is progressively enriched with increasing alteration, but remains less than the overall Na₂O concentrations. Amongst the trace elements Ba, Pb and Sr decrease; Cr, Ni and V are enriched and Cu and Zn illustrate minor variations.

These trends and the dominance of chlorite are not reconcilable with either the typical deuteric or hydrothermal variations described in the preceding sections. The Na and K relationships are indicative of a hydrothermal origin and this is supported by the results of K-Ar isotopic age dating. The ages obtained (see Chapter 12) indicate that alteration was associated with a phase of hydrothermal activity around 230 m.y. resulting in minor mineralisation in the orefield.

The alteration trends in the dolerite are in some respects opposite to those normally involved in hydrothermal alteration. The stability of chlorite reflects high concentrations of Mg and Fe, both normally depleted in hydrothermal alteration, reduction of CaO and low concentrations of CO₂ are also directly opposed to the normal hydrothermal

Table 9.3

TABLE 9.3: Geochemistry of Alteration, Ible Sill

	(1) Unaltered Dolerite (37)*	(2) Altered Dolerite (36)	(3) Altered Dolerite (39)	(4) Highly Altered Dolerite (38)
SiO ₂ %	48.76	44.14	46.40	45.70
TiO ₂	1.86	1.75	1.88	1.84
Al ₂ O ₃	14.60	16.09	16.63	16.71
Fe ₂ O ₃	4.60	4.75	4.52	5.51
FeO	6.06	7.43	8.89	6.92
MgO	8.35	6.78	7.87	6.81
CaO	9.12	4.03	1.21	2.92
Na ₂ O	2.61	3.01	2.24	3.28
K ₂ O	0.79	1.33	2.18	1.17
H ₂ O ⁺	2.36	6.09	6.49	6.37
H ₂ O ⁻	1.26	1.24	1.00	1.26
P ₂ O ₅	0.38	0.26	0.27	0.28
CO ₂	BD	2.28	0.40	1.75
SO ₃	0.05	0.06	0.18	0.09
Total	100.80	99.24	100.16	100.61
Ba (ppm)	302	168	220	168
Co	81	91	107	103
Cr	358	453	473	509
Cu	81	97	89	82
Ni	242	295	272	297
Pb	28	BD	9	BD
Rb	17	12	24	12
Sr	345	99	90	90
V	182	229	231	245
Y	27	24	20	27
Zn	104	128	111	130
Zr	128	101	101	103

*Analyses Number - Appendices 1 to 5

trends. The thin central fissure associated with the Ible alteration contrasts with the 'veinlet-swarm' associated with typical hydrothermal alteration in basalts. Garnett (op.cit.) indicates that the fissure and associated alteration diminish in size and eventually die out with increasing height in the quarry face. A possible explanation for the atypical nature of alteration may be that this represents a locality where the ratio of the volume of wall-rock alteration to hydrothermal fluid was sufficiently large to result in significant geochemical modification of the hydrothermal fluid. It is proposed that the fissure is a minor tectonic feature which allowed the influx of ascensive hydrothermal fluids into the sill. The fissure dies out within the sill and this together with its restricted size severely limited the volume of hydrothermal flow, possibly resulting in conditions of virtual 'stagnation'. Normal hydrothermal wall-rock interactions occurred at lower levels resulting in progressive geochemical modifications of the restricted fluid volume migrating through the fissure. The modifications did not significantly alter the bulk geochemical characteristics of the hydrothermal fluid, i.e. a saline brine capable of H^+ , K^+ and Na^+ metasomatism but enrichment of FeO , Fe_2O_3 and MgO during initial alteration, resulted in the stability of chlorite and wall-rock enrichment at the level exposed by quarrying. Trace elements normally leached during alteration were likewise enriched resulting in the 'atypical' hydrothermal trends.

Vertical wall-rock alteration variations related to progressive geochemical modifications of rising hydrothermal fluids is a common feature typically associated with magma-derived vein deposits (Meyer and Hemley, 1967, p.226). The paucity of such features associated with basalt alteration in the south Pennines is a function of the

minimal volume of wall-rock alteration when compared with the volume of hydrothermal brines involved in the generation of Mississippi Valley Type orebodies. The atypical alteration at Ible Quarry can be explained in terms of the localised reversal of these ratios.

PLATE 3.1 SULPHIDE TEXTURES, ALTERED SHACKLOW WOOD LAVA-MOGSHAW No.3 BOREHOLE.

A). (158/103.2m)* Coarse, euhedral marcasite associated with areas of coarse carbonate and fine-grained pyrite associated with interstitial calcite replacements. Note the preservation of relict textures in the bleached and altered lava-see Plate 3.4.
(0.8mm, ppl)+

B). (158/103.2m)* General view of sulphide impregnations illustrating two distinct generations. Coarse, euhedral marcasite confined to areas of veining and calcite amygdales with finer grained, anhedral "spongy" pyrite occurring in the altered basalt groundmass. (4.0mm, ppl)

C). (159/103.6m) Coarse marcasite aggregates in calcite amygdale illustrating typical strong reflection anisotropy. (0.8mm, pxpl)

D). (159/103.6m) Core of marcasite with an overgrowth of pyrite. (0.8mm, pxpl)

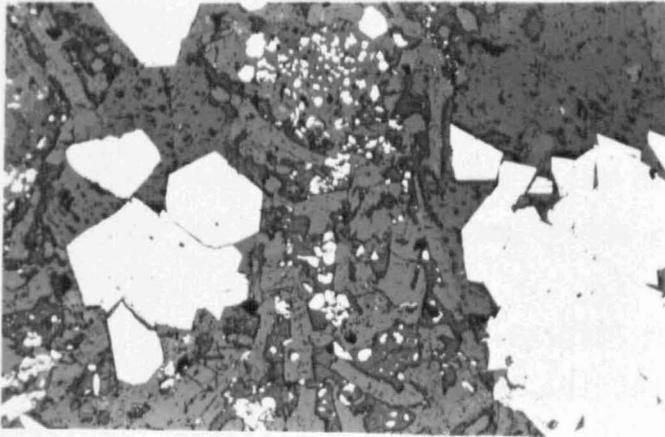
E). and F). (163/105.1m) Cataclastic textures in coarse marcasite, indicating secondary shearing after sulphide impregnation and associated with minor cross cutting veinlets-see Plate 3.4-A4.
(0.8mm, ppl)

(All photomicrographs in reflected light.)

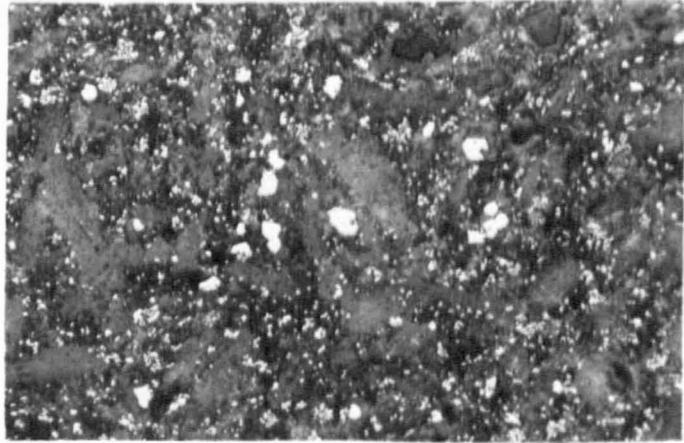
* Analysis number-Appendices 1 to 5, and borehole depth.

+ Width of field of view, ppl-plane polarized light, pxpl-partly crossed polars, xpl-crossed polars.

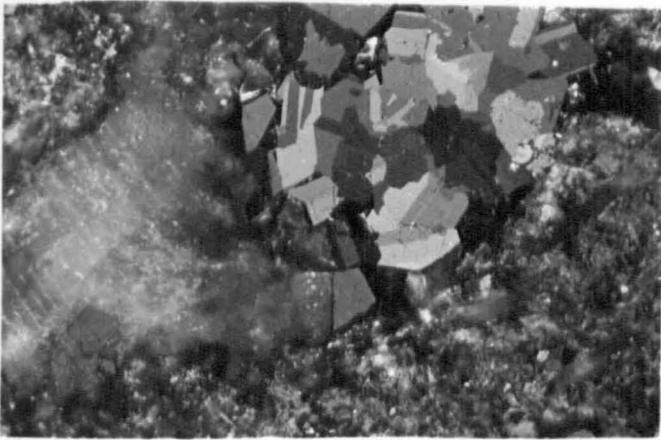
Plate 3.1



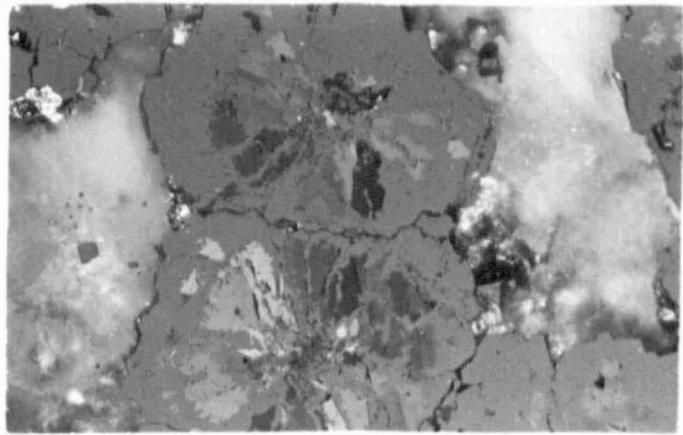
A



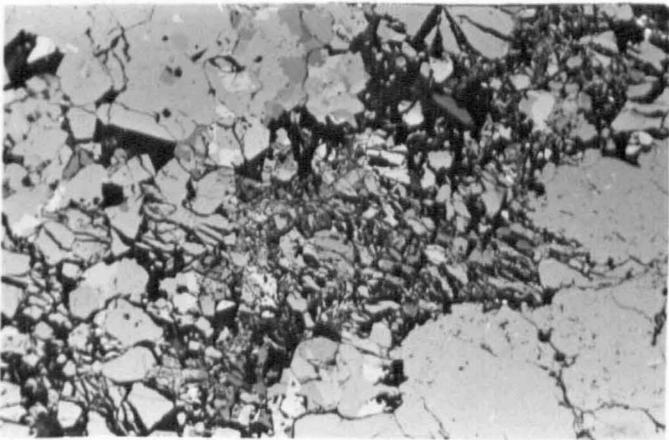
B



C



D



E



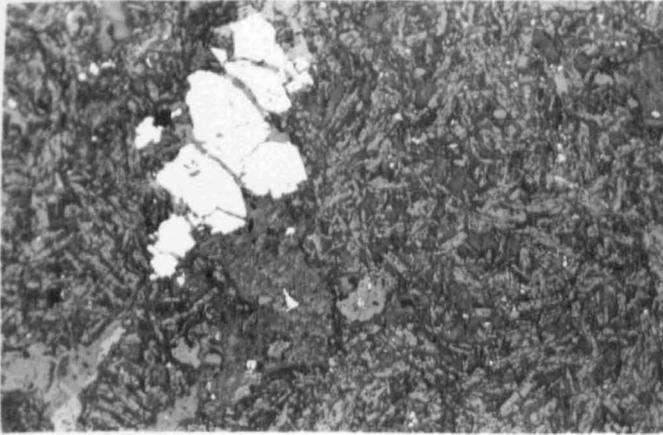
F

PLATE 3.2 OPAQUE PHASES-HYDROTHERMALLY ALTERED LAVAS.

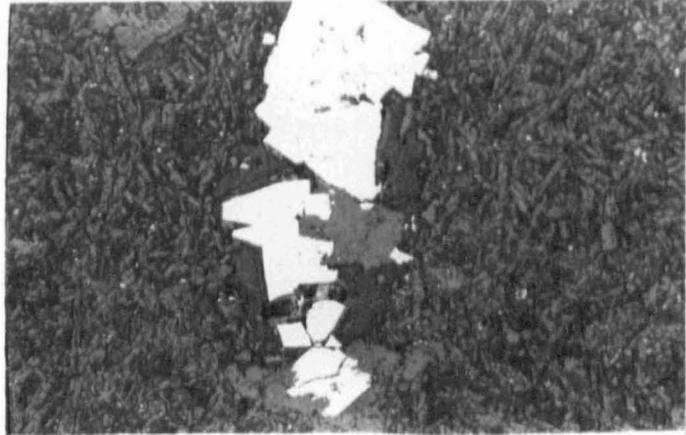
A).and B).CONKS BURY BRIDGE LAVA-CONKS BURY
No. 5 BOREHOLE.(139/56.8m) Restricted veinlet,
occurrences of euhedral pyrite in highly bleached and
altered basalt-see Plate 3.4-B2.Note the preservation
of relict textures.(0.4mm, ppl)

C). to E).MILLERS DALE UPPER LAVA-MAURY
ADIT.(120-122/1.2-1.0m) Association of abundant
cubic and octahedral spinel phases with secondary
silica replacement of calcite pseudomorphs after
olivine microphenocrysts in intensely altered
lava.Density and mode of occurrence suggest a
possible Zn-rich hydrothermal origin for the spinel.
(2.0mm, ppl)

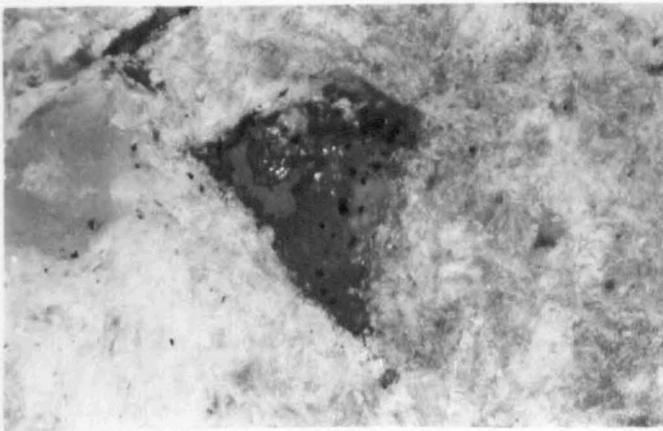
Plate 3.2



A



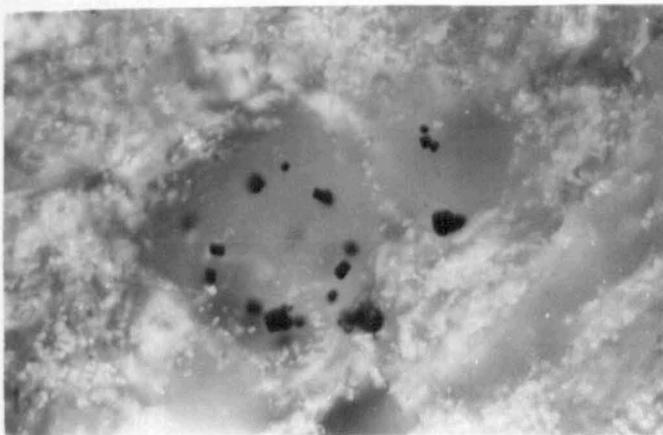
B



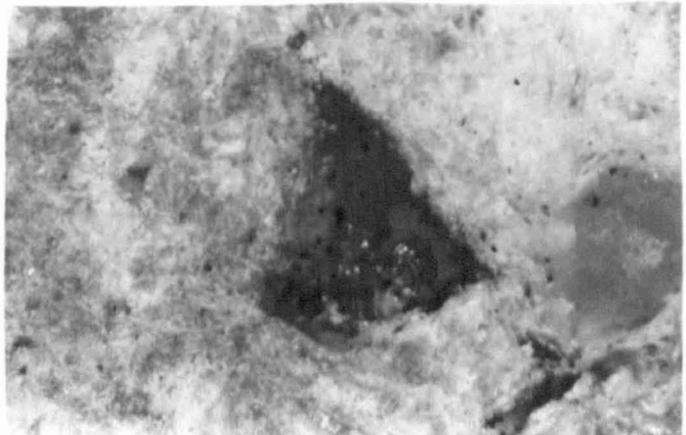
C



D



E



F

PLATE 3.3 HYDROTHERMAL ALTERATION OF FE-TI OXIDES.

A) and B). MATLOCK LOWER LAVA, BONSALL BASALT QUARRY-
VIA GELLIA. (17/Type 1-4)

A). Homogeneous ilmenite with strongly lobate
outline. (0.4mm, pxpl)

B). Titanomagnetite with a slight degree of
ilmenite exsolution. (0.4mm, ppl)

C) to F). MATLOCK LOWER LAVA, HALLICAR WOOD ADIT-
VIA GELLIA. (20-101/Type 1)

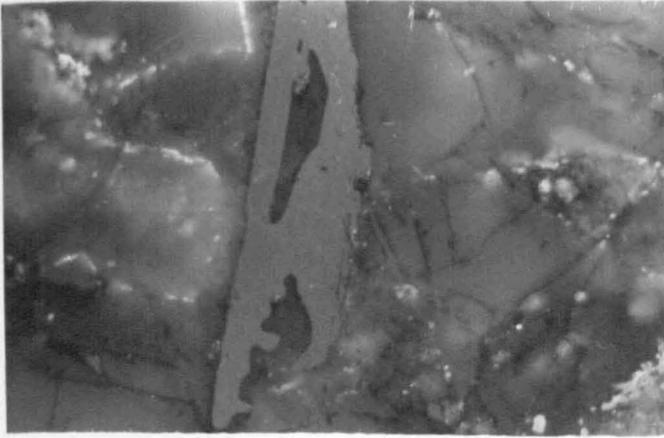
C). Greater degree of oxidation associated
with pyroxene replacement. Patchy exsolution of
titanomagnetite with coarse areas of ilmenite.
Altered pyroxenes can be detected by concentrations
of anatase (white with internal reflections) at
relict grain boundaries. (0.4mm, pxpl)

D). Patchy exsolution textures in oxidized
titanomagnetite. (0.4mm, ppl)

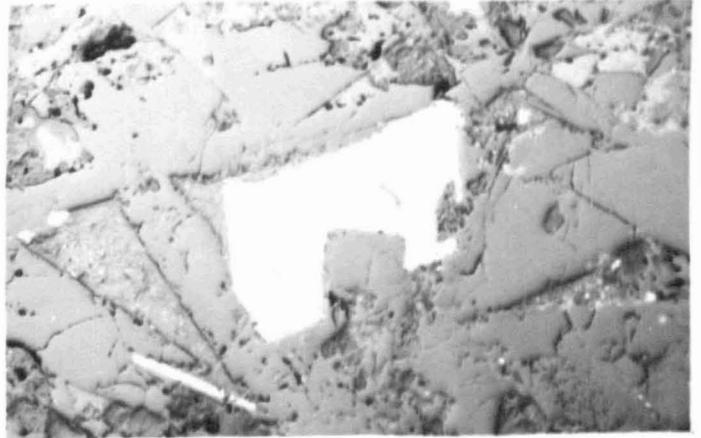
E). Advanced oxidation associated with
hydrothermal alteration. Primary titanomagnetite
completely altered to an aggregate of haematite
(dark areas) and anatase (bright internal reflections)
(0.4mm, xpl)

F). Same field of view as (E) indicating the
original outline of the magnetite grain. (0.4mm, ppl)

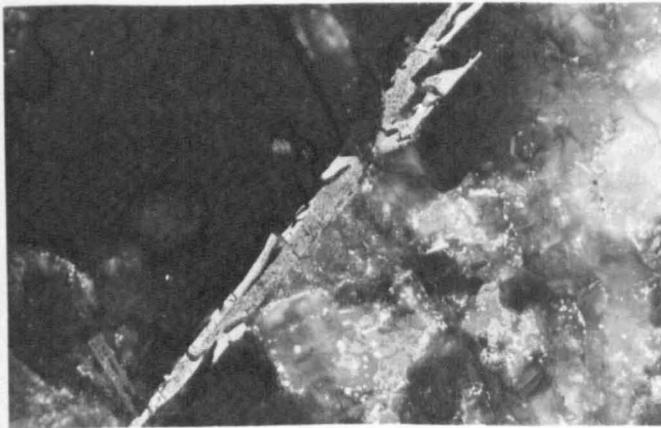
Plate 33



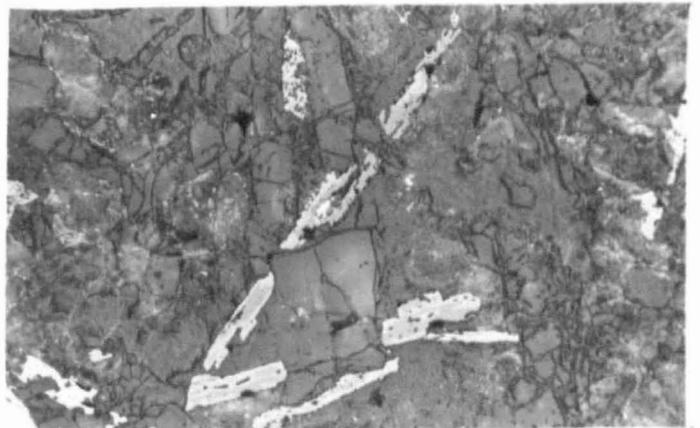
A



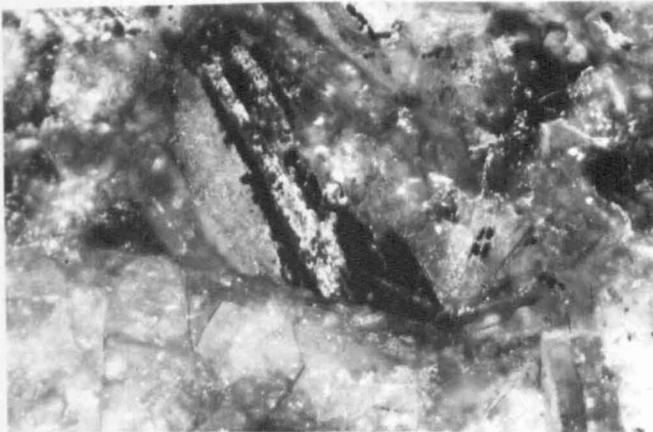
B



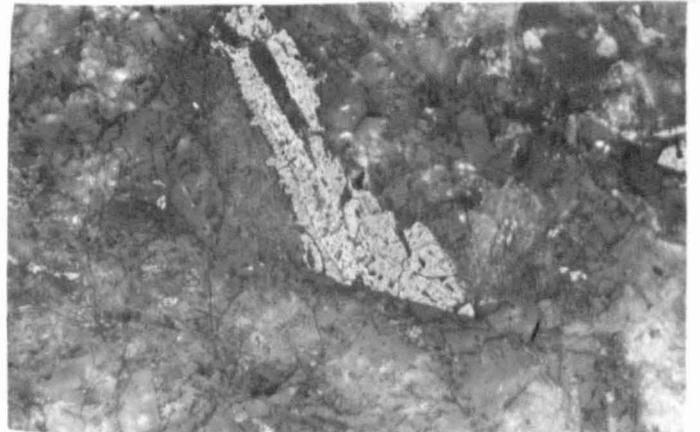
C



D



E



F

PLATE 3.4A HYDROTHERMAL ALTERATION, SHACKLOW WOOD LAVA-
MOGSHAW No. 3 BOREHOLE.

1). (13/110.3m) Unaltered, non-vesicular coarse
'holocrystalline' lava.

2). (12/102m) Iron-stained, vesicular lava
containing calcite amygdales, from close proximity
to mineralization and alteration. The only indications
of this proximity is an enhanced K_2O concentration.

3). (158-159/103-103.5m) Bleached and veined
vesicular lava. Alteration is developed at the contact
of two flow units resulting in a concentration of
calcite amygdales. Restricted development of calcite
veining associated with marcasite and fluorite.

4). (162-164/105-105.2m) Abrupt visual transition
from bleached to unbleached non-vesicular lava across
a calcite veinlet. This transition is typical of the
majority of wall-rock alteration localities and
represents the transition from disseminated haematite
to pyritization or iron depletion and is not
coincident with marked geochemical variations in the
majority of instances.

PLATE 3.4B HYDROTHERMAL ALTERATION, CONKSURRY BRIDGE
LAVA-CONKSURRY No. 5 BOREHOLE

1). (1/51m) Unaltered, nonvesicular fine -
grained olivine phyric lava (see Plate 1.4f).

2). (138/56,5m) Intensely altered and
bleached lava associated with abundant fine-scale
carbonate-silica veining. Despite the intense calcit-
ization and albitization relict textures are preserved
(see Plate 3.2a and b)

3). (143-144/59m) Pale-green, partially altered
lava. Plagioclase is albitized and pyroxenes replaced
but interstitial smectite remains unaffected.

4). (148-149/61.0-61.2m) Calcitized and albitized
bleached lava similar to (2) but with the development
of secondary shearing associated with areas of dark
fault gouge.

Plate 3·4

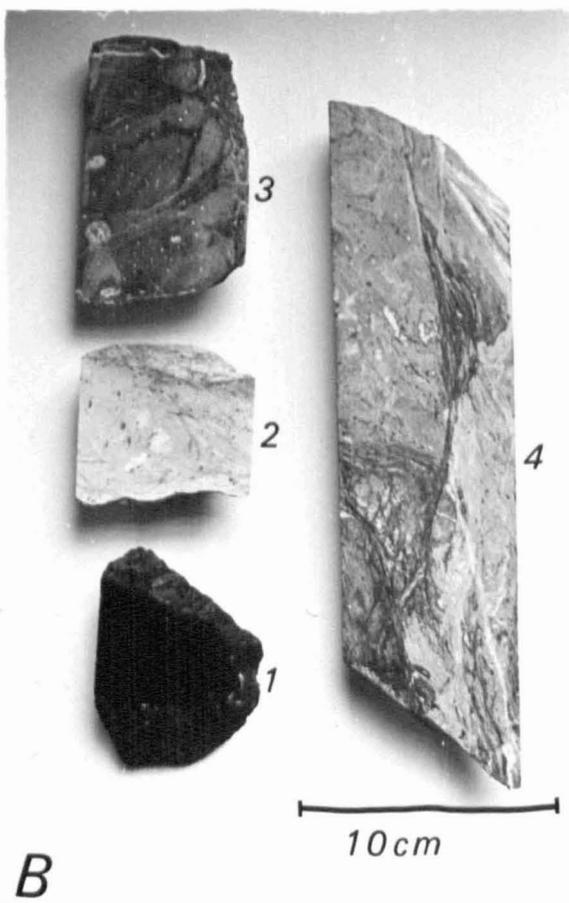
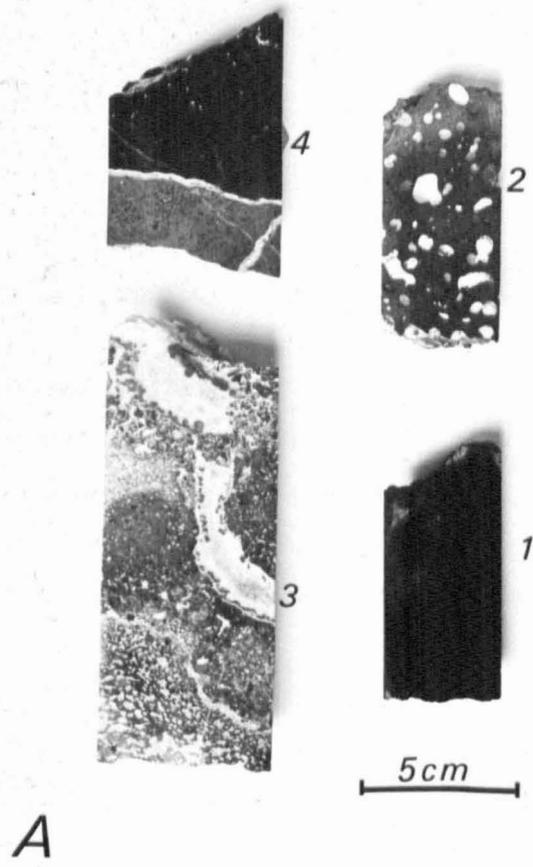
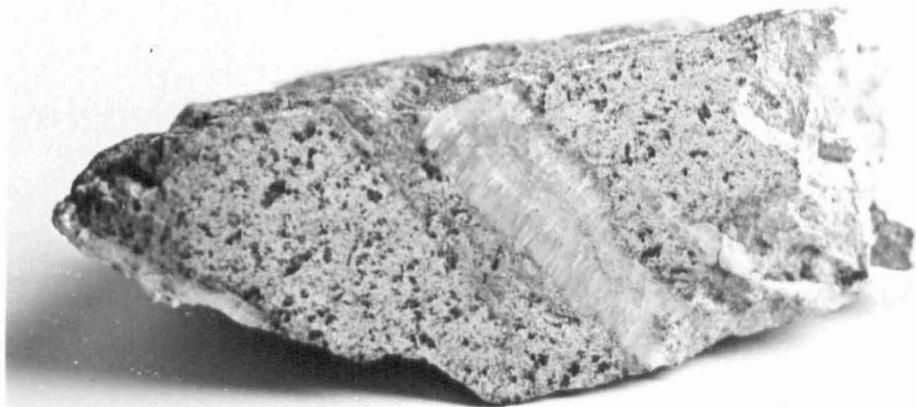


PLATE 3.5A ALTERED POTLUCK SILL DOLERITE, BLACK HILLOCK MINE DUMP.

Calcitized and albitized dolerite with veining. The relict textures of the coarse ophitic dolerite (see Plate 1.5f) are preserved, dark areas represent coarse carbonate replacements of olivine phenocryst pseudomorphs.

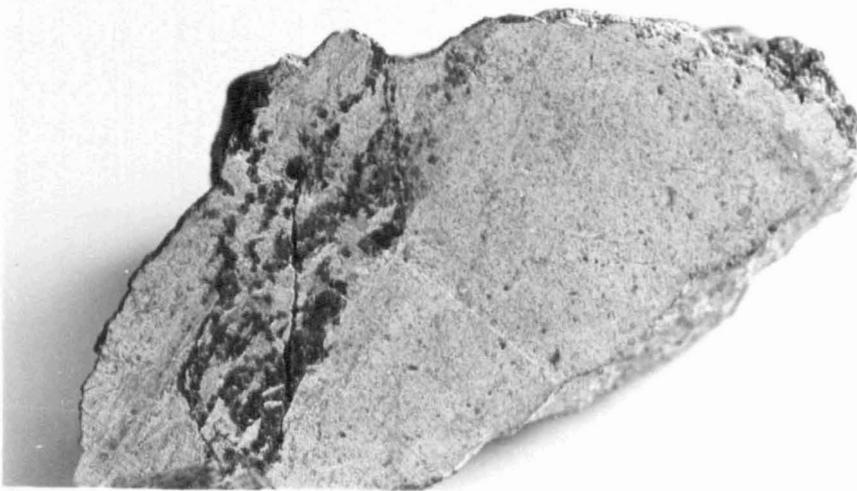
PLATE 3.5B ALTERED MILLERS DALE UPPER LAVA, MAURY MINE DUMPS.

Bleached and altered fine grained lava. Thin, interconnecting veinlets of dark sphalerite with subordinate galena and minor bravoitic pyrite intersect with silica veinlets (light grey) Lava is calcitized and albitized.



A

ACTUAL SIZE



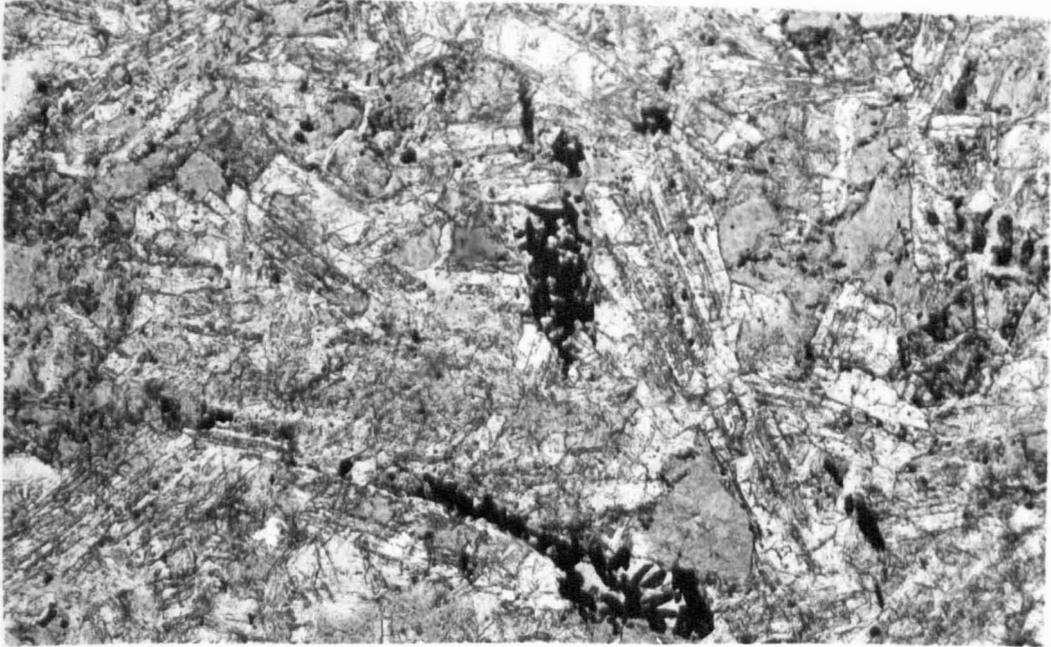
B

PLATE 3.6 ALTERATION OF THE IBLE SILL, IBLE QUARRY.

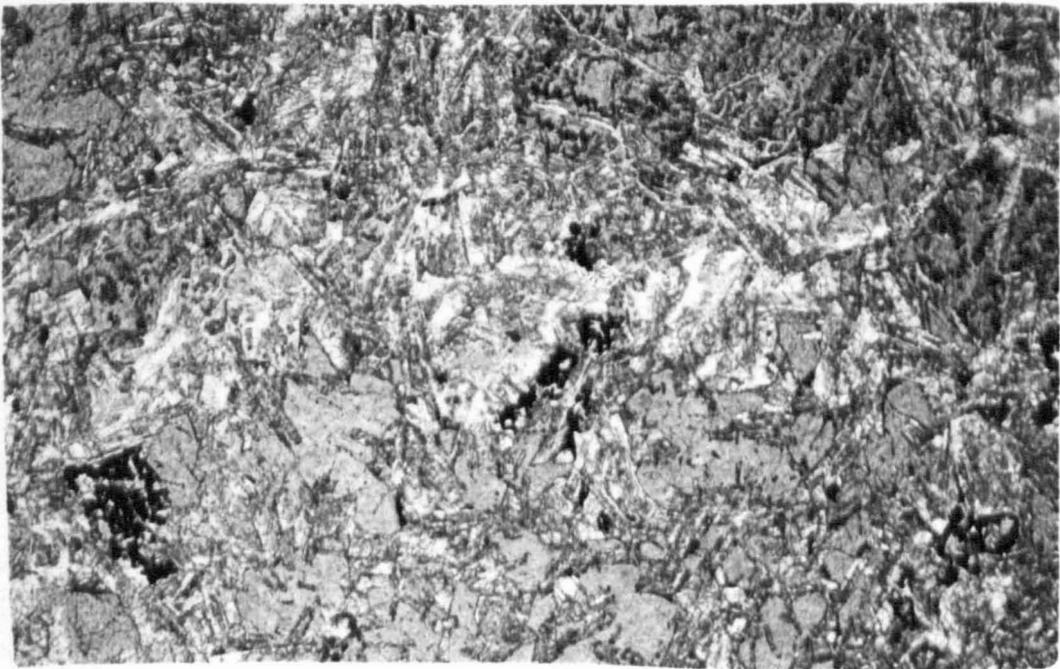
A). Altered dolerite in which the clinopyroxene and pseudomorphs after olivine have been replaced by apple-green chlorite. Ilmenite and magnetite are partly altered to coarse aggregates of euhedral anatase while fine grained, anhedral anatase is concentrated at the relict grain boundaries of pyroxenes. Feldspar is albitized but largely unreplaced by chlorite. (2.0mm, ppl)

B). Highly altered dolerite with no relict ilmenite or magnetite. Albite exhibits partial secondary replacement by chlorite. (4.5mm, ppl)

Plate 3·6



a



b

CHAPTER TEN



Chapter Ten
Occurrence, Geochemistry and Mineralogy of
'Toadstone-Clays'

10:1 Introduction and Previous Research

The tendency for basalts in the south Pennines to exhibit alteration and bleaching localised to the upper and lower margins has long been recognised (e.g. Garnett, 1923). The altered basalt is known locally as 'toadstone-clay' due to its soft, decomposed nature which has resulted from the widespread effects of groundwater interactions and weathering, although when freshly exposed and unweathered 'toadstone-clay' is of a hard, coherent nature. Traill's (1940) description of the toadstone clay associated with the Matlock Upper Lava in Millclose Mine is a typical example:

".... Towards the bottom (of the Lava) there is a gradual change until the lowest 13 or 14 ft. is soft, mottled, light green in colour and highly decomposed. Away from orebodies the upper part of the toadstone is relatively hard and unaltered, but where the main vein cuts through the toadstone the top of the latter is considerably bleached and softened. Wherever one of the mine drives traverses these soft bands the walls and roof have to be supported."

The intensity of bleaching exhibited by the toadstone-clays was related to the proximity of mineralisation by Garnett (1923) and Traill (1940). Material collected by J.G. Traill illustrates this feature at the lower contact of the 129 Fathom Toadstone in Millclose Mine (samples in the Department of Geology, University of Sheffield). Approaching the 129 Fathom orebody, the vesicular lava is bleached from pale green to almost white in colour, associated with pyritisation and areas of coarse grained carbonate.

Garnett (op.cit.) recognised three stages of alteration:

1. 'Dolerite-greenstone' - a calcitised and 'chloritised' basalt, pale green in colour, exhibiting relict textures.
2. 'Green-earth' - a more advanced stage of alteration resulting in progressive 'decomposition' with a substantial portion of clays and pyritisation.
3. 'The end product' - is characterised by a smooth, almost white clay, representing the 'residue' of the original rock. It is more restricted in occurrence than the 'green-earth'.

The work of Garnett (op.cit.) has remained the most authoritative account of the occurrence and geochemistry of toadstone-clays. However, Walkden (1970) investigated the mineralogy of the alteration and Amin (1980) included three major and trace element analyses of the toadstone clay developed at the upper contact of the Matlock Upper Lava as part of a detailed study of the Namurian sediments in the Tansley Borehole.

10:2 Sampling Localities

Toadstone-clay sequences were noted at the contacts of Lavas in a number of boreholes (Appendix 7). Two occurrences were selected for detailed investigation, i.e. the lower toadstone-clay of the Millers Dale Lower Lava in T/B/21 Borehole, Great Rocks Dale and the upper toadstone-clay of the Conksbury Bridge Lava in Haddonfields No.11 Borehole. In addition, toadstone clay sequences exposed in two quarries which showed the effects of weathering were selected for analysis, i.e. the upper toadstone-clay of the Millers Dale Lower Lava, the White Rake Opencast, Tideslow Moor and the 6.5 m thick Matlock Lower Lava in Hoptonwood Quarry, Via Gellia.

Major and trace element analyses are presented in Appendices 1 and 2, while sample location details are contained in Appendices 5 and 7.

10:3 Geochemistry and Mineralogy

a. Lower Millers Dale Lava, T/B/21 Borehole

Toadstone-clay alteration at the base of the Lava is 30 cm thick with an abrupt transition from bleached to unbleached non-vesicular lava and a concentration of pyrite associated with the altered vesicular lava at the lower contact. The altered basalt is hard, coherent and sufficiently durable for the preparation of petrological thin sections. The mineralogy is dominated by calcite and a mixed layer illite smectite with a predominance of expandable layers, together with minor amounts of pyrite, albite, kaolinite and anatase. The geochemistry of the toadstone-clay sequence (Figure 10.1) indicate a reduction in FeO, Fe₂O₃, MgO, Na₂O, Ni, Sr, Ba, Zn and Cu and an increase in K₂O, CaO, CO₂ and Rb.

The altered vesicular basalt is underlain by a sequence of olive-green, uniform clay, 3 m thick with a 'blocky' fracture and an absence of relict textures. The clay exhibits pyritisation, iron-staining and is of a plastic nature towards the contact with the underlying limestone. The mineralogy of the 'clay sequence' is similar to the altered lava apart from the absence of albite and the illite-rich nature of the mixed layer illite-smectite. The immobile and trace element geochemistry, however, is at variance with the toadstone-clay and has not been incorporated in Figure 10.1. The mineralogy and geochemistry of the clay indicates a distal, acidic-ash origin which is described in Chapter 11.

Fig 10.1

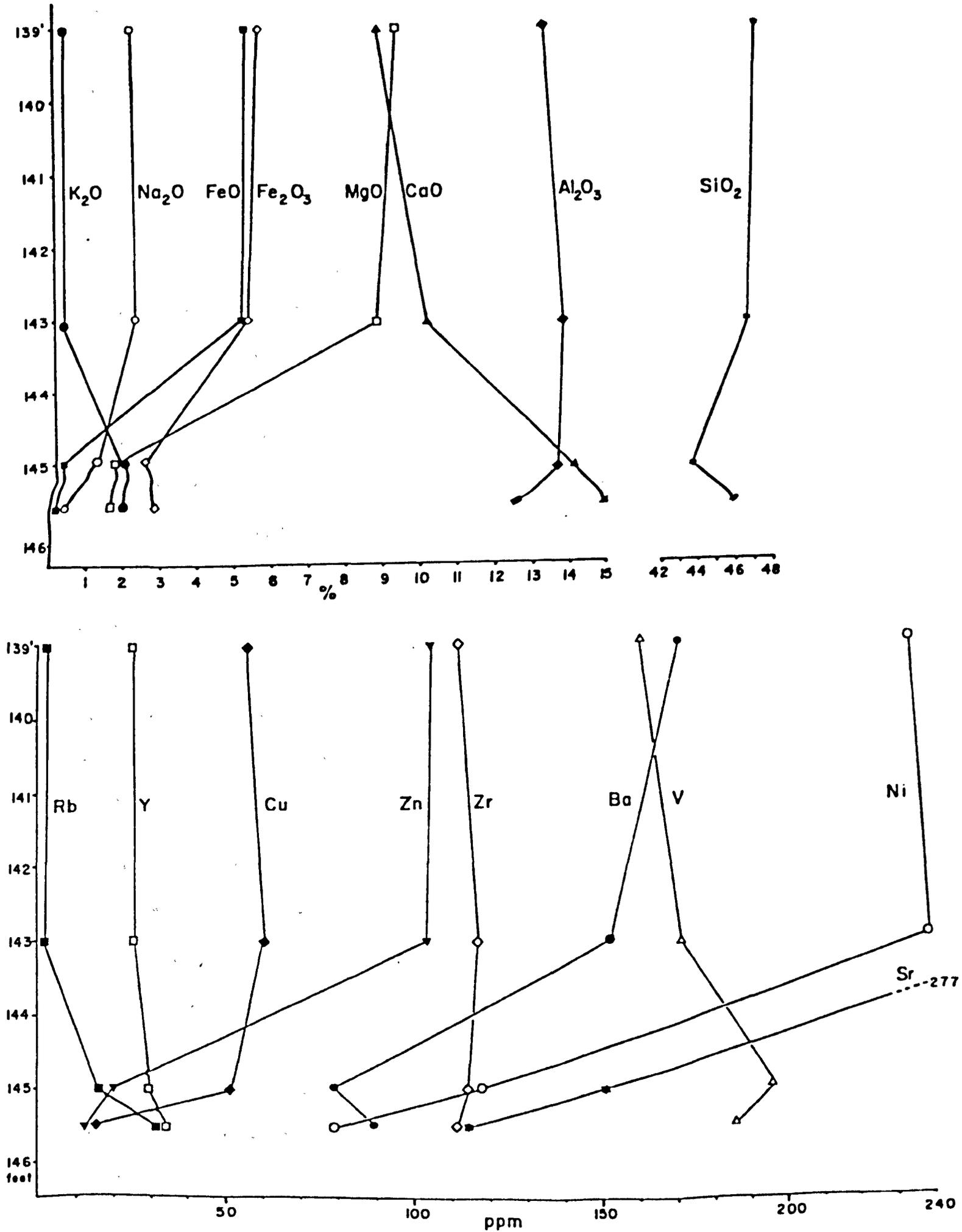


FIG. 10.1 GEOCHEMICAL VARIATIONS - LOWER TOADSTONE CLAY SEQUENCE OF THE MILLERS DALE LOWER LAVA ,TUNSTEAD No.21 BOREHOLE

b. Conksbury Bridge Lava, Haddonfields No. 11 Borehole

The upper 2 m of the Lava is bleached, pyritised and vesicular. The exact thickness of the toadstone clay sequence is unknown due to minimal core recovery in the subsequent 2 m. The altered lava is hard, coherent and suitable for thin sectioning apart from the top 0.3 m which is iron-stained and friable. Preservation of relict textures in the coherent vesicular lava indicate alteration of a fine-grained olivine-phyric basalt. Progressive secondary replacements of olivine pseudomorphs are noted with smectite and carbonate at 52.75 m, followed by silica with carbonates and silicification towards the upper contact. Strong pyritisation is localised in the uppermost 0.5 m of the toadstone-clay and in the overlying limestones. The mineralogy is dominated by calcite and a mixed layer illite-smectite with a high proportion of expandable layers together with minor amounts of pyrite, albite, quartz, kaolinite and anatase.

Geochemical profiles (Figure 10.2) indicate a reduction in Na_2O , FeO , Mg , CO , Zn and Ni (although Ni is not depleted to the same extent as the previous locality) with enrichment of K_2O , CaO , CO_2 , H_2O^+ and Fe_2O_3 the latter correlating with the occurrence of pyrite.

c. Millers Dale Lower Lava, White Rake Opencast

The upper 1.5 m of the Lava exposed in the south wall of the opencast is bleached, altered and friable and a transition from toadstone clay to unaltered lava is not located in the sampled section. The uppermost 0.4 m is an iron-stained clay with no discernable relict textures. This is underlain by pale-green vesicular basalt (0.3 m) which rests on a further iron-stained horizon grading into a sequence of more coherent and bleached vesicular lava.

Figs 10.2 & 10.3

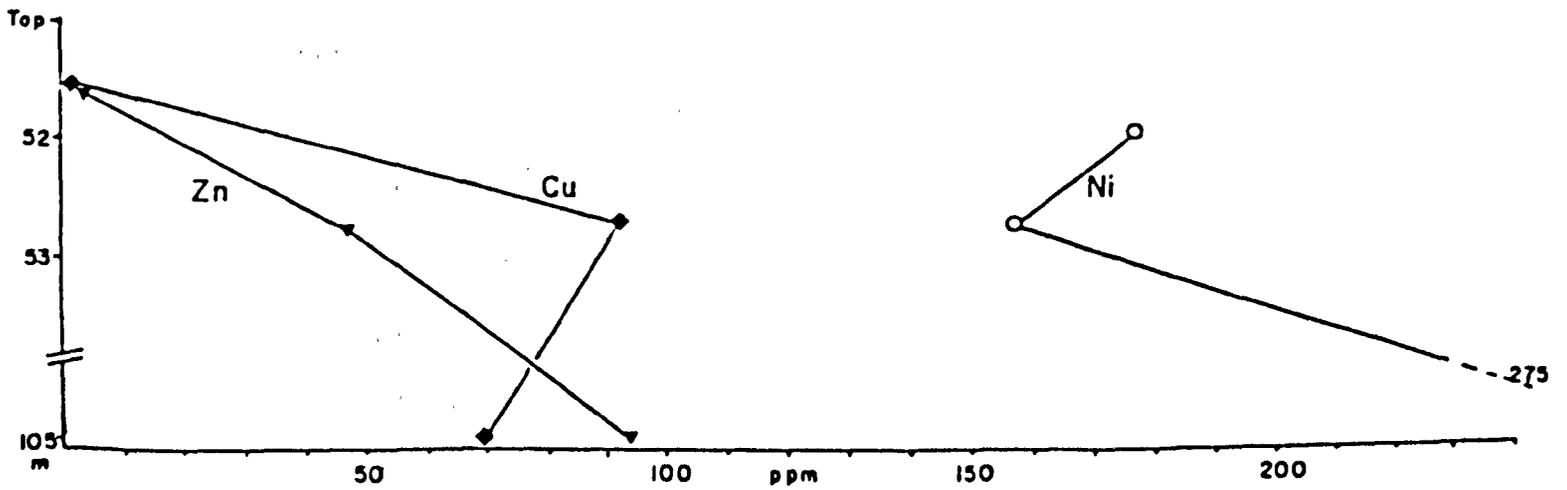
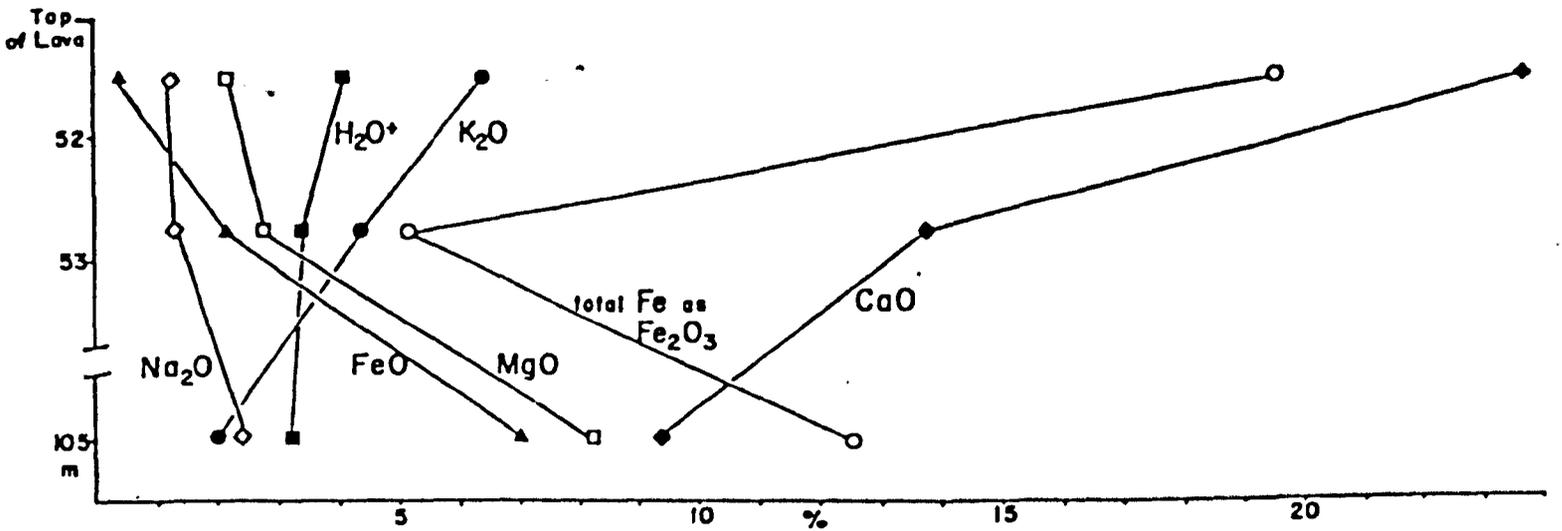


FIG. 10.2 GEOCHEMICAL VARIATIONS - UPPER TOADSTONE CLAY SEQUENCE OF THE CONKSBUARY BRIDGE LAVA, HADDONFIELDS No. 11 BOREHOLE

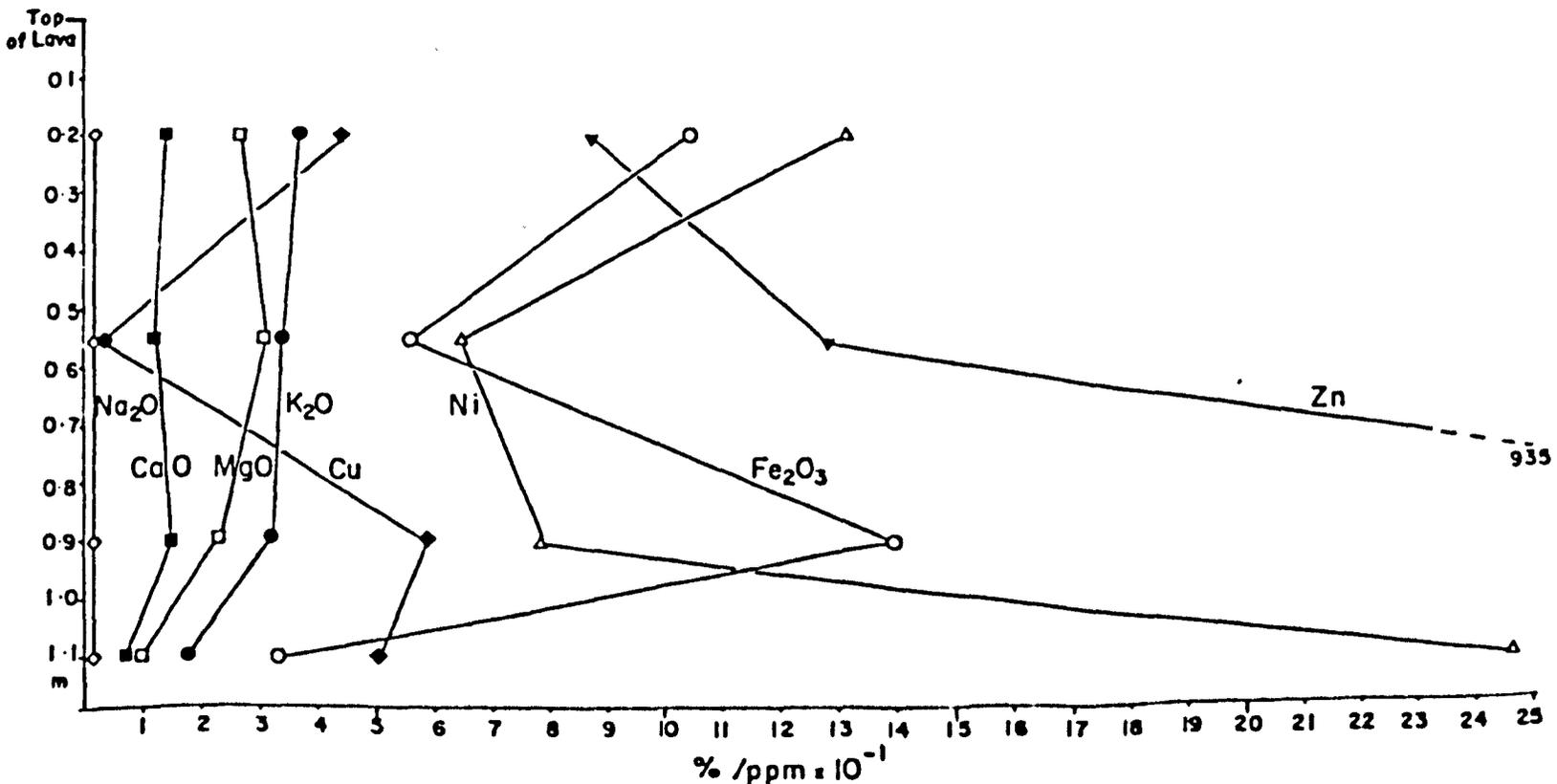
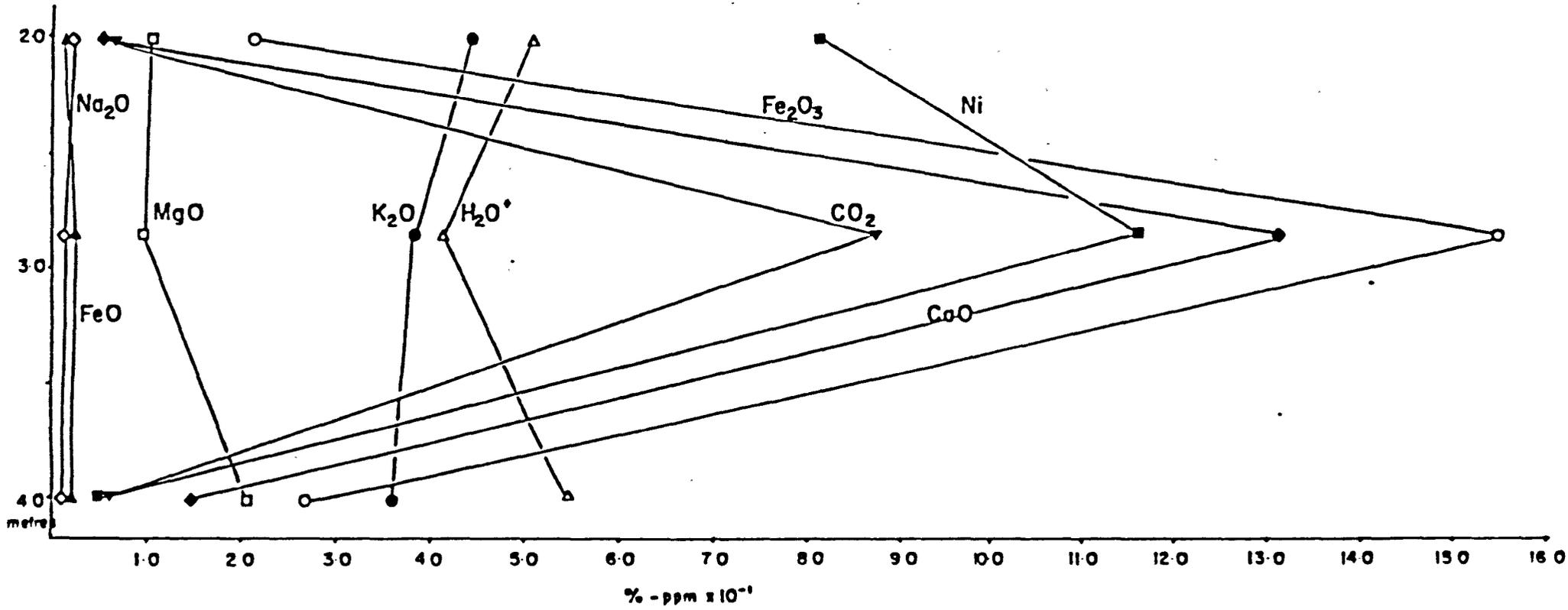


FIG. 10.3 GEOCHEMICAL VARIATIONS - UPPER TOADSTONE CLAY SEQUENCE OF THE MILLERS DALE LOWER LAVA, WHITE RAKE OPENCASE

The geochemistry of the toadstone-clay sequence (Figure 10.3) in comparison with 'average background' concentrations representing analyses of unaltered lava indicate a reduction in Na_2O , MgO and CaO and enrichment in K_2O towards the upper contact. Enhancement of Fe_2O_3 correlates with the occurrence of iron-staining representing pyrite oxidation. The lack of CaO and CO_2 enrichment contrasts with the previous examples, with extensive decalcification probably related to acidification of local groundwaters as a result of pyrite oxidation. This accounts for the more friable, 'clay-like' nature of toadstone clay sequences in exposed situations. Cu variations (Figure 10.3) parallel those of Fe_2O_3 and indicate the pre-oxidation association of chalcopyrite and pyrite. Minimal reduction of Zn is evident at the upper contact with a four-fold enrichment over background concentrations noted at lower horizons in the toadstone-clay sequence. Ni , initially reduced, is similarly enriched at lower horizons. These trends are comparable with those described in Chapter 9 associated with wall-rock alteration adjacent to mineralisation in basalts and it is noted that this locality is next to a major occurrence of such mineralisation (see Appendix 9)

d. Matlock Lower Lava, Hoptonwood Quarry

The Lava is 6.6 m thick and completely altered to a toadstone clay. On initial excavation of the section, relict textures indicated a clear division of the Lava into a lower tuff unit (3 m thick) with fragments of limestone and basalt in a fine-grained matrix and an upper horizon consisting of a single flow unit with thin vesicular margins. When first exposed the basalt and tuff were moderately coherent, although unsuitable for thin sectioning, but became friable and plastic over a short time period resulting in the obliteration of the relict textures. The top 0.35 m is marked by an orange, structureless clay



Cu below detection in all samples
 Zn below 15ppm

FIG. 10.4 GEOCHEMICAL VARIATIONS - TOADSTONE CLAY ALTERATION OF THE MATLOCK LOWER LAVA, HOPTONWOOD QUARRIES

Fig 10.4

overlying some 0.5 of bleached, vesicular lava. The central, non-vesicular, part of the flow unit is similarly bleached and traversed by numerous calcitic veinlets with pyrite. The upper contact of the tuff is pyritised with horizons of marcasite nodules (> 10 cm in diameter). The lower contact is marked by an orange clay overlying a mamillated limestone surface.

The geochemistry of the basalt and the tuff (Figure 10.4) indicates the extent of pervasive alteration that has taken place in that K_2O and H_2O^+ are enriched while Na_2O , MgO , FeO , Cu , Ni and Zn are reduced in all the samples. Enhancement of Fe_2O_3 and CaO at 2.85 m correlate with the occurrence of pyrite and calcite veining and the increased decalcification in the marginal areas arising from closer contact with circulating groundwater.

10:4 The Origin of the Toadstone Clays

A number of proposals regarding the possible origins of toadstone clays have been made by Garnett (1923), Walkden (1970), Ford (1977) and Amin (1980) and these include:

1. Alteration by present-day groundwaters
2. High temperature basalt/seawater interactions
3. Subaerial weathering contemporaneous with extrusion
4. The concentration of deuteric alterations at vesicular flow margins
5. Interactions with hydrothermal fluids related to mineralisation

Garnett (op. cit.) proposed that alteration resulted from the action of 'non-oxidising' groundwaters and that these conditions only prevailed in the presence of overlying limestone sequences. 'Oxidising' conditions were invoked to explain an apparent absence of toadstone clays from

outcrop localities resulting in the formation of a thin veneer of ochreous clays and 'sands'. This apparent anomaly arises from the restriction of toadstone clay sequences to the upper and lower contacts of a Lava or Sill while the exposures associated with red clay represent erosional levels within the basalt horizons, exhibiting the effects of recent weathering.

High temperature basalt/seawater interactions (Amin, 1980) are contrary to the paleo-environment of vulcanicity described in Chapter 3. Extrusive activity was predominantly sub-aerial and instances of localised entry of lava flows into water resulted in palagonite and breccia formation with oxidation and not toadstone clay formation. This proposal also fails to explain the absence of alteration from flow unit margins within composite Lavas.

Contemporaneous subaerial weathering with toadstone clays forming as 'boles' is a possibility in the envisaged paleo-environment. However, as Walkden (1970) recognised, weathering would not be expected to result in extensive alteration of the lower margin of Lavas and fails to explain the absence of toadstone clays within composite Lavas. Examination of discrete contacts between flow units (Appendix 7) indicate a degree of iron-staining and oxidation concentrated at the upper contact of the underlying flow unit and this probably represents the full extent of contemporaneous weathering. The geochemistry of toadstone clay alteration is also inconsistent with the processes of normal weathering (e.g. Lisitsyna, 1968).

The geochemistry and mineralogy of deuteric alteration (Section 9.10) is distinct from the effects of toadstone-clay alteration. However, the development of toadstone clay sequences in the vesicular margins of Lavas involves an overprint of the earlier phase of deuteric activity.

The spatial relationships between the intensity of alteration and mineralisation together with the geochemical and mineralogical similarities with undoubted hydrothermal alteration as well as K-Ar isotopic age dating results (Chapter 12) all indicate that toadstone-clay sequences are the result of interactions with the hydrothermal brines associated with mineralisation. The Lavas and Sills acted as aquicludes controlling the flow of hydrothermal fluids, with increased activity in the vicinity of major channelways such as Rakes or Pipe Veins resulting in the greater intensity of alteration. Toadstone-clay alteration in Millclose Mine (Traill, 1939, 1940) affects the lower margins of the Lavas where they formed 'cap-rocks' to the ascensive ore-bodies, while the upper margins were only altered where faulting had permitted the hydrothermal fluids to migrate through the Lavas.

10:5 Comparisons of Toadstone Clay and Wall-rock Alterations within Basalts

The geochemistry of the toadstone clay profiles (Figure 10.1 to 10.5) and the alteration in basalts (Chapter 9) exhibit similar trends, which are comparable with the smectite-rich argillic alteration described in the previous chapter. The failure to record the more extensive enrichments and depletions associated with advanced kaolinite-rich argillic alteration is attributed to the limited number of toadstone clay profiles sampled. The intense bleaching and alteration described by Garnett (1923) as the 'end product' was not located in the sampled profiles and its development can be inferred to represent the advanced kaolinite-rich alteration type.

Toadstone-clay sequences at the upper and lower contacts of Lavas incorporate altered vesicular and non-vesicular basalts, tuffs and wayboard clays. These pre-alteration variations in geochemistry and

mineralogy impose limitations on the isolation and interpretation of purely hydrothermal trends for which the sampling techniques of alteration within Lavas were specifically designed to overcome. Relict textures in coherent material usually enable the detection of these primary variations, however, the extensive effects of groundwater interactions involving pyrite oxidation and decalcification result in their obliteration. This is illustrated by the upper toadstone clay of the Matlock Lower Lava. Alteration in the Bonsall Basalt Quarry, Via Gellia is represented by some 3 m of iron-stained and green plastic clay. In the nearby Hallicar Wood Adit, decalcification is restricted to the uppermost 0.1 m and the iron stained clay grades into a 3.9 m sequence of bleached but coherent pyritised tuffs with graded bedding and containing fragments of limestone (Walters and Ineson, 1980b). In the excavated exposure of the Lava in Hoptonwood Quarry it is impossible to determine whether the top 0.35 m of iron-stained and decalcified clay represents a weathered tuff or a basalt.

CHAPTER ELEVEN



Chapter Eleven

Geochemistry and Mineralogy of 'Clay-Wayboards' - Geochemical Evidence for their Derivation

11:1 Nature and Occurrence of Wayboards

Thin, laterally persistent clay horizons interbedded with Dinantian carbonate sequences of England and Wales are commonly referred to as 'clay-wayboards' (Walkden, 1972) and the term is retained in the present account. Clay-wayboard horizons can be distinguished from thin shale or mudstone intercalations by their distinctive physical and mineralogical characteristics. These include the lighter colour, lack of fissility, low concentrations of free quartz, low organic carbon and the observation that wayboard clays become plastic and soft when wet with strong swelling characteristics. Mixed-layer illite-smectite, variable concentrations of kaolinite with minor components such as pyrite, gypsum, quartz and anatase are characteristic of wayboards in contrast to the mineralogy of shales and mudstones dominated by high levels of detrital quartz, mica and chlorite. Walkden (1972, 1974) and Somerville (1978) have demonstrated that the wayboards are typical K-bentonites derived from the degradation of volcanic ash. Ash horizons accumulated on lithified, emergent carbonate surfaces of probable eustatic origin. The morphology of the 'mamillated' or 'potholed' paleokarstic surfaces that commonly underlie wayboard horizons suggest prolonged periods of subaerial exposure. Comparisons with modern features of similar origin (Walkden, 1974) suggests that 'average' paleokarstic surfaces with amplitudes in the region of 0.5 m may represent emergence episodes of 30,000 to 100,000 year duration. Paleokarstic horizons of greater amplitude may represent periods of emergence up to one million years (Somerville, 1979a). The development of paleokarstic surfaces and clay-wayboards can be related to a lithostratigraphic cyclicity in the enclosing limestone. However,

cycles are often incomplete and the correlation of the individual wayboards can be speculative.

Dinantian clay-wayboards have been recorded from North Wales by Somerville (1979a,b,c) by Walkden (1972,1974,1977) from the south Pennines and in the Dinant area of Belgium by Thorez and Pirlet (1979). Their occurrence in the Askrigg area can be inferred from the description of 'shale units' by Waltham (1977).

11:2 Origin of Bentonites

Ross and Shannon (1926) defined bentonite as a rock composed essentially of a crystalline, clay-like mineral formed by devitrification and the accompanying chemical alteration of a glassy igneous material, in most cases of tuff or volcanic ash, and commonly containing variable proportions of accessory crystals originally present as phenocrysts in the volcanic glass. Bentonites of Mesozoic and Cainozoic age have montmorillonite as the dominant alteration phase, bentonites of Paleozoic age are potassium enriched with dominant mixed layer illite-montmorillonite and are termed K-bentonites (Schulz, 1962). Kaolinite-rich altered ash horizons typically associated with coal-seams are termed tonsteins (Williamson, 1970).

Relict textures indicative of a pyroclastic origin such as shards or phenocrysts are infrequently preserved in older bentonites due to degradation and diagenesis. Where relict textures are absent the contrasting mineralogy of bentonites and K-bentonites compared with the enclosing sediments, in particular the dominance of smectite or illite-smectite derived from smectite and the restricted heavy mineral suite, are used as indicators of a volcanic origin.

Bentonites, K-bentonites and tonsteins have been recognised from a wide range of sedimentary environments throughout the geological column

(Weaver, 1953; Slaughter and Earley, 1965; Mossler and Hayes, 1966; Cameron and Anderson, 1980). Within the British Carboniferous, in addition to the Dinantian occurrences previously cited, K-bentonites have been recorded from the Namurian shales of North Staffordshire and Derbyshire (Trewin, 1968) and numerous authors have described the occurrence, mineralogy and geochemistry of Westphalian tonsteins (Price and Duff, 1969; Williamson, 1970; Spears, 1971; Spears and Rice, 1973; Spears and Kanaris-Sotiriou, 1979).

11:3 Possible Source Area for the Clay-Wayboards

The majority of Dinantian clay wayboards do not exhibit thickness variations that can be used to infer possible volcanic source areas. Individual wayboards range from a few centimetres to over a metre in thickness. The average thickness of thirty clay-wayboards intersected in boreholes from Asbian limestone in Derbyshire was 13 cm (Cox and Bridge, 1977).

The origin of these thin laterally persistent horizons from volcanic ash falls presents problems with respect to Dinantian volcanicity in Britain which was dominated by localised areas of basaltic activity around Bristol, Derbyshire/Nottinghamshire, Limerick in Northern Ireland, and the Midland Valley of Scotland. The nature of basaltic volcanicity is unlikely to result in widespread ash dispersion, in addition, areas remote from these sources do not exhibit a marked decrease in the frequency of wayboards. The absence of isopachyte relationships in the wayboards has suggested to certain authors (Walkden, 1974; Somerville, 1979a) a derivation from atmospheric air-fall ash originating from the highly explosive eruptions associated with siliceous magmas. Although minor trachytic components have been noted from the Limerick area (Strogen, 1973) with more substantial acid lavas

and tuffs - trachytes and phonolites - recorded from the Midland Valley (Francis, 1967) this activity is insufficient to account for the frequency of the wayboards and more distal sources must be invoked.

However, in areas associated with basaltic activity some ash contributions of a purely local origin are also to be expected. Walkden (1972) noted a lenticle of vesicular basalt apparently degenerating into a 30 cm thick wayboard horizon south of Buxton. Walters and Ineson (1981) indicated that pyroclastic activity in the south Pennines was a minor component of the Lavas, related to phreato-magmatic interactions associated with the onset and cessation of extrusive activity. The explosive nature of this pyroclastic activity resulted in tuff horizons often exhibiting a greater lateral extent than the associated lavas. The Matlock Lower Lava, for example, is a composite unit some 100 m thick near source with the lower 40 m comprised of a variety of tuff and tuffaceous limestone intercalations. These tuffs rapidly thin away from the vent area but persist as a recognisable unit. At a distance of 4 km towards the south-west, at Hopton Wood Quarries, this tuff unit is 3 m thick overlain by only 3 m of lava. Beyond this point the lava dies out but the tuff persists. Pyroclastics associated with other Lavas are less extensive, the Matlock Upper Lava reaches a maximum thickness of some 35 m but over a distance of 3 km degenerates to a tuff horizon only 0.3 m thick. Whilst these thin tuff horizons may contain relict textures indicative of their local basaltic origin it has been observed that such features are obliterated during exposure and weathering.

Whilst a number of 'wayboards' in the south Pennines are likely to be of local basaltic origin, the nature of this activity is insufficient

to account for the frequency of clay-wayboards: over thirty such horizons being recorded from the Lower Asbian, Chee Tor Limestones in Great Rocks Dale by Walkden (1972). A dual origin can be proposed with the majority of wayboards derived from distal ash sources.

Similar relationships have been demonstrated amongst the Westphalian tonsteins. The majority of tonsteins show lateral persistence with no isopachyte indications of source areas. The Stafford Tonstein (Spears, 1970) has been correlated over an area of 7500 km² with an average thickness of 5 cm. Spears and Kanaris-Sotiriou (1979) have demonstrated an origin from distal acidic ash for the majority of tonsteins but in areas associated with local basaltic activity 'basic' tonsteins also occur. In the Midland Valley of Scotland, Francis and Ewing (1961) directly traced the origin of certain tonsteins back to basaltic extrusive centres and noted that these horizons usually extended up to 40 km from the source. The 'Black Rake' tuffaceous siltstone which occurs close to the horizon of the Clay Cross Marine Band in Derbyshire and Nottinghamshire (Francis et al., 1968) has been related to basaltic extrusive centres in the Kelham Hills. The tuff can be traced westwards from this source area and at a distance of some 40 km is represented by a 0.3 m thick horizon.

11:4 Comparisons of the Distribution Patterns of Recent Ash Falls with Clay-Wayboards

The nature of Carboniferous basaltic volcanicity has been shown to be responsible for ash blankets over tens, rather than hundreds, of kilometres. These observations are paralleled in studies of recent basaltic pyroclastic activity associated with Strombolian or Surtseyan (phraeato-magmatic) types of eruption (McDonald, 1972). Violent Strombolian type eruptions of Paracutin in 1946 resulted in a tephra layer

12 m thick in the vicinity of the central cone thinning to 0.3 m over a distance of 10 km. During the phraeato-magmatic phase of the 1963 eruption of Surtsey, basaltic ejecta reached heights of 10 km (Lamb, 1969). However, the total volume of magma involved in the whole eruption was 0.7 km^3 - two to three orders of magnitude less than the eruptions associated with silicic magmas.

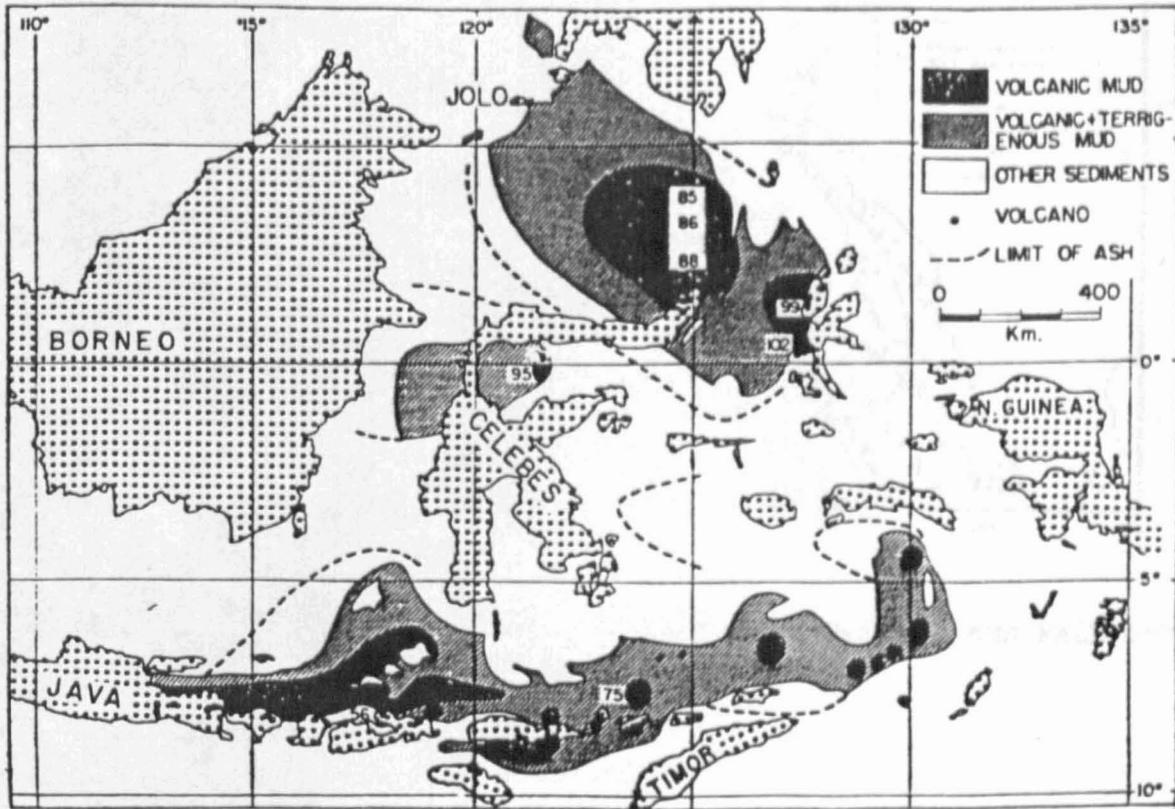
Plinian style eruptions usually involve rhyolitic, dacitic or trachytic magmas, resulting in violent catastrophic eruption of enormous volumes of tephra and caldera formation. The extreme violence of eruption results in ash ejection to heights in excess of 20 km and extensive atmospheric, air-fall, ash blankets. Plinian activity sensu stricto, produces voluminous pumice and ash falls which exhibit strong sorting and gradational characteristics related to distance from source. Variations on Plinian style eruptions are Phraeato-Plinian and co-ignimbritic types. These result in equally as extensive ash falls of more uniform, finer, grain size characteristics.

The Taupo Valley Volcanics, New Zealand (20,000 yrs BP) have been cited as an example of Phraeato-Plinian activity (Self and Sparks, 1978). The interactions of silicic magma and seawater generated some 75 km^3 of air-fall ash. The ash, unlike Plinian eruptions, was finely fragmented and only 5-6 m thick even in the vicinity of the Caldera, whilst at a distance of 800 km the ash layer averages 12 cm in thickness with a grain size $<1 \text{ mm}$. Co-ignimbritic air-fall deposits exhibit similar characteristics and occur as equal volume components with associated ignimbrites (Ninkovich et al. 1978). The eruption of Toba, Sumatra (75,000 yrs BP) is considered to have been amongst the greatest of eruptions during the Quaternary, in the order of two magnitudes greater than the eruption of Krakatoa, (Ninkovich et al., op.cit.). Some 1000 km^3

of ignimbrite and co-ignimbritic tephra resulted in an ash cover of approximately $5 \times 10^6 \text{ km}^2$ which can be traced and correlated in deep sea sediment cores over much of the Indian Ocean. The ash layer averages 40 cm in thickness 500 km from source and 10 cm at 2500 km. The height of the eruption column was estimated to be 50 km. By comparison, the Campanian and Minoan co-ignimbritic and Plinian phase ash falls (25,000 and 2,5000 years BP) extending across the Eastern Mediterranean only involved 60 km^2 and 28 km^2 respectively (Richardson, 1976; Barberi et al., 1978; Watkins et al., 1978). The Campanian eruption resulted in an ash layer 10 cm thick 600 km from source. These distribution relationships are summarised in Figure 11.1.

The Upper Pleistocene Los Chocoyas Ash, Guatemala (Hahn et al., 1979) of co-ignimbritic origin, blankets an area of $1 \times 10^6 \text{ km}^2$ with an estimated volume of 100 km^3 . A similar volume is estimated for the Middle Pleistocene Bishop Tuff, California (Hildreth, 1979). The 1932 eruption of Quizapu, Chile involving easterly dispersal of tephra resulted in a 1 cm thick layer 1000 km from source with fine ash falls detected up to 3000 km from source. Ash from the 1947 eruption of Mt. Hekla, Iceland, was detected over 5000 km away in Finland (MacDonald, 1972).

The dispersal of fine-grained volcanic ash in the atmosphere was investigated by Lamb (1969). The average height of eruption columns involved in Plinian activity is 20-30 km with eruptions of exceptional magnitude reaching 50 km. The bulk of ash-fall occurs over a period of days whilst the residence time of even ultra-fine ash rarely exceeds 15 years. Fine volcanic ash ($< 0.5\mu$) at heights in excess of 40 km resides approximately 12 years, at 25 km for 10 years and 15 km for 3 years. Dust in the 2μ range at 40 km resides only one year. The dispersal pattern of high altitude ash may depart noticeably from the



DISTRIBUTION OF LATE QUATERNARY VOLCANIC ASH IN THE EAST INDIES

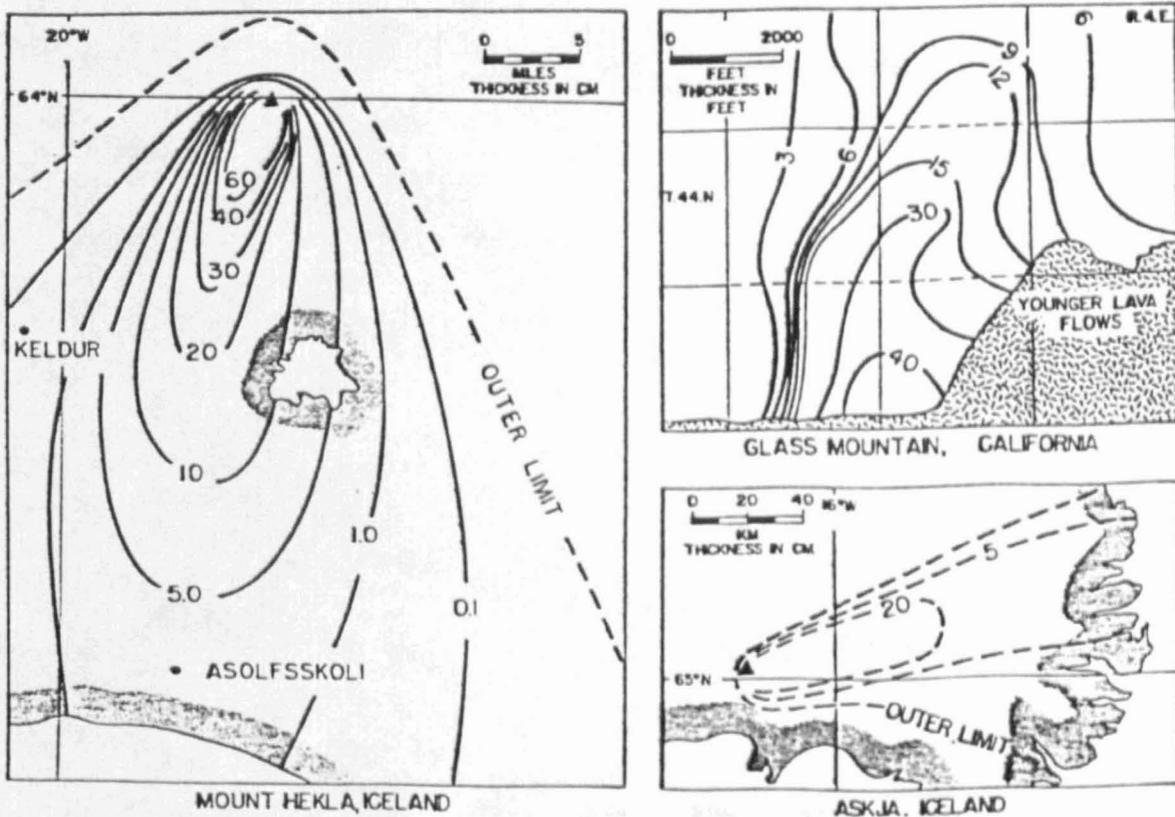


FIG. 11.1 DISTRIBUTION PATTERNS OF RECENT VOLCANIC ASH FALL DEPOSITS (data from Eaton, 1964. and Ninkovich et. al., 1978.)

