

THE GEOCHEMISTRY AND MINERALOGY
OF COAL AND COAL-BEARING STRATA
FROM THE CANNOCK COALFIELD WITH
SPECIAL REFERENCE TO CHLORINE

VOLUME 1

STEPHEN ALLEN CASWELL

Submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

Department of Geology,
University of Sheffield.

January, 1983.

Y112851210
Y34P1

The Geochemistry and Mineralogy of Coal and Coal-Bearing Strata
from the Cannock Coalfield with Specific Reference to Chlorine

The project was conducted on four coals seams, the Shallow and Yard (Lower Coal Measures) from Lea Hall Colliery at Rugeley, and the Park and Eight Feet seams from Littleton Colliery, near Cannock. Ultimate, proximate analyses and moisture contents showed them to be of high volatile bituminous 'B' coal rank, and typical of high Cl^- coals.

The Cl^- investigation showed a relationship with organic matter where ash is a dilutant, reaching c. 1% (by weight) in the coals, almost an order higher than in the associated mudrocks. It is related to the internal surface area and is thus highest in the vitrinite dominated 'bright rocks' and lowest in the 'dull coals'. Two types of Cl^- were identified, originating from saline ground waters, the former representing present ground water solutions trapped in the larger pores and readily water-soluble, and the latter held in organic combination within smaller or closed pores produced by Hercynian rank imposition. Varying levels of this Cl^- can be released by ion exchange with carbonates in leaching experiments.

The mudrock and coal ash mineralogy was conducted on low temperature ashed material which suffered the side-effect of gypsum formation during oxidation. The mudrock mineralogy is dominated by detrital minerals, quartz and clays predominating. Diagenetic minerals rarely account for 7% of the normative minerals except in localised pyrite and siderite nodules. Climate played an important role in the detrital mineralogy, the lower seam floor measures being dominated by a tropically leached suite of kaolinite and quartz. Continental movement led to increased aridity characterised by illite and chlorite which dominate the higher seams. The intraseam dirt bands are composed of very fine clays, rapidly deposited over wide areas by minor base-level changes or river

bank bursts. The roof measures show least evidence of leaching and are often highest in diagenetic siderite. Ba, Sr, Rb (illite) and Zr (zircon) are predominantly detrital trace elements whilst oxyhydroxide material was the transporting media for the diagenetically located elements, Ni, Pb (pyrite), Co and Mn (siderite). Cu is primarily associated with organic matter.

The detrital coal mineralogy reflects the fine mudrock material and is usually highest associated with the dirt bands. Diagenetic minerals dominate the ash, reaching 95% (by weight), the major component being late diagenetic cleat. A paragenetic sequence of mineralisation follows a widespread trend from sulphides, silicates to carbonates reflecting changing ground water composition. The cleat fractures represent micro-jointing produced with stress release during uplift. Its frequency decreases with bed thickness, and the brittle nature of vitrinite causes it to have the earliest formed and most abundant cleat. The strength of multimaceral lithotypes such as durain is much greater and therefore fracture least, later and with a greater dilation.

ACKNOWLEDGEMENTS

This research project was undertaken with the financial support of a C.A.S.E. Award sponsored by the Central Electricity Generating Board (C.E.R.L., Leatherhead) and the Natural Environmental Research Council and to these establishments my appreciation is gratefully acknowledged. To the following I extend my thanks:-

Dr. D. A. Spears, as my supervisor at Sheffield University, for many fruitful discussions and much encouragement; Dr. C. D. Curtis, as my temporary supervisor and for showing continued interest in my project; Dr. J. Bettelheim (external supervisor) and Dr. K. G. Saunders of the C.E.R.L., for their continued interest, help and access to C.E.R.L. data; Mr. J. H. Atkin (Chief Scientific Officer, Western Division) and Mr. R. H. Hoare (Chief Geologist, Western Division) of the N.C.B. who arranged for my underground visits and for technical information. Mr. T. Halker and Mr. K. Whitworth (N. C. B. geologists) in their help during sample collection; Mr. K. Kendal (C.E.G.B.) for conducting ultimate and proximate analyses on my coal samples; Mr. E. Hall (Water Research Centre) for high speed centrifuging of coal samples; Dr. I. F. Holmes, in close co-operation and discussions in the Chlorine study; Dr. R. Kanaris-Sotiriou, for his help in X-ray techniques; Dr. N. J. Soper, for discussions on joint formation; Mr. V. A. Somogyi, Mr. A. Saxby and Mrs. S. M. Rhodes in helping a non-chemist in wet chemical analysis; Mr. H. Brockley, in T.E.M. microscopy and preparation; Mr. M. G. Cooper, for help and instruction in the art of cartography and the Appendix diagrams. Mr. G. Mulhearn, for thin section preparation; Mr. B. Piggott, for help in photographic matters; Mr. S. T. Reynolds, for trace element analysis and discussion in the follow-up work to this thesis; Mr. A. Sheldon (Department of Metallurgy), for S.E.M. operation .

Finally, but not least, to the secretaries who suffered from my protracted pestering during typing, without whom this thesis would not have been completed:-

Miss S. Forster; Miss P. M. Mellor; Mrs. M. Townsend and Mrs. B. M. Wilson.

VOLUME 1LIST OF CONTENTS

	page number
SUMMARY	i
ACKNOWLEDGEMENTS	iii
LIST OF CONTENTS	v
CHAPTER 1	
INTRODUCTION	1
Sample Locations	2
Sampling Scheme	5
Coal Sample Description	6
Mudrocks	9
Mudrock Colour	11
Sample Numbering	12
Coal Analysis	14
Classification of Coal by Rank	17
Macroscopic Seam Sections and Formation Curves	18
CHAPTER 2	
REGIONAL GEOLOGY - THE CANNOCK COALFIELD	21
General	21
The South Staffordshire Coalfield and its Extensions	22
Stratigraphy	23
Igneous Intrusions	31
Structure	32
CHAPTER 3	
WATER-SOLUBLE ELEMENTS IN COAL AND ASSOCIATED STRATA	34
Section 1 LEACHING EXPERIMENTS	36

	Page Number
Preliminary Studies	36
Water-soluble Leaching Experiments	37
30-72 B.S.S. Mesh Fraction-Eight Feet Seam	37
150-200 B.S.S. Mesh Coal	40
Tema Coal	41
Seam Profiles	41
Conclusions	43
Section 2 DIFFUSION STUDY	45
Theory of Diffusion	46
Eight Feet Seam - Diffusion Experiments	48
Conclusions	52
Section 3 TEMA GROUND ANALYSIS OF WATER-SOLUBLE ELEMENTS	53
Method	53
Discussion of Seam Profiles	55
Element Distribution within Seam Profiles	57
Sodium	57
Potassium	60
Calcium	61
Magnesium	62
Bicarbonate	63
Hydrogen - ion Activity	65
Sulphate	66
Chlorine	68
CHAPTER 4 TOTAL CHLORINE	73
The Origin of Chlorine	73
Nature of Chlorine in Coal	74
Chlorine Distribution	75
Variation with Rank	75
Variation with Depth	77

	Page Number
Small Scale Local Variations	78
Within Seam Variations	78
Association with Coal Types	78
Mode and Time of Chlorine Introduction	79
Peat Growth	79
During Deposition	79
Diagenetic Alteration of Ground Waters	80
Total Cl ⁻ Profiles, Lea Hall and Littleton Collieries	82
Discussion of Profiles	82
The Influence of very Saline Ground Waters- an overriding example.	87
Total Cl ⁻ and Depth	89
Prediction of Cl ⁻ Leaching Levels	89
Influence of Ground Water on Leachable Cl ⁻	90
Location of Cl ⁻ in Coal	90
Time of Cl ⁻ Introduction	91
Conclusions	92
CHAPTER 5 LOW TEMPERATURE ASHING	95
Apparatus	95
L.T.A. Side Effects	96
Temperature of Ashing	100
Ashing- The Colour of Mineral Matter	100
Mineral Matter Profiles	101
CHAPTER 6 MUDROCK ANALYSES	102
Section 1 WHOLE ROCK GEOCHEMISTRY	102
XRF Preparation	103
Major Element Geochemistry	105
Normative Mineralogy	107

	Page Number
Quartz	108
Combined Silica and Alumina	111
Titania	112
Ferrous Iron	113
Ferric Iron	114
Manganese	115
Calcium	117
Magnesium	118
Sodium and Potassium	120
Phosphorous	121
Conclusions	123
Section 2 CLAY MINERAL ANALYSIS	126
Method	126
Sample Preparation	126
Pre-treatment Procedures	129
Peak Area Estimation	130
Clay Proportions	133
Clay Minerals in the Coal	134
Clay Mineral Distribution in the Mudrocks	135
Clay Mineral Variation	135
Chlorite Composition	139
Illite	141
Illite Polytypes	142
Crystallinity Index and Sharpness Ratio	143
Mixed-layer Clays	145
Kaolinite	148
Crystallinity	149
The Significance of Kaolinite in Diagenesis	151

	The Implications of the Kaolinite Content in the Floor Measures	152
	Conclusions	154
Section 3	TRACE ELEMENTS	157
	Sample Preparation	157
	Past Study	158
	Trace Elements in Early Sulphide Diagenesis, Nodules, Cleat and Associated Strata	158
	Trace Element Comparisons	159
	Seam Profile Description - General	159
	Trace Element Associations	160
	Further Evidence on Trace Element Location	170
	Summary of Trace Element Locations	171
	Source of Trace Elements	171
	Conclusions	175
Section 4	PHYSICAL PROPERTIES OF MUDROCKS	177
	N.C.B. Cone Indenter	177
	The Influence of Mineralogy, Fabric and Organic Matter	177
	Conclusions	180
CHAPTER 7	EXCHANGEABLE CATIONS	181
	Method	181
	Cation Exchange - Theory	182
	Clay Mineral Content and C.E.C.	184
	Clay Mineral Associationships	185
	Seam Profiles	186
	Cation Ratios	189
	Exchangeable Cations in Coals	191
	Conclusions	191

	Page Number
CHAPTER 8	
COAL MINERALOGY AND GEOCHEMISTRY	193
The Origin of Minerals in Coal Seams	193
Inorganic Matter in Vegetation	194
Coal Mineral Matter Analysis - XRD	196
Minerals Present	196
Sulphide Group	199
Clay Group including Quartz	201
Carbonate Group	204
Other Minerals	205
Summary of Coal Minerals	206
Coal Ash Geochemistry - XRF	207
Constraints	207
Total Silica and Alumina	208
Titania	210
Total Iron	213
Calcium, Magnesium and Manganese	215
Sodium and Potassium	218
Phosphorous	220
The Relative Contributions of Detrital and Diagenetic Minerals in Coal Ash and Associated Strata	221
Conclusions	224
CHAPTER 9	
CLEAT	228
Cleat Origins	229
Cleat Frequency	231
Influence of Bed Thickness	232
Physical Properties of Coal Types	233

	Page Number
Cleat Mineralogy	234
Minerals Present	234
Between Colliery Comparisons	235
Yorkshire, Nottinghamshire, S. Wales and U.S.A.	
S.E.M. Study of Pyrite and Kaolinite	236
Microscope Photographs	237
Kaolinite Form T.E.M.	238
Kaolinite Crystallinity	238
Carbonate Mineralogy	239
Chemical Analyses of Carbonates	239
Paragenetic Sequence of Cleat Mineralisation	240
Relative Dating of Cleat by Mineralogy	241
Coal Type - Cleat Association	241
L.T.A. Colour	242
Thin Sections	242
Cleat Classification	245
Conclusions	249
CHAPTER 10 SUMMARY	251
REFERENCES	259

VOLUME 2

TABLES

FIGURES

PLATES

APPENDIX 1

APPENDIX 2

APPENDIX 3

CHAPTER 1

INTRODUCTION

The present project has been designed to investigate the geochemistry and mineralogy of coal, its immediately associated strata and the origin, form and distribution of chlorine therein. The study is under the tenureship of a C.A.S.E. Award sponsored by the Central Electricity Generating Board and the Natural Environmental Research Council to provide geological information on high chlorine coals from the Cannock Coalfield. The presence of chlorine can lead to serious fire-side corrosion problems to power-station superheater tubes. Seams sampled from Lea Hall and Littleton Collieries provide the framework for the study.

The thesis is divided into three sections. The first covers sampling, classification, formational environment and stratigraphy of the rocks. The second deals with the chlorine research and the third with the mineralogical and geochemical investigation of the coal ash and associated strata. A through seam investigation of the mineralogy and geochemistry is not only of geological significance, but is also of paramount importance in understanding the behaviour of the chlorine, and its leaching, which has previously been disguised by bulk run-of-mine studies.

An investigation into the differing depositional environments has been attempted to show variations between floors, dirt bands, roofs and detrital coal mineral matter. The role of diagenesis has been examined in terms of ground waters, exchangeable cations and mineralogy and their varying contributions to coal and mudrock samples.

Sample Locations

Four coal seams and associated mudrock strata were sampled from the Cannock Coalfield (Figure 1.1). Of the collieries mining the coalfield: Littleton, West Cannock No. 5, Cannock Wood and Lea Hall it was decided that Littleton and Lea Hall would be chosen. As the project was a CASE Award and the C.E.G.B. were interested in the form and distribution of chlorine in coal, with the prediction of chloride leachability from Park Colliery an overriding factor, those collieries most closely related geographically to the proposed Park site (north-east and east of Stafford) were chosen. Lea Hall Colliery at Rugeley, providing coal for the power station thereat, has had a history of chlorine problems. Work by the C.E.R.L. in chlorine leachability prediction was based on Lea Hall and Hem Heath (N. Staffordshire Coalfield) Collieries. Both show markedly different behaviour with Cl^- leachability being more difficult at Hem Heath. Littleton Colliery was found to have characteristics similar to those of Hem Heath. Both Lea Hall and Littleton Collieries have high chlorine coals. They lie inside the boundary faults and mine the concealed portions of the coalfield.

The coal seams found in the South Staffordshire Coalfield can be traced through the Cannock area, to the North Staffordshire Coalfield via Park. Progressing northwards from the stabilising influence of St. Georges Land, greater subsidence led to seam thinning and splitting. However, all the seams found in the Cannock Coalfield are to be found at Park. Final choices of seams to be sampled was based on importance and accessibility. The Eight Feet and Park Seams were sampled at Littleton and the Yard and Shallow Seams at Lea Hall.

Freshly mined sections were sampled and this is of paramount importance in studying the geochemistry of included ground waters, water-soluble elements and minerals that will oxidise with long exposure to air. Mud-

rock samples were taken from the end of roadways as they are not exposed on the working coal face. Mudrocks, thus sampled are therefore older than the coalface exposures, but rarely more than a few days. The associated mudrocks, including the intraseam dirt bands, were analysed to provide a framework in which the differences or peculiarities of the coal and its mineral matter could be isolated.

Lea Hall Colliery

Of the seams sampled, all but the Yard Seams were advance faces. Being a retreat face, the main and return gates for the Yard Seam had been open for some period and dehydration and contamination of the seam may have taken place. Sampling was carried out on the freshly cut face, approximately 5m from the nearest roadway thus eliminating the problems. However, further complications arise with this seam. The roof measures are extremely fissile, organic rich and physically weak so that the top 30cm of the coal seam are left in as a roof support. Samples Y8 and Y9, representing this part of the seam were taken from a roadway and must have been exposed for a long period and are not fresh. The geochemistry of these samples do show characteristics dissimilar from newly cut faces, notably in the analysis of water-soluble sodium and chloride.

The Yard Seam was sampled at:

National Grid Reference (N.G.R.)	E	406150
	W	316340
Level		10270' A.M.D.*
Depth Below Surface (D.B.S.)		1370'
Depth Below Trias (D.B.T.)		840'

*A.M.D. - Above mining datum. Mining datum is 10,000' below O.D.

The Shallow Seam was sampled at:

N.G.R.	E 407180
	N 315900
Level	10320' A.M.D.
D.B.S.	1485'
D.B.T.	1090'

Littleton Colliery

The Eight Feet Seam was sampled in the tail gate of the 317^S

District.

N.G.R.	E 397647
	N 315570
Level	8920' A.M.D.
D.B.S.	1800'
D.B.T.	1550'

The Park Seam was sampled in two locations - one in a roadway man-hole and consequently a long exposed section and the other in a newly exposed section on the working face. In the final analysis, the former samples were rarely used except for a XRD investigation of the clay minerals in the mudrocks.

1. 455^S Return Gate (man-hole)

N.G.R.	E 397565
	N 315712
Level estimated	8680' A.M.D.
D.B.S.	2000'
D.B.T.	1780'

2. 455^S Tail Gate (new section)

N.G.R.	E 397305
	N 316060

Level estimated	8290' A.M.D.
D.B.S.	2340'
D.B.T.	2120'

Sampling Scheme

A similar sampling procedure was used on all the seams. Floor and roof measures were sampled immediately adjacent to the seam and as many samples as possible taken at a vertical interval of 20 cm. This depended upon the thickness of the exposed succession and varied from the Yard Seam where two floor and three roof samples were taken to the Park Seam where only the immediate floor and roof were accessible. Floor samples were designated a prefix 'F' and roof samples 'R'. Intraseam dirt bands were sampled wherever they occurred. Their designation varies between seams.

Coal samples were taken immediately adjacent to the floor and roof measures and thereafter - whenever possible - at a sample interval of 20cm. An exception was made in the Shallow Seam, where, because of its size, coal samples were taken at a 25cm interval. Samples of 1 to 2kg were taken from Littleton Colliery from the end of roadways. At Lea Hall, samples were taken from the face and the greater difficulty in extraction meant smaller samples. All samples were immediately sealed in moisture-proof bags and marked corresponding to their position within the seam which was logged with the assistance of Mr. C.O. Hunt. Thanks are due to the co-operation of the N.C.B., in particular Mr. J.H. Atkin (Chief Scientist, Western Division) and Mr. R.H. Hoare (Chief Geologist, Western Division) and the geologists Mr. T. Halker (Lea Hall) and Mr. K. Whitworth (Littleton).

Coal Sample Description

The coal specimens from each sample were classified on a macroscopic basis. Although microscopic identification of coal is established down to the maceral level a much more broadly based scheme was used as each sample was investigated on a whole sample basis. Maceral variations would thus be homogenised and the overall characteristics likely to control the mineralogical and geochemical properties of the sample. Coal sample description is given on each of the seam profiles (Figure 1.2).

The coal samples were divided into four groups based on their macroscopic appearance. They are: Bright, Bright Banded, Dull Banded and Dull Coals. Such a terminology is in common usage in seam profile descriptions, for example, by the N.C.B. A more detailed description of the microscopic constituents of coal, from a physical aspect, is given in the cleat mineral section. For a detailed description of coal constituents down to the maceral level, Stach et al. (1975) and the International Committee for Coal Petrology (1957, 1975) are recommended. In the hand specimen, four different types of coal may be distinguished. These 'lithotypes' are vitrain, clarain, durain and fusain. Combinations of these lithotypes to greater or lesser extents form the Sub-classes of coal: Bright and Dull coal (Stach et al., 1975). The coal Sub-classes reflect the predominance of one or more lithotypes. If there is a mixture of dull and bright coal bands, the coal may be described on the predominance of bright over dull coal - 'Bright Banded' and dull over bright coal - hence 'Dull Banded' coal. The terminology is self-explanatory. The term lithotype was proposed by Seyler (1948) to designate the different macroscopically recognisable bands of humic coals. These bands were described by Stopes (1919) as the four visible ingredients in bituminous coals (I.C.C.P., 1957).

Bright Coal

Bright coal is composed of the lithotypes vitrain and clarain.

Vitrain

The term was introduced by Stopes (op. cit.) to designate the macroscopically recognisable very bright bands of coals. The bands are usually a few mm in width, thick bands being rare. Vitrain is very shiny, black and clean to the touch. Its brittle nature means that it is very susceptible to breakage, cubic or with conchoidal surfaces and to cleat development.

In the macroscopic description of coal seams, only the very bright bands greater than 3 to 5mm are recorded as vitrain. After clarain, vitrain is the most widely distributed common macroscopic constituent of humic coals.

Clarain

The term was introduced by Stopes (op. cit.) to describe the macroscopically recognisable bright lustrous constituents of coal which, in contrast to vitrain, is interbanded by dull intercalations. More recently, the term has been used to describe all finely striated bands of coal the appearance of which is intermediate between vitrain and durain (I.C.C.P., 1957).

The bands are of variable thickness having a lustre between that of vitrain and durain. The thickness of the fine bright and dull striations must be less than 3mm, or otherwise should be described as separate lithotypes. Bands made from the bright and dull striations having a thickness exceeding 3-5mm are usually recorded as clarain.

Generally, clarain is the most widely distributed and common macroscopic constituent of all humic coals.

Dull Coal

Dull coal is composed of the two lithotypes durain and the normally less common fusain.

Durain

Stopes (op. cit.) introduced the term durain for dull bands in coal observable on the macroscopic scale. Bands of durain are characterised by their grey to brownish black colour and rough surface, with dull or faintly greasy lustre. Reflection is diffuse. Unlike vitrain, durain is not brittle and consequently has markedly few fractures or cleat developed. When fractures are found, the surfaces are granular.

Bands thicker than 3-5mm are recorded as durain. In some cases, it may be difficult to distinguish durain from carbonaceous mudrocks and dirty coals. In the present samples, durain is either dark brown or predominantly black in colour.

Durain occurs in bands often many cm thick. Although widely distributed, such bands are rarely abundant. An exception is to be found near the top of the Eight Feet Seam where dull coal, predominantly durain, forms a band approximately 70cm thick.

Fusain

The term was introduced by Stopes (op. cit.) to designate the black silky, lustrous macroscopic bands in coal.

It is grey-black or black in colour, has a silky lustre, is fibrous and extremely friable. It is this fraction of the coal which blackens objects with which it comes into contact. It is similar to charcoal in appearance, being porous and crumbly, and is sometimes termed 'mineral charcoal'. It may contain a high proportion of mineral material, which strengthens it and reduces its friability. Bands of more than 3 to 5mm are regarded as fusain.

Fusain occurs as fine bands or lenses in almost all humic coals.

It is not abundant but is widely distributed.

Mudrocks

Despite the abundance of fine-grained sedimentary rocks, constituting approximately half of the geological column (Picard, 1971) investigation has been limited in view of the grain size and poor exposure. Problems arise in nomenclature in the absence of any generally accepted terms to distinguish between texture and mineral composition (Blatt, Middleton and Murray, 1972). Fine-grained rocks are variously defined (Spears, 1980) so that all those fine-grained sediments in the present study have been designated 'mudrock' as a general term (Blatt, Middleton and Murray, op. cit., Spears, 1980, Taylor and Spears, 1981). Distinction may be made on grain size, depending upon the relative proportions of clay, mud and sand, and the presence or absence of fissility. A shale is fissile whilst a mudstone is neither fissile nor laminated (Spears, 1980). A mudrock classification has been proposed (Spears op. cit., Taylor and Spears, 1981) using quartz content as a grain size measure. The former paper showed that for British Carboniferous rocks, quartz is absent from the finest fraction and that a positive relationship is found between TiO_2/Al_2O_3 and quartz. The grain size decrease from siltstones through mudrocks is continuous and accompanied by a decrease in the quartz percentage. 40% quartz was shown to correspond to a grain size of $1/100$ mm which bears a close resemblance to the division between mudrock and siltstone based on field evidence. A similar relationship is found in the present rocks ($r = +0.70$, 99.9% significance) although the correlation is strengthened by a non-normal distribution of data (Figure 1.3).

Spears (op. cit.) proposed the division of mudrock categories on the quartz percentages shown in Table 1.1. Two samples, SSF1 and YF1

would thus be classified as siltstones and furthermore are gritty to the teeth and would be classified as such in the field situation. Two samples 8R2 and I.D.2.11 fall into the very fine category, the remainder in fine and mainly coarse mudrocks and 8F1 in the very coarse category. Spears (op. cit.) found that non-marine mudstones fall into the coarse and very coarse categories as is generally found here. Of the four samples in the fine category, the 'finer' two are intraseam dirt samples, Ydb1 and 8S10c whilst I.D.2.11 has no quartz.

The large scale characteristics are given on the seam profiles (Figure 1.2). Bedding is visible in some of the samples, invariably from the roof of seams. The floors show no structure and have clearly been disturbed by vegetation roots and may represent fossil soils. Root impressions and stigmata are common in the Lea Hall Colliery samples.

Spears (1980) defined lamina as a stratum of less than 1cm thick. Bedding is variable and the frequency rarely falls into this range. All the samples may thus be termed mudstones, with the exception of SSF1 and YF1. Spears (1976) considered laminations to be varves and preserved through an absence of benthos. The present samples have non-systematic bedding which probably result from occasional still-stand events allowing periodic accumulation of organic matter. This is best seen in YR2 where occasional thin films (<0.5mm) of discontinuous organic matter can be observed. Occasionally thin vitrain rich layers, which may represent brief periods of renewed coal vegetation accumulation, or the washing in of woody material, can be distinguished.

The finest grained samples, invariably those with little or no quartz show well developed listric surfaces. Of the seven samples with listric surfaces all but Ydb2 fall within the fine mudstone category with <20% quartz. The presence of quartz increases the strength of the material, increasing the internal friction. An absence of quartz

would allow greater preferred orientation of clay flakes and thus greater susceptibility to shearing, smearing and hence the development of listric surfaces.

Mudrock Colour

The colour of mudrocks is often a distinctive and often important characteristic. Colour can be used for stratigraphic correlation and may be indicative of the environment of deposition and diagenesis. Unfortunately, several environments may produce similar colours (Potter et al., 1980). Tomlinson (1916) showed that the colour of slates is independent of the total iron, controlled by the Fe^{2+}/Fe^{3+} ratio. The progression from red-yellow-green-grey corresponds to decreasing Fe^{3+} due to reduction. The percentage carbon is also important (Potter et al., 1980). However, the type organic matter and its distribution are important (Spears, 1980). Thus black shales may have a darker colour with perhaps 5%C than organic rich mudrocks in the present work with c.40%C.

Colour was identified using a streak plate and comparison with the Munsell colour chart. The use of the streak removes bias caused by mineralogical variations and by surface weathering. The colours are given in Table 1.2, together with organic carbon (based on XRF losses - see XRF mudrock analysis) and the $mFe^{2+} : mFe^{2+} + mFe^{3+}$ ratio.

It is evident that the organic matter content is the major influence on mudrock colour, notably when the iron ratio is constant. As the levels are so marked, reaching 45 to 50%, this is not unexpected, nor are brownish black and black being the major colours. Where the organic matter contents and iron ratios are reasonably constant, as in groups (Y2, Ydb2, YR1 and to some extent YR2), (Ydb1, YF2, YF1) and (SSR1, SSR2, SSR3) the colours are internally comparable. Where the organic matter content is low, the colour is generally light grey. An exception, not readily explained is the brownish-black of 8F1 (9.7%C).

The role of the iron ratio is uncertain in the face of such extreme organic matter contents. Thus the black 8R2 may well be a function of this factor but probably due to both. To determine the role of the iron ratio, plasma (L.T.A.) ashed samples would need investigating. However, if organic matter contents and carbonate is high, this may produce sufficient sulphate (Miller et al., 1979) to affect the colour. It was not attempted. The colour of the L.T.A. of the coal samples is, however, related to the pyrite content (Chapter 5).

Sample Numbering

As the sample interval used was constant, except where notable lithological and section changes, the number of coal samples depended upon the thickness of the seam. The thicknesses are as follows at the point of sampling:

Eight Feet Seam	248cm
Park Seam	230cm
Yard Seam	154cm
Shallow Seam	265cm

The profiles together with predominant coal type and sample location and numbers are given in Figure 1.2.

The Shallow Seam was designated as follows. The coal samples were given the prefix SS (Shallow Seam) followed by a number, from the top of the seam downwards from SS1 to SS11. The floor mudrock was described SSF1 (Shallow Seam Floor) and the roof samples from the highest (SSR1) to adjacent the seam top (SSR3).

The Yard Seam coal was sampled at nine points, Y9 being the top and Y1, the floor of the seam. Samples Y8 and Y9 were taken from the 'old' roof support section. The floor samples were described as YF1 and YF2, the latter being the immediate seam floor. The actual coal seam

floor is gradational with increasing organic content. The sample Y1 had a stigmara which indicates that Y1 includes the top of the floor. The roof samples YR1, YR2 and YR3 were taken such that YR1 is the immediate coal seam roof. The intraseam dirt band is separated by a thin coal, Y2. The dirt bands are described as Y dirt band 1 and Y dirt band 2, abbreviated to Ydb1 and Ydb2, the former being lower in the seam.

The Park Seam, sampled at two locations was given different prefixes. The 'old section' taken from the manhole were described 'P'. The working face samples were given a prefix of '2'. The samples are numbered from 2.1 at the top of the seam to 2.12 at the base. The immediate floor and roof are described 2F1 and 2R1 respectively. A dirt band was encountered near the base of the seam and sampled as I.D.2.11. This is not a coal sample. A thinner dirt occurs higher up the seam and is included in sample 2.8. It was not realised that a thin dirt was here when sampling took place and was consequently mixed in with the coal sample. No attempt was made at separation. This was located in the manhole section also.

The Eight Feet Seam was sampled from roof to floor and numbered from 8S1 at the roof to 8S13 at the base. The floor is 8F1 and the roof samples 8R1 and 8R2 the latter being an organic rich siderite band forming the immediate roof. Towards the floor of the seam is a dirt band. This, like that in the Yard Seam, is divided into three sections and all fell into the sample position 8S10. Thus, they were subdivided 8S10a, b and c, from the top to base. 8S10a consists largely of a pyritous nodule band enclosed in a thin mudrock. Although the mudrock was studied by XRD there was not enough sample for detailed geochemical study. 8S10b is a thin bright coal sandwiched between the overlying pyritous mudrock 8S10a and the major dirt band 8S10c, beneath the coal.

Coal Analysis

Coal analyses were provided by the N.C.B. (Chatterley Whitfield) of those seams sampled and others closely associated from Lea Hall, Littleton and Hem Heath (North Staffordshire Coalfield) for comparative purposes. Of the four seams studied in detail in the present work, samples were made up using equal weight from each sample. Mudrocks and dirt bands were excluded. This was analysed by the C.E.G.B. Central Services Laboratory, Ratcliffe-on-Soar, and thanks are due to K. Kendal of the Analytical Chemistry Section. As these composite samples are not complete seam sections they may not be entirely representative. Nor is it known how much dirt is included in the analyses carried out by the N.C.B., and the duplicated seam analyses (N.C.B. and C.E.G.B.) were not sampled at the same time. Variations are thus expected and found. Coal analysis is covered by Montgomery in Karr (1978).

Proximate Analysis

"The determination by prescribed methods of moisture, volatile matter, fixed carbon (by difference) and ash. The term has evolved from 'approximate analysis' as it was, today the analytical procedures are empirical and precise, and if carried out by the prescribed method may be duplicated by all laboratories" (Karr, op. cit.).

Moisture: essentially water, quantitatively determined by definite prescribed methods, which may vary according to the nature of the material.

Ash: inorganic residue remaining after ignition of combustible substances, determined by definite prescribed means. Ash is not synonymous with mineral matter. Alteration takes place with high temperature combustion, CO_2 is lost from carbonates and water of hydration is lost from silicates such as clays.

Pyrite is converted to ferric oxides resulting in a loss of sulphur. The amount lost depends upon the composition of the ash. If there is a high calcium carbonate, the calcium may combine with sulphur lost by the pyrite, thus forming calcium sulphate. This is also true for sulphur lost from organically combined sulphur compounds as sulphur dioxide. Sodium and chlorine are also lost. The ratio of ash to mineral matter depends upon the original mineral matter. Various formulas have been constructed to recalculate mineral matter such as that of Parr (1932) and King et al. (1936) and are covered in Karr (op. cit.). The Parr formula uses only ash and sulphur values:

$$MM = 1.08A + 0.55S$$

A = ash

S = sulphur

The King et al. formula needs the determination of ash, pyritic sulphur, mineral CO_2 , and sulphur trioxide in both the coal and ash, and chlorine in the coal:

$$MM = 1.09A + 0.5S(\text{pyrite}) + 0.8 CO_2 - 1.1SO_3(\text{ash}) + SO_3(\text{coal}) + 0.5 Cl$$

Separate sulphur analyses have not been attempted, nor have carbon dioxide. No attempt has been made to recalculate mineral matter although the Parr formula could be used.

Volatile matter: those products, exclusive of moisture, given off by a material as a gas or vapour, determined by definite prescribed methods, which vary according to the nature of the material.

Fixed carbon: in the case of coal or coke and bituminous materials, the solid residue other than ash obtained by destructive distillation by definite prescribed methods.

Proximate analyses of seams by the N.C.B. and C.E.G.B. are given in Table 1.3. The C.E.G.B. analyses were determined on dried samples. These results were re-expressed on a dry ash free (d.a.f.) basis.

Ultimate Analysis

"In the case of coal and coke, the determination of carbon and hydrogen in the material, as found in the gaseous products of its complete combustion, the determination of sulphur, nitrogen and ash in the material as a whole and the estimation of oxygen" (Karr, op. cit.).

Carbon and hydrogen are determined in one operation. The determined values include, in addition to the carbon and hydrogen of the organic substance, carbon present in the carbonates, and hydrogen in the free moisture of the sample and from the water of hydration of the minerals associated with the coal. When the data are reported on the dry basis, the hydrogen is corrected for the moisture present in the sample as analysed. Nitrogen was not analysed. Oxygen is determined by summing the other components and subtracting from 100. The result is affected by errors incurred in the determinations of the analysis and also by the changes in weight of the ash-forming constituents on ignition. By definition, oxygen calculated as a weight percentage of the analysis sample according to this procedure does not include oxygen in the mineral matter or in the ash, but does include oxygen in the free water (moisture) associated with the analysis sample. As nitrogen was not calculated, both oxygen and nitrogen were calculated by difference and given grouped together. Ultimate analysis based on dried samples of the four seams studied are given in Table 1.3, and have also been re-expressed on a dry ash free basis (d.a.f.) and not a mineral matter free (m.m.f.) basis. The difference is likely to be small as mudrocks were excluded.

In terms of elemental composition, plants consist almost entirely of carbon, hydrogen, nitrogen and sulphur. In the process of coalification, there is a progressive loss of oxygen and a corresponding increase in

the proportion of carbon. The hydrogen content remains fairly constant within bituminous coals, but decreases progressively in passing from these to the anthracites.

Other properties of the material undergoing coalification also show well-defined changes; the volatile matter decreases at a variable rate, the calorific value increases to a maximum in the low volatile steam coals (Coal Rank Code 200), and then decreases, and the moisture shows the opposite trend, reaching a maximum in bituminous coals. These trends with rank are covered in Stach et al. (1975).

The Classification of Coal by Rank

In order to classify coal by rank, use can be made of one or more properties that vary in the same direction throughout the rank range, for example carbon, oxygen and volatile matter. Several classification systems have been devised, probably the best known by Seyler (1948). A simplification of the system used by the N.C.B. for coal classification can be used to indicate the rank of coal expected in the four Lea Hall and Littleton Colliery seams studied in detail.

Volatile matter expressed on a d.a.f. basis (though should be m.m.f.) ranges from 37.2% (Shallow Seam) to 40.9% (Yard Seam). Over 32.0% V.M. are classed as 'High volatile' coals with a coal rank code of 400 to 900, and as H.V. 'A' bituminous coals have volatile matter content of 31% or less, must be in the H.V.B. or H.V.C. class (Karr, 1978). Further subdivision uses the calorific value, which, unfortunately, is not available. The carbon content (d.a.f.) ranges from 79.56% (Yard) to 82.69% (Eight Feet) and this falls into the range 700, 800, 900. The N.C.B. 'The Coalfields of Great Britain, Variations in Rank of Coal' by Wandless (1960), gives Lea Hall as predominantly 800 (high volatile, very weakly caking) and limited 900 (high-volatile, non-caking) and Littleton slightly

higher in rank, a function of greater tectonism and burial, as predominantly 800, with some 700 (high-volatile, very weakly caking). The major uses of coal of these ranks are: 700 'general purposes', 800 and 900 'high volatile steam and house coals'. N.C.B. information (Chatterley Whitfield, provided by Mr. J. Atkin) gives the seams as 800, and work based on the moisture holding capacity (Thomas and Damberger, 1976) shows the coals to be high-volatile bituminous 'B' based on the moisture content.

Macroscopic Seam Sections and Formation Curves

A subdivision of seams can be made by a 'naked eye' appraisal of the coal types on the relative proportions of coal lithotypes and then expressed on a sub-class basis of bright, bright banded, dull banded and dull coals, and carbonaceous shale and shale. Tasch (1960), summarised in Stach et al. (1975), showed that lithotype formation results from different subsidence rates within the swamp. Fusain, for example, represents low rates of subsidence, shallow water and frequent access to air. Vitrain and clarain represent shallow flooding, durain deeper water and carbonaceous shale and shale representing the deepest water, or 'wettest' conditions. Adopting this order to represent the six layers the curve of the measured seam section is drawn by Tasch (op. cit.) in the following way:

"If the lithotype occurring at the floor of the seam is overlain by a second lithotype represented at a higher level in the diagram, an oblique line is drawn from the lower boundary line of the band in the diagram corresponding to the bottom lithotype to the upper boundary line of the second lithotype. The horizontal distance on the diagram between the two points of intersection of this oblique line with the boundary lines of the two bands in question represents the thickness of the lower-

most lithotype. If the next (third) lithotype of the seam, moving towards the roof, is represented by a lower band in the diagram, an oblique line is drawn through the band representing the second lithotype, down to its lower boundary line, the horizontal distance between the two points of intersection again representing the thickness of the lithotype. If the third lithotype is not adjacent to the second in the diagram, a vertical line is first drawn down to the band representing the third. The length of this depends on the nature of the next (the 4th) lithotype. The vertical line will be extended to the lower boundary line or stop at the upper boundary line of the band corresponding to the third lithotype according to whether the fourth is located above or below the third in the diagram. From this point onward, the same procedure as described continues.

If however, a subsequent lithotype finds its proper place on the diagram in the band immediately below the band representing the underlying lithotype, no vertical line is drawn. In such a case, an oblique line is drawn from the lower boundary line of the higher band which coincides with the upper boundary line of the lower band, up to the lower boundary line of the latter. The angle should be so chosen that the horizontal distance between the intersections of the oblique line with the upper and the lower boundaries respectively corresponds to the thickness of the lithotype."

The curve reflects the rate of subsidence and reveals phases in seam formation. It forms the basis for comparing profiles relatively independent of lithotype composition. For example a dull coal may be a carbonaceous shale elsewhere with a small change in the subsidence rate. The occurrences can be used to show a similar trend, as seam formation is simultaneous over the whole area although lithotypes may not. Dull layers are often of wide lateral extent as are dirt bands (and tonsteins).

The present profiles have been drawn from two sources, those of the present research only from those samples taken - and thus are not whole seam profiles - and those whole seam profiles sampled by the N.C.B. for Dr. I. Holmes' chlorine research. 'Average' characteristics have been used in both groups, divisions being made at a sub-class level. The seams studied and shown in Figure 1.4 are the Littleton Benches, Eight Feet, Park and Shallow and the Lea Hall Yard (twice), Shallow and Deep seams. No attempt has been made to standardise the sampling intervals, hence the two Shallow seam profiles are, in reality, of similar thickness. Comparisons are difficult. It is obvious that the coal forming basins changed across the accumulation area, from the characteristics of the Shallow Seam at Lea Hall and Littleton. There is more variation at Littleton in the lower part of the seam and shallower water bright coal predominates at Lea Hall. Further evidence of greater subsidence at Littleton is in the occurrence of two dirt bands which are not found at Lea Hall. There is an overall trend to deeper water towards the top of the seam with a durain rich horizon before returning to shallower bright coals. The Yard Seam, sampled twice at Lea Hall, also shows variation. The dirt band near the floor is well established in both sections but in the section that I sampled, the variations through the band have been emphasised, as have the variations in the roof samples. If the roof section is ignored, then similar profiles result. There is a shallow, bright coal below and above the dirt band, succeeded by the deposition of a deeper water dull coal horizon followed in turn, by a return to shallower bright banded coals in the N.C.B. section and becoming predominantly bright at the top of the seam in the samples that I have taken. As the divisions between coal types are subjective, and not made on a quantitative basis, minor differences may not be significant.

CHAPTER 2REGIONAL GEOLOGY - THE CANNOCK COALFIELDGeneral

The Cannock Coalfield or Cannock Chase Region is applied to the whole northern region of the South Staffordshire Coalfield lying north of the Bentley Faults (Mitchell et al., 1945). These faults, which run generally westwards from Walsall to Short Heath, conveniently divide the coalfield into the productive measures of the north from the largely exhausted but historically important "Black Country" between Wolverhampton, Walsall and Halesowen to the south - the limit of economic coal. Recent mining developments are to be found in the north of the Cannock Coalfield and the extensions of this field beyond the 'boundary faults' beneath a thick covering of Triassic strata. The proved extension of this field to the north reaches the proposed site of Park Colliery immediately east and north-east of Stafford. A location map is given in Figure 1.1.

Surveying the area dates back to 1852-56 by Ramsay et al. for the 'Old Series' one-inch map Sheet 62. Partial revision extended up to 1886. Jukes (1853) described the coalfield in 'The Geology of the South Staffordshire Coalfield, First Edition', and in the Second Edition (1859). The northern area was re-surveyed by Gibson and Cantrill, and the corresponding memoir, "The Geology of the Country around Lichfield" (Barrow et al.) appeared in 1919. The one-inch 'New Series' map, 'Drift Edition' was published in 1922 and the 'Solid' edition in 1926. The western section of the coalfield is covered by the 'New Series' Sheet 153 - Wolverhampton (1929) and the accompanying memoir by Whitehead et al. (1928). The years 1942-43 saw the revision of the Cannock Chase Region with particular reference to mining information obtained from underground and opencast exploration. This work, 'The Geology of the Northern Part

of the South Staffordshire Coalfield (Cannock Chase Region)' by Mitchell, Stubblefield and Crookall (1945) is the most detailed account of the stratigraphy, structure and palaeontology of the region. The British Regional Geological Guide, Central England (Hains, B.A. and Horton, A., 1969) gives the most up-to-date overall coverage.

Before studying the peculiarities of the Cannock Chase Region it is necessary to study the stratigraphy and structure of the South Staffordshire Coalfield in its entirety.

The South Staffordshire Coalfield and its Extensions

The South Staffordshire (Staffs.) Coalfield is a spindle-shaped area of Coal Measure strata surrounded by younger rock of Permo-Triassic age. It appears as an 'island' of Upper Palaeozoic rocks into which anticlinal folds have exposed small areas of older rocks (Mitchell, in Trueman, 1954).

The coalfield is some 40km long about its north-south axis reaching Brereton, near Rugeley in the north, to its southernmost termination, the Lickey Hills (Figure 2.1). The coalfield is generally bounded by major faults which are roughly parallel and are 16km apart in the central portion of the coalfield (Hains and Horton, 1969). To the north-west, the concealed coalfield reaches at least to Sandonbank, 4.5km north-east of Stafford. A full Coal Measures sequence has been proved to the south-east of Rugeley as far as the Whittington Heath borehole, near Lichfield (Hains and Horton op. cit.). To the east of Rugeley, the sub-Triassic extension is mined by Lea Hall Colliery, 1.6km south-east of the town. To the west of the coalfield, beneath the Triassic unconformity, Coal Measures strata are found at depth but the area is subjected to much faulting (Mitchell, op. cit.).

Stratigraphy

Pre-Coal Measures

The Lower Cambrian is found outcropping in the extreme south of the coalfield forming the N.N.W. trending Lower Lickey Hills (Hains and Horton, 1969). No Ordovician rocks are to be found in the area, nor in Central England and the majority of the Coal Measures floor is Silurian in age. Ordovician and Silurian sedimentation was controlled by the stable Midland Block and the subsiding Welsh geosyncline (Wills, 1951; 1956) or the southern continental margin of the Iapetus Ocean in contemporary thinking (Anderton et al., 1979). Continental collision in Upper Ordovician - Silurian times destroyed previous 'basin' and 'shelf' facies.

Upper Llandovery

Rocks of this age are confined in general to Great Barr (eastern coalfield) and the North Lickey Hills near Rubery (south of coalfield). The outcrop is close to the surface in the south-west at Stourbridge and at Walsall is found to be composed of fine sandstone with shale partings, occasionally calcareous and sometimes fossiliferous. Younger breccias and conglomerates often contain Upper Llandovery rocks indicating that the outcrop was considerably larger in pre-Upper Coal Measures and Triassic times (Hains and Horton, op. cit.).

Wenlock Series

Wenlock Series rocks are found in the inlier to the east of Walsall, dipping north-westerly. Borehole and shaft evidence proves the strata between Walsall and Rowley Regis along the same strike. The Barr Limestone, a limestone/shale sequence with a shelf facies is the basal member. The Wenlock Shales, 152 to 213m of grey/green shales with occasional thin limestone are exposed and proved in boreholes along the

south-eastern side of the coalfield between Halesowen and Walsall. A limestone/shale sequence, the Wenlock or Dudley Limestone, including Calymene blumenbachii (the 'Dudley locust'), is located in the Walsall inlier and in the small faulted folds at Wren's Nest Hill, Dudley Castle, Hurst Hill and beneath the Coal Measures at Rowley Regis.

Ludlow Series

Confined to the inliers at Dudley, Sedgley, Turner's Hill and Walsall are the flaggy and nodular Ammestry or Sedgley Limestone and the Upper Ludlow Shales composed of sandy, calcareous flags with limestone nodules, silty shales and sandstone with a benthonic fauna (Hains and Horton, 1969).

Old Red Sandstone

The end of the Silurian saw the climax of the Caledonian Orogeny. Folding, however, had little effect on Central England until well into O.R.S. times. The environment changed from the Upper Ludlow shelf sea to subsiding delta plains supplied by sediment from the newly formed mountains. The intensifying orogeny during the Silurian produced progressively coarser sediments passing from marine to deltaic, brackish water deposits, confined largely to the north west of the Midland block (Hains and Horton, 1969).

Downton Series

The floor of the north west and south west coalfield is formed by Downton Series rocks, exposed in a number of inliers in the south west, especially at Turners Hill and Gornal (south of Sedgley). The succession is composed of sands, silty sands, shales and muds and includes the fishes Didymaspis, Hemicyclaspis and Onchus (Hains and Horton, op. cit.).

Carboniferous

The Carboniferous Period saw markedly changing environments. A return to marine conditions during the Dinantian was succeeded by the shallowing of the seas and detrital, often coarse sandstones associated with delta formation, the cyclothems of the Namurian. The succeeding Coal Measures extend the rhythmic sedimentation of the Namurian but with a much reduced marine component. The Upper Coal Measures saw the progression into entirely non-marine red measures, and expression of the oncoming Hercynian Orogeny.

Carboniferous Limestone Series

Rocks belonging to the Carboniferous Limestone Series are exposed only in a few small inliers, boreholes and colliery workings in the northern part of the South Staffordshire Coalfield. The influence of St. Georges Land and the Mercian Highlands basement was instrumental in the distribution of these strata, lying with marked unconformity on the Lower Palaeozoic rocks and thinning rapidly to the south. The rocks are typical of the 'block facies', slowly sedimented, well bedded limestones with a rich coral and brachiopod fauna.

Namurian

Uplift and erosion produced a marked unconformity before Namurian rocks were deposited. A series of deltas along the northern side of St. Georges Land saw a primarily marine environment, becoming rhythmic, passing from marine to deltaic including thin fire clays and coals. Fossils are rare except in the marine component, especially goniatites, lamellibranchs, brachiopods and fish. Subsidence northwards away from the block saw increased thickness of Millstone Grit strata. Thus in a borehole at Rugeley, 23m of Millstone Grit strata are penetrated, decreasing to nothing in the south (Hains and Horton, 1969).

Lower and Middle Coal Measures

Coal Measures rocks were deposited on the Namurian Millstone Grit deltas, their source in the north, spreading and covering most of the north Midlands. The centre of subsidence lay in the area now occupied by Manchester, and thinned as the sediments approached and overlapped the stable basement massifs such as St. Georges Land to the south. This had a marked effect on the sediments and the thickness of the succession. Supply generally exceeded subsidence producing delta flats on which vegetation flourished when above sea level. Marine incursions were few and far between even when compared with the Namurian. The effect of differential subsidence is seen in progressive thinning of Lower and Middle Coal Measures successions (Figure 2.2). Together they represent 1220m of deposits in the North Staffordshire Coalfield, 550m at Cannock and 200m in the South Staffordshire Coalfield. The coal portion of the succession becomes progressively more dominant and the seams thicken in this direction reaching a maximum in the historically important Dudley region. The classic example is the Thick Coal, reaching 9 to 11m at Dudley, produced by long periods of stability with little subsidence. Further north intraseam dirt bands increase their thickness and the seam is split into the Park, Eight Feet and Benches Seams. At Lea Hall Colliery, 64m of sediments represent the Thick Coal of Dudley. South of Dudley, the coals deteriorate and thin, the lower coals failing first. South of Stourbridge and Halesowen coal is no longer workable and 'seat earths', once the basis of the refractory industry, predominate.

Rhythmic Sedimentation

The characteristic Millstone Grit rhythmic sedimentation continued in the Coal Measures but the lithology changed. The sediments became increasingly terrestrial and the stratigraphically important marine bands, with their characteristic goniatite fauna, diminished in frequency and

thickness. The coals thickened and became more common and the sandstones thinner, finer and more localised. A typical 'complete' rhythm or 'cyclothem' is:- seat earth, coal, marine mudstone, non-marine mudstone, siltstone, sandstone, seat earth. This is rarely complete and considerable lateral variations, due to channel position, often (randomly) controlled the sub-environment of deposition. The depth of downcutting often affects the completeness of the rhythm. Duff and Walton (1962) in an attempt to define statistically the most typical Coal Measures cycle, using the interval between successive rootlet horizons, identified 1200 cycles of which there were 320 different types.

On average, only 2% of the Lower and Middle Coal Measures is coal (Hains and Horton, 1969). Grey and black mudstones and shales, collectively termed 'mudrocks' (Black, Middleton and Murray, 1972; Taylor and Spears, 1981) dominate the succession. Their colour is controlled by organic matter and the oxidation state of the iron present (Potter, Maynard and Prior, 1980). Sandstones are fine grained, cross-bedded and often lenticular, passing laterally into mudrocks. The floor measures, rootlet beds or seat earths, vary from mudstone rich fireclays with a high kaolinite content, to sandstone rich 'gannisters' (Rayner, 1976).

Coal Measures Division

Many schemes have been proposed to divide the Coal Measures using fossil plants, non-marine lamellibranchs and marine bands. A summary of the divisions is given in Table 2.1. Kidston (1894, 1905) proposed a four-fold division based on plants, modified by Crookall (1931, 1955) but which suffers from vague boundaries. Three major marine bands were thus included to delineate the divisions between the lower two divisions (Westphalian A and B), as proposed by the Heerlen Congress of 1927 (Hains and Horton, 1969), and together with the use of palynology, this system is used with some success in correlation. Hind (in Hains and Horton,

op. cit.) proposed the use of non-marine lamellibranchs but this conflicted with the plant division and fell from favour. In conjunction with coal seams and marine bands to overcome poorly defined boundaries, they can be widely used (Trueman and Weir, 1946). Marine bands were often used locally but with the realisation that the major marine bands are continental in extent, wide geographical correlation using marine fauna was possible. Stubblefield and Trotter (1957) re-defined the Lower Middle and Upper Coal Measures using the goniatites Gastrioceras subcrenatum (base), Anthracoceras vanderbeckei, (base of Middle Coal Measures) and Anthracoceras cambriense (base of Upper Coal Measures). The latter is found only in parts of the South and North Staffordshire Coalfields due to the diachronous nature of the boundary (Hains and Horton, 1969) and the unconformable Permo-Triassic strata.

The Cannock Coalfield Succession

The lowest productive Coal Measures of the Cannock area are relatively unfossiliferous but near the base is the Fair Oak Marine Band (Gastrioceras listeri and Gastrioceras retrorsum), located near Rugeley. The Stinking Marine Band divides the Lower and Middle Coal Measures. The Middle and Upper Coal Measures boundary is represented by the Bay Marine Band of the North Staffordshire Coalfield and appears to correlate with the marine band above the Silvester's Bridge Marine Band of the Cannock area. Approximately 85m of grey Productive Coal Measures are present above the highest mussel band at Cannock Chase, but are not found to the south and their age is not certain (Mitchell, 1954).

The succession through the Coal Measures at Lea Hall Colliery is given in Figure 2.3. This is typical of the Cannock Chase Coalfield and thus applicable to Littleton Colliery. The unconformity between the Triassic and Carboniferous is marked and leads to rapid lateral changes in the level of the seams below the unconformity leading to quite thick barren

Upper Coal Measures in places (R.H. Hoare, N.C.B. Western Area, Chief Geologist, personal communication). A detailed account of the Coal Measures succession in the Cannock Chase area covering the seams and palaeontology in detail is given in Mitchell et al. (1945) from which a review follows.

Some 76m of strata, including the Fair Oak and West Hill Marine Bands, are found below the lowest workable coal in the north, being reduced to 15m in the south (Mitchell, 1954). The Mealy Grey Coal of the north fails southwards. The Deep, Little Deep and Shallow coals come together to form the Bottom Coal in the south. Local basalt 'trap' or 'green rock' intrusions are found in the Shallow Seam. The Bass Rider, Bass and Yard Seam (Cannock) become the New Mine Seam in the south. The sulphurous Stinking Coal has been produced by the marine band of that name which forms its roof. Locally important sandstones are found in the measures above. The Heathen Coal sometimes splits into an upper and lower leaf. The Park, Eight Feet (or Wyrley Bottom) and Benches coalesce to form the Staffordshire Thick Coal south of the Bentley Faults where it is largely worked out. The Sub-Brooch Marine Band lies 15m below the Brooch Coal. This is the highest persistent coal (Mitchell, op. cit.). The Charles Marine Band and coal are locally important in the north of the coalfield together with other less economic seams, the Wyrley Yard, Bottom and Top Robbins, Heath Hays and Wimbleberry Cannel above the marine band. The Silvester's Bridge Marine Band overlies the Top Robbins Seam followed by mussel-bearing shales. The highest grey Coal Measures pass into the Etruria Marl, their boundary being uncertain (Mitchell, 1954).

Nodular ironstone horizons were once extensively worked. The most important, the 'Diamond', 'Silver Threads' and 'Blue Flats' lie below the 'Deep Coal' and the 'Pennystone' and 'New Mine' between the Stinking and

Heathen Coals (Mitchell, op. cit.).

Upper Coal Measures

The succession of the Upper Coal Measures is still rhythmic but this is less obvious in the red beds. Deposited in the same basin as the North Staffordshire Coalfield, the succession is similar from the Etruria Marl upwards. The Middle and Upper Coal Measures boundary is diachronous and conformable with increasingly thick productive Grey Measures present when traced northerly away from the basement influence. Local unconformities due to the oncoming Hercynian Orogeny are frequent.

Etruria Marl Group

The Middle Coal Measures grade into red, purple, ochrous, mottled unstratified marls of the Etruria Marl Group, with common breccia horizons, the 'Esplay Rocks'. Well developed in the west of the coalfield, they thin eastwards (Mitchell et al., 1945).

Halesowen Group

The Halesowen Group are red mottled marls including a buff and purple sandstone. Near the top of the succession is a 0.6m spirorbis limestone which contains gastropods and fish remains (Mitchell et al., 1945). Exposures are confined to the southern margin of the coalfield.

Keele Group

Well exposed along the southern margin of the coalfield, and proved by borings and shafts in the east, the Keele Group is present in few places in the west. The succession base is a conglomerate of marl, limestone, sandstone, chert and quartzite, followed by a sequence of red, purple marls and sandstones with a spirorbis limestone. The succession is 198m thick (Mitchell et al., 1945).

