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GEOCHEMISTRY AND SEDIMENTOLOGY OF TWO CRETACEOUS COAL DEPOSITS IN CANADA

by

Eileen Van der Flier

Department of Geology

Submitted in partial fulfillment of the requirements for the degree

of Doctor of Philosophy

Faculty of Graduate Studies

The University of Western Ontario

London, Ontario

1985

ABSTRACT

Many potentially harmful, useful, and environmentally important trace elements are found in coal. In recent years attention has been focused on the siting and distribution of these elements. The sedimentology and the mineralogy of coals and sediments in a coal-bearing sequence have an important influence on the geochemistry and trace element siting and distribution. These aspects have however not been examined in an integrated fashion. Such an integrated analysis is the objective of this study.

The two Lower Cretaceous coal-bearing sequences studied are in the Moose River Basin in northern Ontario and the Monkman region in eastern British Columbia.

The sequences were deposited in entirely continental fluvial and upper delta plain/fluvial environments respectively. The mineralogy of the Moose River Basin sediments emphasises their deposition in highly weathered terrain. Quartz, kaolinite, minor illite/muscovite, pyrite, calcite, siderite and rare gibbsite are found. The lignites are relatively clean containing dominantly quartz and kaolinite. The Monkman sediments contain ankerite, marcasite and mixed layer clays in addition to the assemblage mentioned above. The Monkman coals have a higher proportion of mineral-rich bands and contain a greater variety of minerals than the Moose River Basin lignites, however kaolinite is the dominant mineral associated with the more detrital-free lithotypes.

Major and trace elements were analysed by XRF, AA, NAA, DNC, DCP, EMS, and ESCA. Pearson correlation coefficients coupled with SEM-EDX were used to examine the modes of occurrence of trace elements in the coals and sediments. Trace element concentrations and associations were found to be extremely variable. Certain elements in some sample groups are associated with several phases, both inorganic and organic.

Elements which exhibit organic affinities in some sample groups are Sr, Zr, Ga, Pb, Cu, Zn, Ba, Ni, Co, Mo, W, Cl, PGE, U and Th. In the Moose River Basin lignites Cl, Zn, Mo and Pb are associated entirely with the organics. Ga is the only element entirely associated with the organic matter in the Monkman coals. The most common mode of trace element occurrence (e.g. for Cu, Rb, Cr, Au, U, Ti, V, Ni, Zn and in part P, Co, As, Sr, Y, Zr, Nb, Mo, Pb and Th) is in association with the clay minerals. Zirconium, Ti, Th and in some cases Cr and U occur associated with detrital heavy minerals. Cobalt, As and W in some sample sets are identified as being associated with the sulphides. Phosphorous and Sr are found to be associated with carbonates.

Behaviour of some of the elements can be explained using information from the different lithologies, affected by different physical and geochemical conditions.

Due to the mobility of trace elements in coals and sediments, trace elements sites may have varied considerably through time. Organically bound trace elements are less common in the higher rank coals examined. The mode of occurrence of certain elements such as Zn and Ni also varies with concentration. Ni in Ni-poor lignite is organically associated while in Ni-rich samples it is present in pyrite.

Several factors which influence the trace element characteristics of the coal and sediments are proposed. These include mineralogy, variations between and within depositional environments, original vegetation type, composition of the groundwater and flow patterns, nature of the surrounding rocks, diagenetic factors including depth of burial etc., coal rank and postdepositional effects.

ACKNOWLEDGEMENTS

I would like to thank Bill Fyfe for supervising this study. Thanks Bill for your support and contagious enthusiasm.

Thanks are due to Ed Schiller and Ed Santiago of PetroCanada for making my fieldwork at Monkman possible. Field support in the Moose River Basin was provided by the Ontario Geological Survey and Lignasco Resources allowed access to their drill core. Their help is gratefully acknowledged.

Thanks to all my fellow grad students, especially Bill Shotyk for many stimulating discussions, Mike Powell for introducing me to the SEM and Tsai Way Wu for help with the XRF. Thanks are also due to Jim Brown for ESCA work and much useful discussion, and to Gordon Winder for reading the manuscript. Peggy, thanks for all your moral support and for lending a hand whenever it was most needed.

Special thanks to Jill for passing on many of her Ossie manipulating skills and to her, Marcie, Leesa et al for putting up with extreme antisocial behaviour during the final stages of production of this thesis.