Map showing the distribution of the Toba tephra layer

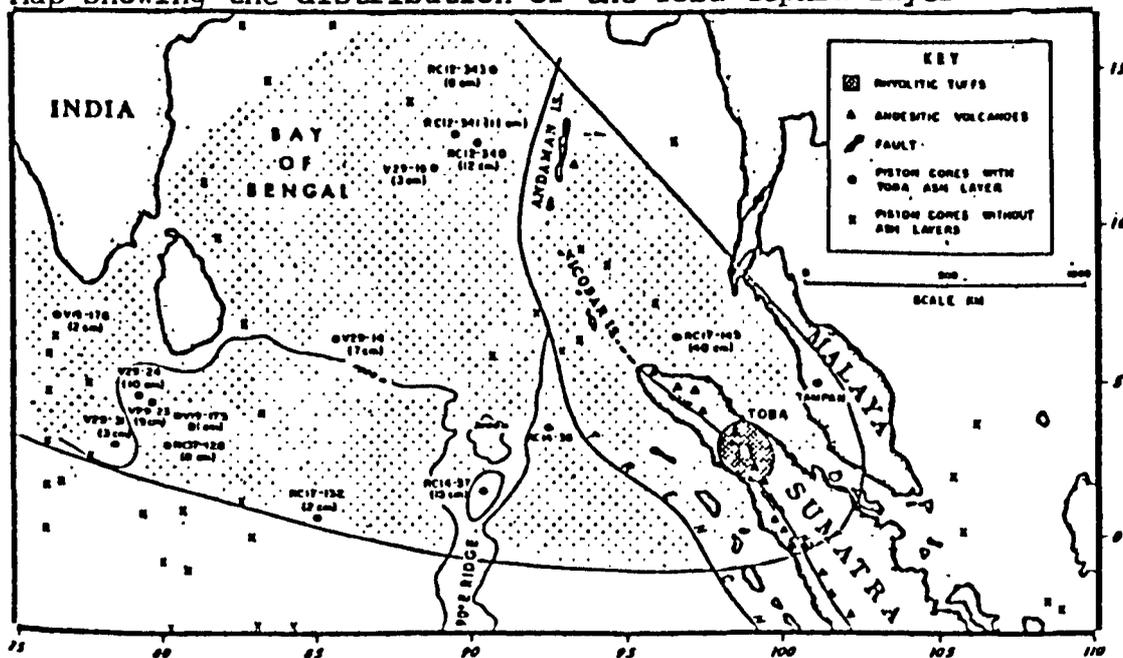
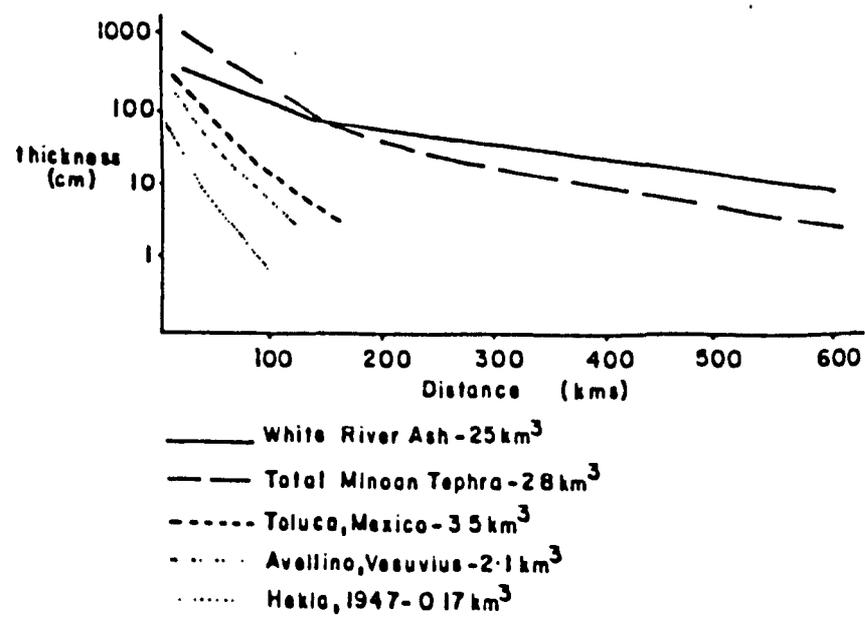
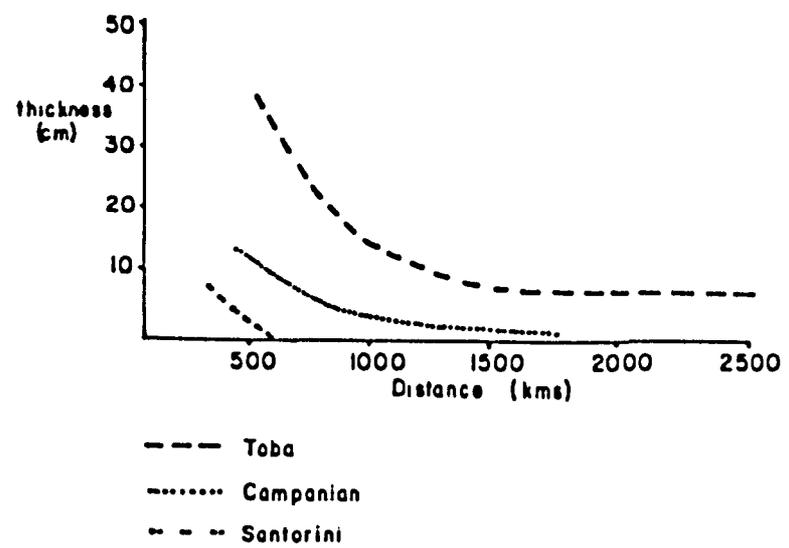


FIG 11.1 DISTRIBUTION PATTERNS OF RECENT VOLCANIC ASH FALL DEPOSITS (CONT.)



distribution of more voluminous lower altitude tephra influenced by local climatic factors. The coarse tephra blankets may be asymmetric and lobate with respect to its source (e.g. Kittleman, 1979) whilst ultra-fine dust is distributed globally as a 'dust-veil'.

Tephra eruptions associated with silicic magmas are capable of producing the widespread ash blankets of uniform thickness and fine grain size invoked as the origin of the majority of clay-wayboards. The question arises whether the frequency and volumes of the Dinantian clay-wayboards is compatible with this proposal. Ninkovich et al. (1978) noted that a study of Quaternary (duration 1.8 ma) deep sea sediments revealed 'hundreds of recognisable (discrete) tephra layers'. Sediments in the vicinity of Mount Rainier National Park, Washington (Kittlemann, 1979) contain 25 tephra layers produced within the last 20,000 years. There is no evidence that volcanic activity during the Quaternary was at an anomalously high level compared to the Carboniferous (MacDonald, 1972). Noting that compaction ratios of recent ash layers can exceed half the original, unconsolidated, ash thickness (Watkins et al., 1978), thicknesses in excess of 20 cm for Dinantian wayboards associated with emergence episodes in the region of 0.1 ma would suggest an origin from multiple ash falls. Namurian K-bentonites incorporated into sedimentary sequences represent individual ash falls and average 0.5 to 1.5 cm (Trewin, 1968), the Westphalian Stafford Tonstein averages 5 cm (Spears, 1970) further suggesting a multiple origin for the thicker Dinantian wayboards. Relict stratification within such wayboards is difficult to assess. The undulose base but planar upper surfaces implies some degree of reworking or deflation. However, certain wayboards exhibit clear stratifications (Worley and Dorning, 1977), whether this represents relict

stratification or structuring within a paleosol is uncertain. Vertical variations in composition and texture within thin wayboard horizons were noted by Thorez and Pirlet (1979).

11:5 The Application of Geochemistry to the Study of Volcanic Ash

Tephrochronology has been widely applied to the study of tephra layers within Quaternary sediments. Correlations on the basis of geochemistry and mineralogy have been reported by Bowles et al. (1973), Richardson and Ninkovich (1976); Hahn et al. (1979), Rose et al. (1979), Hildreth (1979) and Kettleman (1979). Richardson and Ninkovich (op.cit.) utilised K_2O , SiO_2 , Rb, Zr and Y concentrations for correlation whilst Hahn et al. (op.cit.) advocated ternary plots of Ba-Ti-Mn, Sr-Zr-Pb and Sc-Th-Hf. However, as Barberi et al. (1978) note, although comparative geochemical studies are readily applicable to recent ash deposits free from alteration phases, processes such as incipient zeolitization and the transition of ash to bentonite involve complex mobilisation effects of elements such as SiO_2 , Na_2O , K_2O , Sr and Ba.

In addition to selective alterations modifying original geochemistry, primary variations within tephra layers also occur. The geochemistry of fine-grained tephra is not identical to the bulk geochemistry of the pre-eruptive magma. Processes of selective vitric-crystal fractionation or 'aeolian' differentiation' have been documented by Walker (1972). The greater density of crystals relative to glass results in differential settling of phenocrysts and phenocryst rich pumice enriching the remaining ash in vitric components. In ignimbritic eruptions this effect is most marked with neither the geochemistry of ignimbrite nor co-ignimbritic tephra corresponding to the bulk geochemistry of the pre-eruptive magma. The net effect of vitric enrichment is to produce fine-grained tephra falls with a bulk geochemistry more 'evolved' than the

pre-eruptive magmas and depleted in elements associated with phenocryst phases such as apatite or zircon. An additional complexity is introduced by the possibility of varying magma compositions during an eruptive phase. Variations in composition may result in differing dispersal patterns, resulting in primary lateral geochemical variations within an individual tephra layer, e.g. see Hahn et al. (1979).

11.6 Objectives of the Present Study

Given the proposals outlined earlier that the majority of wayboards are derived from fine-grained acidic ash of distal origin but that in areas with contemporaneous basaltic activity, less extensive wayboards resulting from local basalt pyroclastic eruptions are also likely to be present, a pilot geochemical study was undertaken to ascertain whether this could be substantiated. Samples of wayboards from the Alston and Askrigg Blocks, the Mendips and Swansea areas and the south Pennines were obtained. The majority were collected from massive limestone sequences of Asbian age (further location details are given in Appendix 5). Samples from the south Pennines include a number of wayboard horizons suspected of having a local, basaltic origin either on the basis of indications of relict textures or stratigraphic horizons. Also included were less altered samples of undoubted basalt pyroclastic origin and altered basalts of 'toadstone-clay' type. As Walkden (1972) noted: on the basis of simple mineralogy altered igneous material of (basalt) pyroclastic or extrusive origin are indistinguishable from the wayboard clays. It was anticipated that the application of stable trace element techniques could be developed to discriminate wayboards of 'basalt' or 'acid' origin.

11:7 Mineralogy of the Clay Wayboards

Samples were prepared for XRD analysis as both whole rock smears and sedimented clay fractions. No significant differences in overall mineralogy were evident as a result of different preparation methods. The relative intensity of the reflections due to chlorite, however, were enhanced in clay fraction mounts whilst those samples with significant quartz reflections were enhanced in whole rock diffractograms. All samples were glycolated and heated to 450°C for 1 hour in order to test for the expansion and dehydration of smectites. The results are summarised in Table 11.1.

The clay mineralogy of the wayboards exhibit a high degree of uniformity. The dominant clay phase is interlayered illite-smectite. Combined (001)/(001) peaks are broad and asymmetric in the 10 to 11Å region. Many samples show only minimal displacement from the 10.0Å pure illite position but are distinctly asymmetric indicating a low percentage of the smectite component. Comparisons with the data of Hower and Mowatt (1966) indicate 10-15% smectite concentrations. Glycolation of combined peaks close to 10Å results in a small displacement to <10Å with indications of a broad and diffuse 'hump' in the 12Å region. Glycolation of combined peaks initially in the 11Å region results in the production of two new broad peaks in the 9.5-9.9Å and 12-13Å regions representing combined (001)/(001) and (001)/(002) peaks after expansion of the smectite phase. The majority of samples exhibit the former behaviour and do not resolve into two new peaks on glycolation. These can be compared with the low-smectite wayboard clays typically associated with pure, massive bedded shelf carbonate sequences noted by Walkden (1972). Heating to 450°C resulted in collapse of all combined peaks, producing a sharp peak at 10.0Å.

The response of illite-smectites to K^+ saturation is believed to indicate the nature of the parental clay species. Mixed-layering developed from an illite phase collapsing to 10.0\AA on saturation whilst mixed-layering developed from primary smectite exhibits only partial collapse towards 10\AA , (Weaver, 1958). Partial collapse during K^+ saturation has been cited as a diagnostic criterion in the identification of K-bentonites (Trewin, 1968; Walkden, 1972; Cameron and Anderson, 1980). The K^+ saturation responses of the wayboards analysed during the present study (Table 11.1) indicate partial collapse or, in the situation where initial combined peaks plotted close to 10.0\AA , retention of asymmetry, confirming their bentonitic origin.

All diffractograms exhibited further strong illite reflections at $c.5\text{\AA}$ and 3.3\AA with weak reflections at $c.4.5\text{\AA}$. The absence of non-basal reflections, particularly those at 3.6\AA and 3.05\AA and the weak 4.5\AA reflection suggest that the illite is a poorly crystalline polymorph, typical of K-bentonite (Yoder and Eugster, 1955; Mossler and Hayes, 1966). In addition to the dominant illite-smectite phase, moderate to strong reflections attributable to well-ordered kaolinite were present in four samples. Weak reflections at 3.5\AA are present in all samples, except when obscured by chlorite peaks, and represent anatase. Moderate quartz peaks are present in half of the samples, often enhanced by interference with the 3.3\AA illite peak, with weak or absent secondary quartz peaks. Traces of quartz, usually less than 5% are common in wayboards, (e.g. Walkden, 1972; Somerville, 1978). Traces of pyrite are noted in the majority of samples, an extremely high concentration ($>10\%$) is present in the Holme Park Quarry wayboards.

Chlorite is present in four samples, in the Mumbles Head wayboard in roughly equal concentration with the illite-smectite component. High chlorite concentrations are not typical of Dinantian wayboards

Table 11.1

TABLE 11.1 (Cont.): XRD Analysis of Clay Wayboards

Specimen Number*	Treatments		
	Glycolation	K+ Saturation	450°C for 1 hour
1	ND	10.80	10.00
2	9.55 & diffuse peak at 12.90	10.70	10.00
3	9.44 & diffuse peak at 12.63	ND	10.05
4	ND	10.30	10.05
5	10.0	10.0 (ayssm.)	10.00 (sharp)
6	10.05	10.0 (ayssm.)	10.00 (sharp)
7	9.83	ND	10.05
8	9.93 & diffuse peak around 12 ^o A	10.30	10.00
9	9.98	10.45	10.04
10	9.80 (broad)	10.45	10.00
11	9.85	10.10	10.00
12	10.04	10.20	10.00

Specimen Number*	Kaolinite	Chlorite	Quartz	Calcite	Anatase	Others
1 44	St	-	vw	St	m	-
2 45	St	-	vw	v.St	w to m	albite
3 47	St	-	-	-	m	albite
4 46	-	m	w to m	-	w	-
5 48	m	-	-	-	w	-
6 43	-	-	m	-	w	-
7 51	w	-	m	-	m	-
8 53	-	-	m	-	w	-
9 49	w	w	vw	-	w to m	-
10 50	-	St	vw	-	w	-
11 34	-	-	m	-	w	-
12 52	-	m	vw	-	w to m	-

(Walkden 1972) but have been noted as important components of certain Belgium Dinantian wayboards by Thorez and Pirlet (1979), of Silurian metabentonites (Cameron and Anderson, 1980) and from Ordovician K-bentonites by Weaver (1963b). Weaver (op.cit.) suggested that chlorite formation was favoured by Mg-availability under conditions of slow ash accumulation in shallow, carbonate rich waters. Whilst this may provide a possible explanation for the high chlorite concentration of the Mumbles Head wayboard its mineralogy is clearly atypical. An absence of detrital mica and low quartz concentration does not support a sedimentary 'contamination' origin & the significance of the chlorite remains uncertain.

All samples containing chlorite exhibited reflections at c.14.13, 7.07, 4.72 and 3.5Å, these were unaffected by glycolation but heating at 450°C for 1 hour resulted in a migration of the 14.13Å (001) peak to c.13.16Å with a reduction in intensity. The (001) and (003)-4.72Å peaks were enhanced relative to the 7.07 and 3.05Å peaks. In addition to chlorite, pyrite, quartz and anatase, a small number of samples contained additional components with traces of albite and high concentrations of calcite (Table 11.1).

The XRD results confirm that the wayboards have a dominant bentonitic origin. However, unlike bentonites occurring within sequences of continuous sedimentation which represent discrete volcanic events, clay-wayboards represent the coincidence of vulcanism with prolonged periods of emergence and subaerial weathering. Multiple ash accumulations, the possibility of non-volcanic contributions and the influence of non-volcanic components on geochemical discriminations must be assessed.

These components can be divided into three groups:

1. Residual: paleokarstic surfaces with a 'mamillated' relief in excess of 1 metre would be anticipated to result in a concentration of limestone insoluble residues available for incorporation into the overlying wayboard.
2. Terrigenous: thin sedimentary horizons - marls, mudstones and shales - interbedded with sequences of massive carbonates (e.g. see Somerville, 1979a - p.318, 1979b - p.398) may superficially resemble wayboards and raises the possibility of a terrigenous component in wayboards.
3. Non-volcanic atmospheric dust: slow but continuous accumulation of atmospheric dust, similar in composition and origin to that responsible for loess deposits, given emergence episodes in the order of 0.1 ma may result in significant contributions to the wayboards.

Quartz constitutes the main component of limestone insoluble residues; as euhedral authigenic crystals, detrital grains, silicified fossil debris or chert. In chert-free, high purity Asbian limestones, insoluble residue concentrations rarely exceed 1%. The data of Cox and Bridge (1977) for the Derbyshire area indicate an average residue concentration of 0.2%. After quartz, illite and organic matter constitute the dominant components of residues with minor kaolinite or illite-smectite (Cox and Bridge, op.cit.; Walkden, 1972). A paleokarstic surface involving the dissolution of 1 m of limestone with a residue content of 0.2% would result in the concentration of a layer of insoluble residues 0.2 cm thick (of a similar order to the dark insoluble linings coating many stylolite surfaces). Incorporation of this residue into an 'average' volcanic paleosol 10 cm thick results in a non-volcanic component of 2% of which some 1.6% represents quartz. The addition of quartz has no effect on the application of trace-element discriminations

and it can be concluded that in the majority of instances the incorporation of insoluble residues will not be geochemically significant. The main indications of an abnormally high insoluble component would be high concentrations of euhedral, authigenic, quartz grains, phosphate material and discrete illite.

Discrete 10\AA 'illite' or 'mica' is characteristic of a terrigenous component (Spears and Kanaris-Sotiriou, 1979) and its absence from wayboard clays is a strong indication for an absence of 'sedimentary contamination'. High concentrations of detrital quartz can also be diagnostic of sedimentary components, free quartz contents below 5% are typical of Carboniferous K-bentonites (Walkden, 1972; Somerville, 1978; Spears and Kanaris-Sotiriou, 1979). However, secondary siliceous alteration of basalts in the southern Pennines is a common feature and the high quartz content of the Alport Borehole 'palagonite tuff' for example, can be attributed to such an origin. Thorez and Pirlet (1979) noted the occurrence of quartz 'splinters' or acicular fragments in Belgian wayboards representing replaced pyroclastic material.

The application of heavy mineral analysis to detect 'contaminations' has been advocated by Weaver (1963a). Euhedral apatite and zircon, together with biotite and Fe-Ti oxides, were considered to represent the 'primary' suite of bentonites (Weaver op.cit.). Tourmaline, muscovite, light coloured garnets and metamorphic minerals such as kyanite, staurolite, etc. are indicators of sedimentary components. Weaver (1963b) noted rounded tourmalines and zircons together with a high concentration of colophonane bone fragments as the dominant insoluble components of Ordovician limestones. Restricted heavy mineral suites have been used to indicate the absence of sedimentary contamination in tonsteins (Spears, 1970). Few detailed studies of wayboard heavy mineral suites have been undertaken. Somerville (1978) indicated a restricted

suite of apatites and zircons in wayboards from North Wales, whilst Thorez and Pirlet (1979) noted euhedral apatites and zircons with biotite constituting the heavy mineral assemblage of Belgian wayboards. The systematic investigation of heavy mineral suites and the nature of the free quartz component could provide important evidence concerning possible non-volcanic contributions to bentonites, but this was beyond the scope of the present study.

The detection of atmospheric dust components is difficult and has not been appraised by previous authors. Modern loess deposits consist of over 80% silt size quartz grains (Pettijohn, 1975). Presumably wind derived material of sedimentary origin would also contain a small proportion of the characteristic heavy mineral suite and high concentrations of discrete mica. A wind-borne component in limestone insoluble residues would also be expected. In the absence of detailed studies of heavy mineral suites the main indicator for an absence of significant non-volcanic, atmospheric, components must be the minimal geochemical modifications exhibited by pyroclastic horizons of undoubted basaltic origin accumulated on paleokarstic surfaces compared with the primary compositions of pyroclastic material incorporated into volcanic sequences.

11:8 Application of Geochemical 'Fingerprinting' to the Study of Carboniferous K-Bentonites and Tonsteins

Somerville (1979a) raised the possibility that individual Dinantian clay-wayboards might have their own geochemical 'fingerprints' which could be used for large scale correlations. Unpublished major element analyses of thirty clay-wayboards from the Asbian of North Wales with 'semi-quantitative' values for Zr, Sr, Rb and Ba (Somerville, 1978) and 'semi-quantitative' trace element data for eight wayboards from Masson Hill Quarry (Ixer, 1972) comprised the only geochemical wayboard

data available prior to the present study and this data was unsuitable on which to test this proposal.

By way of contrast, the Westphalian tonsteins have received considerable geochemical investigations. Spears and Rice (1973) established that certain trace elements, particularly Zr, Y, Sn, Ti, Cr, V, Th and Ga, were quantitatively retained in resitate minerals during the transition of ash to bentonite and tonstein (see Figure 11.2).

Fig 11.2

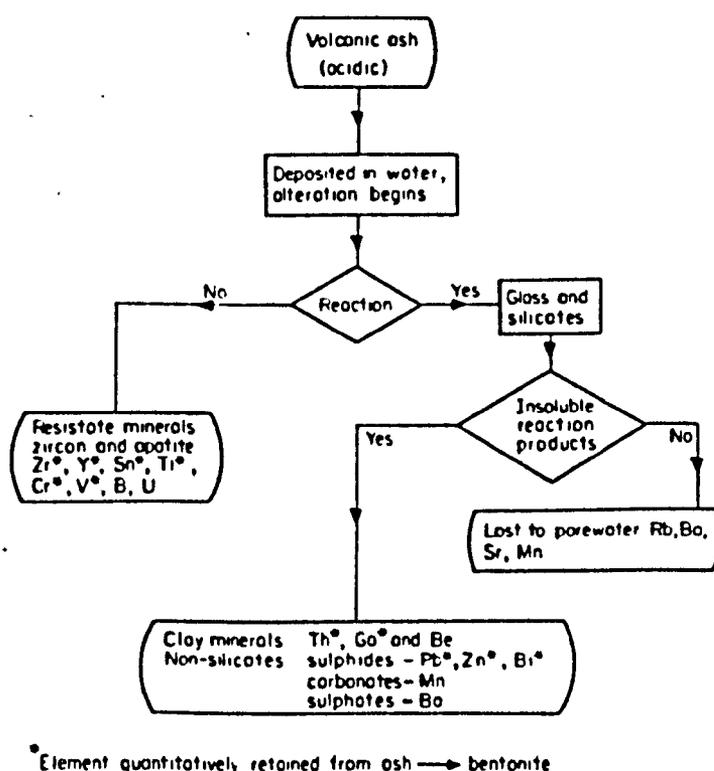


FIG. 11.2 TRACE ELEMENT BEHAVIOUR AND LOCATION DURING DIAGENESIS OF THE SUPRA WYRLEY TONSTEIN. (from Spears and Kanaris-Sotiriou, 1979)

The technique was developed further by Spears and Kanaris-Sotiriou (1979), in which multivariate discriminant groupings based on Ti, Ni, Cr, Zr relative to Al_2O_3 were used to compare tonsteins with 'average' basalt, mudrock, andesite and granite analyses. Tonsteins of local, basaltic, origin and distal acidic derivation were discriminated using these groupings.

It was anticipated that similar techniques applied to a study of Dinantian wayboards might clarify the proposals regarding their dual origin. However, the multivariate discriminant approach of Spears and Kanaris-Sotiriou (op.cit.) has a number of inherent short-comings. The geochemical definition of the discriminant groups is wholly reliant on the suitability and applicability of the analyses utilised in their construction. The definition of 'basalts' in Spears and Kanaris-Sotiriou based on the data of Livingstone and McKissock (1974) fails to recognise the implications that this represents the results from a single borehole and that the basalts exhibit strong pervasive alterations. The definition of 'acid' tuffs using granite analyses fails to recognise modifications resulting from the crystal/vitric aeolian differentiation processes outlined earlier. A discriminant grouping for mudrocks is of dubious applicability, its apparently successful application in Spears and Kanaris-Sotiriou arising from the dominance of kaolinite in tonsteins relative to mudrocks (and normal bentonites) related to the special conditions of coal formation (Spears, 1971) and the expression of trace element concentrations relative to $Al_2O_3\%$. As Pettijohn notes (1975, p.305) the geochemistry of acid pyroclastics is similar to that of a range of immature sediments.

A furtherpoint of distinction between tonsteins and wayboards is the almost ubiquitous association of low-temperature Pb-Zn-F-Ba mineralisation in the 'block' areas of Dinantian carbonate sedimentation (e.g.

see Ford, 1976; Ineson, 1976). The interactions between the hydrothermal brines and basalts in the south Pennines have been outlined in the preceding chapters and involved complex leaching and enrichment relationships. The clay mineralogy of 'toadstone-clays' and wayboard clays are identical and similar geochemical modifications to that exhibited by the altered basalts can be presumed to have taken place within the wayboard horizons. This is supported by the results of K-Ar dating (Ineson and Mitchell, 1973) which indicates K-enrichment of wayboards may relate to episodic mineralisation rather than diagenesis. Any assessment of bentonite parental compositions must exclude elements associated with mineralisation. Amongst the trace-elements these include Pb, Zn, Cu, Ni and Ba. Ni, used as a discriminant element by Spears and Kanaris-Sotiriou (op. cit.) is highly mobile. Geochemical study of altered basalts and tuffs further indicates the mobility of Sr and Rb, invalidating their use by Somerville (1978). As outlined in sections 7.7 and 8.4, TiO_2 , Zr and P_2O_5 can be regarded as 'immobile' elements during basalt alteration, in addition Al_2O_3 , Y and V exhibit minimal mobilisation even under conditions of intense hydrothermal leaching. The 'immobile' element geochemistry of the wayboard clays, basalt tuffs, altered basalts, some common igneous rocks and fine grained sediments are displayed in a series of ternary plots (Figures 11.3, 11.4, 11.5, 11.6, 11.7).

The relative K-enrichment of the majority of wayboards is evident on a plot of $\text{K}_2\text{O}-\text{TiO}_2-\text{Al}_2\text{O}_3$. Certain wayboards and hydrothermally altered basalts and tuffs exhibit a slightly reduced relative K-enrichment. On plots of $\text{TiO}_2-\text{Zr}-\text{Y}$, $\text{TiO}_2-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$, $\text{TiO}_2-\text{Al}_2\text{O}_3-\text{Zr}$ and $\text{TiO}_2-\text{V}-\text{Zr}$ the altered basalts and tuffs and those wayboards suspected of having a basaltic origin all fall within the restricted field defined by analyses

FIG. 11.3 TiO_2 -Zr- Al_2O_3
GEOCHEMISTRY OF WAYBOARDS,
LAVAS, TUFFS & SEDIMENTS

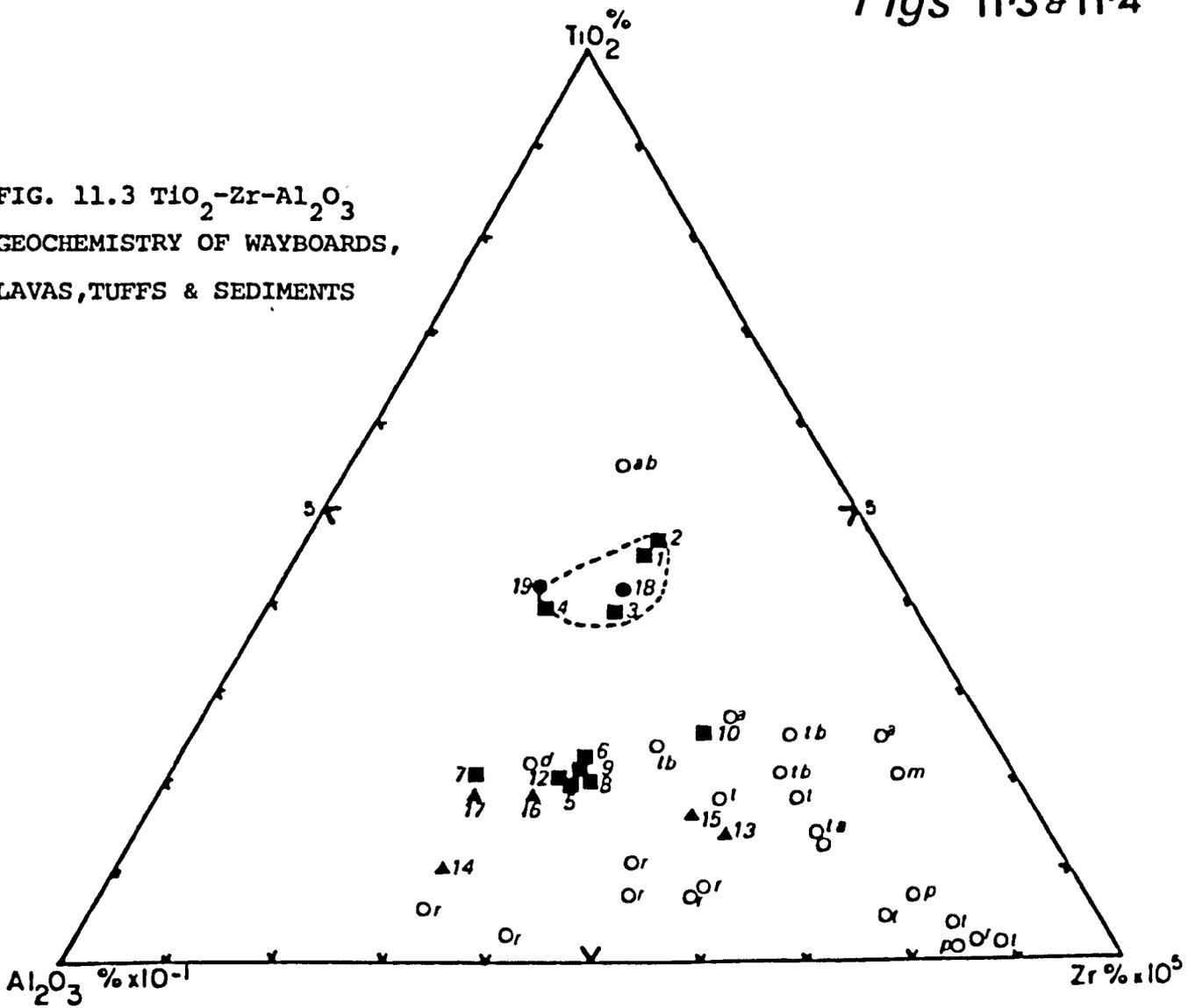


FIG 11.4 TiO_2 - Al_2O_3 - K_2O
GEOCHEMISTRY OF WAYBOARDS,
LAVAS, TUFFS & SEDIMENTS

FOR KEY SEE FIG. 11.7

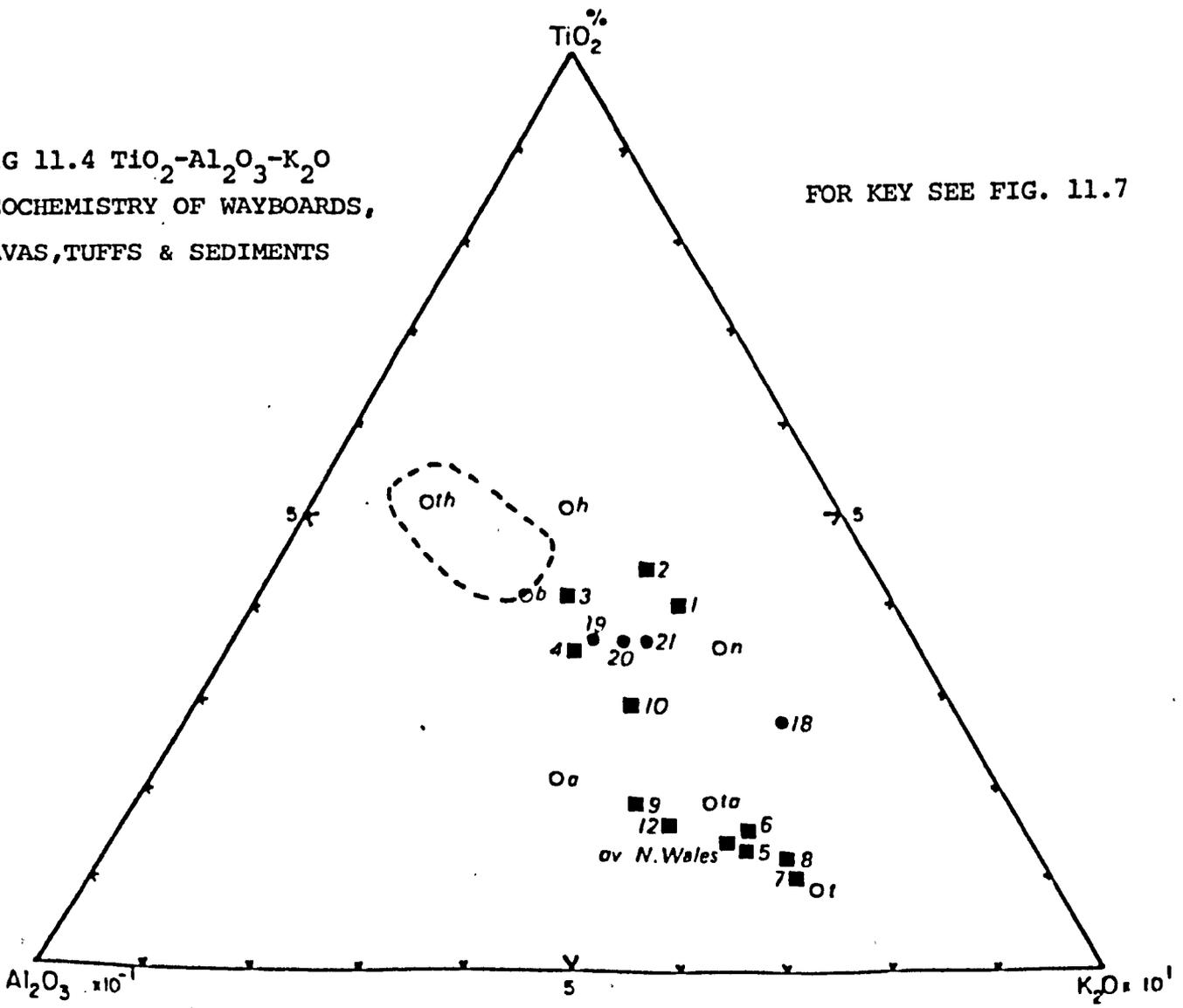


FIG. 11.5 TiO_2 -Y-Zr
GEOCHEMISTRY OF WAYBOARDS,
LAVAS, TUFFS & SEDIMENTS

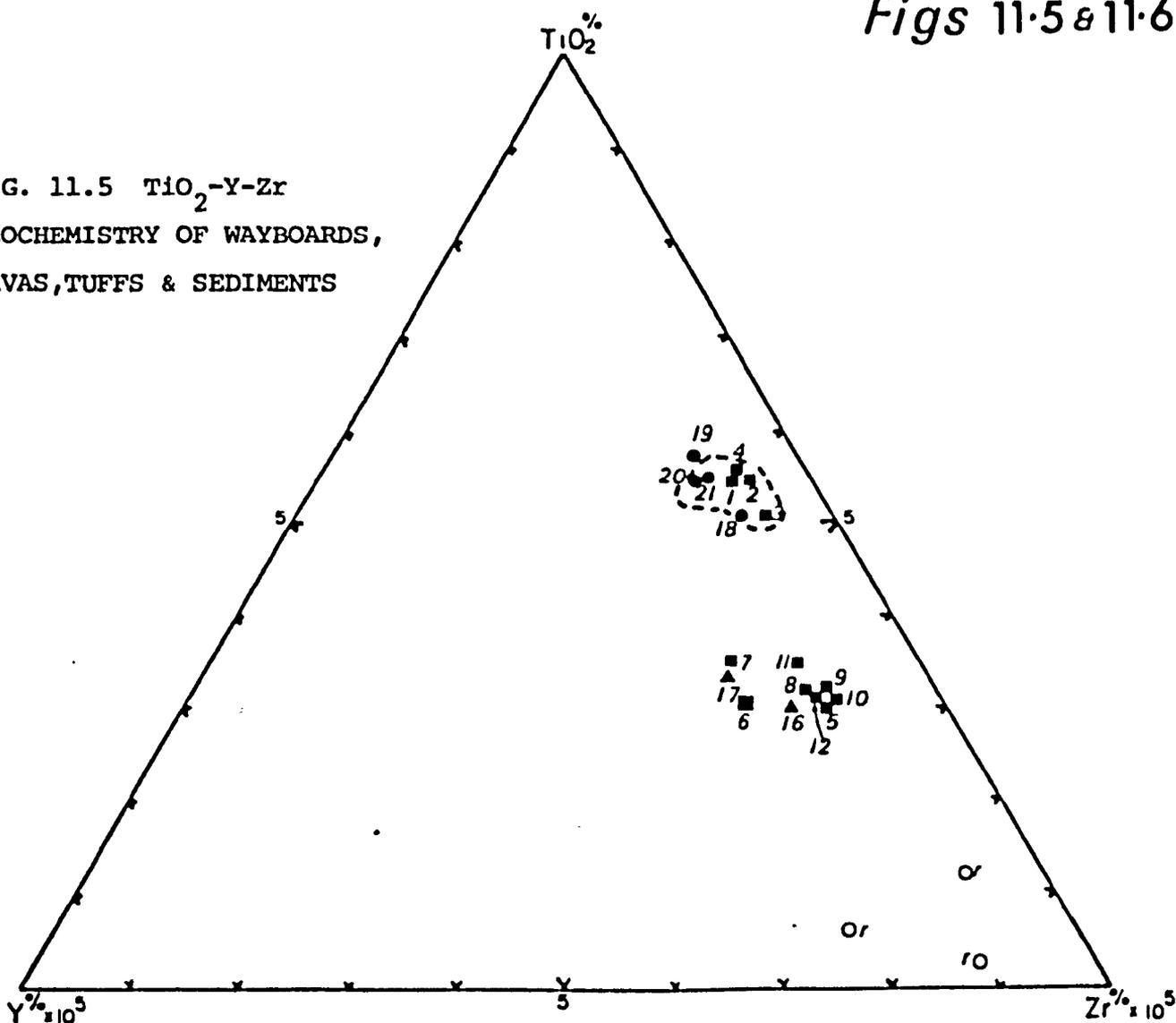


FIG 11.6 TiO_2 - Al_2O_3 - P_2O_5
GEOCHEMISTRY OF WAYBOARDS,
LAVAS, TUFFS & SEDIMENTS

FOR KEY SEE FIG 11.7

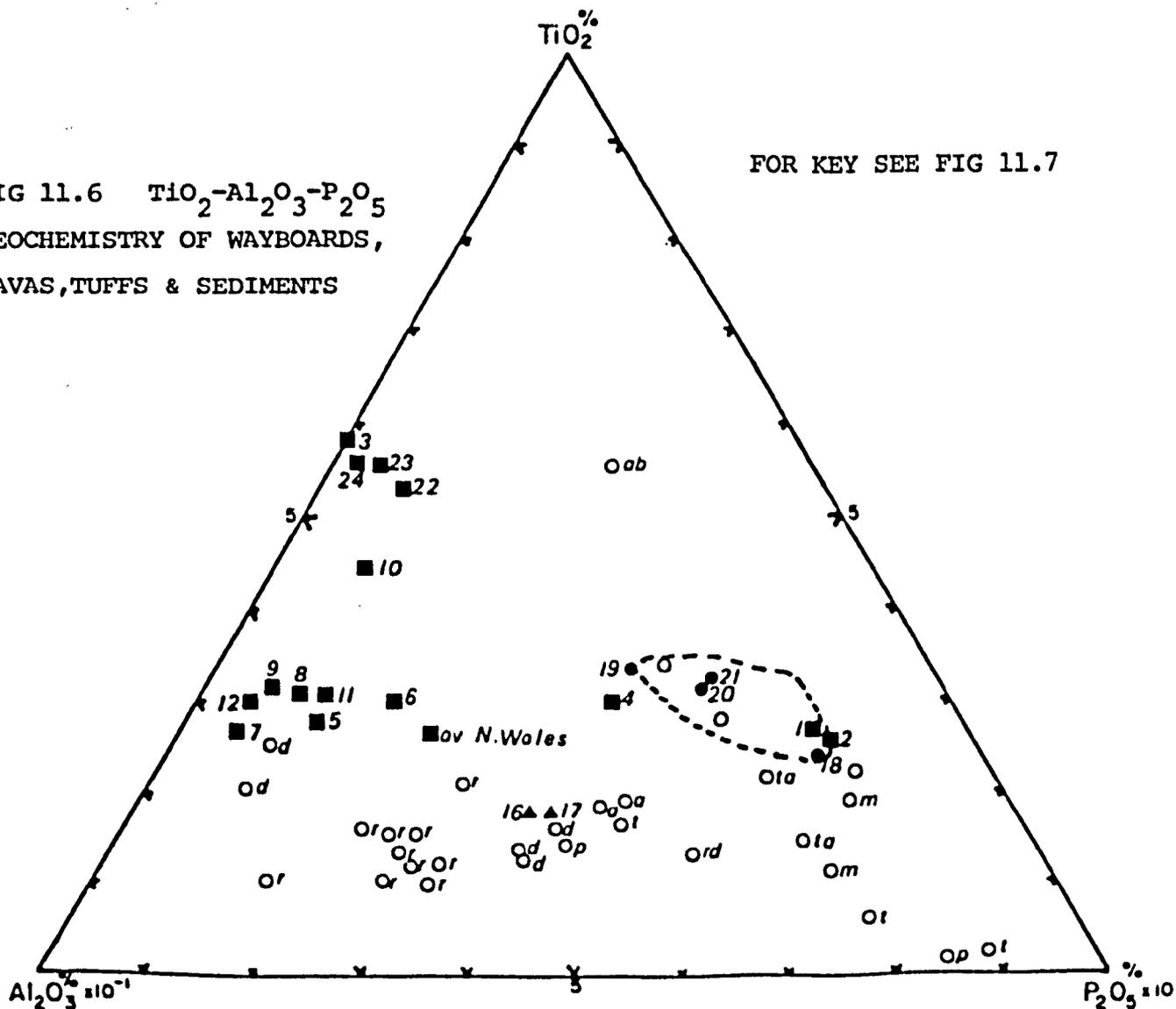
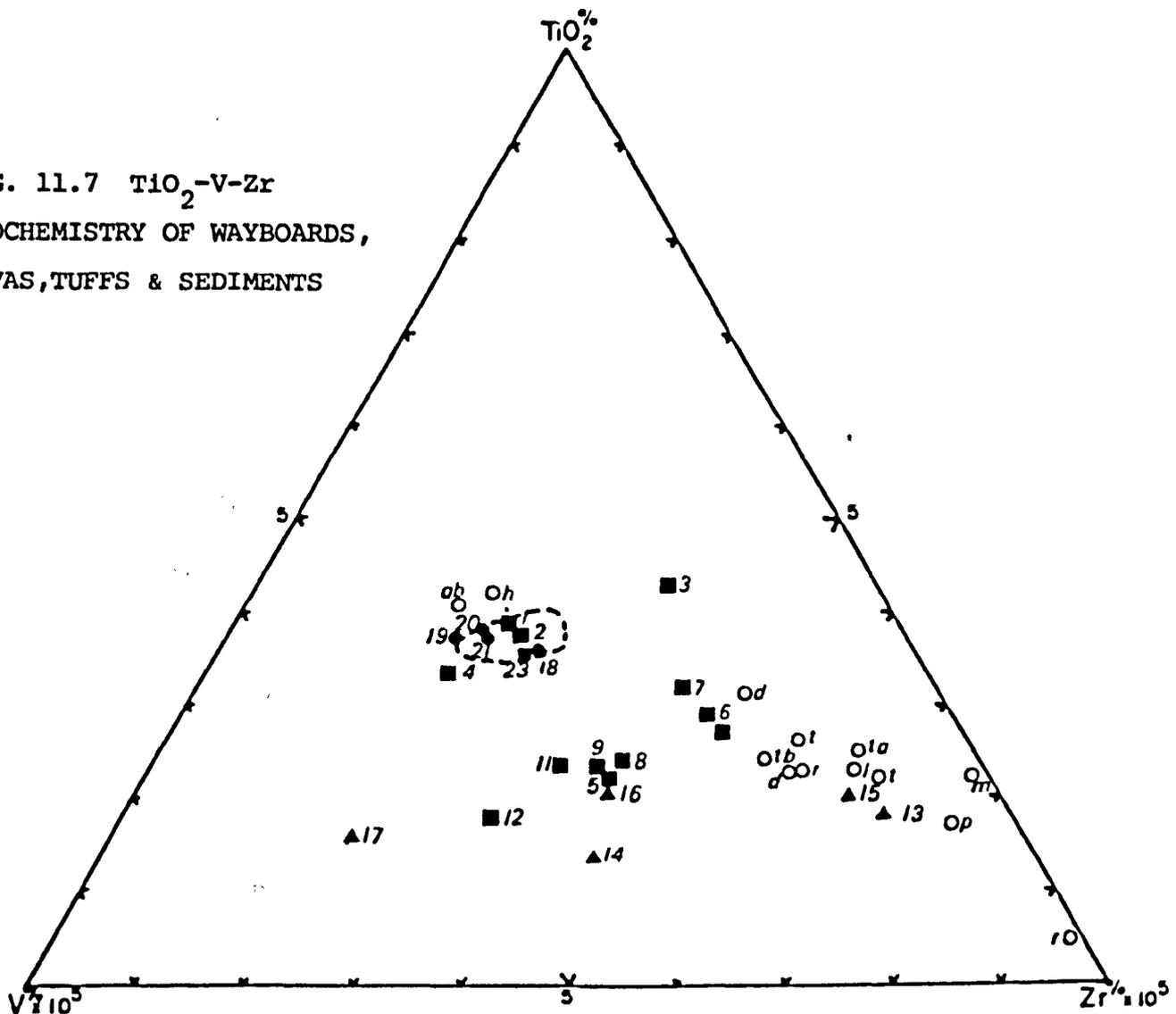


FIG. 11.7 TiO_2 -V-Zr
GEOCHEMISTRY OF WAYBOARDS,
LAVAS, TUFFS & SEDIMENTS



Wayboard samples (numbers refer to Table 11.1)



Altered basaltic tuffs and lavas. 18-Upper toadstone clay, Conksbury Bridge Lava. 19-tuff at top of Cressbrook Dale Lava. 20, 21-Lower Toadstone clay, Millers Dale Lower Lava. 22, 23, 24-Upper toadstone clay, Matlock Upper Lava (Amin, 1980.)



Average sediment compositions. 13-average silty shale, 14-calcareous mudstone, 15-sideritic shale:-Rookhope Borehole (Hirst & Kaye, 1971.) 16-average Namurian non-marine shale, 17-average Namurian marine shale;-Tansley Borehole (Amin, 1980.)



Lava, tuff and ignimbrite analyses. ab-alkali basalt, th-tholeiite, h-hawaiite, b-avrage basalt, a-andesite, tb-trachybasalt, m-mugearite, ta-trachyandesite, t-trachyte, d-dacite tuff, p-phonolite, r-rhyolite, (data from Cook, 1966. Coates, 1968. Johnson & Arculus, 1978. Le Maitre, 1976. McBirney, 1969. Carmichael et. al., 1974. Hahn et.al. 1979.)



Field of south Pennines basalt analyses.

of unaltered basalts from the South Pennines. The remaining wayboard clays fall in a restricted field clearly separate from the basalts. The chlorite-rich Mumbles Head wayboard occupies an intermediate position on a number of plots. Average analyses of Upper Visean and Namurian mudstones and shales (Hirst and Kay, 1971; Amin, 1980) although often distinct from the wayboard field, represent averages within which compositions identical to certain wayboard clays can be found confirming the observation of Pettijohn (1975) noted earlier.

A more complex relationship is apparent on a plot of $\text{TiO}_2\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5$. Although the dominant feature is the two-fold wayboard groupings present on all plots, a number of samples - representing basalt tuffs - exhibit anomalously low P_2O_5 concentrations whilst retaining the $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratios characteristic of basalts. These samples either contain high pyrite concentrations or have been in proximity to such concentrations. As Weaver (1963a) and Spears (1966) note, apatite is a stable mineral under normal conditions but can be mobilised by solutions with a low pH. It is envisaged that P_2O_5 has been selectively leached from these samples due to the action of groundwaters locally acidified by pyrite oxidation.

It is of interest to note that the 'basic' wayboards fall within the fields defined by unaltered basalts. This suggests that the influence of non-volcanic components discussed previously was not significant. The 'Little Toadstone' horizon is in fact a tuffaceous limestone further indicating that components such as calcite or quartz have no effect on trace-element discriminations.

Comparisons of the 'non-basic' wayboard geochemistry with a range of volcanic products does not indicate a close correlation in the majority of cases. Concentrations of P_2O_5 and Zr are relatively low compared with expected rhyolitic or andesitic compositions. A few

analyses of dacitic tuffs fall in the wayboard field but on the whole the wayboards appear to represent compositions 'more evolved' than even highly acidic volcanic products. This lack of correspondance may be a function of the dominance of lava analyses rather than tuffs in the comparisons and the influence of extreme selective vitric/crystal enrichment operating on distal pyroclastic compositions. Analyses of proximal pyroclastic falls of rhyolitic and dacitic type do exhibit a degree of Zr and P_2O_5 depletion suggesting that the wayboards represent the products of distal ash fall of 'acidic' origin.

11:9 Summary and Application of the Geochemical Results and Suggestions for Future Research

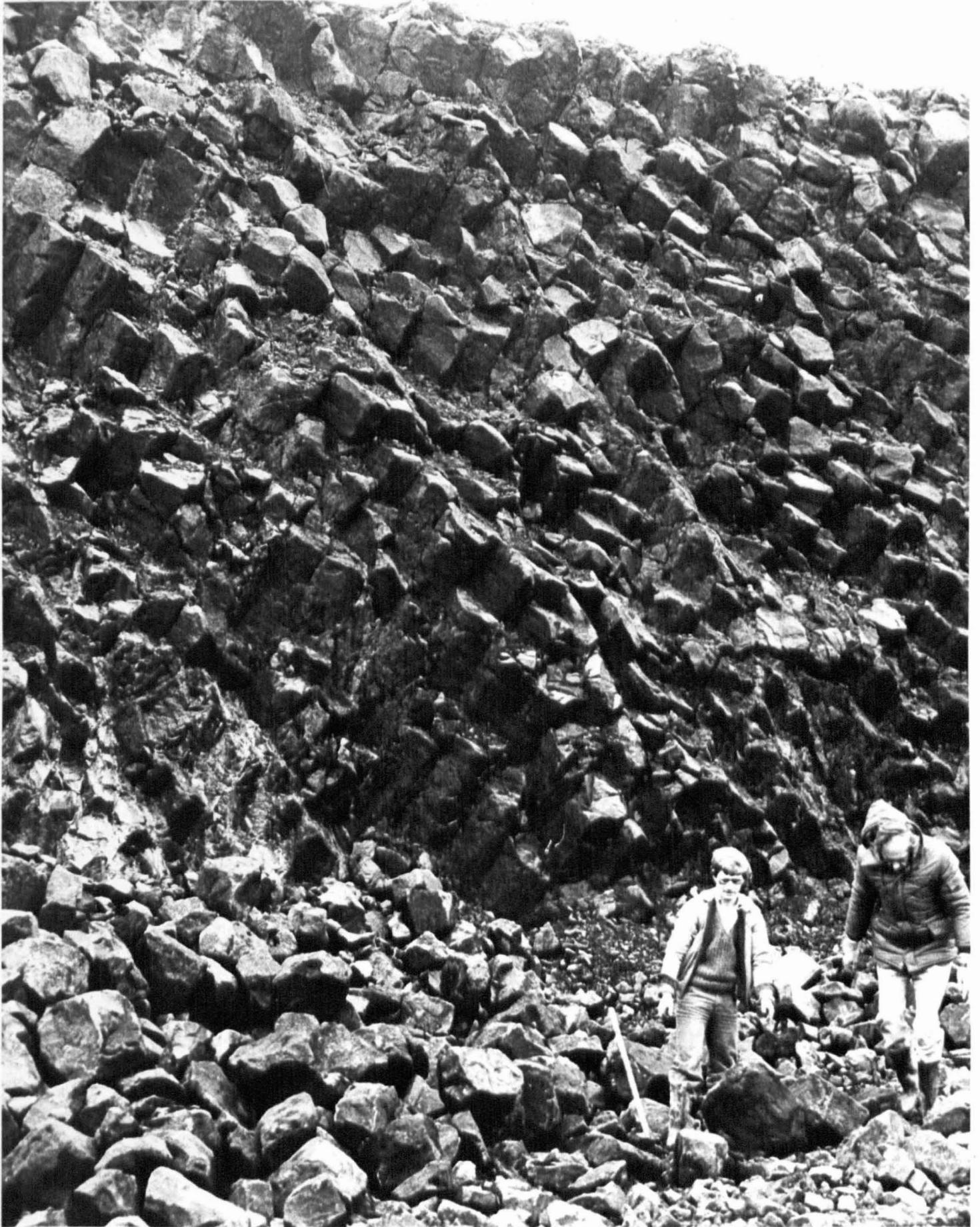
Considering the small number of analysed wayboards and their wide geographic distribution, this aspect of the present study must be regarded as a 'pilot' project. The aims of this project were to assess possible shortcomings, to prove the validity of various proposals and to outline profitable areas for further research.

It is concluded that stable-element discriminations can distinguish between 'basic' and 'acidic' wayboards. Whilst the geochemistry of altered and degraded basaltic material is sufficiently distinctive to contrast with associated sediments, 'acid' bentonites and immature clastic sediments cannot be distinguished on the basis of geochemistry alone and their distinction is based on mineralogical criteria. The assessment of 'non-volcanic' contributions has not received sufficient attention and the study of heavy mineral suites and quartz components to detect 'contamination' is necessary. Regarding the possibility of geochemical 'fingerprinting' and its application in correlations, there appears little prospect of developing an applicable technique. Primary geochemical variations within individual wayboards, multiple ash falls during a single

emergence episode and localised effects of non-volcanic components would be expected to introduce variable modifications to any 'unique' geochemistry.

However, in areas with associated basaltic activity, in particular the south Pennines, the recognition of basic wayboards distributed over tens rather than hundreds of kilometres could be an important tool in local stratigraphic correlations. Over thirty discrete basaltic Lava and Tuff horizons have been recorded from the South Pennines (Walters and Ineson, 1981) and it should be possible to erect a 'basalt stratigraphy' over the area resulting in a vastly improved stratigraphic framework. Given the continuation of basalt volcanism during the Namurian in the Nottingham area and the general westerly paleowinds the technique may also be applicable to a study of Namurian bentonites in the south Pennines.

CHAPTER TWELVE



Chapter Twelve

K-Ar Isotopic Age Determinations

12:1 Introduction and Analytical Techniques

Whole rock K-Ar isotopic age dating of basalts is one of the most important aspects of the technique and its applications are described by Dalrymple and Lanphere (1969), and York and Farquhar (1972). The susceptibility of basaltic material to undergo hydrothermal alteration, with attendant potassium enrichment, led Fitch et al. (1964, 1970) Dunham et al. (1968) and Ineson and Mitchell (1973) to propose that the K-Ar ages from such material could be related to the age of the associated hydrothermal event.

Fifty K-Ar isotopic age determinations were undertaken on basalts from the south Pennines (Table 12.1) by Dr. J.G. Mitchell at the School of Physics, University of Newcastle. K_2O concentrations were determined as triplicate analyses using an E.E.L. 450 Flame Photometer with a lithium internal standard. Duplicate analyses of radiogenic argon were determined by standard isotope-dilution techniques employing an M.S.10 Mass Spectrometer coupled to an on-line gas-extraction system. Theoretical aspects of the dating technique were described in Dalrymple and Lanphere (1969) and Mitchell (1972). The decay constants used are those proposed by Stöiiger and Jäger (1977) and all age determinations are quoted with one standard deviation estimates of experimental precision.

Coarse-grained 'unaltered' samples were analysed as whole-rock chips in order to avoid possible argon loss during fine grinding. The hydrothermally altered basalts were analysed as both whole rock chips, powder and clay concentrates. Clay concentrates were prepared by a sedimentation technique from disaggregated or minimally ground material. The mineralogy of the altered samples is described in Chapter 9. Mixed

layer illite-smectite, kaolinite and calcite constitute the dominant phases with subordinate albite, quartz, anatase and sulphides.

The investigation had three objectives:

- i. To appraise the suitability for dating of the least altered basalts and dolerites, employing strict selection criteria.
- ii. An extension of the work of Ineson and Mitchell (1973) in resolving the thermal events associated with mineralisation in the south Pennines.
- iii. To examine the relationships between the intensity of alteration and variations in the apparent ages previously reported (op.cit.).

12:2 Dating of Unaltered Basalts

Inherent limitations in the application of K-Ar isotopic dating of basalts and in particular with respect to material in excess of 200 m.y. old, were outlined by York and Farquhar (1972). Basalts are particularly susceptible to the effects of incipient alteration and weathering. Webb and McDougall (1967) indicated that alteration, devitrification or recrystallisation of the potassium bearing phases results in the loss of radiogenic argon accumulated up to the time of alteration. The finer-grained alteration products may subsequently lose argon by continuous diffusion at low temperatures. In assessing the suitability of basalt material for dating an understanding of the relationships between potassium distribution, alteration phases and their capacity for argon retention is essential. Material characterised by a concentration of fine-grained alteration phases with a low argon retention capacity will not therefore yield geologically significant ages.

Miller and Musset (1963), and Dalrymple and Lanphere (1969 - Figure 10.13) have demonstrated potassium enrichment in the residual fraction

of basalt melts which crystallise as interstitial glass, quartzo-feldspathic intergrowths or potash feldspars. Direct correlation between anomalously young K-Ar ages attributed to argon loss and the degree of alteration exhibited by the interstitial phases have been reported by Miller and Musset (1963), Webb and McDougall (1967), Vandoros et al. (1966) and Dalrymple and Lanphere (1969). Practical difficulties are encountered in the detection of incipient alteration involving fine-grained phases and Amaral et al. (1966) noted that even with the application of strict petrographic selection criteria age variation of up to 8% occurred amongst samples of Mid-Cretaceous Brazilian basalts from identical stratigraphic horizons. Irrespective of secondary alteration, primary undevitrified glass can be of either an argon retentive or unretentive nature. York and Farquhar (1972) noted that an undevitrified Pre-Cambrian pseudo-tachylite from Quebec gave an age of 975 m.y. while in a number of instances similar material of much younger stratigraphic age exhibited excessive argon loss resulting in anomalously young ages. Webb and McDougall (1967) found that samples of Middle Tertiary Australian basalts containing between 15 to 20% altered interstitial phases gave K-Ar ages 15 to 20% lower than concordant ages obtained on sanidine from interbedded trachyte flows. However, samples exhibiting partial, but still significant, alteration of interstitial phases yielded geologically acceptable ages. Vandoros et al. (1966) concluded that although relict interstitial glass resulted in argon loss, complete deuteric alteration associated with 'chlorites', etc. was associated with minimal argon diffusion and yielded acceptable ages.

Previous K-Ar age determinations on south Pennine basalts (Fitch et al., 1964, 1970) represented random sampling from a limited number of Lavas and Sills where no attempt was made to select the least

altered material or to assess the possibility of selective argon loss. Accordingly the results exhibited a spread of anomalously young ages which were attributed (Fitch et al., 1970) to the interactions between subsequent magmatic and hydrothermal events. Samples from the Waterswallows Sill (Stevenson et al. 1970) yielded three 'concordant' ages of 311 ± 6 m.y. which were interpreted as indicating the true age of emplacement. However, no attempt was made to assess the suitability of the dolerite for whole-rock dating.

Interstitial phases and plagioclase constitute the principal potassium bearing phases of the basalts. Microprobe analyses of plagioclase (Appendix 6) indicate an average K_2O content of 0.2% (range 0.1 to 0.4%) and given average plagioclase contents of 50% (Appendix 4) some 0.1% of the 'whole rock' K_2O is accommodated in the plagioclase phase. The average whole rock K_2O (0.75%) is therefore concentrated in the interstitial phases which average 15% by volume. Primary phases are represented by glass and rare analcite. Partial devitrification accompanied by exsolution of iron oxides and smectite replacement is a ubiquitous feature and in the majority of instances complete replacement by iron-rich smectite aggregates is noted (see sections 4.5, 4.6 and Plates 2.1 and 2.2). Samples selected for dating either exhibited a proportion of relict glass or minor concentrations of interstitial phases.

The stratigraphical range of the Lavas is from Middle Asbian to Middle Brigantian. This delimits their 'true' radiometric ages to between 330 to 340 m.y. (George et al. 1976) and enables a check on the validity of the whole rock dating. There is no such control on the interpretation of the K-Ar ages obtained for dolerite sills and the age of the 311 m.y. (i.e. upper Namurian) reported by Stevenson et al. (1970) for the Waterswallows dolerite is the only previously available

result with respect to the age of intrusive activity in the south Pennines.

The whole-rock ages obtained for 'unaltered' basalts (Table 12.1) range from 334 to 230 m.y. with distinct groupings around 310 and 280 m.y. The Shacklow Wood Lava (Sample 16) contains a high proportion of relict glass and the age of 331 ± 3 m.y. can be regarded as a 'true' age. The remaining basalt lavas give anomalous ages of 316 ± 6 and 317 ± 3 (9), 312 ± 4 (101), 281 ± 3 (1) and 288 ± 5 (28). These results are comparable with those obtained by Fitch et al. (1970) of 311 ± 9 and 315 ± 12 for the Millers Dale Upper Lava, and 313 ± 16 for the Shacklow Wood Lava attributed to "... a subsequent period of hydrothermal activity, possibly one associated with a repetition of basaltic magmatism". Considering the ubiquitous occurrence of interstitial alteration phases it is more probable that partial argon diffusion rather than a hydrothermal resetting of the K-Ar 'clock' is responsible for the discrepantly low ages. A 'true' age of 335 m.y. can be 'converted' into an 'apparent' age of 315 m.y. by the loss of 6.7% radiogenic argon and 280 m.y. by the loss of 17% argon.

Petrographically, it was not possible to distinguish samples giving ages of 310 m.y. or 280 m.y. likewise potassium enrichment related to hydrothermal alteration (Chapter 9) was not noted. A number of whole-rock samples were subjected to fine-grinding in a Tema Mill and left to stand for six months before being dated. The results indicate (Table 12.2) that where K-Ar ages of around 330 to 310 m.y. were obtained on unground chip samples, fine-grinding of the same material resulted in ages around 280 m.y. Where the initial chip material gave ages of 280 m.y. fine-grinding did not significantly alter this age. It is proposed therefore that the grouping of ages around 280 m.y. represents the maximum level of argon loss by

TABLE 12.1: K-Ar Dating Results

Locality Reference Number*	Sample Horizon	Sample Type [†]	K ₂ O Content (%)	Radiogenic Argon Content (mm ³ /gm ⁻¹)	Atmospheric Contamination (%)	Age (m.y.)
9	Haddonfield Lower Lava	Holocrystalline lava (WR)	0.62	$(6.90 \pm 0.06)10^{-3}$	32.2	316 ± 6
			0.51	$(5.73 \pm 0.05)10^{-3}$	32.1	317 ± 3
55	Waterswallows Sill-Lower Horizon	Holocrystalline dolerite (WR)	0.34	$(2.70 \pm 0.02)10^{-3}$	45.4	230 ± 4
		Holocrystalline dolerite (WR)	r.a.(x)	$(2.72 \pm 0.02)10^{-3}$	49.7	232 ± 4
		Holocrystalline dolerite (WR)	0.28	$(2.41 \pm 0.02)10^{-3}$	47.5	246 ± 3
		Holocrystalline dolerite (WR)	r.a.	$(2.48 \pm 0.02)10^{-3}$	47.0	253 ± 3
		Holocrystalline dolerite (WR)	0.57	$(5.49 \pm 0.05)10^{-3}$	31.3	278 ± 3
		Holocrystalline dolerite (WR)	r.a.	$(5.54 \pm 0.05)10^{-3}$	34.0	280 ± 3
1	Conksbury Bridge Lava	Holocrystalline lava (WR)	0.87	$(8.52 \pm 0.09)10^{-3}$	43.2	281 ± 3
			0.85	$(8.42 \pm 0.07)10^{-3}$	24.0	284 ± 3
137		Partly altered lava (WR)	1.60	$(1.16 \pm 0.01)10^{-2}$	41.0	212 ± 3
139		Hydrothermally altered and bleached lava (CF)	1.94	$(1.36 \pm 0.01)10^{-2}$	47.3	205 ± 2
28	Millers Dale Lower Lava	Holocrystalline lava (WR)	0.22	$(2.22 \pm 0.04)10^{-3}$	69.7	288 ± 5
29		Altered non-vesicular lava, part of 'toadstone clay' sequence (WR)	1.86	$(1.27 \pm 0.01)10^{-2}$	49.0	200 ± 2
			r.a.	$(1.26 \pm 0.01)10^{-2}$	46.0	199 ± 2
30		Altered vesicular lava, part of 'toadstone clay' sequence (WR)	1.94	$(1.48 \pm 0.02)10^{-2}$	48.1	222 ± 3
			r.a.	$(1.45 \pm 0.02)10^{-2}$	45.4	218 ± 3
3	Conksbury Bridge Lava	Altered vesicular lava, part of 'toadstone clay' sequence (WR)	4.09	$(3.34 \pm 0.03)10^{-2}$	24.6	237 ± 2
162	Shacklow Wood Lava	Bleached and pyritized non-vesicular lava adjacent to mineralisation (WR)	1.17	$(1.01 \pm 0.01)10^{-2}$	36.7	249 ± 3
163		Pyritized, non-vesicular lava (WR)	1.08	$(9.76 \pm 0.10)10^{-3}$	45.7	260 ± 3
16		Unaltered, holocrystalline lava (WR)	0.61	$(7.10 \pm 0.06)10^{-3}$	31.2	331 ± 3
41	Potluck Sill	Coarse, ophitic dolerite (WR)	0.74	$(8.25 \pm 0.08)10^{-3}$	28.2	316 ± 5
42		Bleached and altered dolerite (WR)	0.86	$(6.03 \pm 0.09)10^{-3}$	62.8	205 ± 3
			r.a.	$(5.94 \pm 0.09)10^{-3}$	66.6	202 ± 3

37	Ible Sill	Coarse, ophitic dolerite (WR)	0.66	$(7.81 \pm 0.07)10^{-3}$	41.3	334 \pm 10
36a		Chloritised, albitised dolerite (WR)	1.21	$(1.17 \pm 0.01)10^{-2}$	26.4	277 \pm 3
36b		Chloritised, albitised dolerite (WR)	1.33	$(1.11 \pm 0.01)10^{-2}$	34.0	242 \pm 3
38a		Chloritised, albitised dolerite (WR)	1.17	$(1.01 \pm 0.01)10^{-2}$	36.0	249 \pm 2
38b		Chloritised, albitised dolerite (WR)	1.07	$(1.15 \pm 0.01)10^{-2}$	21.8	306 \pm 3
39a		Chloritised, albitised dolerite (WR)	2.18	$(1.84 \pm 0.01)10^{-2}$	26.8	244 \pm 2
39b		Chloritised, albitised dolerite (WR)	2.24	$(1.87 \pm 0.01)10^{-2}$	15.7	242 \pm 2
101	Matlock Lower Lava	Sampling traverse adjacent to small mineral vein, +2.2 m from datum - partly altered holocrystalline lava (WR)	0.54	$(5.94 \pm 0.08)10^{-3}$	63.2	312 \pm 4
104		+0.8 m from datum (WR)	1.14	$(7.82 \pm 0.06)10^{-3}$	24.9	201 \pm 2
107		+0.2 m calcitised lava (WR)	1.15	$(8.83 \pm 0.10)10^{-3}$	49.2	224 \pm 3
		r.a.		$(8.94 \pm 0.09)10^{-3}$	44.4	226 \pm 3
109		0.0 m datum, calcitised and bleached lava (WR)	3.51	$(2.97 \pm 0.03)10^{-2}$	23.6	245 \pm 3
111		-0.2 m, bleached-argillised lava (CF)	4.32	$(3.54 \pm 0.03)10^{-2}$	19.5	237 \pm 3
114		-0.5 m, bleached-argillised lava (CF)	6.17	$(6.05 \pm 0.05)10^{-2}$	13.4	281 \pm 3
115	Millers Dale Upper Lava	Sample traverse adjacent to Pb-Zn vein, +1.7 m from datum - iron stained, calcitised non-vesicular lava (WR)	1.76	$(1.03 \pm 0.01)10^{-2}$	37.4	173 \pm 3
120		+1.2 m from datum (WR)	2.95	$(1.64 \pm 0.01)10^{-2}$	20.3	165 \pm 2
123		+0.9 m (WR)	3.56	$(1.46 \pm 0.01)10^{-2}$	28.8	123 \pm 1
127		+0.5 m bleached-argillised lava (WR)	5.27	$(2.81 \pm 0.02)10^{-2}$	23.3	158 \pm 1
130		+0.3 m bleached-argillised lava (WR)	3.64	$(1.93 \pm 0.02)10^{-2}$	23.1	157 \pm 2
131		+0.2 m bleached-argillised lava (WR)	3.70	$(1.98 \pm 0.02)10^{-2}$	27.3	159 \pm 2
132		+0.1 m bleached-argillised lava (WR)	1.95	$(1.17 \pm 0.01)10^{-2}$	34.4	177 \pm 2

All K_2O are average triplicate analyses, rounded to two decimal places, Argon values are average duplicate determinants.

* - Further location details are given in Appendix 5

† - WR - whole rock; CF - clay fraction

(x) - Repeat argon determinations

$$\begin{aligned} \text{Decay constants: } \lambda_e &= 0.581 \times 10^{-10} \text{ yr}^{-1} \\ \lambda_\beta &= 4.962 \times 10^{-10} \text{ yr}^{-1} \\ \frac{40x}{x} &= 1.167 \times 10^{-2} \text{ atom.} \end{aligned}$$

Table 12.1
(cont)

TABLE 12.2: K-Ar Dating Results for Whole Rock Chip and Tema Ground Samples

Locality Reference Number*	Sample Horizon	Sample Type	K ₂ O Content (%)	Radiogenic Argon Content (mm ³ /gm ⁻¹)	Atmospheric Contamination (%)	Age (m.y.)
1	Conksbury Bridge Lava	Whole-rock, chips	0.85	$(8.42 \pm 0.07)10^{-3}$	24.0	284 ± 3
1a	Conksbury Bridge Lava	Whole-rock, powder (stood for 6 months)	0.87	$(8.52 \pm 0.09)10^{-3}$	43.2	281 ± 3
41	Potluck Sill	Whole-rock, chips	0.74	$(8.25 \pm 0.08)10^{-3}$	28.2	316 ± 5
41a	Potluck Sill	Whole-rock, powder	0.89	$(8.67 \pm 0.09)10^{-3}$	41.4	279 ± 3
37	Ible Sill	Whole-rock, chips	0.66	$(7.81 \pm 0.07)10^{-3}$	41.3	334 ± 10
37a	Ible Sill	Whole-rock, powder	0.79	$(7.92 \pm 0.08)10^{-3}$	44.5	287 ± 3
9	Haddonfields Lower Lava	Whole-rock, chips	0.62	$(6.90 \pm 0.06)10^{-3}$	32.3	316 ± 6
9	Haddonfields Lower Lava	Whole-rock, chips	0.51	$(5.73 \pm 0.05)10^{-3}$	32.1	317 ± 3
9a	Haddonfields Lower Lava	Whole-rock, powder	0.74	$(7.16 \pm 0.07)10^{-3}$	40.9	277 ± 3
16	Shacklow Wood Lava	Whole-rock, chips	0.61	$(7.10 \pm 0.06)10^{-3}$	31.2	331 ± 3
16a	Shacklow Wood Lava	Whole-rock, powder	0.66	$(6.48 \pm 0.07)10^{-3}$	42.0	281 ± 3

*See Table 12.1 for explanation of all parameters

diffusion (around 17%) from the secondary smectite phase. Although this diffusion may be promoted by a subsequent thermal event, there is no resetting of the K-Ar 'clock' and the resulting apparent age has no geological significance. A similar relationship was noted by Miller and Musset (1964) where a loss of 7.5% radiogenic argon during fine grinding of material from the Whin Sill was attributed to the liberation of argon from interstitial potash-feldspar grain boundaries.

In the interpretation of three 'concordant' ages of 312 ± 7 , 310 ± 7 and 312 ± 6 m.y. from the Waterswallows Sill as representing the age of intrusion, Stevenson et al. (1970) did not include an assessment of the nature or extent of interstitial alteration phases. In rejecting material which gave ages of 267 ± 7 and 274 ± 5 m.y. it was concluded that argon loss had occurred for which there was no obvious petrographic evidence. Although detailed petrographic descriptions were not included by Stevenson et al. (1970), Stevenson and Gaunt (1971) indicated a high degree of interstitial alteration and this is confirmed by a re-investigation of similar material (Plate 1). Recent extensions to the quarry have exposed fine-grained dolerite with relict interstitial glass exhibiting only partial or incipient devitrification (see Plate 2.1). However, dating of this 'fresh' dolerite gave a range from 280 to 230 m.y. (Table 12.2). It is concluded therefore that the dolerite is unsuitable for K-Ar whole-rock dating. Radiogenic argon loss is a factor in all samples, including the 'concordant' age samples of Stevenson et al. (op.cit.). In addition the anomalous ages associated with the 'fresh' dolerite is in agreement with the observations of Vandoros et al. (1966) that partly devitrified glass exhibits greater argon loss than pseudomorphous secondary phases.

There is no reliable evidence in support of an upper Namurian phase of intrusive activity in the south Pennines and an alternative

relationship is suggested by the age of 334 ± 10 m.y. obtained from the Ible Sill. The dolerite is a typical coarse-grained, ophitic type in comparison with the Waterswallows Sill with minor concentration of interstitial phases. The implications are of a Lower Brigantian emplacement of the Ible Sill into Middle Asbian strata and not one of a long hiatus between extrusive and intrusive activity. Although based on a single analysis this proposal gains credence by the close spatial and geochemical affinities between the Lavas and Sills (Chapters 3 and 7). It is envisaged that repeated minor magmatic episodes during the Viséan replenished a number of shallow crustal magma chambers. This resulted in lava outpourings contemporaneous with high-level intrusions where the magma failed to reach the surface, in the majority of instances by encountering the 'line of weakness' along previous Lava horizons. Similar relationships between intrusive and extrusive activity have been noted by Francis et al. (1968) in the Westphalian of the East Midlands.

12:3 Dating of Hydrothermally Altered Basalts

The K-Ar age dates (Table 12.1) exhibit a broad spread from within individually sampled localities. The correlation between whole-rock potassium concentrations and the age obtained (Figure 12.1) indicates a relationship between increasing potassium saturation and age reduction. Two inflection points are noted on Figure 12.1, at which potassium enrichment has no effect on the resulting age and it is proposed that these represent distinct hydrothermal events associated with mineralisation in the south Pennine orefield.

Age determinations which are intermediate between the true age of basalt extrusion and the age of the hydrothermal events represent 'apparent' ages. These results have no geological significance and arise from the interaction of four processes:

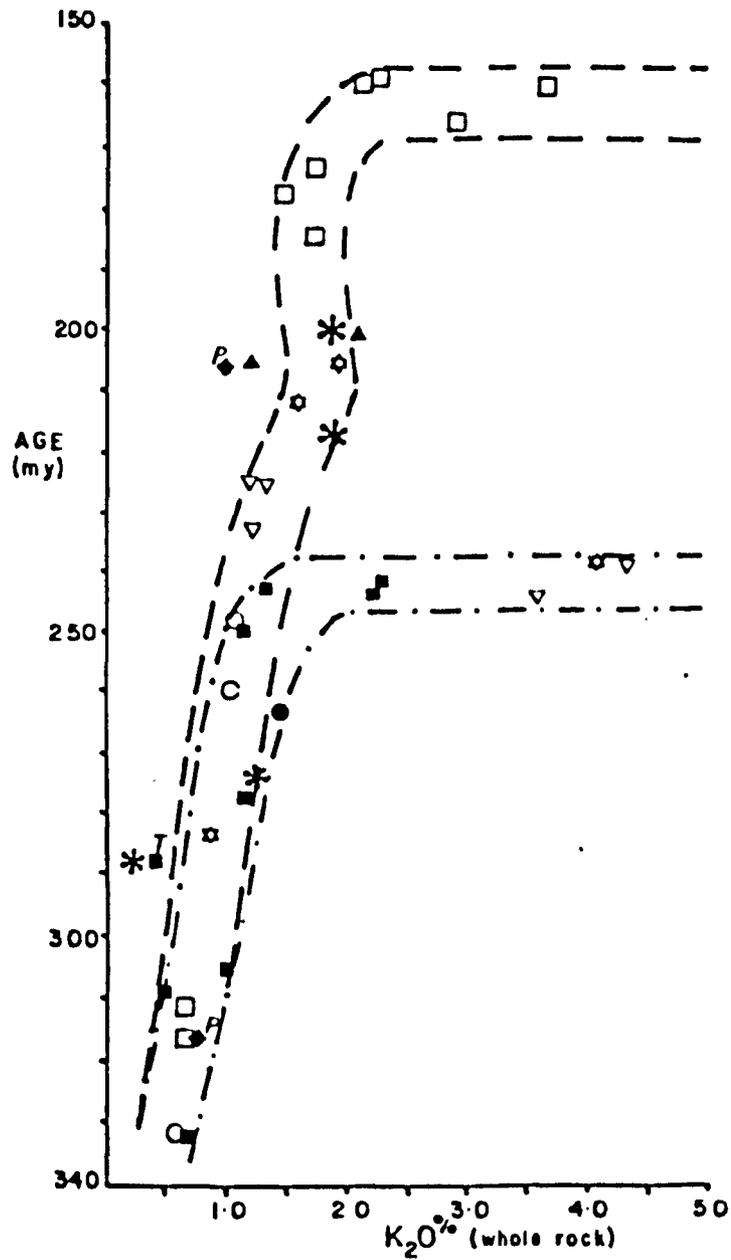


FIG. 12.1 WHOLE ROCK K₂O VERSUS K-Ar Age

Key.

- | | |
|---------------------------|-------------------------------|
| ■ Ible dolerite | ▲ Cressbrook Dale Lava |
| ○ Shacklow Wood Lava | ■ ^T Tideswell Sill |
| * Millers Dale Lower Lava | ■ ^P Potluck Sill |
| □ Millers Dale Upper Lava | |
| ▽ Matlock Lower Lava | |
| ☆ Conksbury Bridge Lava | |

- i. Partial diffusion of radiogenic argon from mineral lattices, accentuated and promoted by elevated temperatures.
- ii. Potassium introduced during hydrothermal alteration.
- iii. Incomplete K-Ar isotopic equilibration associated with phases 'resistant' to processes (i) or (ii) as noted above.
- iv. Partial overprinting arising from repeated hydrothermal events.

The thermal effects of igneous intrusion on the K-Ar characteristics of the host rock have been investigated by Hart (1964) and Hanson and Gast (1967). Argon retentivity was noted for hornblende in close proximity to the intrusion while potash-feldspar readily lost radiogenic argon in the extremities of the thermal aureoles. Host rock mineral separate ages ranged from their true stratigraphic age to the inferred age of intrusion with a continuous spread of intermediate ages.

Unfortunately minimal information is available regarding the argon retention characteristics of the illite-smectite and Fe-rich smectite phases in the altered basalts of the south Pennines. Significant argon loss by diffusion at room temperature/pressure can be discounted due to the rarity of ages younger than 150 m.y., even from material collected at outcrop. In addition, toadstone-clays and wayboard-clays have undergone prolonged contact with thermal groundwaters without resultant argon loss.

The high argon retention capacity of illite was noted by Dalrymple and Lanphere (1969) with detrital illite in recent sediments retaining a Pre-Cambrian K-Ar age. The results described in section 12.2 indicate that deuteritic smectite in the basalts may lose up to 20% argon by diffusion and the characteristics of the illite-rich illite-smectites associated with hydrothermal alteration is probably between these two extremes. However, if the alteration phases were readily susceptible

to argon loss, this would result in a dominant overprint of the youngest thermal event obscuring or obliterating evidence for previous activity. As Figure 12.1 indicates, this is not the case with a distinct resolution between the 240 and 160 m.y. events. The implications of this observation are that potassium introduced into the clay lattices during hydrothermal alteration at 240 m.y. retained its argon during subsequent thermal events and that no new potassium was introduced. It is envisaged that the low temperatures (100 to 160°C) associated with mineralisation (see Chapter 9) were insufficient to reset the K-Ar 'clock' by diffusion and that potassium introduction is the dominant process.

The mineralogy of hydrothermal alteration (Chapter 9) indicates that deuteritic smectite persists into the zone of incipient propylitic alteration associated with potassium enrichment. The proposal that the clay minerals are 'resistant' to total argon diffusion suggests that the apparent ages are the result of the combination of potassium enrichment associated with a hydrothermal event and a 'relict' deuteritic smectite phase exhibiting incomplete argon diffusion. In material with only a minor potassium enrichment the influence of the deuteritic smectite phase is dominant and results in apparent ages older than the hydrothermal event. With increasing potassium enrichment in close proximity to mineralisation the effect of the smectite phase is progressively diminished, resulting in ages corresponding to that of hydrothermal alteration.

This proposal can be tested by comparing the actual results with a series of calculated 'apparent age profiles' (see Figure 12.2). Profile A represents increasing potassium introduced (during a hydrothermal event at 160 m.y.) into a basalt with a modern whole rock K_2O of 0.75% incorporated in deuteritic smectite. The smectite has lost some 17% argon by diffusion converting a true age of 335 m.y. to an

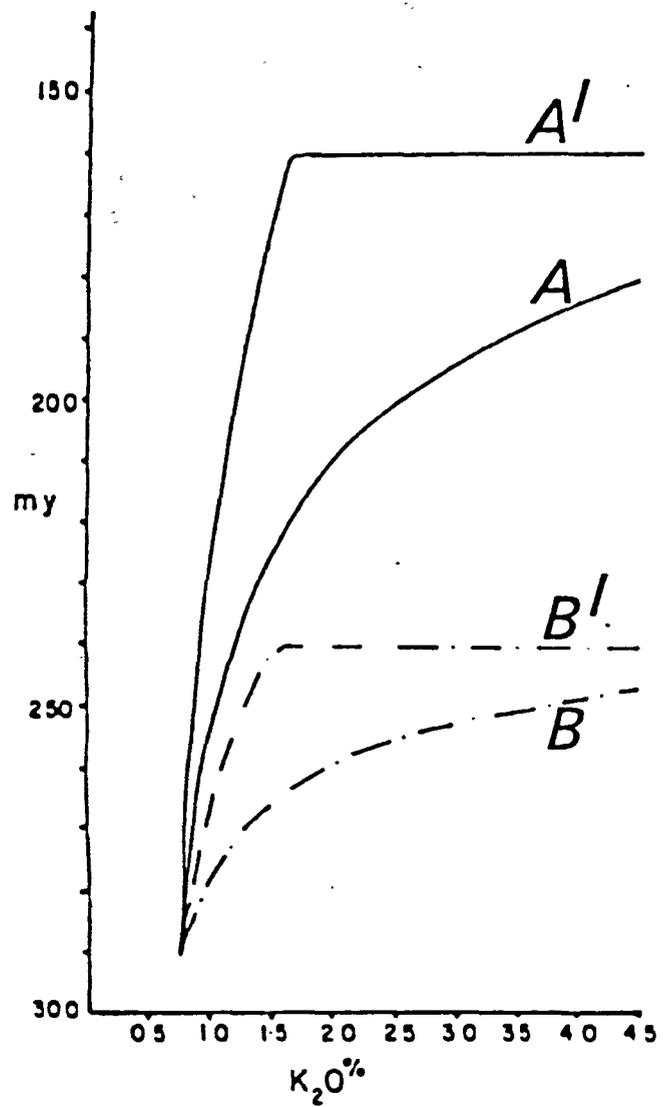


FIG. 12.2 THEORETICAL K-Ar AGE PROFILES
(see text for explanation)

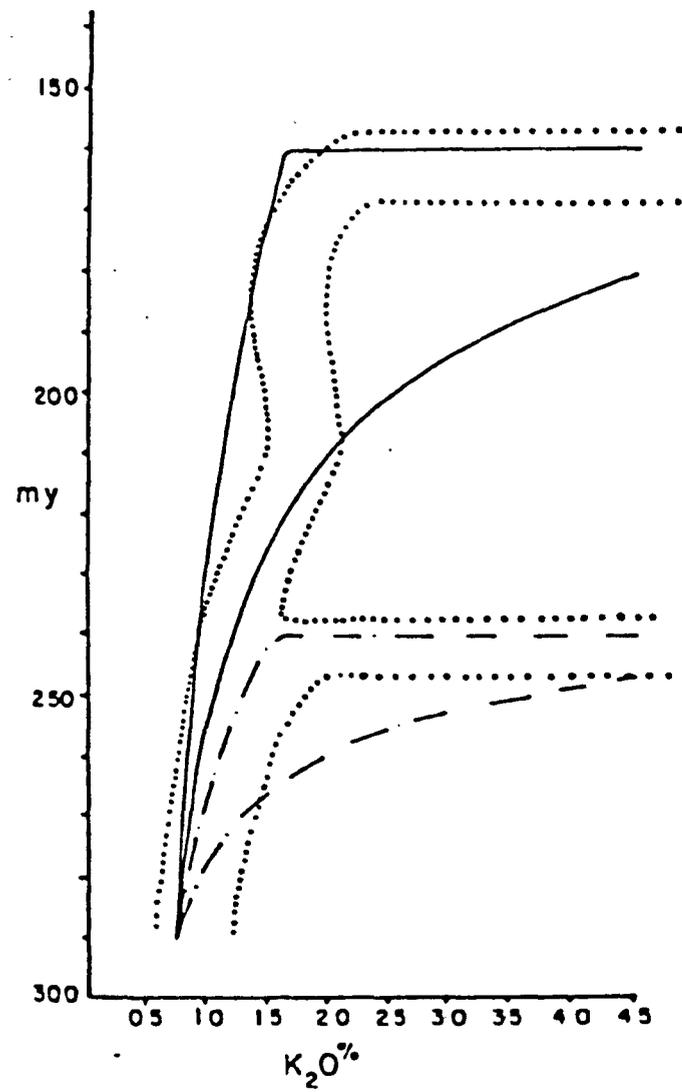


FIG. 12.3 A COMPARISON OF THEORETICAL
& OBSERVED K-Ar AGE PROFILES

apparent age of 290 m.y. before potassium introduction. Profile B represents the same but with potassium enrichment at 240 m.y. These profiles give a spread of ages related to potassium enrichment similar to the observed results. However, in comparison with the actual petrological variations associated with hydrothermal alteration, these 'mixing models' represent an over-simplification. Although deuteritic smectite persists into the outer zones of alteration, calcitisation and albitisation in closer proximity to mineralisation involves the progressive replacement of relict smectite. The potassium liberated during deuteritic smectite replacement is incorporated into the secondary alteration phases, e.g. secondary illite-smectite alteration of albite, and the net effect is a progressive loss of the argon associated with the deuteritic smectite. Profiles A' and B' (Figure 12.2) represents the situation where the addition of 0.1% K_2O (of hydrothermal origin) is accompanied by a 12% argon loss from the deuteritic smectite. Thus at whole rock K_2O concentrations of 1.55% the older 'contaminating' influence of the deuteritic smectite is no longer present.