Permian

Enville Group

The Enville Group has been variously defined as highest Coal Measures (Mitchell et al., 1945; Mitchell, 1954) but is now taken as the Permian base (Smith et al., 1974). Considerable thicknesses of mainly red continental sediments were deposited in a series of troughs and basins in the Midlands. Their correlation is uncertain as is their relationship with the Keele Group. The boundary is located in the Four Ashes borehole and is probably conformable on the eastern side of the coalfield. In the borehole 132m of deposits are found (Mitchell et al., op. cit.) although up to 460m are found elsewhere in the coalfield.

Triassic

There is no palaeontological evidence for the Permo-Triassic boundary. The Hopwas Breccia, underlying the former Bunter Pebble Beds, was taken as the boundary (Mitchell et al., 1945). Warrington et al. (1980) redefined the Triassic nomenclature. The arenaceous lower units of the Bunter and Lower Keuper have become the Sherwood Sandstone Group, the base of which is strongly diachronous. The lowest Triassic strata is the Cannock Chase Formation, a poorly cemented sandy conglomerate. The base is essential knowledge in mining the concealed Cannock Coalfield because of the poor cementation and saturation.

Igneous Intrusions

Intrusions are restricted to the large olivine basalt outcrops at Rowley Regis, Wednesfield and Pouk Hill (Mitchell, 1945). Occasionally they are found in the coal seams destroying or metamorphosing the coal into hard, stony 'black coal'. Detailed coverage of their alteration is given in Mitchell et al. (1945). The intrusions are probably related to Triassic earth-movements (Gibson, 1927; Mitchell, 1954).

Structure

The structure of the coalfield is complex (Figure 2.1). The north-south anticlinal inlier now exposed is essentially Hercynian but pre-Carboniferous activity certainly took place (Gibson, 1927; Mitchell, 1954). Maximum uplift probably succeeded the Enville Group marked by a strong unconformity (Gibson, op.cit.). Late Triassic movements produced gentle folding and the boundary faults (Mitchell, 1954). The Rugeley or Eastern Boundary Fault has a throw of approximately 560m to the east. North of Walsall it becomes the Clayhanger Fault and is joined by the Vigo Fault which dominates the suite, skirting the Lower Palaeozoic inlier at Walsall, terminated eventually by the Birmingham Fault. To the east, Triassic strata overlie thick Coal Measures, at least as far as Whittington Heath, near Lichfield (Bennett and Scurfield, 1951; Mitchell, 1954). North of Cannock Chase, Coal Measures strata reach the Stafford ('Park') area. To the west of the coalfield, Littleton, and previously Hilton Main, collieries mined the concealed measures. Hilton Main revealed strong faulting and sharply folded productive measures (Mitchell, 1954) whilst borehole evidence and surface mapping indicated the presence of the Bushberry Fault, a series of large west throwing fractures. The faulting in this area of the coalfield produces much repetition of the strata. Large faults south of Wolverhampton, the Western Boundary Faults, terminate mining in this direction.

The structure of the Cannock Chase Coalfield is covered in detail by Mitchell et al. (1945). Within the exposed coalfield the strata generally dip westwards, increasing in angle in this direction. Folding is more important south of the Bentley Faults (Mitchell, 1954). These faults lie east-west between Birmingham and Wolverhampton and are associated with a broad arch which separates the historically important Dudley area from the Cannock Chase Coalfield. The Dudley area is a trough which can be

divided into two sub-basins, the exposed coalfield being the exposed arch between the two. The basins are at Wolverhampton in the west, and Birmingham in the east. The coalfield is basement controlled following two trends. The first follows the northerly Lickey Hills, Dudley-Sedgley trend and the second runs from the Netherton axis then parallel to the Dudley Port trough-fault to the eastern outcrop of the Walsall inlier. The major faults follow these trends or their north-south, east-west resultants (Mitchell, 1954). North of Darlestone the Thick Coal crops out and lower measures are introduced until the Deep or Bottom Coal is at a shallow depth on the upthrow (southern) side of the Bentley Faults. North of these faults, higher measures are introduced, striking generally north-south, and the Thick Coal is represented by several thinner seams.

A simplified account of the geology is to be found in the included papers, Caswell, Holmes and Spears, parts 1 and 2 (Appendix 1 and 2).

CHAPTER 3WATER-SOLUBLE ELEMENTS IN COAL AND ASSOCIATED STRATA

The investigation into the major water-soluble elements in coal and associated strata is an important part of this research project. It is an essential part in the understanding of chlorine behaviour and predicting its origins and location within the strata, and hence its potential release. It is to this end that water-soluble elements have been studied, and not primarily as a study of the elements for their own sake.

Work on water-soluble elements in the geological literature is limited. Spears (1974) found water-soluble cations present in Carboniferous shales when studying the relationships between exchangeable cations and palaeosalinity (Spears, 1973). An association of high Ca^{2+} and Mg^{2+} , low Na^+ and K^+ was found with marine strata whilst in the non-marine section the pattern was reversed. Spears (1974) suggested that these water-soluble cations were formerly exchangeable cations which were released into the pore water as diagenesis eliminated some exchange sites. Fellows (1979, Ph.D. Thesis) studied through-seam variations in water-soluble elements in the Barnsley Main and Top Hard Seams. In the field of coal research, water-soluble extractions from coals have long been studied especially in an attempt to predict, then reduce, the level of pollutants such as Na^+ and K^+ , and more recently, Cl^- . Much of the early work involved the analysis of Cl^- in order to predict the Na^+ present, as Cl^- was much more easily analysed. Later, with serious fireside corrosion problems in thermal power-stations, associated with high Cl^- coals, the emphasis of investigation shifted. Cl^- and the associated major cations Na^+ , K^+ , Ca^{2+} and

Mg^{2+} were often analysed, but as these studies were related to bulk coal consumption, run-of-mine samples were used. This may mask within seam variations which may provide important additional information in the understanding of water-soluble element distribution within coal and associated strata.

As a noted high Cl^{-} coalfield, the Cannock Coalfield was chosen for investigation (Daybell and Pringle, 1958; Bettelheim and Hann, 1980; Saunders, 1980). Comparisons between the seams and collieries of the present work was supplemented by additional work carried out for the N.C.B. (see Section 3) by Dr. I.F. Holmes (Post-doctorate research award) on a further seam from both Lea Hall (Deep Seam) and Littleton (Shallow Seam) and from the North Staffordshire colliery Hem Heath (Yard-Ragman Seam).

It is intended to investigate the water-soluble cation and anion behaviour in this section. As this has a major contribution to the behaviour of chlorine, some of the work will be repeated later in this thesis (Chapter 4).

A method devised to identify the association between water-soluble chlorine and coal type using stains and acetate peels is included in Appendix 3 (Caswell, 1981).

SECTION 1LEACHING EXPERIMENTS - PRELIMINARY STUDIES

A series of experiments was set up using different size fractions, sample sizes and dilution factors to investigate different aspects of the water-soluble element distribution. Initial leaching experiments were conducted on run-of-mine coal from the Lea Hall Shallow and Hem Heath Winghay seams supplied by C.E.R.L. An experiment based on the methods of the C.E.R.L. and N.C.B. showed that water-soluble cations and Cl^- determined comparable results with that of the aforementioned industries. The percentage Cl^- extracted was based on the C.E.R.L. figure for total Cl^- and the results given in Table 3.1. The Winghay Seam coal exhibited markedly different leaching characteristics when compared to the Lea Hall seams and shown by the C.E.R.L. to leach a much lower percentage Cl^- . Although the sample from this seam may not have been typical of the whole seam, it was notable that bright coal predominated over dull coal. Leaching experiments were conducted on the two coal types on a relatively coarse size fraction (30-72 B.S.S. mesh) and the major cations determined. Little difference was found except for Na^+ . The values after 24 hours leaching are given in Table 3.1 and indicate far higher chloride (Na^+ is inevitably Cl^- associated in the leachates) leaching from the dull coal. The significance of this observation will become clear in the total chlorine section (Chapter 4). Also notable are the differing leaching rates (Figure 3.1).

Water-soluble leaching experiments

1. As the initial experiments showed promising results, the technique was applied to the Littleton Eight Feet Seam to study both the diffusion rate from the 30 to 72 B.S.S. mesh fraction and the water-soluble elements. Aliquots were taken over set intervals for 25 hours. The samples were crushed in polythene bags by hammer. No attempt was made to separate different coal types within a sample nor to remove mineral matter.
2. The samples crushed for 1 were further sieved through finer meshes. Analysis of water-soluble Cl^- alone was made on the 150-200 B.S.S. mesh fraction.
3. The same sub-samples used in 1 were crushed by hammer then further ground in a mechanical agate. It was thought that terna grinding may have detrimental effects upon the organic matter and thus affect the leaching rates via unwanted side effects (C.E.R.L. internal document). Sub-samples were terna ground for a minimum period and the results compared. Using the F ratio, all major cations except K^+ (the values of which were very low) were shown to be similar at the 95% level. Cl^- determination was made by colourimetric analysis in the initial standardisation experiments. Cl^- investigations made by Holmes at Sheffield for the N.C.B., showed that Mohrs titration was a more accurate and reproducible technique. In subsequent experiments all samples were terna ground for a minimum period and Mohrs titration was used for water-soluble Cl^- determination.

30 to 72 B.S.S. mesh fraction Eight Feet Seam

Method

A large sample (40 g) was diluted in a ratio of 1:12 with distilled water and aliquots were extracted at set intervals over a 25 hour

period following the method of the C.E.R.L. (internal document). The sample was stirred over a mechanical stirrer at slow speed to prevent breakdown of samples to a finer size. Aliquots were extracted from the suspension using a syringe-pipette and the coally matter was removed under suction in a Whatman flask using fine filter paper. The major cations Na^+ , K^+ , Ca^{2+} and Mg^{2+} were analysed by atomic absorption spectroscopy and Cl^- using colourimetric analysis by spectrophotometer. pH was taken in the solution immediately before sampling using a pH electrode. HCO_3^- and SO_4 were determined by titration but found to be negligible. The sample temperature was also monitored and varied over a range of 5°C ($22^\circ\text{C} \pm 2.5^\circ\text{C}$). A similarly prepared blank was run with all the samples. Aliquots were taken at set time intervals for use in the diffusion study. As the leaching rate is markedly exponential and leaching essentially having ceased after a couple of hours, the analyses obtained after 25 hours was used as the final result for this size fraction.

Seam Profile

The profile of major cations and Cl^- are given in Figure 3.2. There are considerable through seam variations that far exceed analytic variation and are thus attributable to true differences between samples. When compared to the 150-200 B.S.S. mesh and tema coal, the values are reduced as would be expected from a far coarser grain size and a considerably smaller surface area available for leaching or reaction. This is particularly notable in the case of Cl^- , Ca^{2+} and Mg^{2+} . Na^+ , although lower in the coarser fraction is not notably different. K^+ is low throughout the profile, rising to a minor peak in the roof sample 8R1. As K^+ is probably clay associated (illite) this may be expected. However, the floor and dirt band samples are

not considerably different to that of the coal samples and may thus be attributable, at least in part, to ground waters.

Ca^{2+} and Mg^{2+} have similar profiles which suggest a similar source, at least within the coals. Similar diffusion rates back this hypothesis. If the ratio of Ca^{2+} to Mg^{2+} is taken, there is considerable variation. Many of the Ca^{2+} values are far in excess of that expected by solution of ankerite and thus it must be concluded that calcite too must be present in some samples. Complications arise at the foot of the seam in 8S11, 8S12 and 8S13. Here, Mg^{2+} exceeds Ca^{2+} and another source, possibly ground waters are making some (variable) contribution. The contribution made by mudrocks is negligible. 8R2 is a contributor to the water-soluble Ca^{2+} and Mg^{2+} but this is essentially a siderite.

Na^+ values exceed the other major cations in solution, varying between a maximum of 1110 $\mu\text{g/g}$ (8S5) and a minimum of 355 $\mu\text{g/g}$ (8S12). The four mudrocks have similar values (615 to 745 $\mu\text{g/g}$) and are slightly higher than the coal seam average. However, the coals show considerably greater variation, reaching a peak about two thirds of the way up the seam.

The Cl^- curve is comparable to that of Na^+ . Their profiles are sub-parallel and Cl^- reaches a maximum of 1735 $\mu\text{g/g}$ in the same sample as the Na^+ . The mudrock Cl^- values are lower than the coal seam average, being comparable to the coal seam average. In the floor (8F1) and roof (8R1), Na^+ exceeds Cl^- but in no other samples does this occur. An association between Na^+ and Cl^- in the coals is seen in their correlation ($r = +0.88$, 99% significance). Much of the early research into the form of chlorine suggested that it was combined with Na^+ . It is evident, however, that although the Na^+ (Cl^- equivalent)

may account for all the Cl^- in some samples, and in the mudrocks exceed the Cl^- , this is not the case in all the coals (Figure 3.2). The reduced major axis regression does not plot through the origin but intersects the Cl^- axis at a value of 340 $\mu\text{g/g}$ which is not Na^+ associated (Figure 3.3). Ca^{2+} also shows a significant correlation with Cl^- ($r = +0.73$, 99% significance) and may also play a role in some of the coal samples. In two coals, 8S5 and 8S6, Na^+ will balance the Cl^- and at the other extreme, 8S7 and 8S12 has only 56.6% and 57.7% balanced by Na^+ . It is interesting to note that the former samples are both dull coals and the latter are bright banded and bright coals respectively. There is a suggestion therefore, that at this size range, dull coals yield more water-soluble Cl^- than bright coals and the former are purely Na^+ associated. This is not the case with the bright coals. The significance of the Ca^{2+} - Cl^- relationship becomes clearer with the tema ground samples and shall be dealt with in the relevant discussion. It is evident that the Cl^- characteristics have no bearing on seam position but rather more fundamental determinants, that of coal type.

150-200 B.S.S. Mesh Coal

The fines of the 30-72 fraction were passed through finer sieves and retained for comparative study. 0.5g of sample was placed in a centrifuge tube with 25ml of distilled water, mechanically shaken for 10 minutes and left to stand overnight. The samples were centrifuged at high speed to separate the suspension from the leachate which was then pipetted off for analysis after 25 hours. Cl^- only was determined and shown in Figure 3.2. No longer is there a relationship between high water-soluble Cl^- and dull coals and low levels from the bright coals. The dull coal 8S5 still yields a significant peak but the bright banded coal 8S1 is marginally higher.

The ratio of the 150-200 to 30-72 B.S.S. mesh coals is shown in Figure 3.4. It is significant that the higher ratios are associated with the bright banded coals, dull and dull banded coals are lower and bright coals are the lowest. This indicates that the relative increased leachability from the dull coals is being reduced, the bright coals are little changed whilst the bright banded coals are leaching predominantly more Cl^- . Further support is thus forwarded for a fundamental structural change in the Cl^- holding capacity of the different coal types.

Tema coal

The distribution of the major water-soluble cations, pH, Cl^- , $\text{SO}_4^{=}$ and HCO_3^- will be covered in greater detail later in this chapter. Here a comparison is made with the leachates of the two coarser fractions. The method was based on Spears (1974) but a sample of 0.5g, 30ml of distilled water and a 25 hour leach was used. Spears (op. cit.) considered 1 hour to be sufficient. A time interval comparable to the coarser fractions was, however, used.

Seam Profile

The profiles for water-soluble Cl^- in the three size fractions, together with total Cl^- is given in Figure 3.5. The tema profiles including other elements are given later in the chapter in figures 3.12 to 3.14. At the top of the seam (8S2 to 8S7), the water-soluble Cl^- is sub-parallel to total Cl^- . This is not clear in the bottom of the profile but is not seen at all in the 30-72 mesh fraction. Work on total Cl^- has shown bright coal (vitrinite specifically) to be the major host (Saunders, 1980; Caswell, Holmes and Spears, Part 1). Water-soluble Cl^- is highest in the bright coal 8S11, followed by the bright banded coals 8S1 and 8S7. The lowest is found in the dull coal 8S9. This is a considerable reversal to the pattern shown by the coarse 30-72 mesh profile.

The ratio of tema Cl^- to 150-200 mesh is modified when compared to the ratio of the coarser fractions (Figure 3.4). The coals showing the highest leaching ratios are the bright coals. The mudrocks show a ratio close to 1 indicating that the majority of Cl^- was leached from coarser fractions and is more accessible than from the coal. Further evidence of changing Cl^- leachability is shown in the hand specimen where the dull coal is most readily leached of Cl^- (Caswell, 1981). The apparent discrepancy between this work and the vitrinite- Cl^- holding capacity of Saunders (1980), is explained by the changing leaching behaviour of the different size fractions, of changing porosity. The maceral groups have different porosity and pore sizes. Vitrinite thus has a far higher internal surface area (porosity) than other coal macerals (Thomas and Damberger, 1976), those of inertinite and exinite (Harris and Yust, 1979). Caswell, Holmes and Spears, part 1 show that porosity is related to Cl^- holding capacity. The different size fractions are, therefore, opening up progressively smaller pores to allow the release of Cl^- . There are complications in that some of the Cl^- is organically bound, and that fine grinding is essential to release this Cl^- and to provide maximum surface area for exchange reactions to take place.

It is apparent, however, that Na^+ is not correlated with Cl^- so strongly in the tema coal as with the coarser fraction. The diffusion rates of Na^+ are known to be different to Cl^- and are not related to particle size (Neavel et al., 1977; Bettelheim and Hann, 1980). The present work supports this observation. The tema Na^+ can account for between one third and one half of the water-soluble Cl^- . This corresponds to the findings of Edgcombe (1956) and Daybell and Pringle (1958). The ratio of the Na^+ leached from the tema to 30-72 mesh (Figure 3.4) coal

shows peaks in the bright and bright banded coals. The lowest values are found in the mudrocks (8F1 is an exception) indicating that the majority of Na^+ is water-soluble from the coarser fraction. The dull and dull banded coals exhibit similar ratios of between 1.1 and 1.3. The ratio exhibits a pore size distribution similar to that of the Cl^- but the ratios are reduced indicating a difference in concentration, location or form. Either Na^+ is not able to enter (or has been expelled) from the smallest pores, or a large proportion of the Cl^- is attached to organic matter on the internal surfaces of the pores. The ratio of Cl^- to Na^+ (tema), is also shown in Figure 3.4. The peaks in the bright banded (8S1, 8S7) and bright coals (8S11, 8S12) are far in excess of that which can be balanced by Na^+ . The alternative relationships of Cl^- in the tema coal are covered later in section 3.

If the ratio of water-soluble Cl^- (tema) to total Cl^- is taken then no significant pattern emerges (Figure 3.4). The 30-72 mesh profile ratio showed peaks in the mudrocks and some dull and dull banded coals. This is to be expected as the dull coals have highest water-soluble Cl^- and lowest for the bright coals. The 150-200 to total Cl^- profile is more complex with peaks in both dull and bright banded coals whilst the tema profile shows great variation which cannot be controlled by coal type alone. There is a variation between 44.6% (8S10) and 88.5% (8S1) for bright and bright banded coals and 41.5% (8S8) to 74.5% (8S4) for dull and dull banded coals. This is partially at variance with the ratios which show a porosity: coal type control, and thus suggests a further factor in the release of Cl^- .

Conclusions

- 1) Leachability of water-soluble elements increase disproportionately to decreasing grain size.

- 2) In coarse fractions, dull coal yields higher Cl^- values than the bright coal. Na^+ may balance the Cl^- leached from the dull coals but not in the bright coals.
- 3) These relationships change with tema grinding. Bright coals release more Cl^- than the dull coals. Na^+ , however, does not balance water-soluble Cl^- in either coal type and another mechanism is contributing to its release.
- 4) The ratio of $\text{Cl}^-:\text{Na}^+$ at different size fractions show differences in coal porosity. The pore size decreases in the order: dull, banded, bright, but the internal surface area of vitrinite is far in excess of exinite and inertinite.
- 5) The behaviour of the mudrocks differs from that of the coal. Cl^- leached at a coarse size may be balanced by Na^+ . Tema grinding does not significantly increase Cl^- leachability but if the organic matter content is low all the Cl^- may be removed. Na^+ may exceed the equivalent Cl^- in these samples.
- 6) Essentially all the Na^+ is water-soluble in the 30-70 B.S.S. mesh size mudrocks. This is certainly not the case with the coals.
- 7) A different holding mechanism exists between mudrocks and coals. The total extraction of Na^+ and Cl^- from the coarser fraction mudrocks demonstrates either:
 - (i) A larger pore size
 - (ii) Neither element is organically combined
 - (iii) A combination of (i) and (ii)
- 8) If the water-soluble Na^+ is a measure of pore accessibility, then the mudrocks have larger pores and/or permeability greater than the coals.

SECTION 2DIFFUSION STUDY

In order to assess the form of the Cl^- within the coal leaching experiments were carried out on varying sample sizes over differing time intervals. Similar investigations are presented by Bettelheim and Hann, 1980. A pilot study was conducted on two size fractions of 'run-of-mine' sample obtained by the C.E.R.L. of the Lea Hall Shallow Seam. This sample is not to be confused with the seam samples dealt with elsewhere in this thesis. They were sampled at two different localities at different times and may have very different characteristics. The experiment was conducted for comparison of methods and results obtained by the C.E.R.L. The two size fractions used were 1 to 0.5 mm and 0.5 to 0.21 mm ('coarse' and 'fine' coal respectively). Water-soluble Cl^- was determined by Mohr's titration. C.E.R.L. total Cl^- figure of 0.66% weight was used to calculate the water-soluble Cl^- percentage leached. The percentage leached at the various time intervals are given in Table 3.2. The water-soluble Cl^- percentages are comparable with those obtained by the C.E.R.L. (internal paper).

The leaching characteristics of the two coal fractions are different. This is to be expected, and has been shown (Daybell and Gillham, 1959; Bettelheim and Hann, 1980) that the particle size has a bearing on leaching rates. There is, however, little difference in the percentage Cl^- leached after 1400 minutes. The leaching rates are different. The rate of leaching is more rapid in the 'fine' coal until the period 340 to 1400 minutes is reached. If the percentage Cl^- extracted is plotted on log-log paper against time, the gradient is related to the diffusion/dissolution rate. A gradient of 0.5

indicates a purely diffusional removal of the solute from the particle surface into the leach solution (Crank, 1957). The gradients obtained are 0.16 ('coarse' coal) and 0.10 ('fine' coal), far lower than for pure diffusion and shown in Figure 3.6. Bettelheim and Hann (op. cit.) showed that there is considerable variation in samples from different but closely related seams and even between the same seam but different samples. Gradients were shown to vary between 0.43 (Shallow Seam) and 0.17 (Hem Heath Winghay and Florence Rowhurst). The present results are lower but there are complications. The figures given in Bettelheim and Hann (op. cit.) are based on the fraction leached out of that removed under reflux at 100°C. This is not necessarily 100% but is close to this figure. The use of total Cl^- values means that the present gradients are minimum values. Variation in the Cl^- analysis for the coarse coal shows that the gradient may vary between 0.16 and 0.26. The conclusions are that the size is important in the percentage leached and also in the rate of leaching. Of the water-soluble Cl^- leached in 1400 minutes, 50% of this had been removed from the 'fine' coal in little over 1 minute and from the 'coarse' coal in 35 minutes. The gradients indicate that more than simple diffusion is controlling the Cl^- release over the 10 to 100 minute interval. The leaching rate decreases with time.

Theory of Diffusion

The mathematical models describing diffusion are dealt with by Crank (1957) and a description of the steps controlling leaching from a porous body are given in Bettelheim and Hann (1980). The four steps of extraction, any of which may be rate controlling, are given below.

(a) For a porous body initially containing gas in the capillary system, the solvent must at first penetrate the particle interior and

replace the trapped gas. This process ('soaking') can be controlled either by the rate of diffusion of the gas through the advancing column of liquid ('diffusional soaking') or by a capillary flow mechanism. The former is a relatively slow process compared with the latter.

(b) After physical contact between the solid and solvent is established, the solute starts to dissolve. Provided the removal of the dissolved solute from the interface boundary is fast (i.e. the rate of dissolution is not controlled by mass transfer from the interface), the rate will be directly proportional to the interface surface area.

(c) Once dissolved, the solute is removed from the interior to the particle perimeter by diffusion for which two limiting models can be proposed. If the soaking and dissolution are fast, then the particle can be assumed to contain at the start of the leaching a uniform solution of the solute. In this situation the removal process can be described by a single-phase diffusion model. On the other hand the capillaries could be initially filled with solid solute. The soaking period would then be eliminated as the solvent replaces only the dissolved solid. The mathematical description in this case must therefore take account of an initial mixture of solid solute and a saturated solution and can be treated in a similar way to 'diffusional soaking'.

(d) In the final stage the dissolved solute is transferred from particle surfaces into the bulk of the leaching solvent.

If the pores are filled with the same solution that makes up the bulk solvent Crank's (1957) model may be applied.

$$E = \phi \sqrt{\frac{Dt}{R^2}}$$

E = fractional extraction
 R = particle size
 D = diffusivity
 t = time

If the pores contain a mixture of solid solute and its saturated solution an approximate solution of the model was made by Piret et al. (1951).

The model is applicable to the period of diffusional soaking and is slower than capillary flow and therefore represents one limiting case.

For lower range extractions, that is, less than 50%, both models approximate to a straight line with the fractional equation.

$$E \propto \sqrt{t}$$

Bettelheim and Hann (1980) concluded that capillary soaking is approximately one order of magnitude slower than diffusional extraction.

Eight Feet Seam - Diffusion Experiments

When Bettelheim and Hann (1980) looked at the percentage Cl^- extracted from 3-6mm coal (at ambient temperature in 24 hours) the coals which exhibited the lowest leaching were from the North Staffordshire Coalfield and comparable were those of the Littleton Park Seam. The highest extractions were obtained from the Lea Hall seams. Consequently it was decided to study the Eight Feet Seam (Littleton Colliery), which lies above the Park Seam, as an example of a slow leaching coal. A size fraction of 30-72 mesh B.S.S. was taken.

Four coal samples were studied in detail. Three show the extremes in leaching behaviour and this is seen to correspond to coal type. It has been shown that in the 30-72 mesh B.S.S. leachates profiles (Figures 3.5, 3.7 to 3.10) that the highest water-soluble Cl^- levels are to be found in the dull coals and lowest in the bright coals. The Na^+ contents correspond to the leaching curve. In the dull coals 8S5 and 8S6, all the leached Cl^- can be balanced by water-soluble Na^+ and these samples were chosen to represent rapid leaching rates. The bright coal 8S12 has the lowest Na^+ to Cl^- ratio for seam and thus expected to have the slowest

leaching rate. 8S13, another bright coal, had a higher Na^+ content, but much lower water-soluble Ca^{2+} and Mg^{2+} values, compared to 8S12, was also studied. Direct comparisons with the leaching rates given in Bettelheim and Hann (1980) are not possible but approximations can be made. This is because of the aforementioned 'ultimate extractability' leaches of tema ground coal under reflux. † The Cl^- gradients are minimum values but should be close to those of Bettelheim and Hann (op. cit.). Greater difficulties arise when dealing with water-soluble Na^+ , Ca^{2+} and Mg^{2+} . Neavel et al. (1977) shows that all Na^+ is not water-soluble at ambient temperature and this observation is confirmed by Bettelheim and Hann (op. cit.). Therefore, the ultimate extractability values in the Bettelheim and Hann paper will be different to those used here. Percentages were calculated on tema ground water-soluble totals at ambient temperature and must therefore be equal to or less than the values obtained under reflux and must therefore be regarded as maximum values. Quantitative comparisons with Cl^- leachability are thus dubious but will indicate trends. With these drawbacks in mind, the results obtained are as follows.

The percentage Cl^- , Na^+ , Ca^{2+} and Mg^{2+} leached is given in Table 3.3. After 10 minutes, the dull coal (8S5) has leached 67.7% of its water-soluble Cl^- for this size fraction. For the time period 10 to 1500 minutes the leaching gradient of 0.07 was achieved. Obviously for this period leaching is considerably slower than that of pure diffusion (0.5). In the period before 10 minutes (that is 3 to 10 minutes) the gradient is much steeper and 0.30 is achieved (Figure 3.7). For the overall 3 to 100 minute period 0.16 is the average. 8S6 shows very similar characteristics, 55.5% of its water-soluble Cl^- for this size being leached after the first 10 minutes. ‡ For the initial period,

3 to 10 minutes, the gradient is 0.31 (Figure 3.8) almost identical to 8S5. Thereafter, the leaching rates fall but not to the same extent. This is probably because the initial leaching period is slower in 8S6.

The behaviour of the bright coals is somewhat different. Unfortunately, it was not possible to sample 8S12 and 8S13 after 10 minutes so gradients over the period 3 to 100 minutes were used. This gave very similar gradients, 0.40 for 8S12 (Figure 3.9) and 0.39 for 8S13 (Figure 3.10). This is much steeper than the initial leaching rates of the dull coals. Although the rates of the bright coal leaching falls with time, the decrease is nothing like so well marked as that exhibited by the dull coals. For the initial leaching period the gradient approaches that of diffusion. For the dull coals this is not seen because the initial leaching period is so fast that the sampling times do not cover the first 50% of the extraction in which the diffusion rates should approximate to a 0.5 slope (Bettelheim and Hann, 1980). In the dull coal 8S5, 50% extraction is reached after 3.75 minutes, 8S6 after 4 minutes, whilst the bright coals need 57 minutes and 55 minutes for 8S12 and 8S13 respectively to back half their Cl^- for that size fraction. There are fundamental differences in the rate of Cl^- release. Similar fundamental changes in the leaching characteristics have been shown for the different size fractions used on the Eight Feet Seam. The differences between the coal types will be investigated later.

The rate controlling mechanism is obviously not pure diffusion. Dissolution is probably taking place as well. This is indicated by the leaching rates of Ca^{2+} and Mg^{2+} . It has been shown by Daybell and Pringle (1958) that carbonate dissolution is important in Cl^- leaching. This is especially so in the bright coals where the Na^+ leached does not balance the Cl^- .

The gradients of Ca^{2+} and Mg^{2+} are very different in all the samples. However, as there is a close correspondence between Ca^{2+} and Mg^{2+} in samples 8S5 and 8S6 it is suggested that this is dissolution of cleat carbonates. Similar, although not identical ratios, are found for 8S12 and 8S13. The variation in gradients between bright coal samples will be controlled by the amount of carbonate present in each sample. Small quantities or finely dispersed material will go into solution faster and consequently the first 50% dissolution will be achieved before the first sample interval. As 8S5 and 8S6 have comparable water-soluble Ca^{2+} figures and both are higher than 8S13 the rates of dissolution are probably controlled by the level of the carbonate minerals. The most rapid leaching rates were achieved in 8S12 which has the highest water-soluble Ca^{2+} and Mg^{2+} levels. (of the 4 samples studied) when tema ground. However, the ratio between the tema ground and 30-72 mesh B.S.S. Ca^{2+} is twice as high as found in the other three samples suggesting that the carbonate is most massive in 8S12, probably as major cleat. Tema grinding will give a large surface area capable of rapid and prolonged leaching.

If the chloride is balanced by Na^+ , it would be expected that similar Cl^- and Na^+ gradients will exist. The proportion of Na^+ leached from the different size fractions, however, shows the distribution and leaching properties of Na^+ and Cl^- to differ as the coal size is reduced. Different leaching characteristics have been found by Neavel et al. (1977) and Bettelheim and Hann. (1980). Here, leaching rates cannot be directly compared. Suffice to say, in the dull coals Na^+ leaches more rapidly than Cl^- and the role is reversed in the bright coal. The orders are comparable, but for the dull coal (as with Cl^-) the first 50% extraction is not sufficiently sampled for rates to be calculated with any certainty.

Conclusions

- 1) The variability of Cl^- leaching rates indicate that dissolution is the most probable rate-controlling mechanism, combined to varying degrees with diffusion of the ions to the particle surface.
- 2) Different coal types have widely differing leaching characteristics. Dull coals leach more rapidly than bright coals.
- 3) Dissolution of carbonates play an active role in releasing Cl^- through exchange and this is most marked in the bright coals.
- 4) The relative abundancies of different coal types in a seam profile will affect the leaching characteristics of composite samples and may contribute to the differing leaching characteristics found by Bettelheim and Hann (1980). The use of bulk run-of-mine samples will mask lithotype (or smaller) variations.

SECTION 3TEMA GROUND ANALYSIS OF WATER-SOLUBLE ELEMENTS

Standard conditions were based on the method devised by Spears (1974) to determine the water-soluble cations in Coal Measures shale samples. Because further analyses were to be carried out, the sample size was increased as was the volume of water used. To make comparisons for the coarser fractions where time allowed for diffusion and dissolution obviously played a role in rate of leaching, a comparable time with these experiments was used. It is thought, however, that the water-soluble elements would enter solution very rapidly, or at least reach equilibrium with the leachate within a short time (van Moort, 1971 and Spears, 1974 used 1 hour). This is backed up by solutional experiments carried out on gypsum and calcite (Figure 3.11), however, it must be noted that these experiments were carried out in distilled, not acid, waters.

Method

0.5g of tema ground sample was placed in a clean, dry centrifuge tube and 30ml of distilled water added. The tubes were stoppered and mechanically shaken for 10 minutes and then allowed to stand for 25 hours. The tubes were centrifuged at high speed in a high speed centrifuge for 5 minutes to separate the fine material from the leachate. Occasionally, separation of the very fine clays encountered within intraseam dirt bands was difficult and separation with filter paper and a similarly prepared blank was needed. However, in Ydbl this is seen to be unsuccessful and it is thought that fine material was held in suspensions. The analysis gave a falsely high K^+ content probably

derived from the illite fraction of the sample. The top 20ml of leachate was pipetted off for analysis. Na^+ , K^+ , Ca^{2+} and Mg^{2+} were determined by a Perkin-Elmer 303 Atomic Absorption Spectrophotometer using 'flame'. Cl^- was determined by Mohr's titration and bicarbonate by titration with dilute HCl (Vogel, 1978). Sulphate analysis followed the method of Fritz and Yamamura (1955). However, due to sample size and dilution this particular method was not particularly accurate. These particular values are not considered to be precise enough for analytical work but will be used to indicate trends. pH readings were taken immediately before the leachates were pipetted off. Immediate reading is essential for pH determination as a gain or loss of CO_2 or oxidation of, for example, ferrous iron, will alter the solution equilibrium and hence the pH. However, as the experiment was conducted over a period of 25 hours, it is expected that CO_2 may be lost, if once present, thus having some effect on the pH. Water-soluble elements were determined shortly after sampling on an 'as received' basis. Moisture content was determined a short time later and thus may have experienced some dehydration. The moisture content was calculated by weighing before and after oven drying at 105°C . Samples were cooled in a desiccator prior to re-weighing. Water-soluble elements were re-expressed using the moisture content on a 'moisture free-basis'. Total Cl^- , determined at a much later date was carried out on oven (105°C) dried samples. This distinction is important to make at this stage. Included within this thesis in the Appendix section are three papers. The first two are the result of joint work on the form of chlorine carried out by Dr. I.F. Holmes for the N.C.B., Dr. D.A. Spears and the present author. The first paper (Appendix 1) 'Total Chlorine in Coal Seam Profiles from the South Staffordshire (Cannock) Coalfield', Caswell, Holmes and Spears is in

press with the journal Fuel and will henceforward be referred to by the authors' names followed by part 1. The second paper (Appendix 2) 'Water-Soluble Chlorine and Associated Major Cations from the Coal and Mudrocks of the Cannock and North Staffordshire Coalfields', Caswell, Holmes and Spears has also been submitted to Fuel and will be referred to as part 2. Much of the work in this water-soluble element and subsequent chlorine section will be duplicated in these papers which can be used as a summary of the present chlorine investigation. However, a distinction must be made between the data used in these two papers. The second paper is given as an 'as-received' basis and the total Cl^- and necessary water-soluble elements have recalculated because the additional seams, Lea Hall Deep, Littleton Shallow and Hem Heath Yard-Ragman (by Holmes) did not have their moisture contents determined. The data from this paper provided by the present author can be recalculated to correspond with that of this thesis by using the moisture contents for the four seams studied here. The results of Holmes will be covered in this present thesis but this will be indicated.

Discussion of Seam Profiles

The four seam profiles of the major cations, anions and pH are given in Figures 3.12, 3.13 and 3.14. Also given are the correlation coefficients (r) of the water-soluble elements for the combined mudrocks and coal samples (Table 3.4).

The most outstanding feature of the seam profiles is the distinct difference between the ion concentrations leached from the coals and mudrocks. Organic rich mudrocks and dirty coals exhibit intermediate concentrations. Obviously there are major geochemical differences introduced by the presence of high concentrations of organic matter. The mineralogy of the coals is similar to that of the associated mud-

rocks so far as the detrital mineralogy is concerned although proportions are different. The diagenetic mineralisation is, however, somewhat more complex. This is best seen in the cleat minerals which normally terminate at the interface between coal and mudrock. The difference in mineral matter will be shown to play a major role in the composition and distribution of water-soluble elements. Differences, too, are found arising from the physical structure of both coal types and mudrock when dealing with internal surface area (henceforward I.S.A.) or porosity and pore size distributions. As the majority of the smallest coal pores are interconnected (Harris and Yust, 1979) and thus permeable and as the samples were all collected from beneath the water-table, it is reasonable to assume that the moisture contents are an indication of the I.S.A. (Caswell, Holmes and Spears, part 1). Thomas and Damberger (1976) showed that a direct relationship exists between inherent moisture content and the volume % porosity in Illinois coals, although small proportions of gaseous and liquid hydrocarbons and CO_2 are also found within the pores. Considerable variations are thus to be found in moisture content between coals and mudrocks explained by differences in porosity. It has been shown that a significant correlation exists between total Cl^- and moisture content (Figure 4.4) and the moisture centrifuged from Ydbl essentially accounts for the total Cl^- of the sample. The composition is comparable to groundwaters analysed for that seam by the N.C.B. (Table 4.2). As similar element ratios were found from water centrifuged from Shallow Seam coal it is expected that the I.S.A. will play a dominant role in determining some of the water-soluble elements. It has been shown that moisture contents vary with coal type as a direct function of their structure (Caswell, Holmes and Spears, op. cit.) and that cleat mineralogy also varies with coal type (cleat section). Indirect relationships will, therefore, also arise.

Exceptional samples are Y8 and Y9 from the Yard Seam. These samples, and the associated roof measures, represent a non-fresh section. Water-soluble Cl^- and Na^+ values are considerably higher than in the fresh Yard samples, and higher than those found in the other seams. These samples are unusual, but do give evidence for the concentration of NaCl rich groundwaters held within the seam through evaporation.

Element Distribution within Seam Profiles

Sodium

Mudrocks

The seam profiles (Figure 3.12) show that Na^+ contents are generally very constant and only slightly lower, except in that Shallow Seam, in the mudrocks than the coals. It is evident, however, that as the organic content increases, as in the carbonaceous mudrock Ydb2 and dirty coal Y2, Na^+ values increase to become intermediate between the mudrocks and coal.

The 30-72 mesh B.S.S. to total Na^+ ratios for the Eight Feet Seam (Figure 3.4) show that Na^+ is most rapidly leached from the relatively coarse fraction, a phenomenon also observed by Neavel et al. (1977) and Saunders (1980). Neavel et al. (op. cit.) found that the total Na^+ is not water-soluble, but this is probably feldspar or clay associated and hence negligible in the present samples (Whole Rock Geochemistry, XRD and Clay Mineral chapters).

Highly significant correlations exist between Na^+ and water-soluble and total Cl^- ($r = +0.97$ and $+0.95$ respectively, 99.9% significance) indicating a possible NaCl association in organic poor mudrocks. This is emphasised by the correlation with H_2O and the composition of moisture

centrifuged from Ydbl (Table 4.4) thought to represent groundwaters trapped or in transit through the mudrock. Na^+ is seen to balance the majority of water-soluble Cl^- and this can account for the total Cl^- of Ydbl. The rapid release of Na^+ suggests that it is held in the pore water and is released by diffusion alone.

Na^+ increases with depth as the salinity of the ground water increases. Although this is found in the coals, it is not obvious in the mudrocks. Table 3.5 gives the Na^+ means for each of the seam mudrocks (excluding the Yard roof). An increase with depth is seen in all but the stratigraphically lowest Shallow Seam but this may be explained by a lower moisture content. Re-expressed as the Na^+ concentration in the moisture an increase with depth is found within a colliery (Table 3.5).

The low Na^+ values associated with the floor samples YF1 and SSF1 may be explained by dilution introduced by very high quartz and hence low clay contents. However, the Lea Hall Deep Seam roof (investigated by Dr. I.F. Holmes) is also quartz rich and has a very high Na^+ content. Either the porosity of this sample is greatly different to those of the Yard and Shallow Seams or diagenetic quartz has reduced the I.S.A., or the porosity is located in between the quartz in the Deep Seam but in the clays in the other two seams.

Coal

Moisture centrifuged from run-of-mine Shallow Seam coal shows Na^+ to be present (Table 4.4) but lower by an order of magnitude than in the mudrock Ydbl. This may be explained either by an ion concentration gradient within the pores or only certain pores yielding their moisture. The rapid leaching of Na^+ suggests that all the Na^+ is held within pore water hence similar concentrations would be expected between the coal and mudrock centrifuged water.

Table 3.5 shows Na^+ to increase with depth explained by increasing dissolved solids with depth in ground waters (Gluskoter, 1965). As the Littleton Colliery seams have been sampled at a greater depth, the composition is related to stratigraphical depth and may therefore represent Hercynian ground waters as there is no apparent evidence for recent dilution from N.C.B. ground water evidence (Table 4.2).

Expressed on a concentration basis (Table 3.5), the Na^+ increases with depth but is lower than in the associated mudstones. As the coals have a higher moisture content, then only certain pores are available to hold Na^+ or other waters are also present. As total Cl^- is related to moisture content via the I.S.A. (Caswell, Holmes and Spears, part 1), yet Na^+ is essentially all leached together with an equivalent Cl^- weight (Saunders, 1980), it is suggested that only certain, larger pores, hold Na^+ (and some Cl^-). Na^+ has a reduced correlation with the total moisture in the coals when compared to the mudrocks.

Na^+ , like Cl^- , is found to be related to coal type. This is most clearly seen in the Shallow Seam profile (Figure 3.12). The highest Na^+ is to be found in the bright coal SS2, whilst the second lowest value is located in the only dull banded (no dull coals) coal, SS3, in the seam. The pore size and distribution is such that vitrinite has the highest I.S.A. (Thomas and Damberger, 1976) but the dull coal maceral groups have far larger pores (Harris and Yust, 1976, 1979) thus specifically concentrating pore waters in dull coals (Caswell, 1981). This will reduce the correlation with moisture content when compared to Cl^- and coal type. Ground waters will more easily enter and leach from the larger pores of the dull and dull banded coals as seen from the coarse coal leaching experiments and diffusion studies.

Potassium

Values are generally very low but range from 5 to 1585 $\mu\text{g/g}$ and are therefore not normally distributed. - There are clearly two populations, that of the mudrocks being several magnitudes higher than the coals which rarely exceed 30 $\mu\text{g/g}$. For the combined mudrock and coal data, a significant positive correlation exists with the ash content and the seam profiles show K^+ increasing towards floor, intraseam dirt and roofs as the detrital input increases.

Of those cations presently under study, K^+ is the most abundant in sedimentary rocks but is much lower in natural waters than Na^+ (Hem, 1970). It is essentially structurally located in feldspars and illite and may be easily re-introduced into the clays if degraded. Similarly, weathering of illite to give degraded illite type mixed-layer clays (as in the present work) may allow K^+ to be leached which would otherwise be strongly held. The K^+ content of ground waters is negligible (Figure 3.14) and maybe thus illite located in the present samples.

Mudrocks

The absence of feldspars and mica (XRD evidence) limits the K^+ host to illite. Highest values are associated to the dirt bands within the Yard and Park Seams where degraded illites are at a maximum thus allowing K^+ to be leached out. Organic rich mudrocks have values intermediate between the mudrocks and the coals emphasising the detrital host. There is, however, no significant positive correlation with specific clay types and the location may vary and edge sites may play a role.

Coals

The K^+ mean, including the high ash coals is 61 $\mu\text{g/g}$ compared to 416 $\mu\text{g/g}$ for the mudrocks. The major clay in the coal samples, except adjacent to the mudrocks, is kaolinite. Thus there are few K^+ sites in

the low ash coals. The ash content is sufficient to explain the difference between coal and mudrock K^+ contents so long as K^+ is not purely clay associated. Without this eventuality ground water K^+ levels are sufficient to explain the water-soluble K^+ in all but the high ash coals.

Calcium

The distribution of Ca^{2+} (Figure 3.13) is seen to be extremely variable and has a negative relationship with ash content.

Mudrocks

There is negligible Ca^{2+} in the mudrocks from the Shallow, Park and Eight Feet Seams, with the exception of the carbonate rich 8R2. The Yard Seam has Ca^{2+} associated with three of the organic rich mudrocks, Y2, Ydb1 and YR2 but YF2 and Ydb2, also organic rich, have no Ca^{2+} .

Two locations may be postulated, ground waters and carbonate minerals. The latter will be locally concentrated and may explain the differences between the organic rich mudrocks where specific organic rich portions, or thin vitrain bands, may have been created. Ground water evidence and centrifuged water from Ydb1 (Table 4.4) show Ca^{2+} to be present. Thus it is unusual to find an absence of Ca^{2+} in some samples unless it has been removed to exchangeable sites or migrated to sites of carbonate precipitation.

Coals

Values are far in excess of the mudrocks, reaching a maximum of 3120 $\mu\text{g/g}$. The peaks are variable and random with major variations being evident in all the seams. Significant correlations with Mg^{2+} , HCO_3^- and pH suggest a carbonate host which is backed by XRD and thin

section evidence. The correlation with Mg^{2+} is reduced through the almost complete absence of Mg^{2+} in the Shallow Seam. This is explained by the predominance of calcite in the Lea Hall seams whilst ankerite is the dominant carbonate at Littleton Colliery.

Dissolution of the carbonates during leaching also help extract Cl^{-} through ion-exchange (Daybell and Pringle, 1958) hence the relationship with Cl^{-} seen clearly in the element profiles. The correlation with total Cl^{-} is indirect via specific associations of both cleat carbonates and Cl^{-} with coal type. The high I.S.A. of bright coals provide the major host for the Cl^{-} whilst its brittle nature make it most susceptible to cleat formation. Dull coals, however, have lower I.S.A., hence total Cl^{-} is lower and its greater strength is rarely fractured (see cleat section). Thus the Ca^{2+} profile is seen to roughly correlate with coal type and is best seen in the Shallow Seam (SS6 and SS7 excepted), where the dull banded coal SS3 has the lowest water-soluble Ca^{2+} level for the seam.

Magnesium

The distribution of Mg^{2+} is seen to be similar to that of Ca^{2+} but is complicated (Figure 3.13) by other sources. Compared to Ca^{2+} it is reduced in the coals but significantly higher in the mudrocks.

Mudrocks

Although the values are lower than in the coals the levels are very variable. Highly significant correlations are found with the moisture content suggesting a pore water source. Using N.C.B. and Ydbl water data, water-soluble Mg^{2+} may be satisfied in most samples. In the Park Seam, the values are probably in excess of ground water alone and additional Mg^{2+} may have been leached from a non-specific clay source (no significant clay type correlation). Correlations with

SO_4^{2-} and pyrite are probably indirect through an association with organic matter. Similarly, the associations with total and water-soluble Cl^- may result from organic matter, I.S.A. and ground water composition.

The ratio of water-soluble Cl^- to Mg^{2+} for the mudrocks is 32 comparing to a ground water value of 53 to 63 suggesting additional Mg^{2+} in the mudrocks. Similarly, YR1, YR2 and Ydbl cannot be explained purely by ground waters. No evidence is found for carbonates but levels may be too low for XRD identification. YR1 and YR2 both have increased Ca^{2+} suggesting a possible carbonate host. Ydbl, however, has Mg^{2+} in excess of Ca^{2+} and thus a non-specific clay host as suggested for the Park Seam is likely.

Coals

The range is wide but the correlation coefficient is influenced by the low Shallow Seam values. Similarities with the Ca^{2+} profile do still exist and may represent trace levels of ankerite for which there is XRD evidence, or substitution within calcite. Ankerite is common in the other seams, especially the Park and Eight Feet. A higher Mg^{2+} to Ca^{2+} ratio is to be found from N.C.B. ground water data at Littleton Colliery. If the Mg^{2+} is held in coal ground water then the similarity in Na^+ to Mg^{2+} ratios for the Shallow Seam leachate with its ground water composition (29.55 and 30.83 respectively) may explain all its Mg^{2+} in this fashion. A further alternative is a minor clay located source.

Variations in the Mg^{2+} to Ca^{2+} profiles may be explained simply by varying proportions of the two major carbonates, calcite and ankerite.

Bicarbonate

After Cl^- , HCO_3^- is the dominant anion in deep ground waters. Its distribution, shown in Figure 3.13, varies systematically with organic

matter content, carbonate distribution hence pH and coal type. The pH control varies with rock type. The range is from 0 to 2830 $\mu\text{g/g}$.

Mudrocks

There is considerable variation and although the pH control is more obvious in the coals, there is a correlation within the mudrocks. Where the organic matter contents are high, the relationship may be masked by the dominance of diagenetic carbonate minerals. Thus correlations are found with Ca^{2+} via carbonate dissolution. In the presence of organic matter, weak organic acids will lower the pH and dissolve carbonates. If none are present the pH will eventually be buffered at about pH4 (Krauskopf, 1979). However, within the mudrock pH range bicarbonate is the stable carbonate species (Blatt, Middleton and Murray, 1972, p. 363). Sufficient carbonate or little organic matter will establish a near neutral pH and a balance between the carbonate cation and bicarbonate. Higher organic matter, as in 8R2, will lead to increased dissolution and a marked peak in both original carbonate and HCO_3^- .

Coals

A great HCO_3^- range is found in the coals which is strongly related to the pH. As found occasionally in the mudrocks, correlations also exist with Ca^{2+} and Mg^{2+} suggesting a carbonate source. The strong positive correlation with water-soluble Cl^- ($r = +0.57$, 99.9% significance) is through ion exchange allowing Cl^- to be released in the presence of carbonates (Daybell and Pringle, 1958; present work, see water-soluble Cl^-). There is an indirect relationship with H_2O via coal type hence cleat development and high I.S.A. in bright coals, whilst being reduced in dull coals. The relationship with exchangeable Ca^{2+} suggests some carbonate dissolution with the BaNO_3 exchange solution, and is indirect.

Hydrogen-ion Activity (pH)

The pH may be expressed in similar units as the other elements for values of greater than pH 7.0 otherwise the values are negligible. Only when the pH is 4 or less are values comparable to the other ions. The pH is defined as the negative base 10 logarithm of the hydrogen ion concentration in moles per litre. The pH is related to equilibrium and non-equilibrium reactions in solutions, solids and gases where H^+ ions are involved including water dissociation. CO_2 is a major pH control (Hem, 1970). pH is thus controlled by carbonates and organic matter and the correlations with Ca^{2+} , Mg^{2+} , HCO_3^- and ash are not unexpected. In the mudrocks, where the organic matter is low and carbonates are few, there are no significant correlations.

Mudrocks

The pH is generally far higher in the mudrocks than the coal as can be seen in Figure 3.13. In those mudrocks with a low organic matter content the major pH control is probably atmospheric CO_2 in the absence of carbonates, low sulphur and iron. Thus it is not unexpected for the pH to be neutral or slightly alkaline. Where the organic matter is high, the mudrocks behave more like the true coal samples.

Coals

The strong positive correlations with the carbonates, hence Ca^{2+} , Mg^{2+} and HCO_3^- , can be seen in all the seam profiles and is expected from solution of carbonate minerals, probably from the cleat. Correlations with moisture and Cl^- are indirect through coal type associations and exchange reactions respectively. Perhaps the best seam profile to show the comparisons between pH, carbonates and water-soluble Cl^- is the Yard. The pH is generally lower in this seam and shows a fairly constant profile in the absence of carbonates. The low pH may be caused by very

low carbonate content or through increased oxidation through longer exposure because of retreat face mining, thus having long established roadways. The lower section of the Park Seam, however, has no such history and has similar pH levels. The peaks in dissolution products, and hence pH, are found in sample Y5. Similarly found is the maximum in Cl^- leaching, if the unmined roof section is ignored.

Sulphate

Determination of sulphate followed the method proposed by Fritz and Yamamura (1955). This involves passing the sample through exchange columns to remove interfering ions but adds a further dilution correction to already very low $\text{SO}_4^{=}$ values. Consequently the values are not accurate often with greater variation within sub-samples than between samples. Indirect $\text{SO}_4^{=}$ determination using atomic absorption also found values too low for accurate analysis. Re-running the same solutions found the values varying by a factor of four through minor standard solution variations. The results are, therefore, not quantitative and are only used to indicate trends and even here have their limitations (Figure 3.13).

Mudrocks

The values of mudrocks $\text{SO}_4^{=}$ show considerable variation, rarely exceeding $250\mu\text{g/g}$ in the Eight Feet, Park and Shallow Seam (floor only). A maximum of $600\mu\text{g/g}$ is found in the Shallow Seam roof. The Yard Seam, however, is markedly different reaching a maximum in $6345\mu\text{g/g}$ (YR2). No significant positive correlations are found with $\text{SO}_4^{=}$ and ash, but a negative relationship exists with exchangeable Ca^{2+} and Mg^{2+} suggesting an inverse relationships with the detrital clay fraction. Correlations with Na^+ , Ca^{2+} , Mg^{2+} , Cl^- (total and water-soluble) and $\text{H}_2\text{O}^{=}$ indicate

an organic association. There is no XRD evidence of sulphate in fresh samples at the instrument precision level (c. 5%).

Ground water may provide a sulphate source and is indicative of oxidation of sulphide minerals, probably pyrite which, in turn, is organically associated. The N.C.B. ground water evidence (Table 4.2) indicate high Fe and a very low pH and $\text{SO}_4^{=}$ in the Yard Seam, typical of contamination. This may be through old mine workings or in situ oxidation of the rock adjacent to long established roadways. Ground water values alone cannot account for the (suspect?) high values in YF2, YR1 and YR2 and may thus be a combination of ground waters and in situ oxidation. The roof samples may, however, be concentrated through evaporation similar to that seen by Na^+ and Cl^- in the unmined Yard 'roof' section.

Coals

$\text{SO}_4^{=}$ values are generally lowest in the centre of the seam increasing adjacent to floor and roof. This data is unreliable as there is often insufficient cations to balance $\text{SO}_4^{=}$ alone. Excluding $\text{SO}_4^{=}$ a reasonable ion balance is maintained. The trend, however, although non-normally distributed, suggests a correlation with seam position which may relate to ash (?pyrite) content. It will be noted that this is opposite to the mudrock trends.

Forms of Sulphate

1. Organic sulphur.
2. Sulphide sulphur; pyrite, marcasite, galena and sphalerite, often cleat associated.
3. Sulphate sulphur; gypsum.

The presence of gypsum in L.T.A. samples is a by-product of the ashing behaviour and except in an oxidising environment is unlikely to

be found associated with an organic rich, reducing, coal environment. Sulphide sulphur is found in many samples and three of the four highest $\text{SO}_4^{=}$ values are rich in sulphides. However, the highest sulphide levels are found in Y7 which has no water-soluble $\text{SO}_4^{=}$. Only in the Yard Seam is there any apparent correlation between pyrite and $\text{SO}_4^{=}$. The higher values in the Yard Seam may indicate oxidation but other sources, such as ground waters, and poor analyses, make predictions impossible.

Chlorine

Cl^- is the dominant water-soluble anion in the majority of the samples. Only in the low organic matter mudrocks is it exceeded by HCO_3^- . As with other elements there is a vastly differing behaviour between mudrocks and coals.