To my family in Ireland, thanks for your continued support of whatever I've done.

Finally to Pete for sharing all the many ups and downs, thank you for your help, understanding and never-ending drive.

TABLE OF CONTENTS

LIST OF PHOTOGRAPHIC PLATES

LIST OF TABLES

LIST OF FIGURES

1

CHAPTER ONE

INTRODUCTION

While workers such as V.M. Goldschmidt (1935) were fascinated by trace elements in coals and organic matter, adequate study of trace elements in coal is a relatively recent phenomena. Increased traditional use of coal and its expanding use in liquefaction and gasification processes and the production of coal-derived fuels has initiated and emphasised the importance of gathering detailed information about potentially harmful elements such as As, Cd, Pb and Hg, and environmentally important trace elements including Mo, Se and to a lesser extent Cu, Ni, Zn, V, U, Cr and F. The siting of elements such as Cl, the alkalis and S, is of importance in that they can strongly influence boiler efficiency due to corrosion and fouling.

The mode of occurrence and distribution of major mineral phases and thus of major elements in coal has been well established for many coal deposits (Kemezys and Taylor, 1964, Rao and Gluskoter, 1973, Gluskoter, 1977; Cecil _et al_, 1981; Chou and Harvey, 1983; Hsieh and Wert, 1983; Benson _et al_, 1984 and Davis _et al_, 1984).

Information on trace elements in coal is however less abundant. A considerable amount of work has been done in the last few decades, but many studies concentrate on coals which have anomalous concentrations of a particular element (for example Hawley, 1955; Masursky, 1956; Szalay, 1974 and Eskenazy, 1982). Recently as a result of heightened sensitivity to environmental problems in the light of forecasts projecting increased use of coal in the future, attention is being focused on environmentally hazardous trace elements in coal and their fate during utilization. Some such studies include Ruch et al (1974) and Kaakinen (1975). An increasing number of studies on coals from a single area are being carried out. Many of these, for example Gluskoter et al (1977), have examined samples collected systematically from a well known coal-bearing succession. Few studies, with the exception of Nicholls and Loring (1962) and Zodrow (1983), have analysed the sediments from the same succession. In general the various aspects of coal deposits such as sedimentology, mineralogy and geochemistry have been studied separately.

It is the purpose of this study to examine the modes of occurrence of selected trace elements in coal in the context of the coal-bearing sequence as a whole. The locations of two coal deposits chosen for this study are shown in Figure 1.1.

The aims of the study are to examine

a) the sedimentology of the coal bearing sequences. Lithotypes and lithofacies are distinguished and a depositional model is proposed, Chapter 3.

b) the mineralogy of the various sediment types and the coal. A sequence of mineral genesis is derived and maceral/mineral relationships are examined, Chapter 4.

c) the geochemistry of the coals and sediments, Chapter 5, and

d) the significance and interrelationships of each of the above on the others, Chapter 6.

As many elements as possible including major elements, Cr, Rb, Sr, Zr, Cd, Co, Cu, Pb, Mo, Ni, Zn, U, Th, Y, Nb, Ba, Ga, V, As, W, Au and the platinum group elements were analysed. Associations of these elements with mineral matter (including clay minerals, carbonates, heavy minerals or sulphides) or with the organic substance are examined.