12:4. Discussion and Interpretation of Results

The spread of results in Figure 12.1 do not fall on a single well defined line but indicate a definite trend accommodated within a band width of 0.5% K_2O . This is related to the initial variations in potassium concentrations in the unaltered basalts on an inter- and intra- Lava and Sill basis. Whole-rock K_2O values range from 0.2 to 1.2% with the majority between 0.5 and 1.0%.

A comparison of the theoretical profiles (A,A' and B,B') with the analytical results (Figure 12.3) indicates close agreement. The distribution of the analytical results approximately parallels trends A' and B' but the agreement is even further improved by invoking a

combination of A with A' and B with B'. The initial portion of the trend parallels A and B, representing potassium addition with no smectite replacement while the remaining trend parallels A' and B', associated with smectite replacement and argon loss. This is in agreement with the observed petrographic variations (Chapter 9) which indicate that deuteric smectite is unaffected during initial propylitic alteration and potassium enrichment followed by a rapid phase of calcitisation replacing smectite.

The factors affecting K-Ar dating of the south Pennine basalt can be summarised into five categories:

1. 'Fresh' basalts with a high proportion of relict interstitial glass give 'true' stratigraphic ages.
2. Partial devitrification of interstitial glass results in random argon loss.
3. Alteration and replacement of interstitial areas by Fe-rich smectites is a common feature, and the smectite has a maximum argon loss in the region of 17% resulting in apparent ages around 280 m.y.
4. The 'argon depleted' smectite persists during initial hydrothermal alteration and potassium enrichment, the smectite does not undergo further argon loss and therefore exerts an older 'contaminating' influence resulting in 'apparent' ages proportional to the relative potassium enrichment.
5. More advanced hydrothermal alteration is accompanied by the replacement of deuteric smectite, the 'contaminating' influence is no longer present and the K-Ar age relates to the age of the hydrothermal introduction of potassium.

Figure 12.1 indicates that only altered material with whole-rock K_2O concentrations in excess of 1.25% provide K-Ar dates indicative of the age of hydrothermal alteration. Analyses of clay concentrates without initially determining whole-rock 'pre-concentration' K_2O values, invalidates their incorporation into Figure 12.1. The age determinations of Fitch et al. (1970) represent whole-rock analyses and are therefore incorporated while only five of the analyses of Ineson and Mitchell (1973) represent whole-rock basalts. The concept of relative potassium enrichment can only be applied to material whose pre-alteration potassium concentrations are known, i.e. the basalts. Care must be exercised in extrapolating these relationships to the tuffs and more especially the clay-wayboards, the majority of which represent degraded fine-grained acidic ashfalls (Chapter 11).

A further implication of Figure 12.1 is that regardless of whether the whole-rock K_2O value is known, apparent ages of less than 220 m.y. can only relate to the 160 m.y. hydrothermal event. This is emphasised by the results from the altered Shacklow Wood Lava adjacent to the Mogshaw Rake. The three age determinations incorporated in Figure 12.1 indicate a minimum age of 250 m.y. associated with minor potassium enrichment. The allocation of the alteration to either the 240 or 160 m.y. periods cannot be ascertained from these results. However, a clay-concentrate 'dump sample' of the altered lava (Ineson and Mitchell, op.cit.) gave an age of 218 m.y. which can only be correlated with the 160 m.y. event.

The 160 m.y. hydrothermal event is associated with alteration adjacent to the Pb-Zn-F-Ba mineralisation at Long Rake, Mogshaw Rake, Maury Rake, Ball Eye and White Rake (Hucklow). The 240 m.y. event is associated with non-economic mineralisation and alteration in the Ible

Sill and at Hallicar Wood Adit. The upper toadstone-clay alteration of the Conksbury Bridge Lava (3) correlates with the 240 m.y. event while the alteration within the lava adjacent to Long Rake is associated with the 160 m.y. event. This supports the proposal in Section-12.3 that the altered, potassium enriched, basalts are 'resistant' to thermal overprinting and further enrichment.

The concept of 'within site concordancy' (Ineson and Mitchell, op.cit.) as the most reliable indication of the age of alteration is represented on Figure 12.1 by the grouping of samples exhibiting minimal age variation with increasing potassium concentrations at 160 and 240 m.y. However 'within site concordancy' can arise from factors other than a correspondance with the age of alteration, in particular the analysis of similar material. 'Concordant' ages were obtained by Ineson and Mitchell (op.cit.) from six samples of the Sallet Hole Tuff (Longstone Edge Upper Tuff) collected from a single exposure with no spatial relationship to mineralisation. It is proposed that the mean age of 240 m.y. represents a concordant 'apparent' age arising from the dating of similar material. However, five samples representing the transition from altered toadstone-clay to vesicular lava at Temple Pipe, Matlock gave an age range from 191 to 289 m.y. and were interpreted as 'discordant' and probably related to complex multiphase mineralisation by Ineson and Mitchell (op.cit.). This spread of ages, however, is compatible with variations in the degree of potassium enrichment and can be related to a single phase of mineralisation.

In comparing the present results and conclusions with the interpretations of Fitch et al. (1970) and Ineson and Mitchell (op.cit.) a number of discrepancies are noted. The proposed 'event' at 280 m.y. represents apparent ages resulting from argon loss (17%) from the deuteritic smectite. An episode of minor mineralisation at 240 ± 5 m.y.

is substantiated but the main phase of mineralisation is resolved at 160 ± 5 m.y.

12.5 South Pennine Mineralisation in a Regional Chronological Context

The application of isotopic age dating to the study of hydrothermal mineralisation in the British Isles and adjacent areas has resulted in the recognition of a number of distinct and widespread (Mesozoic) phases of activity (Mitchell and Halliday, 1976; Harrison et al., 1979). There is a correlation between the diverse and varied types of mineralisation and magmatism. This correlation has been suggested by certain authors (e.g. Harrison et al., op.cit.) as being due to large scale, plate-tectonic controls over mineralisation and magmatism related to the initial opening of the proto-North Atlantic and associated crustal dislocations in the North Sea.

In a review of Mesozoic mineralisation in the 'North Atlantic Ore Province' Mitchell and Halliday (op.cit.) recognised a major tectonically related mineralisation/magmatic episode around 220 to 180 m.y. (upper Triassic to Lower Jurassic) as a period of primary ore deposition and not simply a hydrothermal overprint. Harrison et al. (op.cit.) recognised hydrothermal events at around 225, 165 and 130 m.y. with temporally associated rifting and magmatism. This is in agreement with the K-Ar results of Fitch et al. (1970) for hydrothermally altered Carboniferous basalts with a concentration of ages around 225, 170 and 130 m.y. and a minor 'peak' at 115 m.y. Alteration adjacent to mineralisation in the Whin Sill (Dunham et al., 1968) likewise indicates 230 and 170 m.y. thermal episodes. The results of further K-Ar dating of basalts from the south Pennine orefield (Table 12.1, Figure 12.1) has confirmed the importance of these 'events', with a major phase of mineralisation around 160 ± 5 m.y. and a less important episode around 240 ± 5 m.y.

It is envisaged that the high heat flow and 'seismic pumping' associated with crustal rifting resulted in the dewatering of thick sedimentary sequences. The expulsion of formational brines into carbonate 'highs' was a major factor in the generation of the Mississippi Valley Type deposits in the Pennines (see Chapter 9). Repeated minor rifting and faulting during the main tectonic episode resulted in numerous 'brine pulses' and is reflected in the complex paragenetic sequences typical of the ore deposits in the south Pennines.

REFERENCES

- ABBEY, S. 1977. 'Standard Samples'. How 'standard' are they?
Geostd. Newsletter 1, pp. 39-45.
- ABBEY, S. 1977. Studies in 'Standard Samples' for use on general
analysis of silicate rocks and minerals. Part 5: 1977 Edition
of 'Usable' Values. Geol. Surv. Can. Pap. 77-34.
- ABBEY, S. 1978. U.S.G.S. II. Revisited. Geostd. Newsletter 2,
pp. 141-146.
- ABBEY, S., MEEDS, R.A. & BELANGER, P.G. 1979. Standard Samples of
rocks, the search for 'Best Values'. Geostd. Newsletter 3,
pp. 121-133.
- ADE-HALL, J.M. & LAWLEY, E.A. 1970. An Unsolved Problem - Opaque
petrological differences between Tertiary basaltic dykes and lavas.
in: Mechanisms of Igneous Intrusion. Newall, G. & Rast, N. (eds)
Geol. J. Spec. Pub. 2, Gallery Press, pp. 217-229.
- AMARAL, G., CORDANI, U.G., KAWASHITA, K. & REYNOLDS, J.H. 1966.
Potassium-Argon dates of basaltic rocks from southern Brazil.
Geochem. Cosmochim. Acta. 30, pp. 159-190.
- AMIN, M.A. 1980. Geochemistry and mineralogy of Namurian sediments
in the Pennine Basin, England. Unpublished Ph.D. Thesis, University
of Sheffield.
- ANDERSON, G.M. 1973. The hydrothermal transport and deposition of
galena and sphalerite near 100°C. Econ. Geol. 68, pp. 480-492.
- ANDERSON, G.M. 1975. Precipitation of Mississippi Valley type ores.
Econ. Geol. 70, pp. 937-942.
- BAKER, I. & HAGGERTY, S.E. 1967. The alteration of olivine in basaltic
and associated lavas. Part II: Intermediate and low temperature
alteration. Contr. Mineral Petrol. 16, pp. 258-272.

- BARBERI, F., BIZOUARD, H. & VARET, J. 1971. Nature of the clinopyroxene and iron enrichment in alkalic and transitional basaltic magmas. *Contr. Mineral. Petrol.* 33, pp. 93-107.
- BARBERI, F., INNOCENTI, F., LIRER, L., MUNINO, R., PESCATORE, T. & SANTACROE, T. 1978. The Campanian Ignimbrite: A major prehistoric eruption in the Neapolitan Area (Italy). *Bull. Volc.* 41, pp. 10-31.
- BEALES, F.W. 1975. Precipitation mechanisms of Mississippi Valley type ore deposits. *Econ. Geol.* 70, pp. 943-948.
- BECKINSALE R.D., PANKHURST, R.J., SKELHORN, R.R. & WALSH, J.N. 1978. Geochemistry and petrogenesis of the early Tertiary lava pile of the Isle of Mull, Scotland. *Contr. Mineral. Petrol.* 66, pp. 415-427.
- ARNOLD-BEMROSE, H.H.A. 1894. On the microscopical structure of the Carboniferous dolerites and tuffs of Derbyshire. *Q. Jl. geol. Soc. Lond.* 50, pp. 603-644.
- ARNOLD-BEMROSE, H.H.A. 1899. Geology of the Ashbourne-Buxton Railway: Ashbourne to Crakelow. *Q. Jl. geol. Soc. Lond.* 55, pp. 224-238.
- ARNOLD-BEMROSE, H.H.A. 1899. On a sill and faulted inlier in Tideswell Dale (Derbyshire). *Q. Jl. geol. Soc. Lond.* 55, pp. 239-250.
- ARNOLD-BEMROSE, H.H.A. 1907. The toadstones of Derbyshire: Their field relations and petrography. *Q. Jl. geol. Soc. Lond.* 63, pp. 241-281.
- ARNOLD-BEMROSE, H.H.A. 1903. Geology of the Ashbourne and Buxton branch of the London and North-Western Railway: Crake Low to Parsley Hay. *Q. Jl. geol. Soc. Lond.* 59, pp. 337-347.
- ARNOLD-BEMROSE, H.H.A. 1910. On olivine nodules in the basalt of Calton Hill, Derbyshire. *Geol. Mag.* 7, pp. 1-4.
- BOAR, P.L. & INGRAM, L.K. 1970. The comprehensive analysis of coal ash and silicate rocks by atomic absorption spectrophotometry by a fusion technique. *The Analyst* 95, pp. 124-130.

- BOWLES, F.A., JACK, R.N. & CARMICHAEL, I.S.E. 1973. Investigations of deep sea volcanic ash layers from equatorial Pacific cores. Geol. Soc. Amer. Bull. 84, pp. 2371-2388.
- BROTZU, P., MORBIDELLI, L., PICCIRILLO, E.M. & TRAVERSA, G. 1974. Transitional basalts of alkaline or tholeiitic affinity in the Somali Trap series. Bull. Vulc. 38, pp. 254-269.
- BROWN, G. & STEPHEN, I. 1959. A structural study of iddingsite from New South Wales, Australia. Am. Mineralogist 44, pp. 251-260.
- BUCKLEY, D.E. & CRANSTON, R.E. 1971. Atomic absorption analysis of 18 elements from a single decomposition of aluminosilicates. Chem. Geol. 7, pp. 273-284.
- BURNHAM, C.W. 1962. Facies and types of hydrothermal alteration. Econ. Geol. 57, pp. 768-784.
- BUTCHER, N.J.D. 1976. Some aspects of structure and fluorite mineralisation in the Southern Pennine Orefield. Unpublished Ph.D. Thesis, University of Leicester.
- BUTLER, L.R.R. & KROKOT, M.L. 1969. Application of atomic absorption to the analysis of upper mantle and other rocks. Geol. Soc. South Africa, Spec. Pub. No.3.
- CAMERON, T.D.J. & ANDERSON, T.B. 1980. Silurian metabentonites in County Down, Northern Ireland. Geol. J. 15, pp. 59-75.
- CARMICHAEL, I.S.E. 1964. Petrology of Thingmuli, a Tertiary volcano in eastern Iceland. J. Petrol. 5, pp. 435-460.
- CARMICHAEL, I.S.E., TURNER, F.J. & VERHOOGEN, J. 1974. Igneous Petrology McGraw-Hill, 737 p.
- CHAYES, F. 1966. Alkaline and sub-alkaline basalts. Amer. J. Sci. 264, pp. 128-145.
- CHESHIRE, S.G. & BELL, J.D. 1977. The Speedwell vent, Castleton, Derbyshire. A Carboniferous littoral cone. Proc. Yorks. geol. Soc. 41, pp. 173-184.

- COATES, R.R. 1968. The Circle Creek rhyolite, Nevada. in: Studies in volcanology. Geol. Soc. Amer. Mem. 116, pp. 69-107.
- COOK, E.F. (ed.) 1966 Tuff Lavas and Ignimbrites. Elsevier, 208 p.
- COOMBS, D.S. 1963. Trends and affinities of basaltic magmas and pyroxenes as illustrated on the diopside-olivine-silica diagram. Mineral. Soc. Amer. Spec. Paper 1, pp. 227-250.
- COPE, F.W. 1933. A tholeiite dyke near Buxton, Derbyshire. Geol. Mag. 70, pp. 414-422.
- COPE, F.W. 1937. Some features in the D₁-D₂ limestones of the Millers Dale region, Derbyshire. Proc. Yorks. geol. Soc., 23, pp. 178-195.
- COX, K.G. 1980. A model for flood basalt vulcanism. J. Petrol. 21, pp. 629-650.
- COX, K.G., BELL, J.D. & PANKHURST, R.J. 1979. The Interpretation of Igneous Rocks. Allen & Unwin, 450 p.
- COX, F.C. & BRIDGE, D. McC. 1977. The limestone and dolomite resources of the country around Monyash, Derbyshire. Description of 1:25,000 Resources Sheet, SK16. HMSO, Lond.
- CRAIG, J.R. & CARPENTER, A.B. 1977. Fletcherite, $\text{Cu}(\text{Ni},\text{CO})_2\text{S}_4$, a new thiospinel from the Viburnum Trend (New Lead Belt), Missouri. Econ. Geol. 75, pp. 480-486.
- CURTIS, C.D. 1976. 'Unmixed' Ca/Mg saponite at Calton Hill, Derbyshire. Clay Minerals 11, pp. 85-89.
- DALRYMPLE, G.B. & LANPHERE, M.A. 1969. Potassium-Argon Dating. W.H. Freeman, 258 pp.
- DEER, W.A., HOWIE, R.A. & ZUSSMAN, J. 1978. Rock Forming Minerals - Vol.2A: Single Chain Silicates. 2nd Ed. John Wiley & Sons 668 p.
- DISSANAYAKE, C.B. & VINCENT, E.A. 1972. Zinc in rocks and minerals from Skaergaard Intrusion, east Greenland. Chem. Geol. 9, pp. 285-297.

- DONALDSON, C.H. 1978. Petrology of the uppermost mantle deduced from spinel lherzolite and harzburgite nodules at Calton Hill, Derbyshire. *Contr. Mineral. Petrol.* 65, pp. 363-377.
- DOZY, J.J. 1970. A geological model for the genesis of the Pb-Zn ores of the Mississippi Valley, U.S.A. *Trans. Instn. Min. Metall.* (Sect. B: Appl. earth sci.) 79, pp. 163-170.
- DUNHAM, A.C. & KAY, M.J. 1965. The petrology of the Little Whin Sill, County Durham. *Proc. Yorks geol. Soc.* 35, pp. 229-276.
- DUNHAM, K.C. 1970. Mineralisation by deep formation waters - A review. *Trans. Instn. Min. Metall.* (Sect. B: Appl. earth sci.) 79, pp. 127-136.
- DUNHAM, K.C. 1973. A recent deep borehole near Eyam, Derbyshire. *Nature (Phys. Sci.)*, 241, pp. 84-85.
- DUNHAM, K.C., DUNHAM, A.C., HODGE, B.L. & JOHNSON, G.A.L. 1965. Granite beneath Viséan sediments with mineralisation at Rookhope, northern Pennines. *Q.Jl. geol. Soc. Lond.* 121, pp. 383-417.
- DUNHAM, K.C., FITCH, F.J., INESON, P.R., MILLER, J.A. & MITCHELL, J.G. 1968. The geochronological significance of argon-39/argon-40 determinations on White Whin from the northern Pennine orefield. *Proc. R. Soc.(A)*, 307, pp. 251-266.
- DUNSMORE, H.E. 1973. Diagenetic process of Pb-Zn emplacement in carbonates. *Trans. Instn. Min. Metall.* (Sect. B: Appl. earth sci.) 82, pp. 168-173.
- EATON, G.P. 1964. Windbourne volcanic ash: A possible index of polar wandering. *J. Geol.* 72, pp. 1-35.
- ELSDON, R. 1971. Clinopyroxene from the Upper Layered Series, Kap Edvard Holm Intrusion, east Greenland. *Min. Mag.* 38, pp. 49-57.
- FALL, H.G. 1980. The petrology and geochemistry of Jurassic igneous rocks from the northern North Sea. Unpublished Ph.D. Thesis, University of Sheffield, 187 p.

- FAREY, J. 1811. A general view of the agriculture and minerals of Derbyshire. 1, 532 pp.
- FAWCETT, J.J. 1965. Alteration products of olivine and pyroxene in basalt lavas from the Isle of Mull. *Min. Mag.* 35, pp. 55-68.
- FEARNSIDES, W.G. & TEMPLEMAN, A. 1932. A boring through Edale Shales to Carboniferous limestone and pillow lavas at Hope Cement Works near Castleton, Derbyshire. *Proc. Yorks geol. Soc.* 22, pp. 100-121.
- FIELDER, G. & WILSON, I. (eds) 1975. *Volcanoes of the Earth, Moon and Mars.* Paul Elek Ltd. 126 p.
- FITCH, F.J. & MILLER, J.A. 1964. The age of the paroxysmal Variscan orogeny in England. *in: The Phanerozoic Time Scale.* Harland, W.B., Gilbert-Smith, A. & Wilcock, B. (eds). *Q. Jl. geol. Soc. Lond.* 120, pp. 159-175.
- FITCH, F.J., MILLER, J.A. & WILLIAMS, S.C. 1970. Isotopic ages of British Carboniferous rocks. *C.R. 6th Int. Congr. Carb. Strat. Geol.* (Sheffield 1967) 2, pp. 771-789.
- FLANAGAN, F.J. 1969. U.S. Geological Survey Standards - II. First compilation of data for the new USGS rocks. *Geochem. Cosmochim. Acta* 33, pp. 81-120.
- FLANAGAN, F.J. 1972. Values for International geochemical reference samples. *Geochem. Cosmochim. Acta* 37, pp. 1189-1200.
- FLANAGAN, F.J. 1976. Descriptions and analyses of eight new USGS rock standards. *U.S. Geol. Surv. Prof. Paper* 840.
- FLOWER, M.F.J. 1973. Evolution of basaltic and differentiated lavas from Anjouan, Comores Archipelago. *Contr. Mineral. Petrol.* 38, pp. 237-260.
- FLOWER, M.F.J. 1973. Trace element distribution in lavas from Anjouan and Grande Comore, Western Indian Ocean. *J. Geol.* 12, pp. 81-98.

- FLOYD, P.A. & WINCHESTER, J.A. 1975. Magma type and tectonic setting discrimination using immobile elements. *Earth Planet Sci. Lett.* 27, pp. 211-222.
- FORD, T.D. 1976. The ores of the South Pennines and Mendip Hills, England. A comparative Study. in: *Handbook of Strata-Bound and Stratiform Ore Deposits*. Wolf, K.H. (ed), Regional Studies, Elsevier. 5, pp. 161-195.
- FORD, T.D. (ed) 1977. Limestones and caves of the Peak District. *Geo. Abstracts*, 469 pp.
- FRANCIS, E.H. 1967. Review of Carboniferous-Permian volcanicity in Scotland. *Geol. Rdsch.* 57, pp. 219-246.
- FRANCIS, E.H. 1970. Review of Carboniferous volcanism in England and Wales. *J. Earth Sci.* 1, pp. 41-56.
- FRANCIS, E.H., SMART, J.G.O. & RAISBECK, D.E. 1968. Westphalian volcanism at the horizon of the Black Rake in Derbyshire and Nottinghamshire. *Proc. Yorks. geol. Soc.* 36, pp. 395-416.
- FROST, D.V. & SMART, J.G.O. 1979. Geology of the country north of Derby. *Mem. geol. Surv. Gt. Br.*, 199 p.
- GARNETT, C.S. 1923. On a peculiar chlorite rock at Ible, Derbyshire. *Miner. Mag.* 20, pp. 60-64.
- GARNETT, C.S. 1923. The toadstone clays of Derbyshire. *Miner. Mag.* 20, pp. 151-157.
- GASS, I.G., MALLICK, D.I.J. & COX, K.G. 1973. Volcanic islands of the Red Sea. *Q. Jl. geol. Soc. Lond.* 129, pp. 275-310.
- GEIKIE, A. 1897. *Ancient volcanoes of Great Britain*. London, 2, pp. 8-22.
- GEORGE, T.N. et al. 1976. A correlation of Dinantian rocks in the British Isles. *Spec. Rep. No.7, geol. Soc. Lond.*, 87 p.

- GIBB, F.G.F. 1973. The zoned clinopyroxenes of the Shiant Isles Sill, Scotland. *J. Petrol.* 14, pp. 203-230.
- GIBSON, W. & HIND, W. 1899. On agglomerates and tuffs in the Carboniferous limestone series of Congleton Edge, with an Appendix on the petrography of the rocks by H.H. Arnold-Bemrose. *Q. Jl. geol. Soc. Lond.* 33, pp. 67-71.
- GUNN, B.M. 1971. Trace element partition during olivine fractionation of Hawaiian basalts. *Chem. Geol.* 8, pp. 1-13.
- HAHN, G.A., ROSE, W.I. & MEYERS, T. 1979. Geochemical correlation of genetically related rhyolitic ash-flow and air-fall ashes, central and western Guatemala and the equatorial Pacific. in: Chapin, C.E. & Elston, W.E. (eds), *Ash Flow Tuffs*. *Geol. Soc. Amer. Spec. Paper* 180, pp. 101-112.
- HAMAD, S. el D. 1963. The chemistry and mineralogy of the olivine nodules of Calton Hill, Derbyshire. *Miner.Mag.* 33, pp. 483-497.
- HANSON, G.N. & GAST, P.W. 1967. Kinetic studies in contact metamorphic zones. *Geochem. Cosmochim Acta.* 31, pp. 1119-1153.
- HARRISON, R.K. 1977. Petrology of the intrusive igneous rocks in the Duffield Borehole, Derbyshire. *Bull. Geol. Surv. G.B.* 59, pp. 41-59.
- HARRISON, R.K., JEANS, C.V. & MERRIMAN, R.J. 1979. Mesozoic igneous rocks, hydrothermal mineralisation and volcanogenic sediments in Britain and adjacent regions. *Bull. Geol. Surv. G.B.* 70, pp. 57-69.
- HART, R.A. 1971. Chemical exchange between sea water and deep ocean basalts. *Earth Planet. Sci. Lett.* 29, pp. 269-279.
- HART, S.R. 1964. The petrology and isotopic mineral age relations of a contact zone in the front range, Colorado. *J. Geol.* 72, pp. 493-525.
- HART, S.R. & DAVIS, K.E. 1978. Nickel partitioning between olivine and silicate melts. *Earth Planet. Sci. Lett.* 40, pp. 203-219.

- HEMLEY, J.J. & JONES, W.R. 1964. Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism. *Econ. Geol.* 59, pp. 538-569.
- HESS, H.H. (ed) 1967. Basalts: The Poldervaart Treatise on rocks of basaltic composition. John Wiley & Sons, 2 volumes.
- HILDRETH, W. 1979. The Bishop Tuff: Evidence for the origin of compositional zoning in silicic magma chambers. in: Chapin, C.E. & Elston, W.E. (eds), Ash Flow Tuffs. *Geol. Soc. Amer. Spec. Paper* 180, pp. 43-75.
- HIRST, D.M. & KAYE, M.J. 1971. Factors controlling the mineralogy and chemistry of an upper Visean sedimentary sequence from Rookhope, County Durham. *Chem. Geol.* 8, pp. 37-59.
- HOLLAND, H.D. 1967. Gangue minerals in hydrothermal deposits. in: Geochemistry of hydrothermal ore deposits. Barnes, H.L. (ed). Holt, Rinehart & Winston Inc. 670 p.
- HOLLAND, J.G. & BROWN, G.M. 1972. Hebridean tholeiitic magmas: A geochemical study of the Ardnamurchan cone sheets. *Contr. Mineral. Petrol.* 37, pp. 139-160.
- HOWER, J. & MOWATT, T.C. 1966. The mineralogy of illites and mixed layer illite/montmorillonites. *Amer. Min.* 51, pp. 825.
- HUDSON, R.G.S. & COTTON, G. 1945a. The lower Carboniferous in a boring at Alport, Derbyshire. *Proc. Yorks. geol. Soc.* 25, pp.254-330.
- HUDSON, R.G.S. & COTTON, G. 1945b. The Carboniferous rocks of the Edale Anticline, Derbyshire. *Q. Jl. geol. Soc. Lond.* 101, pp. 1-36.
- HUTCHINSON, C.S. 1974. Laboratory Handbook of Petrographic Techniques. John Wiley & Sons 527 p.
- INESON, P.R. 1967. Trace-element geochemistry of wallrock alterations in the Pennine orefields and Cumberland ironfield. Unpublished Ph.D. Thesis, University of Durham.

- INESON, P.R. 1968. The petrology and geochemistry of altered quartz-dolerite in the Closehouse Mine area. Proc. Yorks. geol. Soc. 36, pp. 373-384.
- INESON, P.R. 1969. Trace element aureoles in limestone wallrocks adjacent to lead-zinc-barite-fluorite mineralisation in the northern Pennine and Derbyshire orefields. Trans. Instn. Min. Metall., (Sect.B: Appl. earth sci.)78, pp. 29-40
- INESON, P.R. 1970. Trace element aureoles in limestone wallrocks adjacent to fissure veins in the Eyam area of the Derbyshire orefield. Trans. Inst. Min. Metall. (Sect. B. Appl. earth sci.), 79, pp. B238-245.
- INESON, P.R. 1972. Alteration of the Whin Sill adjacent to baryte-witherite mineralisation, Settlingstones Mine, Northumberland. Trans. Instn. Min. Metall.(Sect.B: Appl. earth sci.) 81, pp.67-72.
- INESON, P.R. 1976. Ores of the northern Pennines, the Lake District and North Wales. in: Wolf, K.H. (ed.), Handbook of Strata Bound and Stratiform Ore Deposits. Regional Studies; Elsevier, 5, pp. 197-230.
- INESON, P.R. & AL-KUFAISHI, F.A.M. 1970. The mineralogy and paragenetic sequence of Long Rake Vein at Raper Mine, Derbyshire. Mercian Geol. 3, pp. 337-351.
- INESON, P.R. & MITCHELL, J.G. 1973. Isotopic age determinations on clay minerals from lavas and tuffs of the Derbyshire orefield. Geol. Mag. 109 pp. 501-512.
- INGAMELLS, C.O. 1970. Lithium metaborate flux in silicate analysis. Analytica Chimica Acta. 52, pp. 323-334.
- IRVINE, T.N. & BARAGER, W.R.A. 1971. A guide to the chemical classification of the common volcanic rocks. Can. J. Earth Sci. 8, pp. 523-548.

- IXER, R.A. 1972. Controls of mineralisation in Derbyshire. Unpublished Ph.D. Thesis, University of Manchester.
- JOHNSON, R.W. & ARCULUS, R.J. 1978. Volcanic rocks of the Witu Is., Papua, New Guinea. *Bull. Volc.* 41, pp. 609-655.
- JONES, J.G. & NELSON, P.H.H. 1970. The flow of basalt from air into water: Its structural expression and stratigraphic significance. *Geol. Mag.* 107, pp. 13-19.
- KELMAN, P. 1980. The geology of the Ashover volcanics. *Mercian Geol.* 8, pp. 64-71.
- KITTLEMAN, L.R. 1979. Tephra. *Sci. Amer.* 241, pp. 132-142.
- KRISHNAMURTHY, P. & COX, K.G. 1977. Picrite basalts and related lavas from the Deccan traps of western India. *Contr. Mineral. & Petrol.* 62, pp. 53-75.
- KUNO, H. 1967. Differentiation of basalt magmas. in: *The Poldervaart Treatise on rocks of basaltic composition*. Hess, H.H. (Ed.), Vol. 2.
- LAMB, H.H. 1970. Volcanic dust in the atmosphere; with a chronology and assessment of its meteorological significance. *Proc. R. Soc. (A)* 266, pp. 425-533.
- LA ROCHE, H. de & GOVINDARAJU, K. 1973. Rapport (1972) sur Quatre Standards Geochemiques de L'A.N.R.T. *Bull. de la Soc. France de Ceramique* 100, pp. 49-75.
- LE BAS, M. 1962. The role of aluminium in igneous clinopyroxene with relation to their parentage. *Amer. J. Sci.* 260, pp. 267-288.
- LE MAITRE, R.W. 1976. The chemical variability of some common igneous rocks. *J. Petrol.* 17, pp. 589-637.
- LISITSYNA, N.A. 1968. Geochemistry of weathering zones of basic rocks. *Geochem. Int.* 5, pp. 210-240.

- LIVINGSTONE, A. & McKISSOCK, G.M. 1974. The geochemistry of the igneous rocks in the Lower Carboniferous (Dinantian) at Spilmersford, East Lothian, Scotland. Bull. geol. Surv. G.B. 45, pp. 47-61.
- LLEWELLYN, P.G. & STABBINS, R. 1968. Lower Carboniferous evaporites and mineralisation in the east and central Midlands of Britain. Trans. Instn. Min. Metall. (Sect. B: Appl. earth sci.) 77, pp. 170-173.
- LOVERING, T.S. 1950. The geochemistry of argillic and related types of rock alteration. Q. Colorado School of Mines pp. 231-260.
- LYLE P. 1980. A petrological and geochemical study of the Tertiary basaltic rocks of north-east Ireland. J. Earth Sci. R. Dubl. Soc. 2, pp. 137-152.
- McBIRNEY, A.R. (ed) 1969. Proceedings of the Andesite Conference. State of Oregon Dept. Geol. & Min. Resources Bull. 65, 193p.
- MacDONALD, G.A. 1972. Volcanoes. Prentice Hall, 510 pp.
- MacDONALD, G.A. & KATSURA, T. 1964. Chemical composition of Hawaiian lavas. J. Petrol. 5, pp. 82-133.
- MacDONALD, R. 1975. Petrochemistry of the early Carboniferous (Dinantian) lavas of Scotland. Scott. J. Geol. 11, pp. 269-314.
- MALKI, N. 1966. A re-examination of basaltic horizons of the Lower Carboniferous limestone of Derbyshire. Unpublished M.Sc. Dissertation University of Sheffield.
- MEDLIN, J.H., SUHR, N.H. BODKIN, J.R. 1969. Atomic absorption analysis of silicates employing a LiBO_2 fusion. A.A. Newsletter, 18, pp. 25-29.
- MELSON, W.G. & THOMPSON, G. 1973. Glassy abyssal basalts, Atlantic sea floor near St. Paul's Rock: Petrography and composition of secondary clay minerals. Geol. Soc. Amer. Bull., 84, pp. 703-721.

- MEYER, C. & HEMLEY, J.J. 1967. Wallrock alteration. in: Geochemistry of hydrothermal ore deposits. Barnes, H.L. (ed.), Holt, Rinehart & Winston Inc. 670 p.
- MILLER, J.A. & MUSSET, A.E. 1963. Dating basic rocks by the potassium-argon method - The Whin Sill. *Geophys. J.* 7, pp. 547-553.
- MITCHELL, J.G. 1972. Potassium-argon ages from the Cheviot Hills, Northern England. *Geol. Mag.* 109, pp. 421-426.
- MITCHELL, J.G. & HALLIDAY, A.N. 1976. Extent of Triassic/Jurassic hydrothermal ore deposits on the north Atlantic margins. *Trans. Inst. Min. Metall. (Sect. B: Appl. earth sci.)*, 85, pp. 159-161.
- MOSSLER, J.H. & HAYES, J.B. 1966. Ordovician potassium bentonites of Iowa. *J. Sed. Petrol.* 36, pp. 414-427.
- NICHOLS, R.L. 1936. Flow units in basalt. *J. Geol.* 44, pp. 617-630.
- NINKOVICH, D., SPARKS, R.S.J. & LEDBETTER, M.T. 1978. The exceptional magnitude and intensity of the Toba Eruption, Sumatra: An example of the use of deep sea Tephra layers as a geological tool. *Bull. Volc.* 41, pp. 206-230.
- NISBET, E.G. & PEARCE, J.A. 1977. Clinopyroxene composition in mafic lavas from different tectonic settings. *Contr. Mineral. Petrol.* 63, pp. 149-160.
- NORRISH, K. & HUTTON, J.T. 1969. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochem. Cosmochim. Acta.* 33, pp. 431-453.
- NRIAGRU, T.O. & ANDERSON, G.M. 1970. Calculated solubilities of some base metal sulphides in brine solutions. *Trans. Instn. Min. Metall. (Sect. B: Appl. earth sci.)* 79, pp. 208-212.
- NOE-NYGAARD, A. 1968. On extrusion forms in plateau basalts: Shield volcanoes of 'Scutulum' type. *Scientia Islandica, Ann.* Vol. pp. 10-13.

- O'HARA, M.J. 1977. Geochemical evolution during fractional re-crystallisation of a periodically refilled magma chamber. *Nature*, 266, pp. 503-507.
- O'HARA, M.J. & MATHEWS, R.E. 1981. Geochemical evolution in an advancing, periodically replenished, periodically tapped, continuously fractionated magma chamber. *Q. Jl. geol. Soc. London*, 138, pp. 237-279.
- PARKER, A. 1970. An index of weathering for silicate rocks. *Geol. Mag.* 107, pp. 501-504.
- PARSONS, W.H. 1969. Criteria for the recognition of volcanic breccias: Review. *Geol. Soc. Amer. Mem.* 115, pp. 263-304.
- PEARCE, J.A. & CANN, M.R. 1973. Tectonic setting of basic volcanic rocks determined using trace element variations. *Earth Planet. Sci. Lett.* 19, pp. 290-300.
- PETTIJOHN, E.J. 1975. *Sedimentary Rocks* (3rd ed.) Harper & Row, 628 p.
- PILKINGTON, J. 1789. *A view of the present state of Derbyshire*. Vol.1, 469 pp.
- POLDERVAART, A. 1964. Chemical definition of alkali basalts and tholeiites. *Geol. Soc. Amer. Bull.* 75, pp. 229-232.
- PRICE, N.R. & DUFF, P. McL. D. 1969. Mineralogy and chemistry of tonsteins from Carboniferous sequences in Great Britain. *Sedimentology*, 13, pp. 45-69.
- RAMSBOTTOM, W.G.C., RHYS, G.H. & SMITH, E.G. 1962. Boreholes in the Carboniferous rocks of the Ashover district, Derbyshire. *Bull. geol. Surv. G . B .* 19, pp. 75-168.
- RICHARDSON, D. & NINKOVICH, D. 1976. Use of K_2O , Rb, Zr & Y versus SiO_2 in volcanic ash layers of the eastern Mediterranean to trace their source. *Geol. Soc. Amer. Bull.* 87, pp. 110-116.

- RIDLEY, W.I. 1971. Some chemical features of basalts from the British Tertiary province. *Earth Planet Sci. Lett.* 11, pp. 435-439.
- RODGERS, P.J. 1977. Fluid inclusion studies in fluorite from the Derbyshire orefield. *Trans. Inst. Min. Metall. (Sect. B: Appl. earth sci.)* 86, pp. 128-132.
- RODGERS, P.J. 1978. Fluid inclusion studies on fluorite from the Askrigg Block. *Trans. Instn. Min. Metall. (Sect. B: Appl. earth sci.)* 87, pp. 125-132.
- ROSE, I.W., GRANT, N.K. & EASTER, J. 1979. Geochemistry of the Los Chocoyos Ash, Quezaltenango Valley, Guatemala. in: Chapin, C.E. & Elston, W.E. (eds), *Ash Flow Tuffs. Geol. Soc. Amer. Spec. Paper* 180, pp. 87-99.
- ROSS, C.S. & SHANNON, E.V. 1925. The origin, occurrence, composition and physical properties of the mineral iddingsite. *Proc. U.S. Nat. Museum* 67 (Art.7), pp. 1-19.
- ROSS, C.S. & SHANNON, E.V. 1926. The minerals of bentonite and related clays and their physical properties. *Amer. Ceram. Soc. Bull.* 9, pp. 77-96.
- RUXTON, B.P. 1968. Measures of the degree of chemical weathering of rocks. *J. Geol.* 76, pp. 518-527.
- SARGENT, H.C. 1917. On a spilitic facies of Lower Carboniferous lava flows in Derbyshire. *Q. Jl. geol. Soc. Lond.* 73, pp. 11-25.
- SARGENT, H.C. 1925. An analcite bearing tuff in the Carboniferous Limestone of Derbyshire. *Geol. Mag.* 62, pp. 462-463.
- SARJEANT, W.A.S. 1967. Fibrous chlorites in the volcanic rocks of Derbyshire. *Mercian Geol.* 3, pp. 85-95.
- SCHEIDEGGER, K.F. & STAKES, D.S. 1977. Mineralogy, chemistry and crystallisation sequence of clay minerals in altered theoleiitic basalts from the Peru Trench. *Earth Planet Sci. Lett.* 36, pp.413-422.

- SCHULTZ, L.G. 1962. Non-montmorillonite composition of some bentonite beds. in: Clays and Clay Minerals, 11th Conf. pp. 169-177. Pergamon Press.
- SCHWARZER, R.R. & ROGERS, J.J.W. 1974. A world-wide comparison of alkali olivine basalts and their differentiation trends. Earth Planet. Sci. Lett. 23, pp. 286-296.
- SELF, S. & SPARKS, S.J. 1978. Characteristic of widespread pyroclastic deposits formed by the interaction of silicic magmas and water. Bull. Volc. 41, pp. 196-212.
- SEYFRIED, W.E., SHANKS, W.C. & DIBBLE, W.E. 1978. Clay mineral formation in D.S.D.P. Leg 34 Basalt. Earth Planet. Sci. Lett. 41, pp.265-276.
- SHAPIRO, L. 1967. Rapid analysis of rocks and minerals by a single solution method. U.S.G.S. Prof. Paper 575-B, pp. 187-191.
- SHIRLEY, J. 1950. The stratigraphical distribution of the lead-zinc ores of Mill Close Mine, Derbyshire and the future prospects of the area. XVIII Int. geol. Congr. Lond. (London, the Congress), Pt.7, pp. 353-361.
- SLAUGHTER, M. & EARLEY, J.W. 1965. Mineralogy and geological significance of the Mowry bentonites, Wyoming. Geol. Soc. Amer. Spec. Paper 83, 116 p.
- SMITH, W.W. 1959. Pseudomorphs after olivine in markle basalt. Min. Mag. 32, pp. 324-331.
- SMITH, J.V. 1974. The feldspar minerals: Vol.2 - Chemical and textural properties. Springer-Verlag, 690 p.
- SMITH, F.W. 1974. Factors governing the development of fluorspar orebodies in the North Pennine Orefield. Unpublished Ph.D. Thesis, University of Durham. 247 p.
- SMITH, E.G., RHYS, G.H. & EDEN, R.A. 1967. Geology of the country around Chesterfield, Matlock and Mansfield. Mem. geol. Surv. Gt. Br. 430 pp.

- SMITH, E.G., RHYS, G.H. & GOOSSENS, R.F. 1973. Geology of the Country around East Retford, Worksop and Gainsborough. Mem. geol. Surv. Gt. Br. 348 pp.
- SOMERVILLE, I.D. 1977. The sedimentology and stratigraphy of the Dinantian limestones on the Llangollen area and east of the Clwydian Range, North Wales. Unpublished Ph.D. Thesis. Queen's University, Belfast. 234 p.
- SOMERVILLE, I.D. 1979. Minor sedimentary cyclicity in late Asbian (Upper D₁) Limestones in the Llangollen district of North Wales. Proc. Yorks. geol. Soc. 42, pp. 317-342.
- SOMERVILLE, I.D. 1979. A sedimentary cyclicity in early Asbian (lower D₁) limestones in the Llangollen district of North Wales. Proc. Yorks. geol. Soc. 42, pp. 397-404.
- SOMERVILLE, I.D. 1979. A cyclicity in the early Brigantian (D₂) limestone east of the Clwydian range, North Wales and its use in correlation. Geol. J. 14, pp. 69-85.
- SORENSEN, H. (ed) 1974. The alkaline rocks. John Wiley & Sons, 622 p.
- SPEARS, D.A. 1970. A kaolinite mudstone (tonstein) in the British Coal Measures. J. Sed. Petrol. 40, pp. 386-394.
- SPEARS, D.A. 1971. The mineralogy of the Stafford tonstein. Proc. Yorks. geol. Soc. 38, pp. 497-516.
- SPEARS, D.A. & KANARIS-SOTIRIOU, R. 1979. A geochemical and mineralogical investigation of some British and other European tonsteins. Sedimentology 26, pp. 407-425.
- SPEARS, D.A. & RICE, C.M. 1973. An Upper Carboniferous tonstein of volcanic origin. Sedimentology 20, pp. 281-294.
- STEIGER, R.H. & JAGER, E. 1977. Subcommittee on geochronology: Convention on the use of decay constants in Geo- and Cosmochronology. Earth Planet. Sci. Lett. 36, pp. 359-362.

- STEVENSON, I.P., HARRISON, R.K. & SNELLING, N.J. 1970. Potassium argon age determination of the Waterswallows Sill, Buxton, Derbyshire. Proc. Yorks. geol. Soc. 37, pp. 445-447.
- STEVENSON, I.P. & GAUNT, G.C. 1971. Geology of the country around Chapel-en-le-Frith. Mem. geol. Surv. Gt. Br., 444p.
- STROGEN, P. 1973. The volcanic rocks of the Carrigogunnel area, Co. Limerick. Sci. Proc. Royal Dublin Soc. (Series A), 5, pp. 1-26.
- STROGEN, P. 1973. Brecciated lavas from County Limerick, Ireland, and their significance. Geol. Mag. 110, pp. 351-364.
- SUN, MING-SHAN, 1957. The nature of iddingsite in some basaltic rocks of New Mexico. Am. Mineralogist 42, pp. 525-533.
- SWANSON, G.A. & YULE, J.W. 1969. A rapid method for decomposition and the analysis of silicates and carbonates by atomic absorption spectroscopy. A.A. Newsletter 8, pp. 30-33.
- THOMAS, W.K.L. & KEMPE, D.R.C. 1963. Standard geochemical sample T-1. Geol. Surv. Div. Tanganyika. Dar-es-Salaam, 12 p.
- THOMPSON, R.N. & TILLEY, C.E. 1969. Melting and crystallisation relations of Kilauean basalts of Hawaii. The lavas of the 1959-60 Kilauea eruption. EarthPlanet.Sci. Lett. 5, pp. 469-477.
- THOMPSON, R.N., ESSON, J. & DUNHAM, A.C. 1972. Major element variation in the Eocene lavas of the Isle of Skye, Scotland. J. Petrol. 12, pp. 219-253.
- THOMPSON, R.N., GIBSON, I.L., MARRINER, G.F., MATTEY, D.P. & MORRISON, A.M. 1980. Trace-element evidence of multistage mantle fusion and polybaric fractional crystallisation in the Paleocene lavas of Skye, N.W. Scotland. J.Petrol. 21, pp. 265-293.

- THOREZ, J. & PIRLET, H. 1979. Petrology of K -Bentonite beds in the Carbonate series of the Visean and Tournaisian stages of Belgium. in: Proceedings of the International Clay Conference , 1978. Mortland M.M. & Farmer, V.C. (eds), Elsevier, pp. 323-332.
- THORNTON, C.P. & TUTTLE, O.F. 1960. Chemistry of igneous rocks: Differentiation index. Amer. J. Sci. 258, pp. 664-684.
- TILLEY, C.E. 1950. Some aspects of magmatic evolution. Q. Jl. geol. Soc. Lond. 106, pp. 37-61.
- TILLEY, C.E. & MUIR, I.D. 1962. The Hebridean Plateau magma type. Trans. Edinburgh Geol. Soc. 19, pp. 208-215.
- TOMKEIEFF, S.I. 1926. Some chloritic minerals of the Carboniferous basalts of Derbyshire. Min. Mag. 21, pp. 73-82.
- TOMKEIEFF, S.I. 1928. The volcanic complex of Calton Hill. Q. Jl. geol. Soc. Lond. 84, pp. 703-718.
- TRAILL, J.G. 1939. The geology and development of Mill Close Mine, Derbyshire. Econ. Geol. 34, pp. 851-889.
- TRAILL, J.G. 1940. Notes on the lower Carboniferous limestones and toadstones at Millclose Mine, Derbyshire. Trans. Inst. Min. Engrs. 49, pp. 191-229.
- TREWIN, N.H. 1968. Potassium bentonites in the Namurian of Staffordshire and Derbyshire. Proc. Yorks. geol. Soc. 37, pp. 73-91.
- VANDOROS, P., RUEGG, N.R. & CORDANI, U. 1966. On Potassium-Argon age measurements of basaltic rocks from southern Brazil. Earth Planet. Sci. Lett. 1, pp. 449-452.
- VAN LOON, J.C. & PARISSIS, C.M. 1969. Scheme of silicate analysis based on lithium metaborate fusion followed by atomic absorption spectrophotometry. The Analyst 94, pp. 1057-1062.
- WAGER, L.R. 1929. Metasomatism in the Whin Sill of the north of England. Part I: Metasomatism by lead vein solutions. Geol. Mag. 66, pp. 97-110.

- WALKDEN, G.M. 1970. Environmental studies in the Carboniferous limestone of the Derbyshire Dome. Unpublished Ph.D. Thesis University of Manchester.
- WALKDEN, G.M. 1972. The mineralogy and origin of interbedded clay wayboards in the Lower Carboniferous of the Derbyshire Dome. Geol. J. 8, pp. 143-160.
- WALKDEN, G.M. 1974. Palaeokarstic surfaces in upper Viséan (Carboniferous) limestones of the Derbyshire block, England. J. Sed. Petrol. 44, pp. 1232-1247.
- WALKDEN, G.M. 1977. Volcanic and erosive events in an upper Viséan carbonate platform, north Derbyshire. Proc. Yorks. geol. Soc. 41, pp. 347-366.
- WALKER, G.P.L. 1970. Compound and simple lava flows and flood basalts. Bull. Volc. 35, pp. 579-590.
- WALKER, G.P.L. 1972. Crystal concentration in ignimbrites. Contr. Mineral. Petrol. 36, pp. 135-146.
- WALKER, G.P.L. & CROASDALE, R. 1970. Characteristics of some basaltic pyroclastics. Bull. Vulc. 37, pp. 303-317.
- WALTERS, S.G. 1980. Black Hillock or Clear-the-Way Mine, Tideswell Moor. Bull. Peak Dist. Mines Hist. Soc. 7, pp. 327-332.
- WALTERS, S.G. & INESON, P.R. 1980a. Mineralisation within the igneous rocks of the south Pennine orefield. Bull. Peak Dist. Mines Hist. Soc. 7, pp. 315-325.
- WALTERS, S.G. & INESON, P.R. 1980b. The geology of Hallicar Wood Adit, Via Gellia, Derbyshire. Bull. Peak Dist. mines Hist. Soc. 7, pp. 353-356.
- WALTERS, S.G. & INESON, P.R. 1981. A review of the distribution and correlation of igneous rocks in Derbyshire, England. Mercian Geol. 8, pp. 81-132.

- WALTHAM, A.C. 1971. Shale units in the Great Scar Limestone of the Southern Askrigg Block. *Proc. Yorks. geol. Soc.* 38, pp. 285-292.
- WATKINS, N.D. & HAGGERTY, S.E. 1967. Primary oxidation variation and petrogenesis in a single lava. *Contr. Mineral. Petrol.* 15, pp. 251-271.
- WATKINS, N.D., SPARKS, R.S.J., SIGURDSSON, H., HUANG, T.C., FEDERMAN, A., CAREY, S. & NINKOVICH, D. 1978. Volume and extent of the Minoan Tephra from Santorini Volcano: New evidence from deep sea sediment cores. *Nature* 271, pp. 122-126.
- WATSON, W. 1811. A delineation of the strata of Derbyshire forming the surface from Bolsover in the east to Buxton in the west. Sheffield.
- WEAVER, C.E. 1958. The effects and geological significance of potassium 'fixation' by expandable clay minerals derived from muscovite, biotite, chlorite and volcanic material. *Amer. Min.* 43, pp. 839-861.
- WEAVER, C.E. 1963a. Interpretative value of heavy minerals from bentonites. *J. Sed. Petrol.* 33, pp. 343-349.
- WEAVER, C.E. 1963b. Mineralogy and petrology of some Ordovician K-bentonites and related limestones. *Geol. Soc. Amer. Bull.* 64, pp. 921-944.
- WEAVER, C.E. & POLLARD, L.D. 1973. The chemistry of clay minerals. Elsevier, 213 pp.
- WEBB, A.W. & McDOUGALL, I. 1967. A comparison of mineral and whole-rock potassium-argon ages of Tertiary volcanics from Central Queensland, Australia. *Earth Planet. Sci. Lett.* 3, pp. 41-47.
- WHITEHURST, J. 1778. An inquiry into the original stage and formation of the earth with observations on the strata of Derbyshire. London.

- WILKINSON, P. 1967. Volcanic rocks in the Peak District. in:
Geological Excursions in the Sheffield Region and the Peak
District National Park. Neves, R. & Downie, C. (eds), University
of Sheffield, pp. 47-53.
- WILKINSON, J.F.G. 1968. The petrography of basaltic rocks. in:
Basalts, vol.1, Hess, H.H. & Poldervaart, A. (eds), pp.163-214.
John Wiley & Sons, 862 p.
- WILLIAMSON, I.A. 1970. Tonsteins - their nature, origins and uses.
Min. Mag. 122, pp. 119-125; pp. 203-211.
- WILSHIRE, H.G. 1958. Alteration of olivine and orthopyroxene in
basic lavas and shallow intrusions. Am. Mineralogist 43, pp. 120-147.
- WILSHIRE, H.G. 1959. Deuteric alteration of volcanic rocks. J. Roy.
Soc. New South Wales 93, pp. 105-120.
- WINCHESTER, H.A. & FLOYD, P.A. 1976. Geochemical magma type
discrimination application to altered and metamorphosed basic
igneous rocks. Earth Planet. Sci. Lett. 28, pp. 459-469.
- WORLEY, N.E. & DORNING, K.J. 1977. Carbonaceous and fossiliferous
material from some Derbyshire clay wayboards. Mercian Geol.
6, pp. 145-154.
- WRIGHT, T.L. & DOHERTY, P.C. 1970. A linear programming and least
squares computer method for solving petrological mixing problems.
Bull. Geol. Soc. Amer. 81, pp. 1995-2008.
- WOOD, D.A. 1978. Major and trace element variations in the Tertiary
lavas of eastern Iceland and their significance with respect to
the Iceland geological anomaly. J. Petrol. 19, pp. 393-436.
- WOOD, D.A., GIBSON, I.L. & THOMPSON, R.N. 1976. Elemental mobility
during zeolite facies metamorphism of the Tertiary basalts of
eastern Iceland. Contr. Mineral. Petrol. 55, pp. 241-254.

- YODER, H.S. & EUGSTER, H.P. 1955. Synthetic and natural muscovites.
Geochem. Cosmochim Acta 8, pp. 225.
- YODER, H.S. & TILLEY, C.E. 1962. Origin of basalt magmas: An
experimental study of natural and synthetic rock systems. J.
Petrol. 3, pp. 342-532.
- YORK, D. & FARQUHAR, R.M. 1972. The earth's age and geochronology.
Pergamon Press, 176 pp.

APPENDICES

*Analysis number refers to Appendix 5.

*	TI02	FE203	FE0	MGO	CA0	NA20	K20	H20+	H20-	CO2%	CU	NI	ZN _{ppm}
101	1.55	9.97	4.24	5.27	8.14	2.53	0.54	3.26	1.50	2.50	57	200	170
102	1.60	10.79	5.26	4.95	7.52	2.35	0.59	3.88	1.16	2.73	60	140	150
103	1.53	11.50	6.28	4.94	7.58	1.86	1.16	4.40	1.17	4.68	99	78	64
104	1.56	11.16	5.87	4.62	8.35	1.04	1.05	4.32	0.90	4.67	30	38	48
105	1.53	11.06	6.46	4.94	10.38	1.73	0.78	4.41	1.36	8.05	103	90	46
106	1.50	10.27	6.00	4.55	11.79	2.15	0.78	4.28	0.98	8.02	70	90	47
107	1.42	6.11	3.24	2.70	12.56	2.02	1.15	3.70	1.43	9.01	95	50	30
108	1.38	4.45	2.02	2.53	13.85	1.81	1.66	3.34	1.50	11.90	105	27	32
109	1.50	2.41	0.46	1.87	11.20	1.16	3.51	4.03	1.56	8.45	32	45	15
110	1.50	3.20	0.68	1.91	9.79	1.31	3.43	4.09	1.53	7.75	24	105	11
111	1.88	3.49	0.62	2.53	6.84	1.26	4.32	4.88	2.38	4.74	35	105	45
112	1.32	3.49	1.10	2.53	6.84	0.46	4.51	3.14	1.65	12.76	106	56	14
113	1.13	3.38	2.08	4.42	11.23	0.30	5.50	2.53	1.23	12.92	80	36	45
114	1.25	7.74	2.00	4.70	9.76	0.27	6.17	2.06	1.38	12.87	5	68	45

	TI02	FE203	FE0	MGO	CA0	NA20	K20	H20+	H20-	CO2	CU	NI	ZN
116	1.42	2.63	0.40	0.76	13.09	3.11	2.06	1.34	1.37	8.38	150	43	585
117	1.53	2.86	0.40	0.66	13.26	2.94	3.25	1.26	0.84	8.12	230	25	640
118	1.30	3.21	0.44	0.90	12.02	1.94	3.82	2.14	1.43	8.72	112	192	1500
119	1.05	4.28	0.66	1.70	15.27	1.52	2.60	3.32	1.17	11.98	30	111	700
120	1.60	3.37	0.44	1.15	7.13	2.78	2.05	3.00	2.42	2.98	101	52	28500
121	1.93	5.14	0.52	2.51	4.65	1.23	3.13	5.65	4.82	2.51	105	300	75000
122	1.30	4.62	0.92	2.72	11.35	0.58	2.64	4.54	5.71	7.64	90	180	55000
123	1.36	3.35	0.88	2.83	10.80	1.01	3.56	4.84	1.58	7.82	105	166	65000
124	1.33	5.90	1.10	4.00	3.53	0.57	3.26	5.06	1.49	3.81	355	300	80000
125	0.42	0.52	0.18	0.45	23.74	0.39	1.66	0.82	0.09	19.64	10	114	1000
126	0.74	0.75	0.00	0.31	13.70	0.74	2.87	1.65	0.66	10.86	28	176	850
127	0.55	0.65	0.13	0.22	26.83	1.15	2.21	0.96	0.17	22.88	37	20	480
128	2.31	2.00		0.53	7.67	0.75	5.27				178	145	2000
129	0.76	0.84	0.16	0.45	32.02	0.15	2.13	2.50	0.53	28.87	31	600	400
130	0.76	0.95	0.14	0.62	26.07	0.14	2.28	2.93	1.01	24.06	30	90	600
131	1.43	1.27		0.97	16.18	0.19	3.64				17	182	850
132	1.67	0.42	0.08	0.27	10.22	3.02	1.40	3.40	0.40	7.90		53	1000
133	1.57	0.50	0.08	0.30	11.76	2.38	1.43	4.23	0.50	8.80	45	204	1050
134	2.37	0.63		0.44	8.57	2.94	1.95				70	143	1500

	T102	FE2O3	FeO	HGO	CaO	NA2O	K2O	H2O+	H2O-	CO2	CU	NI	ZN
137	1.07	10.31	5.88	5.70	12.84	1.70	1.60	4.54	1.72	8.45	66	268	300
138	1.98	6.80	3.73	4.30	14.23	2.02	2.85	3.34	1.51	8.18	60	170	290
139	1.85	9.73	0.16	1.11	7.18	2.13	1.94	1.04	2.08	6.38	53	133	365
140	1.75	2.52	0.75	1.52	15.49	0.17	5.07	2.20	1.76	10.26	80	80	23
141	1.45	4.18	2.12	1.91	13.60	1.32	3.72	1.88	0.94	13.02	10	108	0
142	1.45	7.04	3.49	2.16	17.25	1.40	3.44	2.50	1.15	13.60	63	163	290
143	1.05	8.88	4.82	2.24	14.73	1.70	3.31	3.21	1.42	11.32	67	228	500
144	1.75	10.10	4.03	2.55	12.53	1.85	2.05	3.60	1.61	0.97	75	283	275
145	1.24	3.00	0.02	0.85	21.16	0.97	3.17	2.08	1.51	16.65	12	75	86
146	1.61	2.30	0.36	0.53	17.30	0.61	4.77	2.40	0.84	15.33	RD	<10	31
147	1.83	1.64	0.22	0.34	18.41	0.22	5.94	2.64	0.59	15.60	RD	125	5
148	1.91	0.56	0.14	0.24	19.06	3.01	1.28	1.57	0.26	16.83	10	24	25
149	1.35	1.00	0.14	0.27	15.22	2.95	1.37	1.60	0.37	16.83	RD	RD	31
150	1.42	0.74	0.10	0.25	19.97	3.51	1.44	1.77	0.27	15.43	7	43	RD
151	1.92	2.98	0.24	0.38	14.45	4.38	1.43	2.47	0.47	10.44	7	RD	37
152	1.02	8.80	1.04	1.94	16.45	1.88	1.80	2.34	1.53	12.33	48	270	22
153	1.65	5.26	1.06	2.83	13.50	4.36	1.08	2.00	0.86	10.21	70	88	27
154	1.80	8.87	2.91	4.66	7.20	3.90	1.46	4.26	1.86	4.50	80	206	50
155	1.83	0.00	4.84	3.36	11.05	1.05	2.85	4.84	2.53	7.61	42	168	44

APPENDIX 1(A)...continued.

	TI02	FE203	FE0	HGO	CA0	NA2O	K2O	H2O+	H2O-	CO2	CU	NI	ZN
157	0.35	6.10	0.44	1.56	32.20	0.61	1.86			27.73	24	72	35
158	0.42	5.28	0.28	0.98	30.59	1.54	1.88			18.09	80	10	7
159	1.01	11.02	0.80	1.82	11.79	3.66	2.82			0.23	23	132	90
160	0.87	10.28	0.99	2.31	17.62	4.11	0.40			13.51	25	40	60
161	0.99	14.10	0.78	3.01	14.08	1.87	0.92			8.76	80	45	52
162	0.99	18.28	0.64	2.42	13.10	1.53	1.17			8.42	9	240	49
163	0.92	18.99	0.40	2.00	13.11	1.63	1.08			7.34	80	59	57
164	1.40	11.42	1.24	5.08	10.11	2.50	0.84			3.94	80	70	72

165	2.08	12.70	0.14	3.27	1.69	0.13	4.48	7.02	4.61	1.08	44	132	88
166	2.13	6.99	0.30	3.95	1.49	0.19	4.23	5.60	5.07	0.20	80	64	128
167	1.87	15.38	0.16	2.47	1.68	0.18	3.38	6.66	4.35	0.34	50	78	935
168	2.40	4.30	0.10	1.26	1.06	0.18	2.47	7.34	2.70	0.23	50	247	630
169	2.53	2.89	0.18	1.42	0.69	0.17	6.00	6.08	5.02	0.08	80	111	80
170	1.43	11.97	0.16	0.73	10.05	0.13	2.91	3.15	1.46	6.67	45	89	13
171	2.15	3.10	0.20	2.37	1.66	0.12	4.10	6.32	9.58	0.36	80	80	13

	TI02	FE203	FE0	HGO	CA0	NA2O	K2O	H2O+	H2O-	CO2	CU	NI	ZN
172	1.29	11.68	0.16	1.26	14.21	0.77	3.83	2.41	2.20	11.67	80	107	80
173	1.76	0.61	0.28	0.27	16.84	1.96	2.00	4.20	0.46	13.92	80	165	8
174	1.18	0.61		0.50	22.02	3.69	0.15				31	89	10
175	1.52	1.08	0.32	0.63	16.64	1.51	3.22	6.12	1.92	13.45	32	160	18

APPENDIX 1 (A)...continued.

APPENDIX 1(B).....XRF MAJOR ELEMENT ANALYSES.

	1	2	3	4	5	6	7
SI02	45.40	46.10	45.56	45.93	52.60	47.70	51.74
TI02	2.16	2.23	1.96	2.15	1.91	1.72	1.50
AL203	13.76	14.25	12.40	13.92	14.33	15.34	13.37
FF203	5.44	*	2.25	4.83	4.15	5.48	6.60
FE0	5.85	10.79	1.92	6.97	2.32	5.13	4.25
MNO	0.13	0.12	0.09	0.14	0.20	0.16	0.10
MGO	9.87	7.86	3.01	8.24	6.87	8.42	7.45
CA0	8.17	8.31	13.89	9.29	7.09	7.91	6.74
NA20	2.08	2.18	1.18	2.40	3.03	2.77	2.31
K20	0.87	0.95	4.09	0.95	0.56	0.63	0.51
H20+	2.11	2.91	3.13	3.19	2.93	3.03	2.96
H20-	4.14	2.85	2.02	1.32	3.11	2.72	2.09
P205	0.41	0.37	0.49	0.43	0.32	0.26	0.22
CO2	BD	ND	7.30	0.77	1.30	BD	0.14
SO3	0.10	ND	0.99	0.10	0.04	0.02	0.01
TOTAL	100.50	93.92	100.27	100.62	100.82	101.28	99.98
	8	9	10	11	12	13	14
SI02	49.20	47.39	46.87	43.82	46.44	46.58	49.18
TI02	1.79	1.57	1.66	1.78	1.87	1.79	2.15
AL203	14.77	14.10	14.45	14.49	15.23	15.15	13.70
FF203		4.45	4.23	4.02	4.47	4.33	5.57
FF0	9.27	6.03	5.94	4.88	4.70	4.83	4.46
MNO	0.15	0.18	0.20	0.06	0.04	0.07	0.06
MGO	6.81	9.40	8.98	6.92	9.19	8.56	7.19
CA0	8.74	7.90	8.24	9.24	4.58	7.86	6.98
NA20	2.92	2.55	2.36	2.27	2.34	2.18	2.24
K20	0.65	0.74	0.46	0.27	2.24	0.49	0.39
H20+	1.72	3.29	3.02	3.32	5.28	4.27	3.36
H20-	3.31	2.21	3.15	2.32	1.58	3.27	3.54
P205	0.20	0.26	0.28	0.26	0.23	0.26	0.26
CO2	ND	0.17	BD	1.05	1.97	BD	BD
SO3	ND	0.04	0.06	0.12	0.02	0.04	0.32
TOTAL	99.53	100.27	99.90	99.82	100.19	99.68	99.60

* Total iron as FeO.

ND Not determined.

BD Below detection.

APPENDIX 1 (B)...continued.

	15	16	17	18	19	20	21
S102	47.65	49.11	48.71	47.77	48.18	49.78	44.83
T102	1.74	1.89	1.88	1.84	1.85	1.71	2.12
AL2O3	14.16	15.00	15.58	15.34	15.05	15.58	13.47
FE2O3	4.91	4.46	4.71	11.23	10.70	5.57	13.74
FE0	5.68	5.16	5.36	**		4.63	
MNO	0.06	0.09	0.14	0.11	0.08	0.05	0.08
MGO	8.08	7.66	7.36	6.89	7.07	5.68	7.26
CAO	8.45	9.03	8.28	8.52	8.10	7.85	9.45
NA2O	2.26	2.26	2.64	2.47	2.64	2.42	2.36
K2O	0.66	0.58	1.03	1.07	1.10	0.60	1.15
H2O+	3.41	3.05	3.24	3.15	3.44	3.26	3.08
H2O-	2.05	1.94	0.70	0.71	0.51	1.50	1.26
P2O5	0.24	0.24	0.35	0.36	0.35	0.26	0.43
CO2	BD	0.34	BD	0.81	0.55	1.62	1.05
SO3	0.02	0.01	0.03	0.16	0.00	0.06	0.26
TOTAL	99.36	100.80	100.58	100.43	99.70	100.57	100.05
	22	23	24	25	26	27	28
S102	44.42	45.65	46.57	47.84	46.61	46.98	46.19
T102	2.13	1.92	2.18	1.89	1.70	1.67	1.72
AL2O3	13.69	13.22	14.06	14.27	14.06	13.23	13.59
FE2O3	13.08	4.36	11.45	11.59	5.39	5.47	5.16
FF0		6.90			3.49	5.20	5.06
MNO	0.10	0.21	0.12	0.10	0.11	0.11	0.13
MGO	7.10	10.79	8.73	8.26	10.14	9.23	8.65
CAO	10.49	7.38	9.38	8.34	8.04	8.69	9.96
NA2O	2.23	2.00	2.18	2.42	2.14	2.01	2.15
K2O	1.11	0.79	0.87	0.66	0.22	0.30	0.22
H2O+	3.28	4.22	3.51	3.84	3.97	3.78	3.43
H2O-	0.86	1.86	1.11	0.54	3.64	2.41	2.11
P2O5	0.42	0.32	0.38	0.26	0.24	0.23	0.24
CO2	1.34	0.15	BD	BD	BD	0.90	1.32
SO3	0.19	0.06	0.01	0.08	0.04	0.10	0.05
TOTAL	100.42	100.33	100.53	100.07	100.00	100.30	99.97

** Total iron as Fe₂O₃.

APPENDIX 1 (B)...continued.

	29	30	31	32	33	34	35
SI02	43.17	45.60	51.16	45.63	45.20	45.28	44.42
TI02	1.79	1.80	2.68	1.74	1.76	1.76	1.56
AL203	13.36	12.34	11.55	14.00	13.85	14.15	12.76
FE203	2.40	2.36	13.78	11.34	11.20	11.16	9.38
FEO	0.12	0.16					
MNO	0.08	0.09	0.07	0.10	0.08	0.08	0.05
MGO	1.58	1.58	6.88	10.11	7.17	9.31	8.94
CAO	13.87	14.80	4.75	7.11	10.63	7.49	5.12
NA2O	1.10	0.38	2.44	2.11	2.22	2.21	3.35
K2O	1.86	1.94	1.24	0.85	0.90	0.88	1.45
H2O+	3.50	3.44	2.79	4.19	3.03	4.31	6.60
H2O-	1.65	2.41	1.97	2.83	1.70	2.29	2.44
P2O5	0.26	0.26	0.45	0.30	0.33	0.30	0.17
CO2	10.28	10.56	RD	RD	1.50	0.50	3.67
SO3	4.27	4.91	0.11	0.10	0.24	0.08	0.31
TOTAL	99.29	100.13	99.87	100.41	99.89	99.80	100.30
	36	37	38	39	40	41	42
SI02	44.14	48.76	45.70	46.40	48.74	48.62	40.31
TI02	1.75	1.86	1.84	1.88	1.86	1.89	1.43
AL203	16.09	14.60	16.71	16.63	14.73	15.17	10.51
FE203	4.75	4.60	5.51	4.52	4.21	4.17	0.71
FEO	7.43	6.06	6.92	8.89	6.58	5.32	0.32
MNO	0.12	0.16	0.04	0.21	0.17	0.12	0.10
MGO	6.78	8.35	6.81	7.87	8.09	6.65	0.52
CAO	4.03	9.12	2.92	1.21	8.94	9.68	22.96
NA2O	3.01	2.61	3.28	2.24	2.67	3.00	0.78
K2O	1.33	0.79	1.17	2.18	0.80	0.86	0.89
H2O+	6.09	2.36	6.37	6.49	2.43	2.30	3.26
H2O-	1.24	1.26	1.26	1.00	10.95	1.54	0.40
P2O5	0.26	0.38	0.28	0.27	0.30	0.30	0.21
CO2	2.28	RD	1.75	0.40	0.13	0.57	18.32
SO3	0.06	0.05	0.09	0.18	0.04	0.04	0.28
TOTAL	99.36	100.96	100.65	100.37	100.62	100.23	101.09

APPENDIX 1 (B)...continued.

	43	44	45	46	47	48	49
SI02	54.72	34.06	21.17	58.00	52.93	45.87	39.22
TI02	1.48	2.70	2.02	1.41	3.90	1.28	1.43
AL203	24.81	13.70	9.45	12.71	28.24	27.57	27.92
FE203	1.63	1.75	2.77	1.99	0.86	3.14	9.43
FE0	0.26	0.29	0.36	5.41	0.25	0.28	0.46
MNO	0.00	0.03	0.08	0.09	0.01	0.00	0.00
MGO	1.92	1.58	1.14	4.28	0.92	2.02	1.39
CA0	0.51	19.58	30.47	4.04	0.17	1.53	0.55
NA20	0.23	0.03	0.02	1.17	0.07	0.21	0.25
K20	5.66	2.72	1.62	1.35	2.64	6.18	3.85
H20+	5.50	3.84	1.92	3.78	9.60	6.64	8.62
H20-	2.59						
P205	0.09	0.58	0.44	0.17	0.03	0.06	0.03
CO2	80	14.54	23.63	3.00	80	0.76	0.23
SO3	1.26	0.12	5.21	1.77	0.47	4.22	6.86
TOTAL	100.66	100.52	100.30	99.25	100.00	99.76	100.24
	50	51	52	53	54		
SI02	44.07	53.44	43.95	50.88	64.69		
TI02	2.97	1.12	1.56	1.00	0.80		
AL203	31.21	27.85	34.07	19.49	18.44		
FE203	1.06	1.75	1.03	2.27	1.51		
FE0	0.41	1.22	0.59	0.34	0.29		
MNO	0.03	0.03	0.01	0.01	0.00		
MGO	2.23	0.68	1.36	1.31	1.40		
CA0	0.61	0.32	0.23	0.31	0.47		
NA20	0.16	0.15	0.42	0.34	0.19		
K20	4.15	7.75	4.98	5.09	4.74		
H20+	11.24	3.03	10.60	7.90	7.12		
H20-							
P205	0.05	0.02	0.03	0.03	0.03		
CO2	0.53	2.76	0.26	0.24	0.12		
SO3	0.05	0.01	1.08	1.16	0.00		
TOTAL	98.77	100.13	100.17	99.37	99.98		

APPENDIX 1(B)...continued.

	60	61	62	63	64	65	66
SI02	47.34	47.92	45.38	47.68	41.13	46.71	47.41
TI02	1.54	1.54	1.92	1.84	2.01	2.10	1.86
AL203	12.14	13.41	12.38	11.71	11.99	12.49	12.06
FE203	4.30	3.78	9.93	7.61	8.48	8.27	7.20
FE0	6.66	7.79	2.89	2.69	3.74	3.57	3.33
MNO	0.16	0.18	0.08	0.12	0.10	0.09	0.11
MGO	8.06	8.85	6.20	3.70	5.77	5.67	4.97
CA0	10.01	3.58	7.72	10.09	10.08	7.57	9.51
NA20	3.50	2.87	0.82	0.99	0.84	1.11	1.22
K20	0.74	1.03	2.79	2.29	2.92	2.76	2.40
H20+	3.05	1.93	8.33	9.19	10.33	7.48	8.19
H20-	1.51	1.44	1.37	1.36	1.56	1.87	1.44
P205	0.25	0.24	0.38	0.33	0.35	0.35	0.36
CO2							
SO3							
TOTAL	99.26	99.56	100.19	99.60	99.88	100.04	100.07
	67	68	69	70	71	72	73
SI02	46.16	43.33	43.96	52.85	48.30	46.26	47.63
TI02	1.95	1.29	1.30	2.45	1.50	1.79	1.54
AL203	13.02	9.65	9.20	18.16	13.98	12.51	14.41
FE203	8.18	22.88	23.41	6.11	2.99	3.68	7.32
FE0	3.50	0.20	0.38	0.50	7.43	7.45	5.02
MNO	0.10	0.06		0.01	0.12	0.19	0.23
MGO	5.90	1.79	1.89	3.02	8.81	11.09	10.36
CA0	7.53	0.57	0.66	0.68	8.35	7.24	7.09
NA20	1.01	0.15	0.14	0.11	2.12	1.90	2.79
K20	2.68	2.61	2.70	5.13	0.22	0.73	0.75
H20+	7.62	6.19	3.73	5.65	5.30	6.03	2.05
H20-	1.85				0.11	0.32	0.29
P205	0.38	0.02	0.01	0.01	0.18	0.28	0.21
CO2					0.88	0.02	0.16
SO3		10.75	13.28	4.88			
TOTAL	99.88	99.49	100.84	99.56	100.29	99.49	99.85

APPENDIX 1(B)...continued.

	74	75	76	77	78	79	80
S102	45.61	49.03	43.55	43.13	47.93	44.01	43.13
T102	2.04	1.81	1.56	1.52	1.63	2.15	
AL203	14.72	13.57	13.19	11.94	13.29	14.34	23.25
FF203	4.10	3.56	4.78	5.45	2.95	0.44	1.87
FE0	7.29	5.65	5.51	4.16	6.30	1.56	4.81
MNO	0.17	0.13	0.07	0.13	0.18	0.06	0.02
MGO	8.79	5.27	3.29	4.62	6.03	6.24	6.50
CA0	7.74	8.68	13.95	13.70	8.41	6.15	5.58
NA20	2.32	2.17	2.27	2.33	2.20	3.95	3.60
K20	0.78	0.20	0.28	0.37	0.40	1.20	3.04
H20+	5.67	3.93	2.76	4.40	4.90	6.43	3.76
H20-	0.42	0.15	0.17	0.62	0.52	0.63	1.06
P205	0.27	0.21	0.21	0.17	0.20	0.21	
C02	0.35	6.15	8.17	7.74	5.09	3.23	3.50
S03							
TOTAL	100.27	100.51	99.70	100.28	100.12	100.50	100.10
	81	82	83	84	85	86	87
S102	47.03	47.79	48.98	48.23	49.04	45.14	43.94
T102		1.85	1.74	1.19	3.75	1.96	2.03
AL203	22.45	14.60	14.06	14.56	11.86	16.54	15.44
FE203		1.80	3.36	2.68	4.31	2.58	3.90
FE0	7.00	6.93	7.27	8.28	7.81	9.13	8.25
MNO		0.00	0.15	0.16	0.24	0.12	0.02
MGO	8.79	3.97	8.26	8.75	5.60	7.68	9.64
CA0	2.92	11.60	8.62	9.36	11.37	9.29	10.56
NA20	2.63	2.61	2.62	2.74	2.19	2.72	2.81
K20	4.55	0.16	0.44	0.58	0.40	1.16	1.34
H20+	3.65	1.79	1.76	2.44	2.24	2.81	2.33
H20-			1.75	0.69		0.84	0.10
P205		0.19	0.19	0.16	0.26	0.22	
C02	1.90	5.94	0.36	0.07	1.16		
S03			0.15	0.07			
TOTAL	100.92	99.28	99.71	99.96	100.23	100.24	100.43

APPENDIX 1 (B)...continued.

	88	89	90	91	92	93	94
SI02	45.15	43.47	40.13	34.57	44.60	42.79	39.72
TI02	2.06	2.02	1.93	1.93	1.74	1.37	1.49
AL203	13.31	12.19	11.41	10.72	12.43	11.20	11.91
FE203	4.46	5.31	2.62	2.22	3.89	3.16	4.98
FE0	7.10	6.96	7.86	5.11	7.38	5.30	8.68
MNO	0.17	0.19	0.16	0.16	0.09	0.10	0.10
MGO	10.26	12.77	15.76	6.78	14.31	11.08	15.98
CA0	7.74	7.32	4.09	15.12	1.46	7.09	2.16
NA20	2.29	1.54	0.33	1.02	1.60	1.03	1.04
K20	0.74	0.98	0.71	4.20	1.37	2.98	1.22
H20+	6.60	7.21	8.09	4.14	6.54	5.31	7.65
H20-			3.90	1.43	3.85	2.56	3.73
P205	0.31	0.31	0.31	0.24	0.20	0.34	0.19
CO2	0.00	0.00	2.40	11.47	0.30	5.08	1.01
S03				0.95			
TOTAL	100.19	100.27	99.79	99.66	99.74	99.83	100.84
	95	96	97	98	99	100	
SI02	35.89	19.92	36.90	10.48	30.44	35.31	
TI02	1.81	0.50	1.51	0.84	1.33	1.01	
AL203	10.23	10.83	17.29	10.43	12.96	11.36	
FE203	9.52	8.75	13.68	8.02	7.83	9.00	
FE0							
MNO							
MGO	5.14	0.58	4.38	0.81	1.43	2.23	
CA0	14.70	28.44	7.46	29.34	21.30	19.09	
NA20	0.43		1.56			0.62	
K20	0.60		3.25			1.10	
H20+	6.97	8.02	5.21	8.13	7.74	2.38	
H20-	4.00	2.70	2.90	4.56	4.46	3.00	
P205							
CO2	10.73	8.03	5.26	8.10	4.00	14.40	
S03	80	12.03	0.04	6.09	4.80	80	
TOTAL	100.02	99.80	99.43	95.79	96.29	90.27	

APPENDIX 2....XRF TRACE ELEMENT DATA .

	1	2	3	4	5	6	7
BA	262	241	276	264	270	221	193
CO	84		32	91	59	77	75
CR	455		402	387	387	316	300
CU	79		79	70	82	61	53
NI	300		144	275	147	127	135
PR	4	10	4	7	9	23	13
RB	9	6	82	15	3	3	4
SR	658	351	332	441	405	328	289
V	200		186	208	220	134	169
Y	30	25	30	32	32	26	13
ZN	101	61	37	94	224	180	128
ZR	194	74	158	167	148	124	107
	8	9	10	11	12	13	14
BA	241	213	190	136	152	149	180
CO		77	76	80	68	72	80
CR		347	344	269	318	267	194
CU		48	75	48	54	39	62
NI		234	211	122	167	117	106
PB		14	7	3	3	80	4
RB		11	80	80	15	80	4
SR		306	341	338	267	400	417
V		163	183	201	215	200	206
Y	27	18	26	27	27	26	27
ZN	367	147	123	162	138	123	107
ZR	132	112	121	118	115	119	143

APPENDIX 2...continued.

	15	16	17	18	19	20	21
RA	165	185	315	336	300	138	406
CO	82	72	70	69	70	85	111
CR	247	279	188	190	185	236	345
CU	44	85	32	43	32	63	84
NI	115	151	88	83	90	103	299
PB	4	BD	BD	7	10	4	7
RB	9	7	18	19	20	12	24
SR	365	348	401	403	390	377	415
Y	164	162	179	191	195	194	191
Y	31	26	27	26	25	16	26
ZN	103	92	84	117	91	136	115
ZR	118	123	139	140	131	111	172
	22	23	24	25	26	27	28
BA	552	240	370	183	146	172	153
CO	100	90	89	80	85	91	84
CR	340	403	409	382	361	348	386
CU	70	69	74	64	50	56	61
NI	279	296	307	225	220	235	239
PB	11	6	5	PD	BD	BD	BD
RB	19	16	20	12	BD	BD	BD
SR	408	268	372	267	282	256	277
V	195	195	238	177	175	162	172
Y	27	24	29	28	31	25	26
ZN	121	88	100	95	128	105	103
ZR	169	133	155	116	121	113	118

APPENDIX 2...continued.

	29	30	31	32	33	34	35
RA	79	90	334	237	241	290	52
CO	52	38	75	85	67	87	67
CR	398	337	59	384	363	381	363
CU	51	12	84	40	59	60	64
NI	118	79	82	210	220	243	132
PB	9	3	10	5	80	80	10
RB	16	32	27	16	16	11	9
SR	151	113	294	340	351	351	177
V	196	186	211	189	198	207	177
Y	30	34	37	23	23	27	26
ZN	20	13	121	115	135	138	116
ZR	115	112	184	170	126	128	89
	36	37	38	39	40	41	42
BA	168	302	168	220	285	259	82
CO	91	81	103	107	88	81	32
CF	453	358	509	473	303	379	293
CU	97	81	82	99	80	86	15
NI	295	242	297	272	210	275	50
PB	80	26	80	9	17	7	6
RB	12	17	12	24	17	15	9
SR	90	345	90	90	358	402	100
V	229	182	245	231	175	196	155
Y	24	27	27	20	30	25	10
ZN	126	104	130	111	97	74	6
ZR	101	128	103	101	133	130	88

APPENDIX 2...continued.

	60	61	62	63	64	65	66
BA							
CO							
CP	320	315	310	265	310	350	335
CU	20	55	BD	40	10	25	15
NI	255	250	270	120	260	205	220
PB	BD	BD	BD	10	BD	BD	BD
RR	15	20	35	40	20	40	35
SR	315	185	175	200	70	210	215
V	290	275	300	235	315	315	320
Y	15	15	15	10	20	20	15
ZN	70	70	60	45	65	50	55
ZR							
	67	68	69	70			
RA		101	124	91			
CO		86	61	30			
CP	335	166	238	482			
CU	BD	78	67	56			
NI	290	286	298	322			
PB	BD	65	70	24			
RR	40	66	80	154			
SF	185	52	70	116			
V	305	146	168	258			
Y	30	10	6	9			
ZN	60	30	40	44			
ZP		88	117	215			
	83	84	90	91	92	93	94
RA	80	90	100	150	100	100	100
CO	35	30					
CR	310	210	300	250	350	250	400
CU	66	23					
NI	230	160	250	100	200	150	350
PB							
RB							
SR	220	200	80	100	250	100	150
V	170	230	150	150	150	150	150
Y							
ZN							
ZR	100	90	300	150	400	300	400

APPENDIX 3....CIPW NORMS*

	1	2	3	4	5	6	7
Q					8.70		7.60
OR	5.44	6.03		5.85	3.55	3.90	3.19
AB	18.70	19.80		21.32	27.42	25.54	20.65
AN	27.20	28.23		25.52	25.62	28.93	25.95
WO	5.43	5.60		8.20	4.10	4.36	3.26
DI EN	3.39	3.33		4.71	2.95	2.62	1.86
FS	1.71	1.98		3.12	0.78	1.51	1.27
HV EN	12.12	14.54		5.73	15.36	12.16	17.72
FS	6.13	8.64		3.79	4.04	6.99	12.12
OL FO	7.41	2.21		7.73	0.00	5.00	0.00
FA	4.13	1.45		5.64	0.00	3.17	0.00
MT	2.18	2.18		2.18	2.18	2.18	2.18
IL	4.39	4.88		4.27	3.87	3.42	3.00
AP	1.00	0.93		1.09	0.79	0.63	0.54
PY	0.19	0.00		0.09	0.00	0.06	0.02
TOTAL	99.42	99.79		99.25	99.55	99.36	99.36
%AN	59.26	58.78		54.50	48.30	54.02	55.69
A	13.23	15.56		15.52	23.44	16.52	14.72
F	42.49	45.35		44.37	31.68	42.65	46.44
M	44.27	39.09		38.11	44.87	40.84	38.83
	8	9	10	11	12	13	14
Q	0.60			4.82		0.34	7.18
OR	4.08	4.61	2.90	1.72		3.13	2.48
AB	26.15	22.85	21.32	20.65		20.06	20.48
AN	26.77	26.23	29.32	30.65		32.66	28.23
WO	7.41	5.58	5.15	6.99		3.27	3.05
DI EN	4.45	3.45	3.20	4.33		2.11	1.85
FS	2.58	1.80	1.65	2.25		0.95	1.03
HV EN	13.51	12.91	16.49	14.18		21.03	17.45
FS	7.83	6.74	8.51	7.36		9.44	9.66
OL FO	0.00	5.86	2.93	0.00		0.00	0.00
FA	0.00	3.37	1.66	0.00		0.00	0.00
MT	2.18	2.18	2.18	2.18		2.18	2.18
IL	3.61	3.15	3.36	3.65		3.69	4.41
AP	0.49	0.65	0.70	0.65		0.65	0.65
PY	0.00	0.09	0.13	0.24		0.08	0.66
TOTAL	99.64	99.49	99.50	99.66		99.59	99.29
%AN	50.59	53.45	57.89	59.75		61.95	57.95
A	19.85	15.36	13.91	15.22		14.28	14.52
F	42.28	40.82	41.82	43.37		39.98	45.86
M	37.87	43.32	44.27	41.42		45.74	39.62

* All norms calculated on an anhydrous/CO₂ free basis and with Fe₂O₃ standardised to 1.5%.