Mudrocks

The seam profiles (Figure 3.12) show considerable variation between 8030 $\mu\text{g/g}$ in the Yard Seam roof to 550 $\mu\text{g/g}$ in the Shallow Seam floor. Like total chlorine, water-soluble Cl^- is related to the organic matter content of the rock (Caswell, Holmes and Spears, part 1) and is, consequently, higher in the organic rich mudrocks such as Ydb2 and Y2. Ignoring the Yard Roof samples (where evaporation has severely concentrated Cl^-) then the mudrock mean of 1350 $\mu\text{g/g}$ compares closely to the 1386 $\mu\text{g/g}$ mean for 'subsurface shales' (Billings and Williams, 1967). As there is a wide range of organic matter contents in the 'mudrocks', which also includes the 'dirty' coal Y2, from 0.11% to 44.35% (by weight) then this is a potentially major influence on water-soluble Cl^- in some of the samples. A negative correlation with ash content, thus diluting the greater Cl^- holding capacity of organic matter, is, therefore, not unexpected.

As revealed in the previous paragraphs, Cl^- has significant positive relations with total Cl^- , Na^+ , Ca^{2+} , Mg^{2+} and H_2O . The relation with total Cl^- is expected if all Cl^- in organic poor mudrocks is water-soluble (Billings and Williams, op. cit., present work). There is little difference between the means of the total Cl. (2163 $\mu\text{g/g}$) and water-soluble Cl^- (1901 $\mu\text{g/g}$), and this discrepancy can be related to the organic rich mudrocks which behave intermediately between the coals and mudrocks. The Na^+ association results from a predominantly NaCl ground water source as has been seen from N.C.B. data and moisture centrifuged from Ydbl. Deep ground waters have been shown to be NaCl rich, often 'brines' in composition (Gluskoter, 1965; Downing and Howitt, 1969; Skipsey, 1975). As the NaCl is held in the ground water, a covariance between salinity and moisture content is readily explained.

The correlation between Cl^- and Ca^{2+} and Mg^{2+} is created by a few widely distributed values, and as will be shown in the coal samples, is due to ion-exchange of Cl^- with carbonate solution in the organic rich mudrocks. Such carbonates, usually negligible, may represent minor cleat in thin vitrain bands within a few organic rich mudrocks such as YR2.

Coal

Within the coal samples, Cl^- values range from 1565 $\mu\text{g/g}$ (2.12) to 9770 $\mu\text{g/g}$ (Y8, largely due to evaporation). The value falls as the ash content rises although the proportion of the Cl^- that is water-soluble increases. Significant negative correlations are to be found with elements that are associated with the detrital coal ash, exchangeable Ca^{2+} and K^+ , and water-soluble K^+ .

As seen with the mudrocks and discussion of the Na^+ profiles, the association with Na^+ is self evident assuming a NaCl ground water

component. The Cl^- that can be balanced by an equivalent weight of Na^+ is thought to represent this component and is that which is readily leached from relatively coarse coal. However, with tema grinding, the close association of these elements has been seen to fall and the water-soluble Cl^- often exceeds that which can be balanced by Na^+ alone. This relationship is, perhaps, best described by the Shallow Seam where the Na^+ profile is generally constant and the equivalent Cl^- falls well below the water-soluble Cl^- profile (Figure 3.12).

The marked Cl^- peaks are seen to correspond to Ca^{2+} and to a lesser extent, especially in the Shallow Seam, to Mg^{2+} . Corresponding to these profiles are HCO_3^- and pH, the associated carbonate dissolution products. As the Cl^- is not associated with the carbonates, the relationship is secondary (Edgcombe, 1956). Daybell and Pringle (1958) showed that even with ultrafine grinding the proportion of the total Cl^- that is water-soluble may be very low if the carbonate content is low or absent. They postulated an exchange relationship of OH^- , from water dissociation, for Cl^- held loosely on organic surfaces. An excess of H^+ , produced by the organic acids, produces acidity in the leachate (low pH) and exchange is eventually terminated. If carbonate is present, this is dissolved in response to the leachate acidity and prevents the pH falling to low, thus enabling exchange to continue. Thus the Ca^{2+} and Mg^{2+} profiles will balance the Cl^- until either all the Cl^- is exchanged or a lack of carbonates prevent exchange to continue. The correlation between Cl^- and Ca^{2+} and Mg^{2+} is only clearly seen in the tema samples. Ultrafine grinding will open up small pores and create a maximum surface area available for reaction, both for carbonate dissolution and Cl^- exchange. As Na^+ associated Cl^- makes a significant contribution to the total Cl^- (c. one third), the carbonate: Cl^- relation-

ship may be seen more clearly if the former contribution is subtracted. Thus the Cl^- equivalent to the water-soluble Na^+ was subtracted from the water-soluble Cl^- and plotted against Ca^{2+} for the Lea Hall seams, and Ca^{2+} plus Mg^{2+} (on a Ca^{2+} basis) for the Littleton seams. This represents more closely the composition of the carbonates found at each colliery, calcite with subsidiary ankerite at Lea Hall, and ankerite with negligible calcite at Littleton. In both cases, the Ca^{2+} and Mg^{2+} predicted to be contributed by the ground water would be small and was ignored. The relationships are to be found in Figures 3.15 and 3.16, both correlating positively with a high degree of significance (99.9%), $r = +0.92$ at Lea Hall and $r = +0.93$ at Littleton. In the former case, there are exceptions from the Ca^{2+} equivalent to Cl^- curve, with some high Ca^{2+} values being undersaturated with respect to Cl^- . Either the Cl^- holding pores were not all opened for exchange to take place or other (unknown) factors are preventing exchange from taking place. In some of the Yard Seam samples Cl^- is occasionally in excess of Ca^{2+} and may reflect an acid (HCl) solution with insufficient carbonate to be dissolved to maintain an environment capable of exchange. There is no doubt that the pH readings from this seam are very low. Unfortunately, HCO_3^- and pH, although being significantly correlated ($r = +0.83$, 99.9% significance) are insufficiently accurate to continue this line of reasoning. The Littleton Colliery samples too show a close spread about the Ca^{2+} equivalent to Cl^- line, although again in the low carbonate samples there is an apparent excess of Cl^- .

Because of the importance of the Ca^{2+} , Mg^{2+} to Cl^- relationship and, in fact, the higher significance of this correlation than between Na^+ and Cl^- , the relationship between Cl^- and total Cl^- is clearly indirect and arises from the predominant association of cleat, in this

case carbonates, with the major Cl^- host, bright coal. Although the ground water contributed Na^+ associated Cl^- may be associated to a greater degree with dull coal, the dominance of the exchange reaction maintains a higher proportion of water-soluble Cl^- in the bright coals. If the ground waters are concentrated enough, however, as in the Hem Heath Yard-Ragman Seam, this relationship will be altered and dull coal may be found to have the highest total Cl^- values. This does not happen in the Cannock Coalfield samples.

CHAPTER 4TOTAL CHLORINEThe Origin of Chlorine

The sources of chlorine are many and varied as are the relative contributions of these sources. Chloride is present in most rock types, but in lower concentrations than any of the major constituents of natural waters (Horn and Adams, 1966). Johns and Huang (1967) summarised the then available data on chlorine content of rocks and calculated that the concentration of chlorine in the crust to a depth of 10 miles averaged 180 ppm. Taylor (1964) had calculated an average of 130 ppm. Johns and Huang (op. cit.) investigating a sample of 80 shales and clays found a range of 50-450 ppm with an average of 103 ppm. They concluded that considerable dilution and leaching had taken place considering the concentration of NaCl in interstitial ground waters. Billings and Williams (1967) considered that these values were low by as much as 14 times and this probably indicated that the majority of previous analysis had been carried out on surface shale samples in which the majority of the chlorine is water-soluble and leached out. Subsurface samples gave a range of 45-2450 ppm and an average of 1386 ppm, lower, but of a comparable order to the mudrocks presently under study.

A review of the possible origins and form of chlorine in coal is summarised by Kear and Menzies (1956), Watt (1968), Gluskoter and Ruch (1971), and Saunders (1980). The nature and distribution of chlorine in coal has been the subject of much controversy over many years as a consequence of the variations in leaching characteristics of different coals. In order to try to resolve this situation, the possible chemical forms of the chlorine, mode of occurrence, and their distribution with depth, rank, location, seam and maceral group have been considered. It

appears that there is more than one form of chlorine in coal and different coals have different proportions of these forms.

Nature of Chlorine in Coal

Many differing theories have been proposed regarding the chemical form of Cl^- in coal. As a result of the examination of the aqueous extracts from coals, many workers considered Cl^- to occur almost entirely as the inorganic chlorides of Na^+ , K^+ and Ca^{2+} with traces of Mg^{2+} and Fe^{2+} (De Waelle, 1915; Sexton and Davidson, 1923; Crossley, 1952; Whittingham, 1954; Crumley et al., 1955; Gluskoter and Rees, 1964). Crossley (1947, 1963) suggested that Cl^- was present in two forms, as Na^+ or K^+ chlorides and as a component of complex silicate based minerals. Nelson (1953) considered Cl^- to occur in several forms, namely:-

- a) Chloride ions present in water layers adsorbed on the inner surfaces of the coal substance (i.e. in pores).
- b) Chloride ions associated with exchangeable cations in the clay minerals.
- c) Water-soluble minerals such as halite (NaCl) and sylvine (KCl).
- d) Water-insoluble minerals where chlorine is a structural component such as chlorapatite ($9\text{CaO} \cdot 3\text{P}_2\text{O}_5 \cdot \text{CaCl}_2$) or sodalite ($3(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \cdot 2\text{NaCl}$).

However, in some coals it was obvious that all the Cl^- could not be removed, even with fine grinding and reflux at 100°C . Although yields often approached 100% Cl^- extraction and sometimes even achieved this total, it was obvious that Na^+ (or K^+) could not balance the Cl^- . Ca^{2+} , Mg^{2+} and pH, in addition to Na^+ may balance Cl^- but the Ca^{2+} and Mg^{2+} originated as carbonates and not chlorides. A secondary reaction was thought to be releasing Cl^- (Edgcombe, 1956; Daybell and Pringle, 1958) and the Cl^- not balanced by Na^+ thought to be attached to the coal

substance by ion exchange (Daybell and Pringle, op. cit.). Ter Muelen (1929) suggested that some proportion of the Cl^- may be in organic combination and support for this theory was provided by Brame and King (1935). A method for the determination of organically combined Cl^- was developed by Das Gupta and Chakrabarti (1951). Daybell (1967) and Gluskoter and Ruch (1971) concluded that a considerable proportion of the total Cl^- may be attached to the organic matter.

The present work supports the existence of organically held chlorine although the linkage mechanism is not known nor appears to be very strong (Chapter 3). Na^+ can balance an overall average of some 31.40% of the total Cl^- . Water-soluble extracts at ambient temperatures show an ion balance to exist but the Ca^{2+} and Mg^{2+} in solution are the dissolution products of carbonates. The presence of carbonate is essential to high Cl^- leaching as proposed by Daybell and Pringle (1958) and can be seen in the water-soluble element profiles and associated explanations.

Easily water-soluble Cl^- is Na^+ related and thought to be a NaCl 'solution' held in the vitrinite micropores (Saunders, 1980). This is backed by evidence provided by centrifuging water from both mudrocks and coals which are NaCl rich.

Chlorine Distribution

Variation with Rank

The total Cl^- holding capacity is linked to the rank of the coal. Skipsey (1974, 1975) showed that the amount of chlorine associated with a coal seam is dependent upon the rank of that coal. Lower-rank coals, that is those with less than 85-86% carbon (d.m.m.f.), can hold up to 1% Cl^- but coals with a higher rank rarely hold more than 0.2% (by weight) even when associated with brines. This cut off point is attributed by Skipsey (1974) to correspond to changes in the organic structure

and hence porosity of the coal. Bond (summarised in van Krevelen, 1961) postulated a change in the ultrafine structure of the coal. A system of pores, connected by capillaries, allows the penetration of liquids and/or gases into the coal substance. As the carbon content increases, the void area declines for coals of lower ranks. Hirsch (van Krevelin, op. cit.), using XRD, related this phenomenon to the increasing orientation of coal lamellae from a random pattern to greater alignment. This would lead to a reduction in pore space where chloride or other ions could be held by the coal (Figure 4.1).

Hirsch's Model (van Krevelin, 1961)

1) 'Open Structure'

Characteristic of low rank coals up to 85% carbon. Lamellae are cross linked and are randomly orientated constituting a highly porous structure.

2) 'Liquid Structure'

Typical of bituminous coals of 85 to 91% carbon, the lamellae show some orientation. Crystallites of two or more lamellae are present. The number of cross-links has decreased and pores are practically absent.

3) 'Anthracite structure'

Found in high rank coals of greater than 91% carbon, the bridge structures have disappeared altogether. Lamellae orientation has greatly increased. The model suggests that the porous system becomes more orientated.

Alternatively, as the carbon content increases, the number of ion exchange sites decreases thus reducing the coals chlorine holding capacity.

Once very high ranks have been reached, the porosity begins to increase. However, the pores are much smaller (Nandi and Walker, 1971)

and perhaps the effective permeability is considerably reduced. The relationship of coal rank to I.S.A. is shown in Figure 4.2.

Variation with Depth

Borehole evidence from the N.C.B. (Daybell and Pringle, 1958) shows Cl^- to increase with depth. The results for the Cannock Coalfield total Cl^- are given in Table 4.1, and are seen to increase with depth for a given colliery with the exception of the Littleton Shallow Seam. Skipsey (1974) found that for coals of less than 85% C (d.m.m.f.), Cl^- increased with depth to reach a maximum value beyond which a series of high but variable values were encountered. Downward leaching of overlying saline strata (Permian) was found to be negligible except in localised cases such as within the Durham Coalfield. Where the coal rank exceeds 85% C, the Cl^- level was found to decline as the rank increased. In other coalfields Cl^- is found to increase with depth, in Oxfordshire (Poole, 1969), Kent, South Wales (Skipsey, 1975) and Illinois (Gluskoter and Rees, 1964). Gluskoter and Rees (op. cit.) and Skipsey (1975) considered that the Cl^- content of the coal is probably controlled directly by the ground water composition. "In an approach towards equilibrium, solutions intimately associated with the coal will take up or give off chloride ions as the ground water chlorine content increases or decreases. Whatever may have been the original chlorine content of the coal would have long since been obliterated, and the present chlorine content of coals within the Illinois Basin is the result of interaction with the currently associated ground water" (Gluskoter and Rees, op. cit.). That ground waters play an important role in coal chloride content is undeniable and further evidence for this source in the Cannock Coalfield (and elsewhere) will be discussed later in this chapter. It is significant to note that high chlorine coals are never found in areas of chloride deficient ground waters.

Small Scale Local Variations

Local variations are often found to override general trends. For example, the abnormally high Cl^- values in Durham caused by downward saline leaching. Chloride rich ground waters are, however, a world wide phenomenon. In the East Midlands, the eastwards down dip Cl^- increase (Wandless, 1957) is reversed in the anticlines at Thoresby where there is evidence of dilution, whilst concentration has occurred in the associated synclines (Skipsey, 1975). Either folding (Hercynian) took place prior to maximum Cl^- development, or the Cl^- has the capacity to migrate or be diluted (or a combination of these factors) could lead to this distribution.

Within Seam Variations

Although Yearsley (1932) believed that between seam variations in Cl^- were unlikely, the association of Cl^- with specific lithotypes could produce within seam variations (Louis, 1927; Chapman and Mott, 1923; Yearsley, 1932). However, investigations into Cl^- in bulk run-of-mine samples, which are more applicable to the coal consuming industries, will mask smaller scale variations. Fellows (1979, Ph.D.) found through seam variations in water-soluble elements and Cl^- was highest in mid-seam. Total Cl^- , however, was more complex and not related to seam position. The present work shows major variations which are complex and important in the understanding of Cl^- behaviour.

Association with Coal Types

The work of Louis, Chapman and Mott, and Yearsley (op. cit.) found that bright coal is lower in water-soluble salts than dull coal. A similar distribution was found in hand specimen coal (Caswell, 1981). The work of Chapman and Mott, however, was conducted on coals from the North Staffordshire Coalfield, which, as it will be shown later in this chapter, behaves

differently to those coals of the Cannock Coalfield.

Saunders (1980) using S.E.M. microanalysis produced results which apparently conflict with those expressed above. The majority of Cl^- is found to be located in vitrinite whilst values in exinite and inertinite were low and variable, and the Na^+ content of the vitrinite could be used to predict an equivalent weight of Cl^- to be leached from 72 mesh B.S.S. coal.

Mode and Time of Chlorine Introduction

It is evident from the complexity of geological processes acting upon a sediment to the present day, from the depositional environment, through its burial history and diagenesis, all play a role in having the potential of supplying Cl^- to coal and its associated strata.

Peat Growth

Cl^- is present, but low, in natural waters (Hem, 1978) and in rain-water may vary from 1.0 to 10's of $\mu\text{g/g}$ (Junge and Werby, 1958). Thus Cl^- was available in the Coal Measures environment in low but variable quantities. In environments bordering on the seam the salinity would increase. Thus Crumley and McCamley (1958) postulated that the eastwards increase in Cl^- levels in the East Midlands Coalfields represented the increasing influence of the sea. Marine influence, however, is negligible within the Coal Measures, the majority of sediments being fresh water paralic and occasionally brackish (Francis, 1979).

During Deposition

The rhythmic sedimentation of the Coal Measures gives rise to a very varied succession where individual beds may be absent from the cyclothem. Sandstone horizons, for example, are often localised and lenticular. Such a horizon, or that of other finer sediments before compaction, would allow downward percolation of saline waters from the occasional marine

flooding. If the salinity of the Coal Measures seas are comparable to those of today (Rubey, 1951), some ground waters would need further concentration of up to one order of magnitude (De Sitter, 1947). Table 4.2 shows that the ground waters associated with the Shallow and Deep Seams are comparable to that of sea water but those of the Yard, Eight Feet, Benches and Yard Ragman are considerably more saline.

A coal seam with a marine roof (the Mansfield Marine Band) was sampled from Treeton Drift (near Sheffield) and found to have a Cl^- content of 0.07%. It is unlikely, therefore, that a marine source alone would create sufficiently high Cl^- levels to explain the values found in high chlorine coals.

Diagenetic Alteration of Ground Waters

"Subsurface water is nearly always a mixture of juvenile waters, meteoric waters, ocean waters, waters produced from diagenetic or metamorphic reactions, and magmatic waters. Rarely, if ever, is it possible to recognise the relative importance of each of these sources in a subsurface water sample. In addition to the interpretive difficulties generated by the diversity of sources, all formation waters are more or less continuously modified compositionally, by ion exchange reactions, by precipitation of minerals, and by solution of surrounding rock. In summary, the history of almost any sample of subsurface water is extremely complex. In most investigations we are unable to determine the sources and earlier history of each chemical constituent and must be content with simply describing its present abundance and percentage of total dissolved solids, a circumstance that greatly hinders our attempt to understand diagenetic processes in general and the areal distribution of mineral cements in particular," Blatt, Middleton and Murray (1972). Thus the reason for concentration is unclear but the existence of deep chloride rich ground

waters is not in doubt. Sulin (1946) found calcium chloride brines typical of deep stagnant environments associated with U.S. oil reservoirs. De Sitter (1947) proposed 'salt seiving', the concentration of chlorides through selective ion release through clay membranes as a mechanism for its retention at depth. Bredehoft et al. (1963) thought that the concentration of saline ground waters took place through down dip migration, then being forced to rise through the sediment pile leaving the dissolved solids at depth. Billings et al. (1969) though larger radius divalent cations would be unable to escape through a negatively charged clay pile compressed into low porosity and permeability. Similarly, the large radius Cl^- anion may be retained below the clay succession where smaller ions may escape.

An alternative mechanism, perhaps more plausible, is through diagenetic removal of anions. The major anions in ground waters are sulphates, bicarbonate and chloride. Sulphate will not survive in a reducing environment, as is typical of the Coal Measures, but will be reduced and in the presence of iron will precipitate as iron sulphide, probably pyrite. Bicarbonate can be removed from the system as carbonates but chloride concentration will continue until the solution is saturated with respect to halite. Thus chloride will become the predominant anion simply because it is not removed in mineral precipitation reactions.

Brines are thus concentrated at depth. Aquifer horizons, such as sandstones, if continuous, may enable long distance migration of ground waters (Curtis, 1978) which may concentrate these fluids in areas away from where they were produced. Coals have a high porosity (based on moisture content and I.S.A.) and the presence of abundant organic matter will provide a reactive medium for the ground waters to host dissolved mineral matter and hold 'organically bound' Cl^- , or act as an aquifer

horizon itself. Coal Cl^- levels are directly related to ground water salinity in Illinois (Gluskoter and Rees, 1964). Similar relationships have been found in deep East Midlands collieries where Cl^- levels reach 131,000 p.p.m. and high chloride coals are found (Skipsey, 1975), also in Yorkshire and Northumberland. The presence of a mudrock succession in Cl^- concentration is important, and little Cl^- is found to be concentrated below limestones (Downing and Howitt, 1969).

Total Cl^- Profiles, Lea Hall and Littleton Collieries

Total Cl^- was determined on ten ground coal samples oven dried (105°C) for 8 hours. The weight loss was expressed as the weight percentage moisture content of the sample. The method of determination followed B.S.S. 1016 part 8 with the exception that nitrobenzene, used to coat the precipitated AgCl and prevent its interference in the titration, was not used. Kolthoff et al., (1969) found the two methods to have comparable accuracy. The total Cl^- profiles are given in Figure 3.12. A close correlation is achieved between the seam averages and those determined by the C.E.G.B. (Table 4.3).

Discussion of Profiles

Total Cl^- values are found to be considerably higher in the coals than the mudrocks whilst the organic rich mudrocks and dirty coals have intermediate values, perhaps best seen in the Eight Feet and Shallow Seams. The mudrocks barely exceed 0.1% whilst the coal samples are in the range 0.64% (Eight Feet Seam) and 0.92% (Shallow Seam). The high values associated with the Yard Seam roof are seen to be largely Na^+ associated and concentrated through evaporation. The bivariate plot of organic matter (calculated by difference using L.T.A. ash content) versus Cl^- is shown in Figure 4.3. There is a highly significant (99.9%)

negative correlation ($r = -0.88$) but the data is not normally distributed and clearly falls into three groups, the coals, low organic mudrocks, and a small intermediate group of dirty coal and organic rich mudrocks. With the exception of Y2, the coals have more than 60% organic matter, most having greater than 85%, and Cl^- varies between 0.5 and 1.1% (by weight). The mudrocks invariably have less than 10% organic matter and less than 0.25% total Cl^- . Remaining, is a group of 7, of which the altered Yard Roof samples Y9 and YR1 are included. The other 5 samples are the dirty coals or carbonaceous mudrocks. (Y8, also altered by evaporation, is indicated).

It has been demonstrated in the water-soluble element section that most, if not all the Cl^- in the mudrocks is water-soluble, potentially balanced by Na^+ , and represents ground waters held within the pores. The link between ground water chloride levels and total Cl^- in coals (Gluskoter and Rees, 1964) suggest a major link within the true coal samples. Evidence provided by the present work to indicate the role of ground waters in contributing chloride to mudrocks has been provided by the moisture centrifuged from Ydbl, a wet mudrock, following the method of Edmunds and Bath (1976). The major cations were analysed by atomic absorption spectrophotometry and Cl^- by Mohr's titration, the results of which are given in Table 4.4. It is evident, allowing for minor analytic variation, that the total Cl^- can be accounted for by the ground water 'soluble' Cl^- , the majority of which can be balanced by Na^+ .

The Yard Seam 'roof', Y8, Y9, YR1, YR2 and YR3 have far higher than expected total Cl^- levels for their organic matter content (e.g. YR2). Y8 and Y9 have by far the highest total Cl^- for the seam. The water-soluble Na^+ , normally constant through the seam is two to three times as high in these coals and remains high in the true 'roof' samples. There was evidence of surface precipitation on these samples, and this

represents concentration of NaCl through evaporation and further wicking of solutions to the sample surface.

Work by Dr. I.F. Holmes on the Lea Hall Deep Seam roof, showed a total of 0.54% Cl^- , all of which was water-soluble and could be balanced by Na^+ . However, this sample is a sandstone with a high moisture content. As the Cl^- is not associated with the quartz, then the chloride is in the ground water.

The N.C.B. ground water figures (Table 4.2) indicate high Cl^- values, especially in the North Staffordshire Coalfield.

An attempt was made to centrifuge moisture from run-of-mine Shallow Seam coal (provided by C.E.R.L.) but despite its high moisture content (9.98%) none was removed in the Departmental centrifuges. The sample was finely, but not tema, ground as it was believed that this may produce surface tension too great to remove moisture. Using higher speed centrifuges at the Water Research Centre, under the supervision of Mr. E. Hall, a small amount of moisture was removed and analysed (Table 4.4). The increased difficulty in removing moisture from the coal, as compared to the mudrocks, suggests that the coal pores are less accessible, perhaps smaller. There is no definitive literature available on mudrock porosity, form or permeability. The coal water analyses are an order of magnitude lower than those of Ydb1 despite the rapid leaching of Na^+ associated Cl^- from coals suggesting its location in pore water (Saunders, 1980; present work), slightly higher Na^+ in the coals and increased moisture contents. Some of the Cl^- , however, is definitely held in the moisture. The reduced salinity, therefore, suggests that there are problems removing the pore solutions. Perhaps tema grinding is essential to the opening of the smaller pores, and moisture determinations were made on this basis. The composition of water held in the larger pores may, therefore, be different in composition to those of smaller dimensions. Alternatively, the dissolved mineral matter

may be trapped more tightly against pore walls by Stern or Gouy layer effects, producing a concentration gradient of which only the least concentrated moisture is being removed.

A comparison of the relative percentages of ions centrifuged from Ydbl and the Shallow Seam (Table 4.4) indicates the former to have a slightly higher Na^+ content. This is made up by increased Ca^{2+} in the coal sample which may be due to carbonate dissolution. The ratio of Na^+ (equivalent weight of Cl^-) to Cl^- is very comparable between the centrifuged coal water and those for the Shallow and Deep seam ground waters (0.85). This suggests that the centrifuged water represents the ground water but the lowered concentration is therefore due to removal difficulties.

Using the Ydbl centrifuged Na^+ values and the sample moisture contents a comparison can be made with the predicted and achieved water-soluble Na^+ values for the Yard Seam. Excluding the unmined samples, approximately 50% of the Na^+ can be explained by the Ydbl ground water (Table 4.5). However, there is no evidence to suggest that the present ground waters located in Ydbl are the same as those trapped in the coal. Ground water seepage horizons are few and far between and Ydbl may be acting as an aquifer whilst the coal water is trapped. Suffice to say that ground water salinity is an important contributor to Na^+ and Cl^- coal and associated strata. In the mudrocks it may account for the total Cl^- and in the coals the Na^+ associated Cl^- .

It is evident that the relationship between Cl^- and organic matter is indirect, with the non-organic material diluting the Cl^- holding capacity of a rock. A relationship would be expected to exist between Cl^- and the moisture content, if, in fact, this is the source of the Cl^- . Figure 4.4 shows the relationship to be positive and highly significant, $r = +0.51$ for the coals and $r = +0.85$ for the combined coal and mudrock data (both 99.9% significant). Thus it may be suggested that a significant

proportion of the Cl^- is in the coal moisture. As the rocks are below the water-table and thus saturated, the moisture content relates to the porosity. Only small proportions of gases are held in addition (Thomas and Damberger, 1976). Relationships are found between the porosity and I.S.A., which are controlled by coal type and rank (Thomas and Damberger, op. cit.) in Illinois coals.

As the total Cl^- profiles show no association with seam position, the distribution reflects fundamental variations. More detail is given in Caswell, Holmes and Spears, part 1, including the profiles studied by Dr. I.F. Holmes. The profile of the Eight Feet Seam shows a relationship between coal type and total Cl^- . The coal types are based on macroscopic whole rock lithotype descriptions, then expressed on a sub-class basis to describe the dominant lithotype. A large scale classification is justified because it is the whole specimen characteristics that are being investigated. Thus a coal sample dominated by vitrain is described as 'bright' whilst durain rich samples are 'dull'. Varying proportions of bright (vitrain and clarain) and dull coals are described bright or dull banded depending upon the predominance of either bright or dull lithotypes. This classification is thought to be suitable except in borderline cases.

Four of the lowest Cl^- values are dull (3) or dull banded associated. A statistical test for significance between the means of the dull and bright coal was therefore conducted. The dull coal Cl^- content has a mean of 0.607 and a standard deviation of 0.058, whilst the bright coal has a mean of 0.675 and a standard deviation of 0.035. Using the standard error (S.E.) of the means shows a significant difference at the 95% significance level.

The Park Seam is more complex but high and variable ash contents complicate the trend. Re-expressed as a d.m.m.f. basis (Figure 4.5),

Four of the five lowest Cl^- values are found in dull or dull banded coals. The Shallow Seam has only one dull banded (SS3) and no dull coals. This has the lowest total Cl^- whilst the highest values are associated with the bright coals. If re-expressed on a d.m.m.f. basis four out of the five highest values are associated with bright coals (Figure 4.6) and with one exception the bright banded coals fall intermediate between the bright and dull banded coals.

The Yard Seam is more complicated though highly variable ash contents and high evaporation values which together overshadow other factors.

The work of Dr. I.F. Holmes (included in Caswell, Holmes and Spears, part 2) supports these conclusions. The Littleton Shallow Seam dull and dull-banded coals have total Cl^- values in the range 0.26 to 0.35%, whilst the bright coals are higher, between 0.35 and 0.45%. The Lea Hall Deep Seam has only one dull coal which has the lowest total Cl^- for the seam. However, two dull banded coals located near the roof have high Cl^- values but there is evidence to suggest that this is 'recently' added from the chloride saturated sandstone roof. The pattern, however, is reversed in the Hem Heath Yard-Ragman Seam where the highest Cl^- values are found in the dull coals.

The Influence of very Saline Ground Waters - an overriding example

Leaching experiments conducted on the Hem Heath Yard-Ragman and Winghay Seams (Bettelheim and Hann, 1980) found their characteristics to be markedly different to those of the Cannock Coalfield. Differences in the Na^+ leaching behaviour between Winghay Seam dull and bright coals has been shown earlier in this work (Figure 3.1). The Hem Heath coals, although having similar total Cl^- to those coals from Cannock, have a much lower proportion readily water-soluble. The moisture contents of

the former coals, 3.07% and 2 to 3% for the Winghay and Yard-Ragman samples respectively, is far lower than those of the latter coalfield (Shallow Seam, 9.98%). This suggests a lower I.S.A. or the moisture accessible pores are fewer or smaller due to the increased rank (Thomas and Damberger, 1976) in the North Staffordshire Coalfield. The salinity of the ground waters are, however, far greater and may make a considerable contribution to the total Cl^- . Caswell (1981) showed that because of the pore size distribution, the larger dull coal pores hold the most readily leached Cl^- (Na^+ associated) despite the I.S.A. being lower than in bright (vitrinite rich) coals. Despite the low moisture content, 40 to 50% of the total Cl^- may be accounted for by ground water salinity. Holmes showed that only 10.7% of the Cl^- was leached from the bright coal 21, yet 63.2% Cl^- was readily soluble from the dull coal 6, representing the extremes for <72 mesh B.S.S. coal. Moreover, the dull coal has the highest Na^+ , whilst the bright coal has the lowest. Thus the proportion of ground water Cl^- is far higher in dull coal. The Na^+ leached increases as the size of the bright coal is reduced, whilst in the dull coal a peak is reached after which finer fractions leach less Na^+ . This indicates further the existence of differing pore sizes and distributions within the various coal types. If the water-soluble Cl^- (72 mesh B.S.S. size) or the Cl^- equivalent to the water-soluble Na^+ (i.e. 'recent' ground water chloride), is subtracted from the total Cl^- , the 'normal' relationship of highest Cl^- in bright coals, lowest in dull coals, remains. This was attempted for the Cannock Seam profiles (Figure 4.7) and the coal - Cl^- relationship, as originally predicted, remains. This non- Na^+ associated Cl^- is essentially fixed and released only by exchange reactions in leaching when carbonate is present. It is organically bound and controlled by the I.S.A. of the various maceral groups.

In conclusion, two forms of Cl^- are found in the coals controlled by the I.S.A. Organically held Cl^- is thus highest in bright coals and lowest in dull coals. Ground waters, essentially NaCl rich may be located in those accessible pores, the largest of which are found in the dull coals. If, however, the salinity of the ground water is great, as at Hem Heath, then the larger dull coal pores may hold sufficient brine to override the relationship of coal type and Cl^- that would be expected from a simple I.S.A. basis. In the Cannock Coalfield, the ground waters are not concentrated enough to blur the 'normal' high total Cl^- in bright coal, low in dull relationship.

Total Cl^- and Depth

As previously indicated in this chapter, and by Skipsey (1974), Cl^- increases with depth, but only within the same colliery. Holmes' information for the Lea Hall Deep Seam fits this trend but that of the Littleton Shallow Seam does not. There is no evidence that a threshold rank (84% C, d.m.m.f., Skipsey, 1975) has been reached but this may indicate the high but variable Cl^- values found below the Cl^- maximum has been reached (Skipsey, op. cit.). The ratio of Na^+ to total Cl^- is similar for all seams of a colliery (Table 4.6), and as Na^+ increases with depth in ground waters (Gluskoter, 1965; Skipsey, op. cit.; Downing and Howitt, 1969), then the lower total Cl^- must be due to a reduced Cl^- holding potential (i.e. reduced I.S.A.).

Prediction of Cl^- leaching levels

As the leaching behaviour of Cl^- in 72 mesh B.S.S. coal can be predicted from the Na^+ content of the vitrinite, then the similarities between the Na^+ to total Cl^- ratios for the Hem Heath (Yard-Ragman Seam) and the Littleton Colliery samples would predict similar low leaching

characteristics. This has been confirmed for the Yard-Ragman and Eight Feet Seams (Dr. J. Bettelheim, C.E.R.L. personal communication). Similarly, the Lea Hall coals would be expected to leach twice these Cl^- levels. Similar results were obtained by Bettelheim and Hann (1980). The similarities between the Littleton and Hem Heath Colliery ratios are probably coincidental considering the vastly differing moisture contents and ground water compositions.

Influence of Ground Water on Leachable Cl^-

Using the N.C.B. ground water values, there is sufficient Cl^- present to account for Na^+ equivalent Cl^- in all but the Shallow Seam at Lea Hall (Table 4.7). This emphasises the role of ground water salinity in its contribution to coal Cl^- levels. It must be noted that the less saline Shallow Seam ground waters, compared to the stratigraphically higher Yard Seam sample, may have been produced by localised variations, or may not be representative of the seam where the present samples were taken.

Location of Cl^- in Coal

It has been shown that two types of Cl^- are to be found within coal. Na^+ can only account for one-third to one-half of the total Cl^- in those coals studied and this represents ground waters held predominantly in the larger pores. The organically held Cl^- is controlled by the I.S.A. This Cl^- may once have been Na^+ associated but has since been able to migrate out of pore sites because of its smaller atomic radius. Alternatively, dissociation of Na^+ and Cl^- , seen by the differences in the leaching rates (Neavel et al., 1977; Bettelheim and Hann, 1980; present work), may have allowed Cl^- to have been fixed to organic matter exchange sites.

As the relative importance of organically combined and ground water Cl^- varies with coal type, rank and ground water composition, and migration

may take place over long distances along aquifer horizons, then closely associated seams may have differing behaviours. Thus it is difficult to predict a time for Cl^- introduction.

Time of Cl^- Introduction

It has previously shown that only diagenetic alteration of ground waters is capable of producing the necessary Cl^- levels on a world-wide basis. So long as there is a closed system, this probably reaches a peak with maximum burial, hence temperature, to generate diagenetic reactions to their utmost. Similarly the Cl^- holding capacity (I.S.A.) was rank imposed during the Hercynian Orogeny, so both processes probably ran in parallel. Tectonic differences across the Cannock Coalfield may produce the differences seen in the behaviour of the Shallow Seam between Lea Hall and Littleton Collieries. The North Staffordshire Coalfield suffered greater tectonism and hence higher rank. Skipsey (1975), therefore, argued that the Cl^- peak was reached soon after the Hercynian Orogeny. It may be suggested that some of the ground water Cl^- held in the coal during rank imposition is that now found to be organically held, trapped within the smallest pores. Ground waters, those not trapped by rank imposition or are 'recent' obviously make an important contribution. If there was a closed system, ancient ground waters, remaining at the concentration reached with maximum diagenesis would be found. However, uplift, mining and erosion may alter the ground water hydrological system which is certainly not static. The present Cl^- values are thus a combination of fixed 'organic' Cl^- and varying compositional ground water Cl^- . Although the original coal-chlorine pattern in the Cannock Coalfield has not been totally obliterated, especially that of the organically associated Cl^- ,

it may, therefore, have been considerably modified.

Conclusions

- 1) Total chlorine holding capacity of a coal is controlled by its rank via its internal surface area. The porosity of high volatile bituminous coals, that is, those with less than 84% C, is considerable and the pore size is relatively large. High rank coals have comparable internal surface areas but the pores are much smaller and hence not so accessible. High chlorine coals are limited to high volatile bituminous coals.
- 2) The internal surface area/porosity depends upon the coal type.
 - (a) It is high in the lithotypes composed primarily of vitrinite and low in those composed of exinite and inertinite.
 - (b) The associated mudrocks have different characteristics. If the organic matter content is low, then total chlorine contents are low and all is water-soluble.
 - (c) Non-organic matter is a dilutant to the far greater porosity of coal organic matter. Dirty coals and organic rich mudrocks have total chlorine values intermediate between mudrocks and coals.
- 3) There are many origins for the chloride found in coal and coal-bearing strata. Their relative importance depends upon the salinity of all the waters in contact with the coal during its diagenetic history. However, without doubt, the major source of chloride in high chlorine coals is diagenetically altered ground water brines. Moisture centrifuged from mudrocks shows that the

total chlorine is derived from ground waters that are chloride rich and held in pores. Coals also hold ground waters which may contribute all the water-soluble Na^+ , and associated chlorine. However, difficulties in removing this moisture arise as the coal pores are very small and element concentration gradients may exist within the pores.

- 4) The time of the coal-chlorine relationship correlates with the Hercynian Orogeny, although the evidence concerning which came first, concentrated brines or rank imposition, is not unambiguous. It seems possible that both coalification and brine evolution took place in parallel. Ground waters, however, may change in composition until the present day if they exist in an open system. The total chlorine of the coals or mudrocks will alter as a consequence.
- 5) The form of the chlorine depends on the host rock. In the low organic matter mudrocks, all is water-soluble, Na^+ associated and are present in ground waters. This contributes to the chlorine content of the coals but only some 30% to 50% of the total chlorine is in this form at the present. Although the remaining chlorine was probably once Na^+ associated, this is no longer the case and now is held in an 'organic combination'. The removal of this chlorine is not totally achieved at ambient temperature even with terna grinding. Indirectly ion exchange with carbonates is necessary for its release even in moderate quantities in leaching experiments.
- 6) The leachability of 'coarse' coal (<72 mesh B.S.S.) can be predicted by the water-soluble Na^+ content (of the vitrinite, as this is usually the predominant maceral group and its small pore size a controlling factor upon chlorine release in run-of-mine coal).

The chloride content of coals is thus fixed by rank and related to coal type. Its origin is ground water. Present ground waters, however,

may alter in composition and may be diluted or concentrated. If the ground water concentration is great enough it will over-ride the expected coal type-chlorine relationship as seen at Hem Heath and to a lesser extent in the Cannock Chase Coalfield.

CHAPTER 5

LOW TEMPERATURE ASHING

Apparatus

The low temperature ashing (L.T.A.) furnace used during the present study was a 'Plasmod' (Tegal Corporation, Richmond, California). The machine has a single cylindrical chamber, 3¼" internal diameter and 6¼" internal length. Samples of tema ground material, approximately 0.5g in weight are thinly spread in open shallow pyrex dishes arranged within the reaction chamber. The chamber is then evacuated to a mild vacuum (approximately 1Torr) by a mechanical pump. Oxygen is drawn through the chamber and over the sample. Power is applied by a radiofrequency of approximately 13.56MHz. This excites the oxygen molecules and changes some to other species, such as atoms, radicals, ions and free electrons. This oxygen plasma is highly reactive and it causes low temperature combustion of the organic materials. "A plasma resembles a gas in many respects, but with an important difference: the particles (atoms or molecules) of a gas don't carry electrical charges. In a plasma, some fraction of the particles are ionised. In addition, the plasma may contain a substantial population of free radicals. A free radical is a molecular fragment that contains surplus electrons that don't participate in chemical bonding within the fragment. These electrons are available for reactions with other fragments, atoms or molecules." (Bersin, 1975).

The plasma created is equivalent to temperatures of several thousand degrees centigrade, whilst the velocities of the excited atoms and molecules are equivalent to temperatures of a few hundred degrees centigrade only (Price and Jenkins, 1980). Such a plasma can achieve controlled oxidation and volatilisation of organic materials at relatively

low temperatures, the actual surface temperatures depending on oxygen flow rate and radiofrequency power input, but being of the order of 150-200°C (Thomas, 1974). The method has been used to separate mineral matter in a relatively unaltered condition for examination and for quantitative coal mineral matter content calculation (Gluskoter, 1965; Estep et al., 1968; O'Gorman and Walker, 1971; Frazer and Belcher, 1973; Miller et al., 1979).

L.T.A. Side Effects

Low temperature ashing is "undoubtedly the best available method for isolating the minerals from coals in as unaltered a condition as possible . . ." based on the evidence of O'Gorman and Walker (op. cit.) and Frazer and Belcher (op. cit.), ". . . but, as will appear, we have certain reservations as to its accuracy as a method of determining mineral matter contents." (Miller et al., 1979). Frazer and Belcher investigated the major side effects of low temperature ashing. Only those relevant to the present study are covered here.

Chlorine

It is known from the present study that L.T.A. removes chlorine. A sample of 8S13, which has a chlorine percentage of 0.7 by weight in the whole coal, was analysed by the C.E.R.L. and found to have "negligible" chlorine remaining. Similar results were found by Dr. K.G. Saunders (C.E.R.L., personal communication) in studies of L.T.A. using S.E.M. fitted with an energy dispersive X-ray analyser. Gluskoter (1965) reported a chlorine loss with perhaps 10% of the original chlorine remaining after ashing. Fellows (Ph.D., 1979) found that although chloride is the major water-soluble cation in the coal he studied (also found in this present work) that after L.T.A. chloride was negligible and

sulphate was now dominant. Loss of chloride using higher temperature oxidation methods of organic matter removal have been reported (Daybell and Pringle, 1958; Montgomery in Carr, 1978).

Sulphur

Gluskoter (1965) reported that some proportion of total sulphur is lost although pyritic sulphur loss, if any, is small. Frazer and Belcher (1973) noted oxidation of pyrite and Miller et al. (1979) reported quantitative analyses of this phenomenon. The amount of pyrite burned increases with its content in the coal, but of the fraction of the pyrite present, the amount remains relatively constant. Pyrite is oxidised to haematite but burning may be minimised by using a low radio-frequency power level. XRD evidence from the present study did not reveal haematite although levels may have been too low for detection. It is concluded that pyrite oxidation, if it occurs, is negligible as a proportion of the total mineral matter. A 0.2g crushed pyrite sample ashed for 7 hours showed no weight change. However, this is not necessarily comparable to oxidation in an organic rich medium.

Sulphate

Sulphate fixation is reported by Frazer and Belcher (1973) and Miller et al. (1979) from an organic source. This would explain the predominance of the sulphate anion in the water-soluble L.T.A. of Fellows (1979, Ph.D.). Miller et al. (op. cit.) reported that organic sulphur is released as SO_3 or SO_2 and the latter oxidised to SO_3 . This produced needle-like crystals on the window of the ashing chamber, probably a hydrate of SO_3 . A similar phenomenon was observed in the present work. This may react with any carbonate present and CO_2 evolved. Sulphate fixed from organic sulphate increases with decreasing power.

The sulphate is fixed in the form of gypsum. Calcium required for this reaction comes either from that held within the coal moisture or from dissolved carbonate. Recalculation of ground water calcium as gypsum shows it to be insufficient to satisfy the sulphate present. Miller et al. (1979) show that sodium sulphate is to be found in addition to calcium sulphate. The coal moisture will provide a sodium source. An attempt was made to see if a correction existed between carbonate and gypsum. Using XRD peak heights, a correlation of $r = -0.34$ exists between gypsum and samples with a single carbonate. The correlation is not significant at the 95% level but may be overshadowed by the aforementioned cation sources. Dissolution of carbonates may take place but the evidence is not conclusive and neither original nor final 'true' carbonate content was calculated.

Fixation of sulphate as gypsum is a major problem in quantitative mineral matter analysis. There was no evidence from the present work that gypsum is to be found as a detrital or diagenetic mineral and it must be assumed that all gypsum is solely a produce of the L.T.A. procedure. The weight gain makes quantitative mineral matter analysis difficult. "Thus one would predict that L.T.A. mineral matter determination will . . . be too high . . . for H.V.C. coals (as in the present study) . . ." (Miller et al., 1979).

Dehydration

At the temperature of L.T.A. (see below) all non-structural water will be lost. In all mineral matter analyses performed in the present work, all samples were pre-treated by oven drying at 105°C to remove H_2O^- . Some, varying proportion of structural water is also lost. This is most notable in the clay minerals and the amount lost will vary with the clay type. Gluskoter (1965), however, noticed no structural changes.

In the section on sulphate fixation, it will be recalled that gypsum was the mineral reported to have formed. This is not strictly true. XRD study immediately after ashing shows the mineral to be hemihydrate and dehydrated hemihydrate. Such a mineralogy was also noted by Gluskoter (op. cit.). Re-hydration to gypsum soon takes place. A sample of gypsum, ashed alone in the L.T.A. furnace lost 16.4% of its total weight by dehydration, later replaced. It should be noted that the reactions taking place during ashing in a coal medium may have differing side effects.

Ashing Rate

The ashing rate depends primarily on the surface area exposed to the stream of activated oxygen at any one time. Oxidation takes place primarily at the surface of those particles covering the top of the sample and therefore the ashing rate depends on the particle size, position within the chamber (and therefore with respect to the gas stream) and the frequency of stirring. As ashing nears completion, the rate becomes asymptotic. Ashing is never actually completed (Gluskoter, 1965) but is discontinued when the rate becomes too low for practical operation. Thus problems arise in finding an end point. In the present work, ashing was considered complete when the blue ashing discharge seen in the chamber becomes a pale grey or vanishes completely. Small discrepancies may arise in the amount of organic matter remaining. The accuracy of the ashing procedure was calculated on sample 8S13. Approximately 1g of coal was ashed in five dishes. The ash weight is 6.84% with a standard deviation of 0.07%.

Temperature of Ashing

The temperature of ashing is difficult to assess (Gluskoter, 1965). A thermocouple cannot be used in the radio-frequency field as the current will heat the wire. Thermometers placed in an empty but activated chamber indicate 60 to 70°C. A dust layer, produced with ashing of coal, produces temperatures of 220 to 240°C, whilst at or near the coal surface, 105°C was observed. Gluskoter (op. cit.) used gypsum as a thermometer. The dehydration temperature needed to produce dehydrated hemihydrate suggests temperatures of less than 190 to 200°C and may be considerably lower. The present work showed spheres of lead and bismuth found in ashed coal (Plate 5.1). These two metals in a 50:50 mixture form a eutectic in the range 110 to 120°C (Saunders personal communication) thus giving a minimum ashing temperature. Frazer and Belcher (1973) summarised the findings of Estep et al. (1968) who concluded that 145°C was attained using an infra red pyrometer. O'Gorman and Walker (1971) using 'Tempilstocks' considered a maximum temperature of between 149° and 163°C. Breger, reported in Finkelman and Stanton (1978) stated that L.T.A. temperatures do not exceed 150°C.

Ashing - The Colour of Mineral Matter

In addition to the L.T.A., certain samples were ashed at 390°C in a conventional furnace. From the colour of the ash, usually a reddish-brown, it is obvious that oxidation has taken place. Determination of the mineral content of coals using low temperature (excluding L.T.A.) furnaces is covered in Watt (1968).

The colour of the L.T.A. mineral matter shows no sign of oxidation. The relative mineral abundance and composition controls the colour. Using XRD the ashes were investigated and the ash colour attributed to the mineralogy. The results were given in Table 5.1. Essentially the light grey colours are dominated by carbonates, kaolinite and gypsum.

Dark grey or black indicates a predominance of pyrite. The brownish-red of 2.6 is a result of siderite.

Mineral Matter Profiles

After ashing is completed, the samples were allowed to cool in a desiccator and then weighed. This was expressed as a percentage of the original sample weight and given as the mineral matter or 'ash' content of the samples, be they coal or mudrock. The mineral matter profiles for the four seams investigated are given in Figures 5.1 to 5.4.

It is immediately evident that major variations are found in the seam profiles between the mudrocks and the coals. In the mudrocks, organic matter is low. Exceptions occur where there are organic rich mudrocks as in the roof of the Yard and Eight Feet Seams. Some coals, associated with intraseam dirt bands have a high ash content, for example Y1 and Y2. Peaks in ash content within the coal seam may reflect minor dirt bands, abundant cleat mineralisation, as in the Yard Seam sample Y7, or early diagenetic mineralisation seen as siderite in the Park Seam 2.6.

In the mudrocks, the ash content reflects detrital sedimentation and the associated containment or suppression of organic matter accumulation. The coal ash is a result of detrital sedimentation in localised cases but the low detrital background in the true coals is overimpressed by diagenetic mineralisation.

Visual Evidence of Ashing

Plate 5.2, an S.E.M. photomicrograph, shows the difference between coal lithotypes in their reaction to L.T.A.

CHAPTER 6MUDROCK ANALYSESSECTION 1Whole Rock Geochemistry

Sample preparation

Samples were crushed by hammer inside polythene bags and then for a minimum time in the terna mill. Further grinding to a talc-like consistency in an agate mortar followed. Considerable variation in organic matter could be expected from the samples, usually depending on their position in relation to the coal seam. Those mudrocks associated closely with the coal seam often have high organic matter levels. This is shown well by the Yard Seam (Figure 5.2).

Organic matter removal

Various methods are available to remove organic matter. Most commonly used are those involving ignition at various temperatures in a furnace. Standard methods for the determination of organic matter are covered by Montgomery in Karr (1978) and for its removal for mineral identification by Jenkins and Walker, also in Karr. Organic matter leads to problems in geochemical determinations and also acts as a dilutant. Similar pre-treatment of all the samples is necessary as different methods have different side effects. High temperature ashing is certain to remove all organic matter but oxidises reduced species and the more volatile fractions may be lost. Oxidation at 390°C is an alternative but although losses are reduced, ashing time is greatly increased, oxidation is not prevented, clearly seen in the red, brown and orange ash. The low temperature 'plasma' ashing furnace was used as the most viable alternative. This method oxidises organic matter using an activated oxygen source and leaves the mineralogy relatively unaltered. The technique is

studied in more detail elsewhere in this thesis. When oxidation of the sample is complete, cooling is allowed in a desiccator. The samples, previously dried at 105°C to remove H_2O^- (adsorbed water), 'represent' the mineral matter content of the specimen and their percentage weight can be calculated. All samples, for XRF and XRD, mudrocks and coal were prepared in this manner. Because of the relatively low ash contents of the mudrocks ashing is fairly rapid and sufficient sample is available for complete XRF major element analysis. This was not the case with the coal samples and the original samples had to be grouped before analysis.

XRF preparation

Major element analysis by XRF was conducted using a Phillips 2kW Spectrometer under the supervision of Dr. R. Kanaris-Sotiriou. Glass discs were prepared following the fusion method of Norrish and Chappel (1967) and described by Norrish and Hutton (1969). The weight loss on ignition was recorded and is explained by the loss of volatile constituents, SO_3 , CO_2 , H_2O and any remaining organic matter. Against this loss is a weight gain through oxidation of reduced elements, iron and sulphur.

A problem arises in the form of sulphur. If the sulphur is reduced, no loss should take place in the disc preparation and the total is expressed as S. If sulphate is to be found in the original sample then a variable loss could be possible with L.T.A. Sulphate is expressed as SO_3 . If, as in the present case, both sulphide and sulphate (gypsum, a by-product of the ashing) are present then problems arise. Unfortunately insufficient sample prevented a separate sulphate determination. In the mudrocks the most common form is sulphide and no sulphate was recognised by XRD. This does not, however, rule out small quantities (<5%) of sulphate being present. Sulphur is reported as S. The coals are markedly different and gypsum is common and in excess of pyrite. Here the analysis was reported as SO_3 .

Wet chemistry

Na₂O, FeO, total water CO₂ and organic carbon were determined using wet chemical analysis. Analysis of sodium was not possible by XRF because of the use of sodium nitrate as an oxidising agent in the disc preparation. 0.1g of sample was dissolved in a mixture of hydrofluoric and perchloric acids and then analysed by atomic absorption spectrophotometry. FeO determination was made following the colourimetric determination of Shapiro (1960) because small amounts of organic matter remain even after L.T.A. After the necessary correction factor, FeO was subtracted from total iron to leave 'ferric' iron. It should be noted here that pyrite is insoluble in the FeO determination and is therefore reported as Fe₂O₃. Total water was determined by the Penfield (1894) tube method. Problems arose here in samples still containing organic matter and those with high levels of pyrite leading to sulphur precipitation. Multiple determinations were carried out and the mean taken. Adsorbed water (H₂O⁻) was determined by oven drying for 7 hours and subtracted from total water to give combined or structural water (H₂O⁺). Further problems arise here in that some adsorbed water may remain until 300°C. (Deer et al., 1962). This was ignored in view of the analysis problems shown later. CO₂ was calculated by weight adsorbed in soda asbestos U-tubes from gas evolution after nitric acid solution. Organic carbon may be determined by a modification of this method but the results were not used in the analysis.

XRD

Quartz and feldspar determination using peak areas was used following the method of Fellows and Spears (1978). Clay minerals were determined using peak areas (Spears et al., 1971; Spears and Taylor, 1972; Collins, 1976).

Major Element Geochemistry

The major element totals are given in Table 6.1. It is obvious that there is a difference between the totals using calculated CO_2 and H_2O and if loss on ignition is substituted. The former are too low and the totals are short of 100%. After re-melting and re-running those samples with largest variation but with no improvement, some samples were ashed and recalculated from the beginning. Wet chemistry was repeated. As further improvement was not forthcoming it was concluded that L.T.A. was not removing all the organic matter. The XRF discrepancy is significantly correlated with organic matter ($r = +0.81$; 99.9% significance). This had been observed by Gluskoter (1965). Further indirect evidence was supplied during total water analysis when oily organic matter was evolved. If the calculated organic carbon values were substituted for L.T.A. values, then in twelve out of the nineteen samples, totals of greater than 100% were calculated. As organic carbon is only a (major) part of organic matter then these totals would be still higher. Either ashing was incomplete or there is a weight gain during the ashing procedure. Of those seven samples lower than 100%, four were notably lower. Based on the values given by Pitt and Millward, page 6, (1978) for medium rank coals, carbon accounts for 88% of the d.m.m.f. weight. Recalculation of these four samples, which have very large organic matter totals (and hence a suspicion of the organic carbon calculation at high levels) gives reasonable totals for Y2 (99.36%) and Ydb2 (101.78%). YR2 and 8R2 are still too low. YR2 is rich in pyrite and organic matter and 8R2 is an organic rich siderite. In the latter case, the high iron content may mean interpolation far beyond the value of the standard rock and thus be a cause for variation. Samples high in pyrite may suffer oxidation during L.T.A. to haematite (Miller et al.,

1979). If oxidised to sulphate then some of this may be lost on L.T.A. preparation thus producing a low total. Alternatively, if there is much sulphate present and the recalculation supposes sulphur as S, then the total will also be low. Recasting S as SO_3 makes an acceptable total. Gypsum sufficient to satisfy this much SO_3 should be visible on XRD but there is no evidence for this. To complicate matters still further, a weight gain could be produced by the fixation of organic sulphur as sulphate (gypsum). This is common in the coal ash samples and covered in the section on low temperature ashing. With lower organic matter values associated with most mudrocks, the gypsum produced will be minor and probably not sufficient to be seen by XRD. In view of these complications ignition losses were used instead of CO_2 and total H_2O to give good totals in all but YR2 and 8S10c (Table 6.1). The difference between ignition loss and CO_2 plus H_2O was tentatively ascribed to organic matter. All analyses were recalculated as a proportion of 100% and given in Table 6.2.