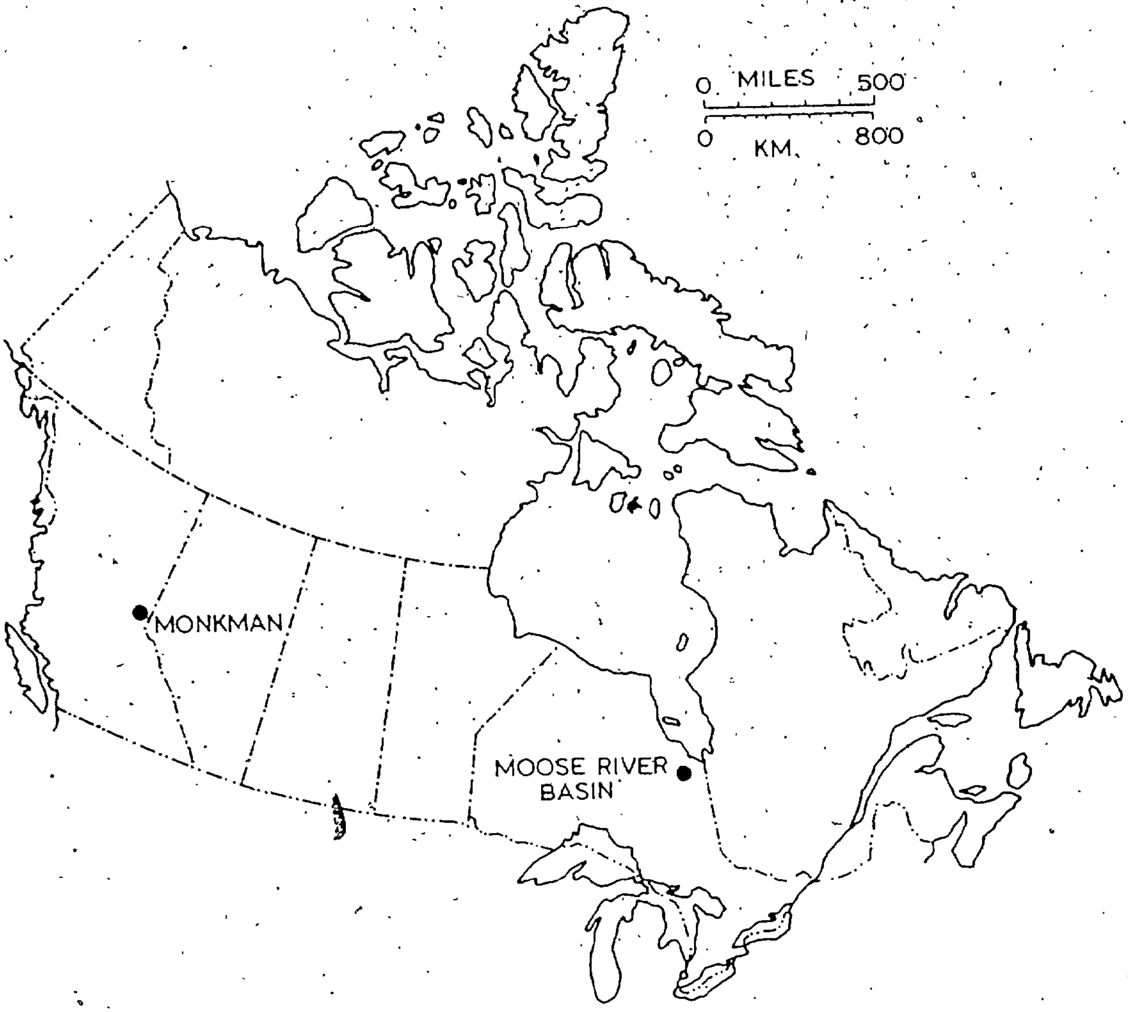


Figure 1.1. Location of study areas.

Many methods have been used to determine the modes of occurrence and in particular the organic inorganic affinities of trace elements in coal. Many of these are summarised in Zubovic et al (1960; 1961), Zubovic (1976), Finkelman (1980) and Palmer and Filby (1983). The most common methods, which include float sink analysis (Gluskoter et al, 1977) and low temperature ashing followed by chemical analyses (Miller and Given, 1977; 1978), involve the disaggregation of the sample as well as removal of the organic material in the latter. To examine trace elements in situ, and in particular their relationships with the macerals, methods such as Scanning Electron Microscopy, Optical Microscopy or Secondary Ion Mass Spectrometry must be employed.

A study by Finkelman (1980) successfully used the SEM to identify the sites of many trace elements in accessory minerals. This method however introduces a bias towards trace elements concentrated in dense easily observed accessory minerals. Trace elements which are associated with the organic material and which are therefore dispersed, are not so readily detected by the SEM. Ion microprobe, and other such techniques must be employed to determine the associations of such trace elements present at ppm levels.

In this study statistical analysis of trace and major element concentrations in the coal and sediments is used in order to gain a more complete picture of trace element systematics in coal-bearing successions. Elements which are organically associated can be distinguished on the basis of their correlation coefficients and suites of elements with which they are associated. Elements associated with the various mineral phases can also be identified. SEM-EDX is also used in conjunction with the statistical analysis and substantiated many of the conclusions arrived at by the latter.

Sources of many of the elements such as U, Zr, Ni and Cr are proposed. This is facilitated by the sampling of all the sediment types.