APPENDIX 3...continued.

	15	16	17	18	19	20	21
Q		2.16				5.64	
OR	4.14	3.55	6.38	4.68	6.91	3.78	7.39
AR	20.39	20.06	23.27	22.09	23.69	21.75	21.66
AN	28.24	30.46	28.73	29.10	27.55	31.71	24.68
WO	6.15	6.20	4.85	5.44	5.49	3.28	6.70
DI	3.65	3.81	2.89	3.10	3.22	1.77	3.60
EN	2.20	2.03	1.72	2.10	2.01	1.41	2.88
FS	17.65	16.20	14.03	13.00	13.49	13.23	7.61
HV	10.64	8.61	8.33	8.80	8.41	10.55	6.07
EN	0.09	0.00	1.53	1.41	1.38	0.00	5.89
FO	0.06	0.00	1.00	1.05	0.95	0.00	5.10
FA	2.18	2.18	2.18	2.18	2.18	2.18	2.18
MT	3.51	3.76	3.70	3.69	3.72	3.44	4.37
II	0.58	0.58	0.86	0.88	0.86	0.63	1.09
AP	0.04	0.02	0.06	0.32	0.17	0.13	0.52
PY	99.51	99.59	99.54	99.82	100.03	99.48	99.84
TOTAL	58.06	60.30	55.25	56.85	53.77	59.32	53.26
%AN	14.74	15.42	19.02	18.42	19.51	17.72	16.37
A	44.50	42.39	42.91	45.76	43.64	49.06	49.79
F	40.76	41.69	38.08	35.81	38.86	33.22	33.85
M							
	22	23	24	25	26	27	28
Q						0.18	
OR	7.15	4.96	5.44	4.14	1.42	1.95	1.36
AR	20.48	18.02	19.46	21.66	19.77	18.28	19.55
AN	26.11	26.32	27.40	27.59	30.64	28.08	28.79
WO	7.60	5.42	7.96	4.01	4.65	6.92	9.41
DI	4.07	3.42	4.82	3.57	3.18	4.26	5.80
EN	3.29	1.66	2.64	2.15	1.10	2.26	3.07
FS	6.35	13.71	10.65	15.88	24.07	20.37	13.89
HV	5.14	6.68	5.77	9.56	8.26	10.80	7.35
EN	6.15	3.02	5.18	1.61	0.17	0.00	2.41
FO	5.48	4.30	3.09	1.07	0.06	0.00	1.41
FA	2.18	2.18	2.18	2.18	2.18	2.18	2.18
MT	4.39	3.89	4.37	3.80	3.70	3.40	3.51
IL	1.07	0.79	0.93	0.63	0.60	0.58	0.60
AP	0.39	0.11	0.02	0.15	0.08	0.21	0.11
PY	99.85	99.50	99.94	99.98	99.81	99.47	99.46
TOTAL	56.05	59.36	58.47	56.02	60.84	60.57	59.56
%AN	15.94	12.07	14.68	15.04	12.11	11.37	12.15
A	50.22	41.30	43.37	44.70	35.86	43.47	43.40
F	33.85	46.63	41.95	40.27	52.03	45.16	44.45
M							

APPENDIX 3...continued.

	29	30	31	32	33	34
Q						
OR			7.80	5.44	5.84	5.73
AB			22.00	19.29	20.73	20.48
AN			17.99	28.39	27.72	28.62
WO			1.66	3.20	7.35	2.71
DI EN			0.87	2.02	4.21	1.68
FS			0.75	0.98	2.82	0.87
HY EN			17.39	16.23	11.53	16.29
FS			14.95	7.91	7.71	8.46
OL FO			0.00	6.30	2.76	5.23
FA			0.00	3.39	2.04	2.99
MT			2.18	2.18	2.12	2.18
IL			5.36	3.57	3.69	3.67
AP			1.17	0.74	0.84	0.77
PY			0.21	0.19	0.49	0.15
TOTAL			99.86	99.84	99.90	99.81
%AN			44.90	59.54	57.21	58.29
A			16.95	13.42	16.21	14.56
F			51.36	40.71	46.56	41.61
M			31.69	46.87	37.23	43.84
	36	37	38	39	40	41
Q						
OR					4.85	5.26
AB					23.27	26.49
AN					26.63	26.54
WO					7.11	8.99
DI EN					4.20	5.35
FS					2.56	3.19
HY EN					11.30	7.32
FS					6.89	4.36
OL FO					3.68	3.23
FA					2.47	2.12
MT					2.18	2.18
IL					3.63	3.76
AP					0.72	0.72
PY					0.08	0.09
TOTAL					99.57	99.62
%AN					53.36	50.05
A					16.82	21.07
F					43.95	42.56
M					39.24	36.37

		60	61	71	72	73	74
Q				1.62			
OR		4.64	6.32	1.36	4.11	4.55	4.91
AB		26.47	25.22	10.12	17.04	24.20	20.90
AN		16.04	21.50	29.75	25.00	25.73	29.78
NE		2.56	0.00	0.00	0.00	0.00	0.00
	WO	14.45	8.82	5.45	4.73	3.93	4.06
DI	EN	8.31	5.09	3.28	2.99	2.34	2.41
	FS	5.49	3.33	1.88	1.44	1.36	1.46
HV	EN	0.00	4.39	20.06	21.27	9.29	11.54
	FS	0.00	2.87	11.50	10.24	5.32	7.00
OL	FO	9.03	9.41	0.00	3.63	10.41	6.58
	FA	6.57	6.79	0.00	1.93	6.57	4.40
MT		2.18	2.18	2.18	2.18	2.18	2.18
IL		3.10	3.04	3.04	3.63	3.00	4.12
AP		0.60	0.58	0.44	0.70	0.51	0.67
PY		0.02	0.02	0.02	0.00	0.00	0.00
TOTAL		99.48	99.56	99.70	99.44	99.60	99.53
%AN		37.80	46.02	60.87	54.39	51.08	58.34
A		19.65	17.20	11.71	11.32	14.73	14.34
F		42.95	43.71	44.24	40.91	42.11	44.96
M		37.41	39.08	44.05	47.78	43.14	40.70
		83	85	86	87	88	89
Q			4.86				
OR		2.77	2.42	7.09	8.04	4.67	6.21
AB		23.10	19.12	20.04	6.15	20.73	13.96
AN		26.39	22.07	30.57	26.04	25.47	25.21
NE		0.00	0.00	2.07	8.70	0.00	0.00
	WO	7.06	14.39	6.54	10.71	5.60	4.86
DI	EN	4.16	7.60	3.62	6.34	3.46	3.11
	FS	2.53	6.36	2.66	3.84	1.81	1.43
HY	EN	16.45	6.80	0.00	0.00	9.99	11.46
	FS	9.96	5.70	0.00	0.00	5.23	5.26
OL	FO	0.59	0.00	11.35	12.18	9.71	13.72
	FA	0.41	0.00	9.19	8.47	5.60	6.94
MT		2.18	2.18	2.18	2.18	2.18	2.18
IL		3.44	7.35	3.86	3.93	4.18	4.12
AP		0.47	0.63	0.54	0.58	0.77	0.77
PY		0.00	0.00	0.00	0.00	0.00	0.00
TOTAL		99.44	99.47	99.70	99.65	99.37	99.21
%AN		53.32	53.58	60.40	76.17	55.13	64.36
A		15.05	13.93	17.94	17.13	13.15	9.79
F		44.27	55.92	46.54	44.04	42.35	40.48
M		40.68	30.15	35.52	30.83	44.50	49.73

APPENDIX 4

MODAL ANALYSES OF 'FRESH' BASALTS

Lava/Sill	Analysis Number	Petrographic* Type	Plagioclase	Pyroxene	Olivine	Opaques	Interstitial Clays
Conksbury Bridge Lava	1	3	33.2	20.8	26.2	7.2	12.6
	4	3	39.6	24.4	18.8	8.2	9.0
Haddonfield Lower Lava	6	3	46.0	16.0	7.0	4.0	27.0
	7	3	46.4	18.2	17.8	4.2	13.4
	9	3	45.2	18.2	0.8	3.2	32.6 ⁺¹
	10	3	42.4	20.6	10.0	3.8	23.2
Shacklow Wood Lava	11	2	34.6 ⁺²	-	14.6	very fine grained groundmass	
	14	1	59.8	15.2	-	3.4	20.6 ⁺¹
	15	1	60.4	16.0	-	3.2	20.4 ⁺¹
	16	1	65.4	17.4	-	2.4	14.8 ⁺¹
Matlock Lower Lava	17	1	48.8	27.8	8.8	5.8	8.8
	18	1	54.8	21.2	9.8	5.0	9.2
	19	1	56.0	21.4	9.4	5.2	8.0
Matlock Upper Lava	21	1	46.1	24.0	19.4	4.6	5.8
	22	1	52.4	21.8	14.6	4.4	6.8
Millers Dale Upper Lava	23	3	25.2	18.6	15.2	7.4	22.6
	24	3	45.8	21.0	21.0	5.6	6.6
	25	3	45.4	25.0	18.8	4.4	6.4
Millers Dale Lower Lava	26	1	49.8	18.2	6.0	4.2	21.8
	27	1	48.4	20.0	9.0	4.4	18.2
	28	1	55.6	17.6	5.6	2.6	18.6

APPENDIX 4 (Cont.)

Lava/Sill	Analysis Number	Petrographic* Type	Plagioclase	Pyroxene	Olivine	Opaques	Interstitial Clays
Cressbrook Dale	31	7	51.0	8.1	-	16.8	24.0 ⁺³
Lava	32	1	46.0	20.4	20.4	2.2	11.0
	33	3	56.4	18.1	10.1	3.6	11.6
	34	3	51.4	17.2	9.8	4.6	17.0
Ible Sill	37	6	56.4	23.6	15.0	2.4	2.6
Potluck Sill	40	6	48.4	22.4	18.4	4.8	6.0
Waterswallows Sill	41	6	46.4	23.2	20.6	4.4	3.2
lower horizon	55	3	38.0	43.6	7.2	7.4	3.8
intermediate type	56	3	46.4	32.6	6.8	7.6	6.8
middle horizon	57	3	46.6	25.6	5.2	6.0	16.6
upper 'gabbroic' horizon	58	3	44.6	17.6	27.0	4.4	6.4
Tunstead North Dyke	59	7	17.7 ⁺²	4.4		fine grained groundmass	
Calton Hill Dolerite	88	4	22.2 ⁺²	19.8		fine grained groundmass	

1000 counts per slide

Olivine is pseudomorphed in all Lavas

Apatite (<0.2%) is present in all samples

* See Chapter 5.2

+1 Coarse texture and interstitial alteration 'obscures' olivine pseudomorphs

+2 Phenocrysts only, groundmass too fine grained for modal analysis

+3 Includes 12.8% in vesicles

APPENDIX 5a. LOCATION DETAILS: PRESENT STUDY

(X.R.F. Analyses)

Analysis 1: Sample CE51 - Conksbury Bridge Lava, olivine-microphyric fine grained lava. Locality: Conksbury East No.5 borehole, 51 m.

Analysis 2: Sample CE5 - Conksbury Bridge Lava, olivine-microphyric fine grained lava. CE5 borehole 56.35 m. Analyst: S. Kirkton, University of Lancaster - unpublished data.

Analysis 3: Sample HF18B - Conksbury Bridge Lava, altered vesicular lava, part of toadstone clay sequence in upper part of lava. Haddonfields 11 borehole, 52.7 m (1.6 m below top of lava).

Analysis 4: Sample HF28A - Conksbury Bridge Lava, olivine-microphyric, fine grained lava identical to CE51 and CE5, HF11 borehole, 105 m.

Analysis 5: Sample HF39B - Haddonfield 'Middle Lava', plagiophyric lava with silica pseudomorphs after olivine. HF 11 borehole 169 m.

Analysis 6: Sample HF52A - Haddonfield 'Lower Lava', coarse non-vesicular lava - part of thick central flow unit. HF11 borehole, 242 m.

Analysis 7: Sample HF53A - Haddonfields 'Lower Lava', coarse 'doleritic' lava with some silica veining. HF11 borehole, 244.7 m.

Analysis 8: Sample HF11 - Haddonfields 'Lower Lava', coarse lava. HF11 borehole 251.6 m. Analyst: S. Kirkton, University of Lancaster - unpublished data.

Analysis 9: Sample HF55B - Haddonfield 'Lower Lava' coarse 'doleritic' lava. HF11 borehole, 259.5 m.

Analysis 10: Sample HF60A - Haddonfields 'Lower Lava', coarse 'doleritic' lava. HF11 borehole, 287 m.

Analysis 11: Sample MG15A - Shacklow Wood Lava, plagiophyric lava with siliceous pseudomorphs after olivine. Mogshaw No.3 borehole, 94 m.

Analysis 12: Sample MG17A - Shacklow Wood Lava, poorly vesicular, iron stained lava above zone of intense alteration. MG3 borehole, 102 m.

Analysis 13: Sample MG18G - Shacklow Wood Lava, coarse lava. MG3 borehole, 110.3 m.

Analysis 14: Sample MG20C - Shacklow Wood Lava, coarse 'doleritic' lava. MG3 borehole, 117 m.

Analysis 15: Sample MG21C - Shacklow Wood Lava, coarse 'doleritic' lava. MG3 borehole, 126 m.

Analysis 16: Sample MG22C - Shacklow Wood Lava, coarse 'doleritic' lava. MG3 borehole, 128 m.

Analysis 17: Sample BB1 - Matlock Lower Lava, coarse olivine-clinopyroxene phyric lava. Recent extensions to Bonsall Basalt Quarry, Via Gellia, (SK 283.574).

Analysis 18: Sample BB2 - Matlock Lower Lava, coarse olivine-clinopyroxene phyric lava. Extensions to Bonsall Basalt Quarry.

Analysis 19: Sample BB3 - Matlock Lower Lava, coarse olivine-clinopyroxene phyric lava. Extensions to Bonsall Basalt Quarry.

Analysis 20: Sample GT23 - Matlock Lower Lava, partly altered coarse lava adjacent to mineralisation, Hallicar Wood Adit, Via Gellia (283572).

Analysis 21: Sample UM1 - Matlock Upper Lava, coarse lava, central portion of large spheroid, Psalters Lane, Masson Hill (287597).

Analysis 22: Sample UM2 - Matlock Upper Lava, coarse lava, central portion of spheroid (different spheroid to UM1). Psalters Lane, Masson Hill (287597).

Analysis 23: Sample MD1 - Millers Dale Upper Lava, coarse 'doleritic' lava, central part of spheroid. Small Quarry near Blackwell Dale (9134730).

Analysis 24: Sample WS2 - Millers Dale Upper Lava, medium grained olivine-pyroxene phyric lava, central part of spheroid. Debris from the Wham Sough Dig, Taddington (129712).

Analysis 25: Sample WS3 - Millers Dale Upper Lava, medium grained lava. Debris from Wham Sough Dig, Taddington.

Analysis 26: Sample TB7 - Millers Dale Lower Lava, coarse olivine-phyric lava. Tunstead borehole 21, Great Rocks Dale, 27.7 m.

Analysis 27: Sample TB16 - Millers Dale Lower Lava, coarse 'doleritic' lava. TB21 borehole, 42.4 m.

Analysis 28: Sample TB17 - Millers Dale Lower Lava, coarse 'doleritic' lava. TB21 borehole, 43.6 m.

Analysis 29: Sample TB18 - Millers Dale Lower Lava, highly altered, coarse lava part of 'toadstone clay' sequence at base of Lava. TB21 borehole, 44.2 m.

Analysis 30: Sample TB19 - Millers Dale Lower Lava, highly altered vesicular lava part of 'toadstone clay' sequence. TB21 borehole, 44.3 m.

- Analysis 31: Sample ED2 - Cressbrook Dale Lava, very coarse almost 'gabbroic' lava part of thick central flow unit. Eyam borehole, 77 m.
- Analysis 32: Sample ED3 - Cressbrook Dale Lava, coarse, olivine-phyric lava, Eyam borehole, 80.2 m.
- Analysis 33: Sample ED12 - Cressbrook Dale Lava, medium grained lava. Eyam borehole, 136.3 m (base of flow).
- Analysis 34: Sample ED22 - Cressbrook Dale Lava, medium grained lava. Eyam borehole, 106.2 m.
- Analysis 35: Sample HE9 - Cressbrook Dale Lava. Inclined exploration borehole, HE9, Hucklow Edge (193777), 188.7 m.
- Analysis 36: Sample IS1A - Ible Sill, slightly altered, intrusive dolerite. Ible Quarry, Via Gellia (253568).
- Analysis 37: Sample IS1B - Ible Sill, unaltered, coarse ophitic olivine-dolerite. Ible Quarry.
- Analysis 38: Sample IS1C - Ible Sill, highly altered dolerite. Ible Quarry.
- Analysis 39: Sample IS1D - Ible Sill, highly altered dolerite. Ible Quarry.
- Analysis 40: Sample BH2A - Potluck Sill, fresh intrusive dolerite with coarse ophitic texture and partly replaced olivines. Dump specimen, Black Hillock Mine, Tideswell Moor (141782).
- Analysis 41: Sample BH2B - Potluck Sill, ophitic dolerite. Dump specimen, Black Hillock Mine.

- Analysis 42: Sample BH1B - Potluck Sill, highly altered dolerite, bleached white consisting largely of calcite, kaolinite and albite. Dump specimen, Black Hillock Mine.
- Analysis 43: Sample TB23 - Olive green structureless clay beneath the Lower Millers Dale Lava. TB21 borehole, 45.7 m.
- Analysis 44: Sample BS1 - 0.3 m clay horizon at level of Upper Matlock Lava showing relict volcanoclastic textures. Bonsall Moor borehole U3, 14.6 m.
- Analysis 45: Sample BS2 - 1.0 m calcareous tuff, the 'Little Toadstone', 5.3 m above the top of the Lower Matlock Lava. Bonsall Moor borehole U3, 35 m.
- Analysis 46: Sample AB1 - altered palagonite tuff. Alport borehole, 457 m.
- Analysis 47: Sample GT40 - 1.0 m wayboard at horizon of Upper Matlock Lava. Hallicar Wood Adit, Via Gellia (283572).
- Analysis 48: Sample PGM3 - Wayboard from Asbian Limestone, below D. septosa band. Ben Bennett's Quarry, Grangemill (242574).
- Analysis 49: Sample HM2 - Major clay horizon with underlying karst in Asbian limestone, North Lancashire. S.W. face of Holme Park Quarry (SD 535788).
- Analysis 50: Sample MH21 - Wayboard from Asbian limestones. Mumbles Head, Swansea Bay, South Wales.
- Analysis 51: Sample RH1 - Pale green structureless clay. Rookhope borehole, Co. Durham, 385.6 m (NY 938428).

Analysis 52: Sample MB29 - Wayboard from Asbian limestones of the Askrigg Block. Mealbank Quarry, near Ingleton (697736).

Analysis 53: Sample HL20 - Wayboard from Asbian limestones of the Mendips. Cooks Wood Quarries, 4 miles NE of Shepton Mallet.

Analysis 54: Sample GS2 - Wayboard from Asbian limestones of the Mendips. Gorney Slate Bottom Quarry (ST 627494).

(Samples 48, 49, 50, 52, 53, 54 - supplied by G.M. Walkden, University of Aberdeen. Sample 51 supplied by D.A. Johnson, University of Durham)

b. LOCATION DETAILS: PREVIOUSLY REPORTED ANALYSES

Analysis 60: Sample Bon.1 - Marginal facies of Bonsall Sill (281588).

Analysis 61: Sample Bon.2 - Normal facies of Bonsall Sill (276593).

Analysis 62: Sample M1 - altered, non-vesicular Upper Matlock Lava
in proximity to mineralisation, Masson Hill (290590).

Analyses 63-67: Samples M2-M6 - Altered, vesicular Upper Matlock Lava
in proximity to mineralisation, Masson Hill (290590). Analyst:
R.A. Ixer, in: Ixer (1972).

Analyses 68-70: Samples ML1-3 - Highly altered 'toadstone clay' sequence
at top of Matlock Upper Lava, Tansley Borehole. Analyst: M. Amin,
in: Amin (1980).

Analysis 71: Sample Malki 1 - Non-vesicular 'fresh' Upper Millers Dale
Lava, Bole Hill Quarry, Millers Dale

Analysis 72: Sample Malki 2 - Non-vesicular 'fresh' Upper Millers Dale
Lava. Small Quarry at foot of Blackwell Dale (134731).

Analysis 73: Sample Malki 3 - Non-vesicular 'fresh' Upper Millers Dale
Lava. Critchley Wood Quarry, Millers Dale

Analysis 74: Sample Malki 4 - Non-vesicular 'fresh' Upper Millers Dale
Lava, Knot Low Quarry, Millers Dale (134735).

Analysis 75: Sample Malki 5 - Vesicular Cave Dale Lava, Cave Dale, nr.
Castleton (148822).

Analysis 76: Sample Malki 6 - Vesicular Lower Millers Dale Lava, ICI
quarries above Buxton Bridge, Tunstead (099760).

- Analysis 77: Sample Malki 7 - Vesicular Lower Millers Dale Lava. Buxton Bridge, Tunstead (097755).
- Analysis 78: Sample Malki 8 - Vesicular Lower Millers Dale Lava. Wormhill Road cutting (124740).
- Analysis 79: Sample Malki 9 - Altered 'spillitic' Lower Millers Dale Lava. In contact with Tideswell Sill. Small Quarry, Tideswell picnic site (153743). Analyst: 71-79, A. Malki, in: Malki (1967).
- Analysis 80: Sample Sp1 - Altered 'spillitic' Lower Millers Dale Lava, Tideswell picnic site (153743). Analyst: E. Sinkinson, in: Sargent (1917).
- Analysis 81: Sample Sp2 - Altered 'spillitic' lava at base of Upper Millers Dale Lava. Knot Low Quarry, Millers Dale (134735). Analyst: E. Sinkinson, in: Sargent (1917).
- Analysis 82: Sample CD2 - Vesicular Cave Dale Lava. Cave Dale, nr. Castleton (148822). Analyst: M. Hepher, in: Cheshire and Bell (1978).
- Analysis 83: Sample WS1 - Dolerite from Waterswallows Sill. Waterswallows Quarry, nr. Buxton (086750). Analyst: W.H. Evans, in: Stevenson et al. (1971).
- Analysis 84: Sample TSD - Buxton South Dyke. ICI northern end of Tunstead Quarry (106751). Analysts: P.R. Kiff and G.A. Sarjeant, in: Stevenson et al. (1971).
- Analysis 85: Sample TND - Buxton North Dyke, nr. Buxton Bridge, Tunstead. Analyst: W.A. Deer, in: Cope (1933).
- Analysis 86: Sample C1 - Calton Hill analcite-dolerite. Calton Hill Quarry (117715). Analyst: S.El.D. Hamad, in: Hamad (1963).

Analysis 87: Sample C2 - Calton Hill analcite dolerite. Calton Hill Quarry. Analyst: S.I. Tomkeieff, in: Tomkeieff (1928).

Analysis 88: Sample 63 - Calton Hill 'basalt'. Calton Hill Quarry. There is some doubt as to whether this is intrusive dolerite or extrusive Lava. Analyst: V.A. Somogyi, in: Curtis (1976).

Analysis 89: Sample C4 - Calton Hill 'basalt', slightly altered adjacent to clay vein. Calton Hill Quarry. Analyst: V.A. Somogyi, in: Curtis (1976).

Analysis 90: Sample Ash 1 - Ashover Tuff. Fallgate Borehole (344622), Ashover, 72.8-74.4 m.

Analysis 91: Sample Ash 2 - Altered vesicular basalt. Fallgate borehole, 113.3-115 m.

Analysis 92: Sample Ash 3 - Chloritised basaltic breccia. Fallgate borehole, 163.4-164.9 m.

Analysis 93: Sample Ash 4 - Altered vesicular basalt. Fallgate borehole, 226.8-228.3 m.

Analysis 94: Sample Ash 5 - Chloritized basaltic breccia. Fallgate borehole, 257.6-258.3 m.

Analysts: 90-94, A.D. Wilson and J.F. Palframan, in: Ramsbottom et al. (1962).

Analysis 95: Sample Ash 6 - Purple Ashover Tuff. Hockley Lime Kilns (352625).

Analysis 96: Sample Ash 7 - Weathered Ashover Tuff. Butts Quarry, Ashover (341631).

Analysis 97: Sample Ash 8 - Basalt Block in tuff. Hockley Lime
Kilns.

Analysis 98: Sample Ash 9 - Weathered Ashover Tuff. Fall Hill Quarry
(355624).

Analysis 99: Sample Ash 10 - Green tuffaceous clay, Ashover Tuff, Fall
Hill Quarry.

Analysis 100: Sample Ash 11 - Purple Ashover Tuff. The 'Drive', Ashover
(351623).

Analyst: 95-100, P. Kelman, in: Kelman (1980).

c. LOCATION DETAILS: PRESENT STUDY

(A.A. Analyses)

Analyses 101-114: Hallicar Wood Adit, Via Gellia (283527). Horizontal collecting traverse adjacent to alteration zone developed within the Matlock Lower Lava. Samples collected at +2.2, +1.5, +0.9, +0.8, +0.4, +0.3, +0.2, +0.1, 0.0, -0.1, -0.2, -0.3, -0.4, and -0.5 m from datum.

Analyses 115-133: Maury Adit, Millers Dale (150731). Horizontal collecting traverse adjacent to zone of mineralisation within the Millers Dale Upper Lava. Samples collected as a continuous channel with each sample representing 0.1 m. Sample centre points at 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, 1.0, 0.9, 0.8, 0.7, 0.6, 0.5 and 0.5 m clay concentrate, 0.4, 0.3 and 0.3 m clay concentrate, 0.2. 0.1 m and 0.1 m clay concentrate from datum point.

Analyses 137-155: Conksbury East No.5 Borehole, Long Rake (212651). Inclined borehole through Conksbury Bridge Lava intersecting a number of alteration zones. Samples of approximately 5 cm in length collected at following depths: 56.1, 56.5, 56.8, 57.3, 57.7, 58.1, 58.7, 59.5, 60.0, 60.4, 60.7, 61.0, 61.3, 61.5, 61.7, 62.0, 62.7, 63.3, and 64.3 m.

Analyses 156-164: Mogshaw No. 3 Borehole (191678). Inclined borehole in Shacklow Wood Lava intersecting probable continuation of the Mogshaw Rake. Samples of split core 10 cm in length collected at following depths: 102, 102.6, 103.2, 103.6, 104.3, 104.8, 104.9, 105.1, and 105.2 m.

Analyses 165-168: Upper Toadstone Clay sequence, Millers Dale Lower Lava-White Rake Opencast (146782). Channel samples collected at 0.0 to 0.4, 0.4 to 0.7, 0.9 and 1.0 to 1.2 m below top of Lava.

Analyses 169-171: Altered Matlock Lower Lava in excavated section above Hoptonwood Quarries, Via Gellia (283556). Samples collected at 2.0, 2.85 and 4.0 m, below top of lava.

Analysis 172: Upper Toadstone clay sequence, Conksbury Bridge Basalt. Haddonfields No.11 Borehole, 51.5 m.

Analysis 173: Altered Potluck Sill, Black Hillock Mine Dumps (141783).

Analysis 174: Altered Millers Dale Upper Lava, Chapmaiden Mine Dumps (147784).

Analysis 175: Altered Bonsall Sill, opencast on Great Rake, west of Low Mine (281586).

d. LOCATION DETAILS: PRESENT STUDY

(Electron Microprobe Analyses)

i. Plagioclase Analyses

Analyses 1-19: Tunstead North Dyke-Buxton Bridge, Great Rocks Dale (59)*.

1,2,3 - phenocryst core to rim. 4, 5, 6, 7 - phenocryst core to rim.

11, 12, 13, 14 - phenocryst core to rim. 15, 16, 17, 18, 19 -

individual groundmass plagioclases.

Analyses 20-21: Millers Dale Lower Lava - TB21 Borehole (27)*. 18,19 -

individual groundmass plagioclase.

Analyses 22-28: Haddonfields Lower Lava, Haddonfields No.11 Borehole (9)*

22 - phenocryst. 23, 24, 25, 26 - resorbed phenocryst core to rim.

27 - groundmass plagioclase. 28 - phenocryst.

Analyses 29-38: Shacklow Wood Lava, Mogshaw No. 3 Borehole (11)*. 29,

30, 31 - phenocryst core to rim. 32, 33, 34 - phenocryst core to

rim. 35 - phenocryst. 36, 37 - individual groundmass plagioclase.

38 - phenocryst.

ii. Clinopyroxene Analyses

Analyses 39-46: Tunstead North Dyke-Buxton Bridge, Great Rocks Dale

(59)*. 39 - groundmass pyroxene. 40 - phenocryst core. 41, 42 -

phenocryst core and rim. 43, 44, 45, 46 - individual phenocrysts.

Analyses 47-50: Millers Dale Upper Lava, Wham Sough Dig (25)*. 47, 48,

49 - zoned phenocryst core to rim. 50 - phenocryst.

*Numbers in brackets refer to analyses number in Appendix 5a

Analyses 51-55: Haddonfields Lower Lava, Haddonfields No.11 Borehole

(9)*. 51, 52, 53, 54, 55 - individual groundmass pyroxenes.

Analyses 56-60: Matlock Lower Lava, Bonsall Basalt Quarry (19)*. 56, 57 -

individual phenocrysts. 58, 59, 60 - individual groundmass pyroxenes.

Analyses 61-64: Potluck Sill, Black Hillock Mine Dumps (41)*. 61, 62,

63, 64 - individual ophitic pyroxenes.

iii. Olivine Analyses

Analyses 65-69: Potluck Sill, Black Hillock Mine Dumps (41)*. 65, 66, 67,

68, 69 - individual olivines in relict microphenocrysts.

APPENDIX 6...ELECTRON MICROPROBE DATA. (A). PLAGIOCLASES.

	1		2		3		4	
SiO2	52.8	2.429	54.0	2.459	53.6	2.434	53.1	2.415
Al2O3	28.6	1.551	28.3	1.521	28.6	1.548	29.2	1.564
FeO	0.5	0.019	0.5	0.020	0.6	0.021	0.7	0.028
CaO	11.9	0.588	11.6	0.568	11.7	0.576	12.4	0.607
Na2O	4.6	0.407	4.7	0.414	4.7	0.415	4.2	0.377
K2O	0.1	0.008	0.2	0.010	0.2	0.010	0.1	0.007
TOTAL	98.6	5.003	99.3	4.992	98.8	5.004	99.7	4.993
%AN		56		57		58		67
	5		6		7		8	
SiO2	52.2	2.391	52.6	2.405	52.0	2.383	51.7	2.368
Al2O3	29.4	1.586	29.3	1.579	29.6	1.560	29.9	1.615
FeO	0.7	0.028	0.5	0.017	0.5	0.020	0.5	0.019
CaO	12.7	0.623	12.4	0.608	12.7	0.623	13.0	0.639
Na2O	4.1	0.367	4.3	0.385	4.2	0.374	4.1	0.361
K2O	0.1	0.007	0.1	0.007	0.1	0.007	0.1	0.007
TOTAL	99.4	5.003	99.2	5.002	99.2	5.007	99.3	5.008
%AN		63		61		65		63
	9		10		11		12	
SiO2	52.3	2.400	54.0	2.431	51.4	2.377	51.6	2.368
Al2O3	29.4	1.587	29.1	1.543	29.5	1.605	29.8	1.613
FeO	0.5	0.019	0.6	0.024	0.5	0.018	0.6	0.027
CaO	12.6	0.620	12.5	0.602	12.6	0.626	13.1	0.647
Na2O	4.2	0.377	4.5	0.389	4.2	0.379	4.0	0.353
K2O	0.1	0.007	0.1	0.008	0.1	0.008	0.1	0.006
TOTAL	99.2	5.002	100.8	4.996	98.4	5.014	99.1	5.005
%AN		61		60		62		64
	13		14		15		16	
SiO2	51.3	2.375	51.7	2.386	55.2	2.517	53.8	2.465
Al2O3	29.5	1.606	29.3	1.595	27.1	1.459	27.8	1.501
FeO	0.7	0.029	0.6	0.024	0.8	0.032	1.1	0.041
CaO	12.7	0.628	12.5	0.616	10.0	0.489	11.0	0.543
Na2O	4.0	0.367	4.3	0.381	5.7	0.500	5.2	0.461
K2O	0.1	0.007	0.1	0.007	0.2	0.014	0.2	0.011
TOTAL	98.4	5.006	98.6	5.010	99.1	5.011	99.0	5.021
%AN		63		61		49		53

	17		18		19		20	
S102	53.7	2.451	53.7	2.438	54.6	2.468	53.0	2.423
AL203	28.1	1.514	28.4	1.536	28.1	1.498	28.9	1.556
FE0	1.3	0.049	0.9	0.036	1.3	0.048	0.4	0.017
CA0	11.3	0.551	11.5	0.563	11.5	0.558	12.3	0.600
NA20	5.0	0.444	4.9	0.433	4.7	0.410	4.5	0.399
K20	0.2	0.011	0.2	0.010	0.2	0.010	0.2	0.009
TOTAL	99.6	5.020	99.1	5.016	100.3	4.992	99.3	5.003
%AN		55		50		57		60
	21		22		23		24	
S102	53.6	2.451	52.8	2.422	51.7	2.364	51.6	2.348
AL203	28.2	1.519	28.8	1.554	30.0	1.615	30.5	1.635
FE0	1.1	0.042	0.9	0.036	0.8	0.029	0.5	0.020
CA0	11.6	0.567	12.2	0.599	13.4	0.654	13.8	0.671
NA20	4.6	0.410	4.1	0.368	3.7	0.325	3.6	0.313
K20	0.2	0.012	0.2	0.012	0.1	0.008	0.1	0.008
TOTAL	99.2	5.000	99.1	4.991	99.6	4.995	100.1	4.995
%AN		57		61		66		68
	25		26		27		28	
S102	53.4	2.410	52.6	2.415	52.0	2.430	51.9	2.416
AL203	29.6	1.573	28.9	1.561	27.2	1.501	28.1	1.545
FE0	0.5	0.020	1.0	0.037	3.4	0.134	2.1	0.083
CA0	12.8	0.617	11.9	0.586	11.2	0.560	11.6	0.577
NA20	4.1	0.361	4.4	0.394	4.1	0.372	4.1	0.367
K20	0.2	0.010	0.3	0.015	0.3	0.015	0.2	0.013
TOTAL	100.6	4.989	99.1	5.009	98.2	5.012	98.0	5.001
%AN		62		59		59		60
	29		30		31		32	
S102	50.6	2.343	51.0	2.354	50.4	2.343	51.7	2.374
AL203	30.0	1.636	29.1	1.614	29.8	1.632	29.7	1.605
FE0	0.5	0.018	1.3	0.051	0.6	0.022	0.5	0.019
CA0	13.4	0.663	12.8	0.647	13.3	0.664	13.1	0.645
NA20	3.9	0.349	3.7	0.341	3.9	0.351	4.0	0.354
K20	0.1	0.007	0.1	0.006	0.1	0.007	0.1	0.007
TOTAL	98.4	5.014	98.0	5.013	98.1	5.020	99.1	5.004
%AN		65		65		65		64

APPENDIX 6(A)...continued.

	33		34		35		36	
SiO ₂	52.6	2.397	52.9	2.385	53.0	2.413	53.5	2.460
Al ₂ O ₃	29.4	1.584	30.0	1.593	29.2	1.563	27.7	1.504
FeO	0.5	0.020	0.4	0.024	0.6	0.021	1.5	0.050
CaO	13.1	0.638	13.3	0.643	12.8	0.622	11.3	0.557
Na ₂ O	4.0	0.356	3.9	0.340	4.1	0.364	4.5	0.401
K ₂ O	0.1	0.007	0.1	0.008	0.1	0.008	0.2	0.013
TOTAL	99.9	4.997	100.8	4.992	99.8	4.991	98.8	4.995
%AN		64		64		62		57
	37		38					
SiO ₂	55.6	2.550	52.3	2.401				
Al ₂ O ₃	26.0	1.406	29.0	1.571				
FeO	1.8	0.071	1.1	0.042				
CaO	9.3	0.458	12.7	0.624				
Na ₂ O	5.6	0.500	3.9	0.347				
K ₂ O	0.4	0.024	0.1	0.007				
TOTAL	98.8	5.010	99.2	4.991				
%AN		64		64				

APPENDIX 6(B)...PYROXENES.

	39		40		41		42	
SiO ₂	51.0	1.918	51.4	1.919	51.2	1.915	51.0	1.934
TiO ₂	0.9	0.027	0.5	0.013	0.6	0.017	0.7	0.021
Al ₂ O ₃	2.9	0.131	3.4	0.157	2.6	0.116	2.2	0.096
FeO	11.1	0.357	8.6	0.267	8.0	0.249	9.9	0.313
MnO	0.2	0.007	0.2	0.008	0.2	0.007	0.2	0.008
MgO	14.5	0.832	17.1	0.955	16.3	0.907	15.5	0.874
CaO	16.7	0.686	15.5	0.525	18.8	0.754	17.7	0.720
Na ₂ O	0.3	0.020	0.4	0.028	0.3	0.024	0.3	0.022
Cr ₂ O ₃	0.5	0.016	0.7	0.021	0.8	0.022	0.5	0.015
TOTAL	98.0	3.992	98.1	3.993	98.8	4.011	98.0	4.001
Mg		44		52		47		46
Ca		37		34		40		38
Fe		19		14		13		16

	43		44		45		46	
SI02	50.8	1.912	50.1	1.900	51.1	1.897	51.6	1.917
TI02	0.5	0.015	0.9	0.025	0.6	0.016	0.5	0.014
AL203	2.6	0.117	3.3	0.149	4.0	0.174	3.5	0.153
FE0	7.9	0.250	8.8	0.278	8.2	0.253	8.4	0.261
MNO	0.2	0.017	0.2	0.007	0.2	0.005	0.2	0.007
MGO	16.2	0.910	14.8	0.836	16.3	0.904	16.9	0.938
CA0	18.8	0.757	18.9	0.767	17.6	0.699	16.4	0.652
NA2O	0.3	0.025	0.4	0.028	0.4	0.029	0.4	0.028
CR2O3	0.8	0.023	0.6	0.018	0.9	0.025	0.9	0.025
TOTAL	98.2	4.015	97.9	4.006	99.1	4.002	98.8	3.994
MG		48		44		49		51
CA		39		41		38		35
FE		13		15		13		14
	47		48		49		50	
SI02	47.3	1.775	47.3	1.791	48.5	1.852	50.2	1.896
TI02	2.0	0.058	2.4	0.067	2.5	0.070	1.3	0.036
AL203	7.8	0.344	6.4	0.286	4.1	0.184	3.4	0.150
FE0	7.3	0.230	7.8	0.248	9.8	0.311	8.0	0.254
MNO	0.1	0.004	0.1	0.003	0.1	0.005	0.2	0.005
MGO	12.4	0.670	12.4	0.701	12.2	0.693	14.1	0.796
CA0	20.9	0.841	21.3	0.966	20.8	0.852	20.4	0.826
NA2O	0.7	0.054	0.5	0.035	0.5	0.040	0.5	0.039
CR2O3	0.5	0.015	0.4	0.012	0.0	0.000	0.2	0.007
TOTAL	99.1	4.015	98.6	4.010	98.5	4.006	98.4	4.008
MG		39		39		37		42
CA		48		48		46		44
FE		13		13		17		14
	51		52		53		54	
SI02	51.4	1.956	50.9	1.956	51.1	1.949	51.8	1.955
TI02	0.8	0.024	1.0	0.028	0.9	0.026	0.7	0.020
AL203	1.8	0.079	1.4	0.065	1.9	0.083	1.7	0.074
FE0	10.6	0.338	12.7	0.407	11.0	0.350	9.8	0.309
MNO	0.3	0.010	0.4	0.011	0.3	0.010	0.2	0.007
MGO	13.8	0.786	13.1	0.750	13.8	0.786	14.9	0.840
CA0	18.8	0.767	18.4	0.755	18.8	0.766	19.0	0.769
NA2O	0.3	0.021	0.3	0.024	0.3	0.023	0.2	0.017
CR2O3	0.2	0.007	0.0	0.000	0.1	0.003	0.1	0.004
TOTAL	98.1	3.987	98.1	3.995	98.1	3.994	98.4	3.994
MG		42		39		41		44
CA		40		40		40		40
FE		18		21		19		16

APPENDIX 6(B)...continued.

	55		56		57		58	
SI02	51.5	1.945	49.8	1.858	50.3	1.863	51.0	1.946
TI02	0.9	0.025	1.0	0.029	0.9	0.026	1.1	0.031
AI203	2.2	0.094	4.6	0.203	4.5	0.194	1.4	0.062
FE0	3.7	0.275	6.9	0.216	6.6	0.205	12.0	0.384
MNO	0.3	0.008	0.1	0.005	0.1	0.004	0.4	0.011
MGO	14.5	0.819	14.4	0.800	14.9	0.873	12.5	0.713
CA0	19.6	0.793	21.3	0.850	21.4	0.847	20.3	0.832
NA20	0.3	0.010	0.4	0.029	0.4	0.028	0.4	0.027
CR203	0.3	0.008	0.8	0.024	0.9	0.026	0.0	0.000
TOTAL	98.1	3.988	99.4	4.014	100.0	4.015	99.1	4.006
MG		43		43		44		37
CA		42		46		45		43
FE		15		11		11		20
	59		60		61		62	
SI02	51.0	1.910	51.0	1.937	51.7	1.936	51.5	1.914
TI02	1.1	0.031	1.1	0.032	1.3	0.035	1.0	0.028
AI203	2.1	0.093	1.5	0.066	1.7	0.076	3.0	0.130
FE0	8.9	0.280	12.0	0.380	10.0	0.313	6.8	0.212
MNO	0.2	0.007	0.4	0.012	0.2	0.008	0.1	0.005
MGO	14.4	0.806	12.0	0.728	14.3	0.797	14.9	0.825
CA0	21.1	0.850	20.5	0.832	20.2	0.812	21.1	0.838
NA20	0.4	0.026	0.4	0.028	0.4	0.026	0.4	0.029
CR203	0.1	0.003	0.0	0.000	0.0	0.000	0.6	0.017
TOTAL	99.1	4.015	99.7	4.013	99.8	4.003	99.4	3.998
MG		42		38		42		44
CA		44		43		34		45
FE		14		19		24		11
	63		64					
SI02	49.8	1.904	50.8	1.904				
TI02	1.4	0.041	1.6	0.044				
AI203	2.1	0.098	2.4	0.107				
FE0	10.0	0.320	9.3	0.291				
MNO	0.2	0.008	0.2	0.007				
MGO	13.6	0.775	14.1	0.787				
CA0	20.6	0.844	21.0	0.845				
NA20	0.5	0.036	0.4	0.027				
CR203	0.0	0.000	0.1	0.002				
TOTAL	98.4	4.024	99.8	4.012				
MG		40		41				
CA		44		44				
FE		14		15				

APPENDIX 6(C)...OLIVINES.

	65		66		67		68	
SiO2	37.9	1.007	38.1	1.032	38.0	1.007	38.7	1.007
NiO	0.2	0.003	0.1	0.003	0.1	0.002	0.2	0.004
FeO	27.6	0.614	31.5	0.715	28.1	0.623	24.9	0.541
MnO	0.4	0.008	0.5	0.011	0.4	0.008	0.3	0.007
MgO	34.1	1.353	29.8	1.202	34.0	1.346	36.9	1.428
CaO	0.3	0.008	0.2	0.007	0.3	0.008	0.3	0.007
TOTAL	100.4	2.993	100.2	2.968	100.8	2.994	101.2	2.994
%FO		69		63		68		72
	69							
SiO2	37.1	1.005						
NiO	0.2	0.003						
FeO	29.0	0.438						
MnO	0.4	0.010						
MgO	33.9	1.333						
CaO	0.3	0.007						
TOTAL	100.8	2.996						
%FO		68						

APPENDIX 7

DETAILED BOREHOLE CORE "LITHOLOGS" AND ABRIDGED BOREHOLE LOGS
(NOT for publication)

7A)....Detailed Borehole Core "Lithologs".

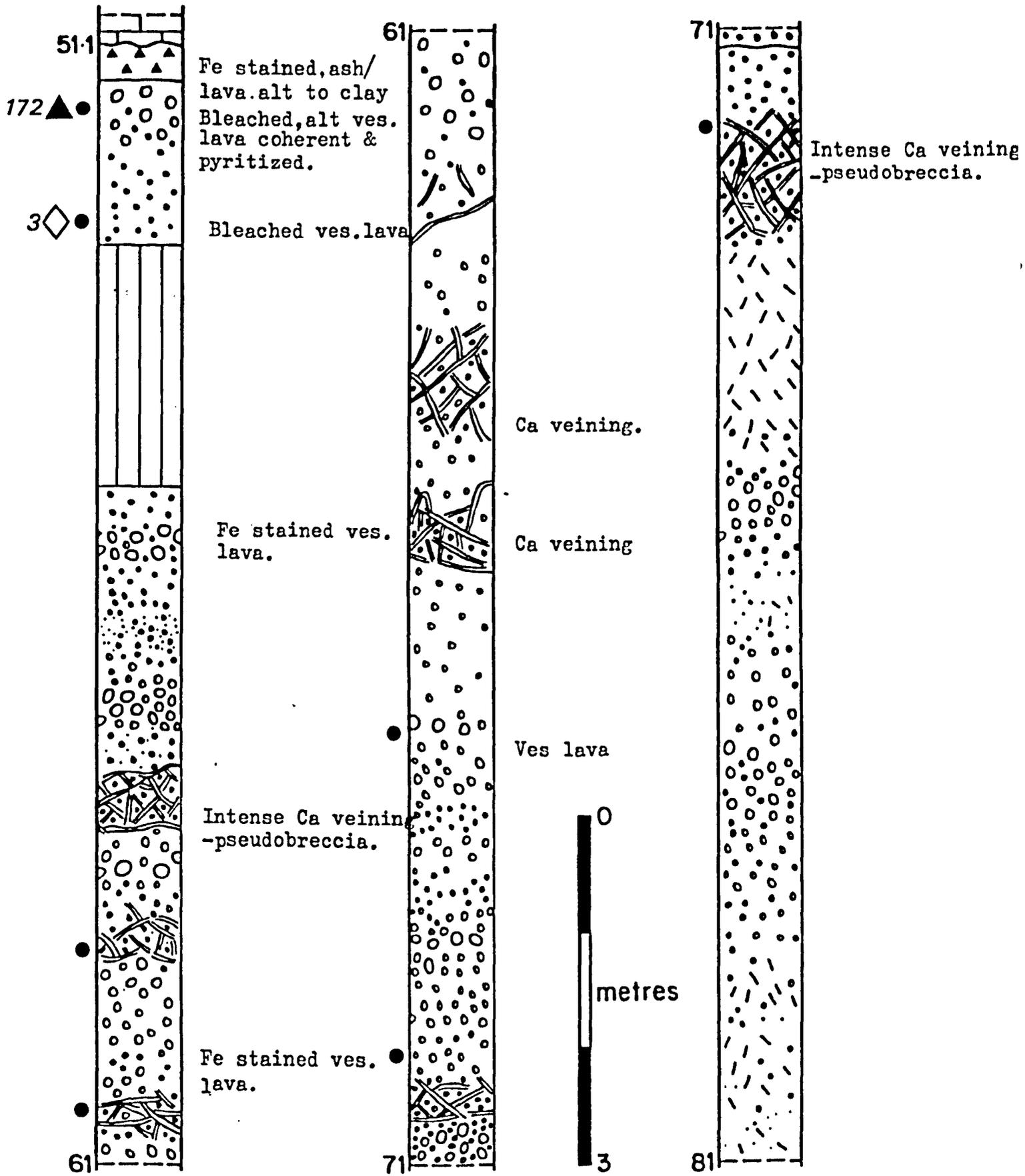
All figure borehole cores were relogged, indicated depths represent actual borehole depths uncorrected for inclinations. Lava thicknesses quoted in the text represent corrected values. Analyses numbers cross-reference with Appendices 1 to 6.

KEY

-  vesicular lava
-  poorly vesicular to non-vesicular lava
-  tuff
-  autobreccias
-  veining
-  intensely bleached and sheared lava
-  limestones

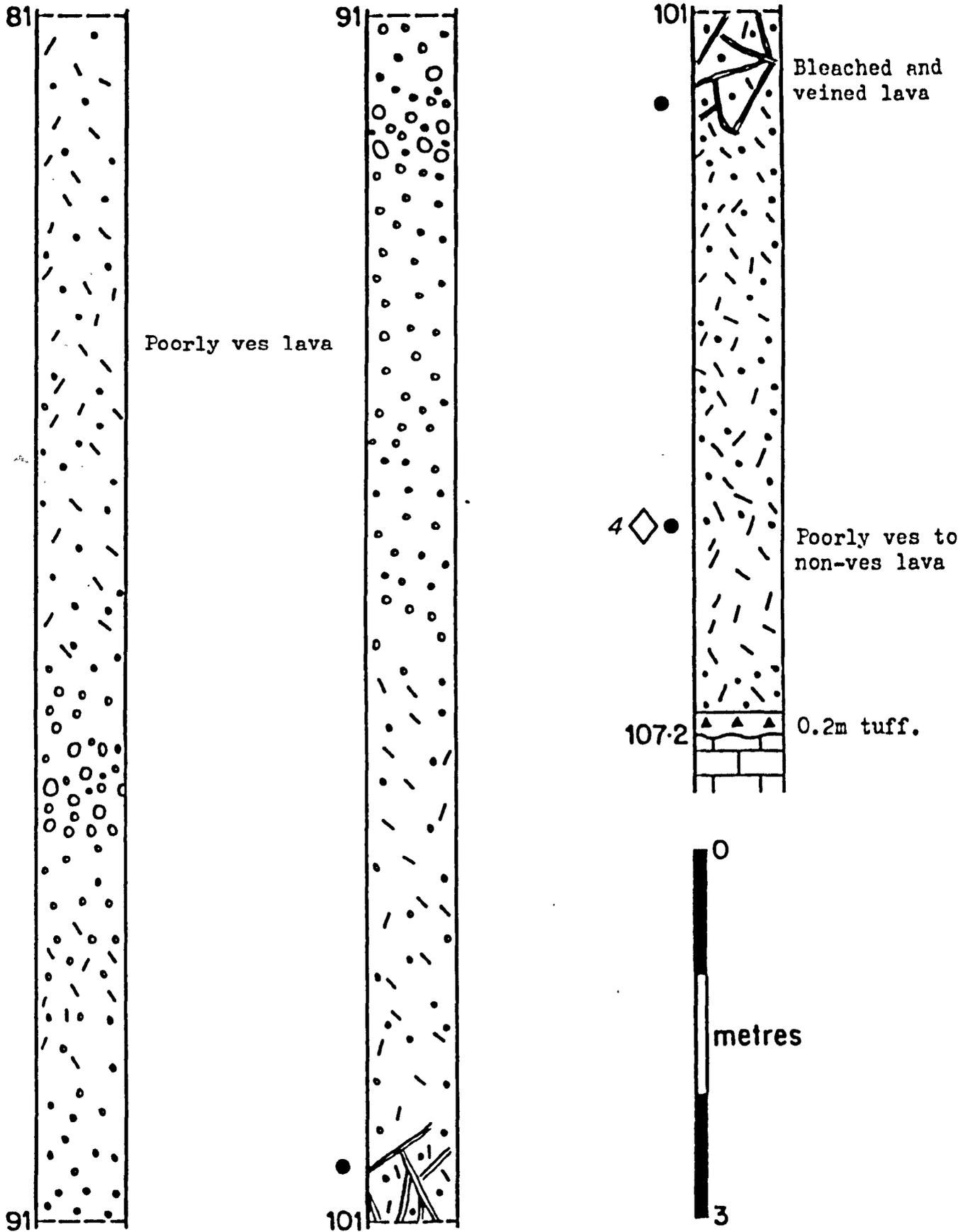
- location of thin section
- ◇ X.R.F. sample and analysis number
- ▲ A.A. sample and analysis number

Conksbury Bridge Lava, Haddonfields No.11 borehole

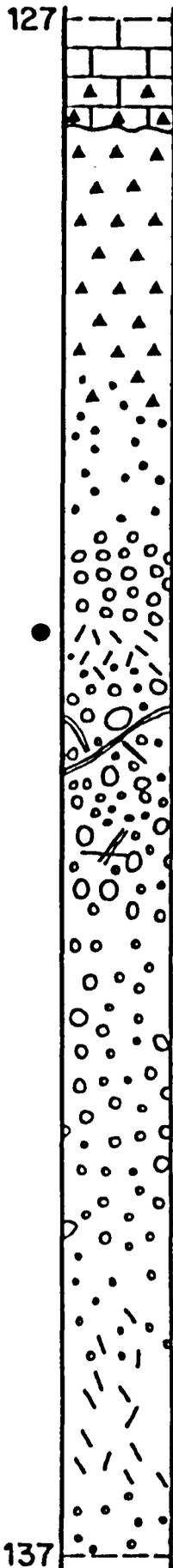


LOCATION.....SK 237 658
 DRILLED.....1970-1971
 INCLINATION.68° at 170°
 COMPANY.....DRESSER MINERALS.

Conksbury Bridge Lava, (CONT) Haddonfields No.11 borehole

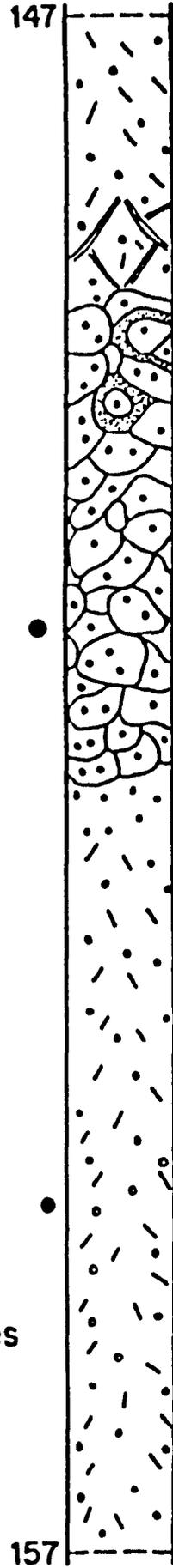
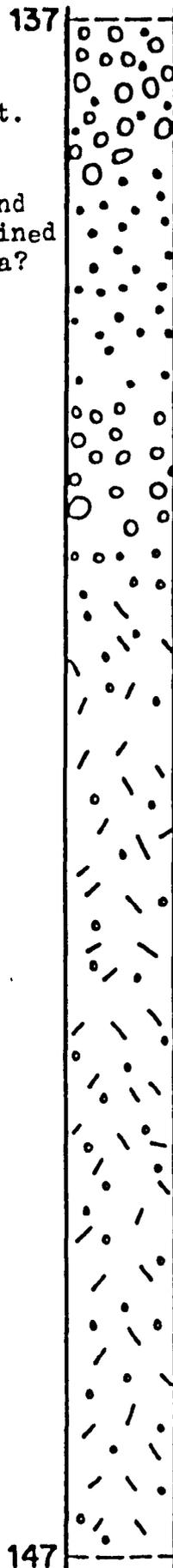


Haddonfields 'Middle Lava', Haddonfields No.11 borehole



Tuffaceous lst.
Deeply wthd and rotten Fe stained tuff &/or lava?

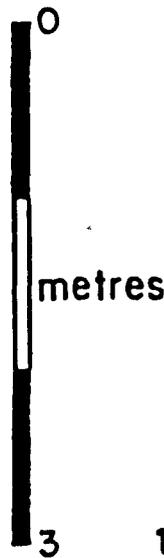
Megavesicles.



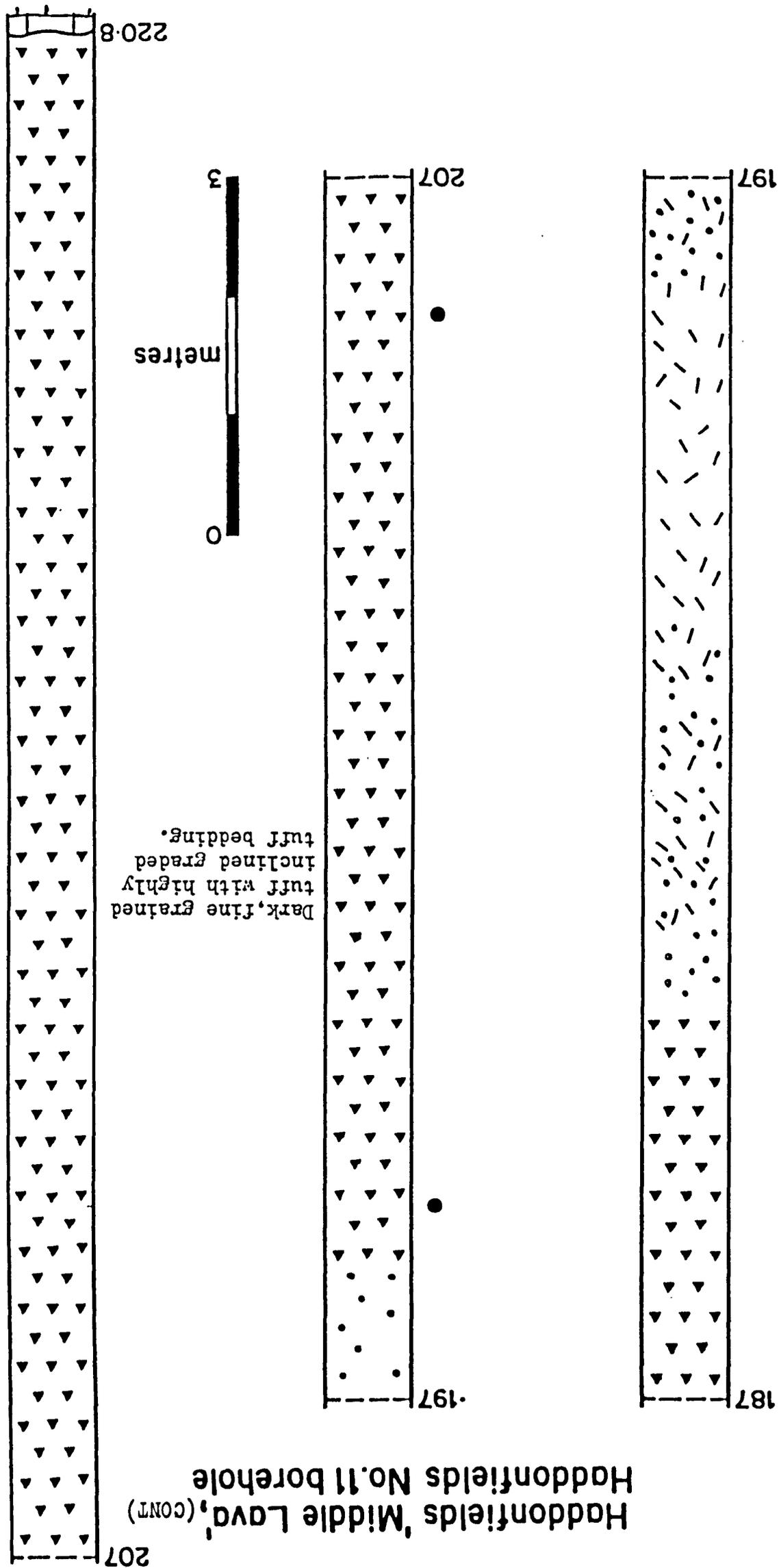
Patchy iron staining giving a "pseudobreccia"

Fe staining

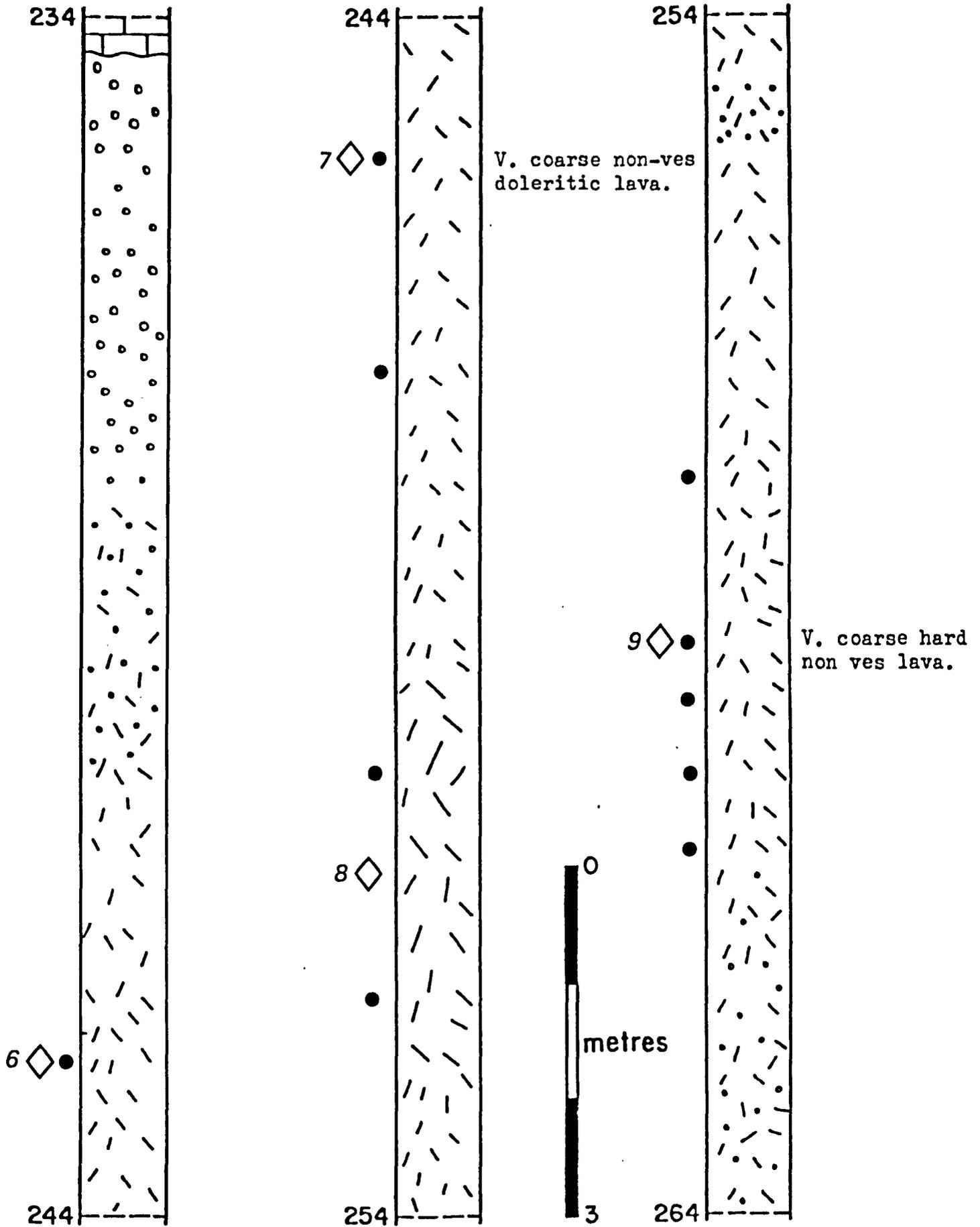
Poorly ves lava



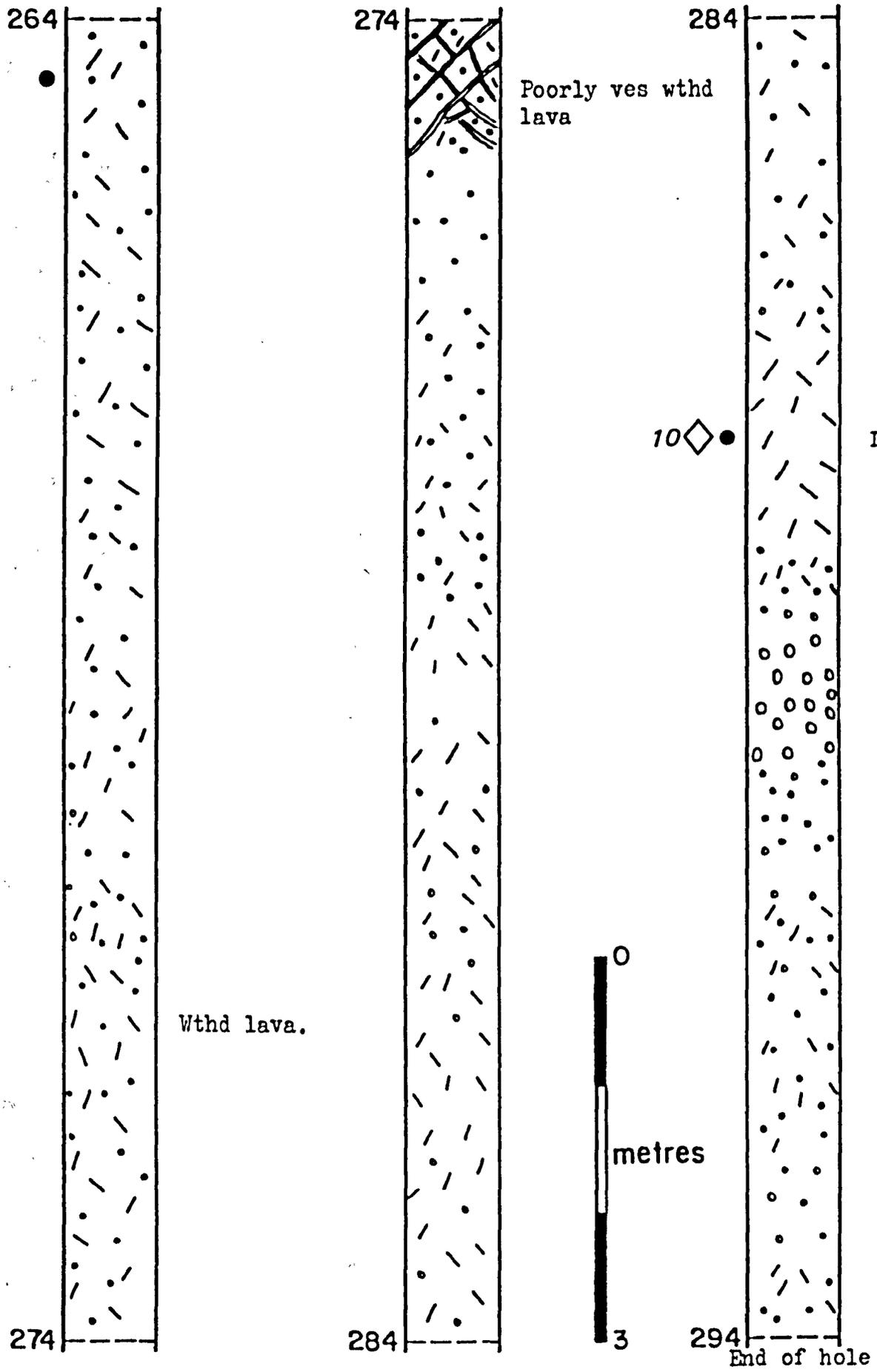
Haddonfields 'Middle Lava', (CONT)
Haddonfields No. 11 borehole



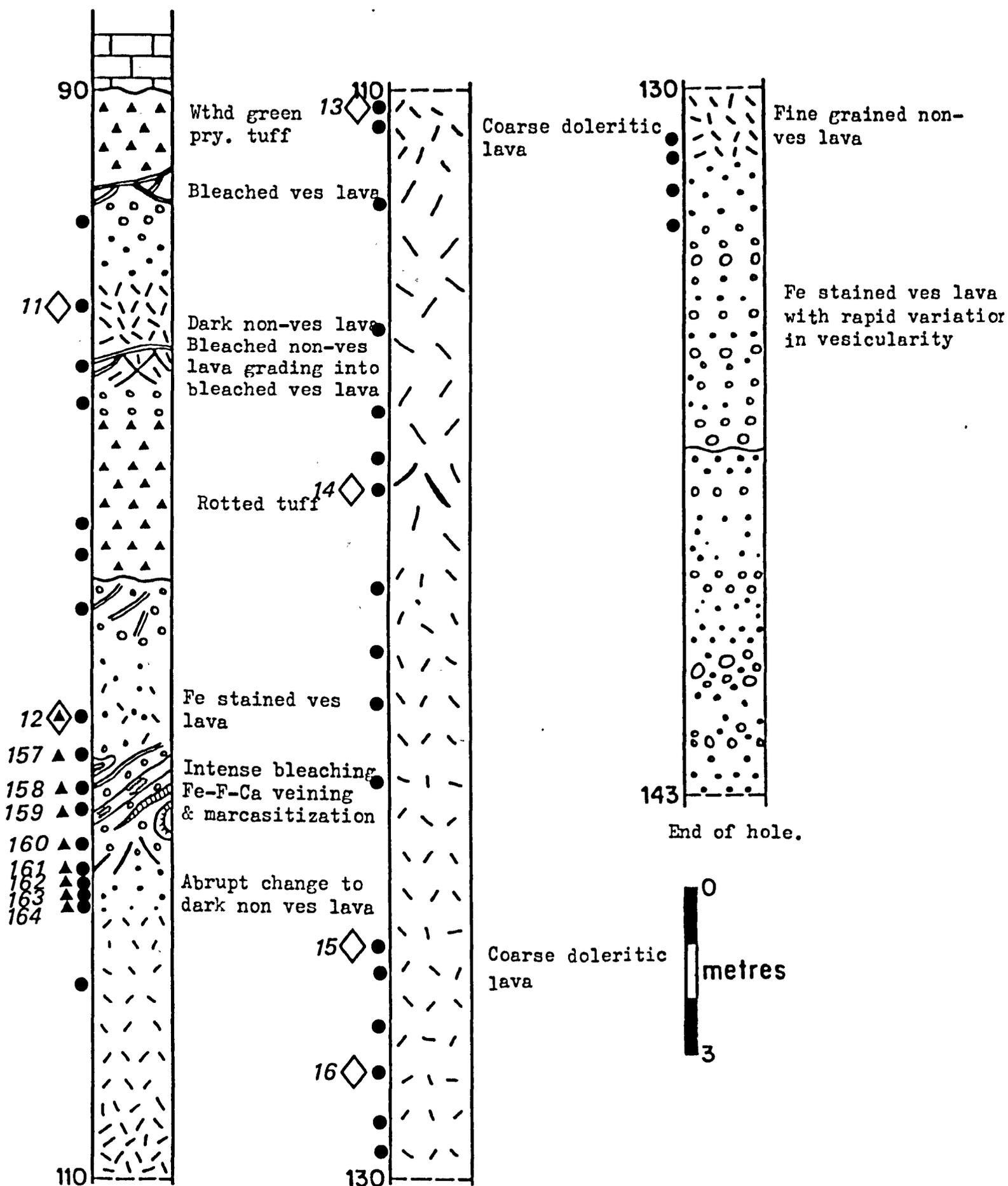
Haddonfields 'Lower Lava', Haddonfields No.11 borehole



Haddonfields 'Lower Lava', (CONT) Haddonfields No.11 borehole

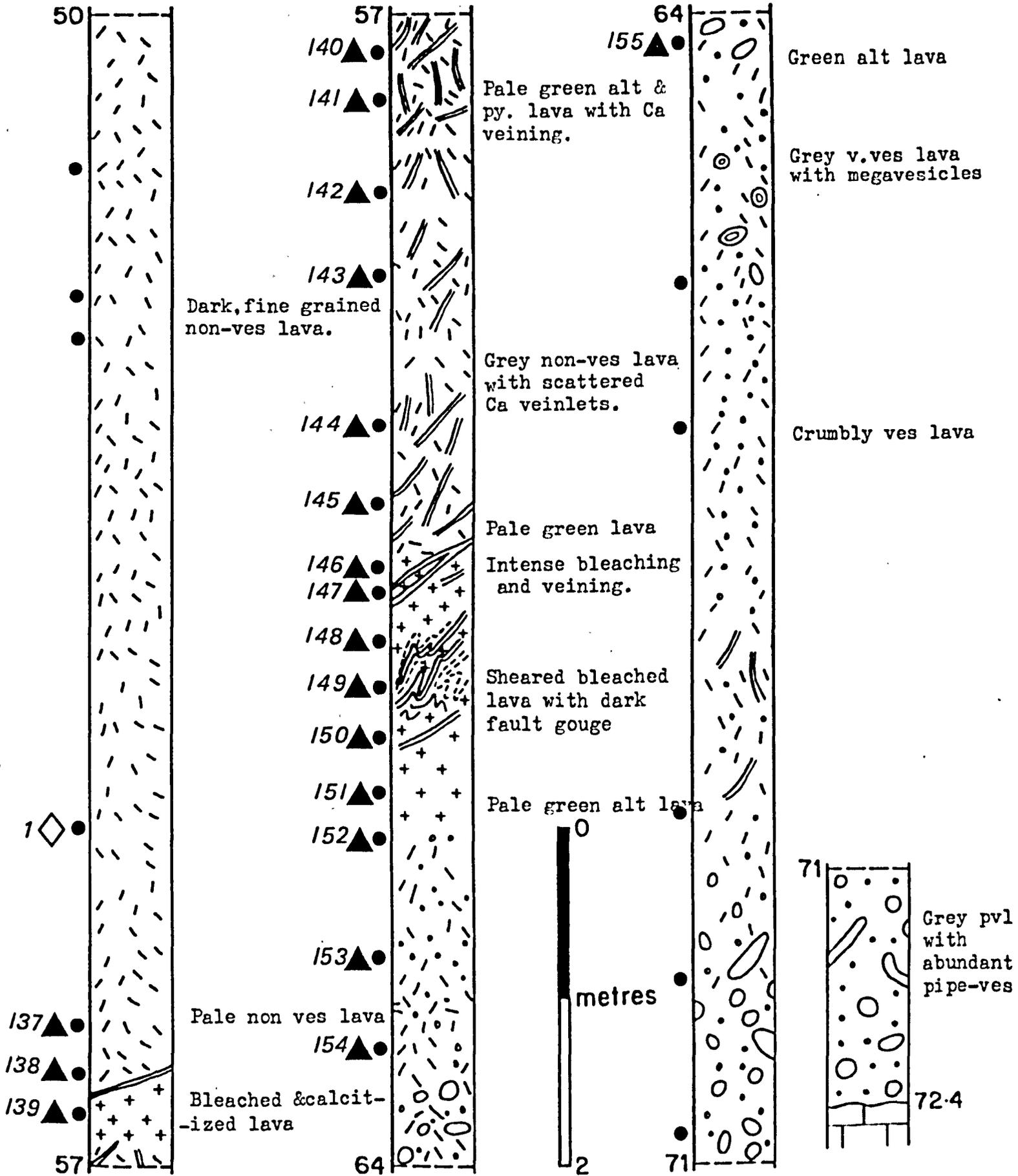


Shacklow Wood Lava, Mogshaw No.3 borehole



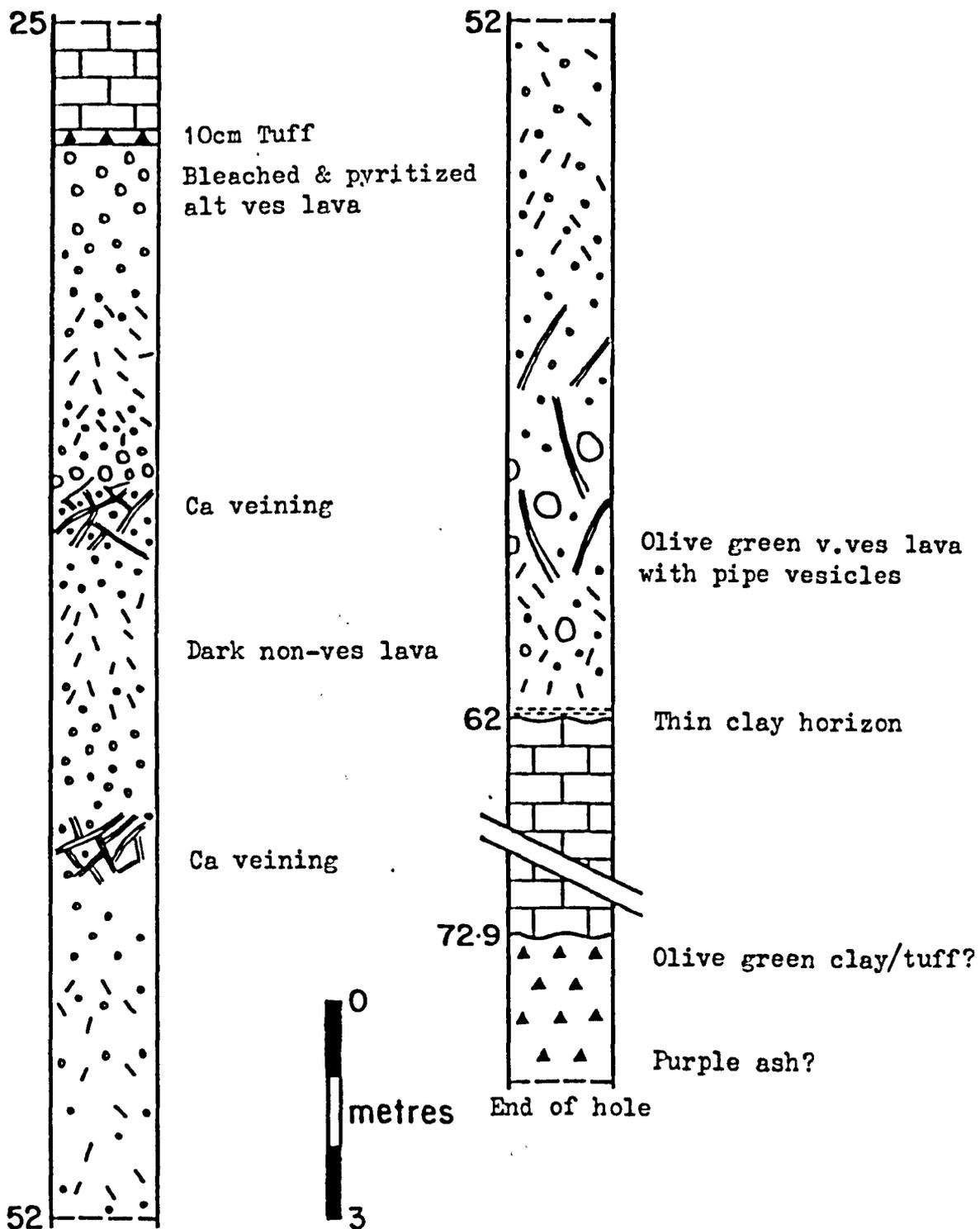
LOCATION....approx SK 191 678
 DRILLED.....July-August 1979
 INCLINATION.67° at 008°
 COMPANY.....DRESSER MINERALS.

Conksbury Bridge Lava, Conksbury East No.5 borehole



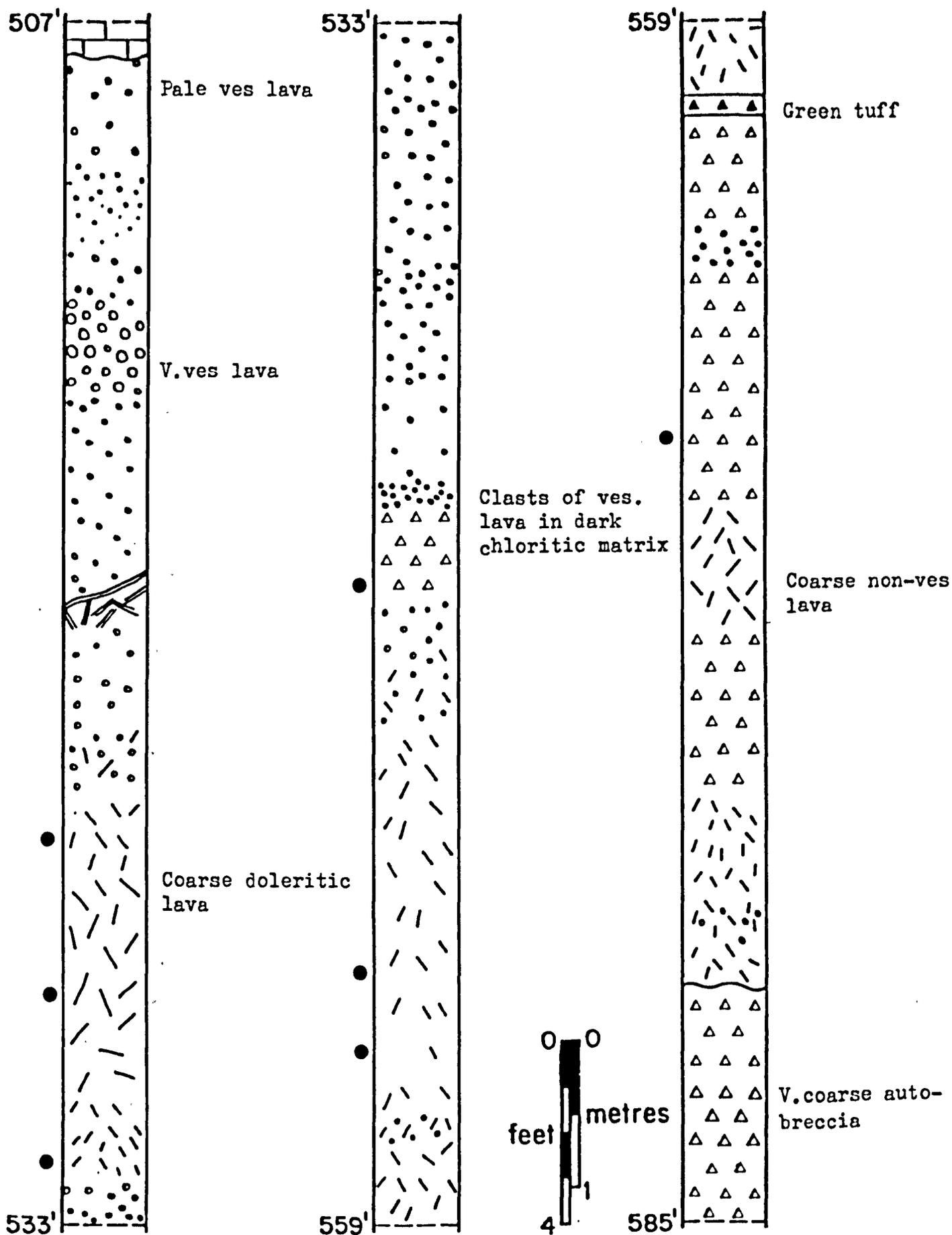
LOCATION....approx SK 212 651
 DRILLED.....1979
 INCLINATION.55° at 180°
 COMPANY.....DRESSER MINERALS.