In view of the problems encountered in this work, possibly the first attempt to analyse L.T.A. by XRF, some suggestions are tentatively made. L.T.A. should be continued for longer than the visual completion point but ashing will never be totally completed. XRD could be used for detailed mineralogical investigation and used as a back-up to XRF analysis. Sulphate analysis should be carried out. The L.T.A. should then be pre-treated to 950°C to remove all organic matter and ensure that the starting material for the XRF disc preparation is of a standard oxidation state. Although the mineralogy will be altered considerably, there will be fewer technical problems with XRF preparation and the results will be quantitative.

Normative Mineralogy

Using the recalculated data, the mineralogy was calculated by apportioning the elements to normative formulae and hence normative minerals, using the method of Nicholls (1962). Modifications were made for the clay minerals because of their extremely variable mineralogy. The proportion to be attributed to the clays was calculated by difference and divided up using XRD peak areas. The use of XRD for clay mineral calculation and identification is dealt with in more detail in the relevant section. Suffice to say, clay mineral abundance was calculated following Schultz (1964) with modifications in using ethylene glycol to determine the proportion expandable clay (Spears et al., 1971; Spears and Taylor, 1972; Collins, 1976).

It is seen from XRD investigation of the ashed material (smear mounts) and whole rock (powder mounts), that feldspars are present. Quantification using the XRD method of Fellows and Spears (1978) was attempted but found to be too low to use this method. Less than 1% of the ash is feldspar. Maximum microcline and high albite were the only feldspars observed as found by Fellows and Spears (op. cit.). In the normative formulae those elements held in feldspar are apportioned to the clays.

The recalculated normative mineralogy is given in Table 6.3 expressed as a fraction of the whole rock. The whole rock data was processed using the computer programme of Till (1969). This programme specifically calculates a correlation matrix of all the data (Table 6.4) and prints the regression lines of significant data. Also calculated are the mean and standard deviation of each variable, and its slope gradient, intercept, and confidence on these variables and data dispersion. The regression is based on a reduced major axis equation (Kermack and Haldane, 1950). Equal error is assigned to both variables and neither variable is specified as dependent.

Quartz

The profile of quartz distribution is given in Figure 6.1 and was positively identified by optics and XRD (Fellows and Spears, 1978). The chemistry of quartz, along with its absence of cleavage, make it resistant to chemical and physical breakdown in most environments. Dissolution will not take place in environments of below pH9 (Krauskopf, 1979) which is highly unlikely in the organic rich coal forming environment. The physical strength of the grains therefore control the size of quartz and its distribution is related to the erosive, then the depositional energy of the environment. The relationship of grain size and sedimentation rate means that quartz can be used as a measure of depositional energy (Spears, 1964). Problems do arise, however, in that its size distribution is restricted in fine sediments.

It is evident from the mudrock profiles that the floors, intraseam dirt bands and roof measures have different characteristics. In all seams, the maximum quartz values are to be found in the floor, notably so in the Yard and Shallow seams. Roof measures are intermediate, although only marginally at Littleton Colliery, whilst the dirt bands are lowest. This is most obvious in I.D.2.11 which has no quartz. The low values in 8R2 are explained by early diagenetic siderite precipitation (Curtis, 1977) preventing compaction, and organic matter dilution. The Yard Seam is complicated by varying depositional energy and organic matter contents. Lowest quartz values are to be found in the dirty coal Y2 and organic rich roof mudrock YR2.

The high quartz levels associated with the Lea Hall Colliery floor measures indicate either a high energy environment with rapid sedimentation, or a weathering regime of a seat earth where leaching has removed labile constituents, thus concentrating the resistate fraction. The Yard

Seam shows a dramatic fall from YF1 to YF2, immediately adjacent to the seam floor. This is expected with the still-stand environment of coal accumulation, which is stable and has reduced energy thus allowing more clay to be retained and held (Wilson, 1965a). Y1 has a relatively high detrital input and is a dirty coal. The first dirt band, Ydb1, shows increased detrital sedimentation following widespread flooding (Wandless et al., 1969), falling again in the coal Y2. Ydb2 saw renewed flooding and detrital sedimentation before the major still-stand and coal accumulation. The roof shows increasing quartz away from the seam with a temporary still-stand seen in the organic rich YR2.

The inverse correlation between quartz and organic matter ($r = -0.55$, 95% significance) is not unexpected as both elements belong to almost mutually exclusive environments of rapid sedimentation and still stand environments respectively. Significant correlations with TiO_2 and Zr confirm a detrital control on these fractions (Figure 6.1).

Floor measures

It is shown in the clay mineral investigation that major differences are found between Lea Hall and Littleton Collieries. Similarly, quartz contents are widely differing and yet, within a colliery, internally consistent. A similar stratigraphic distribution is to be found in the distribution of siliceous seat-earths (+90% silica) which are common in the Lower Coal Measures (Williamson, 1967). Although the present floor samples do not fall into this category they are high in the quartz range for the fireclay category (Williamson, op. cit.).

High quartz content may reflect the source material, in which case a change seems unlikely within the relatively small geographical variation. Both TiO_2 and Zr being detrital but being virtually independent of size, are better indications of depositional rates than quartz (Spears, 1964;

Spears and Kanaris-Sotiriou, 1975, 1979). The high quartz value in the Shallow Seam floor is matched by high TiO_2 and Zr and may therefore reflect rapid deposition. The identical quartz to TiO_2 ratios for SSF1 and YF1, which are considerably higher than for the Littleton seams (Figure 6.1) indicate rapid sedimentation, capable of transporting and depositing more quartz in the Lea Hall seams. The fall seen in YF2 is not mirrored by a fall in TiO_2 and hence the quartz decline is through size segregation rather than a reduced rate of deposition. The carrying capacity may, however, have declined.

There is evidence of authigenic quartz precipitation infilling a stigmaria together with pyrite in Y1. Precipitation of quartz may be a factor in leading to high values. However, only two other examples of authigenic quartz, both in cleat, have been found. Thin section evidence of the mudrocks indicates the quartz grains to be detrital, not authigenic.

Wilson (1965a) considered that changes in seat earths, especially clay minerals, reflected a changing climatic pattern associated with continental movement. Thus a tropical Carboniferous environment changed to a semi-arid, arid environment of the Permo-Trias, from a strongly leaching regime to one where evaporation often exceeded precipitation. In the former environment, the stable quartz would be most resistant to breakdown and would be concentrated relative to other detrital minerals. Later, the clay fraction would assume a greater dominance. Indirect evidence suggests that the approaching Hercynian Orogeny would produce more, rather than less quartz, towards the end of the Coal Measures.

The overall trend of decreasing quartz levels in floor measures appears to be climatic. However, in individual seams, the depositional rates are important and in situ leaching may also emphasize a concentration of resistant minerals.

Intraseam dirt bands

The thin, widespread detrital bands found within coals represent the precarious balance needed for coal vegetation growth. Slight instability or base level changes may produce widespread flooding over an environment which was virtually a peneplain. Similarly, levee burst could produce widespread inundation (Wardless et al., 1969). Channel position would be paramount in this case because flooding would soon find reduced velocity, hence the carrying capacity will be reduced, thus controlling the grain size and type of minerals deposited. Quartz, for example, would be expected close to the channel, fine material such as degraded illites, further away. The thickening or coarsening of the dirt bands may indicate the source direction.

Dirt bands are usually fine grained sediments, mudstones, shales and fireclays, but rarely siltstones (Williamson, op. cit.). The absence of quartz in the Park Seam indicates very fine deposits although the depositional rate, based on TiO_2 evidence, is not necessarily slow.

Roof measures

Quartz profiles indicate increasing energy away from the coal forming environments with subsidence, representing a return to 'normal' detrital sedimentation. Variations may be explained by dilution from diagenetic mineralisation or brief still stands leading to brief coal development.

Combined Silica and Alumina

Clays dominate this group as XRD evidence indicates that mica is minor and feldspar is invariably lower than 1%. The clays are both detrital and diagenetic, the former predominating in the mudrocks, the latter in coals. Clay minerals represent the low temperature (and pressure) surface representatives of the original aluminosilicates,

"... a clay mineral, a compound in which some of the original Al and Si apparently remain combined." (Krauskopf, 1979, p. 91). In the absence of other alumino-silicates, Al_2O_3 is a measure of the clay fraction and its ratio with SiO_2 , the type of clay and their relative proportions.

The association with TiO_2 indicate a detrital source and correlations between Al_2O_3 and SiO_2 , K_2O , H_2O suggest an illite host. This may be indirect, as the illite distribution is fairly typical of the total clay distribution. Correlations with MgO and Na_2O also suggest a clay host. There is no significant correlation with quartz, nor expected, as the hydrodynamic partition and grain size will differentiate clays into low energy, quartz in high energy, environments.

The Al_2O_3 to combined Si ratio (Figure 6.2) was used by Spears (1964) being grain size independent. Variations are present, but similarities are found within sections of a seam. Thus the Shallow and Yard roofs have similar high ratios, floors are similar and the Yard dirt samples are internally consistent. The similarities can be explained by the similarity of clays present within each environment which change as a reflection of degradation and sedimentation rate. The high ratio in Y2 is explained by a high proportion a poorly crystalline (hence detrital) kaolinite. It is interesting to note that kaolinite is often highest in low energy environments. The similarities between the Littleton profiles (8F1 excepted) and Lea Hall roofs indicate a similar overall clay source and mineralogy. The floor clays, however, are sometimes peculiar to their formational environment. It is evident from the ratio that the degradation of illite in I.D.2.11 has not broken the basic Si-Al bond.

Titania

Similarities with Zr and quartz indicate TiO_2 to be detrital (Spears, 1964). 950°C pre-treatment of samples prior to XRD investigations show

its host to be anatase, the low temperature polymorph of rutile. TiO_2 is virtually size independent (Spears and Kanaris-Sotiriou, 1979) and hence the differences in the quartz/ TiO_2 profiles may be explained by size and sorting (Figure 6.1).

The seam profiles (Figure 6.1) show TiO_2 to be highest in the floor, falling towards the seam, then remaining constant or increasing away from the seam. Dilution problems are encountered in the Yard roof and 8R2. In the Park Seam, TiO_2 is highest in the dirt band, contrary to quartz trends and in the Eight Feet Seam dirt band is only slightly lower than in the floor, but higher than in the roof. The Yard Seam shows a similar trend with the coal Y2 being lower in TiO_2 than the associated dirt bands. If the TiO_2 profiles were replotted on an organic free basis, the dirt bands have the highest values for the seam. It is evident therefore that considerable size segregation is producing the apparent conflict between the quartz and TiO_2 levels. Widespread flooding would be expected to produce rapid sedimentation but the low energy would limit its carrying capacity to fine grained (mainly clay) minerals.

Ferrous Iron

The Fe^{2+} profile is not constant (Figure 6.3) and is dominated by the Eight Feet Seam roof. The remaining values are low. It is evident from the distribution of values that correlation significance will, therefore, be suspect, but they do exist between Fe^{2+} and CO_2 , CaO, Mn and P_2O_5 . The latter relationship is indirect through similar diagenetic environments for carbonate and phosphate precipitation, likewise CaO (Spears, 1964; Krauskopf, 1979). The source of the majority of Fe^{2+} , certainly in 8R2 and 8R1 (XRD evidence), is siderite. The seam profiles for normative siderite (Figure 6.4) show, with the exception of the Yard Seam, that siderite is concentrated in the roof samples and is not found

in floors or intraseam dirt bands. The Yard Seam has normative siderite in the floor, minor levels in the dirt bands and a second peak in the roof. The predominant roof association is not controlled by CO_2 availability and hence by Fe^{2+} . Pearson (1979) has shown the seat earths are often depleted in iron and this may in fact represent leaching from the floor measures. The dirt bands may represent reworked 'floor' material and so too would be low in Fe^{2+} . The roof measures may represent 'normal' Fe^{2+} but there is such a non-normal distribution of data that this assumption cannot be followed up.

Clay minerals, especially chlorite, have been shown to be Fe rich, and this therefore, is another iron source. Iron rich chlorites are typical in the British Coal Measures (Collins, 1976). The Fe^{2+} profile is similar to that of chlorite but the clay percentages are very low, especially when compared to the carbonate source.

Ferric Iron

This includes pyrite as it is not taken into solution with the Fe^{2+} acid digestion. A major source of Fe^{3+} is from hydroxides and oxides of iron forming grain coatings which may be mobilised in the reducing environment. As the Fe to Al ratio is far from constant, it is evident that there is not a simple clay association. This may, however, be masked by pyrite, seen in the similarity of Fe_2O_3 and S profiles in the Yard Seam and the significant correlation between the two variables. The other seam profiles do not show the Fe_2O_3 -S relationship and may, therefore, have alternative hosts (Figure 6.5).

The source of pyrite iron may be in solution or sediment (Spears, 1964). Once liberated, iron may migrate long distances before being precipitated. Pearson (1979) showed chlorite to be a major iron source. Early diagenetic pyrite is precipitated at shallow depths (Love, 1967) as

iron monosulphide, altering to pyrite with continued diagenesis (Berner, 1970). In the fresh water environment of the present work, $\text{SO}_4^{=}$ is limited and found to be an order of magnitude lower than in the marine section at Little Smeaton (Spears, op. cit.). Sulphate availability will therefore be the limiting factor in pyrite formation. Pyrite development is complicated by late diagenetic pyrite being present in organic rich samples hence the Yard Seam distribution pattern.

As $\text{SO}_4^{=}$ is limited, hence insufficient S is available to produce high levels of pyrite (exceptions being in the pyrite nodular horizon in 8S10a), the excess Fe^{2+} would be precipitated as siderite, CO_2 being supplied by an organic source (Curtis and Spears, 1967). The normative pyrite curve is given in Figure 6.5.

Manganese

Mn was determined both as a major and a trace element and found to correlate significantly ($r = +0.99$, 99.9% significance). As the trace element determination gave greater detail, this was used. Significant positive correlations were found with apatite (P_2O_5) and carbonates (FeO , CaO , CO_2), as previously noted by Curtis et al. (1975). Negative correlations exist with the detrital elements suggesting dilution in diagenetic environments. Mn may substitute for Ca in carbonate apatite (Krauskopf, 1979).

The Mn profiles are given in Figure 6.3 and show a peak in 8R1, 8R2 and a lesser peak in SSR2. The Park Seam shows a maximum in the roof and the Yard Seam is complex, highest in the roof (YR3) followed by the floor (YF1), the dirt being lowest. The pattern is typical of that predicted by siderite.

Similarities between Fe^{2+} and Mn profiles led Spears (1964) to suggest similar origins (Figure 6.3). The Mn to Fe^{2+} ratio shows

differences occur (Figure 6.4), high ratios indicating Mn being removed preferentially from solution because of its lower solubility. Removal of Fe from chlorite by exchange in pyrite development (Pearson, 1979) is apparently not occurring in siderite diagenesis as witness to 8R2 which has negligible chlorite. Curtis et al. (1975) concluded that ground water solutions may be channelled over great distances, along 'aquifer' horizons, to precipitation sites far from their origins. Similar findings were made by Hallam (1967) and Raiswell (1971). There is, however, no evidence to suggest that 8R2 represented a permeable horizon. Its quartz content (4.2%) is low compared to the adjoining roof sample 8R1 (20.3%), and is still lower when dilution factors for the siderite and organic matter have been applied. It is tentatively suggested that the change from coal to detrital sedimentation was slow. High organic matter (37%) bears this out, together with TiO_2 evidence. Very fine sediments, including soil 'sesquioxides' in large quantities (because of the high surface area to volume ratio) would have been liberated with an equivalent oxidation of organic matter, CO_2 being produced as a by product (Curtis et al., 1975) and the siderite may have developed very soon after burial, probably close to, or at the surface if beneath the oxidation-reduction front. More rapid sedimentation followed (8R1), and coarser sediments, thus less Fe was available and the siderite development was reduced and finally curtailed. Migration of ground waters does not necessarily need to be invoked.

Why Fe and Mn availability reached a maximum in 8R2 is unclear. Perhaps the increasing aridity (Red Beds) of the approaching Upper Coal Measures supplied greater levels of iron oxide coats, or the period marked a long still-stand capable of marked clay sesquioxide development took place.

In taking sections through a siderite 'sheet', Curtis et al. (op. cit.) found systematic and symmetrical variations. The early formed core was Fe and Mn rich leading to later depletion in these cations which are dominated by Ca and Mg, and the carbonate content decreased. The Mn to Fe ratio was highest in the early stages of precipitation. No attempt was made to subsample 8R2, but the ratio is lower than 8R1. Thus siderite precipitation terminated early in 8R1. The only sample (SSR2) to have normative siderite in the Shallow Seam also has a high Mn to Fe ratio.

The change from a siderite core to pistomesite (Mg rich) rim (Curtis et al., op. cit.) is also identified by a doublet siderite peak at c. 2.8\AA (Pearson, 1974). This is not found in the present siderite rich samples (8R2, 8R1, SSR2), nor are abnormally different Mg values. In fact, SSR2 and 8R2 have a Mg depletion when compared to associated samples. Either precipitation ceased before the Mg rich stage (early precipitation is suggested by the high Mn to Fe ratios) or Fe was far more abundant than in the environments studied by Pearson (1974) or Curtis et al. (1975).

Calcium

Ca is significantly correlated with carbonate and phosphates and negatively related with detrital elements. The carbonates are siderite, calcite and ankerite (normative dolomite) but these values are often so low as to be rarely identified by XRD. Ca may be located in apatite and the correlation is further strengthened by the similarities in the geochemical environment which give rise to both diagenetic carbonates and phosphates.

An examination of the relevant profiles shows that although Ca is generally low (Figure 6.6), the peaks are generally associated with the aforementioned carbonates (Figure 6.7) and phosphate but Ca is also

found where CO_2 is absent and normative hydroxyapatite has been accounted for. The highest 'excess' Ca value is 0.16% which compares favourably to the 0.15% ascribed by Spears (1964) to clay minerals.

If the Ca remaining, after apportioning to normative hydroxyapatite, is plotted against CO_2 (Figure 6.8) on an organic free basis, two populations result. Those which are clay associated have been omitted. A cluster lies in the range of less than 0.22% CaO and 0.82% CO_2 and a group of relatively low CaO but high CO_2 consisting of samples 8R1 and 8R2. As both of these samples are siderites, it is not unexpected that the CaO to CO_2 ratio is low. Only SSR3 has been shown by XRD to contain calcite as the only carbonate although trace levels would not be identified. This sample plots a trend approaching that of pure calcite and also has an excess of Ca, probably held in clays. The large cluster of samples lying between that of the siderites and calcite include ankerites and multiple carbonates of varying proportions. It is evident that samples YF1, YF2 and YR1 are all siderites that follow a trend which bears no relationship to that traced by 8R1 and 8R2. The former (Lea Hall) group has a higher Ca to Fe ratio but this may be due to undetected calcite dilution. Ground water evidence does, however, indicate that Ca is higher in relation to Mg at Lea Hall and this is seen in calcite cleat, whilst Littleton has predominantly ankerite cleat minerals.

Magnesium

Significant positive correlations are to be found between magnesium and clay mineral associated elements, probably degraded illites and chlorite. There is no obvious carbonate association as can be seen from a comparison of the CO_2 and MgO profiles (Figure 6.6). YR3 and 8S10c, for example, have no CO_2 and 1.38 and 1.42% MgO (organic free basis) respectively. Other samples have lower Mg values and may be carbonate

located. Detrital MgO is an order of magnitude higher than similarly located CaO. The Mg curves are erratic and may indicate a non-specific clay location over which is printed occasional carbonate sources. If expressed on an organic free basis, MgO is seen to increase from floor to roof in all the seams. If the normative carbonate fraction is subtracted from total MgO, then there is little difference to the distribution except in 8R2.

Mg may be located in chlorite. Although these clays have been shown to be iron-rich, such chlorites still hold some Mg. Chlorite and Mg certainly follow similar trends, increasing with increased rates of deposition. Highest values are found in the roofs, low in the dirt bands. There may be an association with degraded illite but this is likely to be small and would lead to high values in the dirt bands. Exchangeable cation evidence, too, indicates a low Mg to Ca ratio in the dirt bands compared to roof samples. Use of the Mg to Al ratio (Figure 6.7) to avoid dilution problems shows a similar pattern of degraded intraseam dirt bands leached of Mg and a size distribution which would generally omit coarser grained chlorite. Spears (1964) found a similar decrease in the ratio with slow sedimentation indicating Mg sorbtion to be negligible.

There is an overall MgO increase up the stratigraphic profile in those seams sampled. This fits in with a changing climate theory leading to a clay suite dominated by illite and chlorite as aridity increased. Similarly, exchangeable Mg was found to be highest in the youngest, the Eight Feet Seam. The MgO trends are thus a reflection of clay type and abundance, this being a reflection of the hinterland geology, weathering regime, residence time and energy of deposition. The effect of diagenesis is negligible in the clays and is limited to the carbonates.

Sodium and Potassium

Unlike those of the coals, Na and K trends are similar in the mud-rocks, and have therefore been studied together. Na has significant correlations with the detrital aluminosilicate fraction which, in the almost total absence of feldspar (XRD evidence, and no correlation between Na_2O and the minor albite peak heights) is attributed to clay minerals. The contribution of water-soluble Na, even in the Yard Roof, is negligible to whole rock Na_2O . There is a negative relationship with carbonate elements.

The seam profiles (Figure 6.9) show no significant variations. Those in the Shallow and Yard Seams are explained by quartz dilution and 8R2 by siderite and organic matter dilution. Most variation is shown by the Yard Seam with its varying organic matter contents. If re-expressed on an organic free basis, the Yard Seam shows an up seam increase to a peak in YR1.

The K profile (Figure 6.9) is similar to Na, with which it is correlated ($r = +0.54$, 95% significance), but its variation is greater and values are almost an order of magnitude higher. Like Na, there is a close correlation with clay minerals. A negative relationship with both organic matter and S is not unexpected. The major clay host is illite, identified by XRD. Degraded illite, too, will provide a (depleted) K contribution.

Figure 6.9 shows the Na_2O to K_2O ratio, seen generally to be constant but with exceptions in 8R2, Y2, Ydb2 and YR1. Such variations indicate differing clay type, weathering and depositional rate thus controlling the clay size. The K_2O to Al_2O_3 ratio is predicted by XRD illite trends, increasing with depositional rates. Low values in the intraseam dirts are indicative of fine grained K leached degraded illites which often predominate in

this environment. Rapid deposition, on the other hand, allows little time for degradation and a concentration of the coarse illite fraction from which little leaching has taken place. The trends are complicated in the dirt bands by high kaolinite fractions which will enhance the low ratio found in the Yard Seam. The Na to Al ratio (Figure 6.9) is not generally related to a specific clay but a high ratio in Y2, Ydb2 and 8R2 may reflect a location in the degraded illites introduced after its degradation. The peak in YR1, however, cannot be so explained. Variations in the Na_2O to K_2O ratio generally reflect changes in the K level in illite and degraded illite which is a function of grain size and degradation, then separation of illite and degraded illite on a size basis through depositional energy.

K is seen to increase up through the seams and is reflected most clearly in the changing K to Al ratio. XRD evidence confirms this trend as one of increasing illite up the succession.

The clay composition is a product of the weathering environment. Spears (1964) found Na to increase with TiO_2 and quartz and a low Na to K ratio he attributed to time for allowing K exchange and fixation to take place. The present work shows this trend to be reversed. K increases with energy, purely as a function of increasing illite and little or no degradation products in this suite. Cation exchange is of little consequence.

Phosphate

P_2O_5 is associated with the diagenetic fraction and has a negative relationship with detrital sedimentation shown by TiO_2 . Such a relationship may be explained by dilution or by mutually exclusive environments of formation. It should be noted, however, that the P_2O_5 data is not normally distributed and a few extreme values may dominate the correlation.

Apatite is identified by XRD as the phosphate host and Ca shows the most significant correlation ($r = +0.93$, 99.9% significance). The P_2O_5 distribution is given in Figure 6.10.

The Ca needed to form normative hydroxyapatite (Nicholls, 1962; Spears, 1964) does not account for the total CaO in the samples and a varying proportion is carbonate located. The similarity between the distributions of Ca in carbonates and phosphates is a function of a similar geochemical environments leading to their diagenesis (Krauskopf, 1979). Ca is the only common metal in the geologic environment that combines with P_2O_5 . The relative abundance of suitable anions will give rise to fluorapatite or hydroxyapatite (Krauskopf, op. cit.). Hydroxyapatite was identified by XRD. Like carbonates, phosphates have organic matter in common. Spears and Amin (1981) showed that organic matter destruction released P_2O_5 and CO_2 . Curtis et al. (1975) also noted the association of carbonates (siderite) and phosphates.

Krumbein and Garrels (1952) considered that where phosphate is abundant, the pH exceeded 7.0. Values of 0.15% P_2O_5 were "... not thought to have pH significance ..." (Spears, 1964). Only in 8R2 (0.58%) is this exceeded. This sample has fossil lamellibranchs (non-marine species) present and these are the probably hosts of this high P_2O_5 value.. Fellows (1979, Ph.D.) found high P_2O_5 levels to be associated with horizons of fish scales. The P_2O_5 to Ca ratio (Figure 6.10) indicates a fall in sample 8R2 indicating relative limitation of P_2O_5 and hence the association with carbonate in this sample may be more apparent than real. The remaining, lower P_2O_5 values are probably derived from organic matter, as postulated by Spears and Amin (op. cit.), released by the destruction of organic matter by micro-organisms. This would explain the correlation between organic matter content and P_2O_5 .

Conclusions

- 1) The detrital minerals show little evidence of alteration in the diagenetic environment and bear the impression of their origins in terms of mineralogy, weathering environment (climate) and finally size separation through depositional energy.
- 2) The major detrital minerals are quartz and the clay minerals. Anatase is a minor constituent of all the samples. Feldspars and mica, although present, are insignificant.
- 3) The quartz distribution is directed controlled by deposition rate increasing with more rapid sedimentation. However, because of its limited size range, it is excluded from fine sediments as can be seen from the fine grained, yet rapidly deposited intraseam dirt band I.D.2.11. Thus the quartz distribution is found to be lowest in the dirt bands, intermediate in the roof-increasing away from the seam, and highest in the floor. There is an overall trend of falling quartz values in floor measures up the succession. This may be linked to changing climatic patterns with the removal of labile elements, hence concentration of quartz, in the lower seams (Shallow and Yard Seams).
- 4) TiO_2 , located in anatase, is not size dependent like quartz and is thus a more reliable guide to sedimentation rate. It is thus evident, that despite the fine mineral size associated with the dirt bands that they were, in fact, the most rapidly deposited of the mudrock units.
- 5) The proportion of clay minerals increases as the grain size falls. Within individual units of a seam, that is the floor, intraseam dirt bands and roof, the proportion of clay is internally consistent, indicating a grain size control. Kaolinite is variable through the

profiles but in the Yard Seam it is concentrated in the fine dirt band fraction where it is of a low crystallinity. This may represent reworking of kaolinite rich floor measures. Illite, generally the most abundant clay, is typical of the total clay profile. Like quartz, it increases with sedimentation rate. Where weathering has had the opportunity to degrade the illite, it may then be segregated on a size basis. These degraded illites are concentrated in the dirt bands and are lowest where sedimentation rates are high. Chlorite is a minor component of the clay fraction but increases with sedimentation rate.

- 6) Overall climatic trends see kaolinite to be concentrated in the lower (Lea Hall Colliery) seams where the tropical Coal Measures climate produced intense leaching. Increasing aridity towards the Permo-Triassic times is marked by a trend towards increasing illite and chlorite at the expense of decreasing kaolinite. Similarly, K, located in illite, and Mg, non-specific clay or chlorite located, increase up the succession.
- 7) The floor measures appear to be climatically controlled but there is evidence to point to some leaching within the depositional environment.
- 8) The intra-seam dirt bands are fine grained sediments which were rapidly deposited, probably due to widespread flooding associated with bank bursts. The concentration of fine degraded clays is reflected in low K and Mg.
- 9) The roof measures represent 'normal' sedimentation in a subsiding area. Although sedimentation rates increase away from the coal seams, temporary still-stands marked by organic matter accumulation are to be found as in YR2.

- 10) Diagenetic minerals are only locally important as in the pyrite rich 8S10a and the siderite rich 8R2.
- 11) The pyrite profile is variable and is limited by sulphate supply. The iron minerals probably originated in reduced iron sesquioxides once forming grain coats. Once liberated into ground waters, they may be transported over long distances.
- 12) After pyrite precipitation has ceased, the remaining iron will form siderite. In all but the Yard Seam, the distribution of siderite is found to be located only in the roof measures. As iron is the determining step, its absence from floors and dirt bands may be due to leaching from these sediments. Mn shows a similar profile being specifically siderite located. A high Mn to Fe ratio in the major normative siderites indicate very early diagenetic precipitation.
- 13) Ankerite and calcite are relatively insignificant. Calcite predominates at Lea Hall, ankerite at Littleton Colliery, explained by differences in ground water composition.
- 14) Apatite is limited in abundance and its association with the carbonate distribution is explained by similar diagenetic environments. Organic matter is the link with phosphate being liberated by its oxidation. There is little through seam variation, the high value found in 8R2 being attributed to fossil debris.

SECTION 2CLAY MINERAL ANALYSISMethod

XRD was used as the major tool in the identification of the minerals present in both mudrocks and the L.T.A. from the coal samples. The use of XRD as a standard tool in clay mineral studies is well established. Attempts at quantitative analyses of mudrocks have been made by Schultz (1964) and Collins (1976), and "with good practical procedures and some favourable circumstances reasonable results can be achieved," (Brindley and Brown, 1980). It is considered that the estimation of clay mineral abundance is at best 'semi-quantitative', as found by Pierce and Siegal (1969). Using various pretreatment methods, the peak height or better still, the peak area (Cubitt, 1975; Collins, 1976; Brindley and Brown, 1980) can be used to give a relative abundance assessment of the clays present. It must be emphasised that various authors have found considerable analytical variations (Johns, Grim and Bradley, 1954; Gibbs, 1965; Pierce and Siegal, 1969; Carroll, 1970; Ashby and Pearson, 1978) but Brindley and Brown (1980) considered XRD to be "the best of the standard methods available for clay mineral identification, giving a good balance between detail and ease of analysis of a large number of samples".

Sample Preparation

Clay mineral identification and quantification was conducted using orientated smear mounts on glass slides. Such a preparation produces maximum preferred orientation of the platy clay minerals thus enhancing the basal peak reflections and the suppression of all others. Clay mineral analysis was made on both whole rock and a <2 μ m fraction. The <2 μ m fraction is the generally accepted size fraction for clay mineral

investigation (Brindley and Brown, 1980) as it excludes the majority of non-clay minerals and allows good sedimentation of the clays and hence, the best definition of their basal reflections. Small quantities of non-clay minerals, such as quartz, may affect any preferred orientation. It must be realised that the $<2\mu\text{m}$ fraction is calculated on the settling time for a particle with a diameter of this size. As the clays are not spherical, their true dimensions may not correspond to this size fraction. Some clays may also show considerable size range and may therefore be excluded from the fraction because they are too large.

A drawback to any sedimentation technique is that once the suspension has been applied to the glass XRD slide, further sedimentation will take place, leading to a fining upwards gradation which will tend to over emphasise the finest clay fraction (Gibbs, 1965). It is realised that successive clay fractions are needed to separate and identify small contributions made by, for example, smectites, if they are of a minor quantity. However, whole rock samples were used, and backed-up with a selected number of $<2\mu\text{m}$ fractions, as the overall mineralogy was being investigated.

For semi-quantitative analysis, all samples were finely ground and further crushed in an agate mortar with distilled water before being sedimented on to a 2.5 by 3.2cm glass slide. Half of the slide was covered and the sample allowed to evaporate dry. It must be realised that any preparation procedure will affect the mineralogy, grinding more than most (Brindley and Brown, 1980). All samples were treated to a similar procedure and grinding reduced to a minimum period. Stokke and Carson (1973) found that clay thickness affected the peak areas produced and concluded that layers between 3.9 and 7.7 μm thick produced results comparable with other methods. Similar preparation procedures have been used for clay mineral analysis by Spears and Taylor (1972),

Fellows (1979, Ph.D.) and Holmes (1980, Ph.D.).

Selected samples were analysed using a similar procedure but on the $<2\mu\text{m}$ fraction to differentiate possible clay segregation effects. Separation of the $<2\mu\text{m}$ fraction was conducted on whole rock samples that were disaggregated in distilled water in an end-over-end shaker. The samples were re-suspended in an antiflocculant, calgon, then centrifuged at 1000 r.p.m. for 3 minutes 46 seconds at 22°C . Material coarser than $2\mu\text{m}$ was removed from the suspension and the finer fraction decanted off. This was settled using high speed centrifuging, the calgon poured off, and the samples re-suspended in distilled water and prepared on glass slides for identification. A comparison of the results using the two methods is given in Table 6.5.

For crystallinity studies and identification of structural ordering, randomly orientated powder mounts of the whole rock samples were used.

The samples were analysed using a Phillips diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation at 36 kV and 26 mA. A scanning rate of $1^{\circ}2\theta$ per minute from 4° to $44^{\circ}2\theta$ was used for primary investigation. This range is suitable for both clay and non-clay mineral identification. Semi-quantitative clay analyses using various pre-treatments was made on successive scans of the 4° to $14^{\circ}2\theta$ range as all the 001 clay peaks are covered. The count rate was adjusted to give large scale deflection for each sample, usually 1000 or 2000 counts per second (c.p.s.). For a given sample run with the various pre-treatments, a similar count rate was used to enable direct comparisons to be made.

The peak positions for all minerals, including clays, was made at the mid-point of the two-thirds peak height above background, in degrees 2θ . This could be converted to the corresponding d-spacings (Chao, 1969; Brindley and Brown, 1980). The 2θ angle was used to identify the mineral phases present using the ' $2\theta(\text{Cu})$ Table for Common Minerals' (Chao, 1969).

Where present, quartz was used as an internal standard for peak position measurements. The major quartz peak position is at $26.66^{\circ}2\theta$ and the diffractometer is set up using quartz because of its constancy of chemistry and structure and hence minimal peak shift (Brown, in Brindley and Brown, 1980).

The x-ray identification of clay minerals is covered in great detail by Brindley and Brown (1980), together with the pre-treatment procedures.

Pre-treatment Procedures

The following procedures were used to identify and attempt to quantify the clay minerals present:-

- a) Air dried.
- b) Ethylene glycol treatment in a desiccator at 60°C for one hour.
(after Brunton, 1955).
- c) Heating to 300°C for one hour.
- d) Heating to 550°C for one hour.
- e) Acid dissolution (Vivaldi and Gullego, 1961).

All samples were subjected to a), b) and d) using the same sample and diffractometer conditions. Selected samples were also run using c).

Acid dissolution was used on those samples in which chlorite was identified using a) and d) and cation saturation on two samples showing a high proportion of mixed-layer clay. Where any pre-treatment involved heating, diffraction was carried out as soon as practical to reduce rehydration. Its total prevention is unlikely especially where there is a high proportion of expandable mixed-layer clays and high temperatures are being used (Brindley and Brown, op. cit.). All samples used for quantification studies were analysed without cation saturation, 'as received'.

Peak Area Estimation

For each sample run under varying conditions a common background line, traced using french curves to the best fit, was used. The peak form was 'rationalised' or smoothed to give the best outline fit to the diffractogram pattern. The following clay minerals, in varying proportions, were identified:- chlorite, illite and mixed-layer clay (M.L.C.) and kaolinite. The peaks were traced on high quality draughting film, cut out and weighed.

Glycolation

All samples were 'glycolated' to separate any discrete 'mica' (illite) clay from the mixed-layer clay fraction. The mixed-layer clay is identified in the air-dried sample as a markedly asymmetric 10\AA peak which curves gradually towards the higher d-spacing (and lower 2θ angle). The 10\AA illite peak was seen to form an integral part of the structure. In the air dried sample, the whole illite plus mixed-layer clay peak is traced and weighed (Spears and Taylor, 1972).

Certain clay minerals, notably the smectites, have a high interlayer exchange capacity. This has long been appreciated and such clays as the fullers earth have been extensively used for bleaching purposes. These interlayer cations are held ionically and are easily removed or exchanged for others if the chemical environment changes. Polar organic liquids such as ethylene glycol are exchanged for the interlayer cations to give a two layer absorption which give an (001) spacing of 16.85\AA (Hoffman and Brindley, 1961). Such a process will expand the clay to produce a defined peak. After glycolation, a smectite peak position will depend upon the interlayer cation, and where several are present, without a dominance of one species, the peak will be diffuse and difficult to identify, hence the use of cation saturation. If no discrete expandable clays are present,

no discrete smectite peak will be formed with glycolation and the shoulder of the 10\AA clay will 'disappear' leaving a sharper, more symmetrical illite peak. This is the pattern found in the present samples and suggests that the shoulder is not a randomly interlayered mixture of illite and smectite but rather a 'degraded illite', where weathering of the illite flakes has opened up the structure, leaching out potassium and replacing it with other hydrated cations and/or varying amounts of water (Hower and Mowatt, 1966; Jaron, 1967; Paquet, 1969; Sawney, 1972). Examples are given in Figure 6.11.

The illite peak area is traced after glycolation and subtracted from the combined illite and mixed-layer clay peak area to give the relative components of the respective clays. It must be realised that discrete expanding clays may be present but their contribution is less than 10% and thus cannot be identified using the present methods on whole rock samples. Such clays, if present, must, however, be relatively unimportant from a quantitative aspect and would need further separation, for example, a $<0.5\mu\text{m}$ fraction to give positive identification.

Heat Treatment

The reaction of clays to heat varies both within and between types and may be further used to differentiate the clays present.

Heating to 300°C will contract smectite and mixed-layer clays to 10\AA to produce an enhanced 'illite' peak, the area of which should correspond to that of the air dried illite plus mixed-layer clay peak. Both methods are acceptable for the estimation of illite plus mixed-layer clay but the air dried method was used in the present study because of its simplicity and time saving of a further preparation stage. Selected samples were treated at 300°C and compared to the air dried values, given in Table 6.6.

Heat treatment at 550°C will destroy kaolinite structure. This is

necessary to identify chlorite if its presence is suspected. The chlorite (001) peak is to be found in the vicinity of $6.2^{\circ}2\theta$ but this varies with chemical composition. In the present samples, however, the chlorite contribution is small and the (001) peak is often difficult to identify against the low angle background scatter. If the chlorite is present, its (002) peak will fall at about $12.4^{\circ}2\theta$ and this corresponds closely to that of kaolinite, thus increasing the intensity of the 7\AA peak. The relative contributions of chlorite and kaolinite must be identified to establish the relative proportion of kaolinite present. Spears and Taylor (1972) apportioned equal area to the (001) and (002) peaks and subtracted this from the 7\AA peak area. The relative sizes of the (001) and (002) chlorite peaks, however, vary with chemical composition. If the chlorite is iron rich, then the (002) peak may be four times the area of the (001) and hence make a considerable contribution to the 7\AA peak area (Velde and Hower, 1963; Collins, 1976). Heat treatment further changes the relative sizes of the chlorite peaks (Molloy and Kerr, 1961) causing the (001) peak of an iron-rich chlorite to grow and the (002) peak to shrink (Brindley and Robinson, 1951). If, however, the chlorite is diagenetic, it too may be destroyed at temperatures far below 550°C (Powers, 1957).

Acid Treatment

If chlorite has been positively identified from basal peak observation, heat treatment, or separation from kaolinite to give a doublet peak at high 2θ angles, it may be removed by acid treatment. The method of Vivaldi and Gullego (1961) was attempted to remove chlorite. The results, however, were not satisfactory with considerable within sample variation. It is not clear if this was due to side effects caused by the acid dissolution or sample variation and machine response, where the chlorite was not a major contributor to the clay fraction, and thus subjected to relatively

greater variation between samples. It was decided, therefore, to calculate the contribution of chlorite to the 7\AA peak area following the method of Collins (1976). This is dealt with in the Chlorite section of this chapter.

Crystallinity and Ordering of Kaolinite

Many of the kaolinite samples associated with the mudrocks of the present study are what may be termed 'disordered kaolinite' (Brindley and Brown, 1980). Such a kaolinite was once used commercially as refractory clays and termed 'fireclay'. Schultz (1960) showed that kaolinite crystallinity varies and the intensity of the XRD peak increases with the degree of crystallinity. Thus the range of peak area ratios for poorly crystallised kaolinite (fireclay type) to illite, montmorillonite, or mixed-layer illite-montmorillonite in equal amounts is 1:1, compared to 2:1 for well crystallised kaolinite (Schultz, 1964), as found in the cleat.

Using the method of Schultz (1960) the kaolinite crystallinity was calculated and the 7\AA peak area remaining, after subtraction of the (002) chlorite contribution, was adjusted accordingly.

Clay Proportions

The basal peak areas of chlorite (001), illite, mixed-layer clay (had this been identified and measured before and after glycolation), together with the (002) chlorite peak, were calculated and subtracted from the 7\AA (combined kaolinite plus chlorite) peak, then the remaining kaolinite peak was adjusted for crystallinity. The relative peak weights for each sample were thus summed and re-expressed as a relative percentage of the clays present and given in Figure 6.12.

The percentage clay minerals in the whole rock was calculated based on these relative proportions and on the normative XRF calculations

(Nicholls, 1962). The percentage clay fraction was based on Nicholls (op. cit.) re-calculation scheme but instead of applying this method to the clay minerals, the XRD clay proportions were substituted and re-expressed as a percentage of the whole rock mineralogy. It will be noted that two assumptions have been made. Firstly, that the feldspar content is negligible and therefore does not have to be subtracted from the 'clay percentage' of the normative recalculation, and secondly that the 10\AA peak has been ascribed illite, rather than a mixture of illite and muscovite. 'Mica' is perhaps a better description of the 10\AA peak. It has been shown that feldspar, although identified by XRD, is negligible using the method of Fellows and Spears (1978), certainly less than 1%, and has thus been ignored in the normative re-calculation. The presence of muscovite is suggested in the sharp 10\AA peak traces. Muscovite would, however, be concentrated in the coarse fraction and illite in the clay fraction. A comparison of the two methods (Table 6.5) shows that although the $<2\mu\text{m}$ fraction does have a smaller percentage 10\AA mineral, there is in fact, not a great deal of difference. Thus the 10\AA peak has been treated as 'illite'. Peak shape is not notably different if the illite is well crystallised.

Clay Minerals in the Coal

A direct comparison of the percentage clays in the coal mineral matter (L.T.A.) and the mudrocks was not possible, as the clay percentage could not be calculated on the limited coal ash sample available. Further drawbacks arise with the varying crystallinity of kaolinite present in the coal samples and the absence of an internal standard against which the clay peaks, when present, could be measured. Semi-quantitative analysis of the clays present in the coal mineral matter was, therefore, not attempted.

The clay mineralogy of the coal samples is very simple. Where the clays are detrital, in the high ash coals found close to the floors, dirt

bands and roof, the ash mineralogy is very similar to that of the mudrocks but reduced considerably in absolute terms. In the true coals where the detrital input is small, diagenetic kaolinite is the dominant clay. Its character is obviously different to the detrital kaolinite as can be seen from the XRD diffractogram peak shape as a function of its crystallinity, also seen in the S.E.M. and T.E.M. studies of its form (Cleat Mineral Section).

Clay Mineral Distribution in the Mudrocks

It is apparent from Figure 6.12 that the pattern of relative clay proportions is complex. Because of the large number of mudrock samples, the Yard Seam provides the most significant profile showing clear differences between the floor, intraseam dirt bands and associated dirty coal, and the roof measures. Similar variations are to be found in the other seams, but only in the roof of the Shallow Seam are there sufficient samples to show significant trends.

The total clay percentage shows marked variation. Except where the organic matter content is high, as in parts of the Yard Seam, there is an inverse relationship between total clay and quartz content. The percentage 'clay fraction' is shown in Figure 6.13 and the relative clay percentages in the whole rock are given in the whole rock XRF recalculation Table 6.3.

Clay Mineral Variation

Chlorite

The contribution of chlorite to the total clay fraction is generally small. This is to be expected from studies of similar Coal Measures rocks (Spears and Taylor, 1972; Fellows, 1979, Ph.D. Thesis) that have not undergone high grade diagenesis (Dunoyer de Segonzac, 1970). In all

samples but Y2, the chlorite contribution follows a trend which can be related to depositional energy. The approaching still-stand conditions associated with coal vegetation development sees a decline in the chlorite content in both relative and absolute terms. Thus the chlorite content of the intraseam dirt bands is negligible or non-existent. It is not clear, therefore, why the dirty coal Y2 should have chlorite despite lower quartz and higher organic matter contents than the adjacent Ydb1 and Ydb2. There is no evidence to suggest that the chlorite is diagenetic and it may be a function of reworking of the sediment. The floor of the Shallow Seam has no chlorite despite being a high energy deposit. It is possible that it has not survived weathering and deposition in an environment not compatible with its preservation (Wilson, 1965a) but this does not explain its presence in the Yard Seam. The Eight Feet Seam dirt band 8SlOc shows a reduction in chlorite when compared to the remainder of the seam. Chlorite content invariably increases in the roof samples away from the seam. Such a trend is to be found in both the Yard and Shallow Seams. Insufficient roof samples prevent similar observations being made in the Littleton Colliery seams but in both, chlorite is highest in the roof.

Illite

The intraseam dirt bands exhibit the lowest illite values as a fraction of the clay content. In the roof of both the Yard and Shallow Seams, illite increases away from the seam. The floor values are intermediate between that of the dirt bands and roof measures. In the Shallow Seam, which has no dirt band, the illite proportion in the floor is higher than in the lower two roof samples. In all the seams the highest illite content is to be found in a roof, and the lowest in the dirt bands.

In the Lea Hall Colliery samples, the illite percentage is lower than that of kaolinite, except in the Yard Roof. At Littleton, illite exceeds

kaolinite in both the Eight Feet and Park Seams.

Mixed-layer Clay

This is taken as the difference between the air dried and glycolated diffractogram traces and at this stage no attempt is being made to predict its form or origin. In the Shallow Seam, the highest relative mixed-layer clay value is to be found in the floor. Those of the roof are lower but fairly constant. In the Yard Seam, the fraction increases towards the base of the coal and falls, from a maximum in YR1, away from the coal seam. The mixed-layer clay associated with the intraseam dirt bands are intermediate between those in the roof and floor, the highest to be found in the dirty coal Y2. The more organic rich of the dirt band samples, Ydb2, has a higher mixed-layer clay content. The Park Seam has the highest mixed layer clay content in the intraseam dirt band, intermediate in the floor and lowest in the roof. An inverse relationship with illite is to be found in the Park Seam. A gradual decline from floor through dirt band to roof is exhibited by the Eight Feet Seam.

A similar origin of illite and mixed-layer clay, suggesting that the latter is a degraded illite and concentrated in the finer size fraction, can be seen in the profile (Figure 6.13) of the illite to illite plus mixed-layer clay ratio (Gluskoter, 1967). This pattern is clearly detrital. The ratio generally shows an increase in illite away from the coal seams and values are highest in the roof measures. Floors are roughly similar in ratio and the dirt bands have the lowest illite component. This is the best seen in the Yard Seam where the dirt bands have the lowest ratio in Y2. Such a pattern can be explained entirely on the rate of deposition and hence a segregation of the coarser illite from the more degraded, finer mixed-layer clays which are predominantly associated with tranquil deposition.

Kaolinite

The kaolinite distribution is quite complex. In general it follows the trend of total clay indicating that it is detrital. As a percentage of the clay present, however, its contribution is variable. Both the Yard and Shallow seams have kaolinite rich floor samples and if expressed as a percentage of the clay content, the two floors are extremely similar ranging from 45.5% (YF1) to 42.6% (YF2) compared to 44.9% (SSF1). The floor samples from the Park (23.1%) and Eight Feet Seams (21.7%) are similar but markedly lower than those of the geographically distinct and stratigraphically older Lea Hall Colliery seams. There is evidence to support the findings of Wilson (1965a) who suggested that the kaolinite content of seat earths decreased through the Coal Measures in response to a changing climate. This theme is explored in more detail later in this chapter. The Shallow Seam roof clearly demonstrates a relative decline in the kaolinite content away from the seam, whilst the Yard roof is constant. The Park Seam is fairly constant from floor, dirt band to roof, with perhaps, a slight peak in the dirt band. The kaolinite content of the Eight Feet roof is complicated by the siderite band in 8R2 which is diluting the detrital component. 8R1 is, however, lower than the floor and dirt band. The intraseam dirt bands of the Yard and Eight Feet Seam exhibit the highest kaolinite contents for those seams. A diagenetic kaolinite origin in the organic matter must be rejected on the grounds of kaolinite crystallinity (Schultz, 1960) which indicates a lower, not higher index for these samples. The suggestion is that, like mixed-layer clay, kaolinite is predominantly associated with the finer clay fraction (Ashby and Pearson, 1978). It may reflect a re-working of the floor material.

Chlorite Composition

A knowledge of the chemical composition of chlorite is not only important from the mineralogical and geochemical aspect, but also to predict the contribution the (002) peak makes to that of the combined kaolinite, chlorite peak found at 7\AA . The presence of chlorite was identified by the following mean basal spacings:- (001) 14.096\AA , (002) 7.059\AA , (003) 4.715\AA , (004) 3.527\AA . The (002) peak is sometimes identified as a shoulder or doublet on the high angle side (smaller d-spacing) of the kaolinite peak. For a given chlorite composition the intensity of the chlorite peak would depend upon the relative proportions of chlorite and kaolinite. The various methods evolved to study chlorite composition from XRD traces are reviewed in Collins (1976). He states that acid dissolution is the most accurate because it is most direct, but the precision is lost when the chlorite contribution to the 7\AA peak is less than 30%, as is often the case in the present samples. The method of Schoen (1962) was used which compares the structure factor ratios of the first four basal reflections with theoretical values for various compositions. Collins (1976) modified the scheme so that the (002) peak measurement is not needed in the calculation. With three reflections known, the fourth (002) can be calculated. Once the average (001) to (002) ratio is known the (002) peak area can be calculated and subtracted from the 7\AA peak area to leave the kaolinite proportion. A knowledge of the relative peak areas also allows semi-quantitative assessment of the chlorite composition to be made. Unfortunately, as the chlorite peaks are so small in many of the present samples little faith is placed on the results but the average chemical composition may be surmised. The following calculations are to be found on Table 6.7. The ratio of I002 to I001 was thus calculated and an average of 3.95 attained. This compares favourably with 4 of Sudo et al. (1961) and 3.96 of Collins

(1976) for similar rocks. Using the measured (001) peak area, the (002) contribution to the 7\AA peak was calculated and subtracted to give kaolinite peak area.

Using the table given in Schoen (1962) the structure factors for F002 and F004 the number of Fe ions per unit cell were deduced and averaged out at 9Fe per 12 octahedral sites. This gives an average formula of $(\text{Mg}_{3-x}\text{Fe}_9\text{Al}_x)(\text{Si}_{8-x}\text{Al}_x)\text{O}_{20}(\text{OH})_{16}$. The basal spacing of the chlorite 14\AA peak was used to calculate the number of Al-for-Si replacements following the equations:-

$$d(001) = 14.648\text{\AA} - 0.378x \text{ (Kepezhinskis, 1965)}$$

and

$$d(001) = 14.55\text{\AA} - 0.29x \text{ (Brindley, 1961),}$$

considered by Bailey (1972, 1975) as the best estimates of tetrahedral aluminium. The average of the two methods gives 1.5 thus an average formula of $(\text{Mg}_{1.5}\text{Fe}_9\text{Al}_{1.5})(\text{Si}_{6.5}\text{Al}_{1.5})\text{O}_{20}(\text{OH})_{16}$ was calculated. The preciseness of this calculation is in doubt but it does show that the chlorite is iron rich. This is supported by acid dissolution evidence. Mg^{2+} chlorites undergo little decomposition (Shaw, 1973). The relative peak size of small (001) and (003), compared to large (calculated) (002) and (004) are also typical of a highly ferruginous chlorite (Brindley and Gillery, 1956; Brown, 1961). This seems to be typical of Coal Measures chlorites (Collins, 1976; Ashby and Pearson, 1978) although Fellows (1979, Ph.D. Thesis) calculated that the chlorites associated with the Barnsley and Top Hard Seams were Mg^{2+} rich. In an attempt to simplify chlorite nomenclature, Bayliss (1975) suggested that such iron rich chlorites be termed 'chamosite'.

A comparison of the $<2\mu\text{m}$ with the whole rock fraction shows that the percentage chlorite is reduced in 4 out of 7 samples. This does not provide unequivocal evidence to suggest a concentration of chlorite in either fraction.

On glycolation, no peak shift or alteration is found which seems to rule out mixed-layer chlorite/smectite or vermiculite phases. Its stability to heating suggests that the chlorite is detrital rather than diagenetic as the latter is often altered or decomposed at temperatures below 450-500°C (Brindley and Brown, 1980), sometimes considerably so (Powers, 1957).

Illite

Illite is a 2:1 layer silicate held together by large univalent cations, usually potassium. Potassium fits between the clay layers by charge deficiency in the tetrahedral sheets. Thus it is held very strongly and is only partly replaceable by other cations. In the ideal formula, illite is non-expanding and resembles muscovite, sericite mica and glauconite (Greensmith, 1978). Illite is a transitional stage to muscovite but has less potassium (Krauskopf, 1979) and more SiO_2 and H_2O . The chemistry is variable with the percentage mixed-layer clay (Weaver and Pollard, 1973). It is extremely uncommon for illite to be the pure end member. Substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and monovalent cations for divalent or trivalent cations in the octahedral sheet leave vacancies in the octahedral sheet. The size of the potassium interlayer cation is slightly too large for the site available because of tetrahedral rotation, hence the basal spacing is 10\AA , slightly larger than the basal layer thickness 9.3 to 9.5\AA . The presence of smaller cations associated with mixed layering leads to a peak shift (Brindley and Brown, 1980). Without chemical analysis it is difficult to calculate the precise composition of illite. XRD is by far the most widely used tool for clay mineral identification owing to its ease of operation and speed. However, the identification of less than 10% smectite is not obvious using this technique (Hower and Mowatt, 1966). Illite, is therefore, used as a group name as originally suggested by Grim, Bray and Bradley (1937) and this broad description was re-stated by Bradley and Grim (1961).

In addition to mixed-layer clays being present, the precise peak position may also depend upon the size of the illite crystallites, and very fine particles may shift up to 1\AA at the 10\AA d-spacing (Brindley and Brown, op. cit.).

Illite Polytypes

Illite crystallises in two major polymorphic groups, the 1M and 2M types. If the 2M polymorph is present, it indicates high temperatures and pressures and will eventually grade into muscovite mica. In the present samples muscovite may be present and is evident in some thin sections. As the $<2\mu\text{m}$ fraction was taken on limited samples it is difficult to assess the contribution of muscovite to that described as 'illite'. As there is not a great deal of difference in the data provided it has been grouped as 'illite'. The XRD traces suggest that illite plus mixed-layer clay is concentrated in the $<2\mu\text{m}$ which dictates against much muscovite. The diffractogram traces indicate a 10\AA peak that is reasonably broad and asymmetric towards the higher d-spacing. This is typical of illite with a 'mixed-layer' component. After glycolation, the mixed-layer component is expanded leaving a much more symmetrical trace but not the sharp, narrow peak of muscovite. This holds for both the whole rock samples and for the selected $<2\mu\text{m}$ fraction. Thus it is concluded that the muscovite contribution is negligible and the illite is the dominant mica polytype.