CHAPTER TWO

REGIONAL GEOLOGY

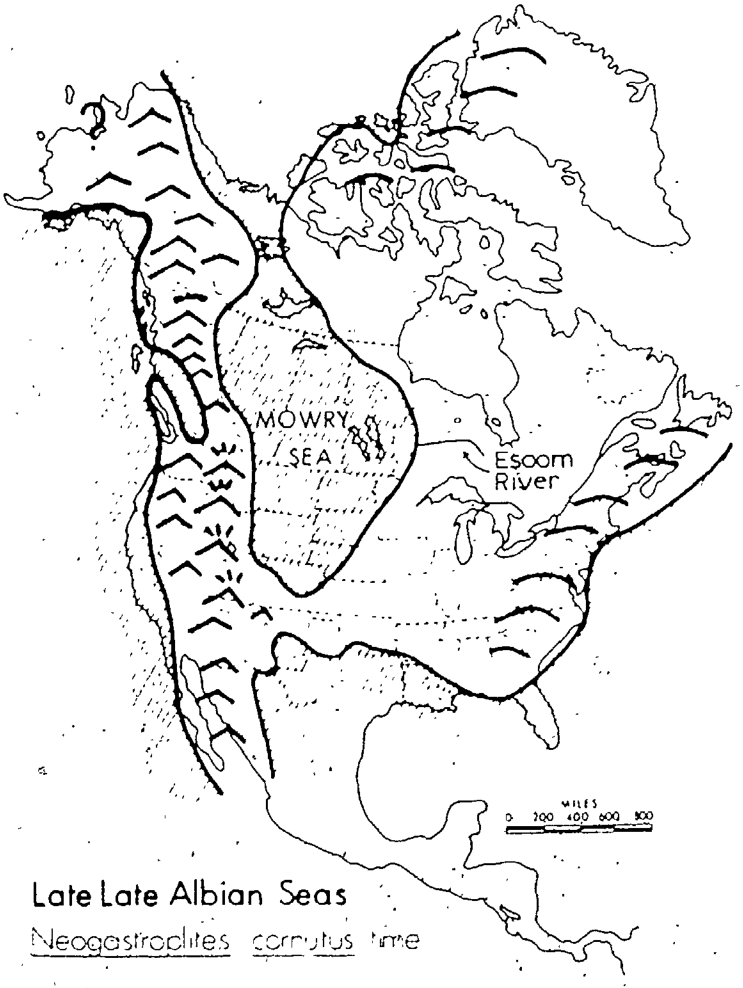
The Mattagami and Gates Formations represent sequences of Lower Cretaceous age which were deposited on two sides of a mid-continental seaway. The regional settings, structure, age and sampling methods will be examined.

2.1 Mattagami Formation, Moose River Basin

The Mattagami Formation occurs in the Mesozoic succession of the Moose River Basin of Northern Ontario. This Phanerozoic sedimentary basin is located southwest of and slightly overlapping the western edge of James Bay. It is separated from the larger Hudson Bay basin to the north by the Cape Henrietta Maria Arch. Both basins are infilled by thick sedimentary packages ranging in age from Middle and Late Ordovician to Upper Devonian in the Hudson Bay Basin and up to Lower Cretaceous in the Moose River Basin. A thin skin of Ordovician and Silurian rocks partly overlies the northwest trending separating arch. Large areas of Precambrian outcrop occur in this area. The sequences are thought to be erosional remnants of a once much more extensive cratonic cover which joined with the Arctic platform in the north, the Allegheny, Michigan and Williston Basins to the south and perhaps was laterally equivalent to the Rocky Mountain sedimentary pile in Alberta and British Columbia to the west.

The palaeogeography during late late Albian time is illustrated in Figure 2.1. Clastic sediments derived from the Appalachian region to the east (Try, 1983; Try et al, 1984) were being deposited on a broad, relatively flat alluvial plain where the major river, the Esoom (Winder

Figure 2.1. Palaeogeography during late late Albian time.



(after Williams and Stelck 1975 and Try et al 1984) et al, 1982 and Fyfe et al, 1983) debouched into the eastern margin of the Albian Mowry sea of Western Canada. The thick deltaic sequences of Lower Cretaceous age in the Rocky Mountain Foothills Belt were being deposited synchronously on the western margin of this seaway.