Conksbury Bridge Lava and Lathkill Lodge Lava/ Lower Alport Lava, Conksbury East No.1 borehole



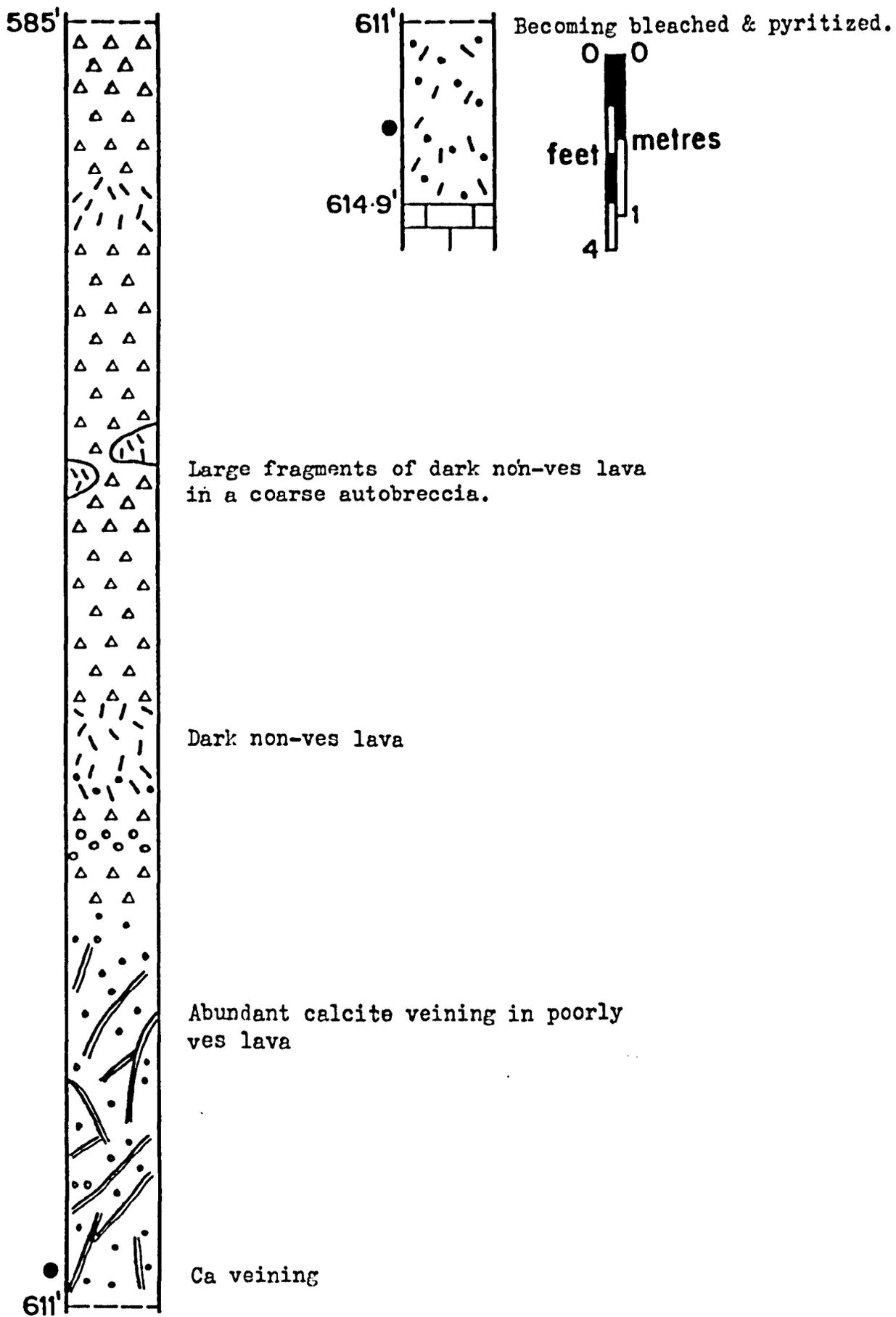
LOCATION.....approx SK 212 653.
 DRILLED.....1979
 INCLINATION.VERTICAL
 COMPANY.....DRESSER MINERALS.

Cressbrook Dale Lava, Wardlow Mires No.1 borehole



LOCATION.....SK 1850 7553
 DRILLED.....1966-1967
 INCLINATION.VERTICAL.
 COMPANY.....INSTITUTE OF GEOLOGICAL SCIENCES.

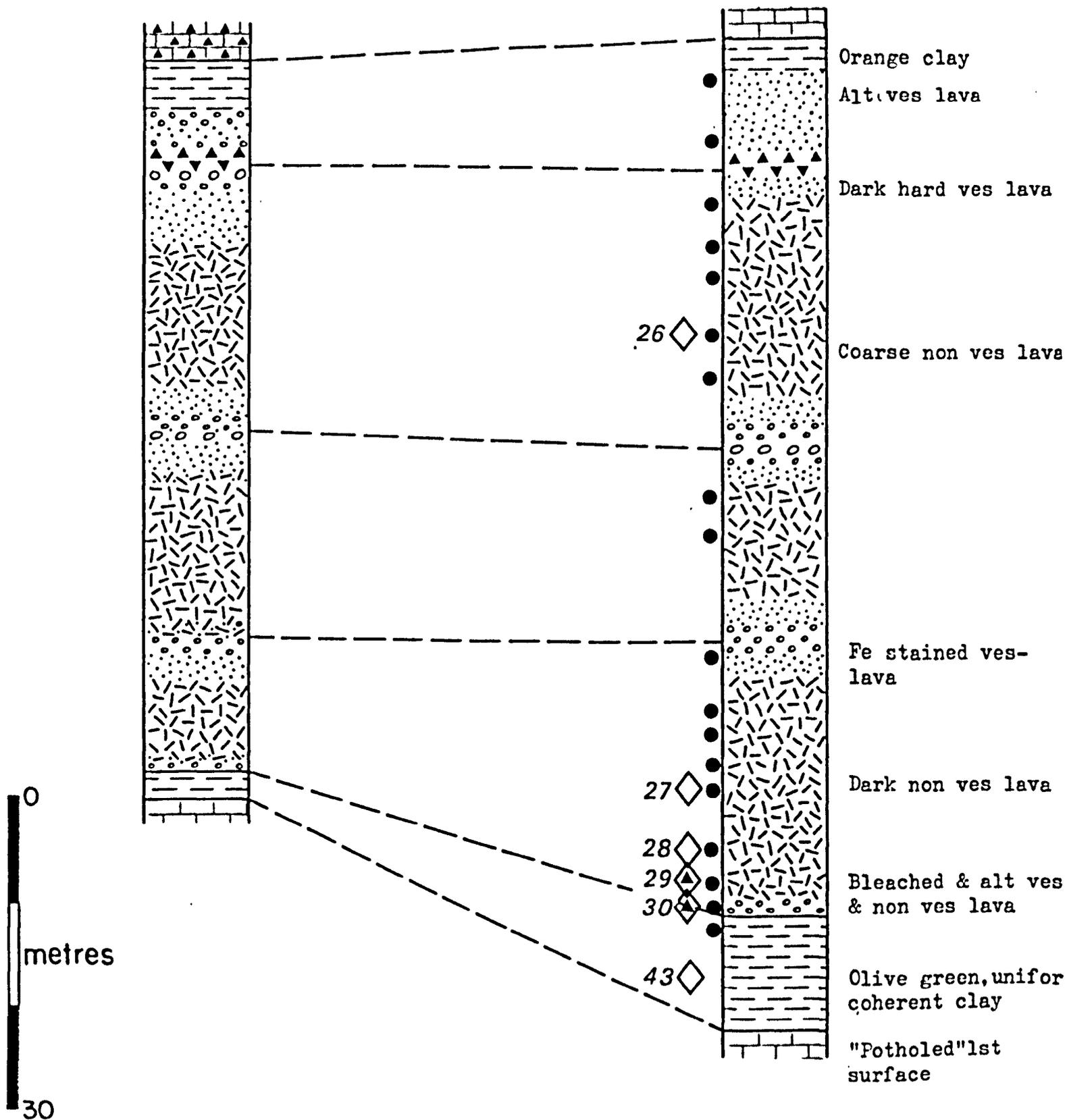
Cressbrook Dale Lava (CONT) Wardlow Mires No.1 borehole



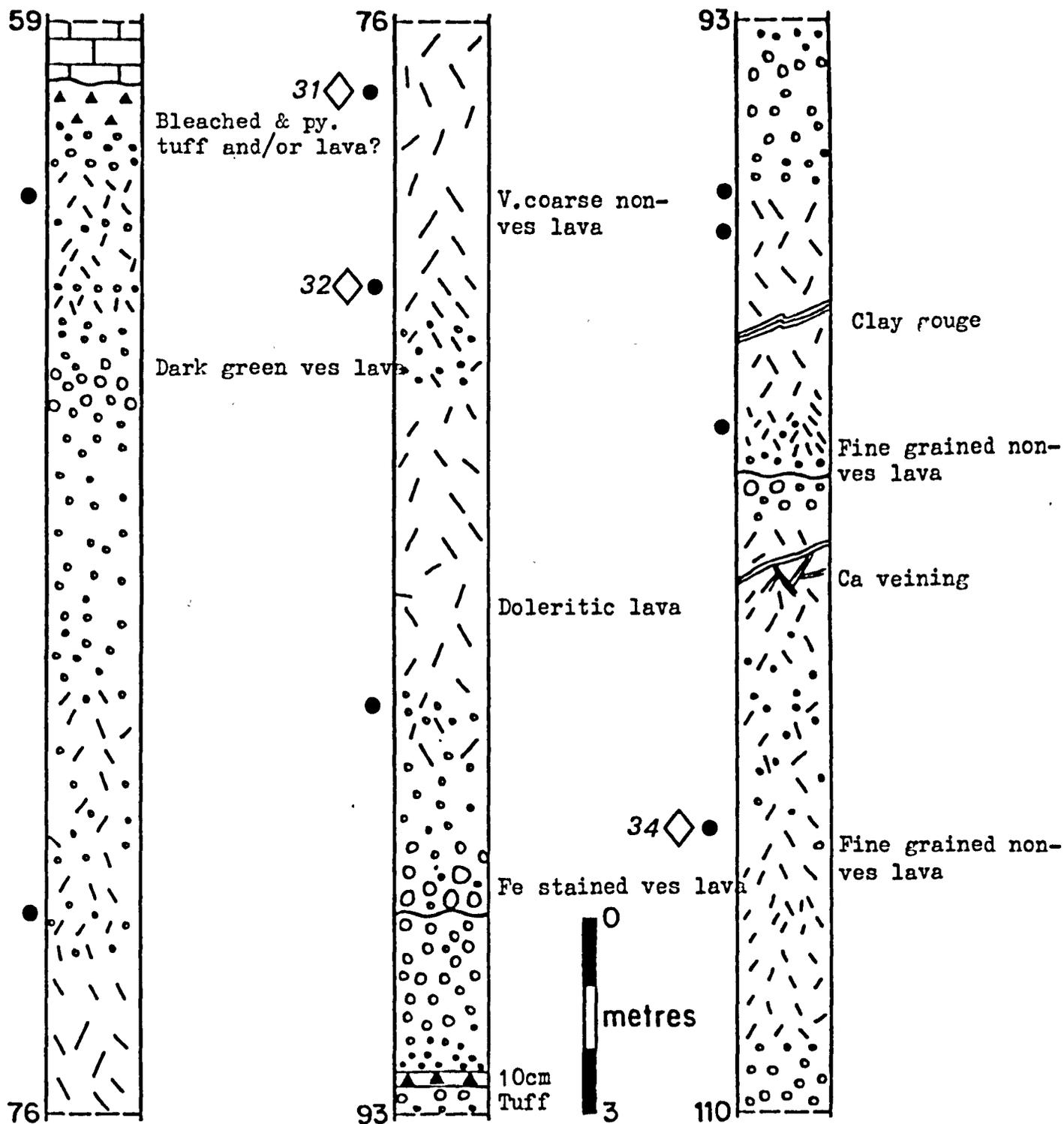
Millers Dale Lower Lava Tunstead Boreholes

T/B/22
(099762)

T/B/21
(103754)

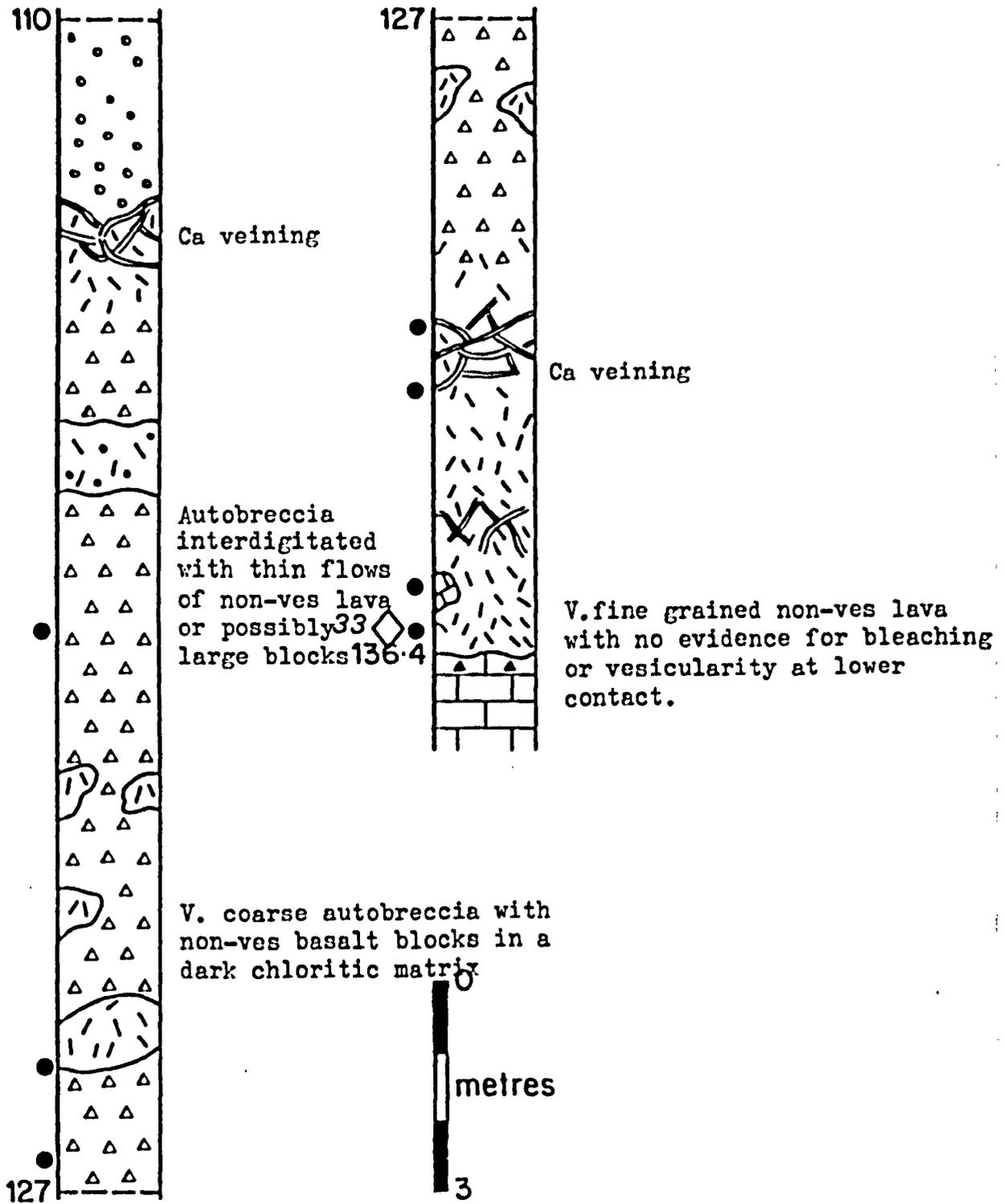


Cressbrook Dale Lava, Eyam borehole

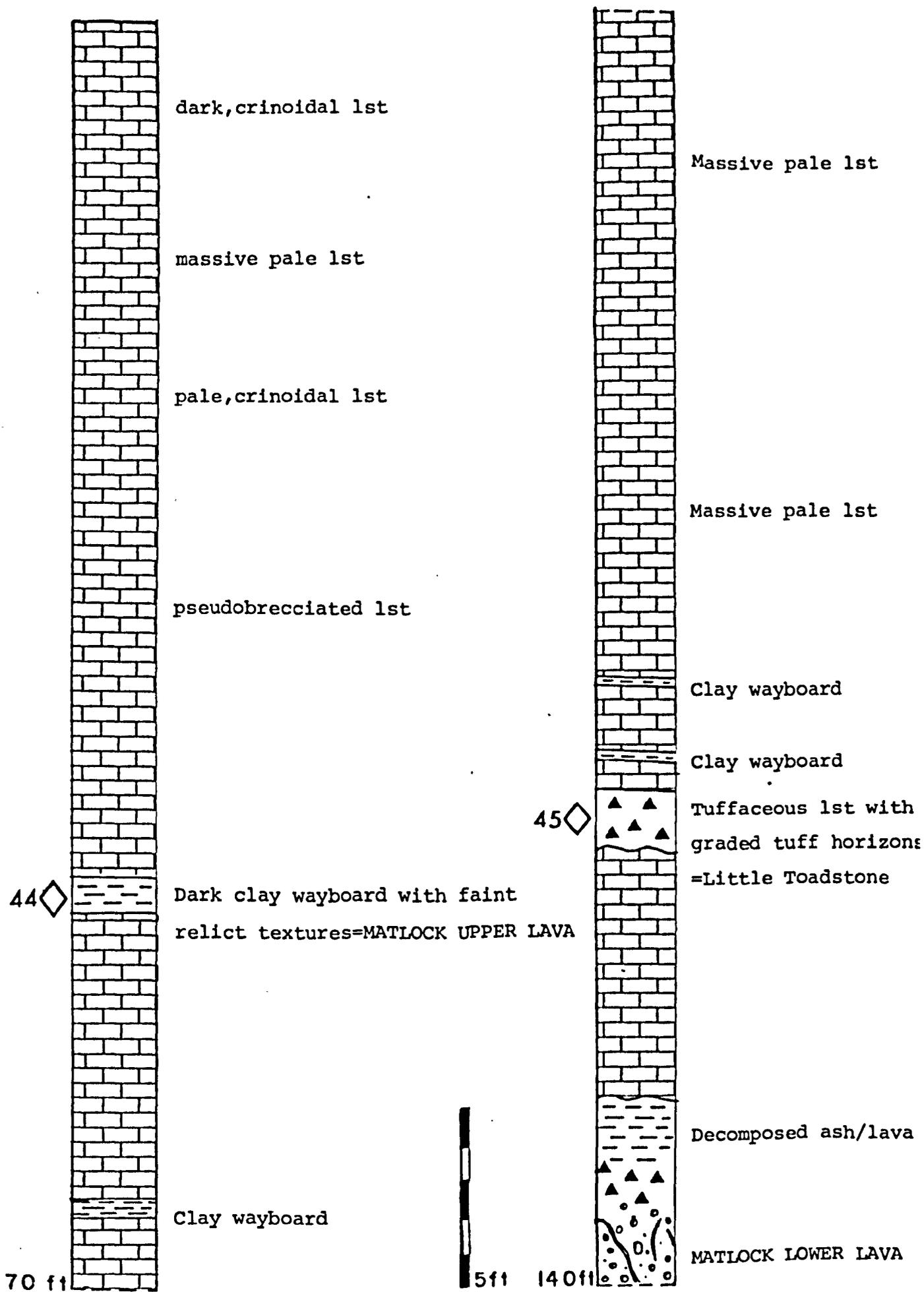


LOCATION...SK 2096 7603
 DRILLED....1970-1972.
 INCLINATION...VERTICAL.
 COMPANY....INSTITUTE OF GEOLOGICAL SCIENCES.

Cressbrook Dale Lava, Eyam borehole (CONT.)



Matlock Upper and Lower Lavas Bonsall Moor U3 Borehole



LOCATION....SK 2579 5850
DRILLED.....1977

INCLINATION..VERTICAL
COMPANY.....NCC MINERALS

ABRIDGED LOGS OF BOREHOLES

(NOT FOR PUBLICATION)

Location: SK 6478 2327 (Stanton Area)

Drilled: 1974

Inclination: 60° at 160°

Company: Allied Chemical Corporation

From	To	
(Metres)		
0	3.3	Overburden
3.3	99.37	Fossiliferous and cherty limestone
99.37	130.07	Basalt, altered to green clay in top 0.2 m = Conksbury Bridge Lava
130.07	133.72	Massive limestones

End of Hole

Location: SK 6479 2367 (Stanton Area)

Drilled: 1974

Inclination: 69° at 030°

Company: Allied Chemical Corporation

From	To	
(Metres)		
0	10.05	Overburden
10.05	104.21	Fossiliferous and cherty limestone
104.21	131.36	Basalt, altered to green clay in top 1.0 m = Conksbury Bridge Lava
131.36	136.26	Massive limestone

End of Hole

Location: SK 6488 2337 (Stanton Area)
 Drilled: 1974
 Inclination: 48° to 325°
 Company: Allied Chemical Corporation

From (Metres)	To	
0	105.06	Limestones
105.06	107.17	Soft green vesicular basalt = Conksbury Bridge Lava
End of Hole		

Location: SK 4288 3582 (Matlock Area)
 Drilled: 1971
 Inclination: Vertical
 Company: Exsud Ltd.

From (Metres)	To	
0	25.50	Porous dolomite
25.50	31.10	Basalt, altered to clay in top 0.6 m = Matlock Upper Lava
End of Hole		

Location: SK 4290 3581 (Matlock Area)
 Drilled: 1971
 Inclination: Vertical
 Company: Exsud Ltd.

From (Metres)	To	
0	25.90	Porous dolomite
25.90	27.40	Dark grey limestone, pyritized at contact with lava

27.40 32.30 Vesicular basalt, bleached and pyritised in top 2m
= Matlock Upper Lava

End of Hole

Location: SK 4286 3581 (Matlock Area)

Drilled: 1971

Inclination: Vertical

Company: Exsud Ltd.

From To
(Metres)

0	15.20	Porous Dolomite
15.20	16.75	Dolomite breccia
16.75	30.00	Dark basalt, very few vesicles = Matlock Upper Lava
30.00	42.40	Porous dolomite
42.40	42.70	Clay horizon
42.70	65.70	Dolomite
65.70	68.90	Altered vesicular basalt = Matlock Lower Lava

End of Hole

Location: SK 4291 3576 (Matlock Area)

Drilled: 1971

Inclination: Vertical

Company: Exsud Ltd.

From To
(Metres)

0	32.20	Dolomite with 0.25 m clay horizon at 6.65 m
32.20	41.00	Basalt = Matlock Upper Lava
41.00	78.80	Dolomite
78.80	82.20	Basalt, altered to toadstone in clay in upper 2m = Matlock Lower Lava

End of Hole

Location: SK 4288 3586 (Matlock Area)
 Drilled: 1972
 Inclination: Vertical
 Company: Exsud Ltd.

From (Metres)	To	
0	28.8	Dolomite
28.8	32.6	Altered vesicular basalt = Matlock Lower Lava
End of Hole		

Location: SK 4288 3584 (Matlock Area)
 Drilled: 1971-1972
 Inclination: Vertical
 Company: Exsud Ltd.

From (Metres)	To	
0	35.6	Dolomite
35.6	64.4	Basalt, altered to toadstone clay in top 1.2 m = Matlock Upper Lava
End of Hole		

Location: SK 4247 3586 (Low Mine)
 Drilled: 1972
 Inclination: 46° at 015°
 Company: Exsud Ltd.

From (Metres)	To	
0	26.40	Grey-green basalt = Matlock Lower Lava
26.40	60.30	Green basalt with abundant limestone and lava fragments, almost 'agglomeratic'
60.30	61.59	Tuff and tuffaceous limestone
61.59	68.60	Limestone and tuffaceous limestone with mineralisation may represent a vein within the Lava
68.60	83.51	Clay and tuffs with limestone fragments
83.51	90.36	Tuffaceous limestone and mineralisation
90.36	98.00	Green lava, tuffs and clays
98.00	138.05	Light grey limestones with thin clay horizons common towards the top

End of Hole

Location: SK 4289 3585 (Low Mine)
 Drilled: 1972
 Inclination: 59° at 000°
 Company: Exsud Ltd.

From (Metres)	To	
0	17.85	Dolomite
17.85	117.56	Basalt, with ash horizons towards base and with abundant limestone and lava fragments between 109.7 and 112.3 = Matlock Lower Lava
117.56	172.65	Grey limestone with 1.08m clay horizon and 163.4 m.

End of Hole

Location: SK 2385 6155 (Coast Rake)

Drilled: 1979 (?)

Inclination: Vertical

Company: Dresser Minerals

From (Metres)	To	
0	81	Black shale and thin limestones
81	84	Thick wayboard = base of Cawdor Group
84	121	Dark limestones
121	189	Dolomites and altered limestones
189	197	Pale limestones
197	205.9	Dark, cherty limestones
205.9	-	Entered into vesicular lava = Matlock Upper Lava
End of Hole		

Location: SK 6180 2453 (Coast Rake)

Drilled: 1974

Inclination: 59° at 266°

Company: Allied Chemical Corporation

From (Metres)	To	
0	215.26	Interbedded shale and thin sandstones
215.26	223.60	Interbedded shale and limestone
223.60	330.08	Limestone with thin (av. 20 cm) clay horizons at 252.0, 258.3, 266.8, 267.6, 273.5 m
330.08	359.12	Basalt = Matlock Upper Lava
359.12	371.52	Limestone
End of Hole		

Location: SK 142 733 (Millers Dale)
Inclination: Vertical
Company: North Derbyshire Water Board

From (Metres)	To	
0	15.2	Massive, pure limestones
15.2	34.7	Basalt with tuff horizons near base = Millers Dale Lower Lava
34.7	106.7	Pure limestones (Chee Tor Beds) with 'black calcareous shale' horizons at 70 m
106.7	304.8	Dark limestones and dolomitic limestones (Woo Dale Beds)

End of Hole

Appendices 8, 9, 10, 12 and 13 - Published Papers

Appendices 9, 10 and 12 represent joint publications with P.R. Ineson, who was responsible for all decisions in the final format of the text and diagrams, and was instrumental in obtaining certain borehole cores and logs together with permission to publish previously confidential information.

Appendix 13 represents a paper in preparation which contains important unpublished borehole and geochemical information obtained subsequent to the final compilation of the thesis, and is included for completeness.

Appendix

8

CLEAR-THE-WAY OR BLACK HILLOCK MINE

TIDESLOW MOOR

by S. G. Walters

SUMMARY

An exceptional thickness of some 200 metres of "toadstone" was intersected at Black Hillock Mine near Peak Forest. A study of contemporary documents and the geology of the surrounding area has shown that the "toadstone" was in fact a dolerite intrusion, possibly related to a complex sequence of lavas and tuffs in adjacent mines. Old man's workings were enlarged and an engine shaft was sunk to a depth of 98 fathoms in 1764-1771. Water was raised by a tub engine and turned into a swallow in the toadstone at 60 fathoms. A further episode of deepening carried the shaft to 120 fathoms in 1789-1793 when water broke in, though it is not known whether the toadstone had been bottomed.

INTRODUCTION

Clear-the-Way or Black Hillock Mine (SK 141 782) was situated on the Hucklow Edge-Tideslow Rake system in the western portion known as White Rake. White Rake had been followed into what was thought to be one of the lava horizons of the area, the 'third toadstone at its basset (outcrop)' according to Farey (1811). At Black Hillock Mine the vein had persisted into and had been worked in at least the upper part of the 'toadstone'. It was logical, therefore, to suppose that this would be the ideal site to follow the vein through the toadstone in the hope of discovering virgin ore in the underlying limestone.

Unfortunately, the toadstone proved to be of exceptional thickness and the predicted rich veins were never discovered. The failure of the venture was documented by Whitchurst (1778) in which he contrasted the great thickness of toadstone at Black Hillock Shaft (183 m not bottomed) with the thin toadstones seen in adjacent mines (Fig. 2). His account has been reiterated many times and created doubts and confusion which may now be examined in the light of recent investigations.

Information of the 'tryal' is found in two reckoning books (Bagshawe Collection 401 and 402) together with a number of Barmasters' Books for the liberty. In the earlier reckonings the mine is known as Clear-the-Way, and only later did the predominance of dark toadstone on the spoil heap earn it the alternative name of Black Hillock (only this latter name will be used to distinguish it from another Clear-the Way mine on Moss Rake).

BLACK HILLOCK MINE, 1764-1771

The initial deep sinking of the Black Hillock Shaft dates from 1764 to 1771, but earlier and later episodes of activity can be recognised. Evidence for the former is from numerous references to the 'old man' in the reckonings of this period. Prior to shaft sinking unworked veins in the vicinity were 'possessed' to form a consolidated 'Black Hillock Title'. These include portions of White Rake, Little Calfestones and Old Calfestones Veins, Chap Maiden Rakes, Bull Rake at Tideslow Top, Stoney Low Vein, Dawsons Rake and the Rattock.

By December 1764, the foot of the Engine Shaft stood at 20 fathoms, still in toadstone. Details of the 'engine' are sparse; for example an entry for

March, 1765, noted that:

A new tub engine - £30 0s. 0d.

Later entries recorded new ropes and kibbles for this engine which seems likely to have been a simple balanced horse-whim. Water was not initially a problem due, no doubt, to the impervious nature of the toadstone. At deeper levels water was drained into a swallow, at 60 fathoms. It is difficult to envisage a swallow in the 'toadstone' at such great depth. It may have been a cavernous portion of the vein draining towards Peak Forest. Water was drawn up from below this level by a horse-whim.

In March, 1767 the 'old man's sumps were opened for air and climbing' by connecting them with a cross-cut from the foot of the engine shaft at 54 fathoms. It becomes increasingly obvious that the miners had little or no idea of the extent of those old workings. In June, 1768, with the engine shaft foot at 82 fathoms, still in toadstone, an investigation was made of both new and old workings (Bagshawe Collection 401). This recorded the 'old man' as descending in a series of typical shallow climbing shafts, variously referred to as sumps or turns. The upper turns were sunk at a particular hade or inclination and suggest they were following the vein. At a depth of some 74 fathoms this vein appears to have been lost in the head of a 20 fathom perpendicular sump, at this time partly flooded. The results of this investigation indicated that 'the old gates stood at 96 fathoms deep' (Fig. 1).

The flooded sumps had been pumped dry by September 1768, as shown by the entries:

Geo. Boam and Co. emptying the old mens sump 22 fathoms and 4 ft. at 22/6 per fathom	£25 10s. 0d.
Widow Rawlin's horses drawing the water out of the old mens sumps	£ 2 2s. 0d.

When pumped dry the bottom of the sump was resurveyed as 94 fathoms deep and discovered to be connected via a short drift to another sump of 4 fathoms giving a total depth of 98 fathoms. This was some 16 fathoms lower than the foot of the Engine Shaft and presented somewhat of a dilemma. The first option was to abandon sinking the engine shaft and concentrate work in the deeper parts of the old sumps. This would entail having to raise water from the sumps by hand to a cross-cut driven from the Engine Shaft foot at 84 fathoms to draw it up to the swallow. The second option was simply to carry on sinking the engine shaft to connect first with the old man at 98 fathoms and then to carry the trial even deeper, a more expensive proposition.

Eventually, however, both plans were put into action in order to provide two interconnected shaft systems which would help considerably with deep ventilation. (Fig. 1).

By the end of 1768 work was in hand to drive the 84 fathom cross-cut to continue sinking the engine shaft and enlarging and deepening the lower reaches of the old sumps. Clearly the fact that the workings were still in toadstone at this depth had not dampened their enthusiasm for the trial. Indeed a short note seems full of optimism:

'... the 16 yard drift lies at or near 94 fathoms deep to which place we must let down our shaft, and then enlarge the 16 yard drift, and from the head of the 20 fathom sump bring our vein with us to the bottom of the toadstone, there we stand prepared with everything for a full tryal of the under Lime, and for air to carry on afterwards.'

This optimism is puzzling. There is a strong implication that either the base of the toadstone had been reached or that there was some indication that it soon would be encountered. Whether or not Black Hillock Shaft

Figure 1 - Black Hillock Mine
Representation of the extent of workings, Spring 1769

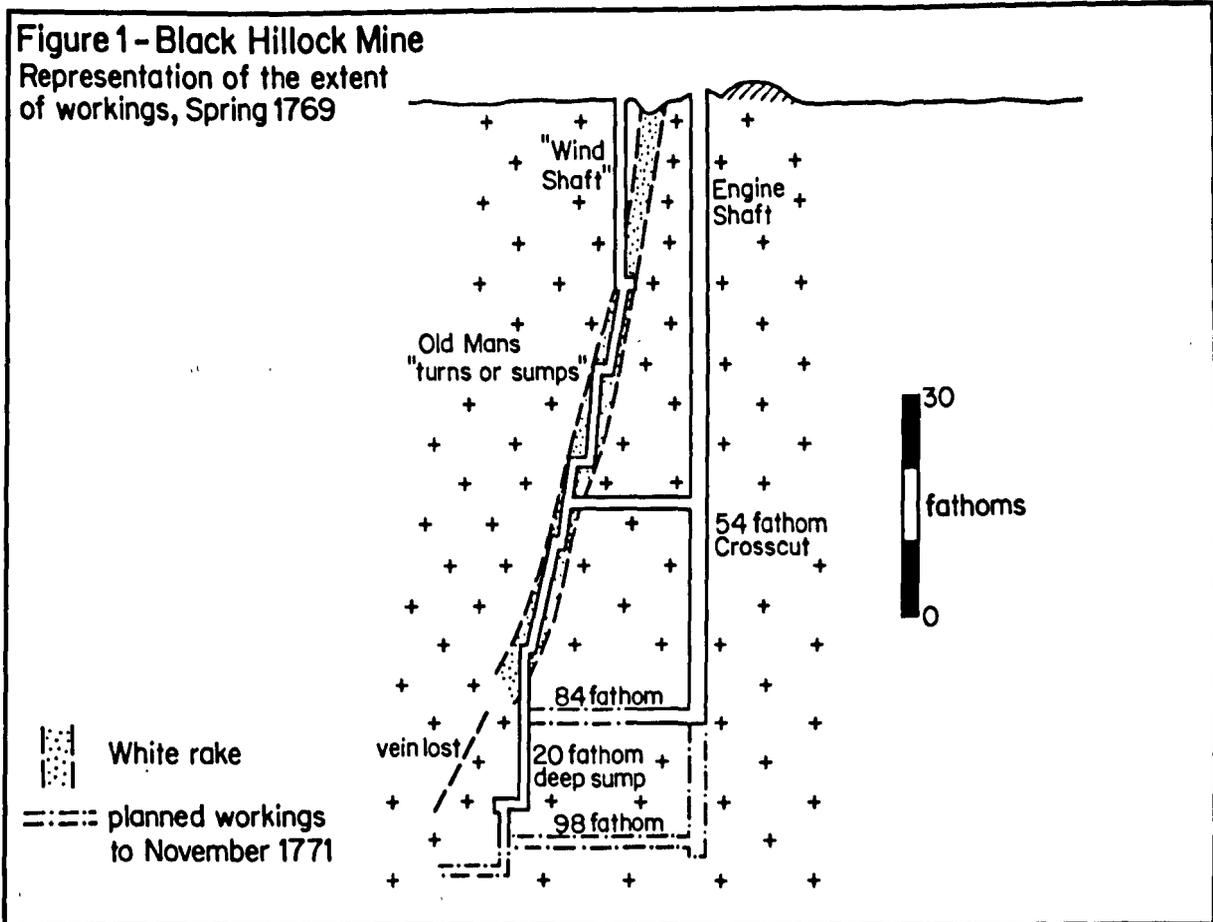
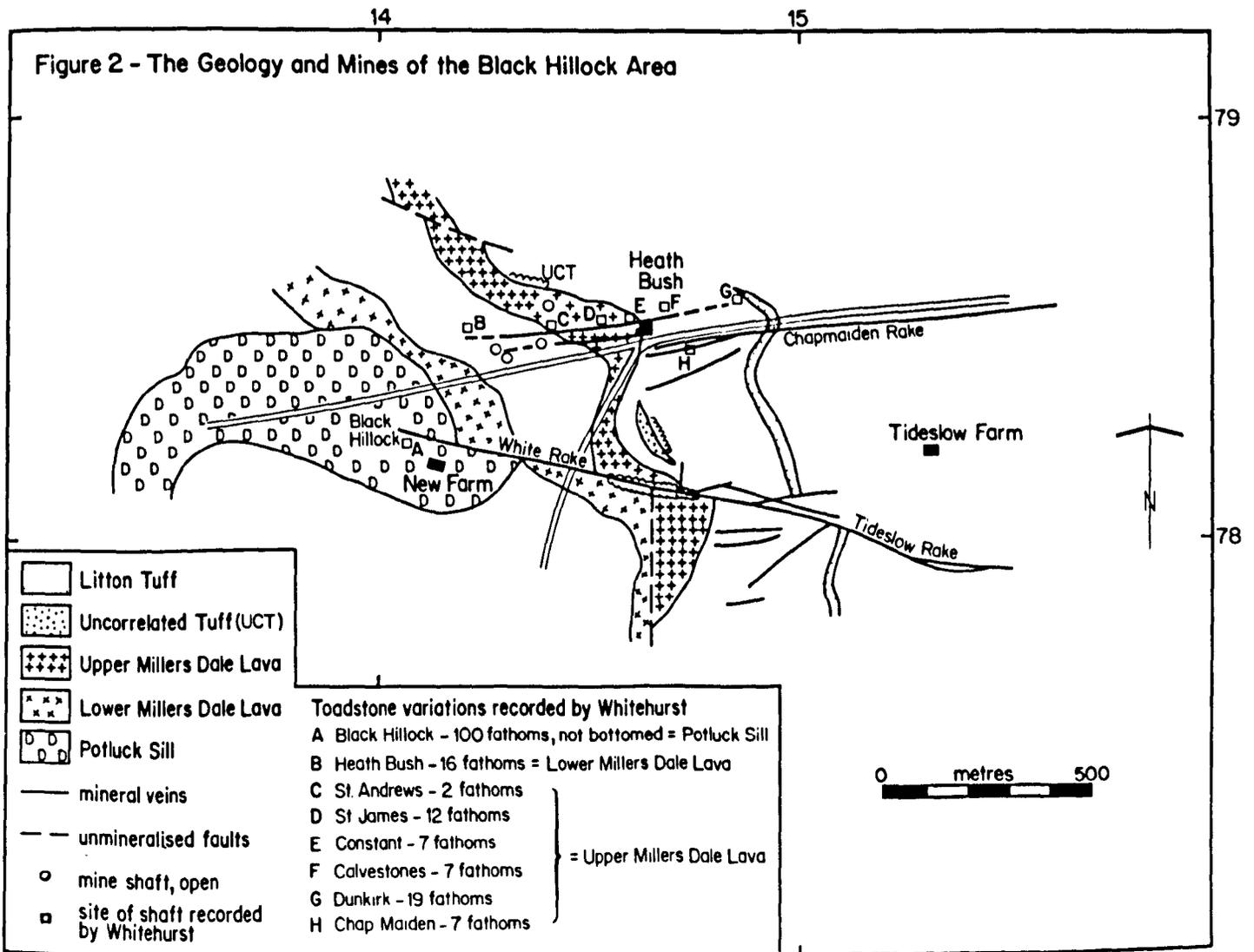


Figure 2 - The Geology and Mines of the Black Hillock Area



ever did reach the limestone has been a point of dispute. Whitehurst (1778) clearly stated that the workings were abandoned in toadstone at 100 fathoms, but Farey (1811) attributed a sudden inundation at the foot of the shaft to a breaching of the limestone.

Although during 1769 work continued at depth to try to intersect the vein, all was not well. The veins within the 'Black Hillock Title' had lain idle for many years and on a number of occasions the Barmaster threatened to give these to other miners. To prevent this, the Black Hillock miners had periodically carried out some semblance of work at each of the veins.

In the period 1770-1771 activity at the mine entered into decline. In the final reckonings there are few details as to why the venture was finally abandoned after so much effort. There are vague references to an increase of water but nothing that matches the sudden inundation noted by Farey. Despite continually 'driving towards the vein' no ore output is ever recorded and it is more likely that this failure to find mineralisation at depth was the deciding factor. The Barmaster became no longer satisfied with their 'sham' workings of the vein, and gave these away in November, 1771, and this may also have been a major factor. The total losses incurred by the shareholders amounted to £5,532 (B.C. 401).

BLACK HILLOCK MINE, 1789-1793

This did not, however, mark the end of activity at the mine. If water had been a problem in 1771, it presented no difficulties in 1789 when sinking was recommenced at the foot of the engine shaft. In the three months ending November, 1789, over 15 fathoms were sunk making the engine shaft in all some 120 fathoms deep. Following this there was a sudden and dramatic drop in activity. The final reckoning was for a 3¼ year period to September 1793, and contained a short note of great interest:

'..... drawing water and endeavouring to sink at the shaft foot but the water could not be managed though as dry a summer as can be remembered.'

This implies that the inrush of water recorded by Farey (1811) was encountered in the summer of 1790 at a depth of 120 fathoms, twelve years after Whitehurst's (1778) initial account.

The abandonment of this second venture with a loss of £60 marks the end to all deep activity in Black Hillock Mine. Sporadic hillocking took place along White Rake from 1794-1824, with small profits from belland ore whilst there is a brief period of mined ore production (December, 1806 - June, 1807).

There is little in the way of surface remains today other than grassed over hillocks and a few open shafts. The most obvious relic is the large mound of dark toadstone at Black Hillock from which the mine was named.

RECENT ACTIVITY

The area has not been without one last surprise. In recent years the White Rake east of Black Hillock has been worked opencast revealing a strong fluorite-rich vein up to 1.5 m wide that persisted into the Upper and Lower Millers Dale lava. Such a strong continuation of a vein through a lava is unusual and the high grade fluorite fill contrasts sharply with the more typical calcite-baryte dominant assemblages seen in the Tideslow Rake portion of the vein system to the east.

GEOLOGY OF THE BLACK HILLOCK AREA

The geological situation at Black Hillock, is far more complex than could have been envisaged by Whitehurst or Farey. Green et al (1887) considered the great thickness of toadstone as due to the shaft being sunk into a feeder structure to the lava. Bemrose (1907) was the first to recognise that the 'lava' at Black Hillock was in fact intrusive dolerite, part of his Potluck Sill. Farey had correlated this sill and the Cressbrook Dale

lava encountered in High Rake Mine further east as his '3rd toadstone'. The stratigraphic level of the intrusion is considerably below the horizon of the Cressbrookdale Lava. This provides an explanation for the thickness variations recorded by Whitehurst and Farey's four 'chance toadstone' beds in Chapmaiden Mine. The map first produced by Whitehurst (1778, incorporated into Fig. 2) shows the mines in question to lie within the areas underlain by the Lower and Upper Millers Dale Lavas. An eastward continuation of Potluck sill towards Chapmaiden Mine may correspond to the third of Farey's 'chance beds'. The presence of four beds, however, in the absence of any fault repetition requires further explanation. The fourth horizon may correspond to the small tuff outcrop outlined by augering on recent Geological Survey maps (Stevenson et al., 1976) from south of Chapmaiden Mine (Fig. 2). Bemrose (1907) recorded tuff from a similar horizon below the old quarry north-west of Heath Bush, now obscured, and the author has collected tuffaceous limestone from shaft spoil near to Bemrose's locality. Another possible explanation can be seen in the recent White Rake opencast. The Lower Millers Dale 'lava' shows two distinct flows separated by a limestone unit some 3 m thick. Seen underground this could have given rise to the interpretation of two or more 'chance beds'. Unfortunately, Farey gave no details as to the thickness and relative position of his 'chance toadstones'. There are a number of open shafts in good condition in the area (Fig. 2) which may give access into the mines and the author would be interested to hear from anyone who has descended these.

Thus, it seems that the Black Hillock Shaft was sunk into a dolerite sill not related to the thin lavas seen at adjacent mines. A thickness of over 215 m however, is still remarkable for a Derbyshire Sill and must represent a sill feeder structure or a 'step down' similar to those seen from the Whin Sill in the North Pennine Orefield. Green et al. noted (1887, p.135):

'..... the toadstone (dolerite) contained many fragments of limestone, differing scarcely at all in appearance from the parent rock. Specimens abound in the hillock.'

This is a peculiar and highly unlikely statement. Many blocks of unaltered limestone can still be found in the hillock strongly suggesting the limestone had been reached. No specimens can be found of limestone caught up in the dolerite in an 'agglomerate' texture.

Apart from the variety of igneous horizons the area is also geologically important for the unusual persistence of mineralisation in these horizons. Farey (1811) recorded a number of mines in this vicinity which 'worked ore in the toadstone' and the recent White Rake opencast supports these observations. At Chapmaiden Mine galena-fluorite-calcite-baryte vein samples within blocks of bleached and altered vesicular and non-vesicular basalts are present. The White Rake at Black Hillock Mine is known to have persisted to at least a depth of 135 m within the Potluck Sill. Occasional specimens of mineralised dolerite can be found on the dump. Adjacent to these veins the dolerite shows zones of bleaching and argillisation producing an altered rock very similar to the 'White Whin' of the North Pennine Orefield.

CONCLUSIONS

The Black Hillock trial failed due to the complexity of the intrusive and extrusive activity in the area and the understandable failure of the miners to recognise the attendant implications. As far as a trial of 'under lime' it is an unfortunate fact that without realising it, mines such as Chapmaiden had already followed the veins down to beneath the lowest lava horizon of the area. It was, as Farey recorded, although he himself failed to recognise the real situation:

'..... a trial suggested only by the grossest ignorance of the stratum.'

ACKNOWLEDGMENTS

The author thanks the staff of Sheffield City Library for their assistance with the Bagshawe Collection; Dr. P.R. Ineson for his critical readings of the manuscript; Mr. M. Cooper for drafting the diagrams; and the various farmers who willingly gave access to their land.

REFERENCES

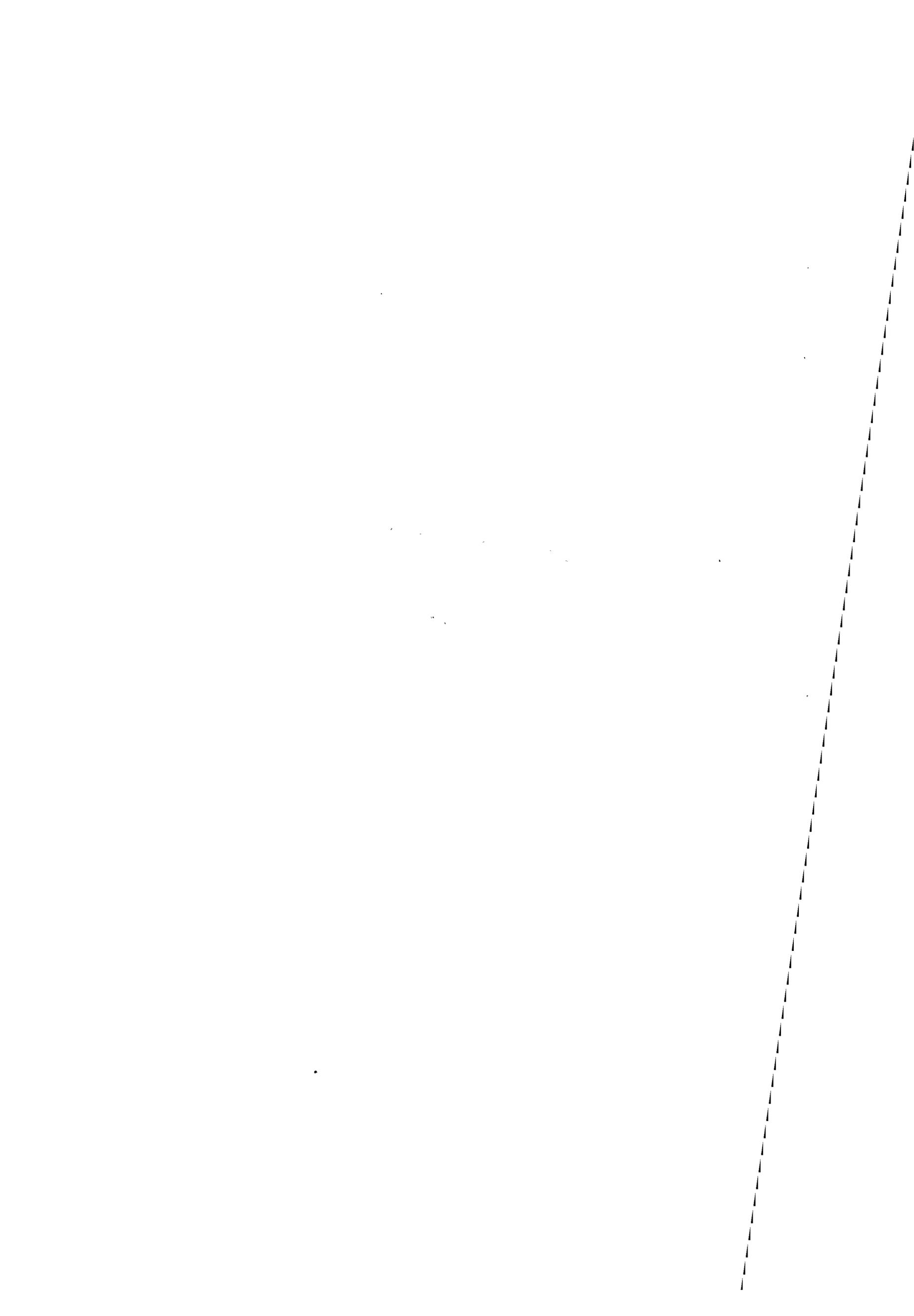
- BEMROSE H.H. ARNOLD, 1907. The toadstones of Derbyshire: Their field relations and petrography. Q.Jl. geol. Soc. Lond., Vol. 63, pp. 241-81.
- FAREY, J., 1811. General View of the Agriculture and Minerals of Derbyshire. London, Vol.1, 532 pp.
- GREEN, A.H., LE NEVE FOSTER, C. and DAKYNS, T.R., 1887. Geology of the Carboniferous Limestone, Yoredale Rocks and Millstone Grit of North Derbyshire and the Adjoining Parts of Yorkshire. Mem. Geol. Surv. Gt. Brit., 2nd Edition.
- STEVENSON, I.P. and EDEN, R.A., 1976. 1:25,000 Geological Map Sheet SK 17, Millers Dale, Inst. Geol. Sciences, London.
- WHITEHURST, J., 1778. An Enquiry into the Original State and Formation of the Earth. 1st Edition.

Received April 1980

S. G. Walters,
Department of Geology,
University of Sheffield,
Mappin Street,
Sheffield,
S1 3JD

Appendix

9



MINERALISATION WITHIN THE IGNEOUS ROCKS OF
THE SOUTH PENNINE OREFIELD

by

S.G. Walters and P.R. Incson

ABSTRACT

In spite of the long-standing tradition that ore is poor or non-existent within the toadstone of Derbyshire, a list has been compiled of some sixty localities with minerals of the hydrothermal suite within lavas or tuffs. Some of these were noted by Farey in 1811. Both these and other recorded occurrences have been checked as far as possible in the field. More localities have been added from field observations.

INTRODUCTION

The Carboniferous igneous rocks of the South Pennine Orefield constitute a varied assemblage of contemporary basaltic lava flows, tuffs, vents and a few intrusive dolerite sills emplaced within the Dinantian limestones. The igneous rocks are known locally as 'toadstones'. It has long been thought that this old mining term may have been derived from the German 'Todt stein' meaning dead or unproductive rock. This derives from the general belief that all toadstones were devoid of exploitable mineral deposits (Firman and Bagshaw, 1974). This tradition has not been supported, however, by the investigation of early mining literature and manuscripts. Examples of mineralisation within toadstones have also been recorded from recent exploration of old mines and from some recent boreholes.

The mineral deposits of the orefield are subdivided into rakes, scrins, pipes and flats (Ford, 1977). Pipes and flats are mineral infills of solutionally enlarged pre-mineralisation pathways in the limestones, i.e. along bedding planes and joints. This complex paleokarstic 'plumbing system' only developed in the carbonate host rocks and therefore, such solutional features are absent from the toadstones. Rake veins are major mineralised faults displacing toadstones and creating 'belts' of open fractures. Scrins may be in minor faults, or in solutionally enlarged joints. In many instances both scrins and rakes were infilled with a clay gouge of decomposed toadstone.

During the propagation of a rake vein from limestone into toadstone the vein often underwent a marked change in character. Whereas 'limestone mineralisation' occurred as single, or a small number of thick veins with distinct vein-walls, in toadstones these veins may split into a swarm of interconnecting veinlets (Fig. 1). Such a change in character was well documented in Seven Rakes Mine, Matlock by De Villiers et al. (1826). Veinlets produce a well-defined zone of bleaching and alteration in the basaltic host rocks similar to, but often more intense, than the 'toadstone-clay' type of alteration developed at the upper and lower contacts of toadstones with limestones (Garnett, 1923).

Pipe veins may be localised above or below lava horizons. Examples of a pipe vein above a lava are from Oxclose and Masson Hill, while at Millclose Mine pipes were developed below a lava. In both these situations the lavas are intensely bleached and intersected with minor veins. Thus the presence of bleached toadstone on a mine dump does not necessarily imply that a vein had been worked 'in the toadstone'. However, in pipes under toadstones, collapse during or after mineralisation may result in adventitious blocks within the ore

deposit. A few localities determined from blocks of altered toadstone in the waste dumps may be of this category.

Toadstones are usually regarded as impermeable aquicludes that controlled the flow of mineralising fluids in the limestones (Firman & Bagshaw, 1974). However, the presence of open fractures transgressing some toadstones could have allowed leakage of fluids from one limestone horizon to another. In some instances this phenomenon was a major factor in the localisation of ore-bodies, as exemplified at the 'boil-up' in Millclose Mine (Traill, 1939), where the rich 129 fathom orebody suddenly ascended through an open fracture in the Upper 129 Toadstone and continued into the overlying limestones.

Such spectacular control cannot be demonstrated easily elsewhere. In the majority of cases thin veinlets in toadstones were infilled with an early-phase of calcite. The rarity of vugs in these veinlets suggest that from a very early stage in the history of mineralisation the fracture zones were effectively 'sealed' and the toadstones reverted to acting as aquicludes. This early infill would account for the 'barren spar leaders' in toadstone often referred to in mining documents. Only the largest fractures remained open long enough to permit the passage of the main phase of mineralisation as in High Rake at Sallet Hole Mine.

In the early mining literature the Rake veins are often depicted as being continuous in limestones above and beneath toadstone layers but cut off by the toadstone, e.g. Whitehurst (1778). Although Pilkington (1789) considered that veins were generally barren in toadstone he noted a vein with a rib of galena 10 inches (25 cm) thick in a mine in toadstone on Tideswell Moor. Farey (1811) noted that during the continuation of a vein through a toadstone it became 'pinched' and was squinted or refracted from its expected position in the underlying limestone (Fig. 1). He also commented that "the vein underneath a toadstone bed, is seldom nearly of the same width, or of the same nature exactly, as that above it".

Farey was the first to recognise that the toadstones were not totally 'un-productive' and in his list of mines (1811) he gave nineteen localities where veins carried ore in the toadstone (although in two of these he misidentified clay and sand bodies around Brassington as decomposed toadstone). He commented ".... doubtless the instances are more numerous". He also listed thirteen mines 'in toadstone' but not specifically working ore in toadstone. A possible logical explanation in these cases is that veins had been followed into toadstones but had proven to be impoverished in galena. Watson (1813) also recorded a number of mines as "very productive in the toadstone".

The strong belief, prior to Farey, that toadstones did not host mineralisation, seems puzzling given these occurrences. However, the unwillingness of the miners to test their veins in the toadstones is less surprising when it is remembered that only some of the larger rake veins carry ore in toadstone. As a percentage of the total of all the other types of mineral bodies in the orefield, scrins, flats, etc., these occurrences appear to be so few as to discourage any trials within toadstone. Practical difficulties of working veins in toadstones would also discourage such ventures. As De Villiers et al. (1826) noted, decomposed toadstone was difficult and expensive to support. Where the toadstone was fresh its hardness and lack of jointing were a major obstacle to the early miners. Whereas miners would drive long distances on thin, barren veins in limestone in the hope of encountering rich bellies or pipes, veins in toadstone were unlikely to strike rich ore suddenly. When a vein had been worked down to a toadstone horizon it was easier to drive crosscuts in search of new veins in the limestone than to attempt to follow the vein down into the toadstone even though it might appear promising. Sinking and driving in toadstone would also be fraught with problems of drainage.

Despite this apparent lack of interest in mineralisation within toadstones nearly sixty instances are given which range from the occurrence of rich, ore-bearing veins to swarms of barren calcite veinlets.

The list does not include instances where one wall only of the vein is in toadstone, owing to faulting. In cases other than those of Farey's list, that cannot be confirmed, where swarms of barren calcite veinlets are noted these have produced strong wall-rock alteration in the toadstones. This distinguishes them from calcite veins present in toadstones which are the product of deuteritic activity, and which show no alteration features. Those mines given in Farey's (1811) list (reprinted in Vol.1, part 7, of the Bulletin, 1962, pp. 38-47) have been located (Fig. 2) and their various 'toadstones' identified in terms of a modern stratigraphic nomenclature. Mineralisation in lavas, dolerites and vents have all been recognised herein.

The stratigraphy of the igneous rocks in the orefield has recently been reviewed (Walters and Ineson, 1980 a & b) and the reader is referred to these accounts for further details of nomenclature and correlation.

At present, the authors do not feel that there is any point in categorising the occurrence into different types, although clearly a partial separation is possible into: (a) adventitious, faulted-in mineralised toadstone; (b) adventitious due to collapse into pipe cavities; (c) replacement of calcitised toadstone; (d) deuteritic mineralisation; and (e) epigenetic, but not part of the Pb-Zn-F-Ba ore suite.

The authors realise that their list is incomplete and would welcome news of further localities.

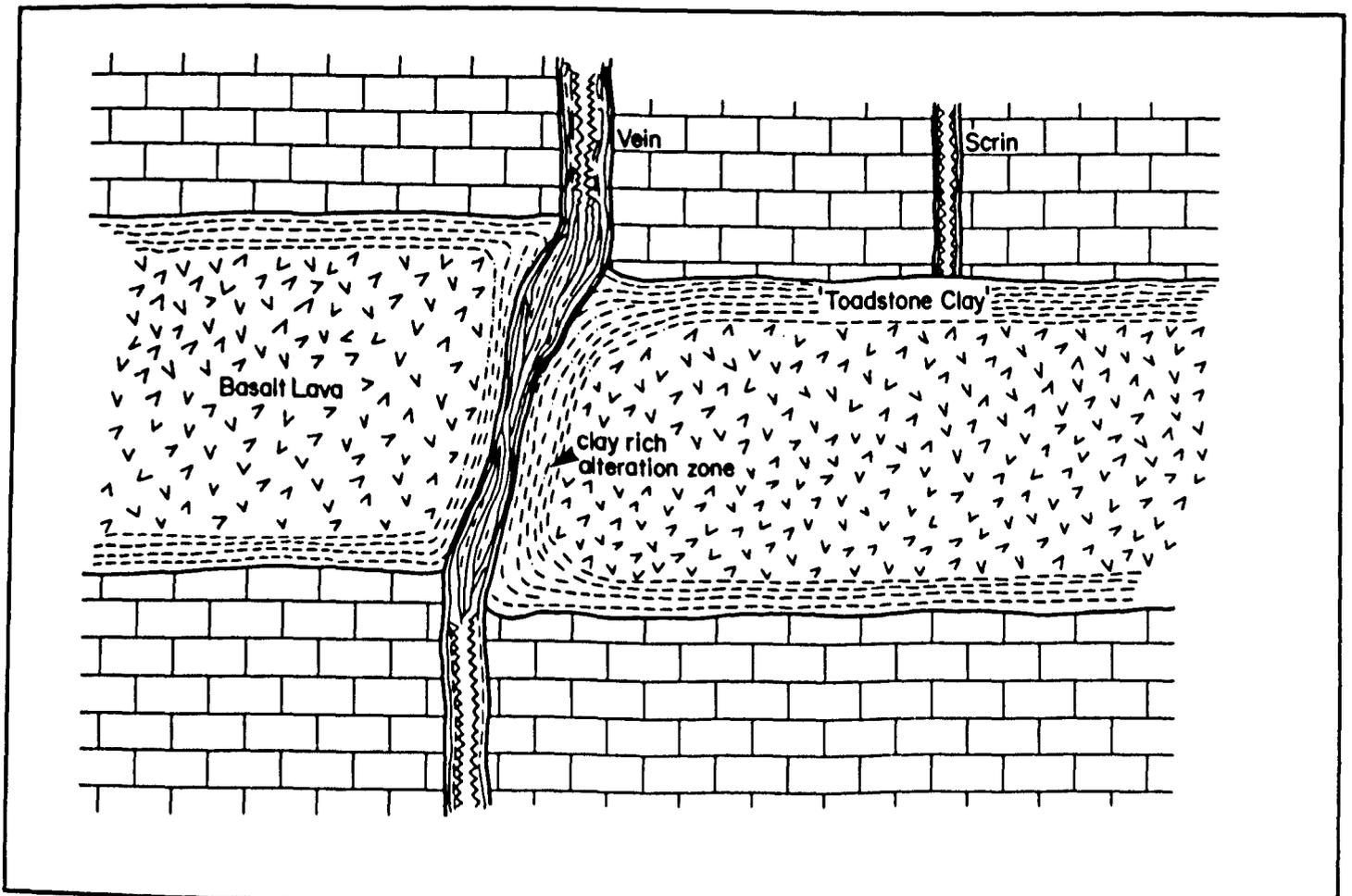


Fig. 1. A typical example of vein - lava relationships.

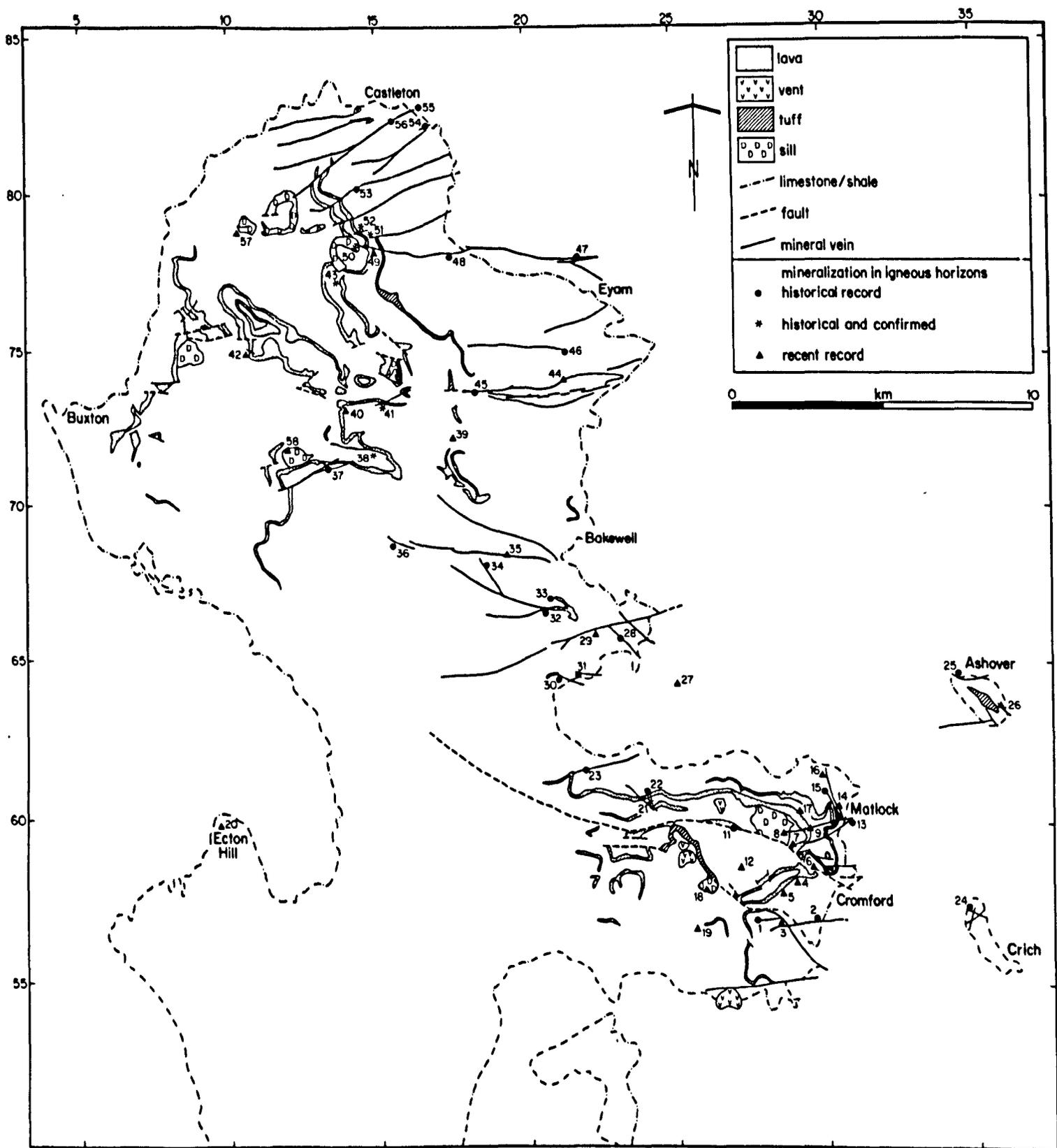


Fig. 2. Mineral localities within the igneous rocks of the South Pennine orefield.

SPECIFIC OCCURRENCES OF MINERALISATION WITHIN IGNEOUS OREBODIES

(Numbers refer to locations given in Fig. 2)

1. Bondog-Hole (or Dog Holes) Middleton by Wirksworth: An E-W rake that crosses Middleton Moor and intersects the Gulph Fault to the north of Middleton. It was an important ore producer in the latter part of the 18th century (Flindall et al., 1973). Bondog Hole Mine is situated at the western end (SK 266.560) and intersects the Matlock Lower Lava, approximately 10 m thick, at a depth of 30 m. Bondog Hole workings in a small rake and associated pipe caverns have been intersected in Middleton Limestone Mine, and both show fallen blocks of the overlying Lower Matlock Lava.
2. Gang Vein: A powerful E-W mineralised fault ranging from Middleton by Wirksworth to Black Rocks, Cromford. Farey (1811) gave no specific indication where the vein carried ore in toadstone. The vein crosses the 'Great Clay'; the clay has been equated with the thin and deeply weathered Matlock Lower Lava (Alsop, 1845). Farey (1811, p.250) however, referred to the "hard 1st toadstone" in the Gang Mine without mentioning clay. It seems likely that as the thickness of the lava will not be in excess of 5 m in this area that even when freshly exposed in a hard state, it would rapidly weather to the 'great clay' lithology, especially adjacent to the vein.
3. Middleton Limestone Mine, Wirksworth: The so-called western extension of the Gang Vein has been intersected and old man's lead workings encountered in a number of places. The limestone workings are in the Hoptonwood Limestones beneath the Lower Matlock Lava, and in places it appears that both walls of this fissure vein are in altered toadstone, much of which has fallen into the old workings giving a spurious effect of toadstone 'in' a vein. Elsewhere in the mine veins have been worked in thick wayboards (1-2 m) along minor faults.
4. Groaning Tor Adit (or Hallicar Wood Sough), Via Gellia: Extension to the adit have recently provided a section in the Matlock Lower Lava and its overlying tuff. Within the coarse, doleritic central portion of the lava occur a number of clay-rich, green, bleached zones associated with calcite veinlets. Tracing thin amygdaloidal horizons across these zones show that they are small mineralised faults with displacements up to 0.4 m. Pyrite is the only other mineral present and no stoping has taken place. These alteration zones lie on the strike of the SW-NE Goodluck Sough veins (Flindall, Hayes and Rieuwerts, 1977).
5. Jacob's Dream Mine: This adit high on the south side of Via Gellia is driven along a scin through a 'wall' of toadstone some 5 m thick, with short workings along the two contacts of the dyke-like toadstone body. In spite of its shape the toadstone mass is a faulted-in slice and the mineralisation is mainly along the contacts with only stringers of calcite in the bleached toadstone.
6. Ball Eye Quarry: High at the back of the quarry a rake vein has been worked for fluor-spar along the line of the Bonsall Fault or one of its branches, in a thick altered toadstone. The vein had a fill with a high content of fluorite and had diffuse calcitic walls in bleached and altered toadstone.
7. Superfine Vein, Bonsall: This locality constitutes the only case recognised to date of mineralisation within a vent. The vein lies on the extrapolation of Coalpit Rake westwards beneath the Matlock Lower Lava. A line of old workings extends across the area of the Ember Lane Vent (Walters and Ineson, 1980) and shaft spoil (SK 283.582) includes blocks of agglomerate. Some of the agglomerate blocks show the replacement of the calcareous matrix and limestone clasts by fluorite and quartz.
8. Great Rake, West of Low Mine: The Great Rake continues into the eastern edge of the Bonsall Sill. It appears that the sill interfingers with the limestone in this region and the vein transgresses one of these leaves. Trenching has exposed the sill at the western end of the Rake and the vein has been worked opencast for a short distance in the dolerite. Blocks of variously bleached and altered dolerite can be found in the opencast walls. In extreme cases it has been converted into an almost white rock consisting of calcite, kaolinite with minor albite, similar to the 'white trap' of the north Pennines.
9. Great Rake, East of Low Mine: On Masson Hill the vein has been worked opencast for a width of 3 m in the upper part of the Matlock Lower Lava. Both vesicular and non-vesicular basalts are exposed and are intensely bleached adjacent to the vein.

10. Porters Mine, Bonsall: Noted by Farey (1811) as being 'in toadstone'. According to Pilkington (1789) the mine was "about 2 miles south of Snitterton", this places it north of Ball Eye Mine. Pilkington (1789) also referred to the "uncommonly strong dip of the measures" which could indicate a position close to the Bonsall Fault Zone, while Watson (1813) placed Porters Shaft to the south of Masson Hill..
11. Salters Way, Brightgate: According to Whitehurst (1778), this was a "fissure, part filled up with toadstone and in part with minerals, etc.". Farey (1811) referred to "chance toadstone beds, and filling fissures?". Whether this represents a true instance of ore within a toadstone is not clear. The mine lay on the Bonsall Fault, west of Bonsall and has also been referred to as Blackstone Shaft (Watson, 1813).
12. Slaley Sough, Via Gellia: This exploratory adit was driven to test veins beneath the Lower Matlock Lava on the north side of the Via Gellia. In its further reaches, the adit was driven along the E-W Parsons Rake. Rises in the vein up into the lava have allowed blocks of lava to fall into the level. These blocks are often strongly altered and veined with calcite which carries minor galena and pyrite in some blocks. This is inferred to represent the continuation of Parsons Rake through the lava.
13. Side Rake, Matlock: A SW-NE vein off the Great Rake in the Riber Mine area yielded ore in toadstone (Matlock Upper Lava) according to Farey (1811).
14. High Tor Rake, Matlock: A NNW-SSE rake that parallels and connects with the Seven Rakes/ Slitt Rake system. High Tor Rake crosses the outcrop of the Matlock Upper Lava below High Tor (SK 296.593) and has been worked in a series of shallow opencasts within the lava.
15. Seven Rakes Mine: 16. Smarts Quarry Borehole, Matlock: Seven Rakes is one of the most widely quoted and best documented cases of the occurrence of ore in toadstone. Workings at Seven Rakes Mine in toadstone were referred to by Pilkington (1803), Farey (1811) and Watson (1813), who also noted ore in toadstone at Dickey Mine on the Seven Rakes further south. De Villiers et al. (1826) gave an account of a visit to Seven Rakes Mine to examine the workings in toadstone.
- At its northern end, the vein was intersected within the Matlock Upper Lavas by an inclined borehole in 1957, at Smarts Quarry (Smith et al., 1967). Mineralisation was present as a 20 cm thick vein containing galena, zinc blende, fluorite, calcite and pyrite.
17. Masson Opencast: The complex system of fluorspar replacement pipes and flats is in dolomitised Lower Matlock Limestones resting on the Lower Matlock Lava. These limestones carry several clay-wayboards which are variably mineralised with fluorite, or which merge into the replacement ore so as to lose their identity.
18. Ible Sill, Via Gellia: A shaft was sunk in the floor of the old dolerite quarry in the 1920's following leads of thin calcite and quartz stringers alleged to carry gold. Samples have revealed only chalcopyrite.
19. Golconda Mine, Brassington: A thick clay wayboard in the roof of a stope near the start of the northeast decline carried large numbers of euhedral calcite scalenohedra, which appear to have grown freely in the altered tuff.
20. Salt's Level, Ecton: A thin steeply dipping clay wayboard (altered tuff) about 5 cm thick carries galena and calcite crystals in the clay near the end of the level.
21. Whitelow Rake, Winster: A NW-SE vein that crosses the outcrop of the Matlock Lower Lava. Ore was worked in the toadstone (Green et al., 1887). The vein has been opencast within the lava in recent years (Butcher, 1976).
22. Mossey Meer Mine, Winster: Situated on one of the series of veins parallel and to the east of the Whitelow Rake that also cross the outcrop of the Matlock Lower Lava. These veins are also known as the Lickpenny Veins (Green et al., 1887).
23. Old Isaacs Venture, Elton: Situated on the Raithe Rake portion of the Coast Rake east of Gratton Dale. It yielded ore in lava (Matlock Lower Lava) according to Farey (1811).
24. Wakebridge Mine, Crich: Stopping for lead in lava (probably, the Matlock Lower Lava) was described by Bemrose (1894). He noted that the ore was "as good as that in the limestone" and gave a brief description of the alteration of the lava adjacent to the vein.

25. Westedge, Ashover: In a strong E-W mineralised fault which bounds the northeast side of the inlier. Lead ore occurred in toadstone (Farey, 1811) which is inferred to be the northern continuation of the Ashover Tuff and associated lava flows.
26. Fall Hill, Ashover: A large fluorspar ore-body has been worked in the limestone overlying the Ashover tuff, along a NW-SE rake. Replacement 'wings' extend into the limestones on each side, and recently one has been worked in the highly altered upper part of the tuff, which may have been very calcareous before mineralisation.
27. Mill Close Mine: The occurrence of ore in toadstone at the 'boil up' has already been mentioned. Traill (1939, p.866) whilst noting that open fissures were much less common in toadstone than limestone nevertheless asserted that at Millclose "... several instances have been found where the existence of an open channel on a fault (in toadstone) has permitted ore solutions to rise from below a bed of toadstone to a higher horizon".
28. Wheels Rake, Alport: This is one of the major NW-SE veins of the Alport mining area. Watson (1811) noted Wheels Rake as "very productive" in toadstone (the Conksbury Bridge/Upper Alport Lava). This rich vein appears to be that discovered in 1786 in toadstone, at the forefield of Wheels Rake Old Sough (Kirkham, 1964). As the sough was driven along Wheels Rake, the vein in the forefield probably equates with one of the NE-SW cross veins in the Baltic Wood area. Although the sough was eventually driven in toadstone to the Long Rake, it is improbable that this was the rich vein mentioned as the sough was still being driven after 1786. Kirkham (1964) also included a section (dated 1836) which depicts the Amos Cross branch of Wheels Rake persisting through the lava into the underlying limestones.
29. Long Rake, Conksbury: Recent exploratory boreholes sunk in connection with the opencast workings around Conksbury have intersected the Long Rake within the Conksbury Bridge Lava. The vein comprised two zones of intense bleaching and calcitisation which show evidence of poly-phase movement and shearing.
30. Nick Sough, Youlgreave: Noted by Farey (1811) as "in toadstone". Nick Sough was driven along the NW-SE Nick Vein from Bradford Dale. The sough tail is situated on the outcrop of the Bradford Dale/Lathkill Lodge Lava.
31. Black Shale Pits, Youlgreave: Another mine "in toadstone" from Farey's (1811) list. It is located on a WNW-ESE vein close to Nick Vein and the toadstone referred to is likely also to be the Lathkill Lodge Lava.
32. Dale, Over Haddon: The Lathkill Dale Vein Sough, being driven in 1743 (Rieuwerts, 1973) passed beneath the river at Lathkill Lodge. The sough was initially in the Lathkill Lodge Lava and followed the vein in this lava for a short distance.
33. Robinstye Flat Work, Over Haddon: Probably situated to the north of Lathkill Dale Sough tail (Rieuwerts, 1973). Ore occurred in the Lathkill Lodge Lava (Farey, 1811).
34. Warm Bath, Sheldon: A NW-SE rake branching from Mandale Rake, north of Lathkill Dale, and trending towards the Magpie Mine area. According to Watson (1811) this was a particularly rich vein and in a section he depicted the vein descending into the upper part of the toadstone. Farey (1811) also noted the vein as carrying ore in toadstone. In the Magpie area the vein transgresses the ground underlain by the Shacklow Wood Lava and it is probable that this is the toadstone referred to by Watson and Farey.
35. Mogshaw Rake, Sheldon: Recent borehole information has supported the statement that major faults are often mineralised within lavas. Mogshaw Rake has been intersected in the Shacklow Wood Lava. It is represented by a zone of intense bleaching and calcitisation. Vuggy veinlets carry calcite and green fluorite together with minor amounts of marcasite, pyrite and chalcopyrite.
36. High Low Pipe, Sheldon: Noted by Farey as "in toadstone" the western end of this WNW-ESE rake is underlain by the Upper Millers Dale Lava. For the mine to have intersected this horizon it would have to have exceeded a depth of 200 m.
37. Wham Rake, Taddington: The NW-SE Wham and Grove Rakes intersect and displace the outcrop of the Millers Dale Upper Lava. Lines of hillocks cross the lava outcrop suggesting the veins were worked in this horizon. Farey (1811) also noted their continuation into toadstone.

38. Horse Steads Mine, Taddington: An E-W vein, that transgresses the outcrop of the Upper Millers Dale Lava at Horse Steads Mine (SK 143.716). Farey (1811) noted the presence of a lower toadstone (Lower Millers Dale Lava) and that the vein was followed down through both these lava horizons.

39. Putwell Hill Mine, Monsal Dale: Once worked for lead, this vein was extensively worked for calcite in the 1920's and the lowest workings, in the Monsal Dale Limestones, worked down into the top of an underlying toadstone, without substantial change in the vein.

40. Basalt Quarry, Millers Dale: In a small quarry above Millers Dale (SK 134.731) an E-W zone of alteration is exposed within part of a coarse non-vesicular, central flow unit of the Upper Millers Dale Lava. The alteration zone is 1.0 m wide and is associated with a swarm of calcitic veinlets with a central, thicker vein with vuggy dog-tooth calcite and pyrite.

41. Maury Mine, Millers Dale: This locality is one of the few mines from Farey's list that is accessible and provides an excellent example of the nature of the continuation of a rake vein in toadstone. Maury vein can be observed in limestone beneath the disused railway track where it is a single thick vein with sharply defined walls, slickensided in places. Columnar calcite is the main fill.

Above the railway track an excavated entrance (SK 150.731) allows access into a section of adit where the vein can be observed in the Upper Millers Dale Lava. Within the lava the rake continues as a swarm of thin calcite and quartz veinlets. These are associated with a well-defined zone, up to 3 m wide, of intense bleaching and argillisation which has a central zone of almost white, kaolinite-rich clay alteration produced in the most intense area of leaching. Some 60 m of adit are currently accessible but over this distance the veinlets have not been observed to carry lead or zinc mineralisation. However, the dumps yield abundant blocks of mineralised and altered lava. Sphalerite and smithsonite predominate with lesser amounts of galena, pyrite and bravoite.

42. Calcite Vein, Tunstead: A 4.9 m wide calcite vein is exposed near Tunstead Quarry (SK 104.748) within the Lower Millers Dale Lava. The vein comprises a number of closely spaced columnar calcite-filled veinlets separated by a thin and highly altered segment of lava. There is a bleached and altered zone developed in the lava adjacent to this set of veins. Disturbed ground suggests that the vein was investigated by the old lead miners; however no ore minerals were observed in the present exposure.

43. Edge Rake, Wheston: This E-W vein transgresses and displaces the outcrop of the Upper Millers Dale Lava. Surface spoil contain blocks of bleached and mineralised lava and support Farey's (1811) statement that ore was worked in toadstone.

44. Sallet Hole Mine, Coombs Dale: This modern mine driven into High Rake and its branches beneath Longstone Edge, has confirmed William Wager's early 19th century reports of a vein in toadstone. The vein, carrying mainly fluorspar, has been stoped out in both limestone and toadstone, in some cases showing little change in its character even when both walls of the fissure were in toadstone, here a bedded tuff carrying much dispersed pyrite, and subordinate amounts of other sulphides such as bravoite, chalcopyrite, etc.

45. Robin Wash, Longstone: Situated in Hay Dale on the western end of the Longstone Edge vein system (SK 180.732), this locality was referred to by Farey (1811) as "in the 1st toadstone". The complex volcanic stratigraphy of this area is far from clear but Robin Wash may be part of the lava exposed at the foot of Cressbrookdale. This lies at the same stratigraphic horizon as the Upper Millers Dale Lava, but appears to be unrelated to it with an extrusive centre in the Longstone Edge area.

46. High Field, Stoney Middleton: Situated at the eastern end of the White Rake (Wardlow) vein. Farey (1811) noted High Field Sough as driven from Coombs Dale and intersecting toadstone. Which toadstone this refers to is uncertain. The area is underlain by the Cressbrook Dale Lava, but the toadstone may be the northern extension of a tuff horizon located above the horizon of Cressbrook Dale Lava in the Longstone Edge area.

47. Ladywash Mine, Eyam: According to Farey (1811) ore was worked, from the continuation of the powerful Hucklow Edge vein into the top of the Cressbrookdale Lava. Modern workings have confirmed this, as parts of the vein have been stoped with both walls in lava.

48. High Rake Mine, Hucklow: This constitutes one of the most thoroughly documented cases of the occurrence of exploitable mineralisation in toadstone on part of the Hucklow Edge/White Rake mineralised fault system. Three main periods of working in the toadstone can be recognised around 1757, 1784 and 1834 (Rieuwerts, 1964). Only the earliest episodes in 1757

and 1784 could have been noted by Farey (1811). As early as 1757 toadstone had been penetrated to the remarkable depth of 49 fathoms (89.6 m) giving a total depth to the shaft of 96 fathoms (175.6 m). Plans (Bagshawe Collection No. 587/18 in Sheffield City Library) from the second period of working clearly state that payable ore was located at a depth of 62 m in the toadstone and the vein could be traced even deeper in the toadstone to a depth of 74.9 m as a thick 'barren spar vein'. A further, parallel, vein was discovered north of the main vein toadstone but this was uneconomic to work.

The High Rake Mining Company was formed in 1834 with the express intention of bottoming the toadstone. In 1846 the shaft foot was standing at a depth of 98.8 m in toadstone. Borings from the shaft bottom to an unknown depth also failed to locate limestone and the attempt was finally abandoned as a financial disaster in 1852. During this period the vein was stoped in the uppermost 55 m of the toadstone to the east of the engine shaft (Bagshawe Collection 203).

The minimum thickness of 100 m for the toadstone in High Rake Mine is exceptional, the most likely explanation being that the Cressbrookdale Lava had been intruded by a thick dolerite sill at this locality.

49. White Rake Opencast, Tideslow: Recent opencast workings on the western end of the Hucklow Edge vein system has exploited a fluorite-rich portion of the vein where the Upper and Lower Millers Dale Lavas have been juxtaposed by faulting. The vein also contains calcite, marcasite and galena with secondary goethite, pyromorphite and cerussite. The geology of this locality and localities 50, 51 and 52 have been described in detail by Walters (1980).
50. Black Hillock Mine, Tideslow: The White Rake, at its western extremity, continued into the outcrop of the Potluck Sill as far as Black Hillock shaft (SK 141.783). The vein was traced to a depth of some 80 fathoms (146.3 m) within the dolerite. The interaction of mineralisation on the dolerite produced a highly altered white rock consisting of kaolinite and calcite with albite.
51. Chapmaiden Mine, Tideslow: Situated on Maiden Rake to the north of White Rake opencast (SK 147.784). Blocks of altered toadstone with veins of calcite-fluorite-galena-baryte are common on the dumps. The geology of the area is complicated by the 'chance toadstone beds' of Farey (1811).
52. Calvestones, Tideslow: A small parallel rake north of Chapmaiden Mine (Whitehurst, 1778). This was also mentioned by Watson (1811) as 'very productive' in toadstone. The rake transgresses the outcrop of the Upper Millers Dale Lava and at its western end there is a much overgrown opencast in the lava.
53. Rake Head Mine, Bradwell Moor: This lies on Moss Rake (SK 143.800) and both the Upper and Lower Millers Dale Lavas are present. Ore was found both in and under the toadstone (Green et al., 1887).
54. Nunleys (Nunlowend) Mine, Castleton: This is situated on the eastern end of Long Rake, to the west of Hope Cement Works. Faujas de St. Fond (1799), in describing a visit to Nunleys Mine, noted the continuation of the rake into 'channel'. This 'channel' is the Pindale Tuff formerly exposed in the Hope Cement Quarry. The vein carried some ore in the tuff but was apparently uneconomic to exploit. The mine was also visited by De Villiers et al. (1826).
55. Ashton's (Pindale) Mine, Castleton: Ashton's Mine (SK 163.825) exploited the eastern extremity of the Dirlow Rake System beneath the Namurian shale cover. According to Green et al. (1887) a "greenish variety of toadstone was found to underlie the shale, without any limestone intervening". The rake could be traced in the toadstone as a network of veinlets that carried small quantities of galena.
56. Dirlow Mine, Castleton: Situated further west on Dirlow Rake north of Pindale (SK 175.822), Dirlow Mine extracted ore within the Pindale Tuff, some 22 m thick at this locality (Green et al., 1887).
57. Vein near Blacklane Farm, Peak Forest: An E-W vein can be traced as a line of disturbed ground and old hillocks into an isolated outcrop of the Peak Forest Sill. In the spoil heaps blocks of bleached dolerite, often strongly veined and brecciated occur together with columnar calcite and minor amounts of galena. This suggests that the vein was exploited within the dolerite.
58. 'Calton Hill Type' Mineralisation: This occurrence of mineralisation differs from all the previous recorded instances in that it cannot be related to a continuation of vein type mineralisation in toadstones. In its classic development - the lava, intrusive dolerite and vent complex at Calton Hill large vugs in unaltered basalt and dolerites are lined with well crystallised quartz, often of amethystine colour. Calcite and baryte occur as overgrowth on this quartz lining. Pyrite and haematite are the only associated metallic minerals. A zonal distribution

of quartz/calcite/baryte infills was at one time evident (Mueller, 1954; Ford, 1967) and suggested a close genetic relationship between the site of the extrusive vent and subsequent silica-rich hydrothermal activity. During the present survey an additional occurrence of this type of mineralisation has been noted from vugs within coarse, non-vesicular basalt of the Upper Millers Dale Lava in a small quarry above Millers Dale (SK 134.730). This occurrence cannot be directly related to the proximity of a vent.