1M illites are the lower temperature polytype, whilst the 2M illite indicates temperatures in excess of 200°C , high pressure (4.5kb) and are stable down to 125°C (Kisch, 1974). The most common detrital illite polytype, if unaffected by high grade diagenesis, is the 1Md type. This is a disordered form of the 1M or 2M illite and is typical of the low temperature weathering environment (Velde and Hower, 1963). In the

Palaeozoic sediments only 1Md and 2M illites are found in appreciable quantity. In more recent environments it has been shown that the proportions of the polytypes can be used to indicate the level of diagenesis. In late diagenesis, 2M exceeds the sum of 1M plus 1Md polytypes (Foscolos and Kodama, 1974) and can be used to indicate the level of diagenesis. The percentage 2M illite increases with depth. Strong hk reflections in the 4.47\AA and 2.56\AA range with other non-basal peaks weak or absent, indicate 1Md polytype (Brindley and Brown, 1980). With KCl saturation and glycolation used in the determination of the sharpness ratio (Weaver, 1961) and crystallinity index (Kubler, 1966) the disordered illites recover their previous 2M structure, if this was once present (Weaver, 1958), providing that weathering was insufficiently severe to destroy the lattice charge and structure.

Crystallinity Index and Sharpness Ratio

It has been demonstrated that with increasing diagenesis, the percentage mixed-layer clay decreases and the proportion of 2M illite increases (Dunoyer de Segonzac, 1970; Foscolos and Kodama, op. cit.). This crystallinity is more sensitive to metamorphic recrystallisation. before petrographic analysis will identify any change (Weaver, 1960, 1961). The Sharpness Ratio (S.R.) of Weaver (1961) and Crystallinity Index (C.I.) of Kubler (1966) are calculated on $<2\mu\text{m}$ fraction, K^+ saturated. The samples were also glycolated but this made little difference in those samples studied, thus indicating that the mixed-layer component was relatively small. The S.R. is a ratio of the (001) peak height above the base line at 10\AA to that of 10.5\AA . The C.I. is a measure of the (001) peak width at half height expressed in m.m. The former exhibits an increase in the ratio with increasing diagenesis, the latter a decreasing peak width. Figure 6.14 shows that, with one

exception, the profiles are inversely related. Similar profiles are achieved by using the reciprocal of the S.R. (Jackson, 1977) and are correlated strongly; ($r = +0.97$; 99.9% significance). There is a spread of S.R. values of 2.00 to 3.33 and for the C.I. between 8 and 13mm. This indicates an origin from within the zone of late diagenesis, the boundary with middle diagenesis being placed by Foscolos and Kodama (1974) at a S.R. of 2.0 or greater and a C.I. of less than or equal to 15mm, and the boundary between diagenesis and the anchizone being <7.75 mm (Kubler, 1968). The late diagenetic zone is also characterised by an absence of kaolinite, clearly not the case in the present sediments. The kaolinite in the mudrocks is not diagenetic and it must be concluded that the illite detrital and its diagenetic grade is a reflection of a previous diagenetic cycle subsequently re-worked and deposited during the Coal Measures.

It is clear from the C.I. and S.R. that no vertical trend in diagenesis can be traced through the samples studied. Evidently local variations in source and supply, the rate of weathering and deposition by far outweigh subsequent diagenetic alteration. As the samples are taken from similar depths (allowing for the greater subsidence at Littleton Colliery) there is, however, little range for distinct diagenetic characteristics to be recognised. It appears that the degree of diagenesis imposed subsequent to Coal Measures deposition was insufficient to remove the evidence of a former burial cycle and thus the illite retained the 'memory' of that previous cycle. Weaver (1958) showed that 2M illite would weather to a 1Md polymorph, as in the present study, and would return to its former structure with K-saturation.

It has been indicated that the shape of the 001 illite peak is a sensitive indicator of relative incipient metamorphism, provided that the Mg/Al ratio of illite is not too high (Esquiven, 1969). The chemical

composition affects the crystallographic properties of illites. A high Al to Fe + Mg ratio in the octahedral layer is indicative of recrystallisation of the illite. With increasing rank, the crystallinity rises and the illite becomes more aluminous. Only where the 002 to 001 peak intensity is greater than 0.3, and the illites can be classified as aluminous (Esquiven, op. cit.) can the ratio be used as an indicator of metamorphic grade. The present ratios are shown in Figure 6.15 and vary between 0.35 and 0.62, and are thus all 'aluminous'. The profiles are conflicting, however, as the most aluminous are often associated with dirt bands where the clays are most degraded. This is not always the case as can be seen by the high ratio in 8R2. There is some evidence from the Park Seam and much of the Yard Seam that the ratio varies directly with the rate of deposition as given by the TiO_2 profile. Again exceptions occur in SSR2, YR2 and 8R2 where the profiles are reversed. These samples do have carbonates present and it is possible that Mg and Fe have been removed from the system during early diagenesis leading to a relative increase in Al. There is no relationship between the ratio and the crystallinity index where the latter was investigated. Al-Jalili (1982, PhD) found that the Al:Fe + Mg ratio increase with crystallinity. The present samples do not exhibit the same range of rank and it has been shown by the S.R. and C.I. that a previous cycle of metamorphism has an overriding effect upon that subsequent to Coal Measures deposition. Thus, it is not entirely unreasonable to find no constant relationship between Al and rank.

Mixed-layer Clays

After glycolation, no discrete peak is to be found in the region 5.3 to $8.7^{\circ}2\theta$ and it is thus concluded that no discrete smectite (Srodon, 1980) nor vermiculite is present. The untreated air-dried 10\AA peak is,

however, decidedly asymmetric, far more than would be produced by angle factors alone. This has been termed a mixed-layer clay (M.L.C.). Its composition and genesis are, however, somewhat more difficult to explain. The most common mixed-layer mineral to be associated with illite is smectite. If there is less than 5% smectite present, this will not be detected by XRD (Brindley and Brown, 1980). Lack of discrete, predictable reflections using the Bragg Law, shows that the mixed-layering is random (Brindley and Brown, op. cit.).

Mixed-layer clays can be formed along two major pathways. They may begin as smectites (or vermiculites), which become degraded either in the weathering environment or with diagenesis. Intense weathering will by leaching remove interlayer cations and lead to the formation of illite via a mixed-layer illite-smectite phase, followed by kaolinite and eventually gibbsite. Burial diagenesis reduces smectite content. It decreases with age (Burst, 1969), with increasing temperature, pressure and time (Maxwell and Hower, 1967) and ground water composition as seen by the exchangeable cations (Caswell, Holmes and Spears, part 2). With depth (4500' in the Gulf of Mexico) no discrete expandable clays are found (Foscolos and Kodama, 1974) and the illite mixed-layer phase becomes prominent, decreasing until only illite remains below 15000' (Burst, 1969). Running parallel to the loss of mixed-layer minerals is a progressive ordering of illite (Hower, 1967). A summary of diagenetic processes, minerals and transformations is to be found in Dunoyer de Segonzac (1970).

The alternative, a weathering approach, sees the opening up of illite layers (Jaron, 1967; Paquet, 1969). With the loss of interlayer potassium, the edges fray and open up looking on an XRD diffractogram trace like a small amount of smectite interstratification. The more K^+ removed, the greater the apparent interlayer spacing. This may allow

large hydrated cations such as Ca^{2+} to enter and hold the edges apart (Sawney, 1972). Alternatively, K^+ deficiency may be made up by water and hydronium molecules (Brown and Norrish, 1952; Hower and Mowatt, 1966). If the weathering is so intense as to leach out all the interlayer cations and destroy the octahedral layer charge, then there is no chance of reconstruction. If, however, the 'memory' is retained, then a K^+ source from oceans, ground water or pre-treatment will reconstitute the degraded illite to its original form due to the great selectivity for K^+ . This was seen when the C.I. and S.R. were calculated indicating that the mixed-layer material was of this type, a degraded illite (Weaver, 1958).

Its distribution shows concentration in the fine fraction which would be expected if greater degradation results from a longer weathering residence time. Similarly the K^+ to Na^+ ratio falls with increasing MLC which suggests leaching of the interlayer K^+ and replacement by Na^+ within the weathering environment or from the Na^+ rich ground waters. As the Na^+ level is generally constant K^+ leached may well be replaced by water.

The C.I. and S.R. indicate that the illite has been subjected to late diagenesis and this in a cycle before Coal Measures deposition. The boundary between middle and late diagenesis falls at 80% illite in the mixed-layers (Foscolos and Kodama, 1974). It is clear that the percentage clay expanded with glycolation, that is, the non-illite fraction, does apparently reach this level and, therefore, must represent disordered and degraded clay. The degradation must have taken place in the Coal Measures environment subsequent to the cycle that imposed the maximum diagenesis.

With increasing mixed-layer material, the 10\AA peak will shift towards a higher d-spacing (Brindley and Brown, 1980). Méring (1949) suggested the peak maximum was governed by the relative intensities of the end members. Foscolos and Stott (1975) showed that with decreasing

M.L.C., the closer the illite peak to 9.98\AA . The illite peak positions were measured (at two-thirds peak height) using quartz where present as an internal standard. Glycolated and air dried positions are given in Table 6.8 and show little peak shift. Rarely do the glycolated peaks allow 10% M.L.C. (Brindley and Brown, op. cit. page 290). As the difference between air dried illite plus M.L.C. and glycolated peak areas show apparently far more M.L.C., this is attributed not to interstratification with other clays but edge 'fraying' of the illite. The 'M.L.C.' tail towards a higher d-spacing shows continuous rate of change in slope in the majority of samples. "... little can be maintained with certainty beyond the observation that illite is interstratified with small (<10%) amounts of smectite" (Brindley and Brown, page 277).

Kaolinite

Kaolinite is a 1:1 layer silicate with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is a dioctahedral clay with Al^{3+} occupying two out of every three octahedral sites. Although the chemical composition varies little, variations in order-disorder of the structure are considerable. The nature of disorder is summarised in Brindley and Brown (1980). The basal reflections at 7.2\AA and 3.6\AA , that is, the (001) and (002) reflections, are least affected by structural disorders which mainly take the form of displacement of Al^{3+} ions from their correct octahedral positions. This, incidentally, makes the (001) probably the most suitable peak area for quantitative measurements (Brindley and Brown, op. cit.).

The degree of order affects the basal peak shape, and hence its area. The basal peaks become less sharp and intense. In randomly orientated powder mounts the peaks in the 20 to $33^\circ 2\theta$ range (021, 111) become blurred and in the 35 to $40^\circ 2\theta$ range, well ordered kaolinites

exhibit two triplet peaks which become two doublets with increasing disorder. As the order declines, the diffractogram peak area declines for a given weight of kaolinite (Schultz, 1960).

Crystallinity

Comparisons of the crystallinity between the mudrocks, coal ash, and cleat minerals were made following the method of Schultz (1960) outlined at the beginning of this chapter. The seam profiles are represented diagrammatically in Figure 6.16. It is immediately evident that a considerable through seam variation in crystallinity exists. The general trend is that the mudrocks have far higher ratios and hence lower crystallinity than the low ash coal samples. The former are highly disordered. The cleat samples, in turn, have higher crystallinity than the coal ash. There are complications in that there is a variation within each of the former groups. The mudrocks show varying degrees of weathering and hence disordering whilst the coal ash is comprised mainly of well ordered diagenetic kaolinite which is diluted with a highly variable amount of disordered detrital kaolinite. Within the mudrocks, the degree of crystallinity varies with the energy of deposition as shown by quartz or TiO_2 . If the quartz content is high, kaolinite is 'moderately disordered' and where low or absent, as in I.D.2.11, the associated kaolinite is 'highly disordered' in the nomenclature of Douillet and Nicholls (1969). This suggests that the more tranquil conditions allow a greater weathering residence time, hence degradation, or that the finer fraction, as a result of prolonged weathering, is more degraded and hence separated into the fine fraction. The higher the degree of weathering, the greater the structural disorder through its destruction (Dunoyer de Segonzac, 1970).

Kaolinite is found to be concentrated in those rocks where the quartz content is low and thus associated predominantly with those finer grained sediments. A similar pattern was found by Ashby and Pearson

(1978). The relative clay percentage of kaolinite has an inverse relationship with the crystallinity and this is well documented by the Yard Seam. The dirt Ybd1 and dirty coal Y2 have the lowest crystallinity and the second and third highest relative proportions of kaolinite in the seam. The floor samples are slightly less disordered and those in the roof least disordered. The relative kaolinite percentage is lowest in the roof and intermediate in the floor. Thus the kaolinite is probably associated with the 'fine' clay fraction. Complications may arise if diagenetic kaolinite is precipitated. Of the floor samples only those of the Yard Seam may be classified as highly disordered 'fire-clay' type kaolinite (Schultz, 1960).

The negative association with quartz suggests that the kaolinite was degraded in the hinterland and segregated on a size basis by transportation into the coal swamp environment. The stability associated with coal swamp formation would also allow prolonged weathering although it is debatable that this alone would produce the crystallinity variations found.

The cleat has the least disordered kaolinite. It is entirely diagenetic and was carried to cleat or pores in solution. The Al^{3+} and Si^{4+} probably originated from solution of silicate minerals. They dissolve separately (Krauskopf, 1956) and may later precipitate in a suitable geochemical environment perhaps via a colloidal phase (Degens, 1965).

The L.T.A. of the coal is more complex. The relative proportions of kaolinite of detrital and diagenetic origin vary with the depositional energy and type of organic matter accumulation. Diagenetic kaolinite also varies with coal type. Where the depositional energy is low the detrital component is at a minimum then the ash is dominated by diagenetic minerals. Where the detrital fraction is high, the kaolinite will

resemble that of the associated mudrocks. The crystallinity will thus be averaged and be a function of the dominant component. Thus there is a similar relationship in the profiles of ash content and kaolinite crystallinity (Figure 6.16).

The Significance of Kaolinite in Diagenesis

The presence of disordered kaolinite associated with the mudrocks and some detrital components of coal mineral matter, together with the diagenetic cleat, can be used to indicate the degree and zone of diagenesis reached by the strata.

Kaolinite is sensitive to the geochemical environment, being stable or neoformed in an acid environment and hence being commonly associated with the floor of coal seams. If the environment becomes alkaline, kaolinite would be destroyed (Dunoyer de Segonzac, 1970). Carbonate follows kaolinite in the paragenetic cleat sequence indicating that those cleat now holding kaolinite were essentially closed to later ground waters which may have destroyed it. It was noticeable, however, that kaolinite and carbonate was not found occupying the same cleat in immediate juxtaposition. Hand specimen evidence showed that cleat containing kaolinite was monomineralic and may thus have been isolated from later groundwaters. Unfortunately it was difficult to prepare slides of cleat samples to study the kaolinite-carbonate relationship and so this assertion has not been conclusively investigated.

With burial diagenesis, kaolinite is destroyed and it is absent from ancient sediments. The depth of this destruction is variable and depends on the pH, ionic strength and temperature but is not a precise indicator of burial depth (Dunoyer de Segonzac, op. cit.). No kaolinite is to be found in the anchizone, the transitional zone of diagenesis to metamorphism, and in deep or late diagenesis, at temperatures in excess of 100°C, kaolinite is transformed irreversibly to dickite in an acid

environment (Dunoyer de Segonzac, op. cit.). This indicates that the burial diagenesis has not exceeded 'middle diagenesis'. Oxygen isotope work on cleat kaolinite from Illinois and Indiana give temperatures of formation in the range 24°C to 30°C and were formed at or near the surface (Shieh and Suter, 1979).

The Implications of the Kaolinite Content in the Floor Measures

It has already been emphasised that the proportion of kaolinite, out of the total clay content, in the floor measures at Lea Hall are approximately twice that associated with the Littleton seams studied. The close similarities between those seams geographically and stratigraphically associated may be a reflection of a changing depositional environment or be a change in the source material. If kaolinite content is related to depositional energy then the similar quartz and TiO_2 contents found in YF2 and 2F1 would be expected to have similar kaolinite levels. Similarly, the quartz and TiO_2 values in 8F1 are slightly in excess of 2F1 and would expect higher kaolinite. This is not found. If kaolinite is associated with primarily tranquil conditions then the expected trend would be for higher kaolinite content at Littleton based on both quartz or TiO_2 evidence. The marked fall in kaolinite, therefore, suggests a change in the source material with time.

An investigation of published and unpublished (Ph.D.) work was made to see if similar trends could be traced elsewhere within the Coal Measures. Wilson (1965a,b) working on South Wales underclays, concluded from qualitative XRD evidence that Lower and Middle Coal Measures rocks had more kaolinite whilst the Upper Coal Measures exhibited reduced kaolinite and increased illite and chlorite. This he attributed to a relatively drier climate in the Upper Coal Measures. He reasoned that the clay minerals were largely the product of their weathering environment and not due, except in minor amounts, to alteration within the

depositional environment. The approach of desert and semi-desert conditions associated with the Permo-Trias would see a decline in the level of precipitation. Kaolinite is the product of intense leaching (Dunoyer de Segonzac, 1970; Blatt, Middleton and Murray, 1972) and is typical of low latitude, tropical soils. Illite is typical of temperate conditions where precipitation and leaching is moderate (Blatt, Middleton and Murray, 1972; Brindley and Brown, 1980). A change in clay mineral emphasis from kaolinite to illite would be supported by changing environmental factors.

Ashby and Pearson (1978) working on the Alton Marine Band in Yorkshire found kaolinite contents of 70% immediately below the marine band. Unpublished Ph.D. work has been used to supplement the evidence for changing clay mineralogy through the Westphalian A and B. All percentages are expressed as a fraction of the clay component and not the whole rock, unless otherwise stated. Fellows (1979, Ph.D.) working on the Top Hard Seam (Thoresby Colliery) and Barnsley Seam (Yorkshire Main Colliery) found associated kaolinite contents of 18.3% and 23.9% respectively. As this is the same seam in the Nottinghamshire and Yorkshire coalfields respectively, it indicates that geographical location plays a not unexpected role in determining the amount of a clay deposited. Taking an average of 21.1%, this compares closely with stratigraphically similar Eight Feet Seam floor with 21.7%. A mineralogical and geochemical study of the mudrocks associated with selected South Wales coalfield seams by Al-Jalili (1982, Ph.D.) shows an overall increasing trend in kaolinite contents with time. As there is a marked increase in the kaolinite content eastwards across the eastern portion of the coalfield, the two major geographical sampling areas were treated separately. Although the two areas have markedly different kaolinite levels, similar trends are to be found in both areas.

Work carried out on strata associated with major marine bands (Ashby and Pearson, 1978; Sezgin, 1982, Ph.D. Thesis) do raise complications. Although the Pot Clay (Sezgin, op. cit.) and Alton Marine Band (Ashby and Pearson, op. cit.) both have very high kaolinite contents (66.4% and 70% respectively) which is to be expected if the model is to hold true, this is not the case with the Mansfield Marine Band (Sezgin, op. cit.). Here the kaolinite content is 64.8% and is far higher than predicted. This may be explained by variation in source material. There is, however, evidence within the marine bands themselves that major reworking of the sediments is taking place. This could be producing the very high kaolinite levels. It must be appreciated, therefore, that the environmental changes associated with the marine bands may produce different deposits to those associated with those coal seams where more stable conditions find marine bands few and far between.

A comparison of the percentage kaolinite in the clay fraction and relative stratigraphies of the samples is given in Table 6.9. It is evident that the kaolinite proportion of the clay fraction declines through the Westphalian A and B. Unfortunately no clay mineral figures are available for the Westphalian C. This decrease in kaolinite is at the expense of illite and mixed-layer clay in the Cannock area and is seen in the relative clay percentages (Figure 6.12). This fits the model proposed by Wilson (op.cit.) although no attempt was made at semi-quantitative clay analysis nor was any subdivision of the Coal Measures made.

Conclusions

- 1) The relative clay proportions were calculated using the (XRD) 001 peak area calculations with allowance being made for variations in the 7\AA peak by 002 chlorite and kaolinite crystallinity. The method is semi-quantitative.

- 2) A comparison of the whole rock and $<2\mu\text{m}$ fraction 10\AA peak shows little evidence of mica. The whole 10\AA peak was therefore attributed to illite.
- 3) The total clay proportion varies inversely with quartz content. It is specifically concentrated in fine fraction by slower sedimentation rates.
- 4) Four clay 'types' were identified; illite, M.L.C. (degraded illite), kaolinite and traces of chlorite.
- 5) The lowest illite values are found in the intraseam dirt bands, and highest in the roofs, increasing away from the Yard and Shallow Seams. In the floors, illite predominates in the Littleton samples but not in those from Lea Hall Colliery.
- 6) The illites are a disordered 1Md type, typical of a low temperature weathering environment. With K^+ saturation and glycolation their original 2M structure is reconstructed. The Crystallinity Index and Sharpness Ratio indicate reaching a grade of 'late diagenesis'. Though seam variations in crystallinity indicate that this grade of diagenesis was impressed before Coal Measures deposition where weathering and size separation are more important variables.
- 7) The M.L.C. is identified as a degraded illite produced by inter-layer leaching and edge fraying. It is highest in the intraseam dirt bands (e.g. Y2, Ydb2), lowest in the roofs and of a similar level in the floors. The distribution is explained by size separation, with the fine material concentrated in the dirt bands. Degradation of illite probably took place in the Coal Measures environment and subsequent diagenesis or ground water K^+ levels have been insufficient to remove this effect.
- 8) The highest kaolinite values are found in the intraseam dirt band concentrated in the finest fraction, though not necessarily

deposited at the slowest rates. Values fall away from the seam roofs. The floors are more complicated. The stratigraphically lower Lea Hall Shallow and Yard Seams have a kaolinite content twice that of the Littleton Park and Eight Feet Seams (c. 44% compared to 23%). The high values in dirt bands may reflect a similar environment to that of the floor measures or represent re-worked floor material.

- 9) Kaolinite crystallinity is lowest in the fine fractions and increases with sedimentation rate. Coal ash kaolinite crystallinity varies with the relative proportions of well crystallised diagenetic kaolinite and poorly crystallised detrital kaolinite.
- 10) The presence of kaolinite indicates that diagenesis has not exceeded middle diagenesis since being deposited in the Coal Measures.
- 11) Chlorite is a minor component which is generally higher in the Littleton Colliery seams and increases with sedimentation rate. It is an iron rich 'chamosite', typical of the British Coal Measures.
- 12) The changing clay proportions from kaolinite rich to illite and chlorite rich through the Coal Measures is explained by a change in climate through continental movement. Kaolinite is typical of intense tropical leaching associated with the Lower Coal Measures, illite and chlorite with a drier climate related to the approaching semi-arid to arid Permo-Triassic environment.

SECTION 3TRACE ELEMENTSSample Preparation

Analysis of trace elements was limited to those samples classed as 'mudrocks'. As there was insufficient ash available for the investigation of the true coal samples, the behaviour of trace elements in the coal is severely restricted to those dirty coals and organic rich mudrocks. However, such samples may not be representative of coal as those elements concentrated in the inherent ash will be over represented and those in the coal diluted. Elements associated with both fractions will vary in relation to their site and their relative abundance in those sites.

The trace elements analysed were Ba, Co, Cr, Cu, Mn, Ni, Pb, Rb, Sr, V, Y, Zn and Zr using the Phillips 2kV Spectrometer employed for major element analysis but now in the trace element mode. Powder pellets were used in a backing holder of boric acid. Compression of the powder to be analysed into the holder was made in a mechanical press subjecting the sample to a force of between 10 and 15 tons per square inch for 3 minutes. The element concentration was determined against a glass disc prepared by Dr. R. Kanaris-Sotiriou at Sheffield University. Allowance is made for variation in sample mass absorption using the coefficients calculated from the major element results. The calibration constants were based on an igneous rock standard but other workers at Sheffield have shown that when used for sedimentary rock analysis the variation is less than 5% and hence acceptable (Holmes, 1980, Ph.D.). The results are given in Table 6.10. Re-runs of samples SSF1 and SSRI show close agreement.

Past Study

Trace element analysis has been used as a palaeoenvironmental tool in the investigation of shales (Potter et al., 1963; Curtis, 1966; Spears, 1967; Curtis, 1969; Holmes, 1980, Ph.D.; Spears and Amin, 1981). In coal study, trace element study has been directed towards the possibility of mineral removal for industrial use and for pollution assessment (Brown and Swaine, 1964; Nicholls, 1968; O'Gorman and Walker, 1971; Stach et al., 1975; Gluskoter et al., 1977; Snyman, 1978).

Trace Elements in Early Sulphide Diagenetic Nodules, Cleat and Associated Strata

A limited study was conducted on an early diagenetic pyrite nodule from the Eight Feet Seam (8S10a). A comparison was made with a similar nodule from a brackish water sample from the Mansfield Marine Band and from the heavy separate from both brackish water and marine shales from the same section. The Mansfield samples were taken at Treeton Drift Mine, near Sheffield. Cleat samples, representing late diagenetic mineralisation were taken from the Yard (Y7) and Eight Feet seams (8S7).

The heavy mineral separate was removed by centrifuging tena ground sample in bromoform. All the samples were digested in 1M HNO₃, boiled to dryness then made to volume in dilute HNO₃. Trace element analysis was made using the furnace attachment to the Perkin-Elmer 406 Spectrophotometer by Mr. S. Reynolds (Department of Geology, Sheffield University). Co, Cu, Ni, Pb and Zn were analysed and the results given in Table 6.11.

Using the Co/Ni ratio, a value of less than unity indicated syngenetic sedimentary pyrite (Davidson, 1962). Although volcanogenic pyrite may produce a similar ratio (Loftus-Hills and Soloman, 1967), the form and distribution of nodular pyrite, which had comparable Co and Ni levels, is typical of a sedimentary environment.

Trace Element Comparisons

Table 6.12 can be used to compare present values with those found in South Wales Coal Measures mudrocks (Al-Jalili, 1982, Ph.D.), North Wales (Nicholls and Loring, 1962), Mansfield Marine Band (Curtis, 1969) and Ruhr coal samples (Stach et al., 1975), with average marine, freshwater and crustal abundance data. The Cannock values are comparable with those of South Wales and North Wales Coal Measures strata, suggesting a similar mineralogical hinterland and environment of deposition. Most notable is the difference in Mn if the siderite rich samples (8R2 and 8R1) are excluded. It is interesting to note that all traces but Ni, Mn, Zn, Cu and Sr exceed the average crust abundance figures although only Co, Rb and Pb are notably increased. It is evident that trace element distribution varies to such an extent that a palaeoenvironmental study is unwise except within comparable palaeogeographical environments and limited geographical extent. Over widely separated areas, mineralogical differences affect the trace element levels perhaps more than deposition environment.

Seam Profile Description - General

Trace element profiles are given in Figures 6.17, 6.18 and 6.19. Generalisations can be made of the distributions. There are considerable through seam variations and this is most notable in the concentration of Mn in the siderite rich samples 8R2 and 8R1. However, despite the variation, it is evident that intraseam dirt band levels are considerably different to their associated floor and roof measures. In general the organic rich samples are far lower in all elements analysed with the exception of Cu. The Yard Seam, with its greater variation in organic matter, is the best example. It is clear, therefore, that the majority of elements are associated with the mineralogical component.

In the Shallow and Yard Seams (YF1) all elements but Zr and Y are lower in the floor than in the remainder of the seam, with the exception of those samples with very high organic matter levels. These floor samples are very quartz rich and this is probably acting as a dilutant.

The siderite 8R2 also provides a contrast. Mn and Co are at their maximum and Ni and Pb are high but all other elements are reduced. Obviously the type of mineralogy present must affect the trace element distribution though its potential host capacity, however, many of the trace elements are lower than would be predicted by dilution alone. Sozanski and Cronan (1979) attribute low trace-metal contents partially to a rapid rate of formation.

Trace Element Associations

The correlation matrix for all trace and major elements is given in Table 6.4. From the matrix, the following relationships may be deduced.

Ba

Highly significant positive relationships are to be found between Ba and those elements associated with the clay fraction. A correlation with K_2O and not Na_2O suggests an illite host. Similar correlations have been found by Curtis (1969), Nicholls (1968) and Spears and Amin (1981). A correlation with MgO may indicate a chlorite association. However, the chlorites are iron rich and no significant iron correlation is found. An indirect relationship may exist, with MgO in degraded illites or mixed-layer clay and hence a Ba: clay relationship being indicated here. Highly significant correlations with Rb and Sr may also be indirect. Rb may substitute for K in illite and Sr shows a similar distribution. The size of Ba, Rb and Sr make them likely to substitute in a K site. Cr and Y are, however, of much smaller ionic radius and hence this correlation is thought to be indirect. A table of ionic radii is given (Table 6.13).

Co

The distribution of Co is markedly different to Ba. A negative correlation is found with the clay fraction, including Cr and V (suggesting a clay site for these elements) and with TiO_2 which is indicative of depositional energy (Spears, 1964). Positive correlations are to be found with carbonate and phosphate. The former is the probable location as the size of phosphorous is probably too small to allow Co entry. High values are to be found in 8R2 and 8R1 but the Co increase is not proportional to the carbonate present. Either Co was limited and hence fell with time and siderite growth, or there is an indirect relationship. SSR2 is also carbonate rich but Co is comparable to the associated samples. A limited supply of Co in early diagenetic ground waters is suggested. Similarity in ionic size between Co, Fe^{2+} and Mn further suggest a siderite host. As there is no correlation between MgO and Co a dolomite host is dictated against. Correlation with Ni indicates a sulphide host as a possibility.

Investigation of the sulphide separate shows very low Co levels in the sulphides and hence the siderite location is endorsed. The heavy separate fractions have slightly higher Co levels probably as a result of non-sulphide material still remaining. This is confirmed by the Yard Seam cleat. Sample Y2 has 8ppm Co, closely comparable with the Y7 cleat analysis. A higher Co value is found in the Eight Feet Seam cleat. Co levels are lower in the organic rich samples and sulphide material does not form all the non-organic matter in Y2. If the higher Eight Feet Seam sample is typical for the seam, then to achieve the value of 8R2 then sulphide cannot be the sole host. Early diagenetic sulphide values are far lower than those of the cleat suggesting limited Co availability during early diagenesis.

The literature finds Co to be located in many sources from organic (Gluskoter et al., 1977; Krauskopf, 1979), detrital with a clay association (Curtis, 1969; Spears and Amin, 1981), non-detrital (Spears, 1967) and diagenetic in sulphide (Nicholls, 1968) and calcite (Holmes, 1980, Ph.D.). The relationship in the present study is therefore complex, the majority in carbonates but a sulphide host cannot be ruled out.

Cr

A clay association is suggested by the correlation matrix with correlations of SiO_2 , Al_2O_3 , K_2O , Ba, Rb and Rb. Reduced but significant correlations are to be found with MgO, Sr, Y and TiO_2 . The latter further indicates a detrital origin. Negative correlations are to be found with organic matter and carbonate.

A detrital clay correlation has been found by Curtis (1969) who suggested substitution for Al, K or Sr, and Spears and Amin (1981). Organic and diagenetic sulphide locations have been suggested by Gluskoter et al. (1977) but are dictated against in the present work as significant contributors.

Cu

This is the only trace element to show a significant positive correlation with organic matter. A negative correlation with quartz indicates the incompatible environments of organic matter accumulation and that of active detrital sedimentation. Cu is thus highest in Y2 and the intraseam dirt samples. Average Cu values are comparable with those of the average shale (Turekian and Wedepohl, 1961) and slightly in excess of those levels from South Wales (Al-Jalili, 1982, Ph.D.). Only the marine shales give values vastly in excess of the present work.

The sulphide study shows the heavy separate to be in excess of the nodule from the same section again indicating dilution of a simply

sulphide rich separate. The Mansfield nodule indicates more Cu available later in the diagenetic nodule growth. That of 8S10a, however, shows a five-fold depletion out to the rim. Re-newed Cu availability is seen from the high levels found in the cleat. The value from the Eight Feet Seam is three times that of the Yard Seam. XRD investigations show no evidence of discrete chalcopyrite. With the exception of Ni (and Cd, which is negligible) the late diagenetic trace element availability at Littleton is in excess of that at Lea Hall. This has been noted in the cleat section and indicates a more diverse metal rich or more potent metal leaching ground waters to the north-west of the Cannock Coalfield in the vicinity of Littleton Colliery.

It is evident that the high Cu levels associated with Y2 may be attributable to cleat sulphide mineralisation. Such mineralisation would lead to an indirect association of Cu and organic matter. The literature indicates multiple Cu sources from organic (Krauskopf, 1979; Holmes, 1980, Ph.D.), organic and inorganic (Nicholls, 1968; Gluskoter et al., 1978), detrital (Krauskopf, 1979), clay and diagenetic (Spears, 1963) where the insolubility of Cu in the presence of S (Nicholls, 1968) leads to concentrations in sulphides (Brown and Swaine, 1964; Gluskoter et al., 1977; Spears and Amin, 1981). A ratio of Fe (from normative pyrite) to Cu indicates through a high Cu level that some fraction of the Shallow Seam roof sequence, the Yard intraseam dirt samples Ydb1, Y2 and Ydb2, the floor YF1 and roof YR3, the Park Seam and all but the Eight Feet floor may be held in sulphides. If the organic matter to Cu ratio is taken a relationship with inorganic matter is indicated for the Yard Seam dirt band samples, the Park Seam dirt band and 8R2. Obviously, therefore, Cu may have several locations. Where values far exceed the mean, there is good reason to believe that some of the Cu is in an inorganic location.

Mn

The seam profiles indicate that Mn is highly localised into two peaks which are dominant over the variable background. These are in SS2 and 8R2. In the latter case this corresponds to a depletion of all trace elements except Co, Ni and Pb. The correlation matrix indicates a siderite site and siderite is confirmed by major element analysis. A carbonate host is indicated by Spears and Amin (1981). Phosphorous is similarly associated but probably indirectly. The correlation with Co and similarity of ionic radii of Fe, Mn and Co probably show substitution of the Mn and Co for iron. A negative correlation exists with detrital sedimentation seen by TiO_2 and clay associated elements. This indicates carbonate formation in areas of low detrital sedimentation. This may be indirect, for if the dilution factor for siderite and organic matter is taken into account, then TiO_2 is close to the mean value. If dilution is the cause of this relationship, then diagenetic siderite growth must take place very early in the sediment depositional history before recognisable compaction. A further indirect cause for the negative correlation with detrital matter is the necessity for organic matter fermentation as a source of CO_2 . Accumulation of organic matter and high detrital sedimentation are not compatible. A roof location is dominant and dirt bands are usually lowest (see Major Element section).

Ni

A sulphide location is suggested by the correlation matrix. A significant correlation is made with Pb which in turn is correlated with S. Significant correlations exist with Fe_2O_3 (includes pyrite in the method used), Co and Zn. Ni, Co and Zn have similar ionic ratios as Fe^{2+} and may substitute for iron in pyrite. A strong similarity between the calculated pyrite profile and Ni is found in the Yard Seam. This is not seen in the other seams and another source may be predicted in addition to

pyrite. Spears and Amin (1981) found a correlation with Ni with Pb (and also Cu and V). Further sources may be clays (Curtis, 1969), carbonates, especially iron rich (Nicholls, 1968) and organic matter (Spears, 1963). A multiple host of organic matter and sulphide was found for Ni in coals by Gluskoter et al. (1978).

The sulphide analyses indicate that Ni may be concentrated in marine or brackish water samples. As the values are comparable to those of Curtis (1969) for the whole rock and are higher than the associated nodule this indicates further evidence that the heavy separate is far from being a pure sulphide separate. A sulphide and another host are therefore indicated.

The nodule from 8S10a is comparable to that of the Mansfield nodule. That pyrite can hold more Ni, if it is available, is evident from the cleat samples where levels an order of magnitude higher are found.

Pb

Two significant correlations are found, with Ni and S indicating a sulphide association. Such a site has been suggested by Spears and Amin (1981). There is no distinct overall trend in the Pb profiles which can be tied to a specific mineralogical association. In the Yard Seam, however, there is little overall variation with perhaps a slight fall in the intraseam dirt and dirty coal samples. There are, however, two distinct peaks, in YF2 and YR2. The profile in this seam alone correlates with normative pyrite. It must be concluded that other sites for Pb exist or that the availability of Pb varied considerably (which seems unlikely) in the other seams. A clay association may be postulated. Krauskopf (1956) showed that smectite removes Pb from solution. The mixed-layer clays may act in a similar manner even if not so efficiently. An organic association was attributed to Pb by Holmes (1980, Ph.D.) but a

diagenetic host was suggested in coal by Nicholls (1968) and Snyman (1978). Gluskoter et al. (1978) found Pb to be in galena in American coals but no XRD evidence has been found of the mineral in the present mudrocks although limited occurrences have been found in the cleat of the Littleton Colliery seams. Of the mudrocks, there is little to choose between the two collieries and similar Pb levels can be assumed during early diagenesis.

The sulphide investigation indicates a slight rise in Pb content with time. This may be explained by a slowing of nodule growth. If the nodule from 8S10a is typical of all early diagenetic iron sulphide (and there is no evidence that nodules and framboidal pyrite should be similar) then such sulphides cannot be the only Pb host. Cleat Pb contents are, however, much higher by more than two orders of magnitude. Higher values in the Eight Feet Seam support the XRD observation of galena at Littleton Colliery. A multiple host for Pb must be envisaged although where high values are found they are most likely to be sulphide located.

Rb

A clay site is strongly indicated by the correlation matrix and a detrital location is suggested by the type of clays and indirectly inferred by the negative correlation with organic matter. The strong similarity of ionic radius between Rb and K is supported by the +0.99 correlation. An illite location seems highly likely (as there is for Ba and Sr with which Rb is significantly correlated). The correlation with Cr and Y also seen by Ba and Sr indicate a clay relationship for all these elements. A detrital clay location for Rb has been noted by Spears and Amin (1981).

Sr

The seam profiles for Sr are very similar to Rb. The correlation matrix again indicates a clay site. Of the trace elements, significant relationships are to be found with the same elements as Rb. Substitution for K is again suggested. A positive relationship with clay minerals has been found by Curtis (1969), substituting probably for Al, Sr or K, and Nicholls (1968). Carbonate sources are known (Spears and Amin, 1981) but there is no clear evidence for this in the present work. Illite is probably the host.

V

The V profiles do not show any consistent trend. Y2 has the highest value for the Yard Seam followed by the organic rich Ydb2. However, the organic rich roof sample YR2 has the lowest value for the seam. In the Park Seam an organic matter trend is followed but not in the Eight Feet Seam as the organic rich 8R2 is low in V. A complex location is envisaged. Correlation with Al_2O_3 , SiO_2 and H_2O^{\pm} indicates a non-specific clay location as does its relationship with Cr, Rb and Sr. A similar ionic size with Cr may indicate a similar host.

A negative correlation with carbonate elements indicates further a detrital location. A clay location is suggested but there are suggestions of an organic affinity. Spears and Amin (1981) found an organic relationship but a pyrite relationship was also noted. Curtis (1969) and Nicholls (1968) found a clay association, the former author suggesting substitution for Al, K and Sr as possibilities.

Y

From the Y profiles it is evident that values are low where organic matter is high. It is also notable that all of the trace elements studied only Y and Zr have their maximum value in SSF1 where the quartz content

usually acts as a dilutant. In the similarly high quartz sample YF1, Y is again high, exceeded in the Yard Seam only by YR3. A detrital correlation is indicated by the matrix by positive associations with TiO_2 , Zr and Quartz. A clay relationship exists, also noted by Spears and Amin (1981), in evidence of major and trace (Ba, Rb and Sr) element correlations. A negative relationship with organic matter is not unexpected as high detrital influx would swamp plant growth or the unstable conditions conducive to rapid sedimentation would not allow widespread organic development. Organic and detrital environments are thus mutually exclusive as shown by the relatively low detrital component in nearly all the coal samples.

Zn

The average Zn levels in the Cannock samples falls far below that of comparable strata (Table 6.12). It is evident that Zn is not associated with organic matter from the seam profiles and the negative correlation. Nor is it related with the resistrate fraction, the lowest levels being found in the Shallow Seam floor. Correlations with Rb and Sr suggest clay sites but no significant relationship is made with the expectation of major clay elements. A positive correlation with MgO and a similar ionic radius may allow substitution in clays or carbonates. Similarly with Ni, a sulphide location may be possible.

The sulphide study shows no Zn in the 8S10a nodule dictating against a sulphide host in the Cannock samples. However, the Mansfield section indicates high levels of Zn in the nodule and marine 'heavy' separate but not in that of the brackish water separate. Migration of Zn from the enclosing sediment to that of the nodule seems unlikely unless there is actually negligible sulphide in the latter heavy separate to cause its precipitation in framboidal pyrite. The fall in Zn through the nodule shows lowering of Zn levels in the ground waters with time,

possibly by removal or by reduced circulation owing to compaction. The marine heavy separate is comparable to that of the early nodule growth stage and is in excess of the values from the Tansley Marine shales (Spears and Amin, 1981). There may be a sulphide concentration. Absence of Zn from the brackish water separate may be tentatively explained by a far higher porosity in the area of nodule growth (and hence its location) but this does not follow from the distribution of other trace elements.

Cleat formation saw a source of Zn in the ground waters of Littleton Colliery but none at Lea Hall. Although the level found in the cleat is unlikely to be sphalerite, sufficient Zn was available for its development and XRD identification in some Littleton cleat samples. Sphalerite has been identified in cleat by Hatch et al. (1976) and Gluskoter et al. (1977).

If the nodule is typical of Zn in the Cannock samples then another additional or alternative source is necessary to explain the mudrock Zn levels. The association with clay minerals indicated by the correlation matrix is a possibility. The Yard Seam profile also shows similarities with the pyrite profile for that seam. A multiple origin is suggested. Spears and Amin (op. cit.) found Zn to be illite related.

Zr

Zr is characteristic of the detrital resistate fraction (Goldschmidt, 1954). Its profile distribution is comparable to that of quartz and TiO_2 which it is significantly correlated. The negative correlation with organic matter is, therefore, not unexpected. The relationship does not always hold with quartz distribution, YF1 having high quartz and a high but not a Zr peak, and I.D.2.11 having a slight peak but no quartz. The latter argues a size distribution in operation dictating against quartz but not Zr. The source is probably zircon (Brown and

Swaine, 1964; Spears and Amin, 1981) as individual crystals or small inclusions within the clay structures. If this is a source, then the lower than expected Zr value in YF1 may be explained by the low clay content owing to quartz dilution.

Further Evidence on Trace Element Location

Using the reduced major axis intercept further information can be derived for trace metal association. The information is provided by the computer program of Till (1969). If the data is normally distributed, an intersection giving a positive value for the proposed host indicates that host may accommodate all the trace metal. A negative intersection shows that some proportion, given by the intersect distance on the trace element axis, has another location. The following generalisations can be made:

Ba, Rb and Sr can be accommodated by Al_2O_3 and SiO_2 . Furthermore, Rb and Sr have a similar relationship with K_2O . Ba has a negative intercept reading 53ppm which is not related directly to K_2O and may therefore be located elsewhere. This proportion, out of a mean of 468ppm and a range of 197 to 755ppm is a fairly negligible proportion.

Cr, V, Y and Zn have other potential locations in addition to Al_2O_3 , SiO_2 and K_2O but again the levels are low.

It is interesting to note that the two groups identified here correlate to that predicted from the correlation matrix and by ionic radii (Table 6.13). The former is illite located, specifically by substitution for K whilst the latter group has been identified more generally as 'clay associated'.

This approach has not been followed for the sulphide located elements as Fe_2O_3 is likely to be found in other minerals as well as pyrite. The carbonate data is not normally distributed owing to the siderite concentrations found in three samples, SSR2, 8R2 and 8R1.

A similar approach shows that although Cu is organically associated other hosts exist as shown in the preceding discussion.

Summary of Trace Element Locations

The following summary of trace element sites or associations can be made from the preceding mudrock data.

Detrital: Clays; Ba, Rb, Sr probably substituting for K in illite. Cr is possibly illite associated. V and Zn are clay associated but not to a specific clay. Zn may also be held in pyrite. Y is detrital and a clay relationship exists. Zr is a resistate, probably in zircon.

Diagenetic: Carbonates; Co and Mn are specifically siderite associated. Sulphides; Ni and Pb are both associated with pyrite in the mudrocks but both elements have other unspecified locations. Some proportion of Co and Zn may be sulphide located.

Organic: Cu is the only trace element primary organically associated although a further source, probably pyrite is considered in some cases.

Source of Trace Elements

In the organic rich fraction and those samples approaching true coals, all trace elements except Cu are low. Casagrande and Erchull (1976) have shown that with the exceptions of Cd and V, "in most cases virtually all of the metals ... would be accounted for in the peat-forming stage". Although this work was conducted on U.S. coals, a similar relationship may be expected here.

Of the inorganic fraction the close correlations of Ba, Rb and Sr with illite predict a detrital origin substituted for K within the

structure. If such a relationship holds, then given a similar clay type distribution, size range and degree of weathering, then the K_2O to trace element ratio will be constant. The Shallow Seam roof is most constant in its major element mineralogy and clay type. The ratio for the above elements is, as predicted, constant.

The Yard Seam allows a closer investigation of the effect of different mineralogy and clay type. Here the K_2O (used to represent illite content) to trace element ratio mirrors that of the K to Na ratio indicating an increase in trace elements in relation to K_2O in the degraded illites (Figure 6.20). Either proportionately more monovalent K was removed than divalent Ba and Sr from the degraded illite fraction or more trace elements were being added, possibly through cation exchange. A viable alternative is suggested by the K_2O to trace element trends which show marked trace element peaks in the dirt band samples. The size of these sediments is known to be much finer than that found in the associated floors and roof measures. Degraded illite and 'fireclay' type kaolinite predominate in the fine fraction. Thus the relative surface area to weight percentage of these clays are considerably increased and may accommodate the higher trace element levels. This effect will be masked by a simple weight percentage ratio.

Rb, with its specific substitution for K in illite, shows a not unexpected constant ratio, and must have been introduced into the clay structure before weathering and probably during its formation.

Those elements not specifically illite associated, Cr, V and Y, the ratio is similar but more marked (Figure 6.21). A total clay to trace element ratio reduced the variation produced by the dirt bands but this was further improved by correlating total clay minus kaolinite with the metals. As the kaolinite is degraded and hence may host trace elements, this is probably indirect. Cr, V and Y are hence thought to

be detrital and found substituted or in exchange sites in illite, degraded illite and perhaps kaolinite and another source.

The transport mode of the remaining trace elements with the exception of Mn and Zr was also investigated. Mn is believed to have been supplied, along with some iron, by oxyhydroxide material and the concentration due to high mobility of metal-rich fluids and perhaps migration along a horizon of higher porosity to a suitable host location. The mobility of Mn and its concentration make the prediction of a carrier very difficult. The distribution of Co, Cu, Ni, Pb, and Zn were studied in relationship to a possible pyrite location. The ratios showed marked variation which suggested that these elements were controlled not by a specific diagenetic mineral site but by a transporting media. As the Yard Seam has been shown to have the closest resemblance between pyrite and Co, Ni and Pb this seam was studied in detail. Co, although shown to be located specifically in carbonates, shows the closest resemblance between any of the above elements and pyrite in the Yard Seam and this was taken to be representative. Attempts to correlate Co with a clay source show a total clay to Co ratio to be reasonably constant (Figure 6.22) in all but the intraseam dirt band samples where a relative loss in Co is indicated. Cu was also calculated as a ratio with K_2O and this too indicates a clay source in the Shallow Seam. This is not entirely compatible with the organic matter to Cu relationship and this is not seen in the Yard Seam where the dirt band samples have very high Cu levels (Figure 6.22). The constant total clay or K_2O to Cu ratio of the Shallow Seam is thus considered indirect and simply due to the constancy of mineralogy and organic matter. The organic matter to Cu ratio has already been stated to show considerable variation and therefore it must be concluded that the transporting medium of the Cu is not known for certain and considerable redistribution and/or multiple sources must be

postulated. The correlation between organic matter and Cu is therefore not identified, and a knowledge of the relationship between a Cu source being scavenged by organic matter or if Cu preferentially accumulates in an environment which is also suitable to organic matter accumulation is not known.

Zr has not been studied and its detrital association suggests that it is purely a resistate fraction.

Where a correlation between trace element concentration and total clay content is indicated by a reasonably constant ratio a holding mechanism is needed. Redistribution after deposition may have taken place. Holmes (1980, Ph.D.) working on Oligocene sediments found that many trace elements were located in oxide coats surrounding clay minerals. Co, Cr, Mn, Rb, V and Zr were shown to be held in this matter. Spears and Amin (1981) have stated the importance of oxyhydroxide material in modern environments in scavenging trace metals by co-precipitation and adsorption and predicted a similar mechanism in the Carboniferous. The oxyhydroxide material probably originated in the weathering environment and metals would have been incorporated then or later during transportation. Spears and Amin (op. cit.) suggest that the trace elements in the soil are the major contributors to the sedimentary environment. Once deposited and reduced in the diagenetic environment oxyhydroxide material would enter into solution and the elements redistributed. Curtis (1966) has shown the importance of organic matter in marine environments, essentially sapropyl, in concentrating trace metals. He also showed that although organic matter contents were higher in associated non-marine sediments, that land derived organic matter, essentially coally in origin, does not concentrate metals to the same degree. This is seen in the dilution effect of organic matter on all elements but Cu in the present study.

From the sulphide study and XRD investigation into the cleat samples it has been shown that Co, Cu, Ni, Pb and Zn are concentrated in the late diagenetic sulphides when compared to early sulphide nodules by at least a factor of ten. However, even in the cleat samples the trace element concentration is far lower in relation to iron content than in the whole mudrock samples. The indication is that trace elements were effectively removed from circulation during early diagenesis. The source of those metals found in the cleat is not known. Several possibilities exist. They may be those metals not taken into sulphide locations in early diagenesis. Alternatively, they may represent metals leached from the associated mudrock successions by 'aggressive' chloride rich ground waters as has been predicted for major sedimentary Pb-Zn provinces (Dunham, 1970; Carpenter et al., 1974; Edmunds, 1975). A further source to be contemplated is from the coal organic material which may lose trace elements when, through coalification and associated devolatilisation, elements may be driven off. As Cu has been shown to be strongly associated with organic matter and the solubility of Cu in the presence of S is very low, such a source would predictably produce relatively high concentrations of Cu. There is no evidence for such a preferential concentration in the sulphide trace element study. It is concluded, therefore, that the most likely source of late diagenetic trace elements is through the redistribution by chloride rich ground waters of those elements not already located within the early diagenetic sulphides or more distance mudrock successions.

Conclusions

- 1) Trace elements have many sources:
 - a. Clays. Ba, Rb, Sr substituting for K in illite. Cr may be illite associated. V, Y, Zn have non-specific clay associations although Zn may also be located in pyrite.

Zr is concentrated in the resistate fraction, probably in zircon.

b. Diagenetic - Carbonates. Co and Mn are specifically located in siderite.

Sulphides. Ni and Pb are usually located in pyrite although other locations may be found. Some, Co, Cu and Zn may also have a pyrite host.

c. Organic. Cu is the only trace element primarily associated with organic matter.

- 2) The transport modes are complicated. Cr, V and Y may be related to clays by virtue of their locations in oxyhydroxide coats, the probable transporting media. A similar mode of transport could be suggested for Co, Ni, Pb and Zn but later transported through sediments to suitable hosts by ground waters.
- 3) Redistribution of the trace elements takes place in the diagenetic environment where oxidised sources may be reduced and liberated. Their concentration depends upon the availability, geochemical environment, available host and the rate of precipitation.
- 4) The consistency of many trace element to clay ratios indicates little loss or gain from the system. This is explained by the boundary of anoxic conditions being within the sediment thus preventing their loss after reduction (Spears and Amin, 1981).
- 5) The concentration of trace metals is greater in cleat sulphides than early diagenetic pyrite nodules but the former are two orders of magnitude lower than disseminated framboidal pyrite. This indicates the efficiency of early diagenetic framboidal pyrite in scavenging the majority of available trace elements before large nodules can accumulate. Metals found in the cleat were probably leached from mudrock successions by chloride rich ground waters before being redeposited in a suitable geochemical environment.

SECTION 4

PHYSICAL PROPERTIES OF MUDROCKS

N.C.B. Cone Indenter

Engineering properties of the mudrocks were not studied in detail. One aspect was, however, that of the uniaxial compressive strength of the mudrocks using the N.C.B. Cone Indenter. The use of this instrument has been suggested as a basic parameter of measurement in the investigation of the engineering properties of mudrocks (Taylor and Spears, 1981). A cursory investigation was made into the relative influence of rank and mineralogy upon the physical strength of the mudrock.

Apparatus

The N.C.B. Cone Indenter is a portable instrument which has a cone which is screwed into the sample under study. The force applied is measured and the penetration of the cone into the sample is read on a dial via the deflection of a strip of steel. The greater the uniaxial compressive strength of the sample, the smaller the depth of cone penetration. Given that there is a large potential variation between poorly cemented or highly fissile rocks, and igneous or metamorphic rocks of great strength, different scales of pressure are used. Conditions for use are given in the N.C.B. Mining Research and Development Establishment Handbook No. 5.

Measurement

Those samples exhibiting sufficient competence to be investigated were tested using the standard cone indenter pressure. Samples YR1, YR2, YR3, 2F1, I.D.2.11 and 8S10c all fractured before the set pressure. All rocks, SSF1, SSR1, SSR2, SSR3, YR1, YR2, YR3, I.D.2.11, 2R1, 8F1, 8510c, 8R2 and 8R1, were consequently tested using the reduced pressure

of the weak rocks cone indenter scale. It was still impossible to achieve a reading for 2F1 because of failure along the listric surfaces.

For those samples tested using both the standard and weak rocks indenter a correlation of $r = +0.93$ (99.9% significance) was achieved indicating a good agreement between the scales in direction if not precise magnitude. This is shown by the regression line not plotting through the origin and a relationship which is not on a proportional basis (Figure 6.23).

In rocks that have a strong planar fabric, as is often common in detrital sedimentary rocks, major differences - both physical and mineralogical - can be expected between sections taken parallel to and normal to the bedding. This is most marked when such differences are on a small scale. Shales, therefore, displaying a strong fissility (Spears, 1976) will show markedly different characteristics normal and parallel to the bedding. If normal, differences will occur if the layer penetrated is predominantly made of one of the minerals or elements going to produce the fissility, that is, quartz, clay or organic matter. As both fissile and massive specimens were available for investigation, experiments were conducted normal to the bedding.

Sample fragments of similar dimensions, approximately 30 by 15 by 5mm, were used. To ensure that the values were not the result of centering on a 'hard' quartz grain or similar, perhaps uncommon, grain, ten random points were chosen for each specimen and the mean value taken. The results are given in Table 6.14. It is interesting to note that the variation between the determinations has a significant inverse relationship with the cone indenter number ($r = -0.61$, 95% significance). Indenter number consistency increases as the uniaxial compressive strength increases. This can be explained by either machine response at the lower limit of the method being more variable, or by variations in the mudrock

construction, such as organic matter, listric surfaces etc., hence affecting the strength of the rock in a random manner. At the top of the scale, the highly cemented siderite 8R2 is relatively homogenous mineralogically, and very strong. This sample shows the least variation between sampling, and with one exception, the greatest uniaxial compressive strength. This exception is provided by sample SSR2. Two different fragments were tested with markedly differing results. That with the markedly greater strength was found to be impregnated by pyrite. The standard deviation of replicate tests on this sample is, however, greater than that of 8R2. This suggests that although pyrite precipitation is widespread, it is not completely uniform in its distribution, and is probably controlled by the initial rock fabric. Fabric plays a dominant role in the uniaxial compressive strength of mudstones and the values, calculated from the cone indenter number are given in Table 6.14. Given that little rank variation existed between seams, this could not overcome the effect of mineralogy. If samples could be taken over the whole coal rank range, a direct relationship between rank and uniaxial compressive strength may be found but only if the rocks are of comparable mineralogy and fabric. An investigation of this nature was made by M. Al-Jalili (Ph.D. Thesis, 1982) on floor and roof rocks from the South Wales Coalfield. A far greater range of rank is found here than in the Cannock Coalfield. No significant relationship was found.