While the Western Canadian Cretaceous succession contains several cycles of continental sedimentation interrupted by marine sedimentation, the Moose River Basin succession consists of continental sedimentation only. The alluvial plain on the eastern margin was probably considerably broader and with the lesser sediment supply does not appear to have suffered the same regular marine transgressions as noted on the western margin.

The Lower Cretaceous underlies an area of approximately 8380 km.^{2} and possibly up to 13970 km.^{2} (Try et al, 1984), however exposure is limited to the banks of the major rivers and thus information is largely derived from extensive drilling projects. The Lower Cretaceous rocks are generally unconformably underlain by Devonian and Silurian carbonates and clays but recently some drill holes have encountered Middle Jurassic sediments (Mistuskwia Beds) disconformably below the Lower Cretaceous in drillholes 82-01 Lignasco and 75-02 O.G.S. (Telford et al, 1975; Norris et al, 1976 and Norris, 1982; Telford, 1982). The extent of this Middle Jurassic sequence is as yet unknown. The entire area is overlain by a Pleistocene cover (15-90 metres thick), which infills a very irregular palaeotopography.

The Moose River Basin has a faulted southern margin (see Plate 1.), where an abrupt east-west scarp is the contact with the Fraserdale Arch of the Precambrian Canadian Shield. The sedimentary basin is downfaulted relative to the Precambrian. The low lying area between the Fraserdale

Plate 1 Cretaceous/Precambrian boundary in Adam Creek, southern margin of the Moose River Basin.

Arch and the Grand Rapids Precambrian high to the northeast provided a suitable site for the accumulation and preservation of the Cretaceous sediments. The maximum known thickness of Cretaceous accumulation (166 metres) occurs within 10 km. of the Precambrian faulted margin. This also results in the Ordovician to Cretaceous sedimentary sequence being assymetrically located within the basin, with the Lower Cretaceous sediments predominantly in the south and east in the structurally lowest lying areas along the edges of the basin.

There are two main areas of thick lignite- bearing Cretaceous succession, the Onakawana area in the northeast which is adjacent to the northern edge of the Grand Rapids high, and the area around Adam Creek in the southeast of the basin. These thicker successions have formed in structural lows (depressions in the underlying Devonian rocks) adjacent to Precambrian highs.

2.1.1 Age of the Mattagami Formation

Bell (1928) suggested that the sediments of the Mattagami Formation were of Late Jurassic to Lower Cretaceous age. Palynological studies carried out by Telford et al (1975), Hopkins and Sweet (1976); Verma et al (1978), Norris and Dobell (1980) and Norris (1982) confirmed this and determined that the sequence is of Middle to Late Albian (Lower Cretaceous) age. Four zones were recognised (Norris and Dobell, 1980), with the area around Adam Creek containing zones 1 and 2.

2.1.2 Structure and Physiography

The Moose River Basin topographically is a flat lying coastal plain area, which drains towards James Bay by a series of major rivers, the Moose, Abitibi, Mattagami, Missinaibi and Albany rivers. The areas between the rivers and their numerous tributaries are wet and muskeg -covered. Higher ice-thrusted zones exist adjacent to the rivers and these support stands of birch and pine.

The Cretaceous sediments are generally flat-lying or dip very slightly (less than 5 degrees) to the north. Many of the river edge exposures at Adam Creek have substantial dips and appear folded (Fyfe et al, 1983). This is thought to be due to local unloading due to rapid erosion of the Creek and subsequent rotational block slumping towards the river.

Exposure in the area is poor, consisting mainly of small outcrops along river banks. Adam Creek is a diversion channel for four Ontario Hydro dams on the Mattagami river. It has been deeply eroded by excess water from the Little Long Rapids Dam spillway, uncovering good Cretaceous sections lying beneath 20 to 30 metres of Pleistocene cover. Adam Creek provided the only outcrop samples for this study. Access to the area was by helicopter (courtesy of the Ontario Geological Survey).

2.1.3 Previous Work

Lignite was first recognised in the area in the late nineteenth century. Keele (1920) distinguished the lignite-bearing sediments from the overlying Pleistocene deposits of the Missinaibi Formation, and named them the Mattagami Series. This series was changed to formational status by Dyer (1928).

Much drilling has been carried out in the Moose River Basin, beginning in 1929 (Dyer, 1930) and continuing until the present. Early reports of the geology and economic potential of the area include Dyer (1931a; 1931b and 1929). Price (1978) and Verma (1982) summarize the exploration in the area. Much of the initial work concentrated in the northeast in the Onakawana lignite field where substantial lignite reserves were proven.