ACKNOWLEDGEMENTS

The authors would like to thank the staff of Sheffield City Library and the Derbyshire Record Office, Matlock, for their help in consulting collections of mining manuscripts, and Mr. J. Rieuwerts for information concerning the location of many of the mines in the list. Dr. N.J.D. Butcher of Dresser Minerals kindly allowed the examination of borehole material, Miss P. Mellor typed the manuscript, and Mr. M. Cooper produced the diagrams. Particular thanks are extended to Dr. T.D. Ford for advising on field localities as well as critically reading and commenting on the manuscript.

REFERENCES

- Alsop, J., 1845. *On the Toadstones of Derbyshire*. Rep. Brit. Assn. for 1844, Section C, pp. 51-52.
- Arnold-Bemrose, H.H., 1894. *Notes on a Visit to Crich Hill and Wakebridge Lead Mines*. Derbys. Arch Journal, Vol.16, pp.41-51.
- Butcher, N.J.D., 1976. *Some Aspects of Structure and Fluorite Mineralisation in the Southern Pennine Orefield*. Unpublished Ph.D. Thesis, University of Leicester.
- De Villiers, Dufrenoy, and Elie de Beaumont, 1826. *Sur les Mines de Plomb du Cumberland et du Derbyshire*. Ann. des Mines, Vol.12, pp. 339-432.
- Farey, J., 1811. *A General View of the Agriculture and Minerals of Derbyshire*. Vol. 1, 532 pp.
- Faujas de St. Fond, B., 1797. *Voyage en Angleterre avec le description Mineralogique des montagnes de Derbyshire*. Paris. English translation 1799 (Derbys., Vol.11, p.264).
- Firman, R.J. and Bagshawe, G., 1974. *A Re-Appraisal of the Control of Non-Metallic Gangue Mineral Distribution in Derbyshire*. Mercian Geol., Vol.5, pp. 145-161.
- Flindall, R. and Hayes, A., 1973. *The Mines East of Hoptonwood Quarries, Via Gellia*. Bull. Peak Dist. Mines Hist. Soc., Vol. 5, pp. 137-48.
- Flindall, R., Hayes, A. and Rieuwerts, J., 1977. *Mines in the Slingtor Wood Area, Cromford*. Bull. Peak Dist. Mines Hist. Soc., Vol. 6, pp. 263-279.
- Ford, T.D., 1967. *Some Mineral Deposits of the Carboniferous Limestone of Derbyshire*. In: Geological Excursions in the Sheffield Region and the Peak National Park. Ed. R. Neves and C. Downie, University of Sheffield, pp. 53-75.
- Ford, T.D. (Ed.), 1977. *Limestones and Caves of the Peak District*. Geo. Abstracts, Norwich, 469 pp.
- Garnett, C.S. 1923. *The Toadstone clays of Derbyshire*. Miner. Mag. Vol.20.pp.151-7.
- Green, A.H., Le Neve Foster, C. and Dakyns, J.R., 1887. *The Geology of the Carboniferous Limestone, Yoredale Rocks and Millstone Grit of North Derbyshire*. Mem. geol. Surv. Gt. Br., 2nd Ed.
- Kirkham, N., 1964. *Wheels Rake, Alport by Youlgreave*. Bull. Peak Dist. Mines Hist. Soc., Vol. 2, pp. 153-173.
- Mueller, G., 1954. *Enclosures in gangue minerals*. Mining Mag., Vol.90, pp. 148-154 & 208-217.
- Pilkington, J., 1789. *A view of the Present State of Derbyshire*. Vol.1, 469 pp.
- Rieuwerts, J., 1964. *Notes on the High Rake Lead Mine, Windmill*. Bull. Peak Dist. Mines Hist. Soc., Vol.2, pp. 175-78.

- Rieuwert, J., 1973. *Lathkill Dale: Its Mines and Miners*. Moorland Publishing Company, 100 pp.
- Smith, E.G., Rhys, G.H. and Eden, R.A., 1967. *Geology of the Country around Chesterfield, Matlock and Mansfield*. Mem. Geol. Surv. Gt Br., 430 pp.
- Trill, J.G., 1939. *The Geology and Development of Millclose Mine, Derbyshire*. Econ. Geol., Vol.34, pp. 851-89.
- Walters, S.G., 1980. *The Geology of Black Hillock or Clear-the-Way Mine, Tideslow Moor*. Bull. Peak Dist. Mines Hist. Soc., Vol. 7, pp.
- Walters, S.G. and Ineson, P.R., 1980a. *A Review of the Correlation of Igneous Rocks in the South Pennine Orefield (Pt.1. - The Matlock Wirksworth Area, including Ashover and Crich)*. Mercian Geol. (in press).
- Walters, S.G. and Ineson, P.R., 1980b. *A Review of the Correlation of Igneous Rocks in the South Pennine Orefield (Pt. 2 - The Alport-Bakewell-Taddington Dale Area)*. Mercian Geol., (in press).
- Watson, W., 1811. *A Delineation of the Strata of Derbyshire Forming the Surface from Bolsover in the East to Buxton in the West*. Sheffield, 76 pp.
- Watson, W., 1813. *A Section of the Strata Forming the Surface in the Vicinity of Matlock Bath in Derbyshire*. Chesterfield, 19 pp.
- Whitehurst, J., 1778. *An Enquiry into the Original State and Formation of the Earth with Observations on the Strata in Derbyshire*. London.

S.G. Walters and P.R. Ineson,
 Department of Geology,
 University of Sheffield,
 Mappin Street,
 Sheffield,
 S1 3JD

A WIRKSWORTH MINE AGENT'S LETTER
contributed by G. Darnborough

Worksworth December 3d. 1678

Sir

I have yos of ye 30th. last past & note ye contents . It was ye wantt of water in Trent yt hindered our lead geting to ye market in due time . This neither you nor I could helpe & as for Sir Jo . Curzons 500£ . bill you know I hinted to you 700£ . I was to him but brought it to 500£ . & further Sir John had hopes till last weeke that he should have hadd money otherwares in London to pay Sir Ro . Carr . It was promised him but ye party faild otherwares . He had made noe use of my bill . I recd but 100£ . of him till now . I have sent up ye bill & most of ye money is yet behind but I may have it on demand . Sir John is a honest person & my good friend . & I am sorry you are straitened to pay that bill . I have today bought 10 p of lead at bawtry at 9£ . 10s . for a sow & 20 p fr mills at 9£ . per sow & intend to mark it on our partible account & shall buy more as you shall give encorragment . I perceive that state affairs are now at a great height . I hope in God a good issue will be to those high & wicked designs , if the people of this nation walk humbly & uprightly & ply ye thorne of grace with fervent prayer . In some haste I rest

Yr loving & obliged friend

Robt . Hayward

I have **NH** almost ready but do not perfect it till have an account from Hull which I hope will come shortly to me .

Appendix

10



THE GEOLOGY OF HALLICAR WOOD ADIT, VIA GELLIA

by S.G. Walters and P.R. Ineson

ABSTRACT

Situated at SK.2830.5722, Hallicar Wood Adit is some 400 m long. It exposes strata which ranges from above the Matlock Upper Lava, through the Matlock Group (Brigantian) limestones into the Matlock Lower Lava. The clay wayboards, scrins, dolomitised wallrocks and mineralisation exposed in this unsuccessful trial are described.

INTRODUCTION

Hallicar Wood Adit (SK.2830.5722) gives access to approximately 400 m of adit workings on the south side of the Via Gellia to the west of Cromford. It was termed the Hallicar Wood Sough by Flindall et al. (1977) who reported a survey of the then accessible passages. Smith and Ford (1971) briefly described the same locality and called it Groaning Tor Adit. The present authors dispute both names for there is a Groaning Tor Vein on Bar-master's plans to the west of the workings described in this article, and an adit is not indicated. Likewise there is no evidence for the level acting as, or being driven with, the specific purpose of dewatering mineral workings, i.e. a sough. The authors therefore propose the geographical location name in that it does not imply specific connotations.

The adit exposes a 55 m sequence of the Matlock Group (Brigantian) limestones above the horizon of the Matlock Upper Lava. Recent extensions have also provided a section of the Matlock Lower Lava.

GEOLOGY AND MINERALISATION

The initial 150 m of the adit were driven on a NE-SW trending scrin, here termed the 'main scrin'. Other parallel scrins are also seen in cross-cuts and these in turn are cut by a series of SE-NW joints and scrins. The main scrin rarely exceeds 30 cm in width and is usually 10 to 20 cm wide. It illustrates numerous divergent and convergent intersections with dolomitic riders, and where the adit and the main scrin part it is a 2 cm wide calcite veinlet. Evidence for movement along the dislocation in the form of slickensides, is not observed; however, the main scrin displaces cross-courses for up to 0.8 m.

The dominant mineral infill of the main scrin is coarse crystalline calcite with minor amounts of barite and galena. The barite, a pink earth form, occurs either as a pre-calcite phase lining the walls or as stringers in calcite. Galena, where present, is associated with the later phase of barite deposition. As no evidence for the extraction of galena is observed the prime objective of the adit may have been to test veins at depth.

The numerous cross-courses are shown in Fig. 1. Cross-cuts have been driven on the larger of these while a number have been backfilled and stopes are evident, for example at 12 m from the entrance where the adit has partially collapsed.

In addition to the mineralised scrins there are a number of either open or red clay infilled fissures and enlarged bedding planes. The enlarged bedding planes superficially resemble clay-wayboards; however, the clay infill and the discontinuous nature of the horizons are diagnostic of solution cavities rather than stratabound wayboards. The red clay most probably represents karstic action in the vicinity; it is also located infilling vugs in the main scrin.

Adjacent to the mineralised fractures the wall rocks are heavily dolomitised, and for the initial 150 m of the adit the walls are in dolomitised limestone. However the stratigraphical sequence may be elucidated by the presence of five clay-wayboards exposed in the adit (see Fig. 1). The wayboards may represent either atmospheric dust derived 'fossil soils' that mantle emergent surfaces in the limestone sequence (Walkden, 1974) or represent the degraded distal pyroclastic material related to local basaltic vulcanicity. Wayboard No.4 of Flindall et al. (1977) is 1.2-0.8 m thick and may be equivalent to the Matlock Upper Lava. This view is supported by Dr. N.J.D. Butcher (pers.comm.) who believes that the Matlock Upper Lava 'fronts' in the nearby Ball Eye Quarry, as well as the evidence of Walters and Ineson (1980) who gave a geographical distribution of the lava and Rieuwerts (1980, p.306) from a study of contemporary mining documents. The remaining wayboards are all less than 5 cm thick.

At the divergence of the adit and the main scrien the limestone wall-rocks are massive bedded, pale shelly micrites almost porcellanous in character with poorly defined bedding planes. The adit adopts a 'coffin-level' type profile beyond this locality. Approximately 25 m before the Matlock Lower Lava is intersected a marked change in dip occurs which is clearly defined by No. 1 wayboard. The regional dip of 10-15°/135° changes to one of 40°/135° for the rest of the adit. The contact between the limestones and the lava dips at 50°/135°. This marked change in dip may be due to a local structural feature or some palaeotopographical expression related to the lava. 42 m of Lower Matlock Limestone is exposed between Wayboard No.4 and the Matlock Lower Lava.

The Wayboards cannot be correlated into adjacent areas. Worley and Nash (1977) in describing the Jugholes Caves noted that of the six wayboards in the Lower Matlock Limestones only two are laterally persistent. Dunham (1954) and Smith et al. (1967) attempted to erect regionally applicable composite sequences in terms of wayboard stratigraphy; this, it is concluded, cannot, with the evidence available, be undertaken. The 42 m succession of the Lower Matlock Limestones compares with 35 m of beds recorded in boreholes to the north of Ball Eye Quarry, 40 m in Oxclose Mine Shaft and a maximum of 54 m in boreholes at Cawdor Quarry. The limestones thin to the west for they are 28 m thick in the Tearsall area and 24.4 m thick in borholes on Bonsall Moor.

Following Findall et al. (op.cit.) publication, the collapse which blocked the adit at the limestone-lava junction, has been cleared and provided access to over 40 m of workings which exposed the Matlock Lower Lava and an overlying tuff. The tuff (3.5 m thick) is equivalent to the iron-stained clay-rich horizon seen above the lava in Bonsall Basalt Quarry (SK.283.574). Pyrite in the overlying limestones and upper surface of the tuff has weathered and produced a 10 cm thick orange clay which passes into a grey clay and then the typical pale green 'toadstone clay'. Unlike weathered surface exposures, this tuff has not been decalcified and has remained compact and coherent. It grades into a coarse tuff with included blocks and fragments of amygdaloidal basalt and limestone clasts (often > 10cm in diameter) the whole set in a fine-grained clay matrix. Graded bedding is developed towards the base where the overall grain size is coarser but the large basalt and limestone fragments are less frequent in number. The tuff overlies a 0.4 m thick fine grained chocolate-brown clay (the 'Brown Bed' of the present contribution) the uneven base of which rests on weathered vesicular lava. Fragments of the lava are included in the base of the 'clay horizon', which in appearance is similar to the columnar clay beneath the Tideswell Sill and considered to be a volcanic mudflow. A petrographic examination of the clay indicates small limestone clasts (> 85%) basaltic pyroclastic fragments (5%) and organic debris set in a sparry calcite matrix. Visually it is identical with material infilling the Ember Lane Vent, south of Low Mine (SK.284.586). The strong iron-oxide coatings, marked rounding of the clasts and preponderance of country rock fragments suggests that the material represents a pyroclastic explosion breccia associated with strong degassing.

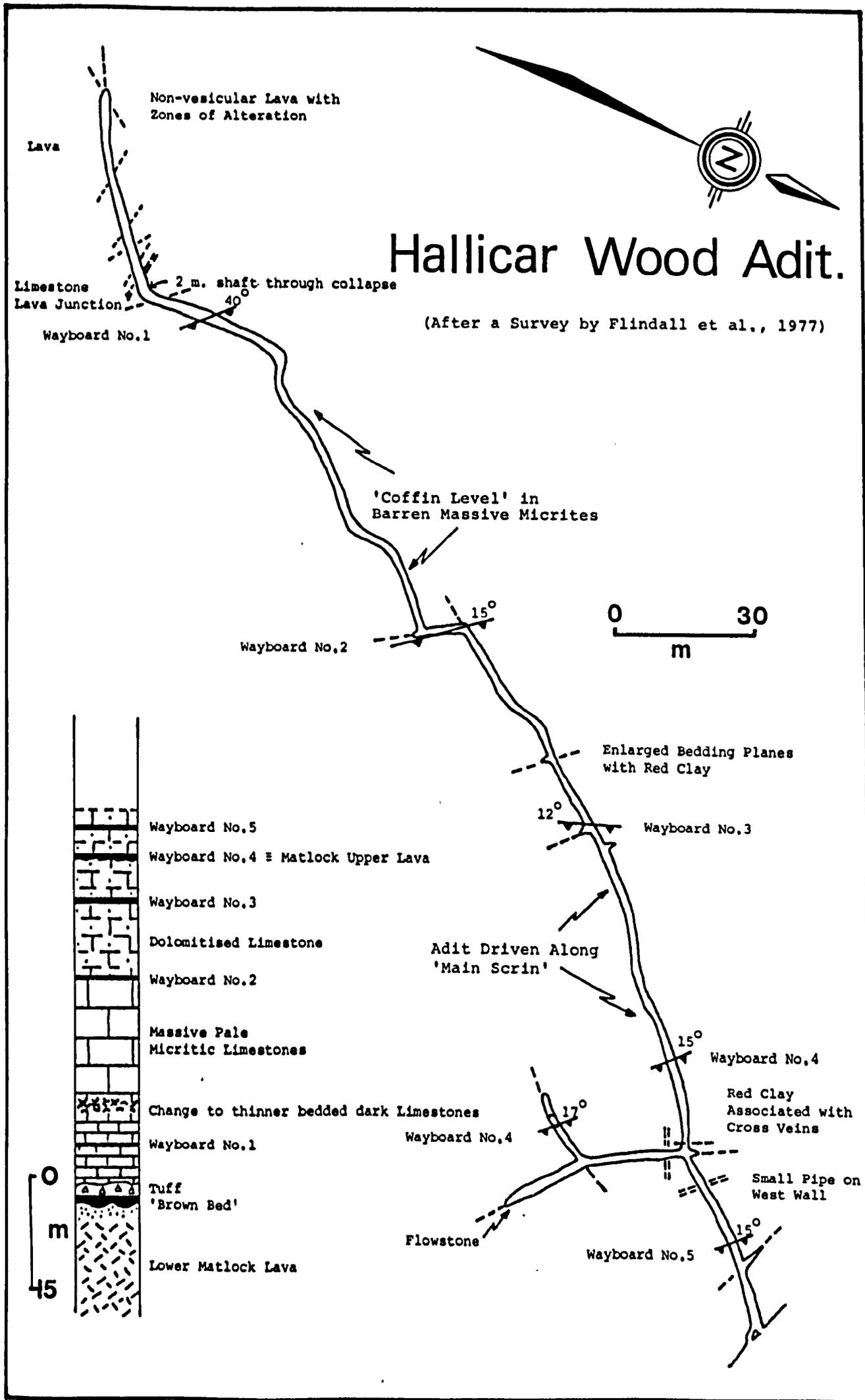
A highly vesicular 1.5 m horizon overlies a non-vesicular, coarse holocrystalline basalt of which 20 m are exposed. As vesicular units are rarely seen, it would imply that the whole succession represents a single flow comparable with exposures in Bonsall Basalt Quarry. In contrast with the hard black lava, the adit is intersected by a number of pale-green clay-rich alteration zones associated with numerous calcite veinlets. The larger alteration zones (> 1.0 m thick) indicated on Fig. 1, trend NE-SW, have a vertical displacement of up to 0.4 m, and as they lie on the projection of the Goodluck Sough Veins to the east most probably represent the peripheral mineral influx, i.e. calcite. As the adit forefield terminates in an intense zone of alteration (where a vein coincides with the line of the adit) it proves that this mining venture did not penetrate the Matlock Lower Lava and was therefore unsuccessful as a trial of veins at depth.

ACKNOWLEDGEMENTS

The authors in particular thank Mr. H.A. Armstrong for his assistance with the underground mapping and collecting in adverse conditions. To the unknown persons who excavated the collapse (? Tony Stubbins and friends) we extend our appreciation.

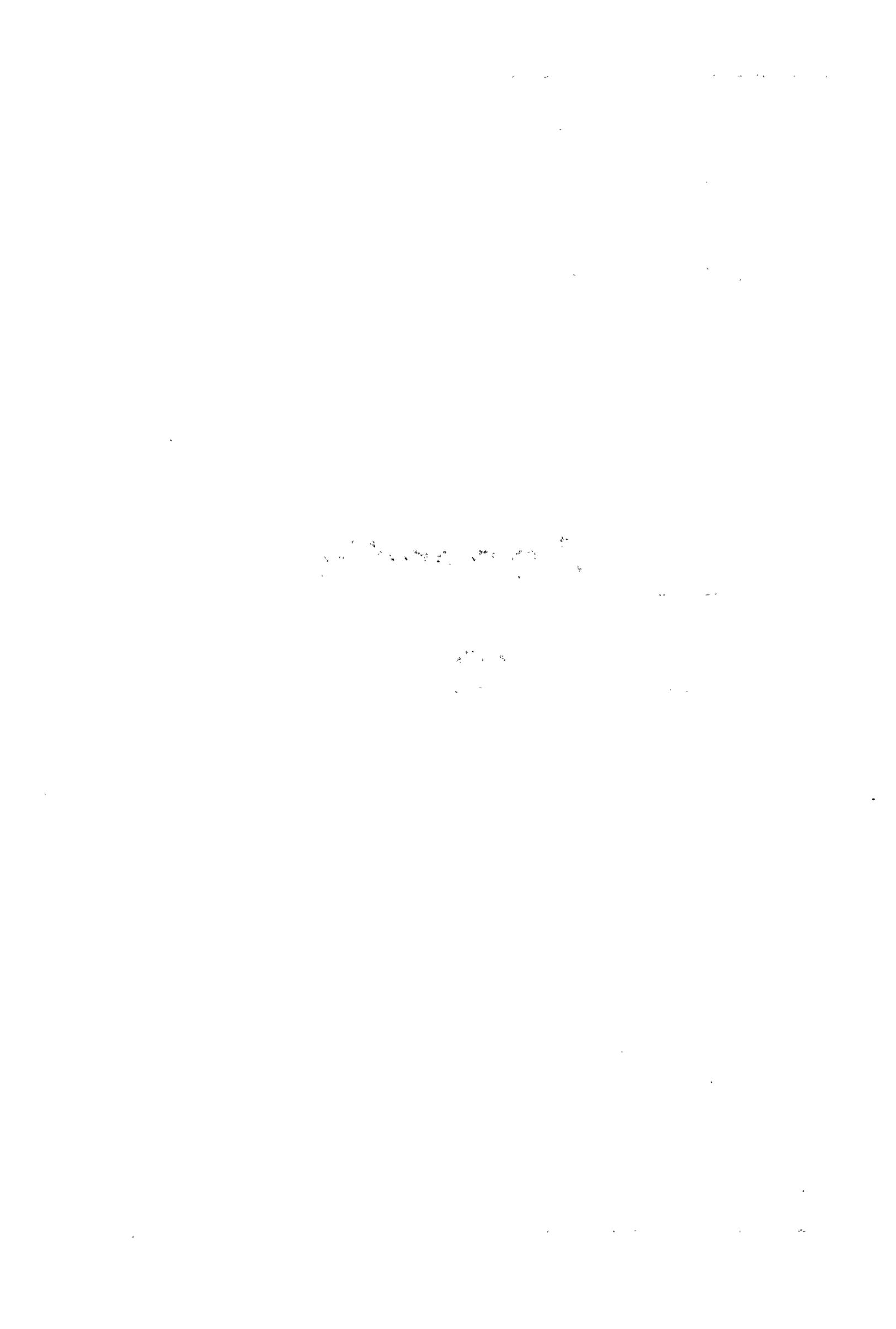
REFERENCES

- Dunham, K.C. 1952. Fluorspar. 4th Edit. Mem. geol. Surv., Spec. Rep. Miner. Resour. Gt. Br. 143 pp.
- Flindall, R.B., Hayes, A.J. and Rieuwerts, J.H. 1977. Mines in the Slingtor Wood Area, Cromford. Bull. Peak Dist. Mines Hist. Soc., Vol.6, pp.263-279.
- Rieuwerts, J.H. 1980. The earliest lead mine soughs in Derbyshire. Bull. Peak Dist. Mines Hist. Soc., Vol.6, pp.241-314.
- Smith, A.D. and Ford, T.D. 1971. Some adits in the Via Gellia. Bull. Peak Dist. Mines Hist. Soc., Vol.4, pp.378-383.
- Smith, E.G., Rhys, G.H. and Eden, R.A. 1967. Geology of the country around Chesterfield, Matlock and Mansfield. Mem. geol. Surv. Gt. Br. 430 pp. + vii.
- Walkden, G.M. 1974. Paleokarstic surfaces in Upper Viséan (Carboniferous) Limestones of the Derbyshire Block, England. J. Sedim. Petrol., 44, pp.1232-1247.
- Walters, S.G. and Ineson, P.R. 1980. A review of the correlation of igneous rocks in the Derbyshire area (Pt. 1 - The Matlock-Wirksworth area including Ashover and Crich). Mercian Geol., Vol.8, (in press)
- Worley, N.E. and Nash, D.A. 1977. The geological evolution of the Jugholes Caves, Matlock, Derbyshire. Trans. British Cave Research Assoc., Vol.4, pp.389-401.



Appendix

12



A REVIEW OF THE DISTRIBUTION AND CORRELATION OF IGNEOUS ROCKS
IN DERBYSHIRE, ENGLAND

by

S.G. Walters and P.R. Ineson

Summary

The classical work on the igneous horizons in Derbyshire was published by Bemrose in 1894 and 1907. Although many of Bemrose's localities have long since been obscured, recent exploratory drilling, mining, opencast work and temporary exposures have provided additional details. The county is subdivided into four geographical regions, the Matlock - Wirksworth, Alport - Bakewell - Taddington Dale, Castleton - Buxton - Tideswell and the Eyam - Longstone - Litton regions.

The geographical distribution and thickness variations as well as the stratigraphical horizon of the sills, lavas/tuffs, wayboards, dykes and vents are described and illustrated in detail. The sills include those at Bonsall, Ible, Waterswallows, Peak Forest, Potluck and Mount Pleasant. Dykes are recorded at Buxton Bridge and in Great Rocks Dale. Grangemill, Ember Lane, Bonsall Moor, Calton Hill, Ditch Cliff and the Speedwell Littoral Cone are examples of previously evoked vent structures. Some of the extensive tuff horizons are located at Shothouse Spring, Ravensdale, Dove Holes, Pindale, Litton and Longstone Edge. In Derbyshire, four lavas are well known, the Matlock Upper and Lower, and the Miller's Dale Upper and Lower Lavas of the Matlock - Wirksworth and Castleton - Buxton - Tideswell regions respectively. However, a number of additional horizons are exposed or have been encountered in mines and boreholes. Included in this group are the Winster Moor, Alport Upper (Conksbury Bridge and Lathkill Lodge), Alport Lower (Bradford Dale), Shacklow Wood, Lees Bottom, Millclose, Cave Dale, Cressbrook Dale and Cressbrook Mill Lavas.

This review, based on previous publications, recent borehole information and present day field observations, includes correlation tables for the above mentioned igneous horizons in Derbyshire.

Nature and Scope of the Review

The Dinantian limestones exposed in the South Pennines contain a varied assemblage of contemporaneous basaltic lava flows, tuff horizons and vents, together with intrusive sills and dykes. In general all the igneous rocks are poorly exposed and especially so in the north between Castleton and Buxton, as well as in the east between Bakewell and Wirksworth; only in the Matlock area are reasonable outcrops encountered.

Merclan Geologist, vol.8, no.2,
1981, pp.81-132; 18 text-figs.,
cover and plates 2-4

A number of igneous horizons are known to extend to the east under the Namurian strata, for volcanic products have been recorded (Ramsbottom *et al.*, 1962) from the limestone inliers at Ashover and Crich. Igneous activity has not been noted in the south-western part of the South Pennines, around Dove Dale nor in the Manifold Valley.

Bemrose's publications in 1894 and 1907 have, in general, remained the only systematic account of the igneous activity in the region. He divided the same into two parts, a north-west or Miller's Dale area, and a south-east or Matlock area, which included Ashover and Crich. Within these two areas, Bemrose (1907) recognised two major lava horizons, the Miller's Dale Upper and Lower and the Matlock Upper and Lower Lavas, but noted that the two sets of lavas lay at different stratigraphical horizons. In doing so, he destroyed the concept advocated by Pilkington (1789), Watson (1811, 1813) and Farey (1811), etc. of the continuity of the 'main toadstones' over the whole South Pennine orefield. In addition to these four lavas, he recognised a number of additional volcanic horizons, which he was unable to correlate.

Subsequent to Bemrose's field observations, information on the stratigraphical complexities and subsurface distribution of the various igneous horizons has increased considerably. Individual, but localised publication (Traill (1940), Shirley (1950) and Walters (1980)), together with general compilations (Institute of Geological Sciences sheets (SK26SW, etc.), mining companies borehole data (personal communications) and the authors' field observations, have added to this knowledge. The inter-relationships of Bemrose's 'uncorrelated lavas' can now be elucidated and many have subsurface developments far in excess of his 'main lavas'. In addition, further lava flows have been recognised that have no surface expression. This was exemplified at Millclose Mine by Traill (1940) and Shirley (1950) who recorded seven lava horizons.

The present compilation attempts to synthesise current knowledge on the stratigraphy of the numerous lava and tuff horizons. This has involved a detailed examination of old mining records (Sheffield City Library and Derbyshire Records Office, Matlock) and early literature sources, e.g. Hopkins (1834). These documents contain a wealth of information, with respect to the location and thickness of the igneous horizons, but must be interpreted with due caution. Information from the above has been combined with details from boreholes, often unpublished but given to the authors,* together with observations from recent mining activity, exploration of disused mines and exposures in opencast sites, mines and quarries developed after Bemrose's publications.

The frequency of surface and subsurface exposures, together with borehole information permit the volcanic horizons to be traced and invariably correlated, over distances of up to 10 km. Elsewhere and especially beneath the Namurian cover, information is scarce and correlation more intuitive. Attempts in using K-Ar isotopic age determinations for correlative purposes have not been successful due to the complex post-extrusive hydrothermal events. Fitch, Miller & Williams (1970) and Ineson & Mitchell (1973) report that the material gives consistently younger ages, more probably related to mineralising episodes than the extrusive activity.

At present, thirty distinct lava or tuff horizons can be recognised, the outcrops of which are poorly exposed. They are often marked by an inconspicuous feature or may be traced over 'marshy ground', the upper limit of which is often a spring line. Recourse to auger holes, animal and mine spoil is often necessary in order to trace an outcrop. Only rarely are actual boundaries observed and in the foregoing text and figures all boundaries and outcrops etc. are conjectural unless otherwise stated. A major part of the South Pennines has recently been resurveyed by the Institute of Geological Sciences and the outcrop distributions given in this paper are based on their published maps with modifications arising from borehole data and the authors' field observations.

*The authors were provided with borehole logs and core, etc. on the understanding that no details be released at this stage, other than for the igneous horizons.

Historical Summary

Mining records indicate a varied and often confusing terminology with respect to these deposits. The most common term is 'toadstone' - a word of uncertain derivation (see Ford, 1977). Records also refer to 'blackstone', this may in a number of instances be equated to either the lavas or to bituminous limestones. 'Channel' - a term used in the northern area may likewise be a synonym for toadstone or refer to 'clay alteration products. Occasionally the term 'dunstone' is used for the igneous horizons at outcrop, but more commonly indicates dolomite. Weathered amygdaloidal lava and toadstone-clays (Garnett, 1923) are cited as 'cat dirt', while 'wayboards' may be either tuffaceous clay partings or residual (clastic/insoluble) clay horizons within the stratigraphical sequence (Walkden, 1972). Whitehurst (1778) initially described these rocks and recognised their intrusive igneous origin. In the Matlock area he depicted three toadstone horizons with 'a vent structure' at Grangemill. Faujas de St. Fond (1779) refuted an intrusive origin, regarding them as 'traps' or sedimentary precipitates, after the Neptunists' school of thought.

An extrusive origin was subsequently proposed and advocated by Pilkington (1789), Watson (1811, 1813), Farey (1811) and Hopkins (1834) all of whom considered that Derbyshire had three toadstone horizons. Farey, in particular, placed emphasis on three continuous toadstone horizons; however, in addition, he recognised areas with 'chance beds', that is, localised toadstones, e.g. Mogshaw Mine at Sheldon.

Significant contributions were the Geological Survey Memoirs (Green *et al.*, 1869, 1887) in which the volcanic nature of the deposits was substantiated, but the validity of their persistent nature was questioned.

Without doubt the most authoritative account of the deposits is Bemrose's 1894 and 1907 papers. In his first paper he provided detailed petrographic descriptions of the lavas and tuffs. The diversity of rock types was enumerated by Geikie (1897), who encouraged Bemrose to remap the field relationships, the results of which he published in 1907.

Geographically the igneous rocks are found in four regions: (1) Matlock to Wirksworth; (2) Alport to Bakewell; (3) Castleton to Buxton; (4) Eyam to Longstone Edge. The two main lava groups erected by Bemrose are retained but are further subdivided to include extensive sub-surface developments of igneous material in the Eyam and Bakewell - Alport areas.

1. The Matlock - Wirksworth region including Ashover and Crich

A number of lavas, tuffs, vents and sills occur in the region (text-fig. 1). The Matlock Upper and Lower Lavas predominate in a varied sequence of igneous rocks, and are to be found from Wirksworth in the south to Gratton Dale in the west. The northerly extent of these horizons is in the area of Millclose Mine (Darley Dale) while the eastern boundary cannot be stated due to insufficient information. One or both of the lavas may extend towards Ashover and in part constitute the complex volcanic sequence located beneath the limestone inlier.

The third lava is the Winster Moor Lava. It has a restricted geographical distribution and is confined to the ground between Gratton Dale, Winster and Bonsall Moors and the workings of Millclose Mine. Considerable confusion has arisen due to previous papers failing to report the Lava, or inserting it at an incorrect stratigraphical horizon.

Two sills, the Ible and Bonsall Sills, named after the villages where they are well exposed, are also described, as well as a number of tuff horizons. The Matlock - Wirksworth region also contains a number of vent structures. Those at Ember Lane and Grangemill are well known and documented, however at least another two are to be found in this region.

A complex volcanic sequence is known to underlie the Ashover Inlier and a less complex, but otherwise insufficiently documented sequence is located in the Crich area. The Ashover area presents considerable difficulties with respect to the correlation of the volcanics with similar strata to the west.

The Winster Moor Lava

The Winster Moor Lava occurs at the Asbian/Brigantian (George *et al.*, 1976) boundary. Exposures are minimal, so much so that the Lava was not recognised until recently as a distinct unit (Shirley, 1950).

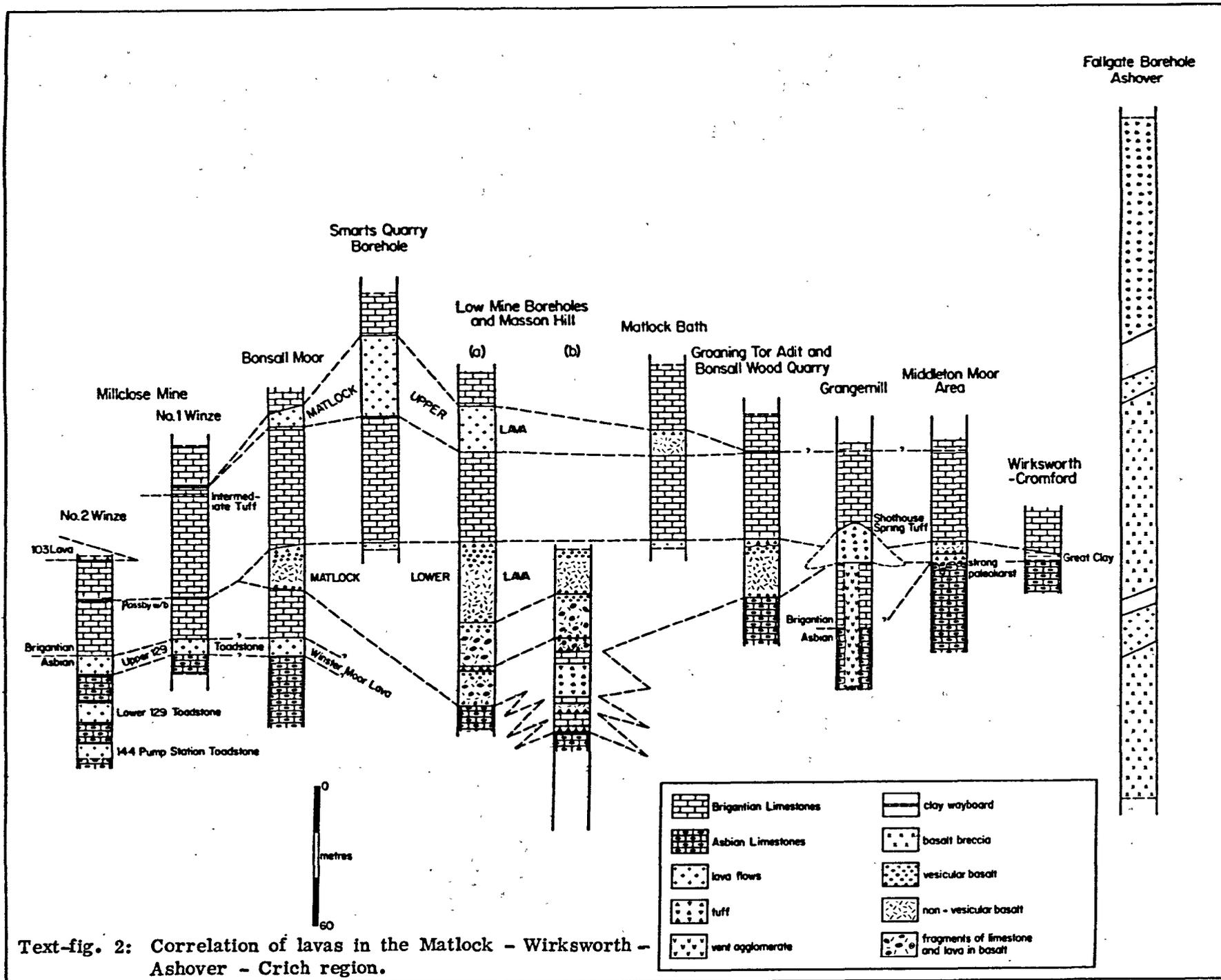
Pilkington (1789) recorded a 'third toadstone' some 10 m thick at Hang Worm Mine (3 miles south-west of Snitterton). Strahan (in: Green *et al.*, 1887) recorded a thin bed of toadstone, east of Winster Moor Farm, below the Matlock Lower Lava, and reported apparent irregularities in toadstone thicknesses at Whitelaw Rake (text-fig. 1). The present authors attribute this apparent irregularity in the thickness of toadstone to the juxtaposition of the Winster Moor Lava and the Matlock Lower Lava and Strahan's failure to recognise the Winster Moor Lava as a separate lava flow in this area. However neither Bemrose (1907) nor Traill (1940) recognised the Winster Moor Lava.

The Lava was named by Shirley (1950) who subsequently reported outcrops on Winster and Bonsall Moors (1959). It has been traced westwards to Gratton Dale where due to rapid thinning, the Lava is represented as a wayboard; the southerly limits and exact extent beneath Bonsall Moor have, as yet, to be defined; The Institute of Geological Sciences map, 1:50,000 Sheet 111 (Buxton), show an isolated outcrop of weathered Winster Moor Lava near Grange Quarry (SK220.560). This is difficult to reconcile with the known geographical distribution of the Lava. The eastern limit of the Lava is at present uncertain.

The northerly extension of the Winster Moor Lava, into the Stanton Syncline and the Millclose workings was, until recently, conjectural. This arose because previous authors failed to recognise the Lava as a distinct horizon, as well as uncertainties with respect to the exact position of the Matlock Lower Lava. Additional complexities were introduced with respect to the location of the Asbian/Brigantian boundary. The latter is based on the change from the massive bedded pale limestones of the (Asbian) Hoptonwood Group to the thinner bedded, darker and more variable facies of the (Brigantian) Matlock Group. In Millclose Mine this change was recognised above the Upper 129 Toadstone, where a thick sequence (30 m) of bituminous limestones are documented (text-fig. 2). At outcrop, Smith *et al.*, (1967) and Shirley (1950) considered the Matlock Lower Lava to lie at this lithological change, but to be overlain by a locally attenuated sequence of bituminous limestones. Traill (1940) considered the Matlock Lower Lava to terminate before Old Millclose Mine. He postulated that it may be correlated, through Millclose Mine by means of the Passby Wayboard - 13.4 to 22.9 m above the Upper 129 Toadstone horizon. The stratigraphical implications of this hypothesis were recognised by Shirley (1950) although his subsequent interpretation, rather confused the problem.

The apparent absence of bituminous limestones beneath the horizon of the Matlock Lower Lava at outcrop was attributed to either a facies change or an erosional episode. Shirley (1950) considered that in Gratton Dale (text-fig. 1) the Matlock Lower Lava (the Tearsall Farm Lava) wedged out. He assigned outcrops of lava in the Gratton Dale area to his 'Gratton Dale Lava' which he considered to be stratigraphically between the horizon of the Winster Moor and the Matlock Lower Lavas. In recognising bituminous limestones from above the "Gratton Dale Lava horizon", that is, from below that which he considered to be the level of the Matlock Lower Lava, he correlated this sequence with the Upper 129 Toadstone and bituminous limestone of Millclose Mine. Subsequently the Matlock Lower Lava and the Gratton Dale Lava have been shown to be the same (Institute Geol. Sci., 1976b) thereby invalidating Shirley's hypothesis.

Smith *et al.* (1967) continued and increased the confusion by not considering the horizon of the Winster Moor Lava in their discussion of the Asbian/Brigantian boundary and the correlation of the Millclose and Matlock Lavas. They considered three possibilities for the correlation



Text-fig. 2: Correlation of lavas in the Matlock - Wirksworth - Ashover - Crich region.

of the Upper 129 Toadstone (Asbian/Brigantian boundary) of Millclose Mine with successions at outcrop:

1. Shirley's (1950) hypothesis outlined above.
2. On the 'grounds of thickness', all lavas in Millclose Mine below the Upper 129 Lava; Upper 129 Toadstone, Lower 129 and 144 Pump Station Lava; pass laterally into the Matlock Lower Lava. This implies that the Matlock Lower Lava straddles the Brigantian/Asbian boundary in the Matlock area and its extrusion represents a period of time equivalent to these three lavas and intervening limestones seen in North Millclose.
3. The Matlock Lower Lava correlates with the Upper 129 Toadstone (not the Passby Wayboard) and the apparent diminution of the bituminous limestones sequence at outcrop is a facies change, as the limestones are traced towards the Matlock Anticline.

Not one of these possibilities is accepted by the present authors. Recent opencast mining north of Moor Farm on Bonsall Moor has exposed a sequence of some 20 m of bituminous limestones between the Winster Moor Lava and the Matlock Lower Lava. This indicates that the failure of previous workers to recognise such a sequence, was due to poor exposures. It is therefore proposed that the Winster Moor Lava is equivalent in age to the Upper 129 Toadstone, and that the two lavas occur at the Asbian/Brigantian boundary. It is possible that these two horizons are part of the same flow.

Shirley (1950) noted some 30 m of bituminous 'D₂' limestones above the Upper 129 Toadstone at Millclose Mine, passing upwards into pale coloured, coral rich horizons above the horizon of the Passby Wayboard. Similar sequences are now recognised at outcrop with 20 m of bituminous limestone beneath the Matlock Lower Lava. At Tearsall Opencast Site, approximately 5 m of bituminous limestones lie on the Lava and are overlain by rich coral horizons. This sequence correlates with the similar facies change seen in Millclose Mine. Thus the Matlock Lower Lava and its probable equivalent, the Passby Wayboard, lie within the Brigantian. The redefined horizon for the base of the Brigantian has been recognised (I.G.S. Buxton Sheet 1:50,000 No.111) and located, around Grangemill, beneath the Matlock Lower Lava even where the Winster Moor Lava is absent.

Worley (1978a) in one of the more recent compilations on the stratigraphical occurrence of the lava horizons, placed the Asbian/Brigantian boundary at Millclose Mine even lower, at the Lower 129 Toadstone horizon. The authors cannot locate supporting evidence to substantiate this hypothesis.

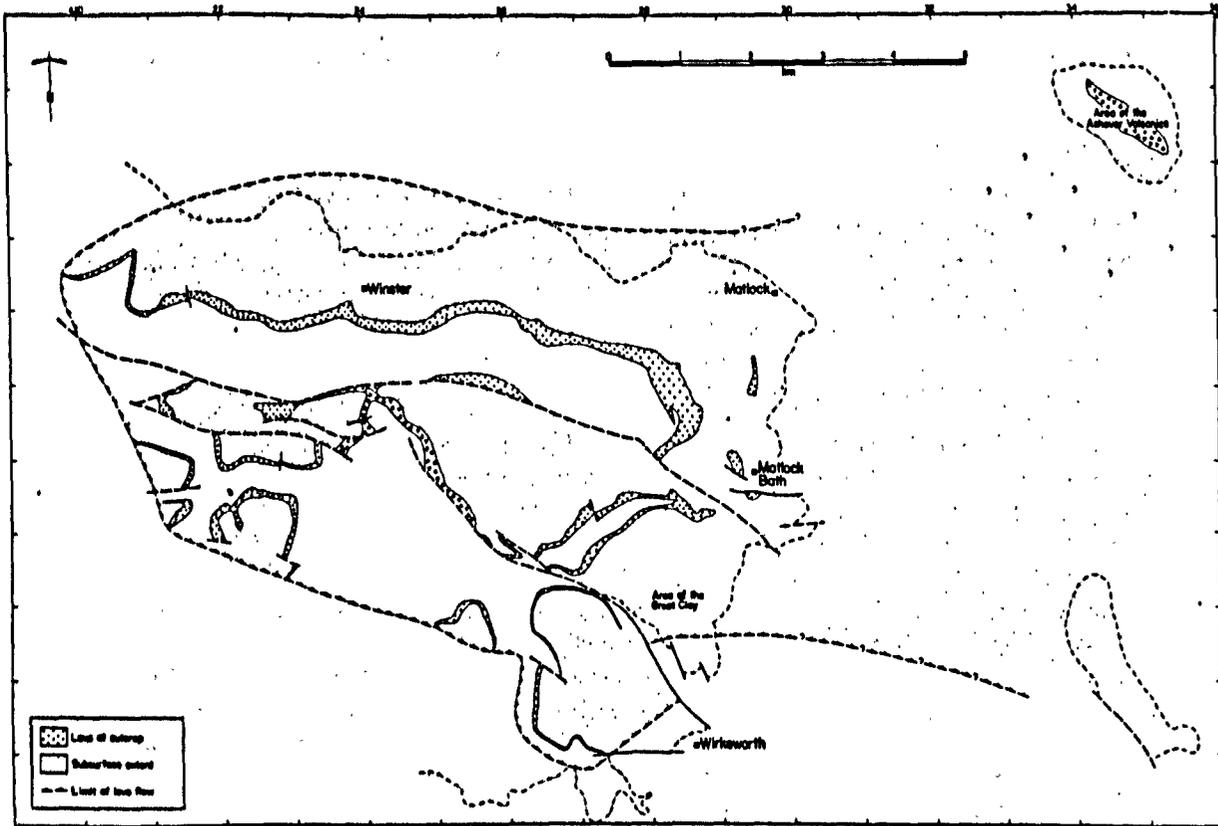
Matlock Lower Lava

Geographical Distribution

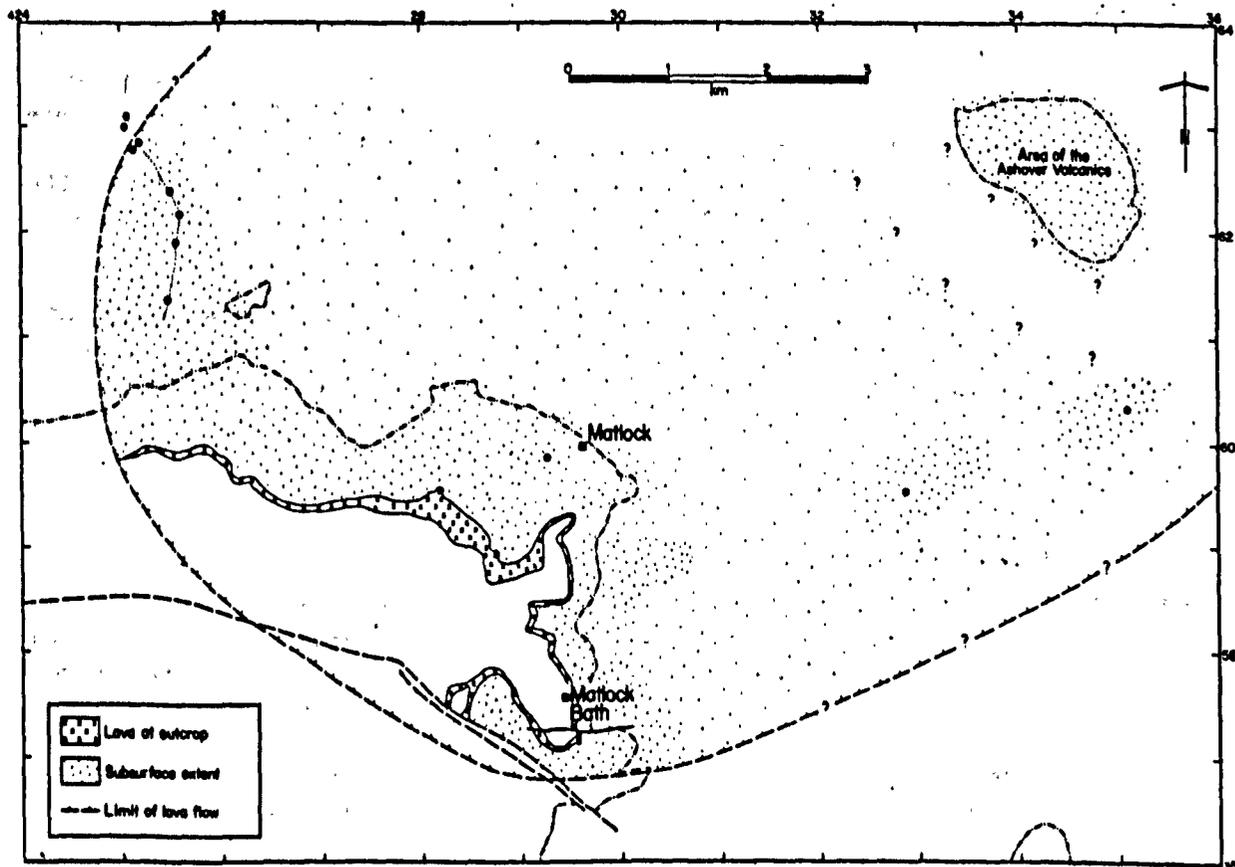
The Matlock Lower Lava has an extensive but poorly exposed outcrop extending from west of Gratton Dale to Masson Hill and the Bonsall area (text-figs. 1 & 3). It is recognised in inliers in the Derwent gorge at Matlock and Matlock Bath. South of the Bonsall Fault, the Lava outcrops at the bottom of the Via Gellia around Ball Eye rising in altitude towards the west. On the northern side of the valley the Lava passes laterally into a tuff associated with the Grangemill vents. The western extremity is to be found in the fault-complicated outcrops at Aldwark. South of the Via Gellia it can be traced to Middleton Moor, but has not been located south of Godfreyhole (text-figs. 2 & 3).

Masson Hill Area

The authors consider that the lava reaches its maximum thickness in the Masson Hill area where a series of boreholes (drilled by Exsud in 1971) on Great Rake proved 99 m of lavas and tuffs (text-fig. 2).



Text-fig. 3: The geographical distribution of the Matlock Lower Lava, stippling denotes subsurface extent and density denotes certainty.



Text-fig. 4: The geographical distribution of the Matlock Upper Lava.

Three distinct flows, characterised by vesicular upper and lower surfaces and separated by ash or decomposed clay, are recognised. The lower two units contain an abundance of marmorised limestone and angular basaltic fragments which result in an almost agglomeratic texture. The upper unit is exposed in an old opencast site on Masson Hill, where Great Rake has been worked within the Lava. The interaction of the mineralisation with the Lava has given rise to a zone of bleached and intensely altered lava.

Beneath the three flows, 40 m of ashes and lavas have been encountered. A varied assemblage of thin flows, ashes, calcareous ashes and tuffaceous limestones are interbedded with thin limestones. The complex sequence is difficult to correlate between individual boreholes. The maximum development may represent the flanks of a developing cone with sporadic and localised pyroclastic eruptions followed by periods of quiescence and inundation. The cone developed and was the precursor to the main effusive phases that culminated in the extrusion of the Matlock Lower Lava.

Associated with the Lava a number of vent feeders have been recognised in the area. They illustrate an alignment parallel to the Matlock anticline. Typical of such vents is at Ember Lane, 350 m southwest of Low Mine (SK284.586). Bemrose (1894) described it initially as a problematical exposure of tuffaceous limestone passing into bedded ash, and subsequently (1907) proposed that the exposures were best explained as an agglomerate filled vent. An unusual feature is the preponderance of limestone clasts with altered pumice fragments in an iron-stained matrix of shards and comminuted volcanic material. Trenching (pers. comm. N.J.D. Butcher) has indicated an intimate relationship between the lava and the 'agglomerate'. This 'vent' may represent the flanks and feeder for a (40 m) tuff rich limestone succession beneath the Matlock Lower Lava around Low Mine.

Smith *et al.* (1967) located an abundance of tuffaceous limestone built into field walls some 600 m north-west of Low Mine and suggested another vent. Bemrose (1907) considered the outcrop to represent a bedded tuff. As its stratigraphical horizon is beneath the Matlock Lower Lava, it is more probably related to the basal ash and lava 'agglomerate' sequence seen at Low Mine.

Ixer (1975) from borehole evidence, indicated that the lava was 80 m thick around Masson Hill Opencast Pit. At Masson Hill the basal 4-13 m of the Matlock Lower Lava is typified by a sequence of lava, tuffaceous limestone and tuff (the Masson Tuff of Ixer) which most probably equates with the sequence at Low Mine. In addition, Worley & Dorning (1977) recognised a 1 m tuff above the Matlock Lower Lava. The 'Little Toadstone' of Dunham (1952) and Ixer (1975) is a thick clay wayboard a few metres above the lava. Dunham (1952) proposed that the Little Toadstone exercised considerable influence on the replacement of limestone by fluorite and the localisation of the mineral deposits. This hypothesis cannot be demonstrated from exposures in the recent extension of Masson Hill Quarry for the wayboard is of such a minimal thickness that in all probability it would not have acted as a temporary cap rock. This wayboard horizon cannot be located in a southerly direction, but a thick and highly variable wayboard occurs in Masson Mine and in Jugholes Mine to the north. Boreholes on Bonsall Moor have located a thick graded tuff with abundant pumice fragments and glass shards in a calcareous matrix at a similar stratigraphical horizon. This unit the authors equate with the 'Little Toadstone' on Masson Hill.

At Tearsall Mine (SK262.600) Bemrose (1907) noted exposures of a fissile, bedded tuff overlying a vesicular lava, which has recently been re-exposed. Smith *et al.* (1967) recorded a thickness of some 25 m for the Matlock Lower Lava at Tearsall Mine which equates with Pilkington's record (1789) of 15 fathoms (27.4 m) of blackstone from this area.

Whitehurst (1778) noted a shaft at Slack Mine (SK257.597) which had been sunk 40 to 50 fathoms in toadstone without reaching the base, while other shafts only some 55 m to the west and east indicated the same horizon as being 20 fathoms (36.5 m) thick. Slack Mine had in fact been sunk into the Bonsall Moor Vent of Smith *et al.* (1967). Tuffaceous agglomerate fragments are present on the mine dumps.

In a southerly direction the lava is interpreted as occupying the southern limb of the Matlock anticline north of the Bonsall Fault. Highly weathered material overlies a silica/fluorite replacement deposit in the Blakemere Lane opencast site (SK261.589) in an area of complex faulting. Bemrose (1907) recorded a problematical outcrop of agglomerate some 500 m south-east from this opencast site along Moor Lane.

Western Outcrop Area

West of Bonsall Moor, Green *et al.* (1887) recorded a thickness of 36 m for the Lower Lava in Wills Founder Mine (SK235.617). Worley (1977) from the same mine, described the uppermost part as exhibiting 'pseudo-spheroidal pillow structures'.

ALCOA boreholes penetrated the lava while investigating Coast Rake, north of Winster, and proved it to be 27-35 m thick. It was also intersected at Portaway Mine, while to the south, an opencast site on Whitelaw Rake (SK232.598) cut through the lava. Further to the west the lava thins and finally disappears west of Gratton Dale. The northern extent of the Lava is certainly south of Milliclose Mine as it was not located in any of the 20th century exploratory drifts from Watts shaft.

South of the Bonsall Fault

The Matlock Lower Lava is exposed in the Bonsall Wood Basalt Quarry where it is 25 m thick. On the south side of the Via Gellia the lava has been intersected in Groaning Tor Adit (SK2830.5722). It is overlain by 3.5 m of tuff, weathered to a toadstone clay in the uppermost 15 cm. The central zone of the tuff contains angular blocks of basalt and limestone which pass into graded tuff. The base is intensely iron-stained and rests on a vesicular basalt. The flow (*sensu-stricto*) has an upper vesicular horizon which quickly grades into a hard 'relatively' fresh compact basalt. The lava is traced along the Via Gellia until displaced by the Gulph Fault.

Around Grange Mill (SK266.569) the Lower Lava has been interpreted by Smith *et al.* (1967) as passing laterally into the Shothouse Spring Tuff which had previously been regarded as being below the Matlock Lower Lava. The Shothouse Spring Tuff is spatially related to the Grangemill vents and dykes associated with the vents. The locality described by Geikie (1897) and Bemrose (1907) is visible opposite Grangemill. West of Grangemill this tuff grades into the basalt which finally terminates in the Aldwark area.

The interplay of the Grangemill vents and the Matlock Lower Lava is difficult to assess. The lava does not increase in thickness adjacent to the vents, as it does at Low Mine, indeed the Shothouse Spring Tuff replaces the lava. It may be the case that the vents are associated with small cones in a localised positive area around which the lava flowed.

South of the Via Gellia the Lava can be traced around Middleton Moor and has been recorded from numerous lead mines. Above Hoptonwood Quarries (SK263.558) recent excavations exposed a thickness of 6.7 m with a 3 m thick tuff overlain by a thin lava. Green *et al.* (1887) recorded some 13 m of tuff at nearby Bradhouse Mine. Worley (1978) refuted this figure and noted the tuff as being 3 m thick, which is consistent with the present reappraisal. The lava in this area, we suggest, may equate with a lobate flow front as it dilates once more in a southerly direction to Godfreyhole. A thickness of 10 m is recorded from boreholes on Middleton Moor (Worley, 1978).

Middleton Moor

In sections above Middleton-by-Wirksworth Limestone Mine (SK277.557) the Matlock Lower Lava is located beneath cambered Matlock limestones. Fresh spheroids of basalt suspended in a toadstone-clay matrix and a diminution in thickness indicate localised 'squeezing' of the lava. In the Mine, the Lower Lava rests on a palaeokarst surface in the Hoptonwood limestones. Karstic pits, up to 10 m deep, infilled with weathered blocks of lava, tuff and limestone in a clay matrix occur beneath the Matlock Lower Lava. This erosional interval may equate with Brigantian Limestones located between the Winster Moor Lava and the Matlock Lower Lava in the northern area (text-fig. 2).

South of Middleton Limestone Mine the Lava rapidly thins. Although no longer exposed, Smith *et al.* (1907) recorded a problematical flow front of 20 m of weathered and brecciated lava interdigitating with limestones (SK278.555, text-fig. 3).

Cromford-Wirksworth Area

The continuation of the Matlock Lower Lava into the Cromford-Wirksworth area is unclear. A thin lava was seen in the floor of Middlepeak Quarry (SK287.546). Farey (1811) recorded a number of mines between Cromford, Middleton and Wirksworth as working veins in the '3rd and 4th lime' which implies recognition of the '3rd Toadstone' or Lower Lava.

Gang Mine yielded galena from the '1st Toadstone'. Old mining records refer to the 'Great Clay' and infer that it was thicker than normal wayboards. Marked on a 1777 plan of Cromford Sough, it was intersected either side of the Bolehill Anticline. The Great Clay was located in Brandrix and Rantertaker Mines working Gang Vein at SK289.557 and SK289.684 respectively. At the former locality, the Meerbrook Sough, some 54 ft. (16.5 m) below Cromford Sough (Oakman, 1978) intersected the Great Clay, here said to be 6 fathoms (11 m) thick. A section by Wheatcroft (1831) depicts the Great Clay displaced by the Gulph Fault, and indicates its location 160 ft. (46.8 m) beneath the base of the shales. Alsop (1845) equated the Matlock Lower Lava with the Great Clay of Wirksworth.

East of River Derwent and Crich

The Matlock Lower Lava can be traced east of Low Mine and in two inliers flooring the Derwent Valley at Matlock and Matlock Bath (text-fig. 1). Between Matlock Bath and Low Mine the position of the top of the lava has been proved in a series of boreholes drilled by Exsud during 1971 and 1972. Watson (1813) recorded a shaft on Bacon Rake as sunk through the 'basaltic amygdaloid with a cinder top' - 40 fathoms thick' (73 m). The weathered upper surface can be located below the pipe deposits in this area, e.g. Wapping Mine.

East of the River Derwent, beneath the Namurian cover, the Matlock Lower Lava has not been located. A lava has been recorded from Crich. The Crich mines were some of the few mines to prove 'rich ore' beneath the toadstone and thus stimulated similar, but unprofitable ventures, elsewhere in the orefield. Bacchus Mine cut through 20 fathoms (36.6 m) of lava whilst Pearsons Venture Mine found an 11 fathom (20 m) development according to Green *et al.* (1887, p.154). In the centre of the anticlinal structure, at Glory Mine (SK343.559) the toadstone was 9½ fathoms thick (17.4 m). Bemrose (1894a) briefly described the occurrence of lead ore in lava and the associated alteration encountered in Glory Vein at Wakebridge Mine. At Old End Mine (SK346.558) the lava was 9½ fathoms thick (17.4 m).

The variable thickness of the toadstone (Lava) in the Crich area was noted by Alsop (1845) who stated: 'a thick bed of toadstone sunk through at one shaft diminishes to a foot or two in thickness at the other'. This statement is difficult to reconcile with published data for the area, but may indicate a local flow front.

The lava at Crich is located at a similar stratigraphical horizon as the Matlock Lower Lava in the Matlock area and may therefore be part of the same flow (Smith, *et al.*, 1967). The eastern limits are unknown; however 'igneous horizons' have been located beneath the Derbyshire coalfield (Smith *et al.*, 1967).

Matlock Upper Lava

The Matlock Upper Lava has, in comparison to the Matlock Lower Lava, a restricted outcrop. It extends from Tearsall Mine (SK262.600) in the west to Masson Hill (SK286.587) and the Derwent gorge in the east. The southernmost extremity is at Ball Eye Quarry in the Via Gellia. South of the Bonsall Fault it does not form a mappable unit (text-fig. 4).

The maximum development is observed in the Masson Hill-Jugholes area (text-fig. 2). According to Dunham (1952) the lava is 21.5 m thick on Masson Hill and at least 24 m thick at Jugholes Mine, where it is exposed in the entrance to the lower adit. A more recent compilation by Worley (1978) indicates 35 m of lava on Masson Hill, while in Oxclose shaft (SK275.599) 29 m is proved.

Vesicular and non-vesicular basalts are exposed along Salters Lane and similar outcrops can be traced below the summit of Masson Hill. From borehole evidence the Matlock Upper Lava can be traced adjacent to Seven Rakes vein at Cawdor Quarry, Matlock, where it is 36 m thick (Smith *et al.*, 1967). Lead ore was recovered (Farey, 1811) from within the Lava at Seven Rakes Mine, and below High Tor (SK296.593) there are old opencast workings in the Lava.

Varvill (1959) noted that in Ribber Mine, the Matlock Upper Lava was some 20 m thick. In a southerly direction it can be traced along the Derwent gorge towards Cromford. Exsud's boreholes at Upperwood proved the Upper Lava to be approximately 10 m thick. Around Ball Eye Quarry, in the Via Gellia, it is involved with the Bonsall Fault zone, where Butcher (1976) proposes fault and thrust repetitions to explain the complexities.

In Groaning Tor adit, on the southern slopes of the Via Gellia (SK283.572), a 1 m wayboard lies some 40 m above the Matlock Lower Lava. This wayboard is the last vestige of the Matlock Upper Lava. A similar correlation may be evoked with thick wayboards located in cores from Bonsall and Middleton Moors, although a definitive statement is not possible.

In a northerly direction the Lava can be traced into Millclose Mine where it is 18 m thick in Watts Shaft and 23 m thick in Lees Shaft (Traill, 1940). North of these localities, Traill recorded a termination prior to No. 1 Winze. Recent borehole information confirms Traill's outline distribution map and supports his hypothesis of an emanative centre to the north of Matlock (text-fig. 4).

East of Matlock, the top of the Matlock Upper Lava has been proved in a series of boreholes in the Ribber Castle, Tansley and Highoredish area (Ramsbottom *et al.*, 1962). The Lava is absent at Crich, although Alsop (1845) reported a clay wayboard varying from 30 cm to 4 m and containing nodules of compact toadstone. A similar relationship cannot today be observed, but Smith *et al.* (1967) considered that Alsop's report may refer to the uppermost clay wayboard in the Matlock Group and equated it with the Upper Lava. If their supposition is correct it may infer the possibility of a flow front in the vicinity. Although the Highoredish borehole intersected the Matlock Upper Lava, the horizon cannot be traced with certainty, into the volcanic sequence at Ashover (1.7 km to the north). Additional clay wayboards, in the Crich area, were reported by Sargent (1912).

Ashover Area

Correlation of the tuff sequence exposed in the core of the Ashover anticline has always been uncertain. As Bemrose (1907) noted, the top of the sequence lies close to the level of the Matlock Upper Lava, but the date of the initial volcanic activity is not known.

Mining during the 18th and 19th centuries proved abnormally dilated 'toadstone' sequences. Cockwell Mine on driving north intersected toadstone on the Great Rake. The Blue Hillock shaft, sunk in 1781, and an exploratory level, proved the 'toadstone' to be 24 yds (22 m) thick. A northward continuation of the exploratory level, towards the centre of the anticline was driven in toadstone while a second exploratory underground shaft, 274 m northwest of Fall Mill, proved 54.9 m of tuff. Band (1976) indicated that, from shaft bottom, a boring for a 'considerable distance' did not bottom the toadstone. Green *et al.* (1887) recorded Milltown Mine shaft as 82 m deep, and stated that it encountered toadstone. New Engine shaft of Gregory Mine, on the western flanks, is depicted on old sections as reaching the top of the toadstone. The toadstone (upper surface) was intersected at a depth of 54.9 m in Westedge Engine shaft in the northern Ashover area. Farey (1811) recorded that lead ore was worked in the toadstone. A shaft on Townhead vein, some 230 m north-north-west of Ashover Church, proved toadstone 55 m beneath the top of the limestone. On the eastern flanks of the inlier, the top of the toadstone was intersected 84 m below the base of the shales, in Hogsland shaft, on Fall Hill vein.

Documentary evidence for the central area was provided by Ramsbottom *et al.* (1962) who indicated that the Fallgate borehole intersected an exceptionally thick (293 m) volcanic assemblage. A 95 m tuff as well as basaltic flows and autobreccias were recorded. The borehole was abandoned

prior to penetrating the full volcanic sequence. The pyroclastic sequence may represent the core and flanks of a volcanic cone. The Milltown borehole, located on the flanks of the anticline, some 183 m south of the Fallgate borehole, indicated a rapid thinning of the tuff as well as failing to penetrate the full sequence in its 137.5 m.

The Ashover area clearly marks the site of a substantial volcanic cone centred on the Fallgate area. Distributional analyses of the Matlock Upper and Lower Lavas do not support the proposition that Ashover was a major contributor to the flows in the Matlock area. Although the Upper Matlock lava has been located between Matlock and Ashover, from borehole evidence it is inferred that the Ashover inlier represents the centre of a large but localised volcanic cone. The stratigraphical horizon of the Ashover 'volcanics' is uncertain, as correlation demands the lower limits, as yet unencountered, to be specified. A recent paper by P. Kelman (1980) provides additional information.

The Bonsall Sill

The Bonsall Sill is one of the largest igneous bodies in the South Pennine area and is intruded into the crest of the Matlock Anticline. It has an outcrop (text-fig. 1) approaching 1 km² but is poorly exposed. The dolerite varies, from a coarse ophitic type with remnants of fresh olivine, to a finer grained marginal facies described by Bemrose (1904) and Gibson & Wedd (1913). The coarse type is exposed in a small quarry at SK276.593 and the marginal type can be found to the south-west of Low Farm at SK281.588. A full petrographic and geochemical analysis of both types was given by Ixer (1972). A series of boreholes in the Becks Mere region (Smith *et al.* (1967), failed to reach the base of the Sill at a depth of 55 m. Becks Mere No. 1 borehole (SK275.593) intersected a 6.4 m thick amygdaloidal horizon with the 'normal' coarse dolerite, at a depth of 33.5 m.

Along its northern margin the dolerite is in contact with the base of the Matlock Lower Lava although the exact relationship is not clear. The sill may have invaded 'a line of weakness' between the lava and limestone, a situation in common with a number of the Derbyshire sills. To the south the sill terminates against the Bonsall Fault zone.

The Ible Sill

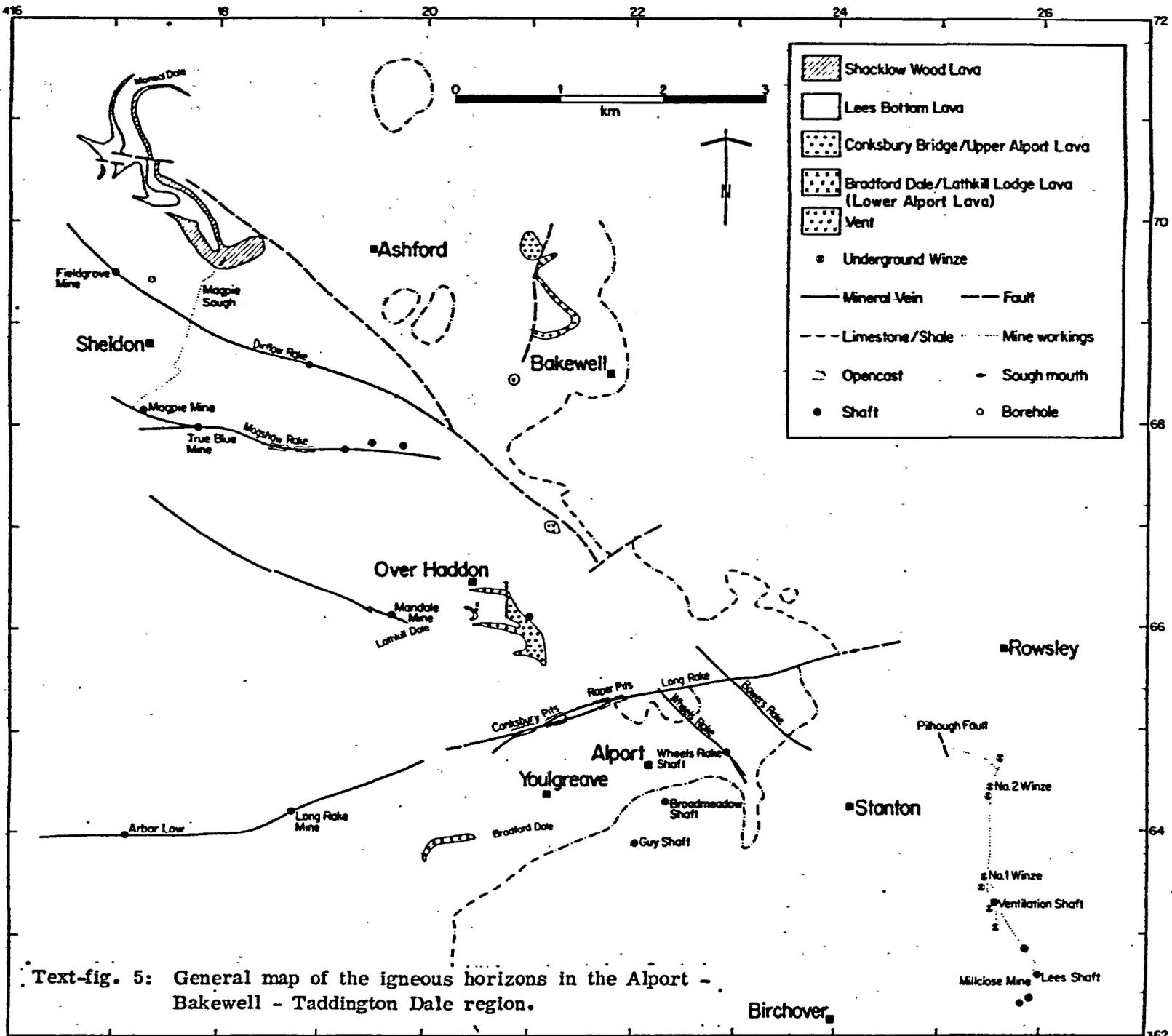
The Ible Sill outcrops at the western end of the Via Gellia (text-fig. 1). It was described by Bemrose (1907) as a typical ophitic olivine-dolerite. An exposure of the sill is located in the disused roadstone quarry at SK253.568 where some 30 m are visible. Bemrose (1907) noted marmorisation of the underlying limestone on the south side of the sill, however, this is now obscured by tip material.

Within the quarry the dolerite is traversed by disorientated calcite veinlets. Fibrous material within the calcite veinlets was thought by Garnett (1923) to be chrysotile asbestos. This suggestion was refuted by Sarjeant (1967) who considered the material to be a chlorite-montmorillonite clay mineral. The dolerite is strongly chloritised and calcitised with ilmenite altered to leucoxene. A distinct pervasive alteration horizon, up to 1.5 m wide, cuts across the sill. The genesis of this horizon is unknown for it is not related to local mineralisation aureoles, but may be connected with a hydrothermal alteration phase related to the cooling of the sill. The alteration has not been observed in the other Derbyshire olivine-dolerite sills.

The Prospect Tuff Mound

Prospect Quarry, Grangemill (SK245.574) reveals a mound-like weathered tuff exposure, against which the enclosing limestones decrease in thickness. From field evidence it appears to be comparable with similar exposures of a tuff mound in the quarries of Associated Portland Cement Manufactures (A.P.C.M.) at Hope (Eden *et al.*, 1964).

The tuff mound, containing blocks of marmorised limestone, is associated with porcellaneous horizons at the top of the Griffe Grange limestones, now thought to be partly Lower Asbian in age. If this is the case, the tuff is older than the Lower Brigantian vents at Grangemill, and represents the oldest known volcanic centre in the southern Pennine orefield. Associated lava flows have not been recorded or located.



2. The Alport - Bakewell - Taddington Dale region

The igneous rocks of this region (text-fig. 5) are poorly represented at outcrop. The isolated, discontinuous nature of which has given rise to difficulties and confusion as to their correlation. They are, however, of considerable sub-surface extent and have been intersected in numerous boreholes and mine workings. Six lava/tuff horizons are located in the region, together with the complex succession in Millclose Mine. The lava/tuffs are: The Alport Upper and Lower, The Bradford Dale, The Conksbury Bridge, The Lathkill Lodge, The Shacklow Wood and The Lees Bottom Lavas. An additional number of lavas are reported from Millclose Mine, some of which can be equated to other lavas in the Alport area, however not all the units have lateral equivalents. Likewise, not all the above lavas are at different stratigraphical horizons, indeed it is proposed that the Alport Lower Lava is equivalent to the Bradford Dale Lava and the Alport Upper Lava is equivalent laterally to both the Conksbury Bridge and the Lathkill Lodge Lavas.

The 18th and 19th centuries witnessed intense mining activity in the Alport area and documentary evidence from that period indicates that the miners only fully understood the location and influence of strata above the Alport Upper Lava.

The Alport Lower Lava

Initial documentary evidence relating to the Alport Lower Lava arose from the exploration in depth at Wheels Rake Shaft (SK228.649) (text-figs. 5 & 7). Deep trials here were the first and only workings in the area to penetrate the hydrological compartment below the Alport Upper Lava, and excessive water was encountered (Oakman, 1978). Even with the erection of a water wheel it proved impossible to drain the shaft and sink it to the Lower Lava. Nevertheless, an exploratory boring was undertaken in the toadstone. Green *et al.* (1887) quote a figure of 56 fathoms (102.4 m) for the thickness of the Alport Lower Lava from 'information supplied by Mr. Toft'. This figure is still quoted on recent maps (Inst. Geol. Sci., 1976b). The present authors considered that this was a remarkable depth for lead miners to drill, and investigation of the original document (Bagshaw Collection No. 587[79]) has indicated that this was a misquote by Green *et al.* (1887) the actual value being a more realistic 56 ft. (17 m). This mistaken thickness of 102.4 m has, however, lead certain authors (Traill, 1940) to postulate a vent feeder for the lava. Such an hypothesis is now clearly erroneous.

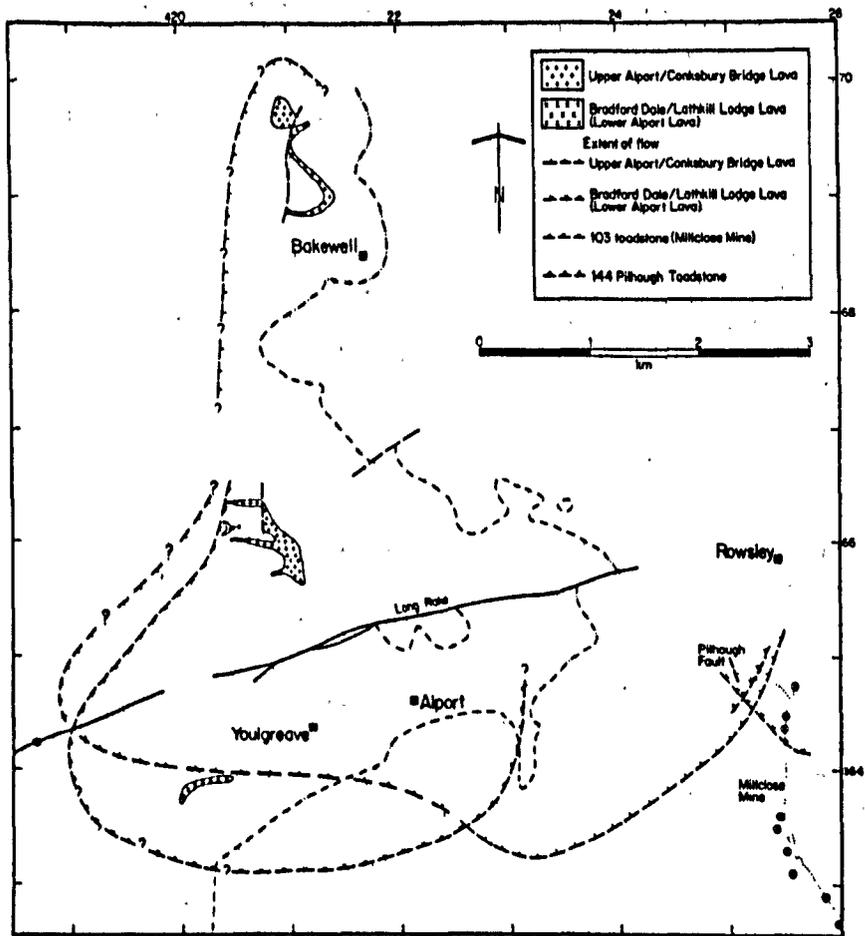
The Alport Lower Lava may also be correlated with the 'Bradford Dale Lava' exposed to the south-west of Youlgreave. Shirley (1957) noted that the Bradford Dale Lava lies 45.7 m below the *Orionastrea placenta* band, whereas the Alport Upper Lava when traced into the Conksbury area lies only 12 m below the *O. placenta* band. This, together with the westerly attenuation of the Alport Upper Lava before Bradford Dale, supports the present correlation (text-fig. 8).

South-east of Alport, the Lower Lava was not intersected by ALCOA in 1974. A vestige of its development in the Alport area is evident, for it is represented by a thick wayboard.

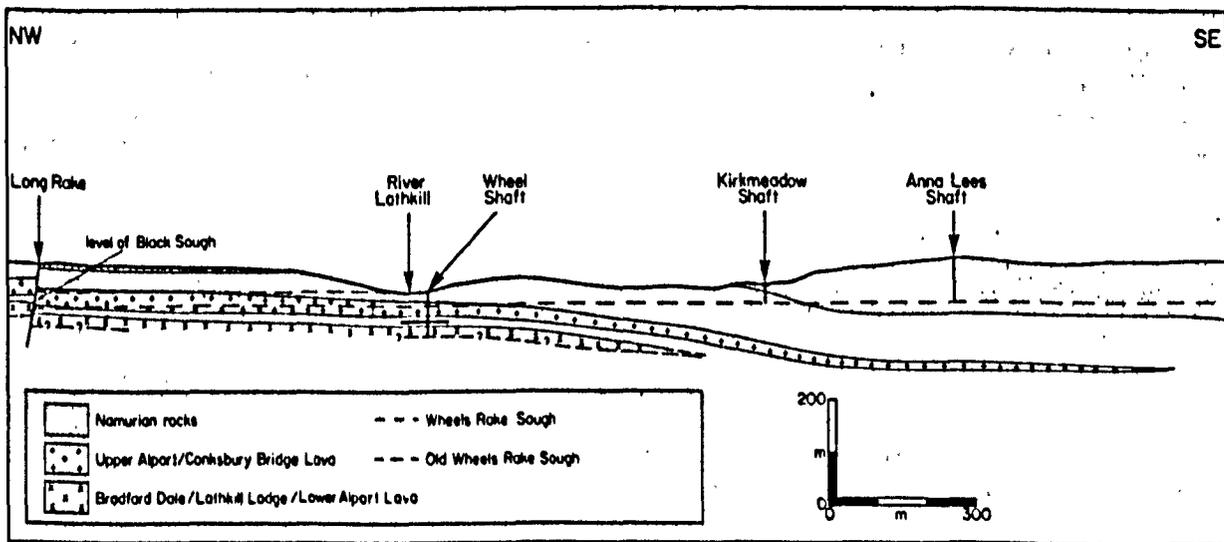
The Alport Lower Lava has been located in a series of boreholes around Conksbury Opencast site. Although the boreholes failed to penetrate the base of the lava, they did indicate a minimum thickness of 15 m. These findings are in accordance with the new interpretation of the Wheels Rake Shaft section, where there is a minimum development of 17 m for the Alport Lower Lava.

The Alport Upper Lava

The Lava is not exposed at surface. It was first encountered when Wheels Rake Old Sough was driven north along the vein from the River Lathkill (SK228.645). During 1786, these workings - in toadstone - encountered a vein in the forefield of the sough. The vein was in all probability Long or Ladies Rake, the powerful east-west reversed fault zone which forms the northern boundary to the mining area.



Text-fig. 6: Geographical distribution of lavas in the Alport - Millclose Mine area.



Text-fig. 7: Section along the line of Wheels Rake (after Butcher, 1976, with additional borehole data).

The Black Sough drainage level was driven westwards along Long Rake from Pickory Corner (SK246.658) on the River Wye. It entered lava near the intersection of Long Rake and Wheels Rake, where Green *et al.* (1887) noted that it was 17 fathoms (31 m) thick. From this intersection a branch was driven south-east along the Wheels Rake 17.4 m below the Old Sough (Oakman, 1978) initially in toadstone and finally passing into the overlying limestone (text-fig. 7).

Deeper drainage was provided by Hillcar Sough and its many branches. The Wheels Rake branch of Hillcar Sough was driven north-west along the vein and encountered the Alport Upper Lava at Wheels Rake Shaft (SK228.649). With the intention of conducting the first deep trial beneath the Upper Lava, a water wheel was erected and sinking commenced. The Upper Lava proved to be 25 m thick and separated from a lower lava by 13.7 m of limestone (Green *et al.*, 1869).

To the south-west of Wheels Rake Shaft, Broadmeadow Shaft (SK224.644) (text-fig. 5) intersected toadstone 21 fathoms (38.4 m) below the level of Hillcar Sough, at a similar stratigraphical horizon to the Alport Upper Lava. Guy Shaft (SK219.641) in the 1840's was sunk beneath Hillcar Sough to a depth of 32.2 m. It failed to locate toadstone, but did intersect two water-bearing wayboards at 65.8 and 80 m below the base of the shales. Tentative correlation places the lower of these two horizons at that of the Upper Lava, intersected in Wheels Rake and Broadmeadow Shafts. The implication of this correlation, is that the Alport Upper Lava decreases in thickness towards the west.

The Upper Lava has been located to the south-east of Alport, in a series of boreholes drilled by ALCOA in 1974. It was some 26 m thick in the area to the south-east of Wheels Rake Shaft, with a diminution in thickness as it was traced in a southerly direction towards Birchover.

Further evidence for the stratigraphical location and thickness of the Alport Upper Lava is from Raper and Conksbury opencast sites (SK217.653 and 210.650 respectively), where it floors these two operations on Long Rake. A thickness of 23 m is recorded (borehole logs) for the lava underlain by some 4.5 m of limestone. Butcher (1976) has shown that the lava thins west of the Conksbury Opencast Site, and is absent to the west of Long Rake spar mines, while to the north-west of the opencast site the lava is represented, at outcrop, by the Conksbury Bridge Lava.