The Influence of Mineralogy, Fabric and Organic Matter

It has been seen that those specimens strongly affected by diagenetic mineralisation may be important in affecting the cone indenter number. The mineralisation must be controlled or control the fabric of the rock in turn. Of the detrital minerals, the hardness of quartz (7 on Moho's Scale) and its abundance in (some) mudrocks makes it an important consideration in controlling their strength. The other major contributors,

percentage clay and organic matter, were plotted against the cone indenter number (Table 6.15). The relationships show a significant correlation with quartz ($r = +0.80$, 99% significant), no correlation with clay, and a negative correlation with organic matter ($r = -0.52$) but only significant at the 90% level. Even though quartz and organic matter both have an effect on the strength, the inverse relationship between quartz and organic matter are a function of the depositional environment being almost mutually exclusive.

Using a number of specimens of Al-Jalili's (op. cit.) a similar investigation was carried out. Although the results were found to be of a different scale to those of Al-Jalili, their direction was similar and the data correlated strongly ($r = +0.98$, 99.9% significance). Thus establishing that similar parameters were being measured, the quartz values of Al-Jalili were correlated with their re-calculated cone indenter numbers (Table 6.16) to give a strong positive correlation ($r = +0.62$, 99% significance).

Conclusions

- 1) In mudrocks of a heterogeneous mineralogy, the uniaxial compressive strength measured normal to the bedding is controlled by the mineralogy. The dominant control is the quartz content. Parallel to the bedding, strength is controlled by the presence or absence of fissility.
- 2) Where diagenetic minerals such as pyrite and siderite are common to 'cement' a rock, they may have a strength far in excess of that predicted by their quartz content.
- 3) In a homogenous suite of mudrocks, their uniaxial compressive strength is expected to increase with rank.
- 4) In coals of above 92°C, the Vickers microhardness increases with rank (Stach et al., 1975).

CHAPTER 7EXCHANGEABLE CATIONSMethod

The major exchangeable cations in the mudrocks were determined following the method of Spears (1973) but using barium nitrate rather than ammonium acetate as the exchange media. The choice of exchange solution is limited by an anion with easily soluble calcium and magnesium salts whilst the cation must be monovalent or a strong base forming divalent cation (Bower and Truog, 1940). $\text{Ba}(\text{NO}_3)_2$ was chosen because of its greater efficiency as an exchange media (Zainal, 1977, Ph.D.). Spears (1973) found problems of carbonate solution when using ammonium acetate, but although this was not entirely overcome (Holmes, 1980, Ph.D.) using the barium salt, it was reduced.

As mudrocks contain water-soluble cations in addition to those which are exchangeable (Spears, 1974), the former contribution must be allowed for. Spears (1973) removed the water-soluble cations before exchange analysis by repeated washing. This, however, will upset the equilibrium and may lead to incorrect values, artificially buffered. Alternatively, parallel experiments were used, the first using the exchange media and the second, distilled water. The water-soluble cations determined were used in the relevant section of this thesis, and subtracted from the water-soluble plus exchangeable cations of this experiment. 0.2g of tema ground sample were mixed with 20ml of 0.05 N $\text{Ba}(\text{NO}_3)_2$, at pH7, in a centrifuge tube. The tubes were stoppered, mechanically shaken for 10 minutes, and then allowed to stand for one hour. Separation was achieved by high speed centrifuging and the top 10mls were pipetted off for analysis. Atomic absorption spectrophotometry was used to analyse for Na^+ , K^+ , Ca^{2+} and Mg^{2+} . Standards were made up

in barium nitrate solutions. A similarly prepared blank was also run. Holmes (1980, Ph.D.) showed that other exchangeable cations do occur in mudrocks in addition to those analysed for in this work. He found, however, little difference between the totals of Na^+ , K^+ , Ca^{2+} and Mg^{2+} and the cation exchange capacity (C.E.C.) and thus C.E.C. was given as exchangeable $\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+}$ on an equivalent weight basis. The same method of C.E.C. determination was used in this present work.

Cation Exchange - Theory

The majority of clay minerals are platey layer lattice structures made up of units of SiO_4 tetrahedra linked with hydroxyl groups forming the 1:1 clay minerals such as kaolinite or those clays where there are two opposing sheets of SiO_4 tetrahedra linking either side of the hydroxyl layer. Examples of 2:1 layer silicates are illites and smectites. Exchangeable cations are of essentially three types (Grim, 1968):-

- 1) Those associated with broken bands and hence associated with edges of clay (or other) minerals.
- 2) Those held within the clay structure to balance charge deficiencies following substitutions within the layer lattices by cations of a lower valance.
- 3) H^+ groups associated with OH^- bands projecting from the end of hydroxyl sheets. Such cations are tightly held and will not be dealt with here.

The 1:1 clays have a very low C.E.C. and are essentially of groups 1) and 3). The C.E.C. of 2:1 clays can be considerably greater than that of the former group because of the added, often dominant, contribution of group 2) cations. The number and type of exchangeable cations in such sites depends upon the type of clay mineral and the co-ordination

of the cation. Illites and chlorites are non-expandable clays and hence the adsorbed cations are held fairly tightly within the structure binding the 2:1 layers (in illites) to the next. The expandable clays in the present study are limited essentially to the mixed-layer clay fraction, which is essentially a degraded illite. Thus the true expandable clay proportion is likely to be very small. The degraded structure may, however, allow cations to be taken into their structure. The type and proportions of the clay minerals present and their percentage of the whole rock are therefore a controlling factor in the C.E.C. of a given rock. The proportions of clay minerals are covered in the relevant section and Figure 7.6.

Exchangeable cations are held in place by Coulomb forces and others are held more firmly by Van der Waals-London forces. In soil organic matter, the C.E.C. is very high, 150 to 500 meq per 100g, but if organic matter has undergone metamorphism the C.E.C. is severely if not completely removed (Grim, 1968) as can be seen in the present coal samples. C.E.C. for clays are:- kaolinite, 3-15; smectite, 8-150; illite 10-40; chlorite 10-40 (Grim, op. cit.). All values are as milliequivalents per 100g.

Where C.E.C. is made up predominantly from broken bands, as in kaolinite and to a lesser extent illite, the size of the clay compared to its volume will determine its C.E.C. A large surface area to volume ratio will result in a higher exchangeable cation total. Consequently, poorly crystallised clays or degraded clays will have a higher C.E.C., for example a fire clay type kaolinite as compared to well crystallised diagenetic kaolinite. Where exchange is controlled by interlayer and within layer substitutions (as in smectites) the size effect is negligible (Grim, op. cit.; Blatt, Middleton and Murray, 1972).

The rate of equilibrium of clays changes with available cations and depends upon the type of clay. Kaolinite equilibrium is rapid because

only the edges are involved and are thus readily accessible. Smectite is slower as penetration to interlayer sites is necessary and is thus proportional to the interlayer spacing and hence the degree of swelling. If the clays are expanded, cation adsorption is rapid. Illite and chlorite react slowly as they are not expanding clays unless the former is degraded. Otherwise diffusion is between narrow interlayer surfaces and is more difficult (Wiklander, 1964).

For any exchange reaction to take place, water must be present. Ions are readily soluble in water and even small quantities are enough to supply or remove cations to or from a clay. Dissolution of other minerals, such as calcite, will obviously affect 'exchangeable cation' ratios. There is some evidence of calcite solution in the Shallow Seam coal samples and 8R2. If mica is degraded on land, K^+ may be leached out (Spears, 1973) and can be replaced by other cations such as Na^+ from the ground waters. If high exchangeable Na^+ are found, it may be a reflection of Na^+ rich groundwaters passing through the strata (Greensmith, 1978; Caswell, Holmes and Spears, part 2). Reconstruction of illites will take place in saline water where K^+ is present (Weaver, 1958; 1967). If the ground waters are low in K^+ then full reconstruction may not be possible. It is evident in light of the very low K^+ values in the centrifuged water samples (Caswell, Holmes and Spears, op. cit.) that K^+ may have been removed but this was insufficient to regrade the often highly degraded illites found in dirt bands.

Clay Mineral Content and C.E.C.

There is a strong positive correlation between the %clay minerals and the C.E.C. ($r = +0.62, 99$ %significance). As the clays will contribute the great majority of exchangeable cations and they form the majority of the minerals present in most of the samples, this relation-

ship is not unexpected. The relationship between C.E.C. and the percentage clay minerals of a specific type is given in Table 7.1. As expected, the 'mixed-layer clays' shows the strongest relationships. This would not be doubted if this fraction was an illite-montmorillonite mixture but the XRD evidence (Clay Minerals section) indicates that the clays are degraded illites. There may be a small proportion of smectite material associated but this is not identified in the $<2\mu\text{m}$ fraction by XRD and is thus unlikely to be more than 5% by weight. The smaller size of the degraded illite, however, allows much greater surface area to be available for exchangeable cation locations and the leaching of inter-layer K^+ allows cations to enter the structure. Illite has a similar correlation with C.E.C. Kaolinite and chlorite correlations are reduced, as the C.E.C. of both clays are low and, in addition, the chlorite percentage is very small. Neither correlations are significant. It is possible, therefore, that the strong correlation between illite and C.E.C. is indirect and rather a function of its abundance and hence, available exchange sites, as well as a highly significant relationship to the percentage clays present. Kaolinite has a stronger correlation with the percentage clay than with the C.E.C. and therefore the C.E.C. correlation may well be indirect. The range of kaolinite crystallinity, too, will play a role in reducing the correlation with C.E.C. The C.E.C. is almost directly related to the percentage clays present. Where the organic matter content is high, as in the organic rich mudrocks and coal samples, the C.E.C. is severely reduced.

Clay Mineral Associationships

Exchangeable Na^+ shows significant correlations (Table 7.2) with illite, mixed-layer clay and kaolinite, whilst K^+ is correlated significantly with illite and mixed-layer clay. Mg^{2+} has correlations with all

the clays but kaolinite with which Ca^{2+} has the only correlation. This is unexpected and probably indirect. It is interesting to note, however, that Ca^{2+} does not have a significant correlation with mixed-layer clay, especially if there is smectite present. A correlation with Na^+ is, however, compatible with a degraded illite host which has removed Na^+ from groundwaters concentrated in this element (Chlorine related chapters). Caswell, Holmes and Spears (part 2) show that the proportions of exchangeable cations are indicative of the ground waters in contact with them. Although the waters at Hem Heath (N. Staffordshire Coalfield) are very concentrated in sodium chloride and give rise to very high exchangeable Na^+ values, the Cannock Coalfield samples too indicate Na^+ as the major cation, although the level is reduced. Within the sections taken, Na^+ is concentrated in the Shallow Seam roof measures, the dirt bands of the Yard and Eight Feet Seams and the floor of the latter. This may indicate more permeable horizons within the strata. The significant correlations between K^+ and illite is not unexpected although the interlayer K^+ is not truly exchangeable except, perhaps, at the edges of clay layers. This may explain the similar correlation with mixed-layer clay whose degradation would allow otherwise fixed K^+ to be available for exchange.

Seam Profiles

Shallow Seam (Figure 7.1)

K^+ is the most abundant exchangeable cation in the mudrock profile. It is lowest in the floor measures and rises in the roof, with the exception of SSR2. The floor value is about half that of the roof, similarly so, are the clay percentages. The high quartz content in the floor is diluting the clay fraction. If the exchangeable K^+ is plotted as a proportion of the clay mineral content, then K^+ is still lower in the floor despite the floor having a higher fraction of illite and mixed-

layer clay. This suggests that K^+ has been leached from the floor measures either prior to deposition or after, by the coal forming vegetation. Rapid sedimentation of the floor, seen in high quartz and TiO_2 values, indicates that leaching probably did not take place during deposition however, and the low exchangeable K^+ is rather a function of a lack of degradation.

Na^+ and the divalent cations Ca^{2+} and Mg^{2+} are low in the floor and fall in the roof, from a maximum adjacent to the seam. Even when expressed as a fraction of the clays present the floor samples are still markedly lower than in the roof. The divalent cations fall gradually away from the seam but the decline in Na^+ is marked. The increase in K^+ is greater than the fall in Na^+ and may be explained in terms of increasing illite and falling mixed-layer clay. A slightly more rapid deposition may indicate a reduction in the illite degradation. Alternatively, greater permeability has allowed ground water Na^+ to be introduced to the samples adjacent to the seam or from the coal seam. It is conceivable that there is 'rapid' ground water movement through the floor sample and instead of regrading clays with Na^+ has opened them to leaching and flushing. Sedimentation rates supporting the former assumption as the most likely cause but seat earth leaching may lead to a similar result.

Yard Seam (Figure 7.2)

The C.E.C. of the Yard Seam is more variable than the Shallow, but so too are the clay percentages and proportions. The highest C.E.C. is to be found in Ydb1 which has the highest clay percentage in the seam. YR2 has the lowest clay percentage and the lowest C.E.C. The C.E.C. closely follows the clay profile (Figure 7.6).

As with the Shallow Seam, K^+ is the major exchangeable cation. Only in sample Ydb1 where Na^+ is high and the Na^+ rich ground water is

found, is this not the case. The exchangeable cations associated with the roof samples YR1 and YR2 are lower than expected from the type and amount of clays present. It is possible that there has been greater degradation and leaching of these samples, removing the exchangeable cations. A brief return to coal forming vegetation, seen in thin vitrain bands in YR2, may mean that YR1 and YR2 acted as a seat earth from which elements were leached by the vegetation. The Na^+ profile is unusual, being very low in all but Ydb1 and YR3. The associated dirt band samples Y2 and Ydb2 have no exchangeable Na^+ . Although the dirt band samples are very degraded, Na^+ has not been taken into the clay structure following the removal of K^+ . Only where Ydb1 acts as an aquifer horizon and holds the brine is Na^+ (very) high. It appears that Na^+ was absent from the depositional environment but not that of diagenesis.

The divalent cations follow similar trends as in the Shallow Seam, but follow no specific clay type.

Park Seam (Figure 7.3)

The Park Seam trends are reasonably simple. The divalent cations are almost identical in all three samples, Ca^{2+} exceeding Mg^{2+} . Na^+ values see a fall from floor, through the dirt to the roof. K^+ is reasonably constant but reaches a peak in the dirt band. Many exchangeable cations may have been leached in this sample. A fall in the C.E.C. in the dirt band when compared to the floor, despite a higher clay fraction, further indicates leaching of Na^+ from this sample. The falling C.E.C. may be explained by an increased kaolinite proportion in the roof sample. Both illite and mixed-layer clay, whilst being high in the intraseam dirt, fall in the roof. K^+ is highest in the dirt band where illite and especially mixed-layer clay reach their maximum for the seam.

Eight Feet Seam (Figure 7.4)

This seam is markedly different to the others studied by virtue of a far higher exchangeable K^+ value. The other cations are, however, comparable, as are the clay percentages. The low values in 8R2 are due to clay dilution in the siderite sheet. It is interesting to note that considerably more Ca^{2+} is being removed from this sample when compared to Mg^{2+} . Solution of the carbonate is taking place.

Although the K^+ corresponds most closely to mixed-layer clay, its proportion is not notably different to that of the other seams. Illite, too, is comparable. There is, therefore, no obvious mechanism for adding K^+ to the system unless it is from ground waters, for which there is no evidence, nor seems likely.

Neither Na^+ , Ca^{2+} or Mg^{2+} follow the trend of any one clay mineral. High values are not found associated with the dirt band despite higher illite and mixed-layer clay percentages. Mg^{2+} values are more variable than in the other seams and exceed Ca^{2+} in the floor and are similar in the dirt and roof sample 8R1. Mg^{2+} is higher in this seam than the others studied.

Cation Ratios

Spears (1973) used the Mg^{2+} to Ca^{2+} ratio to differentiate the marine from non-marine strata at Little Smeaton (Yorkshire). The marine succession had a higher ratio. In the present non-marine sediments, the ratio is more a function of the clays present and their state of degradation. Diagenetic ground waters also play a role. The ratios of monovalent and divalent cations are diagrammatically represented in Figure 7.5.

In the Shallow Seam the Mg^{2+}/Ca^{2+} ratio is fairly constant at approximately 0.5. The values are slightly higher, but of a similar

order of magnitude to the non-marine section of Spears (op. cit.). Spears shows little environmental variation between Na^+/K^+ , although the spread is wider than for the divalent cations. The ratio is lowest in the floor and falls away from the seam in the roof, as the clay fraction falls and quartz increases. If the ratio is a function of depositional rate, then the floor may well have had little Na^+ and the clays in this sample are not degraded enough to allow Na^+ to enter the structure.

The Yard Seam is more complex. Ca^{2+} increases towards the seam in both floor and roof as depositional energy decreases, yet is reduced within the dirt band samples. The immediate roof sample YR1 and YR2 would have been classified as 'marine' in Spears' (op. cit.) section. With these exceptions, the ratios are roughly comparable to the Shallow and Park Seams. There is no marine influence in the immediate roof of the Yard Seam. The Na^+/K^+ ratios follow a trend which is comparable to depositional energy. K^+ increases with decreasing energy. Such a relationship is not to be expected if the mixed-layer clay is an illite-smectite but is explained by increasingly degraded illite in the fine fraction allowing progressively more K^+ to be exchanged as the clay size is reduced. Ydb1 is exceptional and is explained solely by NaCl rich ground waters.

The ratio of divalent cations in the Park Seam shows little variation, and is only slightly higher in the dirt band. As this sample has the highest mixed-layer clay proportion in all the samples, there is no specific correlation with these cations. The Na^+/K^+ ratio is far higher than the similar Yard and Eight Feet Seam values, and is closer to that of the Shallow Seam roof. Again, K^+ is highest in the degraded dirt band and lowest in the floor. Relatively high Na^+ values may indicate a ground water source but for this there is no direct evidence.

The Eight Feet Seam shows the greatest $\text{Mg}^{2+}/\text{Ca}^{2+}$ variation caused

by high Mg^{2+} in the floor and high Ca^{2+} in 8R2. The latter is almost certainly due to carbonate dissolution and may be disregarded. The dirt band and 8R1 are very similar. There is no evidence of a marine floor close to the seam to give the high Mg^{2+} value, nor do the clays appear otherwise unusual. The Na^+/K^+ ratio does not show a great variation. K^+ , as already indicated, is very high. 8R2, which appears to have been slowly deposited, from quartz and TiO_2 evidence, or at least early cemented, has the highest K^+ value.

Exchangeable Cations in Coals

A similar exercise was carried out on the coal samples. As expected from the work of Grim (1968), organic matter that has undergone metamorphism will lose its C.E.C. The ash contents are considerably reduced and the clays are limited to well crystallised cleat kaolinite which has a low C.E.C. Where the detrital ash content is high, the C.E.C. increases. Further problems are involved in the solution of carbonate minerals which increase the divalent cation values. Correlations between exchangeable Ca^{2+} , water-soluble Ca^{2+} and bicarbonate emphasize this problem.

Conclusions

- 1) The C.E.C. is controlled by the total, rather than specific, clay types. This is because none of the clays present in significant quantities has a high C.E.C. Consequently, the overall C.E.C. is low.
- 2) The use of $Ba(NO_3)_2$ produces some dissolution of carbonates.
- 3) The Mg^{2+}/Ca^{2+} and Na^{2+}/K^+ ratios are inversely related, K^+ and Mg^+ usually increasing in low energy environments where degraded illites predominate. The Shallow Seam roof is an exception, as both K^+ and Mg^{2+} increase with illite content and hence with increased depositional

energy. Thus no simple relationships exists, but it is clear that degradation of illite is not releasing all its interlayer K^+ , but may (as in the Shallow Seam) be opening up otherwise fixed K^+ for exchange.

- 4) Na^+ is controlled, often markedly, by NaCl ground water brines as in Ydbl. Few samples are thus affected.
- 5) The coal samples show negligible C.E.C. because of exchange site loss with rank imposition (metamorphism).
- 6) Within a colliery, Na^+ and Ca^{2+} increase with depth and may be a function of their increasing abundance within deeper ground waters. The similarity between Ca^{2+} and Na^+ , Mg^{2+} and K^+ was also found by Fellows (1979, Ph.D.)

CHAPTER 8

COAL MINERALOGY AND GEOCHEMISTRY

The Origin of Minerals in Coal Seams

In his pioneering work on the origins of minerals in coal, Lessing (1925) distinguished five sources. These may be conveniently combined into three major groups:

1. Inorganic matter held in the vegetation.
2. Dissolved or suspended matter in the percolating waters during formation.
3. Dissolved or suspended matter in the percolating ground waters after coal formation.

Mineral matter introduced after the formation of the coal is called 'epigenetic' and that introduced during formation is 'syngenetic'.

Certain minerals are characteristically either syngenetic or epigenetic but many are both or the evidence is insufficient to confirm their origin. This classification is of limited use to the practical user of coal who uses the classification:

a) 'inherent mineral matter' as that material too closely associated with the coal substance to be readily separated by present methods and usually only accounts for less than 2% of the ash (Dixon, Skipsey and Watts, 1964), and

b) 'adventitious mineral matter' representing the material less intimately associated with the coal and can be readily separated. This mineral matter makes up the majority of ash in a coal and comprises of both syngenetic and epigenetic components. Inherent mineral matter is predominantly syngenetic (Watt, 1968). The classification of mineral matter into adventitious and inherent mineral matter was proposed by

Edgcombe and Manning (1952). Even this division is not always realisable in practice (Nelson, 1953). To further complicate matters, the present work will use the geological terminology rather than that of the coal petrologist. Hence mineral matter deposited along with the coal vegetation (syngenetic) will be termed detrital and that introduced later (epigenetic) as diagenetic or authigenic. Diagenetic minerals may be divided in this study into the relative terms of 'early' and 'late' depending on whether formation took place soon after burial or after coalification.

Inorganic Matter in Vegetation

The role of mineral matter arising from the inorganic constituents of the original vegetation has not been studied in this present work as a separate entity. The contribution to the coal ash is minor but is obviously a source of elements. The following is a summary taken from Watts (1968) of the possible elements contributed by the vegetation.

All plants absorb from the soil in which they grow the mineral constituents necessary for their growth. Calcium, magnesium, iron, sodium, potassium, manganese, titanium, sulphur, silicon, chlorine and phosphorous are, after oxygen, the most commonly occurring elements in the earth's crust - and hence in soil - they are also the elements most commonly occurring in plants.

Calcium, magnesium, iron, potassium, phosphorous and sulphur are apparently essential to all plant life and are therefore present in all plant ashes, other elements - silicon, chlorine, sodium, manganese and aluminium - although not apparently essential, appear to have a function in the plants metabolism and are commonly present. The relative proportions and total amounts of these elements may vary considerably with species. Grasses preferentially absorb silica for cell walls;

lycopods, an important contributor to Carboniferous vegetation preferentially absorb a lumina, up to 57% of their ash, compared to levels of less than 1% in most plants.

Mineral matter content of a plant is not large, perhaps 2%, but this is unevenly spread from low values in the woody part of the tree to high values in the leaves. The leaf concentrations are usually precipitated salts left after loss of water.

Elements, too, vary in their distribution between species. The trunk of an oak tree may contain 77% CaO compared with 10% for fir, birch contains 10% MgO compared with 25% for larch; and fir ash can have up to 40% Mn_3O_4 , compared with average values for other trees of about 1%. To interpret these figures in terms of the relative contributions made by the wood, bark and leaves respectively during coal formation it would be necessary to know the relative weight proportions of these structures produced by the tree during its life, but no figures for this have been found in the literature.

Biochemical decay of the plant produces amino acids which in return react with the decay products of the cellulosic parts forming humic acids. Ca, Mg, Fe and Al may survive because of precipitation as insoluble humates (Francis, 1961). Given pH conditions near neutral, the woody parts of the plants will be converted en masse to humates forming vitrinite. Since the bulk of massive humic acid formed from woody materials is almost inaccessible to particulate mineral matter during coal formation then vitrinite will have a low inherent ash. Some coal has lower element values than its constituent organic material indicating diffusion of soluble salts during coalification. (Zalessky, 1915).

Smaller structures such as leaves, spores and twigs will degenerate in a similar manner but will be more liable to be contaminated by

suspended material. During coalification many elements thus introduced may combine with organic matter to become part of the coal mass indistinguishable from elements originally in plants (Deul, 1955).

The coal lithotypes may be expected to reflect differences in ash content and analysis corresponding to their origin. However, because of the very extensive contamination of the smaller plant debris during coalification this is difficult to establish. Diagenetic mineralisation still further complicates this picture and consequently the mineral matter can no longer be directly related to coal type in the samples studied.

Lessing (1925) found that clarain and vitrain had low ash contents, between 1.3 and 1.1% and concluded that these components represented fairly pure vegetable matter. Clarain has the higher content, because of the large proportions of structures of high inherent ash content that it contained, such as cuticles and spores. Much of this ash is comprised of water-soluble salts. Durain has an ash content of 6 to 7%, much of it being rock detritus such as clay. Fusain was found to hold calcium or iron carbonates precipitated from ground waters, - and as seen from the present work, kaolinite and pyrite. Its ash content varies widely from 4 to 30%.

Deul (op. cit.) showed that the organically associated ash, compared to detrital ash was always enriched in B, Be, Fe, Na, Si and U; usually enriched in As, Ga, Ge, Cl, Ti and Zr; occasionally enriched in Co, Ni, Mn, Mo, Pb, Sn, Sr, Y and Yb; and never enriched in Ca.

Coal Mineral Matter Analysis - XRD

The mineralogy of individual coal ash samples was determined by XRD. This is a powerful tool in mineral identification and has been used extensively by various workers in the field of coal mineralogy. The

pre-1968 work is summarised by Watt (1968) of which that of Dixon, Skipsey and Watts (1964) is pre-eminent. Subsequent studies have centred on the work of Gluskoter (1967), O'Gorman and Walker (1971); Gluskoter, Joseph and Lindahl (1973), Mitchell and Gluskoter (1976) and Lin et al. (1978). Unlike the mudrock investigation of this study, it was impossible to make powder mounts for mineral identification as there was insufficient sample available. L.T.A. was further ground in an agate mortar and smear mounts were prepared for analysis. Similar sample weights operating conditions were used so that some degree of comparison was possible.

In addition to the mineral identification, individual and grouped XRD traces were used as a back-up to the XRF study of the coal mineral matter.

Minerals Present

A quantitative determination of minerals is not really possible using smear mounts especially with the limited sample available. The following minerals, in order of their frequency of appearance were found in the coal ash: gypsum (42), pyrite (35), kaolinite (34), ankerite (27), quartz (26), calcite (15), apatite and sphalerite (12), illite and mixed-layer clay (11), marcasite (9), chlorite (4), anatase and siderite (3). A total of 44 samples were studied.

The minerals found in each of the samples are given in Table 8.1, and an indication of their abundance based on peak height (counts per second) in Figures 8.1 to 8.8. Such an analysis of data is assumed qualitative only and abundance has therefore been designated as high, medium, low and trace. In addition to varying mass absorption characteristics of the minerals, the ash content was not allowed for. Analysis of cleat minerals in greater detail has been made elsewhere in this thesis.

Gypsum, the most abundant 'mineral' is a product of L.T.A., the sulphate being derived from organic sulphur and the cations calcium, from carbonate dissolution and ground waters, and sodium from ground waters. The only two samples not to have gypsum identified by XRD are Y2 and I.D.2.11, both are high ash samples of a predominantly detrital origin.

Ball (1935) in his mineralogical investigation into the Illinois No. 6 seam found the mineral similar to that of the present work, as did Fellows (1979, Ph.D. thesis) working on the Barnsley and Top Hard Seams of Yorkshire Main Colliery (Yorkshire) and Thoresley Colliery (Nottinghamshire), with only minor exceptions. In the Illinois Seam, kaolinite, calcite and pyrite comprised of 95% of the minerals present. This is comparable to the present work in order if not quantity, but with ankerite being the dominant carbonate. Quartz, too, is very abundant in frequency if not weight. Mitchell and Gluskoter (1976) in their investigation into American coal ash found quartz and kaolinite in all the samples they studied. It is indicated in the cleat section that the carbonate mineralogy varies from predominantly calcite at Lea Hall to ankerite at Littleton. Regional and indeed local variations may thus be important. More representative sampling over the whole Cannock or even the South Staffordshire Coalfield may well provide a different distribution. Ball (op. cit.) also identified quartz, feldspar, garnet, hornblende, apatite, zircon, muscovite, epidote, biotite, augite, kyanite, rutile, staurolite, topaz, tourmaline and a chlorite type clay. Sprunk and O'Donnell (1942) in a microscopic examination found most of the minerals identified by Ball. Mackowsky (1943a, b) investigated the mineralogy of German coals and Brown and Swaine (1964), and Kemezys and Taylor (1964) that of Australian coal. Nelson (1953) summarised the previous British and American mineralogical research and listed the minerals identified. The list is comprehensive but he concluded that 95% of the minerals may be

grouped as 'shale', 'kaolin', 'sulphide' and 'carbonate'. In the present work, the 'shale group' is, perhaps, reduced in importance, and quartz makes a considerable contribution if not in weight but in frequency.

Stach et al. (1975) found the clay group (including kaolinite) to be the most important, followed by carbonates then sulphides. The clays were found to comprise 60 to 80% of the coal ash. In South African coals, Snyman (1978) found that clays formed the most important group.

Sulphide Group

Pyrite is the most common mineral in the present study of coal mineral matter. Its abundance, at the level of XRD observation, is predominantly due to its concentration in cleat. As a common diagenetic mineral in the highly cleated bright coal the high occurrence of pyrite is not, therefore, unexpected. Early diagenetic pyrite is to be found within the coal matrix as framboids.

Framboidal Pyrite

A study of selected coal samples from the Eight Feet Seam was made using the S.E.M. fitted with an energy dispersive X-ray unit belonging to the Department of Metallurgy (Sheffield University). Samples were cut normal to the bedding and smoothed using emery paper. The surface of the sample was etched by L.T.A. Sample preparation prior to analysis was made by H. Brockley (Department of Geology).

Early diagenetic framboidal pyrite, measuring 20µm in diameter were found in the dull portion of a mixed clarain and durain sample. Similar framboids in coal are not uncommon and have been reported in the literature as far back as 1964 by Kemezys and Taylor although their form was not recognised as such ("...small grains of pyrite may be less than 50µm in diameter ..."). The framboids are both spherical and irregular in outline as can be seen from the photomicrograph plates 8.1 and 8.2.

Closer examination of individual pyrite grains within the framboids show them to be between 1.5 and 2 μ m in diameter (Plate 8.3). Photomicrograph plate 8.2 shows the forms present to be predominantly octahedra. The 'blow-up' (Plate 8.4) shows re-entrant faces along the intersection of the (111) in at least one octahedra. The majority, however, do not show this feature. Plate 8.4 shows octahedral framboids whilst the crystals of Plate 8.3 are 14 sided combination forms.

In addition to pyrite, sphalerite, and to a lesser extent, marcasite are to be found in coal and cleat. Littleton cleat samples have minor galena. At Lea Hall sphalerite is limited to the pyrite rich sample Y7. Marcasite occurs three times, twice in the Shallow Seam. As noted in the cleat section, the mineralogy of the Littleton seams is more diverse. In the Park Seam sphalerite is common but marcasite is limited to two samples. There is no sphalerite, but marcasite is common in the Eight Feet Seam. Pyrite is the more stable sulphide at ordinary temperatures (Watt, 1968) and is more common in British and South African (Snyman, 1978) coals. Australian brown coals are, however, richer in marcasite. With the exception of the detailed study of successive sphalerite deposition in the Illinois No. 6 Coal (Hatch et al., 1976), sphalerite, galena, chalcopyrite and mispickel are to be found in trace levels only and the literature is scarce (Watt, 1967; Stach et al., 1975).

Pyrite is concentrated in bright coal where the properties of vitrain bands make it susceptible to cleat development. Early diagenetic pyrite as framboids (Snyman, 1978) and pore infillings, such as cell lumens and plant structures, of pyrite, marcasite, sphalerite and galena (Kemezys and Taylor, 1964) are shown to be bright coal associated. The present work shows framboids to be found in durain as well.

Undesirable Effects Associated with Sulphides in Coals

The presence of pyrite in coal produces oxides of sulphur during combustion. When sulphur rich coals are being used for metallurgical purposes, sulphur may pass into the metal under treatment. Absorption into oven grate bars may lead to cracking and sulphur dioxide may produce serious corrosion to boiler tubes as well as producing toxic atmospheric pollution. For further information into the combination of sulphur, its determination and removal, reference is made to the relevant chapters in 'Analytical Methods for Coal and Coal Products' (Ed. Karr, 1978). Although pyrite is not the only source of sulphur in coal the form plays an important role in its removal. Pyrite in cleat and larger nodules are readily segregated. The widespread framboidal pyrite is difficult or impossible to separate due to its small size and intimate mixture with the coal substance. Once separated, discarded pyrite may cause further problems such as spoil heap fires due to its oxidation, which is exothermic, and may produce spontaneous combustion in the presence of organic matter (Taylor and Spears, 1981).

Clay Group

Information in the literature into minerals of the 'clay group' is rather scanty. In the present work these minerals are illite and mixed-layer clay, occasional chlorite, and kaolinite. Their through seam distribution is much as expected from a detrital source, being most abundant adjacent to floors, intraseam dirt bands especially, and roofs. This is best shown by the Yard, Park and Eight Feet seams. As expected, quartz follows a similar trend indicating a similar origin, and it is suggested that both are detrital. This is seen to advantage in the Yard Seam. Some complications arise as in the Eight Feet Seam where quartz is to be found in mid-seam without clay. Some of this quartz may be

diagenetic. Clay without quartz in samples associated with the dirt bands show a grain size segregation as indicated by the whole rock mineralogy. The predominantly fine grained nature is seen in the degraded illites which are dominant in these deposits. Such bands, although thin, are persistent (Wanless et al., 1969). The Park Seam intraseam dirt band is, for example, found in both sampling points, although its exact position within the seam varies slightly indicating non-uniform coal accumulation, thus providing a time datum line.

Previous work into minerals of the 'clay group' includes Hicks and Nagelschmidt (1943), Nagelschmidt and Hicks (1943), Sadler (1956), Sadler and Grimshaw (1964) and Dixon, Skipsey and Watts (1964). This last work, the XRD investigations of Illinois clays in coal and associated strata (Gluskoter, 1967) and those of Yorkshire and Nottinghamshire (Fellows, 1979, Ph.D.) are most relevant to the present work and similar trends to be found.

Kaolinite, as indicated by the clay mineralogy and cleat investigations, is both detrital and diagenetic. The differences in crystallinity is clearly shown by XRD traces. The detrital kaolinite has broad peaks and is associated with quartz, illite, mixed-layer clay and occasionally chlorite. Diagenetic kaolinite is common throughout most samples. In addition to cleat mineralisation, kaolinite is also found in coal pores (Ball, 1935; Snyman, 1978), notably in semi-fusinite (Saunders, personal communication). Photomicrograph 8.5 shows crystalline kaolinite. Unfortunately, due to oxidation of the organic matter it is no longer possible to discern whether this was once a pore infill. It is not in a cleat.

Quartz

Although not a clay, the predominantly detrital origin of quartz makes it possible to be considered along with the clay group. Previous works

found quartz levels to be low. No quantitative determination of quartz was possible in the present work but its occurrence is common, if not abundant in terms of weight percentage.

Detrital and diagenetic quartz have been noted by previous authors. Dixon, Skipsey and Watts (1964) are the only authors to find significant levels of quartz, but even here its abundance in coal ash was less than 10%. Sprunk and O'Donnell (1942) and Stach et al. (1975) considered detrital quartz to be wind or water borne, predominantly the latter, and to be rounded. Photomicrograph 8.7 is composed of silica and thought to be a well rounded quartz grain. It is not certain whether the surface relief is due to frosting or incompletely ashed organic matter. 8.6 shows a sub-rounded quartz grain of about 20 μ m diameter. Sprunk and O'Donnell (op. cit.) found that quartz grains fell into a range of 1 to 500 μ m with a mean size range of 20 to 75 μ m. Snyman (1978) found detrital quartz to be rounded, often associated with clays and predominantly held in dull coals, indicating that such coals were deposited in higher energy conditions than bright coals. O'Gorman and Walker (1971) found quartz in dull coal. Kemezys and Taylor (1964) considered that angular, and not rounded quartz to be detrital. This apparent discrepancy may be a function of weathering environment and time, and/or of a size too small to be abraded by attrition.

Sprunk and O'Donnell (op. cit.), Hoehne (1949) and Mackowsky (1956) found diagenetic quartz to be angular. Stach et al. (1975) found it associated with carbargillites where feldspar and mica weathering could give rise to silica precipitation as a finely crystalline cement. Kemezys and Taylor (1964) considered a possible igneous derivation to the chalcedony infilling cell lumens. Direct evidence of diagenetic quartz in the present coal samples is limited to the cleat of Y7, Y9 and 2.2.

It is interesting to note, however, the widespread distribution of quartz throughout the seam without any obvious detrital clay minerals. This quartz is conceivably diagenetic in origin. Finkelman and Stanton (1978) considered the quartz in the lower part of the Pittsburgh No. 8 Seam to be an authigenic infilling of semifusinite pores. Diagenetic quartz infilling the stigmaria found in Y1 shows a form clearly angular and often cusped. There is, however, no evidence that diagenetic quartz within the coal will have a similar form (Plate 8.8, 8.9, 8.10).

The determination of quartz content in coal is important in silicosis prevention (Stach et al., 1975).

Carbonate Group

The carbonate group is dominated by ankerite and calcite with limited occurrences of siderite. Ankerite and calcite are identified as cleat minerals, both being found at Lea Hall, and predominantly ankerite at Littleton. Stach et al. (1975) suggested that some early impregnation of fusain by carbonate took place. There is no evidence of early diagenetic calcite or ankerite in the present coals, but as the limited carbonates in the mudrocks may be pore infilling, it cannot be completely ruled out.

Siderite is found in three samples, SS1, SS2, and, most notably, 2.6 (Park Seam). In this latter sample small spheres and irregular ovoids of siderite approximately 0.5mm in diameter are found in a bright coal. Some spheres coalesce to form discontinuous sheets and are clearly early diagenetic and pre-dating notable compaction. The cleat carbonate is terminated by the siderite nodules which clearly pre-date it. Spherical siderite crystals exhibit a uniaxial cross under crossed nicols indicating a radial arrangement of crystallites. Siderite will form in a geochemical environment similar to that of pyrite but with limited sulphate activity

or pyrite will form (Curtis and Spears, 1967). The two minerals rarely occur together in coal but there is evidence of siderite pre-dating pyrite (Kemezys and Taylor, 1964) probably by the later passage of hydrogen sulphide containing solutions (Smyth, 1966). (Plate 9.20, 9.21).

Other Minerals

Phosphates

Apatite and, limited occurrences of the Sr, Al, phosphate goyazite (SS3, 8S9 and 8S10) represent the phosphate minerals. No phosphates are to be found in the Yard Seam and the occurrence of goyazite and minor apatite in SS3 is the only occurrence in the Shallow Seam. Goyazite was identified by XRF analyses having high P_2O_5 (samples 2 and 14) and insufficient Ca to satisfy the phosphate whilst carbonate was also present, and by XRD. A continuation of the present work in the Department by Mr. S. Reynolds also identified high Sr and phosphate whilst the Ca values were low. Y, also very high, is apparently associated with the goyazite. This mineral has not been identified previously in coal ash.

Both fluorapatite (Dixon et al., 1964; Kemezys and Taylor, 1964; Brown and Swaine, 1964; Stach et al., 1975) and hydroxyapatite (Stach et al., 1975) are found in coal ash but levels are low (Finkelman and Stanton, 1978), ranging from 0.01 to 0.03% in whole coal (Brown and Swaine, op. cit.) which compares favourably with the present samples, excluding the high overall values in the Eight Feet Seam and those with goyazite present.

Two cleat samples, SS1 and SS4 have apatite and must be late diagenetic in origin. In the mudrocks, the association with carbonates suggest an early diagenetic origin. Such a relationship is not observed in the coals but may be swamped by cleat carbonates. The origins of apatite vary from detrital (Kemezys and Taylor, op. cit.), organic

(Kemezys and Taylor, op. cit.; Spears and Amin, 1981) being indicative of proteinaceous albuminous constituents (Stach et al., op. cit.), fish scales (Fellows, 1979, Ph.D.), or diagenetic, as in the present work, although other sources may well play a role.

Anatase

Anatase is found only once in the Lea Hall coal ash (Shallow Seam) and twice at Littleton (Eight Feet). Its association with high ash content in the Eight Feet Seam may indicate a detrital origin as would be expected of a resistate mineral. There is no evidence for a diagenetic origin.

Anatase is practically unknown in the literature on coal mineral matter but was identified by Fellows (1979, Ph.D.). Ball (1935) identified rutile, the high temperature polymorph.

Summary of Coal Mineralogy

The origin of coal mineral matter is summarised in Table 8.2.

The work of Lessing (1925) and O'Gorman and Walker (1971) shows that an association exists between ash content and coal type. Bright coal has a lower inherent or detrital ash content than dull coal. Such a study has not been attempted here. Samples were analysed as 'whole coal' and no attempt was made to separate lithotypes, nor cleat from the coal to leave detrital and early diagenetic minerals. Consequently, the predominance of pyrite in Y7 gives a bright coal a high mineral matter content. Conversely, the dull coal section at the top of the Eight Feet Seam has an ash content no higher than the associated bright coals and much lower than those bright coals associated with the floor and intraseam dirt band.

Coal Ash Geochemistry - XRF

Analysis of the coal ash prepared by L.T.A. by XRF and wet chemical techniques enabled a more quantitative determination than could be attained by XRD alone. There are constraints, however, which make this data, unlike that of the mudrocks, only semi-quantitative.

Constraints

Limited sample weight from individual samples and the long ashing time needed by L.T.A. made individual sample analysis impossible. Samples were grouped based on similar mineralogy (XRD evidence) and seam position. The sample scheme is covered in Table 8.3. Even after grouping some samples still had insufficient to make the minimum 0.28g needed for the Norrish and Hutton (1969) disc preparation. In these cases additions of 'spec-pure' SiO_2 were made and the dilution factor re-calculated after the analyses. As the samples were grouped in proportion to their abundance in the coal the analyses should be proportional to their true abundance. Further problems arise with insufficient sample for the wet chemical analyses. Na_2O was attempted on L.T.A. samples although in a comparison made with 390°C ashing, the former showed some evidence for a sodium loss. The validity of the Na_2O figures is, therefore, questionable. FeO determination (Shapiro, 1960) was made where sufficient sample was available and hence on limited samples only. The FeO values are given in the relevant seam profiles but not in the whole ash analysis. Iron is reported as total iron (Fe_2O_3). This will overestimate the iron content depending upon the FeO contribution. CO_2 was analysed, not on the ash, but similarly grouped whole coal samples. The profile is given but absolute values are not included in the analysis. Water determination was not attempted after the problems associated with organic matter remaining as shown by

the mudrock XRF analysis. Ashing by L.T.A. is never completed and organic matter will always remain. Trace elements were not determined in this study although the follow-up work by Mr. S. Reynolds (Department of Geology, Sheffield University) is rectifying this gap in the analyses. It is known that various 'trace' elements may make a considerable contribution to the coal ash, for example Zn in the cleat sphalerite, and Sr and Y identified with goyazite. Losses on disc ignition were substituted for H₂O, CO₂, organic matter remaining and even then a 100% total was not always achieved. This may be explained by the unaccounted 'trace' elements. A further problem is the production of sulphate as a by-product of L.T.A. The contribution of the coal mineral matter is uncertain (Ca). As both pyrite (and other sulphides) and gypsum is found in the ash and the relative proportions not possible to be determined in the present investigation, sulphur was presented as SO₃ because of the predominance of gypsum. Analyses were, therefore, recalculated as a proportion of 100%. These analyses were used to suggest trends and not for normative recalculation nor detailed analyses. The recalculated totals are given in Table 8.4. Using the grouped ash proportions, their abundance in the whole coal is given in Table 8.5. Included is a 'calculated quartz' value based on an assumption of kaolinite as the only clay present. XRD analysis of similarly grouped samples has been used for a back-up and the relative abundancies of the minerals based on peak height is given in Table 8.6. A correlation matrix (Table 8.7) is given.

Total Silica and Alumina

Total silica comprises of both free silica, essentially quartz, and combined silica, predominantly clays but also perhaps in traces of feldspar and micas. Both the clay minerals and quartz are detrital and diagenetic in origin. The majority of quartz is detrital but there is

XRD evidence of cleat quartz in samples Y7, Y9 and 2.2, and within the stigmata included in sample Y1 (XRF sample 7). There is no XRD evidence for feldspars in the coal ash and consequently their proportion is very small if present at all. It will be noted that the feldspar contribution to the mudrocks was negligible and if the coal ash represents a similar but markedly reduced detrital mineralogy, both in quantity and size distribution, then this would be expected. Increased detrital sedimentary input, seen adjacent to floors, intraseam dirt bands and roofs and the associated increased ash content reflect a change in the composition and abundance of clay minerals. This is clearly seen in individual XRD traces of the coal ash samples. Away from the relative instability of non-coal deposition the detrital clay component, illite, mixed-layer clay, kaolinite and chlorite declines. Diagenetic clays, dominated by well crystallised kaolinite found in the cleat and coal pores becomes dominant along with a progressively finer detrital clay fraction. Because of the complexity of the clay minerals present in some of the ash samples it is not possible to re-calculate the quartz content but an indication may be given.

The highly significant correlation between SiO_2 and Al_2O_3 ($r = +0.98$, 99.9% significance) is evident from the co-variance of their seam profiles (Figure 8.9). It is evident from the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Figure 8.11) that either varying quartz and/or varying clays are present. In those samples remote from detrital influence it is reasonable to assume that diagenetic kaolinite is the predominant clay and hence the quartz content may be calculated. However, if illite, mixed-layer clay and chlorite is present then the re-calculated quartz value will be incorrect and the true quartz value will be lower than that calculated. Quartz determined from the assumption of kaolinite will, therefore, give a maximum value (Figure 8.10).

It is evident that differences exist between the seams. Most notable are those to be found in the Yard Seam which may be predicted from the ash weight and the associated mudrock mineralogy. Major detrital evidence is to be found in sample 7 at the base of the seam. This sample is made up from dirty coals and organic rich intraseam dirt samples and is demonstrated by high SiO_2 and Al_2O_3 values. At the top of the seam, sample 5 reflects the return towards renewed detrital sedimentation and higher energy conditions. The 'calculated quartz' values predictably follows this trend. It is, however, in excess of the quartz calculated for the other seams. On a similar basis, the 'calculated quartz' for the Eight Feet Seam is remarkably constant. Where the detrital influence is strong, the high SiO_2 and Al_2O_3 correspond to high ash contents as shown in the Yard and also samples 11 and 14 from the Eight Feet Seam. Where a peak does not correspond to a high ash content as in sample 2, the detrital influence is probably small and diagenetic kaolinite high.

Titania

Evidence of depositional energy comes from the TiO_2 profiles (Spears, 1964). There is, however, no significant correlation to be found with either SiO_2 or Al_2O_3 thus supporting a complex and varying source of these elements and emphasising the importance of diagenetic mineralisation over detrital deposition in many of the coal samples. It is assumed that the relationship between TiO_2 and quartz (Spears, op. cit.) found in the mudrocks will hold for the coals but that their levels will be reduced in magnitude. Thus, the TiO_2 profile may be used to indicate the energy of the depositional environment and should co-vary with the detrital quartz content. Similar, although not identical profiles between TiO_2 and 'calculated quartz' are to be found (Figure 8.10). Exceptions are to be found in samples 1 and 14.

The TiO_2 content falls towards the roof in sample 1. It may be expected to rise approaching a mudrock depositional environment. There is, however, an increase in the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (Figure 8.11), indicating increased quartz, more 2:1 clays - predominantly illite, or both. A further tool is provided by the K_2O to Al_2O_3 ratio (Figure 8.11). Na_2O may be indicative of clays but there are other sources. In the absence of muscovite and alkali-feldspars (based on XRD evidence) then K_2O is indicative of illite with significant correlations with SiO_2 ($r = +0.96$), Al_2O_3 ($r = +0.96$) and ash ($r = +0.95$). The Shallow Seam profiles of SiO_2 , Al_2O_3 , K_2O (Figure 8.9) and Na_2O (Figure 8.10) co-vary indicating a probable detrital clay influence. Sample 1 shows a peak in the K_2O to Al_2O_3 ratio indicating an illite maximum. If so, the 'calculated quartz' would be reduced and may then follow the TiO_2 curve (Figure 8.10). It must be concluded that TiO_2 is a much more accurate indicator of depositional energy. The unfulfilled expectation of increasing TiO_2 in sample 1 indicates that the change from coal to non-coal forming environments was abrupt.

Sample 14 exhibits a TiO_2 peak but 'calculated quartz' is constant and low. The sample includes material adjacent to and from within the intraseam dirt band. The former (8S9) indicates the continuing influence of the widespread, fine grained sediment deposited intimately with the coal associate with the dirt band. The ash content of sample 14 represents the gradual decline in sedimentation before the very low values reached in the succeeding samples 13 and 12. This is echoed by the TiO_2 , total SiO_2 and Al_2O_3 trends. The K_2O to Al_2O_3 ratios indicate normative illite which is backed by XRD evidence. The low 'calculated quartz' may be a reflection of a grain size control excluding quartz from the fine grained yet rapidly deposited dirt band material.

The relationship between quartz and TiO_2 is controlled further by grain size (Spears, 1964) but this influence may be removed by using the TiO_2 to Al_2O_3 ratio (Spears, op. cit.; Spears, 1980; Spears and Kanaris-Sotiriou, 1975, 1979). Figure 8.11 shows that although the detrital influence was high in sample 14 its carrying power was very low. The suggestion is therefore, that the high ash content was due to a suppression of vegetation growth, probably due to shallow over-bank flooding of very fine grained material deposited rapidly.

Of the remaining samples and seams, the $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio exhibits predictable trends. In the Shallow Seam a decline is seen away from the floor (samples 4 and 3) and then increasing towards the roof (2 and 1). The high detrital ash contents associated with the floor and roof (samples 7 and 5) of the Yard Seam are reflected in a high $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio, and supported by high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios indicating illite and a high 'calculated quartz'. Sample 6, representing 'normal' coal accumulation exhibits the predicted low ratios associated with coal accumulation and reduced detrital influx. The Park Seam is more complex. TiO_2 declines upwards through the seam, increasing adjacent to the roof in sample 8. SiO_2 , Al_2O_3 and 'calculated quartz' show similar profiles. Sample 9 complicates the picture. SiO_2 , K_2O and Na_2O are all high in relation to Al_2O_3 but the TiO_2 to Al_2O_3 ratio is negligible. Illite is suggested but cannot be confirmed by XRD even after siderite dissolution. Kaolinite is present but the total clay fraction is very low. The presence of early diagenetic siderite has greatly retarded cleat development (see cleat section) and it is suggested that the high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio is indicative of the importance of the detrital illite component in this sample. The weight % K_2O is very low indicating low energy deposition and the high ratio must mean low diagenetic clay dilution of the detrital clays present. The evidence suggests, therefore, that the depositional energy

(given by the $\text{TiO}_2/\text{Al}_2\text{O}_3$ ratio) is low but the peaks of SiO_2 , K_2O and Na_2O to Al_2O_3 are due to a lack of dilution by diagenetic kaolinite.

Total Iron

Total iron, expressed in terms of Fe_2O_3 (Figure 8.12) does not show any significant correlation with other oxides. Because of the small amount of ash available ferrous iron determination was not possible for all samples. Where possible, the analysis was determined following the method of Shapiro (1960). These values are not included in the analysis but are shown on the seam profiles (Figure 8.13).

Ferric iron is often found as oxyhydroxide grain coats to clay minerals in the weathering environment (Spears and Amin, 1981) but is unstable under the geochemical conditions of the coal-forming environment. The iron is reduced, mobilised and, together with iron bearing clays (Pearson, 1979), is the iron source for diagenetic sulphides and carbonates. Although the chlorite is iron rich (see Clay Minerals section), its fraction of the mudrock succession is small and is associated with rapid sedimentation. In the coals, there is very little XRD evidence for its presence and hence its contribution to the whole coal is likely to be negligible as are detrital clays in the majority of samples. The majority of iron, therefore, appears to be available from a source outside the coal migrating in ground waters in both early and late diagenesis. In the presence of sulphur, iron sulphide will be precipitated. If absent, organically derived carbonate will lead to iron carbonate precipitation (Curtis and Spears, 1967).

CO_2 calculations made on grouped coal samples (Figure 8.13) indicate the carbonate trends expected in the ash analyses but cannot be used for quantitative analysis. They are included to help differentiate between the iron sulphides and carbonates in the coal ash.

It has been indicated that associations between total iron and sulphate may be spurious. The sources of quantitative sulphate in the present samples appears to be two fold, oxidised pyritic sulphur and a by-product of the plasma ashing procedure. (see relevant section of this thesis). The sulphate values are, therefore, used only to indicate trends (Figure 8.13).

It is evident that the distribution of total iron is far from constant with the possible exception of the Eight Feet Seam (Figure 8.12). Assuming a sulphide source for the iron an association with SO_3 may be expected but the preparation problems must be borne in mind. Similarities are to be found in the Shallow Seam profile and samples 12 and 13 from the Eight Feet Seam, otherwise the discrepancy is considerable. This does not rule out the presence of iron sulphides, as is obvious from individual analysis of the coal ash by XRD, but that sulphide is not the dominant sulphate source and some of the iron may be as carbonate. From the evidence of limited FeO data (which does not determine sulphide FeO) the profile for the Eight Feet Seam indicates the presence of a small amount of iron carbonate. As the trend is not mirrored by calcium or magnesium, this may be siderite. A sub-parallel trend is to be found in samples 1, 2 and 3 of the Shallow Seam suggesting iron carbonate. Similarities are to be found with CO_2 (Figure 8.13), magnesium and calcium profiles (Figure 8.12) but the ratios vary (Figure 8.11). Ankerite is suggested but other carbonates are present in varying quantity.

In the Yard and Park Seams, the SO_3 (Figure 8.13) trend does not correspond to that of total iron. In both seams the losses (Figure 8.14) are inversely related to the SO_3 curves. If the original sulphate levels were constant then varying losses must have taken place during XRF disc preparation. The CO_2 profiles for these two seams are very similar to that of total iron. For example, the well defined peak in sample 9 is

balanced by a CO_2 peak. As SO_3 , CaO and MgO are low in this sample then the iron must be held in siderite. The high loss value can be ascribed to CO_2 . That siderite is the dominant mineral phase of this sample is confirmed by XRD and optical evidence. Excluding this sample, the Park Seam is fairly constant in total iron and SO_3 . The slight overall rise in CO_2 corresponds to a slight rise in calcium and magnesium. In the Yard Seam the high total iron in sample 6 corresponds to a slight CO_2 peak indicating the presence of carbonate. This is not conclusively identified by calcium and magnesium profiles because of the increased magnesium to calcium ratio in the adjacent samples (5 and 7) reflecting the high detrital clay component. In addition to the pyrite identified by XRD in all three Yard samples, 6 has ankerite in addition. The low SO_3 , high loss and slightly lower calcium values than for the other Yard samples, sample 5 may indicate the loss of some sulphate sulphur.

Calcium, Magnesium and Manganese

Unlike the distribution of calcium and magnesium (Figure 8.12) in the mudrocks their role in the coal samples is reversed. Calcium is higher, on average, for all the coal samples, by a factor of 3.8. The two elements are significantly correlated ($r = +0.85$, 99% significance). Magnesium is correlated with manganese ($r = +0.57$) and with losses ($r = +0.53$) at the 95% significance level. The correlation with losses is explained by CO_2 held in carbonate. CO_2 shows a similar profile to calcium however, and to a lesser extent magnesium, exceptions being explained by the presence of siderite. The immediate indication is that magnesium and the correlated but predictably lower manganese levels are located in carbonates. These will be predominantly ankerite, and to a lesser extent, calcite. The pattern will be obscured in high clay samples where magnesium will also be held in the clay structures. The

correspondence between calcium and CO_2 suggests calcite, and where similar to magnesium, with ankerite in the cleat. As there is no significant correlation between losses and calcium it must be assumed that the disparity is caused by other volatile elements as well as CO_2 and that some unknown proportion of calcium may be related to the gypsum produced from ashing.

Although similarities exist between the calcium and magnesium profiles (Figure 8.12), it is very apparent from their ratio that their variation is not stoichiometric (Figure 8.11). In all but sample 1 of the Shallow Seam, where there is proportionately more calcium, the ratio is, however, identical and a common source, calcite and perhaps some ankerite being present. XRD evidence from both coal ash and cleat indicate calcite to be the predominant carbonate. Sample 1 is probably calcite only, with no minor additions of ankerite.

The Yard Seam is complicated by the high detrital contribution to samples 5 and 7. Magnesium exceeds calcium and analogies with the mud-rocks suggest a clay source for the magnesium, perhaps in chlorite or exchange sites in the mixed-layer clay. Calcium is reduced as is predicted from the poor cleat development in coals of a high detrital ash content (Figure 8.14). Sample 6, representing the 'average coal', shows a ratio comparable to that of the Shallow Seam and a cleat carbonate site is again suggested. This is most probably calcite although the presence of ankerite cannot be ruled out from the iron and CO_2 evidence. XRD indicates calcite and ankerite present.

Sample 11, at the base of the Park Seam, shows an excess of magnesium. The ash content is high and XRD shows chlorite, mixed-layer clay, but no carbonate, to be present. The ratios of the remaining three samples show magnesium to be higher than at either of the Lea Hall seams and

ankerite is suggested as the predominant carbonate and identified by XRD. The ratio in sample 9 is higher than for ankerite, and manganese reaches its highest value in this sample. The carbonate is siderite in addition to cleat ankerite.

The Eight Feet Seam has similar ratios and is roughly comparable with the Park Seam. Although sample 14 has a high detrital clay content resulting from the intraseam dirt band the MgO to CaO ratio is not notably increased and is comparable to the overlying low ash sample 13. The very fine nature of the dirt band samples may have precluded chlorite and a very degraded illite leached magnesium, if ever held, from the mixed-layer clays. Ankerite is again the predominant carbonate. Although calcium and magnesium profiles are similar, total iron does not always follow the same path indicating diversity of origins.

Manganese is found in only one Lea Hall sample, 4, which has the highest carbonate content. It is slightly higher at Littleton where substitution for iron in ankerite increases its level. It is highest in the siderite rich sample 9.

It is interesting to note the difference between the cleat mineralogy of Lea Hall and Littleton collieries. Calcite and subsidiary ankerite is found at Lea Hall and ankerite at Littleton. This apparent absence of available iron during late diagenesis is supported by XRD and optical study (Cleat section). Further differences in the ground water composition are seen in higher Mg to Ca ratio (Table 4.2), the greater range in cleat minerals at Littleton and in trace element levels, showing that the ground waters were chemically distinct. The source of the metals may be the associated mudrock strata, leached by aggressive ground waters. With specific reference to the calcium and magnesium levels, it is interesting to note that the average calcium values for

the mudrocks (excluding the siderite 8R2) is very similar, 0.20% and 0.22% at Lea Hall and Littleton respectively. However, the magnesium levels are different, being higher at Littleton with 1.43% compared to 1.03%. The greater availability of magnesium may account for the predominance of ankerite at Littleton, or a reduced calcite level, although the ferrous iron averages are very similar.

Sodium and Potassium

Sodium exhibits a significant positive correlation with SO_3 ($r = +0.68$, 99% significance), and potassium with SiO_2 ($r = +0.96$), Al_2O_3 ($r = +0.96$) and ash ($r = +0.95$). The potassium distribution is explained by the detrital clay fraction represented by illite and perhaps a minor contribution from muscovite and alkali feldspars. The correlation with the losses is explained by the highly significant correlation with ash content and hence the moisture content of the clay minerals. A detailed description of the potassium distribution as in a clay host is given in the section on total silica and aluminium. Similarities between the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio, whole rock K_2O and the ash percentage indicates a detrital origin of the illite. There are exceptions in samples 2 and 9. These variations have been previously explained, 9 in terms of the original detrital K_2O to Al_2O_3 ratio only slightly diluted by subsequent diagenetic kaolinite, and 2 by enhanced kaolinite dilution of the original illite.

The sodium distribution is somewhat more complex. The sources are diverse and not totally understood. Some sodium is held in the clay mineral structures. Additional small amounts may be located in any minor plagioclase feldspar, most probably albite (Fellows and Spears, 1978). However, sodium is significantly correlated with sulphate and a further source must be postulated. This is likely to be pore water sodium. It has been demonstrated in the section on water-soluble elements, that

Na and Cl are major elements in both the ground water and water-soluble extracts from both the coal and mudrocks. It has been demonstrated that chlorine is lost with plasma ashing (Gluskoter, 1965) and that SO_3 becomes the major anion (Fellows, 1979; Ph.D.), originating from oxidation of organic sulphur (Frazer and Belcher, 1973). Miller et al. (1979) found both Ca and Na associated with SO_3 . Such an origin would explain the presently found Na to SO_3 relationships. Using the water-soluble sodium values, grouped as the coal ash samples were, this source of sodium may be calculated as a proportion of the total. The results are not unequivocal. Although most whole coal sodium values exceed the water-soluble data, this is not always the case (Table 8.8). The discrepancy may be explained in four ways. The sodium analysis of the original coal ash may be incorrect owing to the very small amounts of ash available. Any organic matter remaining may give rise to dilution errors. Secondly, discrepancies may arise from the water-soluble sodium analysis although this seems unlikely owing to the systematic through seem variations and its explanation in terms of chloride (Water-Soluble Element section). The third possibility is that in grouping the coal ash into combined samples, that the ash weight from each sample was not proportional to that of the original mineral matter. This may be so but unlikely to explain the range of variation observed. The final possibility is that some sodium was lost during the ashing process. Two samples, 7 and 14, were analysed for sodium on both high temperature (390°C) and low temperature 'plasma' ashing. The results indicate a loss of sodium using the latter method although these results are not beyond suspicion (Table 8.8).

Where possible, the water-soluble sodium contribution has been subtracted to give that associated with the mineral matter. These

adjusted values are comparable, when the values are high, with the ash, silica, alumina and potassium profiles in the Yard Seam. The correspondence in the Eight Feet Seam is also close with the exception of sample 15. XRD shows no detrital clay component for this sample. In the Shallow Seam the sodium profile corresponds to that of potassium and may well be held in clays. In the Park Seam the pattern correlates strongly with that of sulphate even after adjustment.

Phosphorous

Phosphorous in the coal ash shows no significant correlation with any of the oxides analyses and the strong positive correlations found with carbonates in the mudrocks is not evident. The correlation of phosphorous and carbonate is thought to be due to diagenesis under similar geochemical environments (Spears, 1964). Where phosphorous is held in diagenetic minerals, they are of early origin. When values are low then a diagenetic source may be postulated (Spears and Amin, 1981). In the coal samples most carbonate is late diagenetic and found in the cleat. This distribution may obscure any early diagenetic similarities between phosphorous and carbonate formation. Cleat phosphate is rare.

There are three marked phosphorous peaks which are far higher than the background (Figure 8.15). These are in samples 2, 14 and to a lesser extent 10. The background levels are fairly constant and may be detrital phosphorous. Although higher levels have been postulated as diagenetic, they may represent fish scales as found by Fellows (1979, Ph.D.) and indicative of life supporting waters. The normative recalculation scheme of Nicholls (1962) assumes that phosphate is held in hydroxyapatite. Samples 2 and 14, however, have insufficient calcium to satisfy the available phosphorous in this form. XRD examination of the ash samples indicates that carbonate is present but is low. Consider-

able substitution can take place in the majority of sedimentary apatite. Calcium may substitute for phosphate (not in the present case) and sodium and magnesium for calcium (McClellan and Lehr, 1969). In the Eight Feet Seam the magnesium to calcium ratio is very similar in sample 14 to that of the low phosphorous sample 13. In the Shallow Seam, the ratios are very constant despite the high phosphorous level in sample 3. Calcium nor magnesium appear to be substituting for phosphorous. The sodium values with their inherent problems do not provide adequate evidence for substitution. Only the sample 10 peak, which has sufficient calcium to form hydroxyapatite, also shows an outstandingly high sodium level. It appears that substitution may be very complex.

It is interesting to note that in sample 14, there is a correlation with a detrital input clay input. As calcium and magnesium ratios are fairly constant a detrital source, fish scales perhaps, may be inferred but this does not hold for sample 2. XRD evidence, together with additional major and trace element analyses of individual samples completed subsequent to this study, show SS3 (2), 8S9 and 8S10 (14) to contain goyazite, a complex strontium, aluminium sulphate. This mineral is probably diagenetic.

Of the background levels, 0.01 to 0.08%, the likely host is hydroxyapatite. This may be diagenetic, originating in organic matter (Spears and Amin, 1981).

The Relative Contributions of Detrital and Diagenetic Minerals in Coal Ash and Associated Strata

Diagenesis is quantitatively unimportant in mudrock successions in terms of new minerals and alteration of pre-existing minerals. The clay mineralogy is altered little by diagenesis in the present rocks and reflect more closely their weathering history and depositional environ-

ment. Diagenesis is generally restricted to exchangeable and water-soluble cations (Spears, 1973, 1974) in response to changing ground water composition and ion exchange for sulphide precipitation (Pearson, 1979). Quartz is a major detrital mineral which varies with depositional energy (hence grain size) and may be absent from the intraseam dirt bands deposited under tranquil conditions (Wanless et al., 1969). Feldspar is a minor constituent. Anatase, follows the trend of quartz but is apparent not excluded from the finest fraction. Of the diagenetic minerals, normative pyrite dominates the sulphides and calcite, ankerite and siderite represent the carbonates. Locally, the diagenetic minerals are important, pyrite nodules (8S10a) and siderite (8R2) being found, but rare in most samples or succession averages. Fine disseminated pyrite is common but not quantitatively important. Calcite and ankerite is rare except where cleat over-runs the adjacent coal. Apatite is diverse in origin and may represent re-worked igneous or metamorphic material (Deer, Howie and Zussman, 1962), fish scales or organic matter decomposition and diagenesis (Spears and Amin, 1981). The latter seems most likely in the present samples but a detrital contribution cannot be wholly dismissed.

All the detrital minerals can be found in the coal ash but are reduced considerably in level owing to the near still-stand conditions associated with coal vegetation accumulation. It is in the diagenetic minerals that the coal mineralogy differs from that of the associated strata. The early diagenetic minerals, disseminated framboidal pyrite, siderite concretions and apatite are found. As a proportion of the mineral matter, their abundance is slightly increased when compared to the mudrocks. The later diagenetic minerals, however, completely dominate the coal mineral matter. Sulphides, pyrite predominantly, but

also marcasite, sphalerite and galena are widespread and sulphur values are an order of magnitude higher than in the mudrocks (although some may be organic in origin). Kaolinite is the major clay mineral and found in coal pores and cleat like the sulphides. Quartz is not an important diagenetic mineral but is found both early and late. Ankerite and calcite are found in the cleat at Lea Hall (predominantly calcite) whilst ankerite is dominant at Littleton Colliery. Mg and Ca are enriched in the coal ash, the latter by two orders of magnitude reflecting the importance of the cleat.

A generalised comparison can be made between the coal and associated strata in terms of detrital and diagenetic minerals. With the exception of the siderite rich SR2, the maximum diagenetic component is 6.8% (by weight) and the majority of samples are considerably lower. An average has not been taken because the samples taken do not represent the whole Coal Measures non-organic suite. As normative recalculation was not possible for the coal ash, generalisation can be made, but which will over-estimate the diagenetic fraction. In the low ash coals, kaolinite was assumed the only clay and quartz was calculated on this basis. SO_3 was assumed diagenetic, though some is organic and most may be a L.T.A. by-product. Where the ash content is low, the over-simplifications are likely to be small. As the detrital influence increases, the assumptions become less valid, especially where detrital clays will severely affect the calculations. The relative proportions are, however, interesting. Diagenetic minerals account for approximately 70 to 95% of the coal ash. It is evident that in the coals with a low detrital ash content that diagenetic minerals account for an increase of some 1.5 orders of magnitude over the mudrocks. It is the cleat minerals that make the most significant contribution. As a consequence, a more detailed study has been made into the cleat minerals.

Conclusions

- 1) The coal minerals have many sources, variable in importance. The inorganic matter held in vegetation is generally small but varies with vegetation type and abundance. Detrital and diagenetic minerals play the major, but spacially variable, roles.
- 2) Coal petrology nomenclature defines those minerals associated with the organic matter during its formation as 'syngenetic', those deposited later as 'epigenetic'. Coal users terminology are 'inherent mineral matter', being that material not separable from the coal (predominantly syngenetic) and that which is removed with washing, the 'adventitious mineral matter' (predominantly epigenetic). The present work defines minerals on a geological basis of detrital and diagenetic.
- 3) Coal type can control the mineral matter content. Bright coals are low in ash, vitrain about 1.2%, clarain being slightly higher. Durain, which often includes more detrital material may have 6 or 7% and fusain, which can be mineralised, may hold from 4 to 30% ash. As no attempt was made to separate lithotypes, nor cleat from the early diagenetic and detrital ash, this could not be tested in the present investigation.
- 4) Mineral investigation was made by XRD after L.T.A. and the following minerals were identified in order of decreasing occurrence: gypsum, pyrite, kaolinite, ankerite, quartz, calcite, apatite (including goyazite) and sphalerite, illite and M.L.C., marcasite, chlorite, anatase and siderite. Gypsum is a by-product of the L.T.A. Local and regional differences exist in the coal mineralogy, as well as major through seam variations.
- 5) The major (world-wide) mineral groups are sulphides, clays, quartz and carbonates.

- 6) Of the sulphides, pyrite is dominant. It occurs as early diagenetic framboids and late diagenetic cleat. Sphalerite and marcasite are rare at Lea Hall, sphalerite being abundant in the Littleton Park Seam, and marcasite in the Eight Feet Seam. Galena is rare and found only at Littleton Colliery. The nodules and cleat are readily separable in coal processing, the framboids are not.
- 7) The clay group consists of illite and M.L.C. (degraded illite), minor chlorite and kaolinite. All are detrital and their abundance increases adjacent to floors, dirt bands and the roof sections, being similar, though probably finer grained, to their mudrock counterparts. M.L.C. is high in the coal samples adjacent to the dirt bands. Kaolinite is also diagenetic, obviously different from the detrital kaolinite in its XRD peak form. It is the most widespread clay.
- 8) Quartz is a minor component having a similar trend to the detrital clays but reduced in the fine fraction by its grain size. There is occasional evidence of diagenetic quartz both early (Y1) and late (occasional Shallow Seam cleat).
- 9) The carbonates include calcite, ankerite and limited siderite, their abundance being thus the reverse of the mudrocks. This is a reflection of calcite and ankerite being concentrated in the cleat, the former predominating at Lea Hall, the latter at Littleton. Siderite is formed as small early diagenetic nodules in three samples.
- 10) Of the remaining minerals, low levels of phosphates are found, usually apatite, though rarely goyazite. Only three occurrences of anatase have been identified, associated with high detrital ash contents.

- 11) The XRF investigation was hampered by low ash contents. Problems arise because L.T.A. never completely removes all organic matter and fixes gypsum from organic matter oxidation and calcium from pore water and carbonate decomposition. Sodium sulphates are also produced, the Na originating from pore waters. Sulphides, too, may be partially oxidised, though the proportion is small. In the absence of sufficient sample to make the necessary allowances, the present work is semi-quantitative. Detailed XRD investigations provide a good back-up for mineral identification.
- 12) Total Si, Al and K are strongly correlated showing a predominantly clay (illite) association. The quartz content could be indirectly calculated if the composition and abundance of the clays are known (XRD) and the Al equivalent to P_2O_5 (phosphate) is accounted for.
- 13) TiO_2 can be used, as in the mudrocks, to be a measure of sedimentation rate. It indicates that detrital sedimentation, especially association with intraseam dirt bands continues, albeit reduced, after a coal forming environment is re-established. Although these dirt bands are fine grained, they are rapidly deposited.
- 14) In the almost complete absence of chlorite, total iron is accounted for by ankerite and pyrite, and a few localised occurrences of siderite.
- 15) Reversing the mudrock trend, CaO was higher than MgO by an average of 3.8. This is attributable to the importance of cleat carbonates. MnO, usually very low, was found to be marginally higher at Littleton Colliery, reaching a peak in the siderite in sample 9.
- 16) The Na distribution is complicated in having a clay location, and a water-soluble ground water origin, some of which can be fixed as sodium-sulphate by L.T.A.

- 17) The positive relationship between P_2O_5 and Ca seen in the mudrocks is not evident in the coal ash. This is because of the overriding effect of late diagenetic cleat mineralisation which would mask and early diagenetic trends. Overall levels are low but three P_2O_5 'peaks' that could not be balanced by Ca were found to be goyazite.
- 18) The role of diagenesis is only locally important in the mudrocks, usually being restricted to sulphide and carbonate precipitation in early diagenesis. Diagenetic minerals, however, dominate the coal samples where the detrital mineral matter contribution is low. They are spacially variable, early diagenesis being represented by pyrite framboids and siderite nodules (like the mudrocks). Cleat minerals, however, formed in late diagenesis, completely dominate the mineralogy.
- 19) Based on XRF proportions, the diagenetic minerals account for 70 to 95% of the coal ash compared to a maximum 6.8% (excluding 8R2) and a much lower mean in the mudrocks. This increase in diagenetic mineralisation in the coals is largely the function of cleat minerals, rarely if ever found in the mudrocks.

CHAPTER 9CLEAT

Cleat is the name given to the small-scale jointing and faulting that occurs in coal. They are much more highly developed than joints found in all other rock types. Although the origin is not entirely clear, cleat is analagous to 'microjoints' found in finely banded sedimentary rocks (Price, 1966). Cleat or 'slynes' (Williamson, 1967) are to be found in all coal types increasing in frequency to a maximum in low-volatile bituminous coals (Ting, 1977).

Cleat fractures are more or less parallel and their frequency per coal type and thickness is systematic. Often, a conjugate joint set, cross cutting at virtually 90° is found. The major cleat which is most continuous and well developed, is termed the 'main' or 'face' cleat, whilst the conjugate set is the 'back' or 'butt' cleat. The direction of the main cleat is generally fairly constant, being north-west in the Northern Hemisphere (Macrae and Lawson, 1954). This is a generalisation and variations may be found within one colliery (Dron, 1925). The direction is important in mine planning as the fractures form inherent weaknesses. Conjugate cleat sets are used to determine pillar direction and coal mine 'rooms' in Alberta (Campbell, 1979), although in the U.K. coal cutting is often at an angle to the cleat to minimise uncontrolled face collapse. The frequency will affect the ease and feasibility of de-gasing coal prior or during mining, control pillar strength and determine the coal top-size (Ting, 1977).

Cleat fractures are mineralised and often show a paragenetic sequence of deposits depending upon the composition of the ground water and relative time of fracturing and re-activation. Bright coals cleat first and with a higher frequency. Cleat minerals are readily separated

in coal processing and as they play a major role in the coal ash content improve the coal quality and remove significant potential corrosive or pollutant sources. It may be feasible in a suitable economic climate to use some of the cleat minerals as a metal source (Hatch et al., 1976).

Cleat Origins

The origin of cleat is not totally understood. Like joints, they are consistently widespread and common. A summary of the early work is given by Macrae and Lawson (1954). Daubreé (1879) experimenting with sheet glass thought that torsion produced conjugate joint sets at 90° but Butcher (1920) showed that it was tension in the upper and lower surfaces of the glass. Kendall and Briggs (1933) suggested that east-west diurnal earthtides produced torsion and a predominantly north-west cleat trend in the northern hemisphere. The flexing of lithospheric plates due to latitude and great circle changes may produce joints (Hobbs, Means and Williams, 1976) but no constancy of direction is involved, but from the present work is not seen. The main cleat direction at Lea Hall is $N 20^{\circ}E$ and at Littleton $N 10^{\circ}W$. Fellows (1979, Ph.D.) found a trend of $N 47^{\circ}W$ for the Yorkshire and Nottinghamshire coalfields.

Compression through overburden (van Waterschoot and van der Gracht et al., 1942) may control fault orientation but not joints (Price, 1966). Joints in young rocks led Kendall and Briggs (op. cit.) to believe that cleat is early formed but if they are compressional then maximum development will be at depth unless the rocks undergo plastico-viscous deformation. Isotope work on cleat minerals (Shieh and Suter, 1979) show mineralisation to take place near surface at low temperatures, probably with uplift and stress relief. For brittle fracture to take place the coalification process must have rendered the coal competent. A para-

genetic sequence of mineralisation shows multiple re-activations of cleat (Hatch et al., 1976) in which the coal type, cleat and mineral relationships change with time.

Campbell (1979) suggested that the constancy of cleat direction indicated that fracturing took place after rank imposition which often followed a different pattern. Price (1966) found that post compressional jointing probably dominates cleat/joint direction and is related to the orientation of the principal stress during the main tectonic phase. Rank may be retarded with pressure. Vertical shear joints, produced when the intermediate principal stress is vertical is unusual in the field Price (op. cit.). Price (1959) found that 'residual strain' existed after the stress was removed. The lateral stress dissipation is at a different rate to vertical gravitational and overburden stress. Consequently, with uplift there is a change in the pattern of principal stress with tensile stress due to horizontal extension of the beds being approximately half of the change in the gravitation load. Residual strain is released when tensile stress is equal to the tensile strength of the rock. Price (1966, p. 132) describes two variations in stresses which occur in horizontally bedded rocks as a result of uplift leading to the development of orthogonal sets of tension joints. Ting (1977), Campbell (1979) and Shieh and Suter (1979) believed that strain release is one of, probably the major, causes of cleat formation. Campbell (op. cit.) and Nicholson and Hough (1967) found that cleat and associated rock jointing trends are similar. Williamson (1967), however, suggested that normal joints have a relationship with structure, whereas the associated cleat did not, suggesting an independent cause.

Ting (op. cit.) discussed other causes of joint formation in coal, namely through dehydration and devolatilisation. When deposited, peat is 95% moisture which is lost with compression. With intergranular

slippage and cellular collapse, the fragments re-arrange. Vertical compression is dominant until the brown coal stage (c.60% moisture), then vertical and horizontal changes take place and fractures may open in the direction of least compressive stress. Coalification similarly leads to devolatilisation. Such processes may be important in coals below the bituminous rank but higher rank may remove early formed fractures through recrystallisation (Price, 1966). It is conceivable that weaknesses may be reactivated but stress directions may change. In the present coal, stress relief is the most likely cause of cleat development.

Cleat Frequency

The cleat frequency is defined as the 'number of fractures per unit length' (Macrae and Lawson, 1954). Considerable variation is found in different coal types. The frequency was measured on the most highly developed cleat in the sample, usually vitrain bands (unless a great range was found) and given in Table 9.1. Some samples had one or no cleat, as in Y2, 8S10b - both high ash coals, and 2.6, strengthened by layers of early diagenetic siderite nodules and sheets. Dull coals are usually more massive and have a low frequency as seen by SS3 (0.09) and 2.3 (0.08). Maximum values are found in bright coals (often >3.00) although the variation is often considerable. The highest value is found in a thin vitrain band within a dull coal portion of 2.9 (6.00). Banded coals usually have a frequency intermediate between these extremes. Macrae and Lawson (op. cit.) found different joint intervals between coal types and associated strata with dirty coals and carbonaceous dirt having intermediate values. If the mudrocks have low tensile strength, as in I.D.2.11 which has no quartz, then movement is seen in listric surfaces rather than fractures. The cleat frequency is similar in the

present samples to those of Macrae and Lawson (op. cit.). It is evident, however, that the frequency is related to bed thickness as well as coal type.

Influence of Bed Thickness

There is an inverse relationship between cleat frequency and the lithotype thickness also observed by Harris et al. (1960). Durain in banded coals is more highly cleated than massive durain (8S4, 8S5, 8S6). The influence of bed thickness to joint frequency was attributed by Price (1966, p. 144) to frictional forces between adjacent beds. In lithotypes of difference competence, tensile stress in the vitrain will reach a point of failure and a joint will form. This will open until all the stress is released. However, friction with adjacent beds will prevent unlimited opening and consequently, after a set distance, failure will again occur. The distance between cleat will be related to the sum of the traction forces between the lithotypes.

$$\text{Hence} \quad F = \sigma_T \cdot Z$$

F force
 σ_T original stress
 Z bed thickness

For a given stress, therefore, a bed twice as thick will increase the frictional force resisting slippage and the traction force must act over twice the distance, thus doubling the fracture interval. The distance a cleat will dilate is also related to the cleat interval. Major cleat fractures cross cutting all lithotypes are therefore rare but wide, especially when compared to the frequent but negligible displacement found in thin vitrain bands. Thus it can be seen that the cleat frequency cannot be related directly to coal type but also to bed thickness; hence the great variation seen in Table 9.1.

Physical Properties of Coal Types

It is evident from the above discussion that the different coal types have different susceptibilities to fracture. The paragenetic sequence of mineralisation makes it clear that cleat formation takes place at different times in different lithotypes.

Maceral Groups

Vitrinite has an angular or conchoidal fracture and the surfaces are glassy or pitchy. From its degree of fissuring it is obviously brittle (Stach et al., 1975). Alpern (1963) proposed a 'fragility index'. Vitrinite is brittle and easily splinters. Where coal has >15% volatile matter (as at present) it exhibits 'brittle hardness' (Heinze, 1958). Exinite varies; resinite is similar to vitrinite but cutinite and sporinite are very tough. Cracks are seen to stop at spores. "Spore exines in durite rich layers act as iron rods reinforcing concrete" (Stach et al., 1975). Inertinite is generally harder than vitrinite.

Microlithotypes

If they are bi- or trimaceral, the strength of microlithotypes is greatly increased. Vitrite is very brittle. If exinite rich, both clarite and durite are very strong, the latter being stronger for a given exinite content. Thick durain (without fusain) with a high exinite content, is consequently very strong and hence, rarely cleated. It is not unexpected that bright coal develops more cleat.

Vitrite → Clarite → Durite → Mudrocks (increasing strength)

Stach et al. (1975).

Further factors leading to greater strength are:-

- 1) Absence or poorly developed sedimentation planes.
- 2) Thickness of heterogeneous layers in a seam.
- 3) Syngenetic (detrital or early diagenetic) mineral inclusions.

(Stach et al., op. cit.).

Cleat Mineralogy

An XRD investigation into individual cleat samples, and comparisons with whole coal L.T.A. were used to identify the minerals present. S.E.M. and T.E.M. were used to investigate the form and mineral relationships together with thin section (employing carbonate staining) and hand specimen observations. Chemical study was by atomic absorption spectrophotometry, both 'flame' and 'furnace'. Trace element studies in cleat samples are included in the trace element chapter.

Minerals Present

The following cleat minerals were identified in varying quantities:

- 1) Sulphides; sphalerite, marcasite, pyrite, galena.
- 2) Silicates; quartz, kaolinite.
- 3) Carbonate; ankerite, calcite.
- 4) Phosphate; apatite. Follow-up work by Mr. S. Reynolds shows goyazite present in addition, possibly in the cleat.

Cleat minerals identified and comparisons with L.T.A. are given in Table 9.2. The selected cleat samples need not necessarily cover all the types of minerals present but the range of samples was large and the major phases identified. The L.T.A. samples may swamp trace levels of minerals with other phases or types. The XRD investigation is not quantitative. The coal mineral matter section covering XRD investigation gives a semi-quantitative estimation of the importance of diagenetic minerals in the coal ash. Different ash weight and mass absorption coefficients mean that XRD investigations are only qualitative. Using the peak height in the L.T.A. samples, the minerals were designated 'high', 'medium', 'low' and 'trace'. This may be internally consistent but cannot be used to compare between samples. Problems arise in distinguishing early diagenetic minerals from those in the cleat (Table 8.1 and 9.2).

Between Colliery Comparison:

The major groups, sulphide; silicate, carbonate and to a lesser extent, phosphate, are found in both collieries. Littleton Colliery, however, shows more diversity. Pyrite is the most abundant sulphide and is found in both collieries. Marcasite is far less common but its frequency is higher at Littleton. Sphalerite is only found here, in the Park Seam, and once in the Eight Feet Seam. Galena is found in individual cleat samples from the Park Seam. Occurrences may be more common in the L.T.A. but are swamped by other mineral 'interference'.

Kaolinite is widespread, found in all samples. It is clearly different in form (XRD, TEM, SEM) to detrital kaolinite. Quartz is rare, being restricted to the Yard (Y7, Y9) and Park (2.2) seams as positive identifications.

The carbonates, calcite and ankerite, are more abundant in terms of weight than kaolinite but are more localised. At Lea Hall, calcite is dominant over ankerite. Carbonates are rare in the Yard Seam. In the Shallow Seam, SS1 and SS2 have calcite only, the remaining samples (with the exception of SS3 and SS4) being calcite and ankerite. At Littleton Colliery, ankerite predominates. In the Eight Feet Seam a 'trace' of calcite is found in 8S11 and 'low' values in the Park (2.3 and 2.12). Phosphates are uncommon at Lea Hall but more common at Littleton, and goyazite has been identified in SS3, 8S9 and 8S10.

Yorkshire, Nottinghamshire, S. Wales and U.S.A.

The major phases are all present. Fellows (1979, Ph.D.) found pyrite, quartz, kaolinite, ankerite, calcite and baryte, of which ankerite was the most abundant. Macrae and Lawson (1954) found pyrite, kaolinite and calcite common in Yorkshire coals. King, Maries and Crossley (1936), conducting chemical analysis, found calcite and ankerite

(the latter probably early diagenetic) in S. Wales coals. A summary of cleat mineral investigation into British coal is given in Watt (1968).

Most modern cleat investigation has been carried out in the U.S.A. Ball (1934) found pyrite, kaolinite and calcite the dominant cleat minerals in Illinois coal; as did Gluskoter et al. (1973), Harris et al. (1979), Hatch et al. (1976) and Hughes (1971). Shieh and Suter (1979) found kaolinite and calcite to be the major phases. Sphalerite was identified by Gluskoter et al. (op. cit.), Ruch et al. (1973, 1974), and Gluskoter and Lindahl (1973), galena by Ruch et al. (op. cit.) and quartz by Hoehne (1949, 1959).

Scanning Electron Microscope Study of Pyrite and Kaolinite

S.E.M. photographs and semiquantitative chemical analysis was made of Shallow and Yard Seam cleat samples using a Cambridge Instruments S4-10 S.E.M. The machine was operated by Dr. K.G. Saunders of the C.E.R.L. (Leatherhead). The cleat was composite, being made up of kaolinite and pyrite.

Plate 9.1, Shallow Seam, shows a section of pyrite surrounded and overlapped by kaolinite flakes indicating pyrite followed by kaolinite. The pyrite appears to be massive but with a well developed surface ornamentation of rounded and angular blebs and elongated lath-like structures. The kaolinite is well crystallised showing a good euhedral form. There appears to be two major orientations, the kaolinite with c-axes normal to the photograph surface, and the basal sections parallel to the photograph surface. The latter probably represents kaolinite deposited against the cleat wall. This layer is relatively thin. The majority of kaolinite crystals are normal to this and although there are variations, generally trend left-right across the photograph. This may indicate the direction of ground water movement. The kaolinite flakes are clearly terminated against the pyrite.

E.D.A.X. (Energy dispersive analysis of X-rays) microanalysis shows concentrations of trace elements in the pyrite surface ornamentation. Zinc and copper are to be found in the blebs. Copper is also found in the main pyrite sample. The laths are iron and sulphur (pyrite) and contain other light elements. Their concentrations, however, are too small to pick up against the background.

Plate 9.2 is a close up of the pyrite surface. Plate 9.3, a pyrite sample from Y7, shows subhedral pyrite forms. Both pyritohedron and cubes can be distinguished but the majority of crystals show no particular form. Surface ornamentation varies from smooth, with blebs and laths, to a well developed fine, uneven, surface relief.

Plates 9.4 and 9.5 show the small scale surface detail of pyrite. The ornamentation is complex. Plate 9.4 shows a preferred surface ornamentation, suggesting perhaps the direction of cleat water movement, or the surface relief of the coal fracture surface.

Plates 9.6, 9.7 and 9.8 taken of Shallow Seam cleat, show kaolinite crystals. All show good to perfect crystal form. It will be noted, especially from 9.8, that there is considerable porosity between kaolinite books, and sometimes within them, even though mineralisation is apparently completed. Such porosity may form pathways for the migration of recent ground waters.

Microscope Photographs.

Using a camera fitted to a reflecting light microscope, low magnification photographs of Yard Seam Y7 cleat show pyrite and carbonate.

Plate 9.9 shows an overall view of the cleat minerals. Most notable are the variations in cleat surface expression within the pyrite. This varies from coarsely crystalline to fine crystalline and also concentric textures. This difference in form may be related to the cleat wall micro-relief.

Plate 9.10 shows a close-up of the coarse pyrite. It is clearly cubic and occasional pyritohedra may be seen. Crystal form is undoubtedly euhedral. Large crystals indicate slow crystal growth in response to stable ground water concentrations.

Plate 9.11 is a close up of the concentric pattern. This may follow similar relief on the coal surface or be an expression of sequential deposition. If this is so, then conditions of pyrite deposition were different from those which allowed euhedral crystals to form. Alternatively, the form may indicate differences between the lithotypes forming the cleat wall and differences in physical composition and perhaps in time of cleat formation.

Kaolinite Form - T.E.M.

A comparison of the forms of kaolinite crystals were made between cleat and mudrock samples. Pure kaolinite cleat samples were selected and broken down in distilled water. Whole rock samples were used for the mudrocks. The cleat samples show well formed crystals (Plate 9.12), whereas in the mudrocks, the clays are degraded and individual types are difficult to distinguish (Plate 9.13).

Kaolinite Crystallinity

The kaolinite crystallinity was calculated from the peak shape (XRD, 001 peak) after Schultz (1960). Cleat samples are seen to be well crystallised. The crystallinity of the L.T.A. samples is reduced slightly through dilution by poorly crystallised detrital kaolinite found in the mudrocks and detrital coal fraction. Further investigation into kaolinite crystallinity is found in the Clay Minerals section. Crystallinity ratios from cleat and L.T.A. samples are given in Table 9.3.

Carbonate Mineralogy

XRD and stained thin sections were used to distinguish carbonate minerals. Calcite was identified by a peak at $29.43^{\circ}2\theta$ ($d\ 10\bar{1}4$) and ankerite at approximately $30.84^{\circ}2\theta$ (slight changes with chemistry) indicating a ferroan dolomite. Peak positions were calculated for cleat scrapings and L.T.A., and together with those of Fellows (1979, Ph.D.), are given in Table 9.4. Similarity of composition shows similar ground waters from the central (Cannock) to eastern (Yorkshire and Nottinghamshire Coalfields) England before uplift and erosion separated the coalfields. It must be noted, however, that small chemical differences will not be identified.

Chemical Analyses of Carbonates

Selected thick cleat carbonates were separated and taken into solution in dilute HCl and analysed on A.A. for Ca, Mg, Fe and Mn. The elements were recalculated as percentage carbonate (Table 9.5) and plotted on triangular diagrams (Figure 9.1). Fellows (op. cit.) found the composition of both calcite and ankerite to be more constant than in the present study (Table 9.6). Much of the variation in the present samples is due to composite carbonate cleat of differing proportions. A few samples (Y1, 2.4, 2.8) appear to have high iron levels. This is not easily explained unless the composition of the ground waters change considerably or small amounts of siderite have also been brought into solution. The ankerite samples from the Eight Feet Seam show least chemical variation and are very similar to those of Fellows as does the composition of the 'purest' calcite from SS2. Nelson (1953) considered 'ankerite' to cover a range of chemical compositions and not a particular precise composition. Included in the triangular diagrams is carbonate data from the major British Coalfields (figure 9.3) along with a

carbonate classification (Figure 9.2) (Pringle and Bradburn, 1958).

Indiscriminate carbonate dissolution may lead to a variation in carbonate chemistry.

Paragenetic Sequence of Cleat Mineralisation

From hand specimen and thin section evidence the following order is distinguished:-

Sulphides, Silicates, Carbonates (Ankerite, Calcite). The position of phosphate is not known but diagenetic phosphate is formed under similar geochemical conditions as carbonates (Krauskopf, 1979). Further subdivisions are difficult because of the low concentrations. Thus sphalerite, marcasite and pyrite may be found in the same cleat but not individually distinguished by eye. Galena has only been found in monomineralic cleat.

The relative solubilities of the sulphides depend upon the HS^- activity. As this increases, it is difficult to distinguish the order of sphalerite from pyrite. At low levels the order of relative solubility is galena, sphalerite then pyrite (Spears and Rice, 1973).

Quartz is rare and monomineralic although literature evidence suggests that it pre-dates kaolinite (Hatch et al., 1976). Calcite post-dates ankerite (thin section evidence). As kaolinite is sensitive to environment, alkaline solutions precipitating carbonates would probably destroy it unless separated (Dunoyer de Segonzac, 1970). Kaolinite cleat is essentially monomineralic and hence may have been isolated from later ground waters. A similar order was found in the Yorkshire, Nottinghamshire Coalfield by Fellows (1979, Ph.D.) though ankerite may overlap kaolinite in time and baryte was found in a few samples. No sphalerite, marcasite, galena or phosphate was identified. Hatch et al. (op. cit.) identified in Illinois coal a wide range of pyrite precipitation over-

lapping that of sphalerite, then the following minerals:-

Pyrite, sphalerite, pyrite; quartz, kaolinite; ankerite, calcite. Hughes (1971) found contemporaneous deposition of pyrite and kaolinite.

The sequence reflects changing ground water geochemistry in response to relative insolubility of metals and availability of an anion source, most probably from within the coal. The anions S and CO_3 may have been evolved from the organic matter into the ground water during different stages of coalification.

Relative dating of Cleat by Mineralogy

With changing cleat chemistry with time, the order of fracture of coal types can be ascertained. Early cleat will have early minerals, predominantly sulphide rich, hence the first cleat at Littleton are monomineralic galena filled fractures. Successive reactivation of the cleat leads to polyphase deposition, 'crustiform banding', of parallel development from the walls outward into mid-cleat where subsequent opening often fractures the central suture. Mineralogy may therefore be used to back-up the physical evidence for cleat formation order.

Coal Type - Cleat Association

The observed cleat abundance (peak height) can be applied to coal type. This is not conclusive evidence because cleat may develop in a specific coal lithotype (e.g. a thin vitrain band) whilst the coal type description is an average of the sample. Sulphides are predominantly found in the bright coal. The other groups are variable.

Similarly the frequency of occurrence can be investigated.

1) The occurrence of all cleat groups decrease in the order:-

bright, bright banded, dull band and dull, but so do coal types.

Re-expressed as a function of coal type occurrence, there is a

slight overall decline. It must be noted, however, that the abundancies cannot be directly compared between samples, and coal type is still an average composition.

- 2) Sulphide occurrence declines from bright to dull banded.
- 3) Kaolinite is fairly constant but decreases from bright to dull if the coal type frequency is taken into account.
- 4) Carbonate increases from bright to dull banded if frequency of coal type is accounted for.
- 5) With only 5 dull coals, their significance is difficult to assess.
- 6) Similar early diagenetic minerals can lead to complications.

L.T.A. Colour

The L.T.A. colour (see L.T.A. section) is related to mineralogy. As the diagenetic minerals are dominant in the coal ash the colour may be related to coal type. The darker the colour, the higher the pyrite content. White ash is usually quartz, kaolinite and gypsum rich (Table 5.1). Bright coals are thus predominantly pyrite rich, banded coals are dominated by kaolinite and carbonates, whilst dull coals exhibit a range, perhaps because detrital mineralogy may be more important here. The detrital component may mask the effect of cleat mineralisation.

Thin Sections

Where the composite cleat was thick and well developed, sections were cut for microscopic investigation to determine the paragenetic sequence, crystal form and size, and the cleat wall development. Crustiform banding indicates successive depositional phases. Mineralisation is often found to be symmetrical about the centre of the fracture, indicating weakness along the central suture, formed where crystals growing inwards from the walls have interlocked. The cleat walls would act as precipitation

nuclei or the indentations would be a trap for transported crystallites. Later reactivation of a previously sealed cleat may show a markedly different mineralogy indicating a changing ground water composition. A few samples do not have symmetrical mineralisation, showing that the weak point is sometimes the boundary between the minerals and the wall of the cleat.

Thin sections were taken from the carbonaceous siderite 8R2, lying immediately above the Eight Feet Seam. Here, cleat can be traced out of the coal into the siderite. Sample Y7, a predominantly bright coal, shows the most highly developed cleat (by weight). It is dominated by the sulphide stage, especially pyrite. Carbonate minerals (ankerite) are also present. Other samples were taken from a run-of-mine Yard Seam cleat (C.E.R.L. supplied) and 2.6, which includes both early diagenetic siderite (after pyrite) and ankerite cleat. Where carbonates were present they were etched and stained with a potassium ferricyanide and alizarin red S mixture (Dixon, 1965), giving calcite a red, and ankerite a turquoise stain.

Plate 9.14, taken from 8R2, clearly shows the cleat to be dilational as the sides key perfectly together. This is indicative of tension joints. Unfortunately, in this and other plates, the stains show poorly owing to the great contrast in brightness between the rock and minerals, the latter being over-exposed by the automatic camera. Ankerite and calcite are present. The former are small crystals, in the range of 0.01mm. Small groups of calcite have replaced the former carbonate to give larger crystals, approximately 0.1mm in diameter.

Plate 9.15 shows the same cleat with large crystals (vague orange colour) being surrounded by finer, blue, ankerite crystals.

Plate 9.16, although poorly exposed, shows earlier fine ankerite (here a green colour) being cross cut and replaced in the major vein by

calcite. The calcite vein appears colourless, and as occasional larger crystals in the ankerite cleat.

Also within 8R2, immediately adjacent to the coal seam, are thin (approximately 0.3mm) vitrain bands. These show well developed cleat (Plate 9.17) spaced at approximately 0.3 to 0.4mm intervals. The cleat is approximately 0.04mm wide, terminating abruptly at the limits of the vitrain. This demonstrates the difference in the strength and susceptibility to cleating of the various materials. The mineralisation is predominantly ankerite with calcite inclusions.

Plate 9.18 is another of these thin vitrain bands showing displacement of the cleat by thin layers of non-vitain material.

Although most cleat are dilational, a few show a limited lateral movement, as in Plate 9.19 from the siderite rich 8R2.

Plate 9.20 is taken from sample 2.6. This shows clearly the early diagenetic siderite clusters radiating from a central core. Occasionally (Plate 9.21) the core is of pyrite, indicating the limited availability of sulphur in early diagenesis. The cleat fractures (often as white cracks in 9.20) post-date the ankerite, and in the case of the curved fracture, are clearly influenced by the ankerite.

The relationship between pyrite and ankerite is clearly seen in the following series of plates from Y7 and the Yard run-of-mine samples. Within the coal, fracturing is more complex because of its far more brittle nature, and the dilational component is more difficult to identify in the major cleat.

Plates 9.22 and 9.23 predominantly show an early pyrite cleat, approximately 0.6mm wide. The major cleat has been re-activated and has an ankerite core (white crystals). The pyrite is very fine and individual crystals are difficult to recognise. The later ankerite is coarser, shown well in Plate 9.24, and may measure up to 0.2 by 0.1mm. The large

size suggests slow precipitation under near equilibrium conditions (Hatch et al., 1976). Neither phase show a preferred orientation and the form of the pyrite fracture may have controlled the direction of ankerite growth.

Multiple cleat reactivation during the pyrite phase is evident. Plates 9.22 and 9.23 show a fine stock-work of pyrite filled fractures. These have an angular pattern, some intersecting at approximately 90° , typical of conjugate joint sets, but terminated by the main cleat which must pre-date it. The veinlets are in the range of 0.02mm wide, some being narrower, and thin out to nothing away from the major cleat. Veinlets can be terminated by spores (Plate 9.25) indicating the greater strength of the latter material. Further evidence comes from multiple rafting of coal fragments from the cleat walls. A similar phenomena has been recognised by Hatch et al. (op. cit.). This is evident in Plates 9.25, 9.26 and 9.27. (this latter sample from the run-of-mine coal). Plate 9.25 shows two rotated fragments which were either rafted from the wall and then rotated, or represent material being carried within the cleat. This has acted as a nuclei for further sulphide precipitation, followed later by ankerite. Plates 9.26 and 9.27 show a predominantly pyrite cleat with rafted material surrounded by shattered angular fragments of coal with both pyrite and ankerite mineralisation being present.

Cleat Classification

A sequence of cleat formation, based on coal type, thickness and mineralogy, is systematic enough to be classified. A scheme was proposed by Fellows (1979, Ph.D.) and found to be consistent with the present study. It is included in full detail and amended where thought to be necessary. The following cleat types are to be found in Figure 9.4.

Type 1

Type 1 cleat fractures are closely related. They are confined initially to the vitrain bands but begin to penetrate intervening clarain and durain bands. It is the dominant cleat of the vitrain bands.

Type 1a

This type of cleat is restricted vertically to vitrain bands. They are well developed and strongly parallel following the main cleat direction. Rarely do they have an orthogonal ('back cleat') set. The cleat frequency is high, usually every 2mm to 4mm and usually less than 10mm, but this depends on the vitrain band thickness. Dilatation of these cleat is negligible, usually markedly less than 1mm. Such cleat are often monomineralic and sulphide, usually pyrite, rich. The fractures are dilatational with no apparent torsional component. Maximum dilatation is to be found in mid-cleat, thinning to nothing immediately on reaching the next coal band. The nature of the fractures and the rare occurrence of an orthogonal set suggests that they are the initial tension joint set, probably formed normal to the least principal stress at depth.

Type 1b

Similar to type 1a but passes into the intervening coal types, usually thin clarain. The degree of penetration depends upon the thickness of the vitrain band and the closeness of successive vitrain bands. Dilatation is similar to 1a but may be slightly greater. Its frequency is significantly lower averaging every 5mm to 15mm. The cleat initiated within the vitrain band.

Type 1c

In bright coals, composed predominantly of vitrain bands, 1b cleat may unite to form a large vertically penetrating cleat. Where this passes through durain layers the cleat may be refracted but is vertical

within the bright coal. This suggests that the type 1b cleat in the bright coal layers were offset and fracture began in the bright coal and spread across the intervening dull coal layer. The surface is characteristically ribbed and may be termed "augen" (Price, 1966). Within the dull coal, the fracture surface is often rough and undulating. This is probably a reflection of the complex nature of the maceral groups making up the durain band with individually differing strengths. The frequency is low, every 20mm to 50mm and maximum dilation is to be found in the centre of the cleat, between 2mm to 4mm wide, to 1mm at the extremities. The mineralogy of these cleat is predominantly carbonate although kaolinite is also common. Pyrite, although common in the preceding types, is rare.

Thus the type 1 cleat form in the order 1a, 1b and 1c, the thick dull coals being last to undergo tensional jointing because of its greater strength, and often greater thickness. Such cleat may form as type 1a, develop through 1b and finally 1c as the tensional strength of each coal type in turn is exceeded. If this is the case, the mineralogy may be complex, from monomineralic to polymineralic, depending upon which section of the cleat studied and the dilation produced.

Type II cleat. The cleat is often rough and irregular. Of the type II cleat, only type IIc appears to have an association with specific coal types.

Type IIa

These types are dominant in thinner seams otherwise they are difficult to distinguish because of type 1c superimposition. In minor seams they are seen to pass into joints in upper and lower non-coal rocks. They are smooth and unrefracted and may be termed 'minor joints' (Price, op. cit.). They may be single or orthogonal and where superimposed on type 1 cleat is more perfectly developed.

The cleat may be striated or polished or show plume structures indicative of small scale movements according to Fellows. This is not entirely true. Striations may be indicative of movement. Plume structures, however, indicate the joint fracture propagation direction (Hobbs, Means and Williams, 1976) and do not necessarily indicate relative movement.

Dilation is larger than lc cleat, being 2mm to 6mm and thinning is not evident. The repeat distance is 100mm to 200mm. The passing into joints or listric surfaces was not observed in the present work as the relationship of cleat and joints was not observed in situ. However, if these cleat represent joints in the associated strata, it is reasonable to expect late stage mineralisation. This is borne out by Fellows who found them to be predominantly calcitic in composition. These cleat affect the ease of coal working and face stability, together with type lc because of their great vertical extent.

Type IIb

Again these type were not observed in situ because no detailed investigation was made during sampling. They are of irregular occurrence found adjacent to dirt bands or the roof or floor. Their shape and dimensions are irregular. The cleat is often wedge shaped or sinusoidal tears contiguous with the mudrock listric surfaces. These cleat are probably the result of shearing due to differential movement of the coal and mudrocks. It is expected that such cleat are most highly developed where vitrain bands are found adjacent to the mudrocks and the greatest difference between coal types is found. Smearing out of type 1 cleat and lateral shearing of pyrite bands show they post-date type 1 cleat and were found to be of calcite only. Dilation is variable, being between 2mm and 6mm and the frequency random, suggested by Fellows to

represent a random stress field.

Type IIc

Type 1b cleat cut thin dull coal bands. Thicker durain layers have type 1c cleat which are refracted. They may be split by large vertical to sub-vertical fractures with a hackly fracture. Their frequency is low, every 100mm approximately and the dilation is often large, similar to other type II fractures. As it is not associated with mudrocks it is thought to be the development of type 1c in thick durain layers. As the cleat interval is large the dilation too will be greater than in bright coal type 1 fractures. In the Cannock coals these cleat are predominantly mineralised by a very thick 'fluffy' kaolinite looking very different to the thin kaolinite 'skins' found in bright coal. The mineralogy suggests that they are not the first fractures to form and the 'fluffy' appearance is probably due to reactivation of the cleat during kaolinite precipitation. They do, however, exhibit a high degree of crystallinity.

Conclusions

- 1) Cleat is common and widespread. It usually forms an orthogonal set with one direction being dominant. The main cleat direction is reasonably constant but variations can be found.
- 2) Cleat in coals above sub-bituminous grade is caused by stress release with uplift. The cleat direction is controlled by stress directions at depth but the fractures occur near surface.
- 3) The cleat frequency differs with coal type. It is highest in bright and lowest in dull coal for a given thickness of lithotype.
- 4) The thinner the lithotype, the higher the cleat frequency.
- 5) The dilation of the cleat is greater in the widely spaced major cleat.
- 6) The physical properties of the maceral groups control the strength of the microlithotypes and hence the lithotypes. Multimaceral micro-

lithotypes are stronger than monomaceral ones. Exinite greatly reinforces microlithotypes. Strength increases in the order:-
 Vitrite → Clarite → Durite → Mudrock, hence cleat decreases.

7) The minerals present are:-

- (a) Sulphides; galena, sphalerite, marcasite, pyrite.
- (b) Silicates; quartz, kaolinite (well crystallised).
- (c) Carbonates; ankerite, calcite.
- (d) Phosphates; apatite, goyazite.

This is the probable order of deposition with the exception of (d).

8) The major phases:- sulphide, silicate and carbonate, are found continent-wide. Minor differences exist even on a local scale between collieries and even between seams of a colliery. The Littleton Colliery cleat is more complex and probably reflects more exotic ground waters at that colliery when compared to Lea Hall.

9) The order of deposition reflects the relative solubilities of the metals in the ground waters. Suitable anions may have been transported in solution over long distances (hence similarities) or originated from organic matter maturation.

10) A cleat classification based on the frequency, size (dilation) and vertical extent is included. Type 1 cleat are confined predominantly to vitrain bands but are seen to extend to intervening lithotypes. Type 2 cleat are generally non-coal type specific and may pass into joints in associated strata. They are generally larger and may be termed 'micro joints'.

CHAPTER 10SUMMARY

There are two principal aims to this research project, to study the mineralogy and geochemistry of coal and its immediately associated strata, which provides a framework for an investigation into the form and distribution of chlorine in coal with a view towards its potential removal. Chlorine is a major problem in thermal power generation, causing fire-side corrosion of power station super-heater tubes. Co-operation with the C.E.R.L. (C.A.S.E. Award) enabled the use of geological information from Cannock Coalfield collieries at Lea Hall (Rugeley) and Littleton (near Cannock) to predict the behaviour of Cl^- in coal at the site of the proposed new colliery to the east of Stafford, which would mine the northerly extension of the concealed South Staffordshire Coalfield. Four seams were sampled, the Shallow and Yard from Lea Hall (Lower Coal Measures) and the Park and Eight Feet seams from Littleton (Middle Coal Measures). The associated floor, intraseam dirt bands and roof sediments provide a framework with which comparisons between the organic rich coals and essentially non-organic, detrital, mudrocks could be made.

Samples were collected at set intervals through the seams and as the bulk characteristics of each sample were being studied, they were described on a sub-class basis. Coal samples from each seam were analysed by the C.E.G.B. by proximate and ultimate analysis. This provided rank information indicating high volatile bituminous 'B' or 'C' coals (37.2 to 40.9% volatile matter) falling within the N.C.B. Coal Rank Code 700 to 900 (79.6 to 82.7%C). N.C.B. rank information give both collieries as 800 although the Littleton Colliery Seams are of a slightly higher rank following a more complex structural history and greater burial depth. Coal moisture content indicates the coals as high volatile bituminous 'B' rank.

The chlorine research was directed to two fields, the association-ship of total chlorine to coal type (Caswell, Holmes and Spears, in press), and a study of the major water-soluble ions, their distribution and specifically their relationship to chlorine (Caswell, Holmes and Spears, submitted to Fuel). An investigation into the leaching behaviour of different size fractions indicated a not unexpected increase in leachability with falling grain size. In addition, two forms of chlorine were identified, the proportions of which differ with coal type and a function of the pore size distribution within the coal type. Thus in coarse coals, Cl^- is seen to be leached predominantly from dull coals and water-soluble Na^+ can balance all of the Cl^- . Bright coals leach least Cl^- and this is not balanced by Na^+ . Banded coals show intermediate trends. With decreasing grain size, this pattern is seen to shift so that in fine ground coal, highest water-soluble Cl^- is associated with bright coals, lowest in dull coals. The peaks in Cl^- leached, correspond to Ca^{2+} , Mg^{2+} , HCO_3^- and pH, indicating dissolution of carbonates. Na^+ levels, however, show only minor through seam variations being only slightly higher than in the associated mudrocks, and having minor peaks in the bright coals. Na^+ only accounts for some one-third of the total chloride, perhaps half of the water-soluble Cl^- , though this latter level is highly variable. The carbonate-chlorine association indicates exchange reactions releasing Cl^- from organic sites, and this is only achieved to any appreciable degree where fine grinding allows the opening of the small fixed Cl^- holding pores and allowing maximum surface area to be available for reaction and allowing rapid carbonate dissolution. Where carbonates are negligible, the released Cl^- can be balanced by Na^+ and exchange is prevented by the acidity of the leachate.

Diffusion studies indicate that the dull coals leach most rapidly and the rates indicate that a component is already dissolved within the

coal moisture. Na^+ shows similar leaching rates to Cl^- in these coals. The leaching rates associated with bright coal indicate a dissolution component and Cl^- is most closely associated to Ca^{2+} and Mg^{2+} . The leaching behaviours of the different coal types change with decreasing grain size, indicating that progressively different pore size distributions are being opened up. Dull coal pores are relatively large, allowing rapid accessibility, but the I.S.A. is small compared to that of bright coals where vitrinite predominates, the pores are much smaller but the I.S.A. is far larger but consequently less accessible.