Conksbury Bridge and Lathkill Lodge Lavas

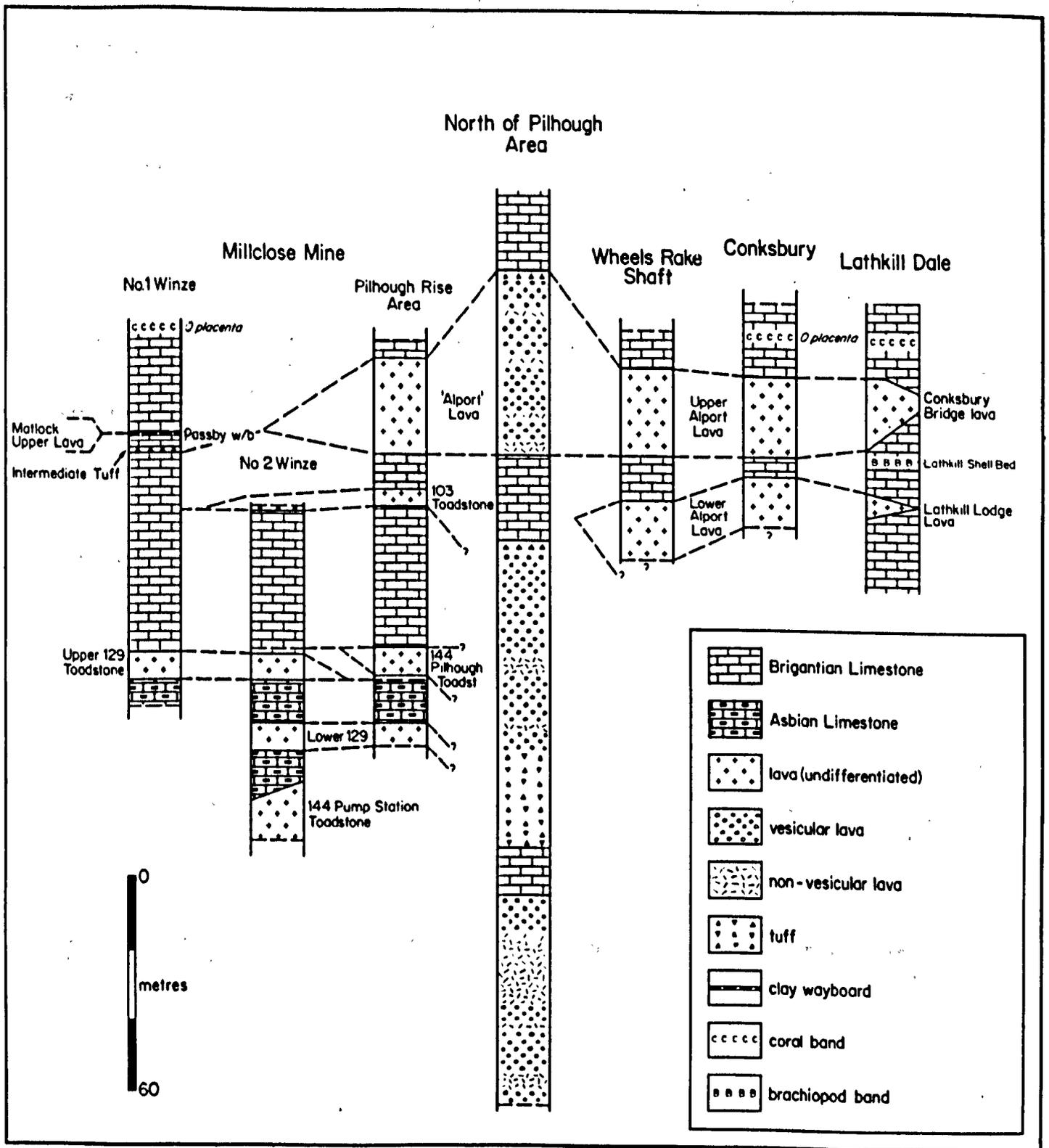
Using the *Orionastraea placenta* band mainly as the stratigraphical reference, the Alport Upper and Lower Lavas equate with the Conksbury Bridge and Lathkill Lodge Lavas, exposed in the lower reaches of Lathkill Dale north of Alport.

Lathkill Dale

The top of the Conksbury Bridge Lava is exposed along the northern side of the Dale (text-fig. 5). The *Orionastraea placenta* band occurs 12 m above the lava. The limestones rest on the vesicular upper margin of a flow which is 5 m thick. The central portion of the flow is characterised by a non-vesicular dolerite and a vesicular base rests on a lower flow. This has a highly vesicular and slightly hematized upper margin which grades downwards into a thick sequence of non-vesicular dolerite.

Lathkill Dale witnessed an unusual mining venture in the 1850's when it was claimed that gold had been discovered in auriferous pyrite associated with the weathered top of the Conksbury lava (Grigor-Taylor, 1972). Auriferous pyritic clay was also supposedly assayed from the weathered top of the Alport Lower Lava in Wheels Rake Shaft. All that remains of the ambitious venture are overgrown hollows and spoil heaps of basaltic fragments at SK209.661.

The Conksbury Bridge Lava is not encountered west of Over Haddon but may equate with a thick wayboard in Mandale Mine (SK196.662). The Lathkill Lodge Lava, according to Shirley



Text-fig. 8: Correlation of lavas in the Millclose Mine - Alport - Lathkill Dale areas.

(1950) is 27 m beneath the Conksbury Bridge Lava (text-fig. 8). At the type locality some 5 m of lava are visible and contain marmorised limestone fragments. Traced in a westerly direction a rapid attenuation may be observed. Farey (1811) noted that the Lathkill Dale Vein Sough commenced in lava into which the vein persisted.

Bakewell Area

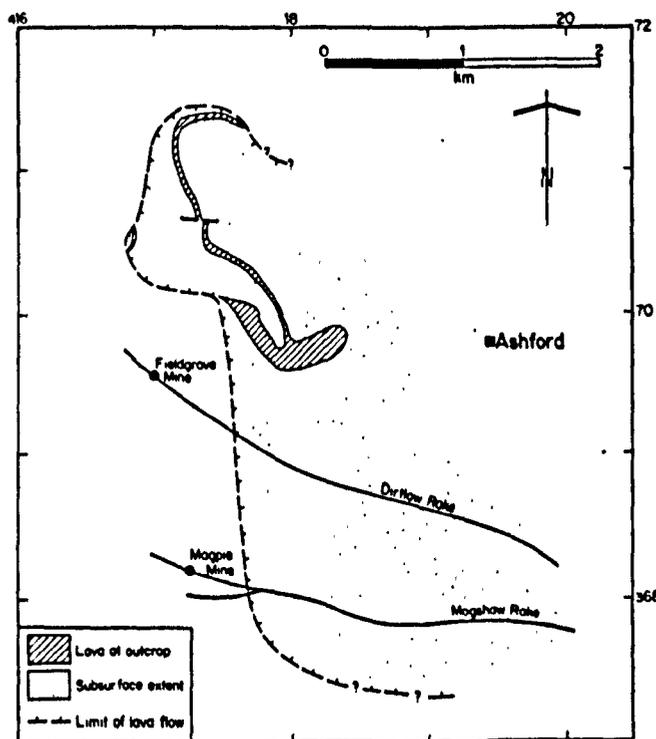
The subsurface extent of the lavas towards Bakewell is unknown due to the paucity of mines and borehole data. The Institute of Geological Sciences (1977b) report two vents, at Ditch Cliff (SK211.670) and adjacent to the Monyash road, at SK207.684. These are minimal in extent and exposure. Officers of the Institute, in noting a lava (the Endcliff flow) to the north of Bakewell at a stratigraphical horizon some 25 m beneath the *Orionastraea placenta* band, have correlated it with the Conksbury Bridge Lava. The Cracknowl 'vent' of Bemrose (1897, 1904) has been reinterpreted as a faulted segment of the same lava (Inst. Geol. Sci. 1977b).

Shacklow Wood and Lees Bottom Lavas

To the west of the Alport-Bakewell area, a number of lavas have been located at outcrop, in mines and boreholes in the general vicinity of Sheldon (text-fig. 5). A number of these lavas may correlate with the Lathkill Dale/Bakewell units.

Two flows, the Shacklow Wood and Lees Bottom Lavas (basalts) - are known from outcrops in Monsal Dale and Shacklow Wood. These units were equated by Butcher and Ford (1973) with the Millers Dale Upper and Lower Lavas, but have been subsequently considered (Inst. Geol. Sci., 1976a) to occur at stratigraphically higher horizons in the Brigantian succession.

The Lees Bottom Lava is exposed at the foot of Taddington Dale and a flow front is located in a southerly direction. It has not been reported from the Magpie Mine area nor from the head of Monsal Dale to the north. Information in the Ashford/Great Longstone area is minimal and hence its distributional limits are problematical.



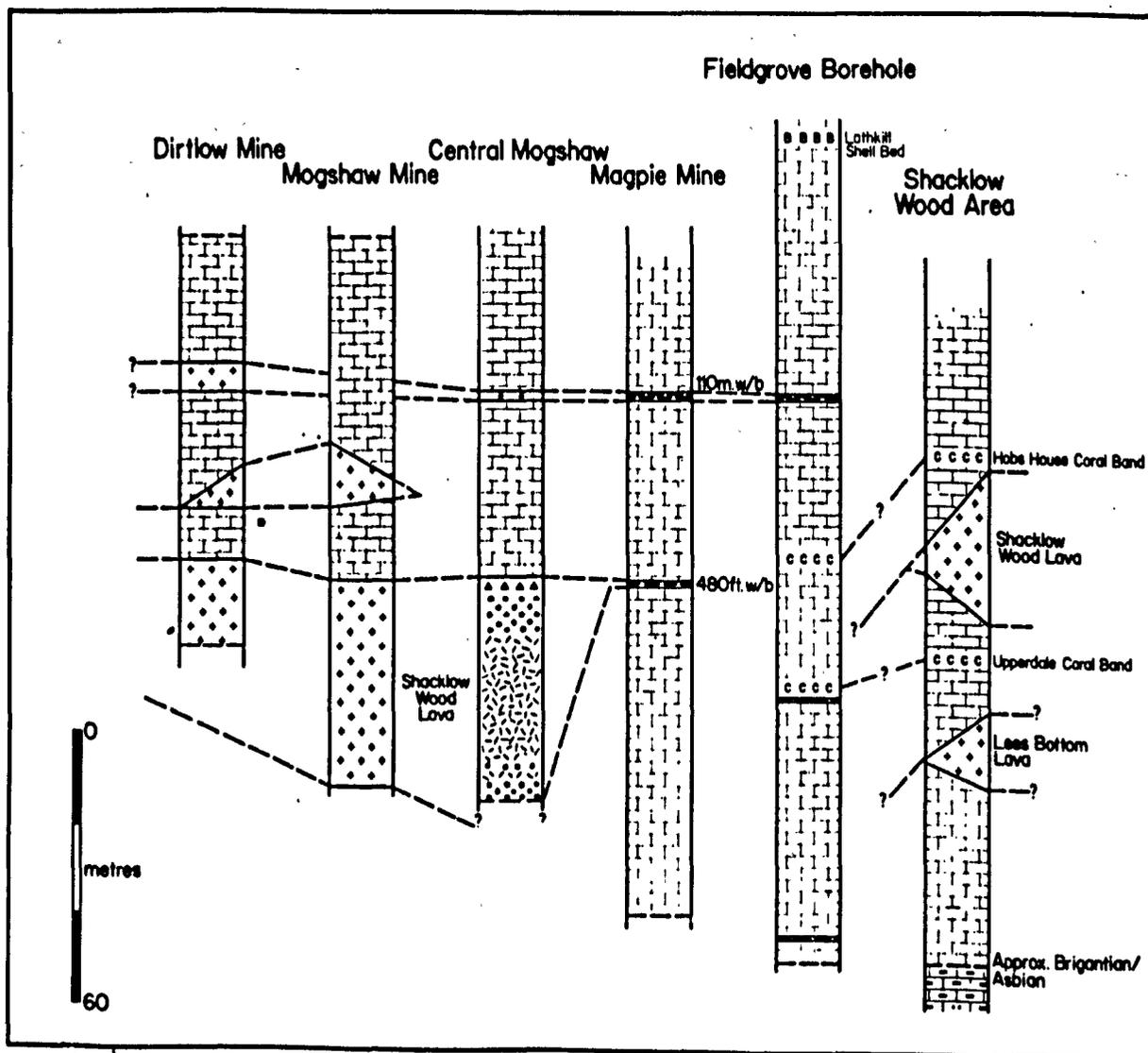
Text-fig. 9: Geographical distribution of the Shacklow Wood Lava, stippling denotes subsurface extent and density denotes certainty.

The Shacklow Wood Lava is exposed in Taddington Dale (text-fig. 9). Near Fin Cop (SK173.704) it is 11.5 m thick and at Black Rock corner (SK177.700) some 18 m are exposed. At this latter locality a vesicular upper surface rapidly grades into a sequence of non-vesicular dolerite. The coarseness of the central flow led Bemrose (1907) to regard it as intrusive - his New Bridge Sill. A more recent description of the area has been given by Miller (1980).

Magpie Mine Area

Magpie Sough intersects the Shacklow Wood Lava over a distance of 457 m, where it is folded into a shallow syncline and so faulted that the base is not exposed. Butcher (1975) described the top as having a spheroidally weathered surface associated with yellow clay and overlain by pyritous limestones. According to Butcher & Ford (1973) Sheldon Shaft (SK177.688) exposed 42 m of lava above sough level, while it was absent at Magpie Mine Shaft (SK172.682), 700 m to the south.

True Blue Mine (SK177.680) to the east of Magpie Mine intersected the base of the Shacklow Wood Lava in a rise 26 m above the Magpie 560 ft. (170.7 m) level (Varvill, 1959). Considering the horizontal attitude of the strata in the area, the thick wayboard at the 480 ft. (146.3 m) level in Magpie Shaft may be the lateral equivalent of the Shacklow Wood Lava seen in the True Blue rise (text-fig. 10). Varvill (1959) equated a clay, intersected at the bottom of the True Blue Shaft, as the top of the lava. If this interpretation had been correct,



Text-fig. 10: Correlation of lavas in the Magpie Mine area, Sheldon

it would have given a thickness of 40 m for the lava. However as Worley (1978) indicated, this clay cannot be equated with the weathered top of the Shacklow Wood Lava, but is more probably the lateral equivalent of a thick wayboard (over 1.5 m) seen in the Redsoil Shafts at depths of between 104 and 110 m.

North of Magpie Mine, the Shacklow Wood Lava diminishes (at outcrop) in the vicinity of Shacklow Wood only to reappear further to the west. At (SK168.705) a small isolated exposure of vesicular lava may represent a lobate flow front (text-figs. 5 & 9). Fieldgrove Engine Shaft (SK170.695) exposed a thick clay at 110 m on the southern, upthrown side of the fault. A recent borehole (Cox & Bridge, 1977) at SK173.695 close to Fieldgrove Shaft, failed to intersect the Shacklow Wood Lava, but proved a number of wayboards. In the same borehole, a 0.55 m pyritic clay with included limestone clasts at 82 m, most probably correlates with the 110 m wayboard in Fieldgrove Shaft. It is not possible to equate a specific wayboard with the Shacklow Wood Lava, but the most obvious equivalents are a group of wayboards between 149 and 157 m. The tentative identification (Cox & Bridge, 1977) of marker horizons in the area, indicates that the Shacklow Wood Lava may equate with stratigraphically higher but less obvious wayboards. A number of marker horizons, the Lathkill Shell Bed and the *Orionastraea placenta* band, can be traced into the area enabling a comparison to be made of the relative stratigraphical horizon of the Lathkill Dale/Monsal Dale Lavas (text-figs. 5, 8 & 10).

East of Magpie Mine

To the east of Magpie Mine three toadstones are recorded. Farey (1811) referred to the 'chance' toadstones in Mogshaw Mine while Green *et al.* (1887) noted old mining records as showing three toadstones at Dirlow Mine (SK188.687). A section at the eastern end of Mogshaw Rake (dated 1840) depicts two toadstones inclined to the east, with the thinner, upper toadstone decreasing westwards (Bagshawe Coll. Sheffield City Library - B.C. 598).

Additional information has been provided by recent exploration drilling which intersected the lower toadstone. The hole failed to penetrate the base of the lower toadstone but proved a minimum thickness of 54 m. Non-vesicular holocrystalline basalts, comparable with the exposures at Black Rock corner, are now correlated with the Shacklow Wood Lava. The upper lava of the Mogshaw Mine section, was not evident; however a pyritic clay and thin basalt are recorded some 36 m above the lava. This horizon may equate with the '110 clay' intersected in the Magpie Mine area.

The mining manuscripts of Dirlow Mine upon which Green *et al.* (1887) based their account (Bagshawe Coll. B.C. 604, 605) depict three toadstones. The 'lower toadstone' is the thickest and correlates with the lower toadstone of Mogshaw Mine and the Shacklow Wood Lava. The 'middle lava' of the Dirlow sections is depicted as occurring 10 m above the Dirlow Mine Lower Lava and as dying out to the west. This can be correlated with the Upper Toadstone of the Mogshaw section which has indications of a similar attenuation to the west. It was not located in the recently drilled Mogshaw Rake Borehole located in the central part of Mogshaw Rake to the west of Mogshaw Mine (text-fig. 10). The 'upper lava' of the Dirlow sections is some 36 m above the top of the 'lower lava' (Shacklow Wood Lava - text-fig. 10). This fact strongly suggests a correlation with the tuff/lava (?) encountered 36 m above the Shacklow Wood Lava in the Mogshaw borehole. A volcanic horizon at a similar stratigraphical level is not depicted on the Mogshaw Mine section but attenuation trends suggest that it may only be a thick wayboard in this area and would not be marked on a section as 'toadstone'.

Extrapolation of the evidence provided by the Fieldgrove Borehole places this 'upper lava' below the Lathkill Shell Bed close to the horizon of the Lathkill Lodge Lava. Attenuation trends, however, support the probability that it represents the continuation of local flows developed, at depth, in the Bakewell-Longstone Edge area.

The Millclose Lavas

The northward extension of Millclose Mine intersected five distinct lavas (text-figs. 2 & 8). These horizons are tentatively correlated with volcanic sequences in adjacent areas. It has been proposed (p. 98, this paper) that three flows, the 144 Pilhough, the Lower 129 and 144 Pump Station toadstones, are located at the base of the Brigantian and within the Asbian Limestones. Comparable stratigraphical horizons with volcanic sequences have not been intersected to the west or north-west (Alport area). These lavas are absent in the Matlock area, but are found at similar stratigraphical horizons to the Millers Dale Lavas, in the northern region of the South Pennine Orefield.

Correlation with Alport Lavas

The Alport lavas occur within the Brigantian succession (text-fig. 8). The only comparable volcanic horizons noted in the northern part of Millclose Mine are the 103 toadstone and the 'Alport' lava of Traill (1940), who assumed that they correlated with the Alport Upper and Lower Lavas. However, as borehole data (pers. comm. by N.J.D. Butcher) indicates, the Alport Lower Lava does not extend towards Millclose Mine. This raises the question of whether the correlation of the Alport Upper Lava and Traill's 'Alport Lava' of Millclose Mine can be accepted. The Alport Upper Lava persists towards the Millclose area, but unfortunately the 'Alport Lava' was only intersected prior to the final abandonment of Millclose Mine. It was 27.4 m thick in the Pilhough Fault area, however its exact stratigraphical location was not proven. A rise in the area of No. 1 Winze south of the Pilhough Fault demonstrated the absence of any 'Alport' Lava.

Traill (1940) tentatively correlated the 'Alport' Lava of the Pilhough area with the Intermediate Tuff of Central Millclose Mine. This thin but persistent tuff horizon formed an important cap-rock to orebodies in the vicinity of No. 1 Winze. The Intermediate Tuff occurred 3.4 to 4.6 m beneath the horizon of the Matlock Upper Lava in the south of Millclose Mine. The horizon, according to Shirley (1950) was some 28-38 m below the *Orionastraea placenta* band.

In the absence of more detailed and definitive information on the stratigraphical horizon of the lavas in Millclose, the available evidence coupled with the general attenuation trends, is compatible with the following hypothesis. The 'Alport Lava' of Millclose Mine, the Alport Upper Lava of Alport and district as well as the Conksbury Bridge basalt of Lathkill Dale may all be regarded as one eruptive unit.

The 103, 144 Pilhough, Lower 129 and 144 Pump Station Toadstones

The 103 Toadstone forms another cap-rock horizon in a manner similar to the Intermediate Tuff. It was infrequently penetrated in the mine workings. In the Pilhough rise, a thickness of 3 to 6.7 m was recorded. The geographical limits of this toadstone are known in detail as it delimited the zone of step-like ascension of the orebodies to the overlying 'Intermediate Tuff'. Traill (1940) indicated that the toadstone terminated south-west of a line between Pilhough and No. 2 Winze (text-figs. 6 & 8). The emanative centre is probably in the vicinity of Rowsley (SK255.660).

The 144 Pilhough Toadstone is only recognised in Millclose Mine. Stratigraphically it occurs above the Upper 129 Toadstone in the central section of the mine. On the Pilhough Fault, it was 8.5 m thick, with a rapid attenuation to the south-east where it is represented by a wayboard.

The Lower 129 Toadstone is located some 12 m beneath the 144 Pilhough Toadstone, between No. 2 Winze and Pilhough. Traill (1940) noted that it lay on an erosion surface with attendant marmorization of the underlying limestones. It is a thin but highly variable flow varying between 3 and 8 m thick. Any attempt to deduce the direction of attenuation and hence a geographical distribution for the flow is not possible. It may correlate with the top of a flow located at a similar horizon in No. 1 Winze to the south, and 10 m below the Upper 129 Toadstone.

The lowest volcanic horizon in the basal Asbian Limestones was the 144 Pump Station Toadstone. It is 9.4 m stratigraphically lower than the Lower 129 Toadstone, and was intersected in the area of No. 2 Winze. The base of the toadstone was never exposed; however, some 15 m of lava were proved. The detailed description given by Traill (1940) of the flow front on the 144 fathom level indicates attenuating limestones with a number of wayboards abutting a 20° slope of pillowed, eroded lava which decreases in thickness towards the south-west.

North of the Pilhough Area

Despite the difficulties already outlined with respect to the correlation of the 'Millockse Lavas' with adjacent areas, a distributional analysis indicates that they are related to an Upper Asbian volcanic centre to the north-east of Pilhough. On the basis of data from the north-west of Pilhough it is suggested that this area also contains the volcanic centres responsible for the majority of the Brigantian extrusive activity at Millockse and Alport.

Three 'flows' were encountered north of Pilhough (text-fig. 8). The upper flow (52 m thick) consists of vesicular and non-vesicular units. To judge from its stratigraphical horizon this lava may correlate with the Alport Upper Lava and the 'Alport Lava' of Millockse Mine. This proposal is consistent with the observed attenuation trends. The middle lava (93 m thick) infers proximity to a vent with a comparable situation to the Low Mine sequences of the Matlock Lower Lava around Bonsall (p.89, this paper). Confirmation of this possibility is supported by the presence of a 60 m tuff sequence. Highly inclined graded tuffs, and auto-brecciated horizons intercalated with thin basalt flows underlie the uppermost 33 m of vesicular/non-vesicular flow units. It is proposed that this represents the flanks of a feeder cone similar to the situation outlined by Ramsbottom *et al.* (1962) for an interpretation of comparable horizons in the Ashover boreholes.

A minimum thickness of 58 m has been indicated for the lower lava which, unlike the middle and upper units, is characterised by the absence of pyroclastic material and the presence of thick coarsely crystalline doleritic centres to the individual flows. These horizons cannot be equated with individual lavas in the Pilhough area. One of the thick lava/tuff sequences may correlate with one or all of the 'Pilhough flows'. In the absence of detailed palaeontological classification of the intercalated limestones, the erection of correlatable horizons is not possible. The expanded volcanic sequence does, however, reconfirm the statement that Rowsley may be regarded as a volcanic centre concealed beneath Namurian shales.

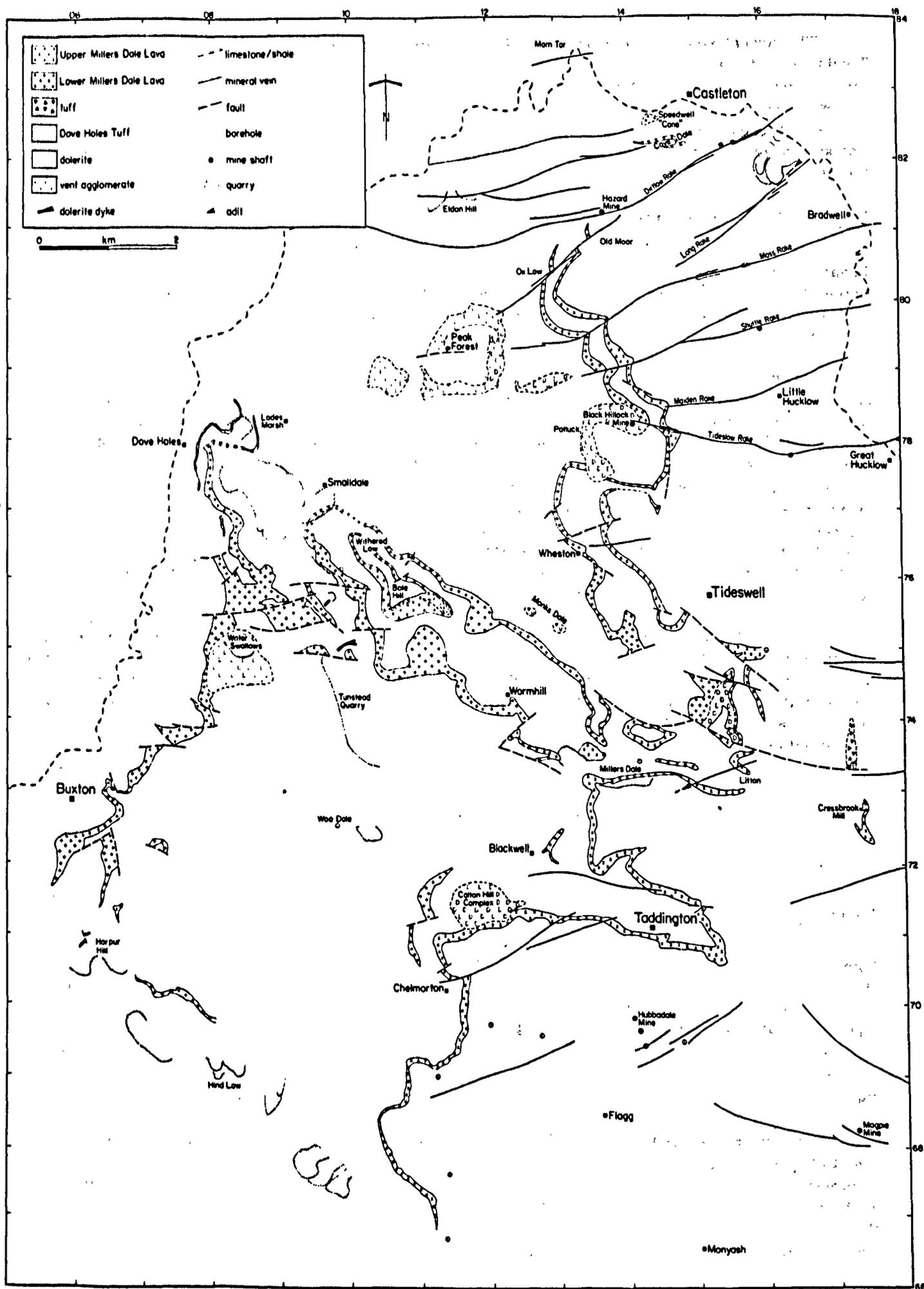
3. The Castleton - Buxton - Tideswell Region

Introduction

Two extensive lavas, the Miller's Dale Upper and Lower Lavas, dominate the igneous horizons in the north western part of the South Pennines. Additional volcanic strata include the Ravensdale Tuff and the Dove Holes Tuff. The region is unusual in that a large number of sills are located within the limestone sequence; the Waterswallows, Peak Forest, Potluck and Mount Pleasant Sills constitute this assemblage. Possibly the Waterswallows Sill is the most well known and the Peak Forest Sill occurs at the lowest stratigraphical horizon, while the remaining sills are of minimal extent and exposure, as are the Monks Dale and Peter Dale vents.

The region also contains one of the most frequented igneous localities in the whole of the South Pennines, The Calton Hill Complex. Unfortunately this locality was never fully documented and is now the site of a refuse tip, however two typical exposures are preserved as Sites of Special Scientific Interest (S.S.S.I.). Although not unique to the South Pennines the region also contains two dykes near ICI's Tunstead Quarry. These are poorly exposed, and as they are located on private land, are difficult to examine and sample.

Included within this subdivision of the South Pennines is the Castleton area, and so complex are the igneous deposits of this geographically restricted area, that it is described



Text-fig. 11: General Map of the Igneous horizons in the Buxton - Tideswell area (excluding Castleton)

in a separate section. The Pindale Tuff and the Cave Dale Lava together with the Speedwell 'vent' are possibly the best known igneous horizons. The Speedwell 'vent' in particular has resulted in a considerable number of publications, far beyond the number normally produced by such a small exposure. It has recently been the subject of a complete reappraisal with the result that it is now considered to be a littoral cone. (Cheshire & Bell, 1977).

Pre-Asbian Extrusive Activity

The Woo Dale Borehole

The Woo Dale Borehole (SK 4099.3726) described by Cope (1949 & 1973) encountered 'volcanics' at a depth of 275.6 m. The upper 26.4 m of the 33 m sequence consists of highly inclined tuffs overlain by horizontal limestones and resting on sub-alkaline lavas (Cope, 1979). Although thought to be pre-Carboniferous, the age of the volcanic sequence has always been doubtful and Cope (1949) initially considered them to be part of the Pre-Cambrian basement, however K-Ar isotopic age dating (Cope, 1979) has indicated a minimum age of 383 ± 6 m.a. (Devonian) for the tuffs.

The Ravensdale Tuff

The oldest Carboniferous igneous rocks in the northern (Tideswell) area, the Ravensdale Tuff, was initially described by Bemrose (1894, 1907), while Sargent (1925) noted analcite infilled vesicles in some of the lapilli. Shirley & Horsfield (1940) placed the Tuff in the D₁ (Asbian) limestones. The bedded tuff sequence may be correlated with similar horizons in the Litton Dale Borehole (SK 160.750) where Stevenson *et al.* (1971) noted that the Tuff was 29.6 m below the base of the Millers Dale Lower Lava, and borehole chippings indicated that a 13.7 m sequence of tuffs and thin lava flows may be present. Further to the west, a Severn-Trent Water Authority's borehole in Millers Dale (SK 142.733) failed to intersect igneous horizons in the 300 m of limestones beneath the Millers Dale Lower Lava. A 'black calcareous shale' logged 30 m below the base of the Lava may represent the last vestige of the Ravensdale Tuff (text-figs. 11 & 14).

The Millers Dale Lower Lava

The lava outcrops from Buxton to Doveholes, around Wormhill and Tunstead east of Great Rocks Dale and forms an inlier in Millers Dale. Towards Tideswell it is intruded by the Tideswell Dale Sill. It can be traced northwards over Tideswell Moor as far as Ox Low, while in the Castleton area local pyroclastic and extrusive activity may have occurred contemporaneously.

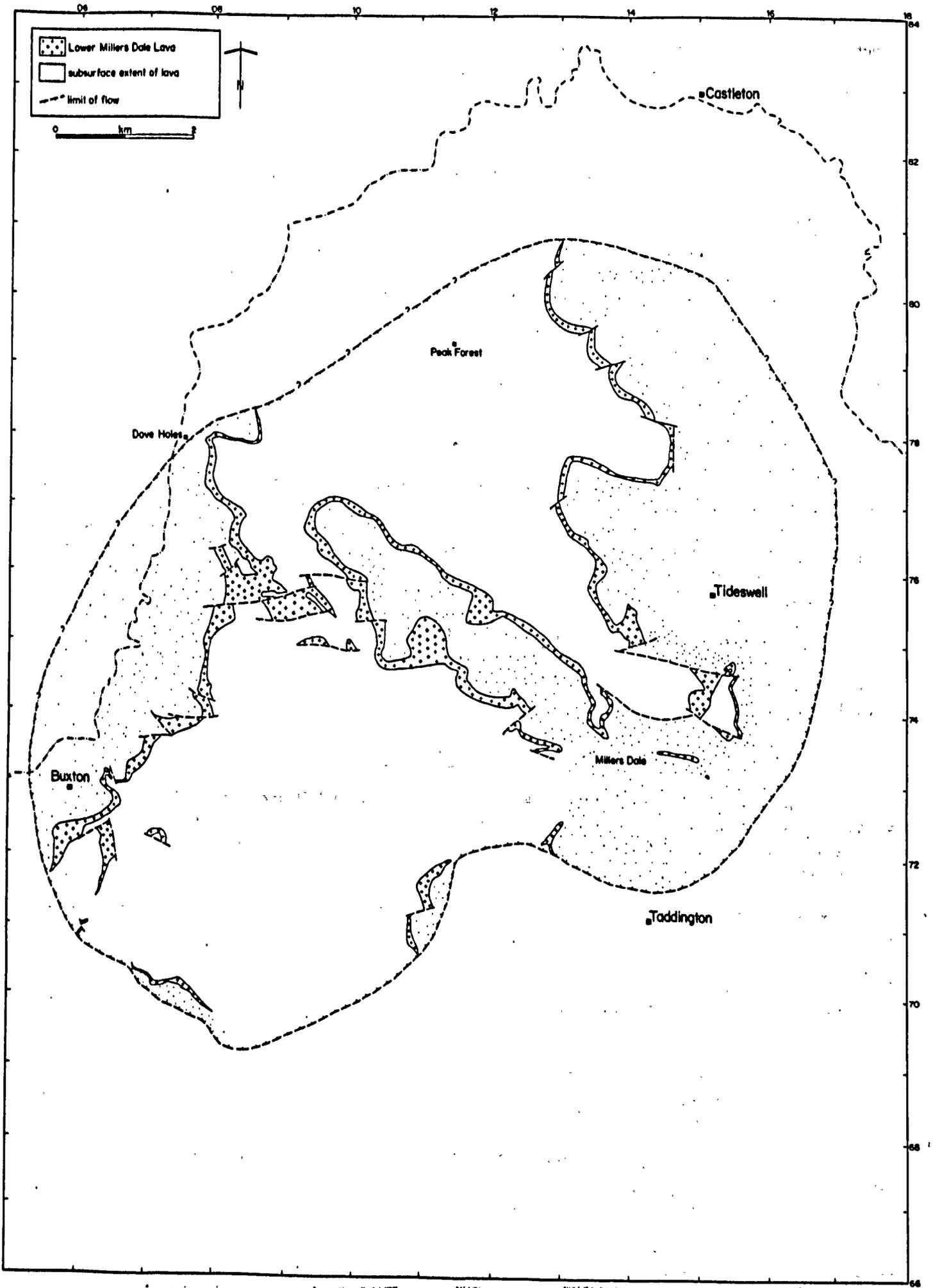
Stratigraphically the lava occurs in the Asbian Limestones and where present it subdivides the Bee Low Limestones into the Upper Millers Dale Beds and the Chee Tor Beds.

Buxton-Taddington Area

East of Buxton, the Millers Dale Lower Lava is 9 m thick but decreases in thickness and terminates south-west of a line from Grindlow (SK 055.717) to Hind Low (SK 082.690) (text-figs. 11 & 12) where a number of flow fronts are complicated by faulting. Walkden (1972) recorded a lenticle of weathered toadstone in the Hind Low quarries, at the horizon of the Lower Lava. This rapidly degenerates into a wayboard and the southern limit of the flow is defined by a number of isolated exposures near Calton Hill (SK 118.715) and Blackwell Dale (text-fig. 12).

Farey (1811) noted that the Millers Dale Lower Lava was present in Horsesteads Mine (SK 142.716) near Taddington, however it is absent in Cressbrook Dale, and this fact enables an approximate eastern limit to be defined.

The top of the lava is exposed below Raven's Tor in Millers Dale (SK 150.733) where it forms a small domed inlier and the full sequence (20.7 m) was proved in the Severn-Trent Water Authority's Millers Dale Borehole.



Text-fig. 12: The geographical distribution of the Lower Millers Dale Lava

Great Rocks Dale/Wormhill - the Waterswallows Sill (Cover, plate 2)

To the north of Buxton the Waterswallows Sill has been intruded at the junction between the limestones and the Millers Dale Lower Lava. The olivine dolerite sill lacks the coarse ophitic texture common to many of the Derbyshire intrusives and Moseley (1966) interpreted the evidence as indicating that Waterswallows was the site of a vent infilled with 'massive basalt'. Subsequently K-Ar isotopic age dating of the dolerite by Stevenson *et al.* (1970) indicated a mean intrusive age of 311 ± 6 m.a. They refuted Moseley's proposition of a vent and supported Bemrose's (1907) interpretation of a sill intruding the lava.

In the 1960's, I.C.I. undertook a feasibility study to the east of Great Rocks Dale in order to ascertain the suitability of the lava for use as a roadstone aggregate. Boreholes at SK 103.755 and SK 099.761 intersected the lava and showed a northerly attenuation over a distance of 600 m, where the lava decreased from 29.9 m to 22.8 m. It is divisible into three extrusive events with a tuffaceous upper unit while the two lower and relatively thicker units display coarse holocrystalline central flows with fresh augite. Sections of the lava are exposed in three small quarries at SK 098.761, near Buxton Bridge which were opened as part of the feasibility study.

The Millers Dale Lower Lava extends from the north-west of Tunstead Quarry, through an intensely faulted area towards Doveholes. Its furthest extent in this direction, is in the region of Lodes Marsh (SK 086.784) while the western extremity of the lava is undefined and may occur beneath the adjacent Namurian strata. The top of the unit was intersected west of Tunstead Quarry (SK 100.740) in boreholes at SK 075.767 and SK 078.763 (Stevenson *et al.*, 1971).

Great Rocks Dale Dykes

Two NE-SW trending dykes, described by Stevenson *et al.* (1971) in Great Rocks Dale, are exposed at SK 097.757 and SK 101.751. The northerly dyke, now minimally exposed, was described by Cope (1933) as being 3.7 m wide and highly weathered. The adjacent limestones illustrate marmorization while Cope noted xenoliths of dolomite and sandstone and suggested that the latter were derived from basement formations. Xenoliths of a similar lithology have also been noted (Smith *et al.*, 1967; p. 92 this paper) from the Ashover Tuff and the Grange Mill Vents. The southerly dyke is distinguished from the northerly one being partly amygdaloidal and excessively altered. They are named by the Institute of Geological Sciences as the Buxton Bridge Dykes.

Wormhill-Ox Low

At Wormhill the Lower Lava (30 m thick) contains zeolite and calcite filled amygdales whilst the olivines and pyroxenes have been replaced and the ilmenite altered to leucoxene. The Lava is exposed in a road cutting at Wormhill (SK 123.741) and thins to the north, where in Smalldale (SK 165.814) it is 9 m thick.

Tideswell Dale (plate 3, plate 4, fig. 2)

The Lava has been intruded by the Tideswell Sill and the two are visible in the old roadstone quarry in Tideswell Dale (SK 155.738). This locality, now a picnic site in the Peak Park, has been described by numerous authors, Wilson (1870), Geikie (1897), Bemrose (1899), Sargent (1917) and Wilkinson (1967). The Sill is transgressive and where it is in contact with the underlying limestone, has resulted in marmorization. Wilson (1870) stated that a baked columnar clay preserved beneath the vesicular lava was a volcanic mudflow. Geikie (1897) was the first to recognise the intrusive origin of the 'crystalline basalt'. The quarry exposes an 18 m thick sill in which Bemrose (1899) recognised five distinct zones characterised by a coarse central, and finer grained outer margins. Sargent (1917) considered the altered vesicular lava underlying the sill to have 'spilitic affinities' an observation based on an alkali content in excess of 6%. The type of alteration he described is typical of the vesicular margins of numerous toadstones in the South Pennines and is a reflection of the complex deuteric and hydrothermal alteration these lavas have undergone rather than any primary 'spilitic' magma. Wilkinson (1967) describing the lavas, exposed in three roadside quarries (SK 154.743) at the entrance to the Picnic Site, stated that a non-vesicular lava, with microphenocrysts of andesine and augite, is in contact with a highly altered vesicular lava. Original pyroxene is absent and only a few olivine pseudomorphs remain in flow-orientated feldspar laths and microlites which are oligoclase in composition. He stated that the soda content is about 4%.

The full sequence of the Lower Lava was proved in the Litton Dale Borehole (SK 160.750) (Stevenson *et al.*, 1971). A sequence of 24 m of lava and tuff were subdivided by a 3.7 m limestone horizon, into an upper 20.3 m unit, and a lower 3.7 m one. The lava thins rapidly to the east and is not seen in Cressbrook Dale.

To the west of Tideswell, in the vicinity of Wheston, the Lava is approximately 27 m thick. Two vents with vent agglomerate are located in Monks Dale and in Peter Dale. Bemrose (1907) and Stevenson *et al.* (1971) recognised the southerly (SK 130.753) and northerly (SK 126.755) occurrences, respectively. The coincidence of these vents with the area of maximum development for the Lower Lava suggests that they may represent the eroded roots of the vents and cones that were the main extrusive centres.

North of Wheston, the Lava is 10.7 m thick at Wall Cliff (SK 140.774). On Tideswell Moor, opencast workings for fluor spar in White Rake, provide an exposure in which the Millers Dale Upper and Lower Lavas are faulted in juxtaposition. The Lower Lava is exposed on the southern wall of the opencast site near Tides Low (SK 146.782) and shows an upper flow unit, with highly vesicular margins, resting on 3 m of limestone which in turn overlies a lower less vesicular but blocky lava. In the Tideswell Moor area the lava has been partly intruded by the Potluck Sill (Walters, 1980).

North of Tideswell Moor, the Lower Lava is poorly exposed at the surface but has been intersected in shafts and mine workings, over Bradwell Moor. At outcrop, it can be traced as far as Conies Dale (SK 131.807), where at Cop Round it is 9 m thick. The northern limit is a weathered horizon 1.8 m thick at a depth of 22.9 m in Hazard Mine Shaft (SK 137.813) 275 m to the west, a 0.6 m thick clay horizon at a depth of 3.6 m in Wham Shaft, may equate with the Lower Lava.

Recent exploration of mine shafts on Moss Rake (Bradwell Moor) has located the upper surface of the Millers Dale Lower Lava. In Kitty Cross Shaft (SK 154.803) the exact thickness is not known, but can be demonstrated to be less than 11 m. At Rake Head Mine (SK 143.800) Green *et al.* (1887) noted 11 m of the lower toadstone. The eastern extent of the Lava is difficult to define, but in all probability it does not extend far beyond Kitty Cross Shaft. Information with respect to its presence in and around Hucklow is not available for neither mines nor boreholes have intersected the stratigraphical horizon of the Millers Dale Lower Lava.

The Dove Holes Tuff

The Dove Holes Tuff was first recognised by Green *et al.* (1869). It has a patchy development, rests on a strongly potholed surface, and reaches a maximum thickness of some 2 m. The Tuff may initially have had the form of a low angle mound related to a vent, but now exhibits greater weathering than similar structures in the Derbyshire area. Stratigraphically it occurs approximately 15 m above the Millers Dale Lower Lava.

Outcrops of the Tuff occur around Batham Gate and Bibbington, northeast of Tunstead Quarry. It is exposed in Holderness Quarry (SK 084.782) as a 1.8 m thick unit, it decreases to 1.1 m thick in a southerly direction and is not located south of Dove Holes. It is exposed east of Peak House (SK 080.766) and was proved to be 1.5 m thick in a borehole near Batham Gate (SK 075.767) although additional boreholes in the general vicinity failed to indicate the Tuff. A borehole at Batham Gate (SK 078.763) is of interest in proving an additional lower tuff horizon 2.3 m thick, only 3.4 m above the Millers Dale Lower Lava (Stevenson *et al.*, 1971) (text-fig. 14).

Tuff sequences in the Upper Asbian are not recorded at outcrop away from the intensely quarried Great Rocks Dale area, but a lenticle of tuff occurs at a similar stratigraphical horizon to the Dove Holes Tuff in Station Quarry, Millers Dale (SK 134.734). This tuff is not associated with a palaeokarst surface which suggests that in the main area of pyroclastic activity around Dove Holes, a highly localised uplift and karstification episode preceded volcanicity (Walkden, 1977).

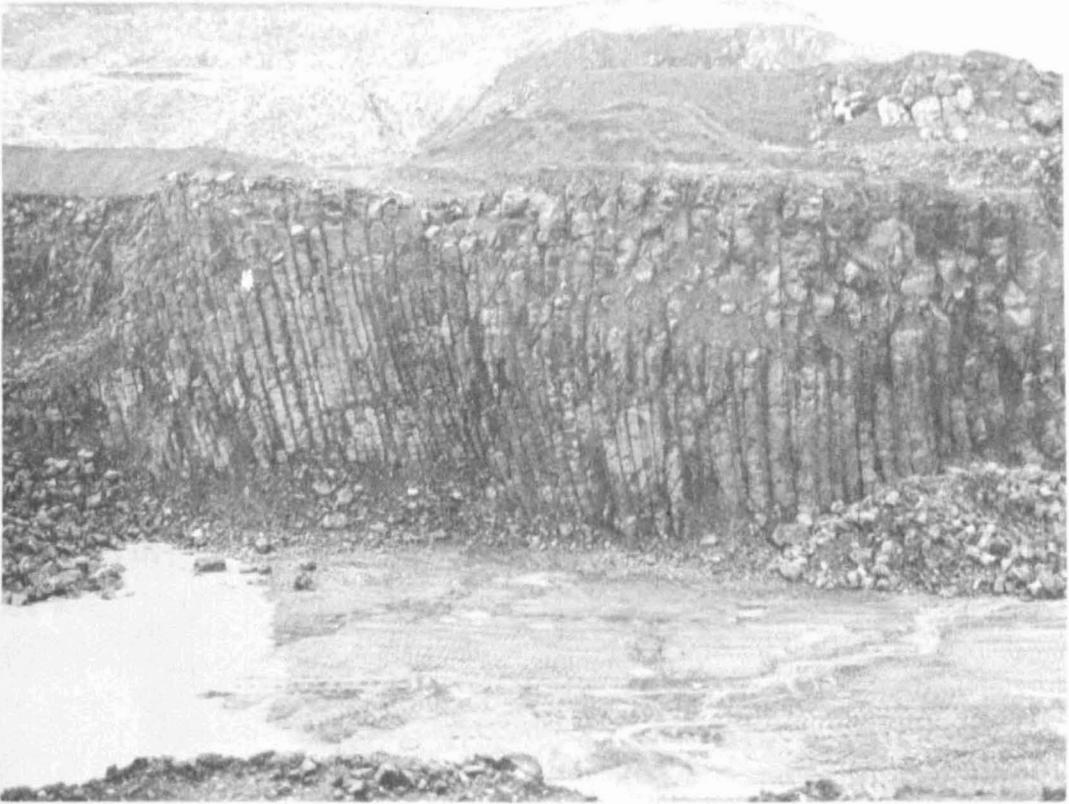


Fig. 1: Waterswallows quarry, Buxton. The Waterswallows Sill is an olivine-dolerite showing vertical columnar structure; face since removed. (Photo: M.G. Lodge, December 1980).

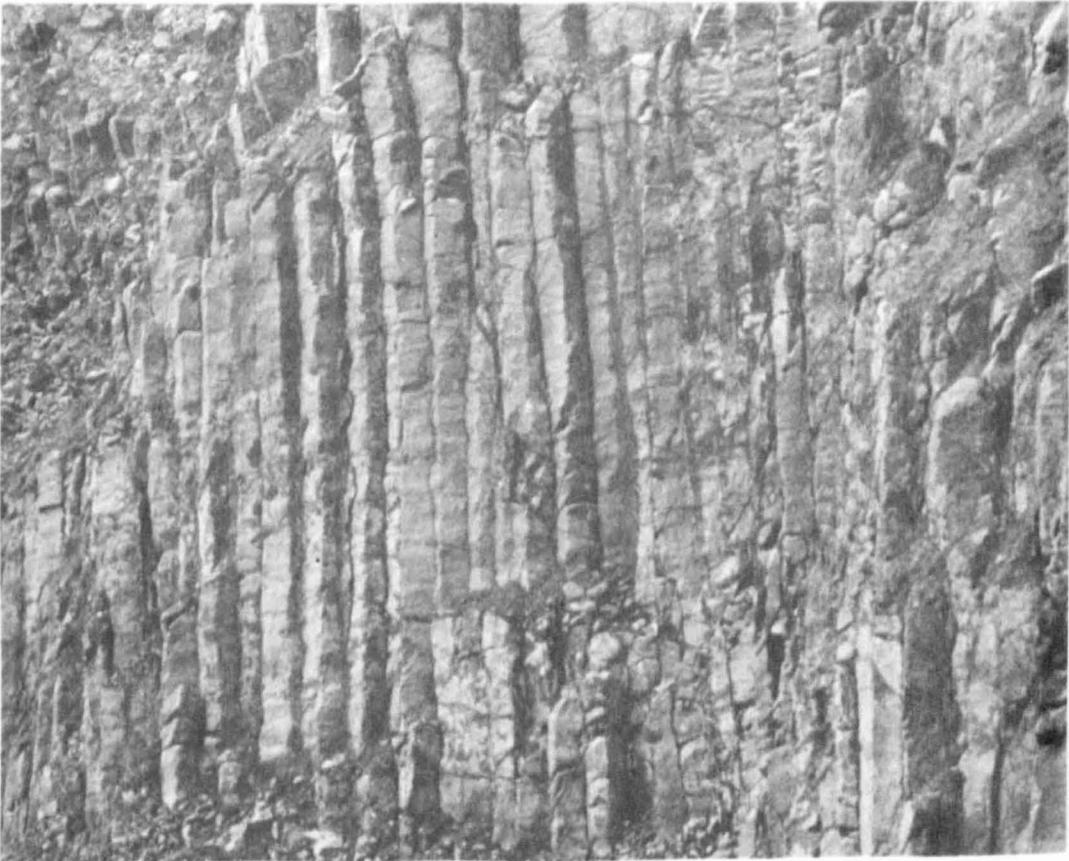


Fig. 2: Close-up of the columnar structure seen in Waterswallows Quarry. (Photo: M.G. Lodge.)



Fig. 1: Millers Dale Lower Lava, Tideswell Dale.



Fig. 2: Close up right-hand side of Fig. 1, showing spheroidal weathering of lava.

The Millers Dale Upper Lava

The Millers Dale Upper Lava (text-fig. 13) can be traced from Earl Sterndale (SK 112.670) northwards to Calton Hill, around Taddington and along the south side of Millers Dale to Litton Mill (SK 160.730). Three small exposures of vesicular lava and vesicular lava in tuff occur in the foot of Cressbrook Dale, at the same stratigraphical horizon and may be a continuation of the Lava. North-west of Millers Dale the Lava forms a cap to Knot Low (SK 134.736) and outcrops around Withered Low (SK 102.764) and Bole Hill (SK 108.767) in the Wormhill area. North of Millers Dale the Lava continues through Tideswell towards Wall Cliff (SK 139.773) where it is replaced locally by a tuff sequence. On Tideslow Moor and northwards to Conies Dale the Lava is poorly exposed but has been intersected by a number of mines. It finally dies out south of Dirtlow Rake.

For the majority of its extent the Millers Dale Upper Lava occurs at the Asbian/Brigantian boundary. In the Millers Dale area a complex interplay of penecontemporaneous subsidence, folding, erosion, and volcanicity has given rise to a locally preserved Brigantian limestone sequence beneath the Lava - the Station Quarry Beds (Cope, 1937; Walkden, 1977).

Chelmorton-Taddington Area

The southerly attenuation of the Millers Dale Upper Lava is defined from recent boreholes reported by the Institute of Geological Sciences (1977b). Previously, information on the Lava came from old mining records and workings at Hubbadale Mine, which intersected it at a depth of 57 fathoms (104.2 m) in Devonshire Shaft (Worley, 1978b). The records indicate that the southerly dipping lava may have formed a sole to some of the rich pipe deposits in the area.

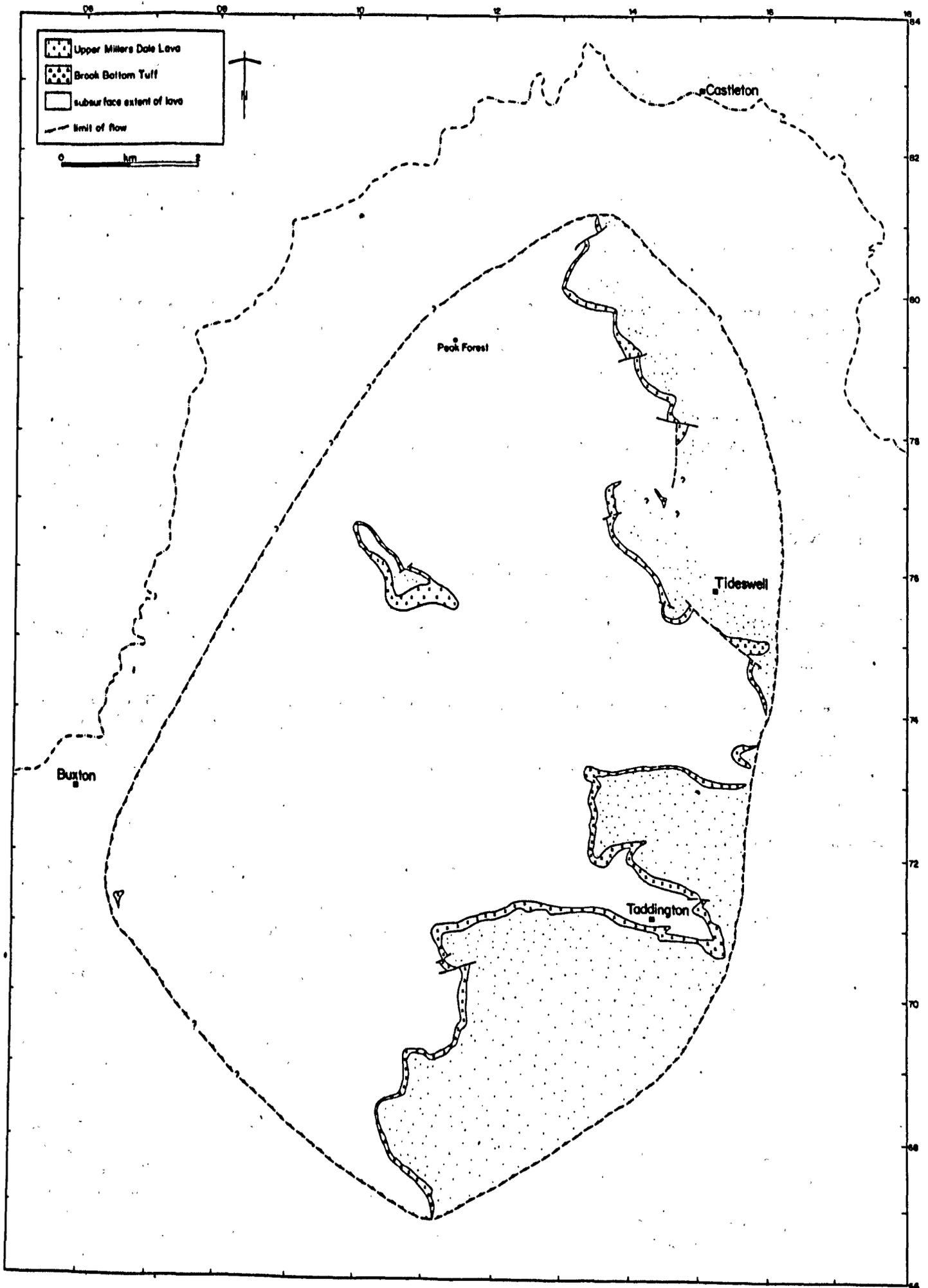
A number of wayboards occur above the Lava. The 'Great White Wayboard' lies 19 m above the Lava and may be the vestige of a lava developed at this horizon to the east, i.e. the Lees Bottom Lava (p.99, this paper). Cox & Bridge (1977), from borehole evidence, confirmed mining records reporting a thick clay horizon 22 m above the weathered amygdaloidal top of the Millers Dale Upper Lava.

To the north of Hubbadale the Lava outcrops around Taddington and Calton Hill where it is intimately associated with the complex intrusive and extrusive sequences (dolerites, tuffs and agglomerates). Between Taddington and Calton Hill the Lava is 15 m thick, while at Taddington (SK 152.711) Cope (1937) recorded a temporary exposure showing a 35° east-facing lava flow-front.

Calton Hill Complex (SK 120.718) (Plate 4, fig. 1)

Calton Hill was recognised by Bemrose (1910) as the site of a vent for the extrusion of the Millers Dale Upper Lava which had subsequently been intruded by a dolerite. He also noted unaltered olivine/pyroxene nodules in the dolerite. The only detailed description of the complex was given by Tomkeieff (1928) who recorded agglomeratic sequences beneath the Upper Lava. The intrusive analcite-dolerite has, in common with a number of Derbyshire sills, invaded a line of weakness along the Lava and large blocks of vesicular lava have been stoped into the dolerite. The roadstone quarry, operated by Derbyshire Stone Ltd. and later by Tarmac, was enlarged subsequent to Tomkeieff's account and a greater complexity of events revealed. Unfortunately no additional general studies were made. Hamad (1963) and Donaldson (1978) investigated the 'peridotite' nodules in the analcite-dolerite and found them to be olivine-orthopyroxene-clinopyroxene-spinel xenoliths, i.e. typical spinel lherzolites in basalts of upper mantle origin.

Subsequent silica-rich hydrothermal activity at Calton Hill (Mueller, 1954; Ford, 1967) gave rise to veining and quartz lined vugs. A zonation of the vugs is apparent, with a central vuggy quartz passing into a zone of calcite on quartz and finally a calcite-barite zone. The pattern suggests an ascension of siliceous fluids via the vent feeder. Prominent fibrous veins are also very common and as at Ible were once thought to be asbestos. They have been shown to consist of clays (saponite) probably replacing a fibrous chlorite (Sarjeant, 1967; Curtis, 1976).



Text-fig. 13: The geographical distribution of the Upper Millers Dale Lava.

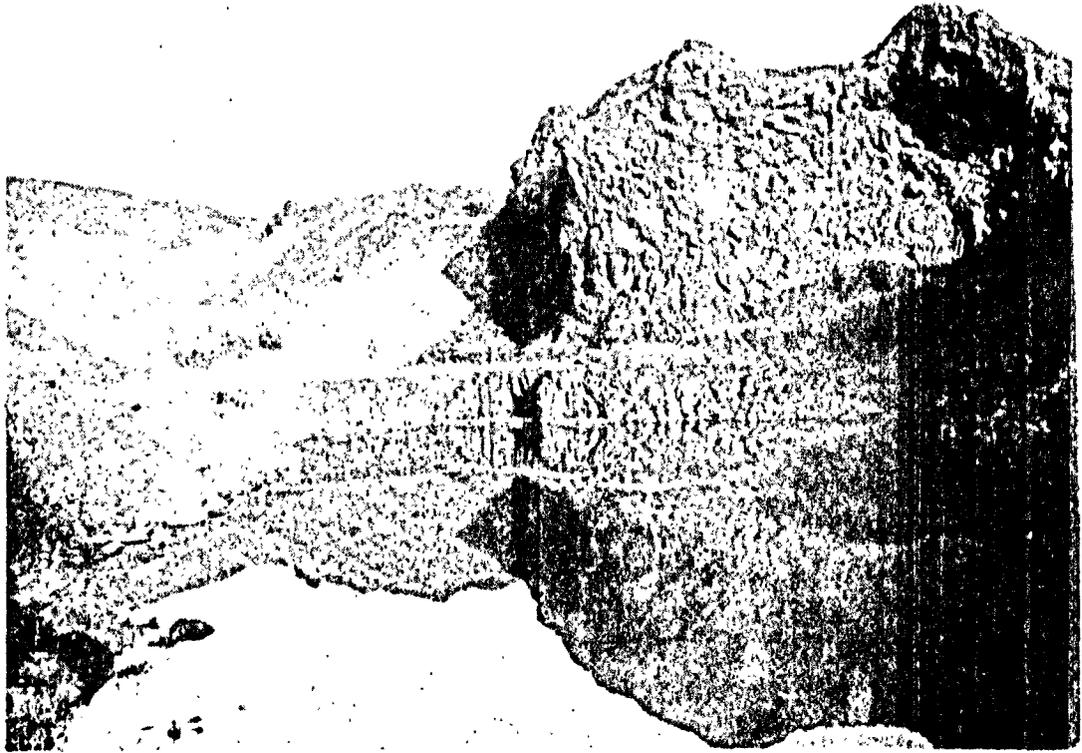


Fig. 1: Calton Hill Site of Special Scientific Interest. Reflection in water of basaltic columns and agglomerate bluff.

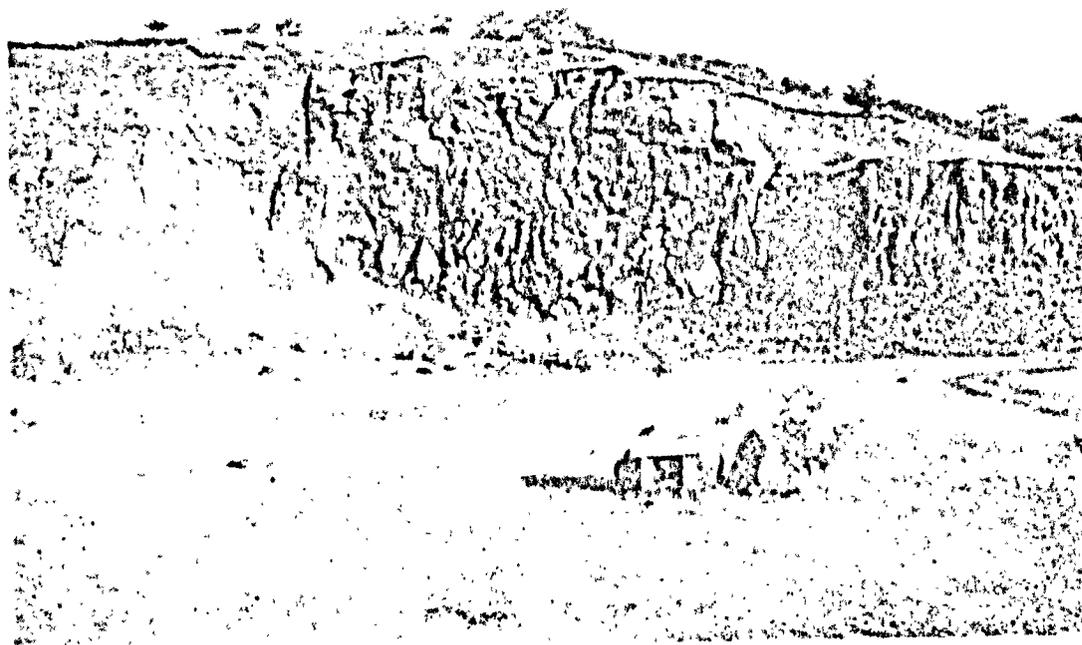


Fig. 2: Tideswell Dale Quarry picnic site. Millers Dale Lower Lava and Dolerite..

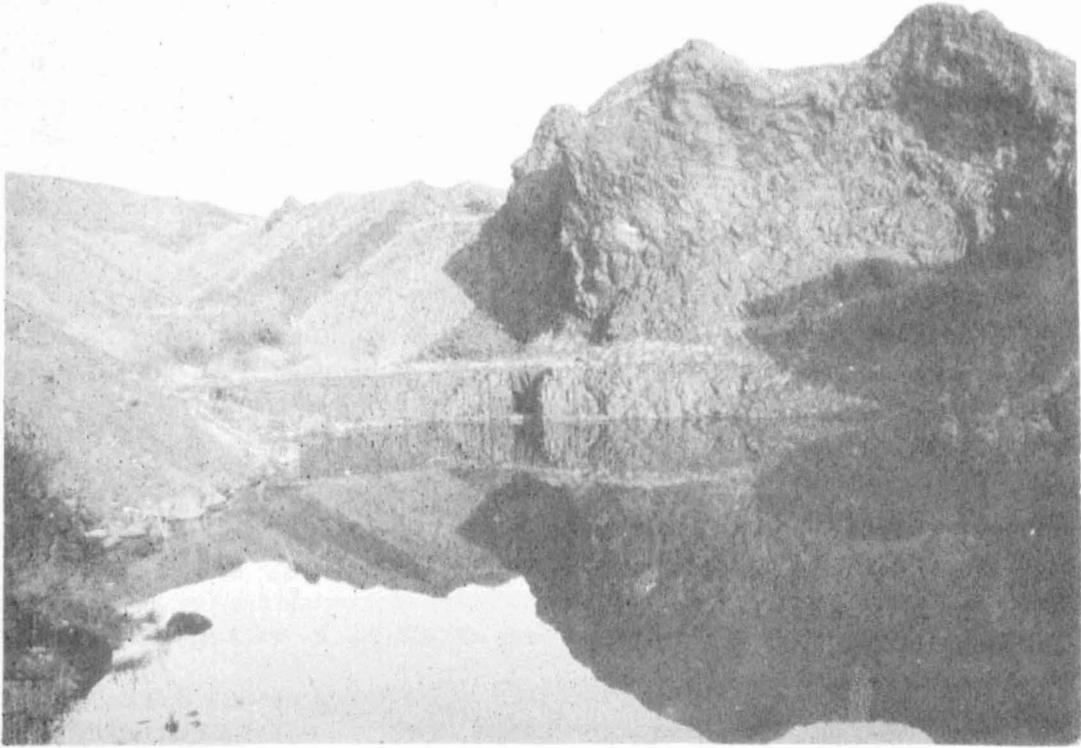


Fig. 1: Calton Hill Site of Special Scientific Interest. Reflection in water of basaltic columns and agglomerate bluff.

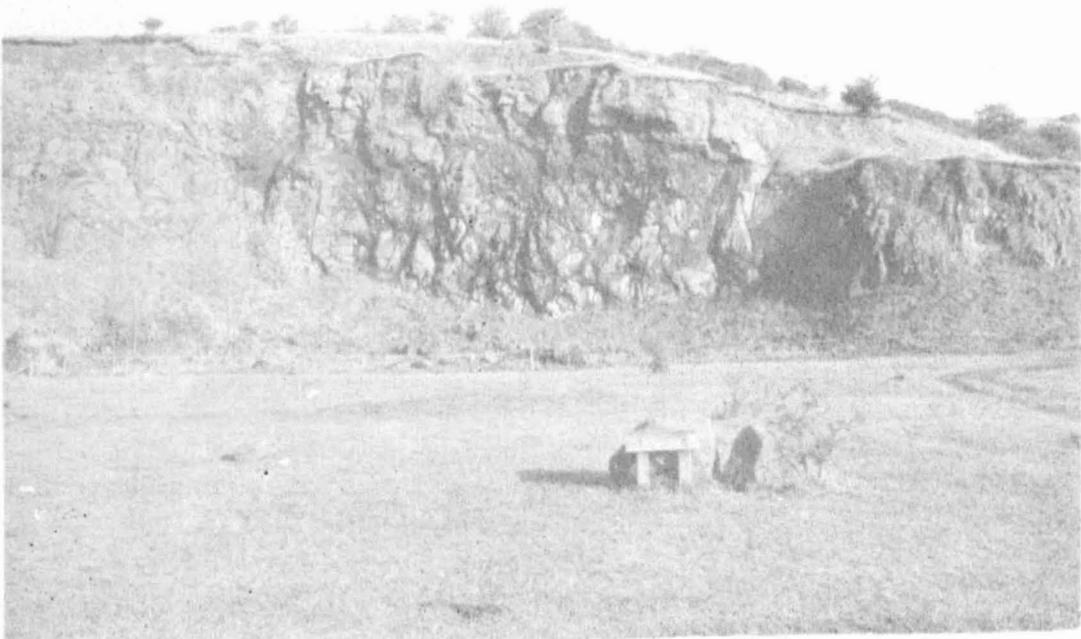


Fig. 2: Tideswell Dale Quarry picnic site. Millers Dale Lower Lava and Dolerite.

Millers Dale

The Upper Lava is exposed in a number of quarries in Millers Dale (SK 134.731). Bemrose (1894, 1907) noted a continuous exposure of the complete sequence of igneous rocks in the Lime Works Quarry (SK 140.730). It was 35 m thick and capable of subdivision into at least two distinct extrusive events, a 5.2 m thick sequence of tuffs with a thin amygdaloidal basalt was overlain by a thick lava (text-fig. 14). Although Bemrose's section is no longer visible, two small quarries (SK 134.731 and 134.730) to the west of the old lime works are clearly in the thick lava sequence and expose 10 m of non-vesicular, holocrystalline basalt with spheroidal weathering. A similar exposure is observed in quarries on Knot Low (SK 134.736) to the north of the dale where Sargent (1917) noted 'spilitic affinities' for the altered, vesicular lower portions of the flow. The maximum development of the Millers Dale Upper Lava is 35 m.

East of the Lime Works the Lava forms a prominent feature above the disused railway line as far as Litton Mills. It is exposed in the adit of Maury Mine (SK 150.731) where a vein persists into the Upper Lava and produces a zone of intense bleaching and argillisation. Farey (1811) recorded the extraction of lead ore from within the Lava and mineralised lava including galena and sphalerite may be found on the old mine dumps. The Lava terminates in a flow front above Litton Mills in the railway embankment near to Litton Tunnel entrance. The rapid attenuation of the Lava was noted by Green *et al.* (1867) but was subsequently interpreted as a fault by Bemrose (1907). Cope (1937) considered it to be a flow front and this was supported by Walkden (1977) who demonstrated a complex relationship between the exposed flow front, flows within the Upper Lava and the local preservation of the Station Quarry Beds.

Bemrose's division into an upper major flow and a lower thinner unit enables the flow front at Litton Mills to be equated with the more extensive upper flow. Each extrusive event was accompanied by a measure of uplift, erosion and folding. At Litton Mills, the upper flow has over-ridden the thinner lower flow. The strong brecciation, palagonitisation and crude stratification seen in the flow front suggest the entry of the lava into shallow water giving a flow front breccia (Jones & Nelson, 1970). The bentonitic clay exposed above the Litton Tunnel entrance exhibits a relict vitroclastic texture in contrast to the typically amorphous bentonitic clays seen in the limestone sequence (Walkden, 1972). This implies that it is the lateral equivalent to the flow front breccia.

Cressbrook Dale

The lava which outcrops at the horizon of the Millers Dale Upper Lava in Cressbrook Dale (SK 174.727) is difficult to reconcile with the geographical distribution of the Millers Dale Upper Lava (text-fig. 13). The partial distributional analysis given by Butcher & Ford (1973) has been invalidated by the Institute of Geological Sciences' officers (1976) who considered that the Shacklow Wood Lava of the Sheldon area (p.100 this paper) lies at a stratigraphically higher horizon than the Millers Dale Upper Lava. Walkden (1977) inferred a deep embayment in the distribution of his 'lower extrusive phase' to accommodate the lava at Cressbrook Dale. It is more probable that this lava which the authors refer to as the Cressbrook Mill Lava represents the western edge of one of the flows from the Longstone Edge area that lies at the same horizon as the Millers Dale Upper Lava.

Wormhill-Harpur Hill

The Upper Lava outcrops on Withered Low and on Bole Hill where the Institute of Geological Sciences' officers (1976a) have mapped limestone intercalations. It thins to the north decreasing from 30 m at Bole Hill to between 3-4.5 m on Withered Low.

The western limit cannot be defined in detail for basal Brigantian strata are not present in the Great Rocks Dale area, and where they are present around Dove Holes, the Lava is absent. This fact implies a limit to the flow in the Great Rocks Dale/Waterswallows area. Likewise the Lava is absent around Buxton and Hind Low to the south, but it is present at Harpur Hill (SK 066.713) and allows a limit to be defined as shown on text-fig. 13.

Tideswell-Dirtlow Moor Area

The flow front above Litton Mills can be traced north towards Tideswell. At the junction of Tideswell and Litton Dales, the Millers Dale Upper Lava is 18 m thick. The Litton Dale Borehole (SK 160.750) located 350 m further east proved only 3 m of weathered lava. To the north-west of Tideswell, the Lava continues as far as Wall Cliff (SK 139.773). In a faulted area with minimal exposure, the Lava is the lateral equivalent to a bedded tuff sequence - the Brook Bottom Tuff of Bemrose (1907). This tuff may represent a small cone against which the lava thins, analagous to the situation at Grange Mill (p. 93 this paper) but on a smaller scale.

The geographical distribution of the Millers Dale Upper Lava (text-fig. 13) is asymmetrical with respect to the position of the known vent at Calton Hill. This implies an additional feeder vent associated with the northern outcrops. The disappearance and reappearance of the lava at Wall Cliff may be a reflection of the interplay between these source areas for the Lava.

The Upper Lava is exposed in White Rake opencast site (SK 146.782) on Tideswell Moor. A minimum thickness of 15 m of weathered lava is observed on the northwall with marmorized limestone inclusions up to a metre in diameter included in the Lava. The Tideswell Moor area is remarkable for the persistence of mineral veins which cut lava flows, for altered and mineralised blocks of lava occur in the spoil from a number of mines (Walters, 1980).

North of Tideslow Farm (SK 154.782) the Lava is poorly exposed, but has been proved in a number of mines and its outcrop is displaced by rake veins. It forms a feature around Cop Round (SK 126.797) where it is some 6 m thick (Moore, 1903) and finally dies out in the region of Old Moor Mine south of Dirtlow Rake (SK 136.811).

Bradwell-Little Hucklow Area

The Millers Dale Upper Lava underlies part of Bradwell Moor and is 9.1 m thick in a shaft on Moss Rake, near Rake Head Mine (SK 143.800). Green *et al.* (1887) noted a toadstone 3.7 m thick at a depth of 87.8 m near this locality which was referred to as 'the clay' in mining records and correlated with the attenuating Upper Lava. Likewise in the Hucklow area, the Lava cannot be accurately defined. A toadstone 45 m thick at a depth of 95 m in Shuttle Rake Mine (SK 160.796) occurs stratigraphically higher than the Upper Lava and its thickness suggests a correlation with the Cressbrook Dale Lava of the Eyam area. Within the Bradwell-Hucklow area the stratigraphical horizon at which the Millers Dale Upper Lava may occur has not been penetrated and hence conclusions cannot be formulated, with respect to its north-eastern extent.

The Peak Forest Sill

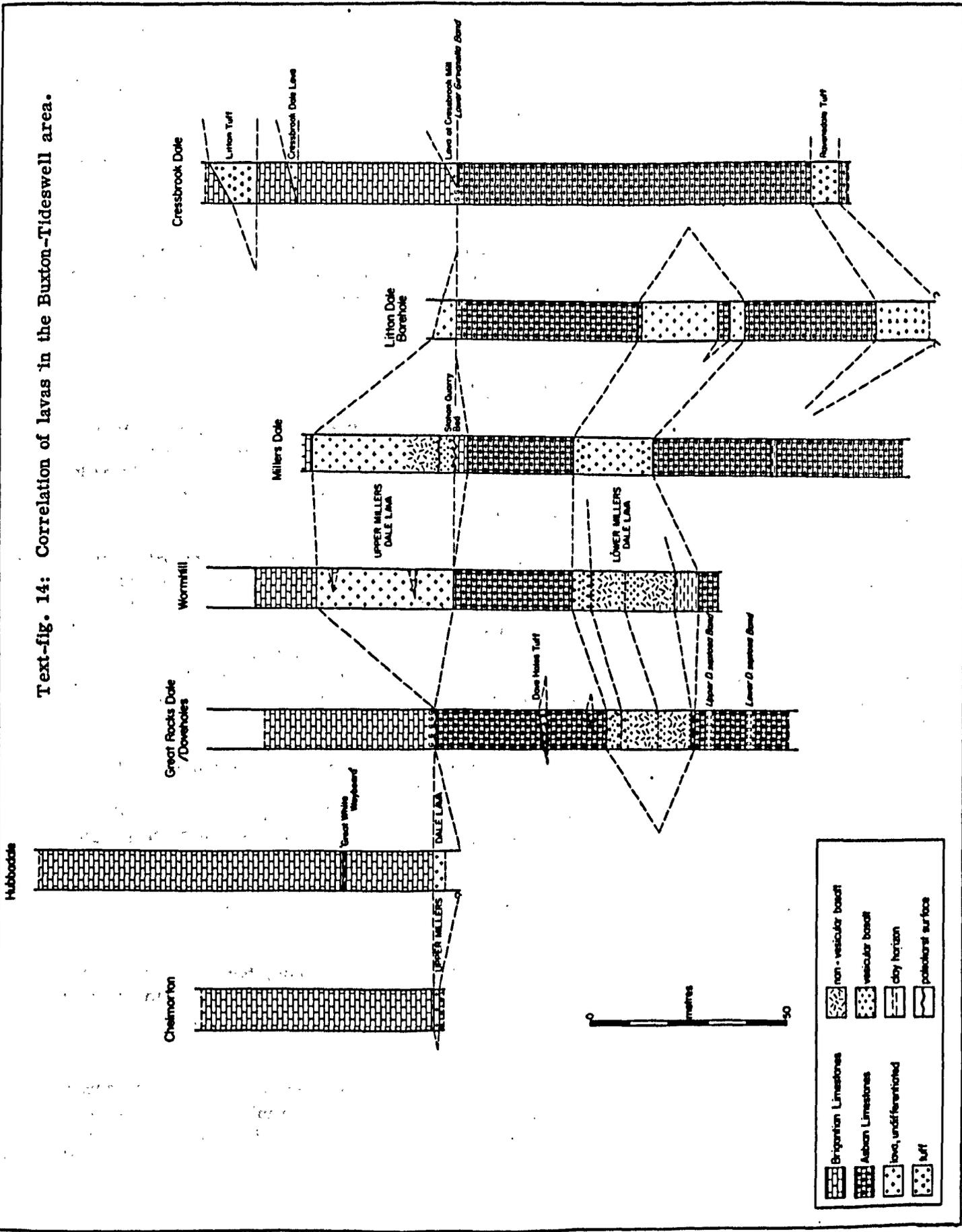
The Peak Forest Sill is a non-vesicular coarse olvine dolerite intruded in the axis of the Peak Forest Anticline. It was first described by Geikie (1897) and its upper contact phenomena were noted by Barnes (1902a and b). The base is not exposed hence a thickness is not known. The exposure, by Mill Cottage in Dam Dale (SK 116.788), shows the attendant marmorisation of the overlying limestones for 10 m from the contact the limestones are strongly dolomitised. The fine grained sub-ophitic dolerite has undergone extensive silicification and calcitisation. Additional localities are located at Damside Farm (SK 115.787), Backlane Farm (SK 107.789 and SK 107.790) and Newhouses Farm (SK 111.785). Text-fig. 11 illustrates the geographical distribution of the sill.

The Potluck Sill

The Potluck Sill, described by Bemrose (1907) occupies much of Tideswell Moor. Exposures are minimal, with the only occurrence at Pittle Meer (SK 136.783). Additional evidence for the geographical extent of the sill is to be found in the debris around old mine shafts and workings.

Green *et al.* (1887) state that Black Hillock Shaft (SK 141.782) proved 600 ft. (183 m) of

Text-fig. 14: Correlation of lavas in the Buxton-Tideswell area.



'toadstone' and the base was not reached. Stevenson *et al.* (1971) proposed that the shaft probably followed a feeder to the sill. A more detailed account of the locality, as recorded in mining documents, has been presented recently by Walters (1980). Stevenson *et al.* (1971) wrote that the Sill is a coarse ophitic olivine-dolerite, gave a modal analysis and a petrological description.

Mount Pleasant Sill

Initially described in 1907, Stevenson *et al.* (1971) noted that Bemrose did not appreciate its full extent. They reported ploughed igneous debris near Batham Gate (SK 126.786 and SK 130.787) as well as similar material further east (SK 131.788).

The sill appears to show an alignment along the line of Shuttle Rake and Faults, south of Hernstone Lane Head (SK 120.787). It has been suggested (Stevenson *et al.*, 1971) that Shuttle Rake exercised considerable influence on the intrusion of the Sill, but this is impossible to substantiate given the extent of exposure.

The Castleton Area

The igneous horizons were first noted by Faujas de St. Fond (1797) in Nunley's Mine, Pindale (SK 158.823). Green *et al.* (1887) reported 12 fathoms (21.9 m) of toadstone in Dirlow Mine (SK 155.822) and a 'light greenish variety of the toadstone' beneath the 'Yoredale Shales' at Pindale (or Ashtons) mine (SK 164.825). The Cave Dale Lava and Speedwell 'vent' were described by Geikie (1897) and Bemrose (1894, 1907).

Holkerian igneous activity was advocated by Stevenson *et al.* (1971). In reporting the log of the Eldon Hill Borehole (SK 113.816) they recorded 30.5 m of tuffaceous material, 68.6 m below the top of the Woo Dale Beds. Ford (1952) noted a thin clay horizon at a similar stratigraphical horizon in Speedwell Cavern. Hudson & Cotton's (1945a) paper on the Alport Borehole (SK 136.911) indicated 'basinal' facies of the S₂ (Holkerian) as containing 6 m of dark limestones and mudstones with tuffaceous bands and fragments of eroded tuff. This horizon, 110 m below the top of the Holkerian limestones, may equate with the Eldon Hill Tuff.

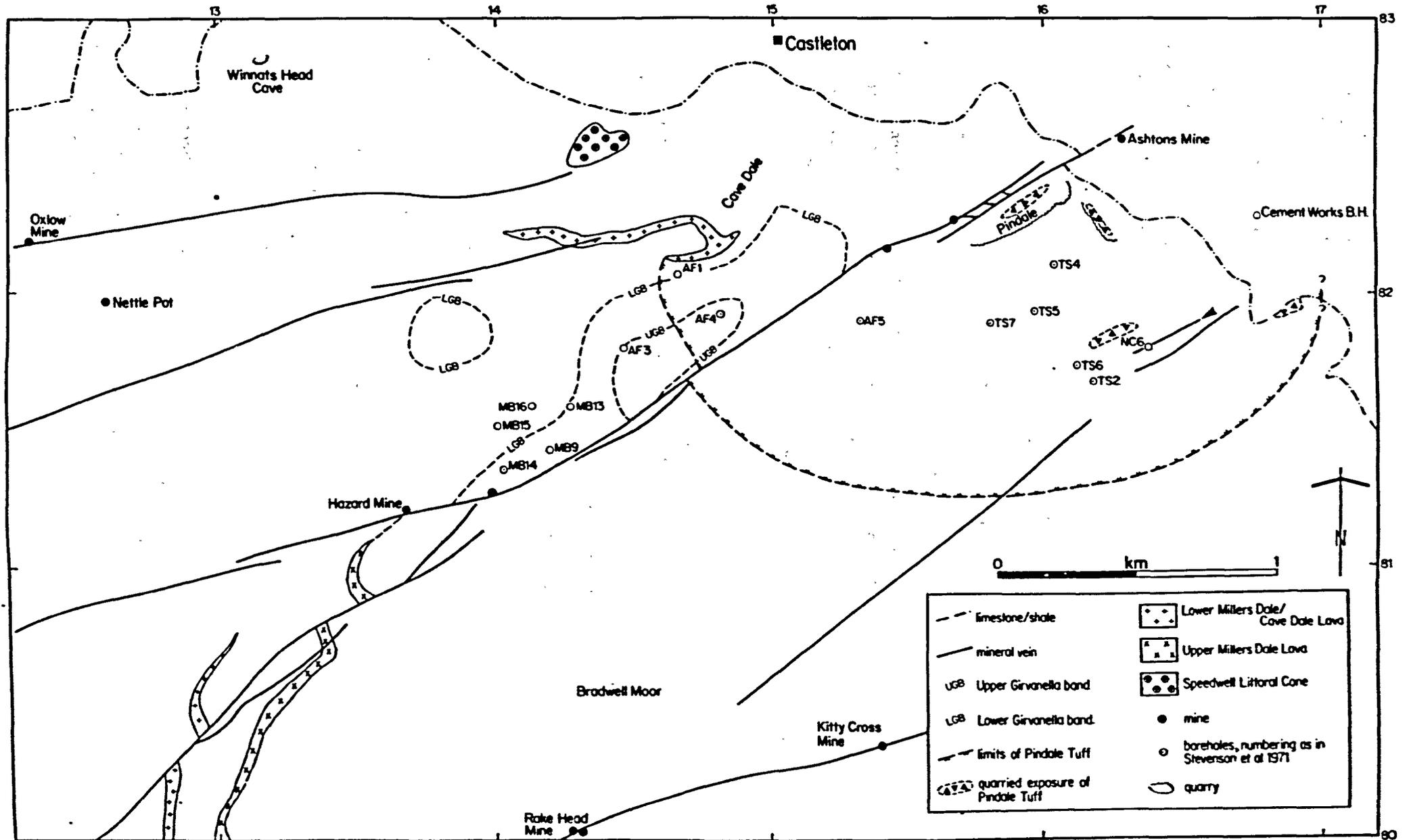
Lower Asbian igneous activity has been intersected in a number of boreholes, and at least two distinct episodes are evident. In the Eldon Hill Borehole, Wright (1979) noted a 3 m thick basalt at a depth of 12 m (i.e. 70 m above the base of the Asbian). This places it below the lowest *Davidsonia septosa* band and hence below the horizon of the Millers Dale Lower Lava. Exploration boreholes on Bradwell Moor have, according to Jefferson (1979, and pers. comm.), intersected a thin tuff at a similar horizon. These two occurrences may be part of the same minor Lower Asbian eruption, however lack of intervening information makes this a very speculative correlation.

To the west of the Blue Circle Group's limestone quarry at Hope, borehole core logs have delineated the eastern limit of a thick tuff sequence stratigraphically beneath the 'Pindale Tuff' (text-fig. 16). It grades downwards into a coarse agglomerate, locally associated with vesicular basalt. The extrusive centre was probably on the Bradwell Moor area.

The igneous activity, spanning from the Holkerian to the Brigantian (S₂ to D₂) is characterised by pyroclastic deposits. The result is a complex palaeogeographic interplay between the volcanics and the back reef, fore reef and basinal calcareous shale facies. The extrusive activity here is unrelated to the contemporaneous proximal events centred on Millers Dale to the south.

The Pindale Tuff

Quarry exposures and the interpretation of numerous borehole logs from the ground to the south of Pindale have demonstrated the presence of a major tuff and volcanic cone - the Nunlow Tuff of Shirley & Horsfield (1940) or the Pindale Tuff of Stevenson *et al.* (1971). Shirley and



Text-fig. 15: A detailed geographical distribution map of igneous horizons in the Castleton area.