The associated mudrocks show very different characteristics. Organic matter content is directly related to the Cl^- holding capacity. The low organic mudrocks have total Cl^- levels a magnitude lower than some of the coals and all the Cl^- is water-soluble, even from the coarse fraction, and can be balanced by Na^+ . Thus the pore size and distribution is markedly different between mudrocks and coal, the latter being much smaller in size and the former having no organically combined Cl^- . The organic rich mudrocks have characteristics that are intermediate between the mudrocks and coals.

The coal type - total Cl^- relationship shows that the highest values are to be found in bright, lowest in dull coals, and this can be related to the moisture content which is a measure of the I.S.A. Thus, vitrinite, with its high I.S.A. is the predominant Cl^- host. As rank controls the I.S.A., the Cl^- holding capacity of a coal seam is related to the maceral groups present, their relative abundance and rank.

Cl^- may be introduced during any stage of coal diagenesis but only the diagenetically altered, chloride rich ground waters provide a plausible world-wide mechanism. Moisture centrifuged from a wet mudrock (Ydbl) and coal (run-of-mine Shallow Seam Coal) show it to be chloride rich and in the mudrock is capable of accounting for the whole rock Cl^- .

This accounts for the Na^+ - Cl^- association and the readily water-soluble nature of the chloride. This cannot be applied to the coal sample because of selective pore water extraction and ion concentration gradients within the pores. Element ratios are, however, typical of the associated ground waters and this may account for the Na^+ associated Cl^- , the remainder being held in organic combination. This organic Cl^- component, too, may have been a ground water brine trapped and fixed during rank imposition (Hercynian Orogeny). As the large dull coal pores are most accessible to ground waters and these are very concentrated, as in the North Staffordshire Coalfield, then the predicted coal type - Cl^- relationship may be overridden and the dull coals found to have the highest total Cl^- . If the Na^+ associated Cl^- is subtracted from the total, the expected association is found. This suggests that the ground water diagenesis is related to post-Hercynian processes.

The coal and mudrock mineralogy and whole rock geochemistry was determined after the initial removal of interfering organic matter by L.T.A. Although this leaves the mineral matter relatively unaltered, there are side effects important in quantitative analysis, most serious of which being the fixation of organic sulphur as gypsum. XRF and wet chemical methods were used to determine the whole rock geochemistry and XRD for mineral identification and to back-up XRF in the calculation of clay percentage, quartz and feldspar determinations.

The mudrocks are dominated by detrital minerals, quartz, clays and minor feldspar and anatase. Diagenesis is generally of little consequence rarely accounting for 6.8% of the mineral matter and usually less except in locally important early diagenetic pyrite (8S10a) and siderite (8R2) nodules. Minor levels of apatite, probably originating from organic matter decomposition, are to be found in most samples. The peak in 8R2 is related to shell material.

Within each mudrock unit of a seam floor, intra-seam dirt band and roof, the mineralogy is internally consistent. The roof measures appear to most closely represent 'normal' sedimentation in a predominantly fresh water environment. The relative lack of leaching is seen in trace element concentrations, and the predominant location for diagenetic siderite development. The quartz content increases, along with titania (anatase), with increased sedimentation and subsidence rates, whilst the total clay proportion declines. Illite and chlorite (at Littleton Colliery) increase as a proportion of the clay fraction. The floor measures are more complicated. There are major differences between the stratigraphically lower Lea Hall seams and those at Littleton, especially in the quartz contribution and relative clay proportions. The Lea Hall seams are quartz rich (c. 44% compared to c. 22%) and kaolinite dominates the clays. There is evidence (XRF) for the leaching of the more labile constituents in a tropical Lower Coal Measures environment where precipitation was intense and typical of kaolinite formation. Similarly, the approaching aridity associated with the Permo-Triassic environment, due to continental movement, is reflected in the predominance of illite and more abundant chlorite in Littleton Colliery Park and Eight Feet Seams. Similar mineralogical variations in quartz and kaolinite levels are found elsewhere in British Coal Measures successions supporting the theory of a climatically controlled mineralogy. Dirt bands are predominantly very fine-grained sediments, thin and of considerable geographical spread (local time planes) rich in very fine poorly crystalline kaolinite and degraded illite. Quartz levels are very low or maybe excluded completely because of its size distribution (I.D.2.11). TiO_2 evidence, however, often supports very rapid sedimentation, probably due to minor base level changes or river bank bursts. The degraded nature of these deposits is reflected in the whole rock geochemistry and exchangeable cations.

Further evidence for the Shallow and Yard Seam floor leaching is provided by low levels of exchangeable cations. Na^+ and Ca^{2+} are seen to increase with depth which may be a reflection of ground water composition. Exchangeable K^+ is high in the degraded illites, reflecting their small size and weathering opened clay layers. There is evidence for carbonate dissolution from 8R2 and the coal seams - which otherwise have negligible C.E.C., even when using barium nitrate as an exchange media.

Physical testing of mudrocks show that the uniaxial compressive strength is directly proportional to the quartz content when calculated normal to the bedding. Parallel to the bedding, fissility or lamination controls the strength. Where diagenetic mineralisation by pyrite or siderite is a major component, the strength is greatly increased and overrides that predicted by the quartz content. The uniaxial compressive strength of a homogeneous suite of mudrocks is expected to increase with rank, as can be seen in coals of greater than 92%C.

The trace element levels in the mudrocks reflect the major element mineralogy. Ba, Rb and Sr are found to substitute for K in illite. Zr, located in zircon, is also concentrated in the detrital fraction. Diagenetic locations are dominated by siderite - Co and Mn, and pyrite - Ni and Pb. Cu is closely associated with organic matter. Other trace elements have no one specific location. Thus V, Y and Zn may be clay-associated although Zn, Co and Cu may also have a pyrite location. The diagenetically hosted trace elements were probably supplied by oxhydroxide grain coats and released with reduction. Because there is little apparent loss of trace elements from the sediment, a reducing level above the sediment (often organic rich) is assumed. This would allow the siderite, 8R2, to be precipitated very early in diagenesis, at or near the surface, and not along a permeable, silty horizon. It is evident that the early diagenetic

framboidal pyrite was more efficient in scavenging their associated trace elements. Concentrations in large nodules may be two orders of magnitude lower because of the relative insolubility and limited abundance of these elements. Those in the cleat sulphides are less concentrated than the framboidal pyrite, and probably represent metals leached from mudrock sequences by aggressive chloride rich ground waters.

The coal mineral matter is dominated by the diagenetic fraction (up to 95%) of which the late diagenetic cleat minerals predominate. The detrital fraction is mineralogically similar to that of the associated mudrocks but concentrating the finer grained fraction. Detrital ash contents are thus highest where associated with the mudrocks, especially in the dirt bands where fine sedimentation often continued after the re-establishment of coal vegetation.

Early diagenetic minerals are quantitatively infrequent, limited to framboidal pyrite and occasional siderite horizons (2.6). Minor levels of phosphate, apatite and rare goyazite, are found.

The cleat minerals are late diagenetic, representing mineralisation of fractures, analagous to micro-joints in other rocks, caused by stress relief produced by uplift. The cleat varies in frequency and dilation according to coal type and thickness. The frequency is highest in vitrain, lowest in durain and decreasing with increasing bed thickness, although the accumulated stress dissipation is allowed for by greater dilation. The frequency and order of fracture is inversely related to maceral group strength, being lowest in vitrinite and increasing with poly-maceral lithotypes, being greatest in durain. The polyphase nature of mineralisation indicates re-activation of some fractures and the paragenetic sequence can be used to give relative dating to the various coal type-cleat associations. The mineralogy follows a wide geographical sequence which can be divided into sulphides, silicates and carbonates in depositional

order. Occasional phosphates (Shallow Seam) are found. The minerals represent changing ground water compositions and the relative solubilities of the minerals therein. Generally, the Littleton Colliery cleat is more exotic in its sulphide minerals and ankerite predominates over calcite in the carbonate phase. This is reflected in a reduced Mg to Ca ratio (XRF). The subtle differences may reflect a host sediment pile less leached of constituent metals at Littleton in comparison to Lea Hall Colliery.

REFERENCES

- AL-JALILI, M.A. (1982). Geochemistry and Mineralogy of Mudrocks from the South Wales Coalfield, with particular reference to diagenesis. Unpublished Ph.D. Thesis, University of Sheffield.
- ALPERN, B. (1963) Fissuration - Fragilité. Cerchar, Rep. F 312, Paris.
- ANDERTON, R. BRIDGES, LEEDER, M.R. and SELLWOOD, B.W. (1979). A Dynamic Stratigraphy of the British Isles. George Allen and Unwin, London.
- ASHBY, D.A. and PEARSON, M.J. (1978). Mineral distribution in sediments associated with the Alton Marine Band near Penistone, South Yorkshire. International Clay Conference 1978 (Eds. M.M. Mortland and V.C. Farmer) Elsevier, Amsterdam.
- BAILEY, S.W. (1975). In: 'Crystal Structures of Clay Minerals and their X-ray Identification (Eds. Brindley, G.W. and Brown, G.). Mineralogical Society. Spottiswoode Ballantyne Ltd., Colchester.
- BAILEY, S.W. (1972). Determination of Chlorite Compositions by X-ray Spacings and Intensities. Clays Clay Miner. 20, 381-388.
- BALL, C.G. (1934). Kaolinite in Illinois Coals. Econ. Geol., 29, 767-776.
- BALL, C.G. (1935). Mineral Matter of No. 6 Bed Coal at West Frankfort, Franklin County, Illinois. Illinois State Geol. Surv. Rpt. Invest. 33. Contributions to the Study of Coal.
- BARROW, G., GIBSON, W., CANTRILL, T.C., DIXON, E.E.L., and CUNNINGTON, C.H. (1919). The Geology of the Country around Lichfield (N.S. Sheet 154). Mem. Geol. Surv.
- BAYLISS, P. (1975). Nomenclature of the trioctahedral chlorites. Can. Mineralogist. 13, 178-180.
- BEAR, F.E. (1964). Chemistry of the Soil. 2nd Ed. Reinhold Publishing Corp., New York.
- BENNETT, R. and SCURFIELD, R.W. (1951). Proving of the North-eastern extension of the Cannock Chase Coalfield. Trans. Inst. Min. Eng., 110, 280-288.

- BERNER, R.A. (1970). Sedimentary Pyrite Formation. *Am. J. Sci.*, 268, 1 - 22.
- BERSIN, R.L. (1975). Industrial applications of plasma, the fourth state of matter. *Industrial Research*.
- BETTELHEIM, J. and HANN, W.W. (1980). An investigator of water leaching of some British coals. *J. Inst. Energy*, 53, 103 - 108.
- BILLINGS, G. K., KESSLER, S.E. and JACKSON, S.A. (1969). Relation of zinc-rich formation waters, northern Alberta, to the Pine Point ore deposit. *Econ. Geol.*, 64, 385 - 391.
- BILLINGS, G.K. and WILLIAMS, H.H. (1967). Distribution of chlorine in terrestrial rocks - a discussion. *Geochim. et Cosmochim. Acta*, 31, 2247.
- BLATT, H., MIDDLETON, G. and MURRAY, R. (1972). *Origin of Sedimentary Rocks*. Prentice-Hall, Englewood Cliffs.
- BOWER, C.A. and TRUOG, F. (1940). Base exchange capacity determinations as influenced by nature of cation employed and formation of basic exchange salts. *Proc. Soil Sci. Soc. Am.*, 5, 86 - 89.
- BRADLEY, W.F. and GRIM, R.E. (1961). Mica clay minerals. In: Brown, G. (Ed.) *X-Ray Identification and Crystal Structure of Clay Minerals*. Mineral Soc., London.
- BROME, J.S.S. and KING, J.G. (1935). 'Fuel Solid Liquid and Gaseous' 4th Ed. Arnold, London.
- BREDEHOEFT, J.D., BLYTH, C.R., WHITE, W.A. and MAXEY, G.B. (1963). Possible Mechanisms for Concentration of Brines in Subsurface Formations. *A.A.P.G. Bull.*, 47, 257 - 269.
- BRINDLEY, G.W. (1961). Chlorite minerals. In: Brown, G. (Ed.) *The X-ray Identification and Crystal Structures of Clay Minerals*. Mineralogical Society, London.

- BRINDLEY, G.W. and BROWN, G. (Eds.) (1980). *Crystal Structures of Clay Minerals and their X-ray Identification*. Mineralogical Society. Spottiswoode Ballantyne Ltd., Colchester.
- BRINDLEY, G.W. and GILLERY, F.H. (1956). X-ray identification of chlorite species. *Am. Miner.*, 41, 169-186.
- BRINDLEY, G.W. and ROBINSON, K. (1951). The chlorite minerals. In: Brindley, G. (Ed.) *X-ray Identification and Crystal Structure of Clay Minerals*. Mineralogical Society, London.
- BROWN, G. (Ed.). (1961). *The X-ray Identification and Crystal Structures of Clay Minerals*. Mineralogical Society, London.
- BROWN, G. and NORRISH, K. (1952). Hydrous micas. *Mineralog. Mag.*, 29, 929-932.
- BROWN, H.J. and SWAINE, D.T. (1964). Inorganic Constituents of Australian Coals. Nature and Mode of Occurrence. *J. Inst. Fuel*, 37, 422-440.
- BRUNTON, G. (1955). Vapour pressure glycolation of oriented clay minerals. *Am. Miner.* 40, 124-126.
- BUCHER, W.H. (1920). The mechanical interpretation of joints. *J. Geol.*, 28, 707 and 29, 1.
- BURST, J.F. (1959). Post diagenetic clay-mineral environmental relationship in the Gulf Coast Eocene. *Proc. Natl. Conf. Clays Clay Minerals*, 6th, Natl. Acad. Sci. Natl. Res. Council, Publ., 1957: 327-341.
- BURST, J.F. (1969). Diagenesis of Gulf Coast clayey sediments and its possible relationships to petroleum migration. *Bull. Am. Ass. Petrol. Geol.*, 53, 73-93.
- CAMPBELL, J.D. (1979). Major cleat trends in Alberta Plains coals. *Can. Min. Metall. Bull.*, 72, No. 802, 69-75.

- CARPENTER, A.B., TROUT, M.L. and PICKETT, E.E. (1974). Preliminary Report on the Origin and Chemical Evolution of Lead- and Zinc-Rich Oil Field Brines in Central Mississippi. Bull. Soc. Econ. Geol., 8, 1191-1206.
- CARROLL, D. (1970). Clay Minerals: A guide to their X-ray identification. Geol. Soc. Am. Spec. Paper 126.
- CASAGRANDE, D.J. and ERCHULL, L.D. (1976). Metals in Okefenokee peat-forming environments: relation to constituents found in coal. Geochim. et Cosmochim. Acta, 40, 387-393.
- CASWELL, S.A. (1981). Distribution of water-soluble chlorine in coals using stains and acetate peels. Fuel, 60, 1164-1166.
- CASWELL, S.A., HOLMES, I.F. and SPEARS, D.A. Total Chlorine in Coal Seam Profiles from the South Staffordshire (Cannock) Coalfield. (In Press - Fuel).
- CHAKRABARTI, J.N. (1978). Analytical Methods for Coal and Coal Products. Volume 1 and 2. (Ed. Karr). Academic Press, New York.
- CHAO, G.Y. (1969). 2 θ (Cu) Table for Common Minerals. Carleton University Geological Paper 69-2. Canada.
- CHAPMAN, W.R. and MOTT, R.A. (1928). The Cleaning of Coal. Chapman and Hall, London.
- COLLINS, R.J. (1976). A method for measuring the mineralogical variation of spoils from British Collieries. Clay Minerals, 11, 31-50.
- CRANK, J. (1957). Mathematics of Diffusion. Oxford University Press.
- CROOKALL, R. (1931). A Critical Revision of Kidston's Coal Measures Floras. Proc. Roy. Phys. Soc. Edin., 22, 1-34.
- CROOKALL, R. (1955). Fossil Plants of the Carboniferous Rocks of Great Britain (2nd Ed.). Mem. Geol. Surv. Palaeont., 4, pt. 1.
- CROSSLEY, H.E. (1947). Boiler Availability Committee Technical Paper 1.
- CROSSLEY, H.E. (1952). J. Inst. Fuel, 25, 224.

- CROSSLEY, H.E. (1963). *J. Inst. Fuel*, 36, 228.
- CRUMLEY, P.H., FLETCHER, A.W. and WILSON, D.S. (1955). *J. Inst. Fuel*, 28, 117-120.
- CRUMLEY, P.H. and McCAMLEY, W. (1958). *Science in the use of Coal. Proc. Inst. Fuel Conf. 'Science in the use of coal'*. Sheffield, Paper 32, D-43-D51.
- CUBITT, J.M. (1975). A regression technique for the analysis of shales by X-ray diffraction. *J. Sed. Pet.*, 45, 546-553.
- CURTIS, C.D. (1966). The incorporation of soluble organic matter into sediments and its effect on trace element assemblages. *Advances in Organic Geochemistry*, 1-13.
- CURTIS, C.D. (1969). Trace element distribution in some British Carboniferous sediments. *Geochim. et Cosmochim. Acta*, 33, 519-523.
- CURTIS, C.D. (1977). Diagenetic processes occurring in compacting clay-rich sediment sequences. *Proc. of 4rd International Symposium on Env. Biochem.*, Wolfenbuttel, 1977.
- CURTIS, C.D. (1978). Possible links between sandstone diagenesis and depth-related geochemical reactions occurring in enclosing mudstones. *Jl. geol. Soc. Lond.*, 135, 107-117.
- CURTIS, C.D., PEARSON, M.J. and SOMOGYI, V.I. (1975). Mineralogy, chemistry and origin of a concretionary siderite sheet (clay-ironstone band) in the Westphalian of Yorkshire. *Min. Mag.*, 40, 385-393.
- CURTIS, C.D. and SPEARS, D.A. (1967). The Formation of Sedimentary Iron Minerals. *Econ. Geol.*, 63, 257-270.
- DAS GUPTA, H.N. and CHAKRABARTI, J.N. (1951). *J. Indian Chem. Soc.*, 28, 664-666.
- DAUBREE, A. (1879). *Étude Synthétiques de Geologie Expérimentale*, Paris.
- DAVIDSON, C.F. (1962). On the cobalt-nickel ratio in ore deposits. *Mining Mag.*, 106, 78-85.

- DAYBELL, G.N. (1967). The Relationship between sodium and chlorine in some British coals. *J. Inst. Fuel.*, 40, 3-6.
- DAYBELL, G.N. and GILLHAM, E.W.F. (1959). The Removal of Chlorides from Coal by Leaching. *J. Inst. Fuel*, 32, 589-596.
- DAYBELL, G.N. and PRINGLE, W.J.S. (1958). The Mode of Occurrence of Chlorine in Coal. *Fuel*, 37, 283-292.
- DEER, W.A., HOWIE, R.A. and ZUSSMAN, J. (1962). *Rock Forming Minerals*. 5 vols. Longman, London.
- DEER, W.A., HOWIE, R.A. and ZUSSMAN, J. (1977). *An Introduction to the Rock Forming Minerals*. Longman, London.
- DEGENS, E.T. (1965). *Geochemistry of sediments*. Prentice-Hall, Englewood Cliffs.
- DE SITTER, L.U. (1947). Diagenesis of Oil-field Brines. *Am. Assoc. Petrol. Bull.*, 31, 2030-2040.
- DEUL, M. (1955). *Econ. Geol.*, 50, 103-4.
- DE WAELE, A. (1915). The Occurrence of Chlorine in Coal. *Analyst*, 40, 146-150.
- DICKSON, J.A.D. (1974). In: *Laboratory Handbook of Petrographic Techniques* (Ed. Hutchinson, C.S.). John Wiley, New York.
- DIXON, K., SKIPSEY, E. and WATTS, J.T. (1964). The Distributions and Composition of Inorganic Matter in British Coals: Part 1 - Initial Study of Seams from the East Midlands Division of the National Coal Board. *J. Inst. Fuel*, 37, 485-493.
- DOUILLET, P. and NICOLAS, J. (1969). Les minéraux du kaolin-Reflexions concernant les diverses classifications et nomenclature. *Bull. Soc. fr. Céram.*, 87-114.
- DOWNING, R.A. and HOWITT, F. (1967). Saline ground-waters in the Carboniferous rocks of the English East Midlands in relation to the geology. *Q. Jl. Engng. Geol.*, 1, 241-269.

- DRON, R.W. (1925). 'Notes on Cleat in Scottish Coalfields'. Trans. Inst. Min. Eng., 70, 115-117.
- DUFF, P. McL. D. and WALTON, E.K. (1962). Statistical basis for cyclothem: a quantitative study of the sedimentary succession in the East Pennine Coalfield. Sedimentology, 1, 235-255.
- DUNHAM, J.C. (1970). Mineralization by deep formation waters: a review. Trans. Instn. Min. Met., 79, B127.
- DUNOYER de SEGONZAC, G.D. (1970). The transformation of clay minerals during diagenesis and low-grade metamorphism - a review. Sedimentology, 15, 281-346.
- EDGCOMBE, L.J. (1956). State of Combination of Chlorine in Coal 1. Fuel, 35, 38-48.
- EDGCOMBE, L.J. and MANNING, A.B. (1952). Origin and Nature of Ash; Sampling and Analysis. J. Inst. Fuel, 25, 166.
- EDMUNDS, W.M. (1975). Geochemistry of brines in the Coal Measures of northeast England. Trans. Instn. Min. and Met., 85, B39-52.
- EDMUNDS, W.M. and BATH, A. (1976). Environ. Sci. Tech., 10, 467.
- ESQUEVIN, J. (169). Influence de la Composition chimique des illites sur leur cristallinite. Bull. Centre-Rech. Pau-SNPA, 3, 147-153.
- ESTEP, P.A. KOVACH, J.J. and KARR, C. (1968). Quantitative Infrared Multicomponent Determination of Minerals Occurring in Coal. Analyt. Chem., 40, 358-363.
- FELLOWS, P.M. (1979). An Investigation of the Water-soluble elements in Coal and Coal-Bearing Strata. Unpublished Ph.D. Thesis, Dept. of Geology, University of Sheffield.
- FELLOWS, P.M. and SPEARS, D.A. (1978). The Determination of Feldspars in Mudrocks using an X-Ray Powder Diffraction Method. Clays Clay Miner., 26, 3, 231-236.
- FINKELMAN, R.B. and STANTON, R.W. (1978). Identification and significance of accessory minerals from a bituminous coal. Fuel, 57, 763-768.

- FOSCOLOS, A.E. and KODOMA, H. (1974). Diagenesis of Clay Minerals from Lower Cretaceous Shales of North Eastern British Columbia. *Clays Clay Miner.*, 22, 313 - 335.
- FOSCOLOS, A.E. and STOTT, D.F. (1975). Degree of diagenesis, stratigraphic correlations and potential sediment sources of Lower Cretaceous Shale of Northeastern British Columbia. *Energy Mines and Resources Canada. Geological Survey Bulletin 250.*
- FRANCIS, E.H. (1979). British Coalfields. *Sci. Prog., Oxf.*, 66, 1 - 23.
- FRANCIS, W. (1961). *Coal: Its Formation and Composition.* 2nd Ed. Edward Arnold, London.
- FRAZER, F.W. and BELCHER, C.B., (1973). Quantitative determination of the mineral-matter content of coal by a radiofrequency-oxidation technique. *Fuel*, 52, 41 - 46.
- FRITZ, J.S. and YAMAMURA, S.S. (1955). *Anal. Chem.*, 27, 1491.
- GIBBS, R.J. (1965). Error due to segregation in quantitative clay mineral X-ray diffraction mounting techniques. *Am. Miner.*, 50, 741 - 751.
- GIBSON, W. (1927). *Coal in Great Britain.* 2nd Ed. Arnold, London.
- GLUSKOTER, H.J. (1965a). Electronic low-temperature Ashing of Bituminous Coal. *Fuel*, 44, 285 - 291.
- GLUSKOTER, H.J. (1965b). Composition of Ground Water Associated with Coal in Illinois and Indiana. *Econ. Geol.*, 60, 614 - 20.
- GLUSKOTER, H.H. (1967). Clay minerals in Illinois Coals. *J. Sed. Pet.*, 37, 1, 205 - 214.
- GLUSKOTER, H.J., HATCH, J.R. and LINDAHL, P.C. (1973). Zinc in coals of the Illinois Basin (abs.). *Geol. Soc. America. Ann. Mtg., Abstracts with Programs*, 5, 637.
- GLUSKOTER, H.J. and REES, O.W. (1964). Chlorine in Illinois Coal. *Illinois State Geology Survey Circular 372*, 23pp.

- GLUSKOTER, H.J., JOSEPH, R. and LINDAHL, P.C. (1973). Zinc in Coals of the Illinois Basin. Geol. Soc. Am. Mtg., Abstracts with Programs, 5, 637.
- GLUSKOTER, H.J. and LINDAHL, P.C. (1973). Cadmium: Mode of Occurrence in Illinois Coals. Science, 181, 264 - 268.
- GLUSKOTER, H. J. and RUCH, R.R. (1971). Chlorine and Sodium in Illinois coals as determined by neutron activation analysis. Fuel, 50, 65-76.
- GLUSKOTER, H.J., RUCH, R.R., MILLER, W.G., CAHILL, R.A., DREHER, G.B. and KUHN, J.K. (1977). Trace Elements in Coal: Occurrence and Distribution. Illinois State Geological Survey Circular 499, 15400.
- GOLDSCHMIDT, V.M. (1954). Geochemistry. Oxford Univ. Press, London.
- GREENSMITH, J.T. (1978). Petrology of the Sedimentary Rocks. 6th Ed. George Allen & Unwin, London.
- GRIM, R.E. (1968). Clay Mineralogy, 2nd Ed. McGraw Hill, New York.
- GRIM, R.E., BRAY, R.H. and BRADLEY, W.F. (1937). The mica in argillaceous sediments. Am. Miner., 22, 813 - 829.
- HAINS, B.A. and HORTON, A. (1969). British Regional Geology - Central England (3rd Edition). N.E.R.C. Inst. of Geol. Sciences, H.M.S.O. London.
- HALLAM, A. (1967). Siderite- and calcite-bearing concretionary nodules in the Lias of Yorkshire. Geol. Mag., 104, 222.
- HARRIS, J.F., TAYLOR, G.L. and WALPER, J.L. (1960). Relation of deformational fractures in sedimentary rocks to regional and local structures. Bull. Am. Ass. Petrol. Geol., 44, 12, 1853.
- HARRIS, L.A., CAVIN, O.B., CROUSE, R.S. and YUST, C.S. (1979). SEM observations and EDX analysis of secondary mineralisation in a bituminous coal. Scanning Electron Microscopy Conference, Washington, D.C. NTIS: CONF - 790418-4.
- HARRIS, L. A. and YUST, C.S. (1976). Transmission electron microscope observations of porosity in coal. Fuel, 55, 233 - 236.

- HARRIS, L.A. and YUST, C.S. (1979). Ultrafine structure of coal determined by electron microscopy. 177th Am. Chem. Soc. National Meeting, Honolulu. NTIS: CONF - 790415-28.
- HATCH, J.R., GLUSKOTER, H.J. and LINDAHL, P.C. (1976). Sphalerite in Coals from the Illinois Basin. *Econ. Geol.*, 71, 613-624.
- HEINZE, G. (1958). *Bergbau-Arch.*, 19, 1-23.
- HEM, J.D. (1970) Study and Interpretation of the Chemical Characteristics of Natural Water. 2nd Ed. Geol. Survey Water Supply Paper 1473. United States Government Printing Office, Washington.
- HICKS, D. and NAGELSCHMIDT, G. (1943). Med. Res. Council Rept. 244(B).
- HOBBS, B.E., MEANS, W.D. and WILLIAMS, P.F. (1976). An Outline of Structural Geology. Wiley International Edition, U.S.A.
- HOEHNE, K. (1949). *Gluckauf*, 85, 661-676.
- HOEHNE, K. (1959). Ost. U.S.A., Westkanda and Nordmexiko: *Geologie*, 8, 280-302.
- HOFFMAN, R.W. and BRINDLEY, G.W. (1961). Adsorption of ethylene glycol and glycerol by montmorillonite. *Am. Miner.*, 46, 450-452.
- HORN, M.K. and ADAMS, J.A.S. (1966). Computer-derived geochemical balances and element abundances. *Geochim. et Cosmochim. Acta*, 30, 279-297.
- HOLMES, I.F. (1980). Geochemistry and Mineralogy of the Bembridge and Hamstead Beds (Oligocene), Isle of Wight. Unpublished Ph.D. Thesis, University of Sheffield.
- HOWER, J. (1967). Order of mixed-layering in illite-montmorillonites. *Clays Clay Miner.*, Proc. Natl. Conf.
- HOWER, J. and MOWATT, T.C. (1966). The Mineralogy of Illites and mixed-layer illite/montmorillonites. *Am. Miner.*, 51, 825-854.
- HUGHES, R.E. (1971). Mineral Matter Associated with Illinois Coals. Unpublished Ph.D. Thesis, University of Illinois.
- B.C.G.R.A. Bull., No. 2, 21-63.

- INESON, J. (1966). Geol. Surv. Water Supply Papers, Hydrogeol. Rep. No. 3.
- INTERNATIONAL COMMITTEE FOR COAL PETROLOGY (1957). Centre National de la Recherche Scientifique, Paris, France.
- INTERNATIONAL COMMITTEE FOR COAL PETROLOGY (1975). Centre National de Recherche Scientifique. Paris, France.
- JACKSON, T.A. (1977). A relationship between crystallographic properties of illite and chemical properties of extractable organic matter in Pre-Phanerozoic and Phanerozoic sediments. *Clays Clay Miner.*, 25, 187-195.
- JARON, M.G. (1967). A method for determining post-depositional alteration in underclays and associated lithologies. *Penn. Topogr. Geol. Surv., Inform. Circ.*, 57, 14pp.
- JENKINS, R.G. and WALKER, P.L. Jr. (1978). Analysis of Mineral Matter, in Coal, in Karr (Ed.).
- JOHNS, W.D., GRIM, R.E. and BRADLEY, W.F. (1954). Quantitative estimation of clay minerals by diffraction methods. *J. Sedim. Petrol.*, 24, 242-251.
- JOHNS, W.D. and HUANG, W.H. (1967). Distribution of chlorine in terrestrial rocks. *Geochim. et Cosmochim. Acta*, 31, 35-49.
- JUKES, J.B. (1859). The South Staffordshire Coalfield. *Mem. Geol. Surv.* 2nd Ed.
- JUNGE, C.E. and WERBY, R.T. (1958). The concentration of chloride, sodium, potassium, calcium and sulphate in rain water over the United States. *J. Meteorology*, 15, 417-425.
- KARR, C. Jr. (Ed.). (1978). Analytical Methods for Coal and Coal Products. Volume 1 and 2. Academic Press, New York.
- KEAR, R.W. and MENZIES, H.M. (1956). 'Chlorine' in coal: its occurrence and behaviour during combustion and carbonisation. *B.C.U.R.A. Bull.*, 20, 2, 53-65.

- KEMEZYS, M. and TAYLOR, G.M. (1964). Occurrence and distribution of minerals in some Australian coal. *J. Inst. Fuel*, 37, 389-397.
- KENDALL, P.F. and BRIGGS, H. (1933). The Formation of Rock Joints and the Cleat of Coal. *Proc. R. Soc. Edinb.*, 53, 164-187.
- KEPEZHINSKAS, K.B. (1965). Composition of chlorites as determined from their physical properties. *Dokl. Akad. Nauk. SSSR, Earth Sci.*, 164, 126-129.
- KERMACK, K.A. and HALDANE, J.B.S. (1950). Organic correlation and allometry. *Biometrika*, 37, 30-41.
- KIDSTON, R. (1894). On the Various Divisions of British Carboniferous Rocks as determined by their Fossil Flora. *Proc. Roy. Phys. Soc. Edin.*, 12, 183-259.
- KIDSTON, R. (1905). On the Divisions and Correlation of the Upper Portion of the Coal-Measures, with special reference to their Development in the Midland Counties of England. *Quart. J. Geol. Soc.*, 61, 308-23.
- KING, J.G., MARIES, M.B. and CROSSLEY, H.E. (1936). *J. Soc. Chem. Ind.*, 55, 266-281.
- KISCH, H.J. (1974). Anthracite and meta-anthracite coal ranks associated with 'anchimetamorphism' and 'very-low-stage' metamorphism. *Proc. K. ned. Akad. Wet. Section B*, 77, 81-118.
- KOLTHOFF, I.M., SANDELL, E.B., MEEHAM, E.J. and BRUCKENSTEIN, S. (1969). *Quantitative Chemical Analysis*. Macmillan.
- KRAUSKOPF, K.B. (1956). Dissolution and precipitation of silica at low temperatures. *Geochim. et Cosmichim. Acta*, 10, 1-26.
- KRAUSKOPF, K.B. (1967). *Introduction to Geochemistry*. McGraw Hill, New York.
- KRAUSKOPF, K.B. (1979). *Introduction to Geochemistry*. 2nd Ed. McGraw Hill, New York.

- KRUMBEIN, W.C. and GARRELS, R.M. (1952). Origin and classification of chemical sediments in terms of pH and oxidation-reduction potentials. *J. Geol.*, 60, 1-23.
- KUBLER, B. (1966). La cristallinite d'illite et les zones tout à fait superieur du metamorphism. Colloque sur les Etages Tectoniques à la Baconniere, 105 - 122.
- KUBLER, B. (1968). Evaluation Quantitative du Métamorphisme par Crystallinité de l'illite. *Bull. Centre Recherches de Pau (Soc. National des Petroles d'Aquitaine)* 2, 385-397.
- LESSING, R. (1925). *Jnl. Soc. Chem. Ind.*, 44, 277.
- LIN, J.S., HENDRICKS, L.A., HARRIS, L.A. and YUST, C.S. (1978). Microporosity and Micromineralogy of Vitrinite in a Bituminous Coal. *J. Applied Cryst.*, 11, 621-625.
- LOFTUS-HILLS, G. and SOLOMAN, M. (1967). Cobalt, nickel and selenium in sulphides as indicators of ore genesis. *Mineralium Deposita*, 2, 228-242.
- LOUIS, H. (1927). *Chem. and Ind.*, 46, 547.
- LOVE, L.G. (1967). Early Diagenetic Iron Sulphide in Recent Sediments of the Wash (England). *Sedimentology*, 9, 327-352.
- MACRAE, J.C. and LAWSON, W. (1954). Cleat in Coal Seams. *Trans. Leeds Geol. Assoc.* VI, 227-242.
- MACKOWSKY, M. Th. (1943a). *Feuerungstech.*, 31, 143-145.
- MACKOWSKY, M. Th. (1943b). *Arch. berbaul. Forschung*, 4(1), 1-16.
- MACKOWSKY, M. Th. (1956). *Proc. Int. Conf. for Coal Petrology*, No. 2, 31-34.
- MAXWELL, D.T. and HOWER, J. (1967). High-grade diagenesis and low-grade metamorphism of illite in the Pre-Cambrian Belt Series. *Am. Miner.*, 52, 843-857.

- MCCLELLAN, G.H. and LEHR, J.R. (1969). Crystal-chemical investigation of natural apatites. *Am. Miner.*, 54, 1374-1391.
- MERING, J. (1949). *Acta crystallogr.*, 2, 371-377.
- MILLER, R.N., YARZAB, R.F. and GIVEN, P.H. (1979). Determination of the mineral-matter contents of coals by low temperature ashing. *Fuel*, 58, 4-10.
- MITCHELL, G.H., STUBBLEFIELD, C.J. and CROOKALL, R. (1945). The Geology of the Northern Part of the South Staffordshire Coalfield (Cannock Chase Region). *Geol. Surv. Wartime Pamphlet*, 43.
- MITCHELL, G.H. (1954). The Coalfields of Great Britain (Ed. Sir. A. Trueman). Arnold.
- MITCHELL, R.S. and GLUSKOTER, H.J. (1976). Mineralogy of ash of some American coals: variations with temperature and source. *Fuel*, 55, 90-96.
- MOLLOY, M.W. and KERR, P.F. (1961). Diffractometer patterns of A.P.I. reference clay minerals. *Am. Miner.*, 46, 583-605.
- MONTGOMERY, W.J. (1978). Standard Laboratory Test Methods for Coal and Coke. In: 'Analytical Methods for Coal and Coal Products'. Karr (Ed.). Academic Press, New York.
- MURCHISON, D. and WESTOLL, T.S. (Eds.) (1968). Coal and Coal-Bearing Strata. Oliver and Boyd, Edinburgh.
- NAGELSCHMIDT, G. and HICKS, D. (1943). *Miner. Mag.*, 26, 297-303.
- NANDI, S.P. and WALKER, P.L., Jr. (1971). *Fuel*, 50, 345-366.
- NATIONAL COAL BOARD (1977). N.C.B. Cone Indentor. M.R.D.E., Handbook, 5, 12pp.
- NEAVEL, R.C., NAHAS, N.C. and KOH, K.K. (1977). Removal of Sodium from Illinois Coal by water extraction. *Soc. Min. Eng., A.I.M.E.*, 262, 263-267.
- NELSON, J.B. (1953). Assessment of the mineral species associated with coal. *B.C.U.R.A. Monthly Bull.*, Vol. 17, 2, 41-55.

- NICHELSEN, R.P. and van HOUGH, N.D. (1967). Jointing in the Appalachian Plateau of Pennsylvania. *Geol. Soc. Amer. Bull.*, 78, 609-630.
- NICHOLLS, G.D. (1962). A Scheme for Recalculating the Chemical Analysis of Argillaceous Rocks for Comparative Purposes. *Am. Miner.*, 47, 34-46.
- NICHOLLS, G.D. (1968). The Geochemistry of Coal Bearing Strata (Coal and Coal Bearing Strata. Eds. Murchison and Westoll). Oliver and Boyd, Edinburgh.
- NICHOLLS, G.D. and LORING, D.H. (1962). The Geochemistry of some British Carboniferous Sediments. *Geochim. et Cosmochim. Acta*, 26, 181-223.
- NORRISH, K. and CHAPPEL, J.T. (1967). In: Norrish and Hutton (1964). *Geochim. et Cosmochim. Acta*, 33, 431-453.
- NORRISH, K. and HUTTON, J.T. (1969). An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. et Cosmochim. Acta*, 33, 431-453.
- O'GORMAN, J.V. and WALKER, P.L. Jr. (1971). Mineral matter characteristics of some American coals. *Fuel*, 50, 135-151.
- PAQUET, A. (1969). *Analcite et Argiles diagenetiques dans les Formations sédimentaires du Bassin d'Agadès*. Unpublished Thesis, University of Strasbourg.
- PARR, S.W. (1932). "The Analysis of Fuel, Gas, Water and Lubricants". 4th Ed. McGraw-Hill, New York.
- PEARSON, M.J. (1974). Magnesian siderite in carbonate concretions from argillaceous sediments in the Westphalian of Yorkshire. *Min. Mag.*, 39, 700-704.
- PEARSON, M.J. (1979). Geochemistry of the Hepworth Carboniferous sediment sequence and origin of the diagenetic iron minerals and concretions. *Geochim. et Cosmochim. Acta*, 43, 927-941.
- PENFIELD, S.L. (1894). On some methods for the determination of water. *Am. J. Sci.*, 48, 30-37.

- PICARD, M.D. (1971) Classification of fine-grained sedimentary rocks. *J. Sed. Pet.*, 41, 179 - 195.
- PIERCE, J.W. and SIEGEL, F.R. (1969). Quantification in Clay Mineral studies of sediments and sedimentary rocks. *J. Sed. Pet.*, Vol. 39, 1, 187 - 193.
- PIRET, E.L., EBEL, R. A., KIANG, C.T. and ARMSTRONG, G.W.P. (1951). *Chem. Eng. Prog.*, 47, 628 - 636.
- PITT, G.J. and MILLWARD, G.R. (Eds.) (1979). *Coal and Modern Coal Processing: An Introduction*. Academic Press, London.
- PLUMPTRE, J.H. (1959). *Trans. Instn. Min. Engrs.*, 119, 3, 155.
- POOLE, E.G. et al. (1969). In: Skipsey, 1974. *Bull. Geol. Surv.*, 39, 1.
- POTTER, P.E., SHIMP, N.F. and WITTERS, J. (1963). Trace elements in marine and freshwater argillaceous sediments. *Geochim. et Cosmochim. Acta*, 27, 669 - 694.
- POTTER, P.E., MAYNARD, J.B. and PRYOR, W.A. (1980). *Sedimentology of Shale, Study Guide and Reference Source*. Springer-Verlag, New York.
- POWERS, M.C. (1957). Adjustment of land derived clays to the marine environment. *J. Sed. Pet.*, 27, 255 - 372.
- PRICE, F.R. and JENKINS, D.A. (1980). Removal of resin from standard soil thin-sections by low temperature ashing as a means of following transmitted optical by scanning electron microscopy. *Clay Minerals*, 15, 309 - 315.
- PRICE, N.J. (1959). Mechanics of jointing in rocks. *Geol. Mag.* 96, 149.
- PRICE, N.J. (1966). *Fault and Joint Development in Brittle and Semi-Brittle Rock*. Pergamon Press.
- PRINGLE, W.J.S. and BRADBURN, E. (1958). The Mineral Matter in Coal II - The Composition of the Carbonate Minerals. *Fuel*, 37, 166 - 180.
- RAISWELL, R. (1971). The growth of Cambrian and Liassic concretions. *Sedimentology*, 17, 147.

- RAMSAY, A.C., JUKES, J.B., HULL, E. and HOWELL, H.H. (1852-56). In Mitchell et al., 1945.
- RAYNER, D.H. (1976). The Stratigraphy of the British Isles. Cambridge University Press, Cambridge.
- READ, H.H. (1970). Rutley's Elements of Mineralogy, 26 Ed. Thomas Murby & Co., London.
- RUBEY, W.W. (1951). Bull. Geol. Soc. Am., 62, 111.
- RUCH, R.R., GLUSKOTER, H.J. and SHIMP, N.F. (1973). Occurrence and distribution of potentially volatile trace elements in coal: an interim report. Illinois Geol. Survey Environmental Geol. Note 61, 43p.
- RUCH, R.R., GLUSKOTER, H.J. and SHIMP, N.F. (1974). Occurrence and distribution of potentially volatile trace elements in coal: a final report. Illinois Geol. Survey Environmental Geology, Note 72, 96p.
- SADLER, A.G. (1956). Unpublished Ph.D. Thesis, Leeds University.
- SADLER, A.G. and GRIMSHAW, R.W. (1964). Canada, Dept. of Min. and Techn. Surv., Mines, Branch, Ottawa, Internal Rept., MPL 61-67.
- SAUNDERS, K.H. (1980). Microstructural studies of chlorine in some British coals. J. Inst. Energy, 53, 109-115.
- SWAHNEY, B.L. (1972). Selective sorption and fixation of cations by clay minerals, a review. Clays Clay Miner., 20, 93-100.
- SCHOEN, R. (1962). Semi-quantitative Analysis of Chlorites by X-ray Diffraction. Am. Miner. 47, 1384-1392.
- SCHULTZ, L.G. (1960). Quantitative X-ray Determinations of Some Aluminous Clay Minerals in Rocks. Clays Clay Miner., Proc. 7th Nat. Conf. 216-224.
- SCHULTZ, L.G. (1964). Quantitative interpretation of mineralogical composition from X-ray and Chemical Data for the Pierre Shale. U.S. Geol. Survey Prof. Paper 391-C, 31p.

- SEXTON, A.H. and DAVIDSON, W.B. (1923). Fuel and Refractory Materials. Van Nostrand, New York.
- SEYLER, C.A. (1948). The past and future of coal - the contribution of coal petrology. Proc. S. Wales Inst. Engrs., 63, 213-243.
- SEZGIN, H.I. (1982). The Occurrence and Formation of Kaolinite and other minerals in Coal Measures Rocks from the East Pennine Coalfield. Unpublished Ph.D. Thesis, University of Sheffield.
- SHAPIRO, L. (1960). A spectrophotometric method for the determination of FeO in rocks. U.S. Geol. Surv. Prof. Paper, 400-B.
- SHAW, H.F. (1973). Clay mineralogy of Quaternary sediments in the Wash embayments, Eastern England. Mer. Geol., 14, 29-45.
- SHIEH, Y.-N. and SUTER, T.G. (1979). Formation conditions of authigenic kaolinite and calcite in coals by stable isotope determinations. Clays Clay Miner., 27, 2, 154-156.
- SKIPSEY, E. (1974). Distribution of alkali chlorides in British Coal Seams. Fuel, 53, 258-267.
- SKIPSEY, E. (1975). Relations between chlorine in coal and the salinity of strata waters. Fuel, 54, 121-125.
- SMITH, D.B., BRUNSTROM, R.G.W., MANNING, P.I., SIMPSON, S. and SHOTTON, F.W. (1974). A correlation of Permian rocks in the British Isles. Jl. geol. Soc. Lond., 130, 1-45.
- SMYTH, M. (1966). The association of minerals with macerals and micro-lithotypes in some Australian coals. C.S.I.R.O. Technical Communication, No. 48, 35pp.
- SNYMAN, C.P. (1978). Mineral Commodities from Coal. Trans. geol. Soc. S. Afr., 81, 241-248.
- SOZANSKI, A.G. and CRONAN, P.S. (1979). Ferromanganese concretions in concretions in Shebandowan Lakes, Ontario. Can. J. Earth Sci., 16, 126-140.

- SPEARS, D.A. (1963). Geochemistry of the Mansfield Marine Band.
Unpublished Ph.D. Thesis, University of Sheffield.
- SPEARS, D.A. (1964). The major element geochemistry of the Mansfield Marine Band in the Westphalian of Yorkshire. *Geochim. et Cosmochim. Acta*, 28, 1679-1696.
- SPEARS, D.A. (1967). Boron, and other elements in some Namurian shales from the North of England. *Compte Rendu 6e Congrès Intern. Strat. Geol. Carbonif.*, Sheffield 1967, 4, 1481-1490.
- SPEARS, D.A. (1973). Relationship between exchangeable cations and palaeosalinity. *Geochim. et Cosmochim. Acta*, 37, 77-85.
- SPEARS, D.A. (1974). Relationships between water-soluble cations and palaeosalinity. *Geochim. et Cosmochim. Acta*, 38, 567-575.
- SPEARS, D.A. (1976). The fissility of some Carboniferous shales. *Sedimentology*, 23, 721-725.
- SPEARS, D.A. (1980). Towards a classification of shales. *J. Geol. Soc. London*, 137, 125-129.
- SPEARS, D.A. and AMIN, M.A. (1981). Geochemistry and mineralogy of marine and non-marine Namurian black shales from the Tansley borehole, Derbyshire. *Sedimentology*, 28, 407-417.
- SPEARS, D.A. and KANARIS-SOTIRIOU, R. (1975). Titanium in some Carboniferous sediments from Great Britain. *Geochim. et Cosmochim. Acta*, 40, 345-351.
- SPEARS, D.A. and KANARIS-SOTIRIOU, R. (1979). A geochemical and mineralogical investigation of some British and other European tonsteins. *Sedimentology*, 26, 407-425.
- SPEARS, D.A. and RICE, C.M. (1973). An Upper Carboniferous tonstein of volcanic origin. *Sedimentology*, 20, 281-294.
- SPEARS, D.A. and TAYLOR, R.K. (1972). The influence of weathering on the composition and engineering properties of in-situ Coal Measures rocks. *Int. J. Rock Mech. Min. Sci.*, 9, 729-756.

- SPEARS, D.A., TAYLOR, R.K. and TILL, R. (1971). A Mineralogical Investigation of a Spoil Heap at Yorkshire Main Colliery. Q.J. Eng. Soc., 3(4), 239-251.
- SPRUNK, G.C. and O'DONNELL, H.J. (1942). Bureau of Mines Tech. Paper, 648m 67pp.
- ŠRODŇ, J. (1980). Precise identification of illite/smectite interstratifications by X-ray powder diffraction. Clays Clay Miner., 28, 401-411.
- STACH, E., MACKOWSKY, M.-TH., TEICHMÜLLER, M., TAYLOR, G.M., CHANDRA, D. and TEICHMÜLLER, R. (1975). Stach's Textbook of Coal Petrology (2nd Ed.). Begründer Borntraeger, Berlin.
- STOKKE, P.P. and CARSON, B. (1973). Variation in clay mineral X-ray diffraction results with the quantity of sample mounted. J. Sedim. Petrol., 43, 957-964.
- STOPES, M.C. (1919). On the four visible ingredients in banded bituminous coal. Proc. Roy. Soc. B, 90, 470-487.
- STUBBLEFIELD, C.J. and TROTTER, F.M. (1957). Divisions of the Coal Measures on Geological Survey Maps of England and Wales. Bull. Geol. Surv. Gt. Brit., No. B, 1-5.
- SULIN, V.A. (1946). Waters of oil reservoirs in the system of natural waters. In: Bredehoeft et al. (1963). A.A.P.G. Bull., 47, 257.
- SUDO, T., OINUMA, K. and KOBAYASHI, K. (1961). Acta Univ. Carol. Geol., p. 189.
- TASCH, K.H. (1960). *Berbau-Rdsch.* 12, 153-157.
- TAYLOR, J.H. (1964). Some Aspects of Diagenesis. *Advancement of Science*, 20, 417-436.
- TAYLOR, R.K. and SPEARS, D.A. (1981). Laboratory investigation of mudrocks. Q. J. Eng. Geol., 14, 291-302.
- TER MUELEN, H. (1929). *Rec. Trav. Chim.*, 48, 938.

- THOMAS, J. and DAMBERGER, H.H. (1976). Internal Surface Area, Moisture Content, and Porosity of Illinois Coals: Variations with Coal Rank. Illinois State Geol. Surv., Circ., 473.
- THOMAS, R.S. (1974). Use of chemically-reactive gas plasmas in preparing specimens for scanning electron microscopy and electron probe microanalysis. Proceedings of the Seventh Annual Scanning Electron Microscopy Symposium (Chicago).
- TILL, R. (1969). Correlation and regression. Comput. Applic. Nat. Soc. Sci., 4. Nottingham University.
- TING, F.T.C. (1977). Origin and spacing of cleats in coal beds. Journal of Pressure Vessel Technology, v. 99, Trans. of ASME, p. 624-626.
- TOMLINSON, C.W. (1916). The Origin of Red Beds. Amer. Jour. Sci., 24, 153-179.
- TRUEMAN, Sir A.E. (Ed.). (1954). The Coalfields of Great Britain. Arnold, London.
- TRUEMAN, Sir A.E. and WEIR, J. (1946). A Monograph of British Carboniferous Non-Marine Lamellibrachia. Palaeontogr. Soc.
- TUREKIAN, K.K. and WEDEPOHL, K.H. (1961). Distribution of the elements in some elements in some major units of the Earth's Crust. Bull. Geol. Soc. Am., 72, 175-192.
- VAN KREVELEN, D.W. (1961). Coal. Elsevier, Amsterdam.
- VAN MOORT, J.C. (1971). A comparative study of the diagenetic alteration of clay minerals in Mesozoic shales from Papua, New Guinea, and in the Tertiary Shales from Louisiana, U.S.A. Clays Clay Miner., 19, 1-20.
- VAN WATERSCHOOT, W.A., VAN DER GRACHT, J.M., JONGMANS, W.J. and TESCH, P. (1942). Meded. Geol. Sticht., Serie C.12, 1. Maastricht.

- VELDE, B. and HOWER, J. (1963). Petrological significance of illite polymorphism in Palaeozoic sedimentary rocks. *Am. Min.*, 48, 1239-1254.
- VIVALDI, J.L.M. and GALLEG0, M.R. (1961). Some problems in the identification of Clay minerals by X-ray diffraction 1. Chlorite - kaolinite mixtures. *Clay Minerals Bull.*, 4, 288-292.
- VOGEL, A.I. (1978). *Vogel's Textbook of Quantitative Inorganic Analysis*. 4th Ed. Longman, London.
- WANDLESS, A.M. (1957). British Coal Seams: a review of their properties with suggestions for research. *J. Inst. Fuel*, 30, 541.
- WANDLESS, A.M. (1960). *The Coalfields of Great Britain. Variations in the Rank of Coal*. N.C.B.
- WANLESS, H.R., BAROFFIO, J.R. and TRESPOTT, P.C. (1969). Conditions of Deposition of Pennsylvanian Coal Beds. In: *Environments of Coal Depositions*, pp. 105-142 (Eds. Dapples, C. and Hopkins, M.E.). *Geol. Soc. Amer. Spec. Pap.* 114, 104-142.
- WARRINGTON, G., AUDLEL-CHARLES, M.G., ELLIOTT, R.E., EVANS, W.B., IVIMEY-COOK, H.C., KENT, P., ROBINSON, P.L., SHOTTON, F.W. and TAYLOR, F.M. (1980). A correlation of Triassic rocks in the British Isles. *Geol Soc. Lond.*, Special Report No. 13, 78pp.
- WATT, J.D. (1968). The physical and chemical behaviour of the mineral matter under the conditions met in combustion plant. Part 1. The occurrence, origin, identity, distribution and estimation of the mineral species in British coals. B.C.U.R.A. Leatherhead, Surrey.
- WEAVER, C.E. (1958a). The effects and geologic significance of potassium expandable clay minerals derived from muscovite, biotite, chlorite and volcanic material. *Am. Miner.*, 43, 839-861.
- WEAVER, C.E. (1958b). Geologic interpretation of argillaceous sediments. Part 1 - Origin and significance of clay minerals in sedimentary rocks. *Bull. Am. Ass. Pet. Geol.*, 42, 254-271.

- WEAVER, C.E. (1960). Possible uses of clay minerals in search of coal. Bull. Am. Assoc. Petrol. Geologists 44, 1505-1518.
- WEAVER, C.E. (1961). Clay Minerals of the Ouchita Structural Belt and Adjacent Foreland. Univ. Texas Bur. Economics Geol. Pub. No. 6120, 147-162.
- WEAVER, C.E. (1967). The significance of clay minerals in sediments. In: Fundamental Aspects of Petroleum Geochemistry (Ed. Nagy, B. and Colombo, V.). Elsevier, New York.
- WEAVER, C.E. and POLLARD, C.E. (1973). The Chemistry of Clay Minerals. Developments in Sedimentology 15. Elsevier, Amsterdam.
- WHITEHEAD, T.H., ROBERTSON, T., POCOCK, R.W. and DIXON, E.E.L. (1928). The Country between Wolverhampton and Oakengates (Sheet 153). Mem. Geol. Surv.
- WHITTINGHAM, G. (1954). B.C.U.R.A. Monthly Bull., 18, 581.
- WIKLANDER, L. (1964). In: Bear (Ed.) 'Chemistry of Soil'.
- WILLIAMSON, I.A. (1967). Coal Mining Geology. Oxford.
- WILLS, L.J. (1951). A Palaeogeographical Atlas. Blackie, London.
- WILLS, L.J. (1956). Concealed Coalfields. Blackie, London.
- WILSON, M.J. (1965a). The Origin and Significance of the South Wales Underclays. J. Sed. Petrol., 35, 1, 91-99.
- WILSON, M.J. (1965b). The Underclays of the South Wales Coalfield east of the Vale of Neath. Min. Engng., 124, 389.
- YEARSLEY, C.W. (1932). Unpublished M.Sc. Thesis, University of London.
- ZAINAL, Y.M. (1977). Mineralogy, Geochemistry and the Origin of some Recently Discovered Tertiary Bentonites in Iraq. Unpublished Ph.D. Thesis, University of Sheffield.
- ZALESSKY, M.D. (1915). Mem. comit. geol. Petrograd. 139, new series, 74pp.