Horsfield considered that it was located at the base of the D₂ (Brigantian) limestones, but Eden *et al.* (1964) demonstrated that the horizon is D₁ (mid-Asbian) in age and is hence at a similar stratigraphical horizon to the Millers Dale Lower Lava.

The Pindale Tuff was exposed in the lower bench of Blue Circle's Hope Cement Works Quarry as an elongate mound-like structure according to Shirley & Horsfield (1940). It marked the site of a WNW-ESE aligned volcanic cone. The exposure, with a maximum dilation of 20 m, illustrated a central coarse ungraded agglomerate with included limestone fragments, while the extremities, with 30° marginal dips, were finer grained and well sorted. Stevenson *et al.* (1971, plate V) illustrated a generalised isopach map of the Pindale Tuff, which inferred the presence of a second unexposed volcanic cone to the north of the quarry. Their interpretation was based on a 65 m thick tuff sequence intersected in borehole TS4 (text-fig. 15). Subsequently D.P. Jefferson (pers. comm.) has proved the presence of a major fault between the quarry and borehole TS4 and postulates that fault repetition may explain the unusual thickness of tuff encountered in that borehole rather than a hypothetical second cone structure.

The southerly limit of the Pindale Tuff is defined in detail (text-fig. 15) and indicates that both the Millers Dale Lower Lava and the Pindale Tuff are either absent or represented by a thin tuffs/clay horizons on Bradwell Moor.

Stevenson *et al.* (1971) indicated that the Millers Dale Lower Lava is stratigraphically above the Pindale Tuff in the Michill Bank area to the west of Hope Cement Works Quarry. The attenuated lava is traced in boreholes as a thin (0-2 m) weathered tuff horizon east of Hazard Mine Shaft (SK 137.813) whilst in borehole AF1 (Stevenson *et al.*, 1971, plate IV) the tuff, noted as a 'clay parting', is recorded some 7 m above the Pindale Tuff and is 10 m above the Cave Dale Lava in Roger Cliff (Cave Dale).

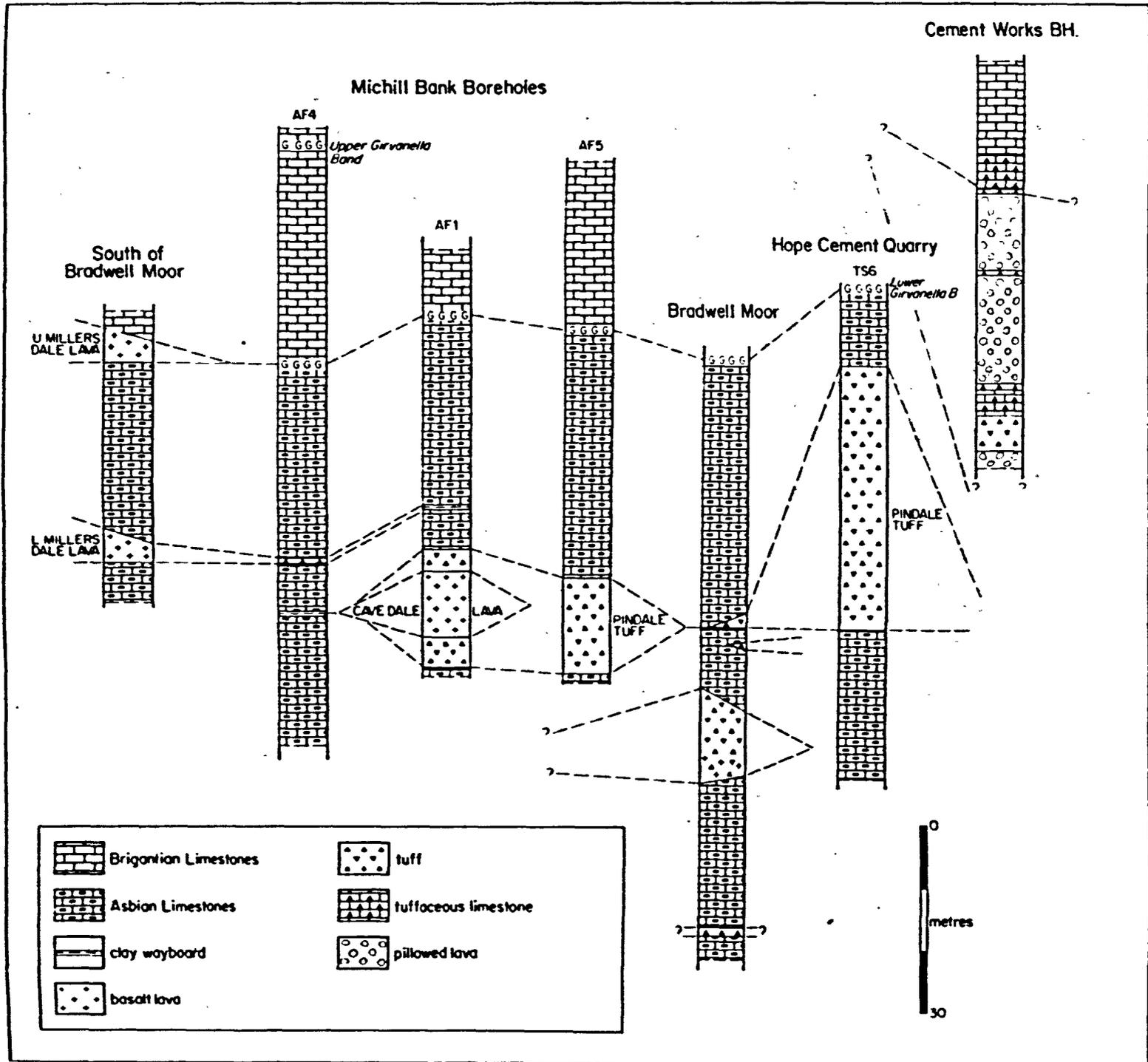
The Cave Dale Lava

The amygdaloidal Cave Dale Lava is exposed near the head of Cave Dale (SK 148.822) where a 7.6 m section is visible. Shirley & Horsfield (1940) proposed that the lava was at the same stratigraphical horizon as the Millers Dale Lower Lava. However, as they considered that the Cave Dale and Millers Dale Lower Lavas were part of the same flow, they attributed the absence of lava in the Dirlow Moor area, S.W. of Cave Dale, as due to the effects of a postulated D₁ (mid-Asbian) erosional episode. Stevenson *et al.* (1971) refuted this proposition and from evidence provided by borehole cores, showed that the Cave Dale Lava was a flank eruption of the main cone, from which the Pindale Tuff was ejected.

The Cave Dale Lava is traced at outcrop for a short distance (700 m) to the west of Cave Dale. A number of wayboards in the mines and caves around Castleton may represent the lava's lateral extent. A 0.3 m weathered clay in Winnat's Head Cave is located at the same stratigraphical horizon as the Cave Dale Lava. Nettle Pot (SK 126.819) exposes two clay horizons, the first at a depth of 45 m is 1.0 m thick and the second thinner horizon is 8 m lower in the succession. Ford (1952) referred to these horizons as 'clay beds with amygdaloids' and implied they were decomposed lava. The upper horizon occurs to the NW where it is exposed in Oxlow Mine (SK 125.822). Subsequently, Ford (1977) considered that these 'clays' represent 'flows in the Cave Dale Lava'. The Millers Dale Lower Lava, it is proposed, may extend as far as Nettle Pot and another explanation is that the two clay horizons are the remnants of both the Cave Dale and Millers Dale Lower Lavas.

Speedwell Littoral Cone

The outcrop of 'igneous material' near Speedwell Cavern (SK 143.825) has been the subject of a number of publications. It was interpreted as a vent by Geikie (1897, p.16), Bemrose (1907, pp.250-1), Shirley & Horsfield (1940, p.294), Wilkinson (1967, p.49) and Stevenson *et al.* (1971, p.301). Broadhurst & Simpson (1973) however, suggested that it represented a fragmented portion of Cave Dale Lava Flow which had spilled over the dry apron reef slope. This interpretation has been supported by Cheshire & Bell (1977) who demonstrated the hyaloclastic nature of the 'agglomerate' and considered it to have been



Text-fig. 16: Correlation of lavas in the Castleton area.

formed in the tidal zone at the foot of the reef slope. This interpretation would imply an emergence of some 100 m in the mid-Asbian. The 'vent' is now considered to be a littoral cone.

Brigantian Activity

Fearnside & Templeman (1932) described the sequence in the Hope Cement Works borehole (SK 1678.8228) which intersected pillow lavas and tuffs 21.3 m below the base of the Namurian. Three vesicular pillow lavas, the lowest not penetrated, totalled 28.3 m in thickness and were separated by 13.1 m of tuff and tuffaceous limestone. Fearnside & Templeman considered that the sequence was unable to be correlated with adjacent volcanic horizons and stated that they represented an unexposed vent in the vicinity. Eden *et al.* (1964) regarded the sequence as equivalent to the Pindale Tuff and hence implied an unconformable junction between the lava and the succeeding limestones. This hypothesis was rejected by Stevenson *et al.* (1971, p.113) who pointed out that the overlying limestones (with a Brigantian fauna) contained tuff bands and tuffaceous partings which suggested an association between the limestones and volcanics. They stated that the igneous rocks are upper P₁ (upper D₂) or P₂ in age and lie near an unexposed eruptive centre. This interpretation is supported by logs of the Alport (SK 136.911) and Edale Boreholes (SK 108.849) described by Hudson & Cotton (1945b). Both showed extensive tuff horizons in lower Brigantian 'basinal' facies. It is proposed that the pyroclastic components of the pillow lava sequence in the Hope Cement Works, Alport and Edale Boreholes are all of the same extrusive event.

The tuff in the Alport Borehole consists of altered palagonite, carbonated shards and glass fragments, indicative of submarine eruptions. It is interesting that the only record of a major pillow lava sequence amongst the Derbyshire volcanics should be associated with deep water 'basinal facies' strata.

4. The Eyam-Longstone-Litton Region

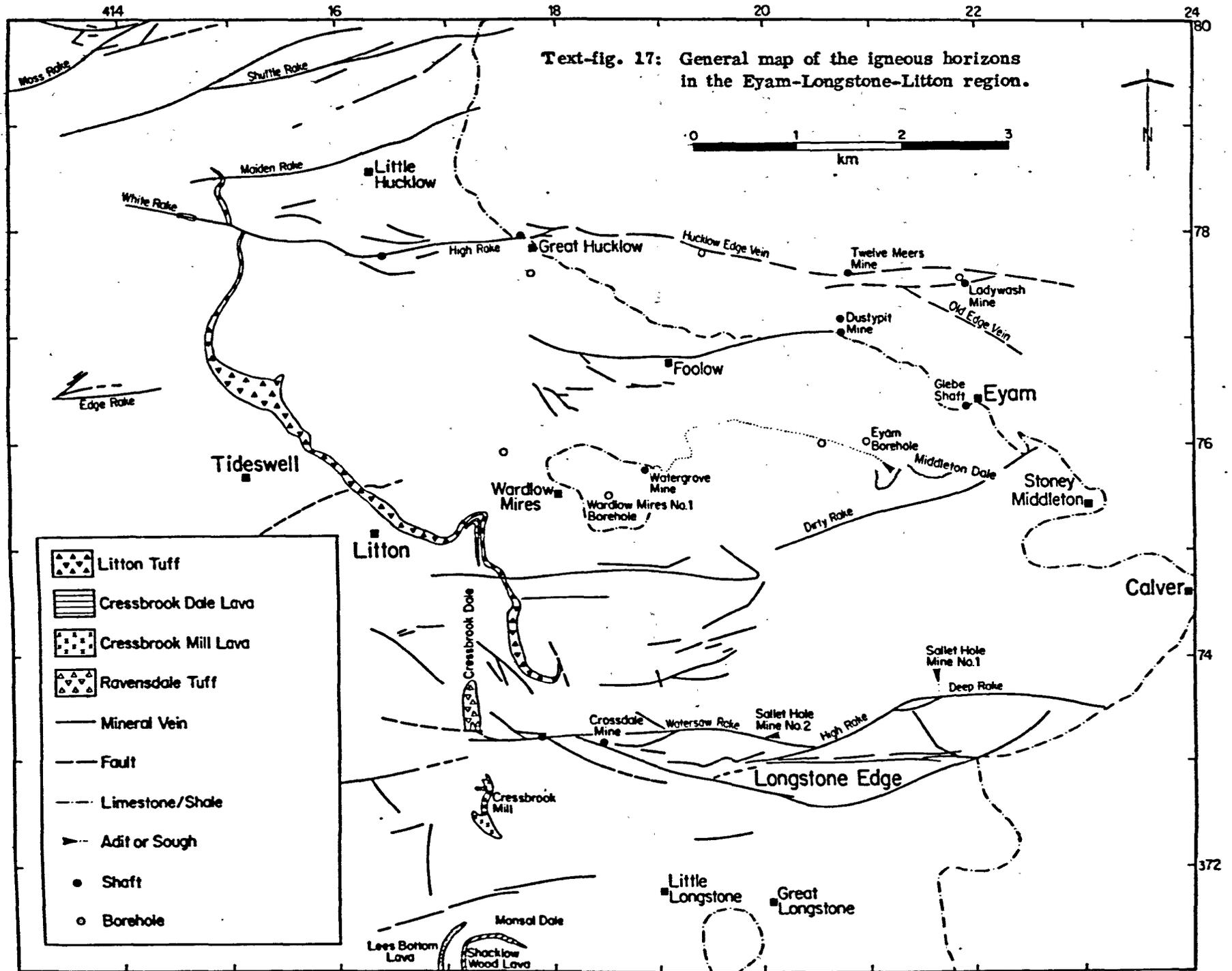
The igneous rocks (lavas and tuffs) in the north-eastern part of Derbyshire are poorly represented at outcrop (text-fig. 17). They have been intersected in numerous mines and boreholes from which it is inferred that they are of considerable sub-surface extent. Indeed many of the units are better developed than the lavas and tuffs in the Matlock and Millers Dale areas.

The Cressbrook Dale Lava and the Litton Tuff are well documented horizons; however a further three major tuff horizons (the Longstone Edge Upper, Middle and Lower Tuffs) are recorded here for the first time and an extensive lava, the Cressbrook Mill Lava, is separated from the Cressbrook Dale Lava.

Stratigraphical Complexities

Brigantian limestones (Monsal Dale and Eyam Limestones) dominate the surface stratigraphical succession where typical exposures are seen in Eyam Dale (Stevenson *et al.*, 1971). Information with respect to the underlying horizons and especially the complete Asbian succession has been provided only by the Eyam Borehole (Dunham, 1973) located to the north of Middleton Dale (SK 2096.7603). A 162 m succession of 'normal massif facies' limestones was intersected in the 1851.0 m deep borehole, which compares favourably with 160 m of Asbian limestones and volcanics intersected by the Severn-Trent Water Authority's borehole and surface exposures in Millers Dale (p.113, this paper). However, the lavas present in Millers Dale are not developed around Eyam. For example, a coarse tuff (18.6 m thick) at a depth of between 256.8 and 275.4 m and a thin (0.63 m) tuff at 286 m, both within the upper Asbian succession of the Eyam Borehole (Dunham, 1973) are not exposed in the Eyam area. They represent localised activity, which post-dated the extrusion of the Millers Dale Lower Lava to the west.

Text-fig. 17: General map of the igneous horizons in the Eyam-Longstone-Litton region.



In contrast to the Asbian succession, the Brigantian Monsal Dale Beds illustrate complex facies and thickness variations related to the development of contemporaneous downwarping with respect to the more stable areas of Longstone Edge to the north and Monyash-Sheldon to the south. This palaeogeographical interplay and facies variation introduces complexities in the attempted correlation of relatively localised volcanic sequences, as palaeontological marker horizons are not well developed. (Shirley & Horsfield, 1945).

The major facies change, which effects the Lower Monsal Dale Beds, particularly below the horizon of the Cressbrook Dale Lava, is an area of subsidence in the Eyam-Calver area. Thus, some 60 m of limestone are present beneath the Cressbrook Dale Lava in Cressbrook Dale and 54 m of limestone beneath the same lava in the Ladywash Borehole (SK 218.776) while 109 m were proved by the Eyam Borehole. Above the horizon of the Cressbrook Dale Lava the main areas of subsidence are centred on Wardlow Mires and Great Longstone (text-fig. 17).

Stevenson *et al.* (1971) reported some 120 m of Monsal Dale Beds above the Cressbrook Dale Lava in Wardlow Mires No.1 Borehole. These limestones decrease in thickness to 100 m in Cressbrook Dale and the Littonfields Borehole (SK 175.759). To the east 70 m are recorded in Dusty Pit Mine Shaft (text-fig. 17), 70 m in the Middleton Dale area and 60 m in the Ladywash Borehole. Hucklow Edge No.1 and 2 Boreholes penetrated 62.5 m according to Stevenson *et al.* (1971). Further to the west, in the region of Great Hucklow, these limestones thicken to approximately 80 m. The major part of this variation is the result of subsidence in the Wardlow Mires area during the deposition of the Lower Monsal Dale Limestones above the Cressbrook Dale Lava and below the Upper Girvanella band; differential subsidence had largely ceased prior to the deposition of the Lower Shell Bed (text-fig. 18).

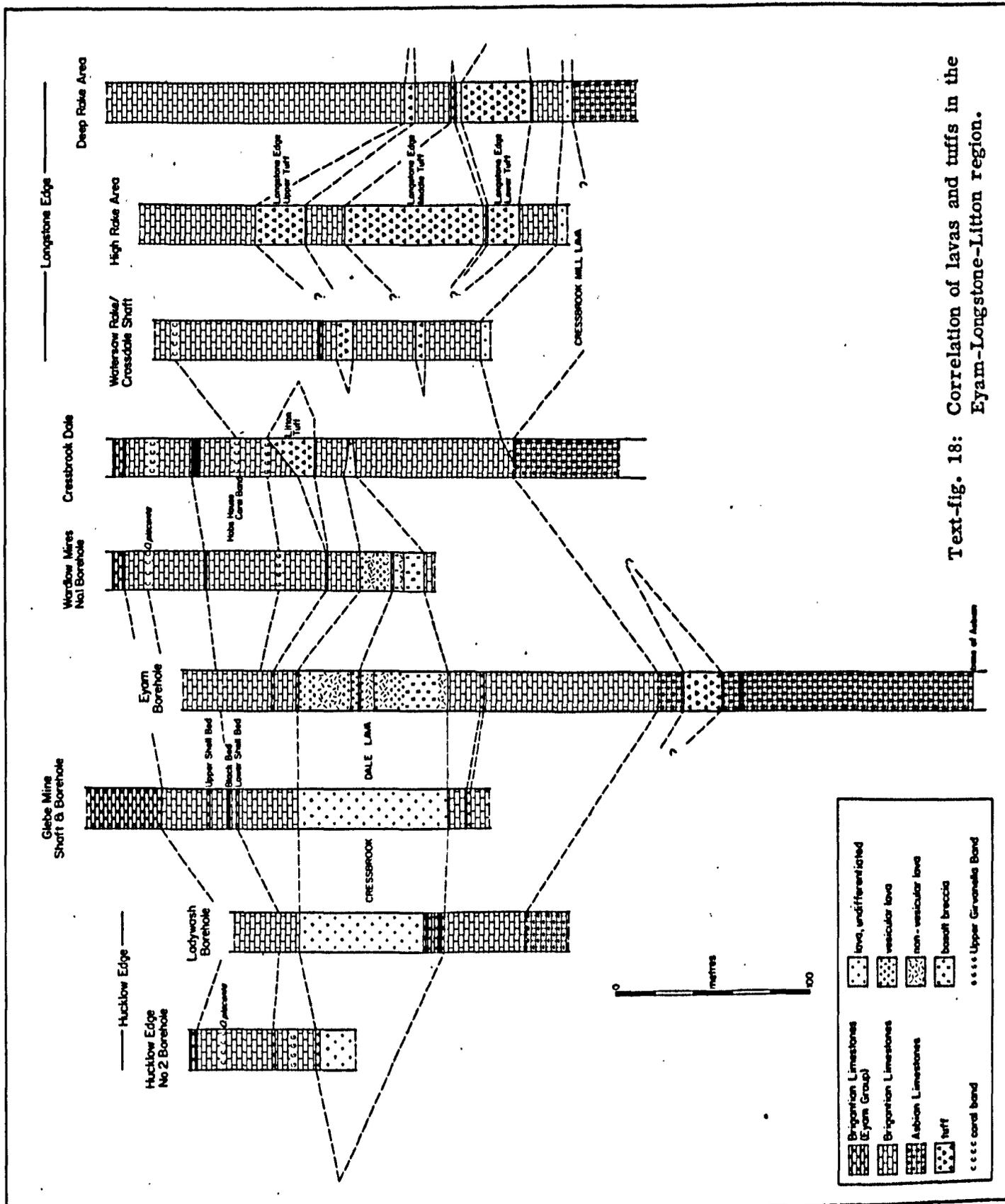
Within this stratigraphical framework the region can be divided into two areas each characterised by extrusive centres. The Eyam-Litton-Hucklow area including the Litton Tuff and the Cressbrook Dale Lava, and Longstone Edge which has complex tuff sequences.

The Cressbrook Dale Lava

The Lava has a restricted, poorly exposed outcrop near the head of Cressbrook Dale where it is 10 m thick and occurs 5 m below the horizon of the Litton Tuff. The Lava thins to the south-east and is absent in a shaft on Wardlow Sough Mine (SK 176.748) some 300 m away. It does not outcrop around Tideswell nor extend into the Longstone Edge area.

In a north-easterly direction it has a considerable sub-surface development. The Littonfields Borehole (SK 175.759) indicated that the Cressbrook Dale Lava was 33.8 m thick, and the Wardlow Mires No.1 Borehole proved a total thickness of 33.5 m. The Lava attains its maximum recorded thickness in the Eyam area, the evidence being provided by a number of boreholes. Dunham (1952) reporting a borehole to the north of Glebe Mine shaft, indicated that the Lava was 76.2 m thick with a 1.5 m thick volcanic horizon 10 m below the base of the Lava. More recently the Eyam Borehole proved the Cressbrook Dale Lava to be 76.6 m thick with a corresponding tuff (1.55 m thick) 14 m stratigraphically lower (Dunham, 1973). Additional confirmation that the Lava attained its maximum development in the Eyam area was provided by the Ladywash Borehole which intersected a 63.4 m thick lava underlain by the 10.7 m thick sequence of thin tuffs, clays and pyritic limestones (Schnellmann and Willson, 1947). The Derwent Water Authority's borehole near the west end of Middleton Dale (SK 205.760) intersected 50 m of lava overlain by a 1.5 m thick tuff, but did not pass through the flow.

Examination of the Wardlow Mires No.1 and the Eyam Borehole cores of the Cressbrook Dale Lava have enabled the internal flow structures to be elucidated (text-fig. 18). The predominant features are breccias in the lower part of the unit, and comparable with the 'auto-breccias' or 'flow breccias' described from the Haddonfields and Ashover area (p.103, this paper, and Ramsbottom *et al.*, 1962). They consist of oxidised angular fragments of either vesicular or non-vesicular basalt set in a matrix of silica and chlorite. The breccias interdigitate with non-brecciated lava flows. In the Eyam Borehole the lower breccia sequence is 22 m thick, while 17 m are developed in the Wardlow Mires area. Core samples indicate the presence of similar breccias in the Ladywash Borehole.



Text-fig. 18: Correlation of lavas and tuffs in the Eyam-Longstone-Litton region.

In a north-westerly direction towards Great Hucklow only the uppermost part of the Cressbrook Dale Lava has been encountered in a number of old lead mines (Farey, 1811) and boreholes, all of which indicate an easterly dip of the upper surface. The Hucklow Edge No.1 Borehole penetrated 3.6 m into vesicular lava with an overlying 2.6 m tuff. Hucklow Edge No.2 Borehole drilled 19.8 m of lava below a 1.4 m thick tuff sequence. Around Great Hucklow the lava was encountered in Milldam Mine and the Derwent Water Authority's borehole (SK 178.776) was sunk through 1.8 m of tuff and into 2.0 m of lava.

The overall variations in thickness together with their geographical distribution imply an emanative centre for the Cressbrook Dale Lava in the area to the south of Eyam. However, closer examination of the available information indicates that extrusion may have been beneath Hucklow Edge to the west of Ladywash Mine for Slater's Engine Borehole at Foolow (SK 193.777) proved that the Lava was 72 m thick (J. Hedges, pers. comm.). The Lava is overlain by only 0.75 m of tuff in the Eyam Borehole and rests with a sharp irregular base on a thin (0.5 m) tuffaceous limestone sequence. When traced northwards towards Ladywash Mine, the basal tuffaceous limestone increases in thickness as does the overlying tuff. In the Twelve Meers Mine region (text-fig. 17) the overlying tuff is coarse and poorly sorted with abundant limestone clasts and is interbedded with fine pyroclastic debris with high angle graded bedding. This observation may imply the proximity of a pyroclastic cone marking the eruptive centre of the Cressbrook Dale Lava.

The westerly extent of the Cressbrook Dale Lava beyond Milldam Mine is uncertain. During the sinking of High Rake Shaft (SK 163.778) at least 133.5 m of 'toadstone' were penetrated, leading to the abandonment of the shaft at a depth of 219.5 m (p.119, this paper). The top of this toadstone lies very close to the stratigraphical position of the Cressbrook Dale Lava. The 133.5 m of toadstone may be due to the intrusion of a dolerite sill into the Cressbrook Dale Lava at this locality, in a situation similar to the Tideswell Dale, Bonsall, Waterswallows and Calton Hill sills. The nearby Black Hillock Mine shaft penetrated 183 m of the Potluck Sill and its associated feeder (Walters, 1980). Another possibility is that the 'toadstone' represents a tuff-mound unrelated to the Cressbrook Dale Lava. A thickness in excess of 130 m indicates a substantial cone structure and this would have to thin rapidly to be absent at outcrop over a distance of less than 2 km. Such a situation is not improbable if it is compared with similar changes in thickness of some of the tuff horizons of Longstone Edge. On Tideswell Moor a distinct tuff horizon stratigraphically below the Litton Tuff may equate with a tuff sequence at High Rake shaft (Walters, 1980).

The implication of this alternative hypothesis is that the Cressbrook Dale Lava rapidly attenuates west of Milldam Mine shaft. In support of this proposition, Green *et al.* (1887) stated that when the top of the lava was traced west of the shaft it was found to be absent from its projected position 'if it had had the same dip as the enclosing limestones'.

North of High Rake, Green *et al.* recorded a 45 m thick toadstone at a depth of 95 m in Shuttle Rake Mine (approx. SK 160.795). This places it at approximately the same stratigraphical horizon as the Cressbrook Dale Lava but again it is difficult to reconcile with the proposed position of the emanative centre. In the absence of further borehole information the igneous stratigraphy of the Great Hucklow area must remain speculative. The subsurface presence of igneous horizons in addition to the Cressbrook Dale Lava is a distinct possibility.

The northern and eastern extent of the Cressbrook Dale Lava cannot be defined. In all probability it extends beneath the Namurian cover to the north of Hucklow Edge and into the Abney Syncline. Likewise the eastern boundary may coincide with the valley of the River Derwent, between Grindleford and Calver, and as it has not been encountered in the Longstone Edge area it is inferred that the southern boundary is beneath Middleton Moor.

The Litton Tuff

The Litton Tuff can be traced from Tideswell Moor through Litton and Cressbrook Dale to Wardlow Hay Cop (SK 180.738). It attains its maximum thickness in excess of 30 m to the

north-east of Litton, where temporary exposures (Stevenson *et al.*, 1971) of an agglomerate which included bombs, indicate proximity to the vent. At outcrop in Cressbrook Dale it decreases in thickness northwards from 12.8 m to 7.6 m, a trend confirmed by the Littonfields Borehole where 3.2 m of fine grained tuff overlies 0.9 m of tuffaceous limestone. In the Wardlow Mires No.1 Borehole 0.5 km from the proposed source area the Litton Tuff is a 0.76 m thick unit illustrating small scale graded bedding (Stevenson *et al.*, 1971, p.124). The Tuff is separated from the Lower Girvanella Band by 24.2 m of oolitic limestone which Stevenson *et al.* related to the effects of sedimentation against the upstanding cone structure. In profile the Tuff represents a low-angle tuff-mound with peripheral slopes in the region of 1°.

In the Hucklow Edge area the Litton Tuff might be expected to be present in a highly attenuated form as a thin, fine-grained tuff or a wayboard, but it has not been detected in either the Hucklow Edge No.1 or No.2 Boreholes. Green *et al.* (1887) recorded a thick clay horizon 3.7 m above the Cressbrook Dale Lava in Milldam Mine as 'hot unlike decomposed toadstone'. The Great Hucklow Borehole (SK 178.776) intersected a 0.3 m thick 'ashy shale' also 3.7 m above the Lava. This horizon lies at a similar stratigraphical position and may well correlate with the attenuated Litton Tuff.

In the Eyam area the Litton Tuff has been correlated with a 1.1 m thick fine-grained tuff 12 m above the Cressbrook Dale Lava in the Eyam Borehole (Dunham, 1973). A thin tuff only 12 m below the horizon of the Lower Shell Bed (text-fig. 18) in Burnt Heath Mine shaft, on Middleton Moor, has also been correlated with the Litton Tuff by Worley (1978). These suppositions may be incorrect for the Eyam area is nearer to Longstone Edge than Litton and it is now becoming evident that major tuffs are located in the Longstone Edge area with which these tuffs may correlate.

Longstone Edge

The mining and exploration boreholes located on the 5 km of Longstone Edge have indicated numerous igneous horizons of which only one is seen at surface. The area has been and is one of the most actively exploited areas of Derbyshire for Laporte Industries Ltd. are mining fluor-spar from Sallet Hole No.1 Mine. At the time of writing detailed information for the area is minimal and this account must be regarded as no more than an introduction to the complexities of the area.

Mining documents of the 18th and 19th centuries recorded an unsuccessful attempt to drive a level from Coombs Dale (Sallet Hole Level) in 1780. It encountered a toadstone. Wager's Level was then driven north into Longstone Edge to work veins beneath the toadstone (Willies, 1976). More recent information has been provided by Ineson (1967 & 1970) and Butcher (1976) with borehole information provided by Laporte Industries Ltd.

The igneous activity is dominated by Brigantian pyroclastic eruptions giving rise to low angle tuff mounds with peripheral slopes of between 2° and 5°. Occasionally these tuff mounds exceed 90 m in thickness but illustrate rapid thinning where limestone intercalations interdigitate and result in a complex relationship between extrusion and sedimentation. The correlation of the major tuffs with their lateral attenuated representatives, that is thin tuffs and wayboards, is extremely difficult as no detailed palaeontological correlation of marker horizons is available and the Monsal Dale Limestones show a strong easterly increase in thickness.

Three major tuffs have been intersected (text-fig. 18) and are designated the Longstone Edge Upper, Middle and Lower Tuffs. The Upper Tuff was intersected in Sallet Hole Mine No.1 adit where it proved a maximum development of some 30 m. The same horizon is 5 m thick at the eastern end of Longstone Edge (Red Rake) and of similar thickness at the west end in the High Rake area. Petrographic details were given in Ineson & Mitchell (1973). The Middle Tuff is centred further west at High Rake where 90 m are recorded; it likewise attenuates in both an easterly and westerly direction, in the former direction at Deep Rake it is 0.7 m thick and it may extend into the Watersaw Rake although a positive correlation is not possible (text-fig. 18). In general terms the western segment of Longstone Edge does not contain major developments of tuff. The Lower Tuff, for which information is at present minimal, appears to be thickest (> 35 m) beneath the Deep/Red Rake area (text-fig. 18).

The lowest igneous horizon so far penetrated is a thin but extensive lava. Crossdale Mine Shaft (SK 184.732) at the west end of Watersaw Rake encountered lava at depth of 110 m while Farey (1811) noted a toadstone in Robinstye Mine in Hay Dale. These two occurrences are the lateral equivalent of the lava exposed near Cressbrook Mill (text-fig. 17) located at the horizon of the Millers Dale Upper Lava. Walkden (1977) postulated a deep embayment in the geographical outline in order to incorporate this locality in the overall extent of the Millers Dale Upper Lava. This suggestion is not substantiated for it is proposed that this lava, now termed the Cressbrook Mill Lava, is part of a separate flow centred in the Longstone area. The Lava, at the Asbian-Brigantian boundary, can be tentatively correlated with similar material intersected in boreholes located in the central and eastern part of Longstone Edge (text-fig. 18). Although only 4 m thick in the Deep/Red Rake area information provided by Mr. J.D. Hedges indicates that 'a substantial thickness' is present beneath the central area of Longstone Edge.

Additional information with respect to the geographical extent of these igneous horizons beneath Longstone Edge is not available. They have not been recorded at outcrop in the Little Longstone-Monsal Dale area to the south and they are largely absent to the north in the Eyam Borehole. Farey (1811) noted toadstone in High Fields Sough located to the north of Coombs Dale. The tuff horizons in the Eyam Borehole and Burnt Heath Shaft may well be the attenuated equivalents of the tuffs beneath Longstone Edge. This suggestion implies the complex inter-fingering of the attenuated Longstone Edge Tuffs and the Cressbrook Dale Lava and Litton Tuff beneath Middleton Moor, a statement which at present cannot be substantiated.

Conclusions

The correlation of the igneous horizons in Derbyshire, and in particular the South Pennine Orefield, has indicated a greater complexity than had been previously proposed for more than thirty major lavas and tuffs have been recognised.

In the Matlock, Wirksworth, Ashover and Crich region the Bonsall Moor area is providing detailed information with respect to the form and attitude of the igneous horizons as well as the influence they have had on the near surface mineralisation. The opencast sites and exploration boreholes for fluorspar have intersected the Matlock Upper Lava and the Winster Moor Lava on Bonsall Moor and have shown that the stratigraphical horizon of the Winster Moor Lava is equivalent to the Upper 129 Toadstone of Millclose Mine. These two units are located in the Asbian-Brigantian boundary.

To the south, in the Middleton-by-Wirksworth area the Winster Moor Lava is absent, whilst the Matlock Lower Lava rests directly on the Asbian limestones. This junction is marked by a palaeokarstic surface indicative of an emergent and erosional period which is equivalent, in the Bonsall Moor area, to the limestone succession between the Winster Moor and Matlock Lower Lavas.

The overall geographical distribution and thickness variations indicate that the main eruptive centre from which the Matlock Lower Lava was emitted is likewise located on Bonsall Moor in the vicinity of Low Mine. The easterly extent of both the Matlock Upper and Lower Lavas may, in part, contribute to the thick sequence of volcanics proved at Ashover. However until detailed palaeontological zonation of the intercalated limestones is undertaken, definitive statements are not possible.

In this southern region the authors conclude that the Grange Mill Vents and the Shothouse Spring Tuff represent localised volcanicity which although contemporaneous with the extrusion of the Matlock Lower Lava, was unrelated to it.

The maximum development of the Matlock Upper Lava (36 m) is in the vicinity of Cawdor Quarry, Matlock.

Further north in the Alport-Bakewell-Taddington Region, of the 7 major lavas recorded in Millclose Mine, only 3; the Matlock Upper Lava, the Upper 129 Toadstone and the 'Alport' Lava

can be correlated with lavas at outcrop. The remaining 4 (the 103, the Pillough, the Lower 129 and the 144 Pump Station Toadstones) represent localised flows beneath the Namurian cover, which were extruded from a volcanic centre in the Rowsley area.

This region has a proliferation of locally named lavas which were thought to be separate horizons. We now conclude, however, that the 'Alport' Lava of Millclose Mine, the Alport Upper Lava, the 'Haddonfields Upper Lava' and the Conksbury Bridge Lava are one and the same eruptive unit. Likewise, but less definite, the Alport Upper Lava is equivalent to both the Lathkill Lodge and the Bradford Dale Lavas. We can find no evidence to support the proposition of a vent in the vicinity of Wheels Rake Shaft on Long Rake Shaft.

A tentative conclusion for the area between Long Rake and Bakewell based on the extrapolation of known igneous horizons in surrounding areas, implies the presence of thick and complex igneous deposits. Unfortunately, there are no exploration boreholes nor old mines situated in this area to confirm or disprove this statement.

In the Castleton-Buxton-Tideswell Region the Millers Dale Lower Lava (30 m thick) occurs in the vicinity of Wormhill and this implies a genetic relationship with the vents in Monks Dale and Peter's Dale, and secondarily that the geographical distribution of the Millers Dale Upper Lava is asymmetrical with respect to a single extrusive vent at Calton Hill. This observation combined with additional information suggests that a second extrusive vent may be present beneath Tideswell Moor. Although the area between Castleton, Bradwell and the villages of Little and Great Hucklow is known to contain a number of volcanic horizons these cannot be correlated with those of adjacent areas, for insufficient details of the stratigraphical succession are available, due to the lack of deep boreholes. The opposite case occurs around Castleton and that area is best regarded as a distinct volcanic centre unrelated to that centred on Millers Dale. Igneous activity, dominated by the extrusion of tuffs, occurred over a period of 20 million years, that is, from the Holkerian to the Brigantian. Pillow lavas associated with 'basinal facies' limestone-shale sequences indicate dominant subaqueous extrusion as opposed to the largely subaerial extrusion associated with the volcanicity in the 'shelf areas'. Six igneous units are recognised in the Castleton area. Pillow lavas occur at the highest stratigraphical horizon and are underlain by the northern limit of the Millers Dale Lower Lava, the Pindale Tuff and Cave Dale Lava, the Bradwell Moor tuffs, and a basalt beneath Eldon Hill Quarry. An agglomerate in Holkerian limestones is the lowest unit proved in the Castleton area, and this, as with other horizons beneath the Pindale Tuff/Cave Dale Lava, cannot be followed laterally to any great extent.

The study of the north-east region of Derbyshire, Eyam-Longstone-Litton, was hampered by 'restricted' information. Sufficient information is available, however, for it to be concluded that the Cressbrook Dale Lava was extruded from the central part of Hucklow Edge rather than to the south of Eyam, as had been previously inferred.

The lava exposed at Cressbrook Mill is not part of the Millers Dale Upper Lava, but is the western edge of a thin but extensive flow traced beneath Longstone Edge, the Cressbrook Mill Lava. Although the limestones beneath Longstone Edge have not been palaeontologically sub-divided it is thought that the Cressbrook Mill Lava is located at the Asbian-Brigantian boundary.

The Longstone Edge area contains a complex Brigantian volcanic sequence dominated by three major tuff horizons, called the Longstone Edge Lower, Middle and Upper Tuffs. Contrary to previous opinions these tuffs are not considered to be the lateral equivalents of either the Litton Tuff or the Cressbrook Dale Lava.

The stratigraphical horizons and geographical distribution of the Derbyshire igneous rocks are important as they effect the hydrology of the limestone area, giving rise to perched water tables. They likewise have had an important influence on the localisation and form of a number of orebodies (Trail, 1940; and Walters & Ineson, 1980).

Although the Matlock and Millers Dale areas were regarded as the main extrusive centres, the present study has shown that virtually the whole of the eastern part of the South Pennine

Orefield is underlain by substantial volcanic sequences as suggested by Ford (1977, p.65). Individual volcanic centres with pyroclastic cones, volcanic breccias and lavas often exceed 100 m in thickness.

It is concluded that the surface exposures represent the western edge of a Lower Carboniferous igneous province, that extends to the east beneath the Namurian cover.

The igneous activity in Derbyshire illustrates a wide range of basaltic rock types with minor geochemical and petrographic variations. Extrusive bodies include lavas, tuffs, auto-breccias and cones which have a stratigraphical range from the Upper Holkerian to Upper Brigantian (S₂ to D₂), i.e., 20 m.y. However, the major phase of activity occurred in the Lower Brigantian. These deposits cannot be considered to be minor in extent or volume for ten lavas have an areal extent in excess of 10 km² and maximum thicknesses of approximately 100 m, with volumes in the order of 4 km³. Intrusive bodies, genetically related to the basaltic volcanism, include vents, sills and dykes. Isotopic age determinations on the sills indicate a Namurian age of emplacement.

The correlations proposed are the best obtainable in the light of available evidence and until a full and comprehensive correlation of the limestones is undertaken, this paper must be regarded as erecting tentative conclusions in certain areas. The value of this exercise is not only in the reconstruction of the past volcanic environments, but may also help mineral operators to locate additional deposits.

Acknowledgements

The authors would like to thank the following people, companies and organisations for information, access to mines, mine plans, documents, borehole data and detailed discussions with respect to the location, thickness, stratigraphical horizon and composition of the various igneous horizons:

Derbyshire Records Office and Sheffield City Libraries
Dr. N.J.D. Butcher and Dresser Minerals International Inc.
Mr. J.D. Hedges and Laporte Industries Limited
Mr. P.H. Dagger and Imperial Chemical Industries Limited
Dr. D.P. Jefferson and the Blue Circle Industries Limited
Mr. L.H. Dowse and Severn-Trent Water Authority
Mr. H. Cowley and Derbyshire County Council
National Coke Carbonising (Minerals) Limited
Members of the Peak District Mines Historical Society Limited
Mineral tributors, farmers, landowners, etc.

Drs. I.P. Stevenson and J.I. Chisholm of the Institute of Geological Sciences kindly commented on the manuscript, while information from a detailed log of the Eyam Borehole by I.P. Stevenson, is published with the permission of the Director of the Institute of Geological Sciences.

National Coke Carbonising (Minerals) Limited, co-sponsored with NERC, the Research Studentship for which Mr. Walters is particularly grateful.

Special thanks are extended to Messrs D. Nash, J. Rieuwerts and M.G. Lodge, for detailed field information and finally, Dr. T.D. Ford's contribution in comments and correlation details as well as critically reading the manuscript is duly acknowledged.

S.G. Walters, B.Sc., AMIMM, FGS;
P.R. Ineson, Ph.D., C.Eng., MIMM, FGS
Department of Geology,
University of Sheffield,
Mappin Street
Sheffield, S1 3 JD

References

- ALSOP, J. 1845. On the toadstones of Derbyshire. *Rep. Brit. Assn. for 1884, Section C*, pp.51-52.
- ARNOLD-BEMROSE, H.H. 1894. On the microscopical structure of the Carboniferous dolerites and tuffs of Derbyshire. *Q. Jl. geol. Soc. Lond.*, vol.50, pp.603-644.
- ARNOLD-BEMROSE, H.H. 1894a. A Note on Crich Hill, Derbys. *Arch. Nat. Hist. Soc.*, vol.16, pp.44-51.
- ARNOLD-BEMROSE, H.H. 1899. On a sill and faulted inlier in Tideswell Dale (Derbyshire). *Q. Jl. geol. Soc. Lond.*, vol.55, pp.239-250.
- ARNOLD-BEMROSE, H.H. 1907. The toadstones of Derbyshire. Their field relations and petrography. *Q. Jl. geol. Soc. Lond.*, vol.63, pp.241-281.
- ARNOLD-BEMROSE, H.H. 1910. On olivine nodules in the basalt of Calton Hill, Derbyshire. *Geol. Mag.*, vol.7, pp.1-4.
- BAND, S. 1976. Lead mining in Ashover: A preliminary survey. *Bull. Peak Dist. Mines Hist. Soc.*, vol.6, pp.129-139.
- BARNES, J. 1902a. On a metamorphosed limestone at Peak Forest. *Trans. Manchr. geol. Soc.*, vol.27, pp.317-321.
- BARNES, J. 1902b. Further observations of the changes brought about by the intrusion of igneous matter into the Carboniferous limestone at Peak Forest. *Trans. Manchr. geol. Soc.*, vol.27, pp.366-369.
- BROADHURST, F.M. & SIMPSON, J.M. 1973. Bathymetry on a Carboniferous reef. *Lethaia*, vol.6, pp.367-381.
- BUTCHER, N.J.D. 1975. The geology of Magple sough and mine. *Bull. Peak Dist. Mines Hist. Soc.*, vol.6, pp.65-70.
- BUTCHER, N.J.D. 1976. Some aspects of structure and fluorite mineralisation in the Southern Pennine Orefield. Unpublished Ph.D. Thesis. University of Leicester, 218pp.
- BUTCHER, N.J.D. & FORD, T.D. 1973. The Carboniferous limestone of Monsal Dale, Derbyshire. *Mercian Geol.*, vol.4, pp.179-195.
- CHESHIRE, S.G. & BELL, J.D. 1977. The Speedwell vent, Castleton, Derbyshire. A Carboniferous littoral cone. *Proc. Yorks. geol. Soc.*, vol.41, pp.173-184.
- COPE, F.W. 1933. A tholeiite dyke near Buxton, Derbyshire. *Geol. Mag.*, vol.70, pp.414-422.
- COPE, F.W. 1937. Some features in the D₁ - D₂ limestones of the Miller's Dale region, Derbyshire. *Proc. Yorks. geol. Soc.*, vol.23, pp.178-195.

- COPE, F.W. 1949. Woo Dale Borehole near Buxton, Derbyshire. *Abstr. Proc. geol. Soc. Lond.*, 1446, p.24.
- COPE, F.W. 1973. Woo Dale borehole near Buxton, Derbyshire. *Nature (Phys. Sci.)*, vol.243, pp.29-30.
- COPE, F.W. 1979. The age of the volcanic rocks in the Woo Dale Borehole, Derbyshire, *Geol. Mag.*, vol.116, pp.319-320.
- COX, F.C. & BRIDGE, D. McC. 1977. *The limestone and dolomite resources of the country around Monyash, Derbyshire*. Description of 1:25,000 resources sheet, SK 16, HMSO, Lond. 137pp.
- CURTIS, C.D. 1976. 'Unmixed' Ca^{2+}/Mg^{2+} saponite at Calton Hill, Derbyshire. *Clay Minerals*, vol.11, pp.85-89.
- DONALDSON, C.H. 1978. Petrology of the uppermost upper mantle deduced from spinel lherzolite and harzburgite nodules at Calton Hill, Derbyshire. *Contrib. Mineral Petrol.*, vol.65, pp.363-377.
- DUNHAM, K.C. 1952. Fluorspar. 4th Edit. *Mem. geol. Surv., Spec. Rep. Miner Resour. Gt. Br.*; 143pp.
- DUNHAM, K.C. 1973. A recent deep borehole near Eyam, Derbyshire. *Nature (Phys. Sci.)*, vol.241, pp.84-85.
- EDEN, R.A., ORME, G.R., MITCHELL, M. & SHIRLEY, J. 1964. A study of part of the margin of the Carboniferous limestone 'massif' in the Pindale area of Derbyshire. *Bull. geol. Surv. Gt. Br.*, vol.21, pp.73-118.
- FAREY, J. 1811. *A general view of the agriculture and minerals of Derbyshire*, vol.1, 532pp.
- FAREY, J. 1812. On toadstones in Derbyshire. *Min. Mag.*, vol.33, pp.513-516.
- FAUJUS DE ST. FOND, B. 1797. *Voyage en Angleterre ... avec la description Mineralogique ... des montagnes de Derbyshire*. Paris. English translation 1799 (Derbys. vol.ii, p.264).
- FEARNSIDES, W.G. & TEMPLEMAN, A. 1932. A boring through Edale Shales to Carboniferous limestone and pillow lavas at Hope Cement Works near Castleton, Derbyshire. *Proc. Yorks. geol. Soc.*, vol.22, pp.100-121.
- FITCH, F.J., MILLER, J.A. & WILLIAMS, S.C. 1970. Isotopic ages of British Carboniferous rocks. *Cr. 6th Int. Congr. Carb. Strat. Geol.* (Sheffield, 1967), vol.2, pp.771-789.
- FORD, T.D. 1952. New evidence on the correlation of the Lower Carboniferous reefs at Castleton, Derbyshire. *Geol. Mag.*, vol.89, pp.346-356.
- FORD, T.D. 1967. Some mineral deposits of the Carboniferous limestone of Derbyshire. In: *Geological Excursions in the Sheffield Region and the Peak District National Park*. Ed. R. Neves & C. Downie, University of Sheffield, pp.53-75.

- FORD, T.D. (ed.) 1977. Limestones and caves of the Peak District. *Geo. Abstracts*, 469pp.
- GARNETT, C.S. 1923. The toadstone clays of Derbyshire. *Min. Mag.*, vol.2, pp.151-157.
- GEMKIE, A. 1897. *Ancient volcanoes of Great Britain*. London, vol.2, pp.8-22.
- GEORGE, T.N. *et al.* 1976. A correlation of Dinantian rocks in the British Isles. *Spec. Rep. No.7, geol. Soc. Lond.*, 87pp.
- GIBSON, W. & WEDD, C.B. 1913. The geology of the northern part of the Derbyshire Coalfield and bordering tracts. *Mem. geol. Surv. E. & W.*, 186pp.
- GREEN, A.H., LE NEVE FOSTER, C. & DAKYNS, J.R. 1869. The geology of the Carboniferous limestone, Yoredale rocks and Millstone grit of North Derbyshire. *Mem. geol. Surv. Gt. Br.*, 1st ed. 150pp.
- GREEN, A.H., LE NEVE FOSTER, C. & DAKYNS, J.R. 1887. The geology of the Carboniferous limestone, Yoredale rocks and Millstone grit of North Derbyshire. *Mem. geol. Surv. Gt. Br.*, 2nd ed., 212pp.
- GRIGOR-TAYLOR, W.R. 1972. Notes on the Lathkill Gold Mine 1854-1856. *Bull. Peak Dist. Mines Hist. Soc.*, vol.5, (1), pp.43-49.
- HAMAD, S. EL D. 1963. The chemistry and mineralogy of the olivine nodules of Calton Hill, Derbyshire. *Min. Mag.*, vol.33, pp.483-497.
- HOPKINS, W. 1834. *On the stratification of the limestone district of Derbyshire*. Private Publication, 47pp.
- HUDSON, R.G.S. & COTTON, G. 1945a. The lower Carboniferous in a boring at Alport, Derbyshire. *Proc. Yorks. geol. Soc.*, vol.25, pp.254-330.
- HUDSON, R.G.S. & COTTON, G. 1945b. The Carboniferous rocks of the Edale Anticline, Derbyshire. *Q. Jl. geol. Soc. Lond.*, vol.101, pp.1-36.
- INESON, P.R. 1967. Trace-element geochemistry of wallrock alteration in the Pennine orefields and Cumberland ironfield. Unpublished Ph.D. Thesis, University of Durham, 286pp.
- INESON, P.R. 1970. Trace element aureoles in limestone wallrocks adjacent to fissure veins in the Eyam area of the Derbyshire orefield. *Trans. Inst. Min. Metall. (Sect. B, Appl. earth Sci.)*, vol.79, pp.B238-245.
- INESON, P.R. & MITCHELL, J.G. 1973. Isotopic age determinations on clay minerals from lavas and tuffs of the Derbyshire orefield. *Geol. Mag.*, vol.109(6), pp.501-512.
- INSTITUTE OF GEOLOGICAL SCIENCES 1969. Classical areas of British geology, Sheet SK 18 and part of SK 17 (Solid & Drift) - Edale & Castleton, 1:25,000. *Inst. geol. Sci. Col.*
- INSTITUTE OF GEOLOGICAL SCIENCES 1970. Classical areas of British geology. Parts SK 25, 26, 35 and 36 (Solid & Drift) - Matlock: 1:25,000, *Inst. geol. Sci. Col.*

- INSTITUTE OF GEOLOGICAL SCIENCES 1975. Classical areas of British geology. Sheet SK 07 (Solid & Drift) - Buxton: 1:25,000 Inst. geol. Sci. Col.
- INSTITUTE OF GEOLOGICAL SCIENCES 1975. Classical areas of British geology. Sheet SK 18 (Solid & Drift) - Castleton: 1:25,000, Inst. geol. Sci. Col.
- INSTITUTE OF GEOLOGICAL SCIENCES 1976a. Classical areas of British geology. Sheet SK 17 (Solid & Drift) - Millers Dale: 1:25,000, Inst. geol. Sci. Col.
- INSTITUTE OF GEOLOGICAL SCIENCES 1976b. Geological Survey map, Sheet SK 25 NW (Solid & Drift). 1:10,560, Inst. geol. Sci. Col.
- INSTITUTE OF GEOLOGICAL SCIENCES 1977a. Classical areas of British geology. Sheet SK 16 (Solid & Drift) - Monyash: 1:25,000, Inst. geol. Sci. Col.
- INSTITUTE OF GEOLOGICAL SCIENCES 1977b. Geological Survey map, Sheet SK 26 NW (Solid & Drift). 1:10,560, Inst. geol. Sci. Col.
- IXER, R.A. 1972. Controls of mineralisation in Derbyshire. Unpublished Ph.D. Thesis. University of Manchester. 117pp.
- IXER, R.A. 1975. A revision of part of the Matlock group at Masson Hill, Matlock, Derbyshire. *Mercian Geol.*, vol.5, pp.181-186.
- JEFFERSON, D.P. 1979. *Guide book to the Midlands of England, field excursion guide E5*. Sixth International Clay Conference, 1978. Oxford. pp.34-39.
- JONES, J.G. & NELSON, P.H.H. 1970. The flow of basalt from air into water: Its structural expression and stratigraphic significance. *Geol. Mag.*, vol.107, pp.13-19.
- KELMAN, P. 1980. The geology of the Ashover Volcanics. *Merc. Geol.*, vol.8, pp.11-28.
- MILLER, G. 1980. Now you see it, now you don't, or the case of the disappearing sill. *Amat. geol.*, vol.VIII (1), pp.14-18.
- MOORE, S. 1903. Note on an unmapped toadstone in Derbyshire. *Geol. Mag.*, vol.10, pp.84-96.
- MOSELEY, F. 1966. The volcanic vents and pocket deposits of Derbyshire. *Mercian Geol.*, vol.1, (3), pp.283-285.
- MUELLER, G. 1954. Enclosures in gangue minerals. *Min. Mag.*, vol.90, pp.148-154 and 208-217.
- OAKMAN, C.D. 1978. Sough Hydrology of the Wirksworth-Matlock-Youlgreave area. Unpublished M.Phil. Thesis, University of Leicester, 209pp.
- PILKINGTON, J. 1789. *A view of the present state of Derbyshire*, vol.1, 469pp.

- RAMSBOTTOM, W.G.C.,
RHYS, G.H. & SMITH, E.G.
1962. Boreholes in the Carboniferous rocks of the Ashover district, Derbyshire. *Bull. geol. Surv. GB.*, no.19, pp.75-168.
- SARGENT, H.C.
1912. On the origin of certain clay bands in the limestones of the Crich inlier. *Geol. Mag.*, vol.9, pp.406-412.
- SARGENT, H.C.
1917. On a spilitic facies of Lower Carboniferous lava flows in Derbyshire. *Q. Jl. geol. Soc. Lond.*, vol.73, pp.11-25.
- SARGENT, H.C.
1925. An analcite bearing tuff in the Carboniferous limestone of Derbyshire. *Geol. Mag.*, vol.62, pp.462-463.
- SARJEANT, W.A.S.
1967. Fibrous chlorites in the volcanic rocks of Derbyshire. *Mercian Geol.*, vol.3 (1), pp.85-95.
- SCHNELLMANN, G.A. &
WILLSON, J.D.
1947. Lead-zinc mineralisation in North Derbyshire. *Trans. Instn. Min. Metall.*, vol.485, pp.411-429.
- SHIRLEY, J.
1950. The stratigraphical distribution of the lead-zinc ores of Mill Close Mine, Derbyshire and the future prospects of the area. *XVIII Int. geol. Congr. Lond.* (London, the Congress), Pt.7, pp.353-361.
- SHIRLEY, J.
1959. The Carboniferous limestone of the Monyash-Wirksworth area, Derbyshire. *Q. Jl. geol. Soc. Lond.*, vol.114, pp.411-429.
- SHIRLEY, J. &
HORSFIELD, E.L.
1940. The Carboniferous limestone of the Castleton-Bradwell area, North Derbyshire. *Q. Jl. geol. Soc. Lond.*, vol.96, pp.271-299.
- SHIRLEY, J. &
HORSFIELD, E.L.
1945. The structure and ore deposits of the Carboniferous limestone of the Eyam district, Derbyshire. *Q. Jl. geol. Soc. Lond.*, vol.100, pp.289-310.
- SMITH, E.G.
RHYS, G.H. &
EDEN, R.A.
1967. Geology of the country around Chesterfield, Matlock and Mansfield. *Mem. geol. Surv. GB.* 430pp + vii.
- SPEED, P.H.
1964. The volcanic rocks of the Wirksworth area. An excursion report. *Mercian geol.*, vol.1, pp.71-72.
- STEVENSON, I.P. &
GAUNT, G.C.
1971. Geology of the country around Chapel-en-le-Frith. *Mem. geol. Surv. GB.*, 444pp.
- STEVENSON, I.P.,
HARRISON, R.K. &
SNELLING, N.J.
1970. Potassium argon age determination of the Water-swallows Sill, Buxton, Derbyshire. *Proc. Yorks. geol. Soc.*, vol.37, pp.445-447.
- TOMKEIEFF, S.I.
1928. The volcanic complex of Calton Hill. *Q. Jl. geol. Soc. Lond.*, vol.84, pp.703-718.
- TRAILL, J.G.
1940. Notes on the Lower Carboniferous Limestones and toadstones at Millclose Mine, Derbyshire. *Trans. Instn. Min. Engrs.*, vol.49, pp.191-229.

- VARVILL, W.W. 1959. The future of lead-zinc and fluorspar mining in Derbyshire. In: *The Future of Non-Ferrous Mining in Great Britain and Ireland*. Lond. Instn. Min. Metall., pp.175-232.
- WALKDEN, G.M. 1972. The mineralogy and origin of interbedded clay wayboards in the Lower Carboniferous of the Derbyshire Dome. *Geol. J.*, vol.8, pp.143-160.
- WALKDEN, G.M. 1977. Volcanic and erosive events in an upper Viséan carbonate platform, north Derbyshire. *Proc. Yorks. geol. Soc.*, vol.41, pp.347-366.
- WALTERS, S.G. 1980. The geology of the Black Hillock or Clear-the-Way Mine, Tideswell Moor. *Bull. Peak Dist. Mines Hist. Soc.*, vol.7, pp.327-333.
- WALTERS, S.G. & INESON, P.R. 1980. Mineralisation within the igneous rocks of the South Pennine Orefield. *Bull. Peak Dist. Mines Hist. Soc.* vol.7, pp.315-325.
- WATSON, W. 1811. *A delineation of the strata of Derbyshire forming the surface from Bolsover in the east to Buxton in the west*. Sheffield. 76pp.
- WATSON, W. 1813. *A section of the strata forming the surface in the vicinity of Matlock Bath in Derbyshire*. Chesterfield, 19pp.
- WHEATCROFT, J. 1831. Uncatalogued MS. Peak Dist. Mines Hist. Soc., Derbyshire Records Office, Matlock.
- WHITEHURST, J. 1778. *An inquiry into the original stage and formation of the earth with observations on the strata of Derbyshire*. London.
- WILKINSON, P. 1967. Volcanic rocks in the Peak District. In: *Geological Excursions in the Sheffield Region and the Peak District National Park*. Ed. R. Neves and C. Downie. University of Sheffield, pp.47-53.
- WILLIES, J. 1976. John Taylor in Derbyshire, 1839-1851. *Bull. Peak Dist. Mines Hist. Soc.*, vol.6, pp.146-161.
- WILSON, E. 1870. Altered clay bed and sections in Tideswell Dale, Derbyshire. *Geol. Mag.*, vol.VII, pp.394 & 520-523.
- WORLEY, N.E. 1977. The Geology of Will's Founder Shaft. *Bull. Peak Dist. Mines Hist. Soc.*, vol.6, pp.257-262.
- WORLEY, N.E. 1978a. Stratigraphic controls of mineralisation in the Peak District of Derbyshire. Unpublished Ph.D. Thesis, University of Leicester, 263pp.
- WORLEY, N.E., WORTHINGTON, T. & RILEY, L. 1978b. The geology and exploration of Hubbadale Mines, Taddington. *Bull. Peak Dist. Mines Hist. Soc.*, vol.7, pp.31-39.
- WORLEY, N.E. & DORNING, K.J. 1977. Carbonaceous and fossiliferous material from some Derbyshire clay wayboards. *Mercian Geol.*, vol.6, pp.145-154.
- WRIGHT, A. 1979. A geochemical investigation of massive limestones of North Derbyshire. Unpublished M.Sc. Thesis, University of Sheffield. 177pp.

APPENDIX THIRTEEN.

The Waterswallows Sill, Derbyshire.

Paper in preparation for submission to the Yorkshire Geological Society, November 1981. The authors are Walters, S.G. and Ineson, P.R. Until publication all borehole information and analyses can not be reproduced without permission.

The Waterswallows Sill, located 3km north-east of Buxton, has a circular outcrop area some 0.8km in diameter (Fig. 13.1). The intrusive dolerite is exposed in the roadstone quarry owned by Tarmac Roadstone (Northern) Holdings Ltd. Recent quarry extensions and exploratory boreholes have enabled a detailed investigation of the internal structures, geochemical variations and form of the intrusion to be undertaken. The sill was briefly recorded by Bemrose (1907), whilst Moseley (1964) interpreted the then available evidence as indicating an extrusive origin. This proposition was refuted by Stevenson et. al. (1970) and Stevenson and Gaunt (1971) who on the basis of K-Ar age determinations, petrology and field relationships confirmed an intrusive origin. However, the present study has indicated numerous aspects which are at variance with these latter descriptions.

The Waterswallows Sill, in common with the majority of intrusions in the south Pennines (Walters and Ineson, 1981), has been intruded along the line of weakness afforded by a Lava/limestone interface - in this instance the Lower Millers Dale Lava. Over much of its present area the Sill was intruded within the Lower Millers Dale Lava, however to the east the sill becomes gently transgressive into the underlying Chee Tor Limestones whilst to the west the Sill is more strongly discordant, transgressing into the overlying Millers Dale Limestones. The overall form of the Sill resembles a small lopolith (Fig. 13.2 and 13.3) with strongly upturned margins dipping at 40° to the west and south-west. Contours constructed on the base of the sill (Fig. 13.2) indicates this overall form but also illustrates the undulate nature of its basal contact. Exposures on the lower levels of the quarry and all recent boreholes indicate a variable sequence of lava and tuff directly beneath the intrusive dolerite in the central quarry area (borehole logs dating from the early programme of exploration carried out by Hughes Brothers unfortunately fail to recognize or record this basal sequence.) The Lava/tuff sequences underly the dolerite despite the large scale undulations of the lower contact indicating that it represents a post-intrusive, tectonic feature in keeping with the observed regional dip variations which approaches 12° . A minimum

thickness of 80m has been proven for the Sill in the area of maximum downwarping in the north-eastern area.

The sharply defined, undulating basal contact of the sill is at present (July 1981) well exposed in the lowest level of the quarry. The dolerite is in contact with some 4m of non-vesicular to poorly vesicular lava with a concentration of calcite veinlets around the actual contact. The petrographic alteration of even the hard, dark non-vesicular lava contrasts with the fresh nature of the overlying dolerite. The upward "bulges" of vesicular lava into the dolerite noted by Moseley (1966) are not present, neither is the thin limestone horizon between the lava and underlying tuff (Moseley, op. cit.) Towards the lower contact of the lava it becomes more vesicular and bleached to a coherent "Toadstone clay" type lithology. Coarse tuffs with abundant limestone inclusions and iron stained tuffaceous limestones are present below the lava and have likewise been proved in boreholes under the western and central parts of the sill. There are indications that the basal tuff thins and finally disappears to the south-east and it is also absent some 2km to the north-east, i.e. in the vicinity of Buxton Bridge (see Appendix 7, borehole T/B/21.) The coarse nature of the tuff in the quarry area indicates proximal activity which is confirmed by the rapid increase in thickness of both tuff and lava in a north-westerly direction beneath the area of the processing plant. The increase in thickness of the tuff to over 20m indicated the site of the central cone responsible for the extrusion of the Lower Millers Dale Lava. Likewise the close association of the tuff cone with the area of maximum thickness of the dolerite and greatest discordance of the sill suggests a common feeder for both extrusive and intrusive activity.

Three distinct petrographic types can be recognized in the Sill and enables a division into lower, middle and upper horizons. The lower horizon and the middle horizon are characterized by fine-grained dolerite lacking the ophitic texture common to the majority of south Pennine intrusions. The lower horizon averages 20-30m in thickness (Fig 13.3)

and is associated with spectacular columnar jointing (see Frontispiece to Chapter 4). The fine-grained dolerite is olivine-microphyric with some 7% of olivine exhibiting incipient smectite alteration, rare partly resorbed plagioclase microphenocrysts are noted but augite phenocrysts have not been observed. The groundmass consists of labradorite laths (less than 0.25mm) exhibiting a degree of fluxioning together with granular augite and lobate Fe-Ti oxides of late stage crystallization. Intersertal areas are composed of primary glass associated with apatite concentrations, partial devitrification is present with exsolution of iron oxides and smectite alteration. (see Table 13.2 and Plates 1.7, 2.1 and 2.2) The middle horizon is a fine grained olivine microphyric dolerite with a slightly coarser texture than the lower horizon. It contains no relict olivine and a high percentage of interstitial secondary smectite areas. In addition, the middle horizon is enriched in plagioclase and depleted in augite in comparison with the lower horizon (Table 13.2) The contact between these two horizons is well defined and has been located in all recent boreholes (Fig. 13.3) There are no detectable chilling relationships, although a slight "transitional" type in terms of plagioclase and augite percentages is noted towards the top of the lower horizon (Table 13.2). The lower horizon exhibits minor deuteric alterations in comparison with the middle horizon and recent developments of the quarry have been designed to exploit the lower horizon as a high quality roadstone.

The upper horizon represents a "gabbroic" development and has been largely removed by erosion and quarrying with only isolated areas remaining in situ in the north-west area of the quarry. Average grain size exceeds 2mm, with smectite pseudomorphs after olivine phenocrysts in excess of 4mm and constituting over 25%. Coarse intergrowths of augite and labradorite lack the ophitic texture (see plates 1.7 and 2.2), while interstitial areas contain zoned smectites. The detailed relationships between the gabbro and the middle horizon are not known but all evidence indicates that the Sill is a composite intrusion with at least three distinct phases of intrusion.

The geochemistry (Table 13,1) indicates minimal variations between the lower and middle horizons. The gabbroic horizon, however, is distinctly "less evolved", contrasting, for example, with the high state of evolution of the Conksbury Bridge Lava which although much finer grained is of the same petrographic type with a high proportion of olivine pseudomorphs. The gabbro exhibits many similarities with the basal picritic layer of the Duffield Sill (see Fig 7.11). However, its location above the thick dolerite horizons does not support an in situ cumulus origin. The most plausible explanation is that the gabbro represents the olivine enriched basal layer of the sub-intrusive magma chamber which was intruded as the final product of intrusive activity, thus reversing the normal vertical geochemical variations associated with in site differentiation and crystal settling.

Major element variations in the Sill fall within the "liquid line of descent" for the south Pennine basalts. In terms of evolution the Waterswallows dolerite is less "evolved" in comparison with other sills and shows strong affinities with the least evolved lavas, in particular the Lower and Upper Millers Dale Lavas (Fig. 7.1). This is emphasized when the average analyses of incompatible and minor elements (Fig. 7.7) are compared. These indicate a close correspondance with the Lower Millers Dale Lava, in particular with respect to K_2O , Zr and P_2O_5 levels. The spatial and geochemical correlations between intrusive and extrusive activity in the south Pennines is indicative of consanguineous activity. The concept of a prolonged hiatus between intrusive and extrusive activity has been based on the results of K-Ar dating on dolerite from the Waterswallows Sill (Stevenson et. al., 1970), however, as Chapter 12 indicates this material is wholly unsuitable for K-Ar dating and any apparent "concordant ages" are the result of Ar loss from the interstitial smectite, the main potassium bearing phase.

TABLE MAJOR AND TRACE ELEMENT GEOCHEMISTRY

13.1

%	1	2	3	4	5	6	7
SiO ₂	49.98	50.42	50.13	49.85	43.64	46.24	49.98
TiO ₂	1.81	1.81	1.79	1.83	1.44	1.53	1.74
Al ₂ O ₃	14.02	13.72	13.70	13.84	11.42	12.56	14.06
Fe ₂ O ₃	2.97	2.78	2.69	2.90	4.31	3.63	3.36
FeO	8.40	8.90	8.88	8.22	8.63	8.54	7.27
MnO	0.16	0.14	0.15	0.15	0.14	0.13	0.15
MgO	8.66	9.07	8.78	8.70	13.20	10.99	8.26
CaO	8.60	8.55	8.34	8.69	5.74	7.01	8.62
Na ₂ O	2.62	2.60	2.66	2.49	1.56	1.99	2.62
K ₂ O	0.38	0.34	0.58	0.33	0.41	0.42	0.44
H ₂ O ⁺	1.78	1.48	1.35	1.52	4.35	3.07	1.76
H ₂ O ⁻	1.05	0.54	0.40	1.03	4.92	3.53	1.75
P ₂ O ₅	0.24	0.23	0.23	0.24	0.16	0.18	0.19
CO ₂	0.08	0.08	0.03	0.13	0.16	0.06	0.36
SO ₃	0.00	0.00	0.02	0.05	0.00	0.01	0.15
Total	100.81	100.66	99.73	99.97	100.08	99.89	99.71

ppm.

Ga	24	21	21	21	16	18	18
Nb	13	13	12	12	9	8	-
Pb	7	8	6	9	7	4	-
Rb	9	11	15	5	8	10	-
Sr	311	327	252	322	151	212	220
Y	23	23	23	22	16	19	-
Zn	107	109	109	109	114	107	-
Zr	125	125	122	127	91	98	100

1- Lower horizon, bulk sample of chips.

2-Lower horizon, 4m above basal contact.

3-Lower horizon, transitional type.

4-Middle horizon, bulk sample of chips.

5-Upper horizon.

6-Upper horizon.

7-Stevenson and Gaunt (1971)

TABLE

NORMATIVE

ANALYSES

13.2

	1	2	3	4	5	6	7
OR	2.31	2.01	3.49	2.01	2.66	2.66	1.42
AB	22.68	22.34	23.02	21.66	14.56	18.11	23.86
AN	25.89	25.10	24.22	26.33	25.33	25.85	32.66
WO	6.69	6.85	6.91	6.87	2.04	4.27	0.00
DI EN	3.90	4.00	4.00	4.05	1.26	2.57	0.00
FS	2.48	2.53	2.59	2.49	0.66	1.47	0.00
HY EN	17.59	18.42	16.36	18.23	20.79	19.45	12.93
FS	11.17	11.63	10.59	11.14	10.90	11.14	12.04
OL FO	0.39	0.35	1.37	0.00	9.94	5.15	0.00
FA	0.27	0.24	0.99	0.00	5.74	3.25	0.00
MT	2.18	2.18	2.18	2.18	2.18	2.18	2.18
IL	3.51	3.50	3.47	3.57	3.02	3.11	3.77
AP	0.58	0.54	0.54	0.56	0.42	0.44	0.57
Q				0.61			9.75
Total	99.63	99.67	99.71	99.69	99.50	99.64	99.56

TABLE AVERAGE MODAL ANALYSES.

13.3

	(A)	(B)	(C)	(D)
Plagioclase.	38.0	46.4	46.6	44.6
Augite.	43.6	32.6	25.6	17.6
Olivine.*	7.2	6.8	5.2	27.0
Fe-Ti Oxides	7.4	7.6	6.0	4.4
Interstitial areas.	3.8	6.8	16.6	6.4

(A)-Lower horizon

(B)-Lower horizon-'transitional' type.

(C)-Middle horizon

(D)-Upper horizon.

*-Includes relict olivine and smectite replacements.

X-RAY DIFFRACTION ANALYSIS RESULTS.

	Air dried, 4-30° 2θ	Glycolated, 4-10°	1 hr 450°C 4-10° 2θ
Whole rock smear			
Lower horizon.....	15.1 ⁰ , 7.4, 3.04	16.8	9.83
Clay fraction			
Lower horizon.....	15.1, 7.4, 3.04	16.7	9.77
Whole rock smear			
Middle horizon....	15.0, 7.5	16.2	10.0
Olivine pseudomorph			
Upper horizon.....	14.8, 7.4	16.3	9.8
Fibrous vein infills			
at basal contact....	15.2, 7.5	16.8	9.8

WATERSWALLOWS SILL-LOCATION DETAILS....

- 55A- Lower horizon,bulk sample of chips.
- 55B-Lower horizon,hand specimen approx 4m above basal contact.
- 56- "Intermediate" type below upper contact of Lower Type,hand specimen.
- 57- Middle horizon,bulk sample of chips.
- 58A-Upper "gabbroic" horizon,hand specimen.
- 58B-Upper "gabbroic" horizon,hand specimen.

Samples 55 to 58 collected within Waterswallows Quarry.

- 59- Tunstead North dyke,Buxton Bridge-Great Rocks Dale.

PLATES

- 1.1 (frontispiece to Chapter 5) photomicrograph,lower horizon.
- 1.3 Photomicrographs,Tunstead North Dyke.
- 1.7 Photomicrographs,petrographic variations in the Waterswallows Sill.
- 2.1 E & F. Photomicrographs,interstitial phase in the Middle and Lower horizons.
- 2.2 D & E. Photomicrographs,olivine pseudomorphs-Lower and Gabbroic horizons.

FIGURES

- 13.1 General location map,Waterswallows Sill.
- 13.2 Contours on the base of the Sill and borehole locations.
- 13.3 Geological cross sections,Waterswallows Sill.

TABLES

- 13.1 Major and Trace element analyses.
- 13.2 Normative and modal analyses.

FIGURE 13.1

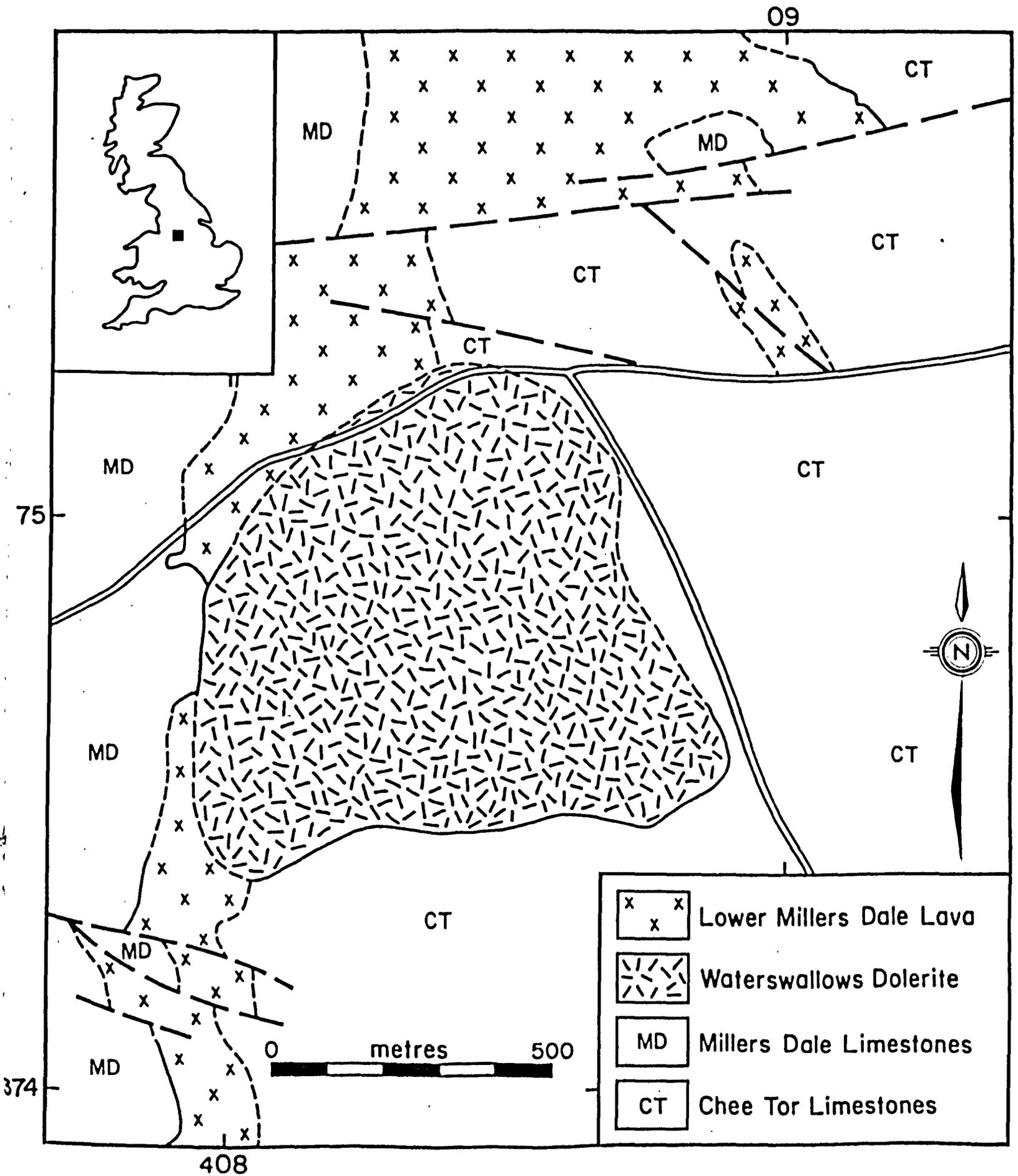
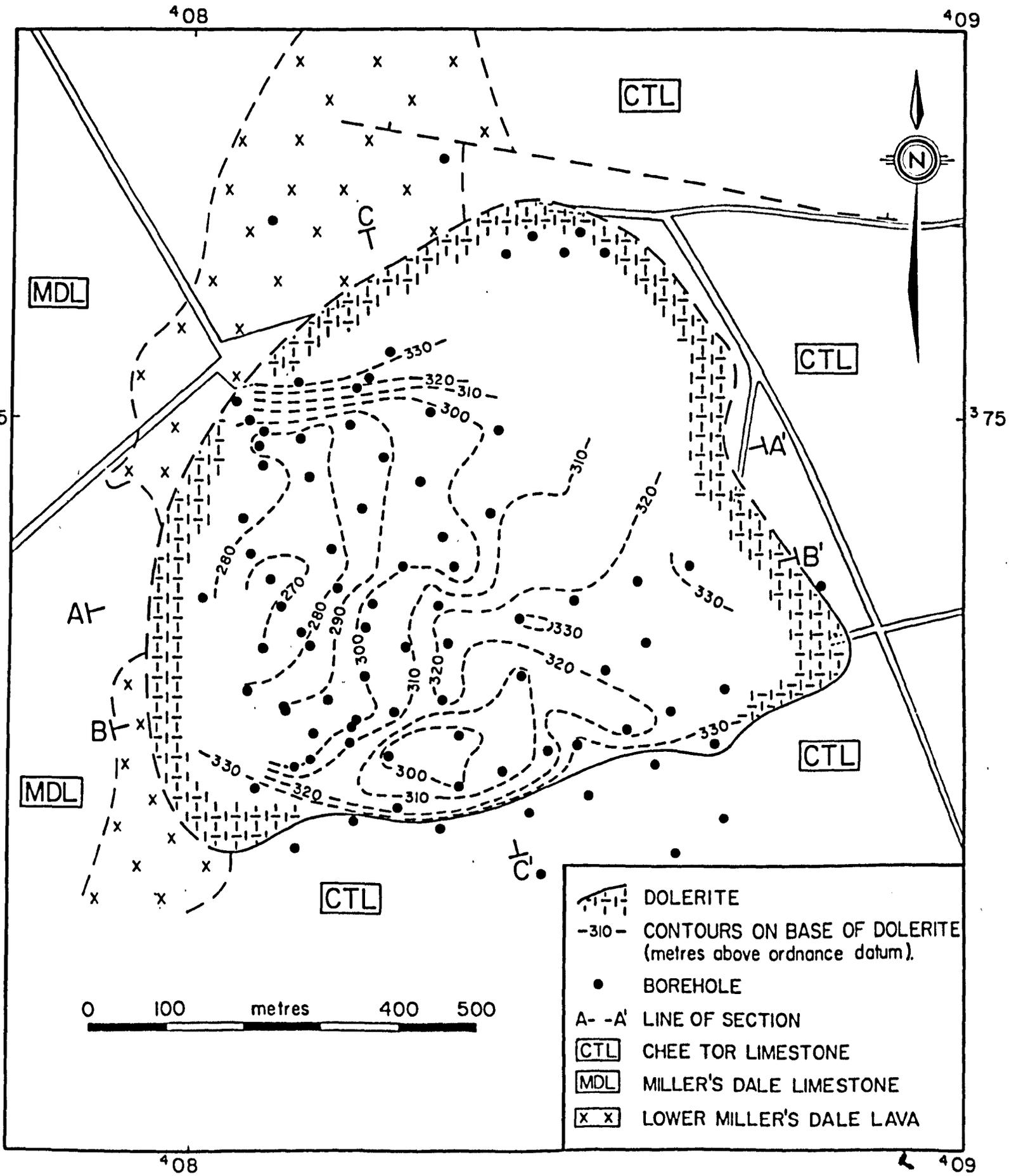
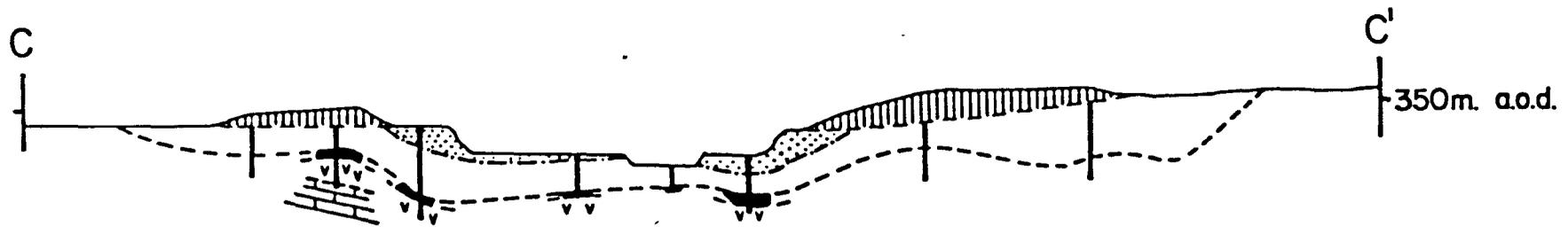
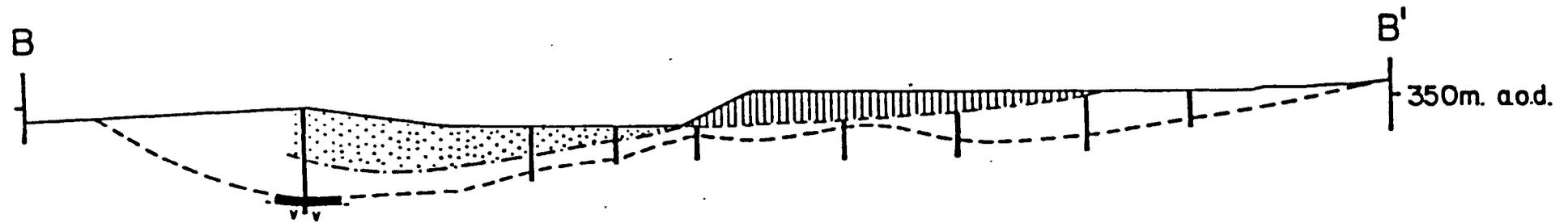
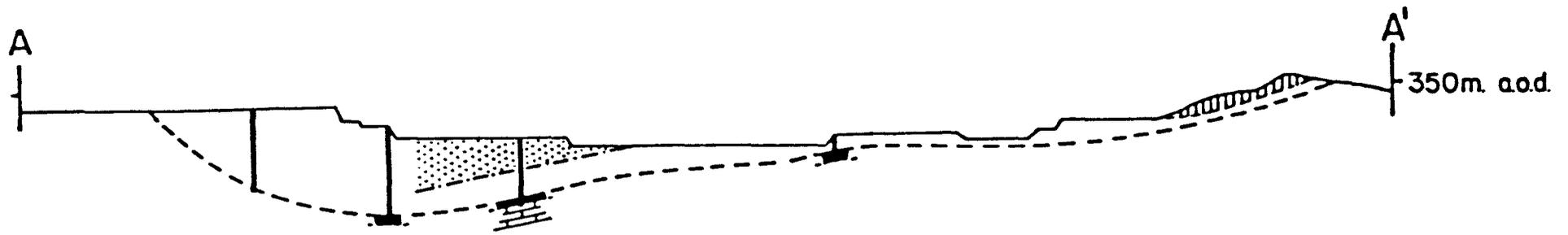


FIGURE 13.2



-  DOLERITE
-  -310- CONTOURS ON BASE OF DOLERITE (metres above ordnance datum).
-  BOREHOLE
-  A- -A' LINE OF SECTION
-  CTL CHEE TOR LIMESTONE
-  MDL MILLER'S DALE LIMESTONE
-  x x LOWER MILLER'S DALE LAVA



-  Present Surface
-  Tip Material
-  Base of Sill
-  Contact of Lower-Middle horizon
(where differentiated)
-  Lava
-  Tuff
-  Limestone

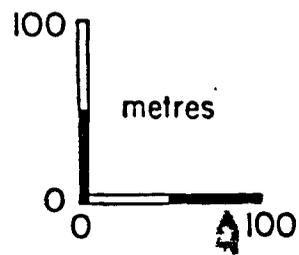


FIGURE 13.3