The lignite occurs in two seams, the upper being thinner and higher in ash than the lower. A 0.3 to 4.6 metre clay band separates the seams whose total thickness is approximately 15 metres (Vos, 1982). The lignite seams are largely continuous throughout the Onakawana area.

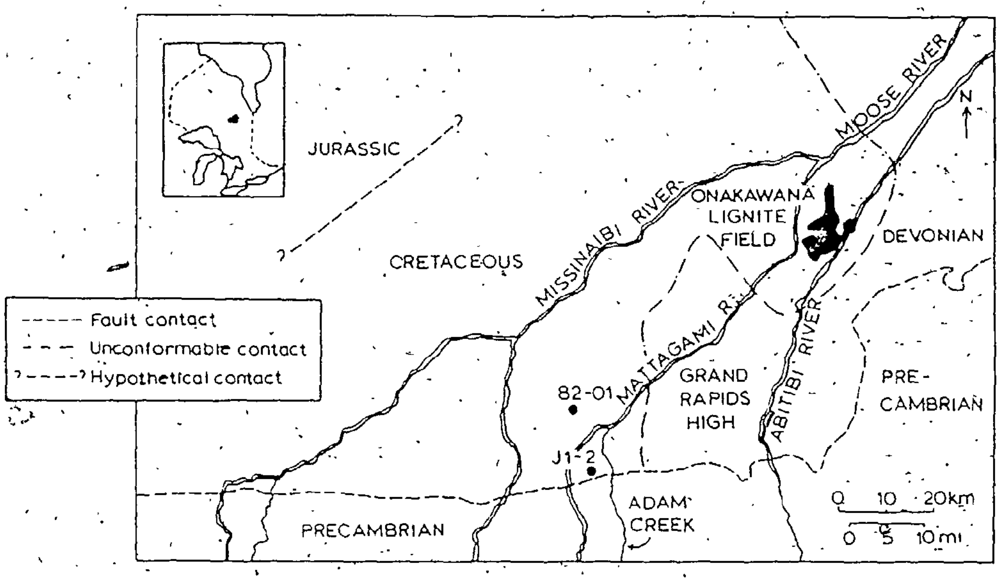
Attention subsequently shifted to the southern part of the basin, where lignite and farther reserves of kaolin and refractory clays were found. Telford and Verma (1979) and Telford (1982) have documented the results of drilling in this area. The Ontario Geological Survey, Ontario Energy Corporation and Lignasco Resources are presently active in the Moose River Basin.

Geochemical and sedimentological studies on the sediments and lignites from the south of the basin are documented in Fyfe et al (1983) and Try et al (1984).

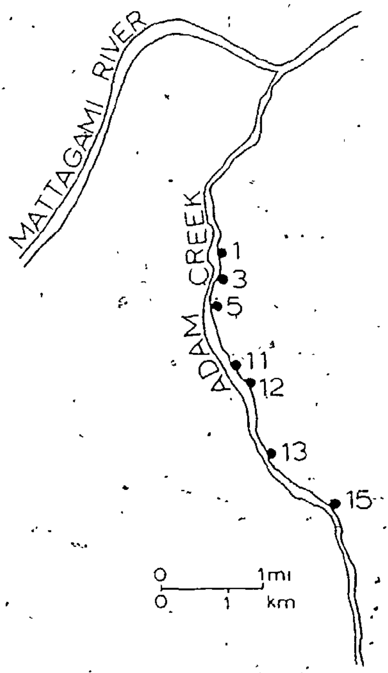
2.1.4 Sampling

Sampling was concentrated in the southeast part of the basin, due to the availability of recent drillcore and the outcrop along Adam Creek. Sections were measured and sampled on visits to Adam Creek in 1981 and 1982. Other samples are from two Lignasco drillholes 8 km to the northwest of Adam Creek, which were examined and sampled in Thunder Bay in late 1983. The holes were drilled by the vibracore technique thus disturbing the sample as little as possible and providing 16 cm diameter core. The location of all sampling sites are shown in Figures 2.2 A and B. Samples collected from Adam Creek are identified by the suffix AC and the year of collection follows the sample number. The samples from

Figure 2.2A. Geology of the Moose River Basin and location of drill holes sampled.



B. Location of sample sites on Adam Creek.



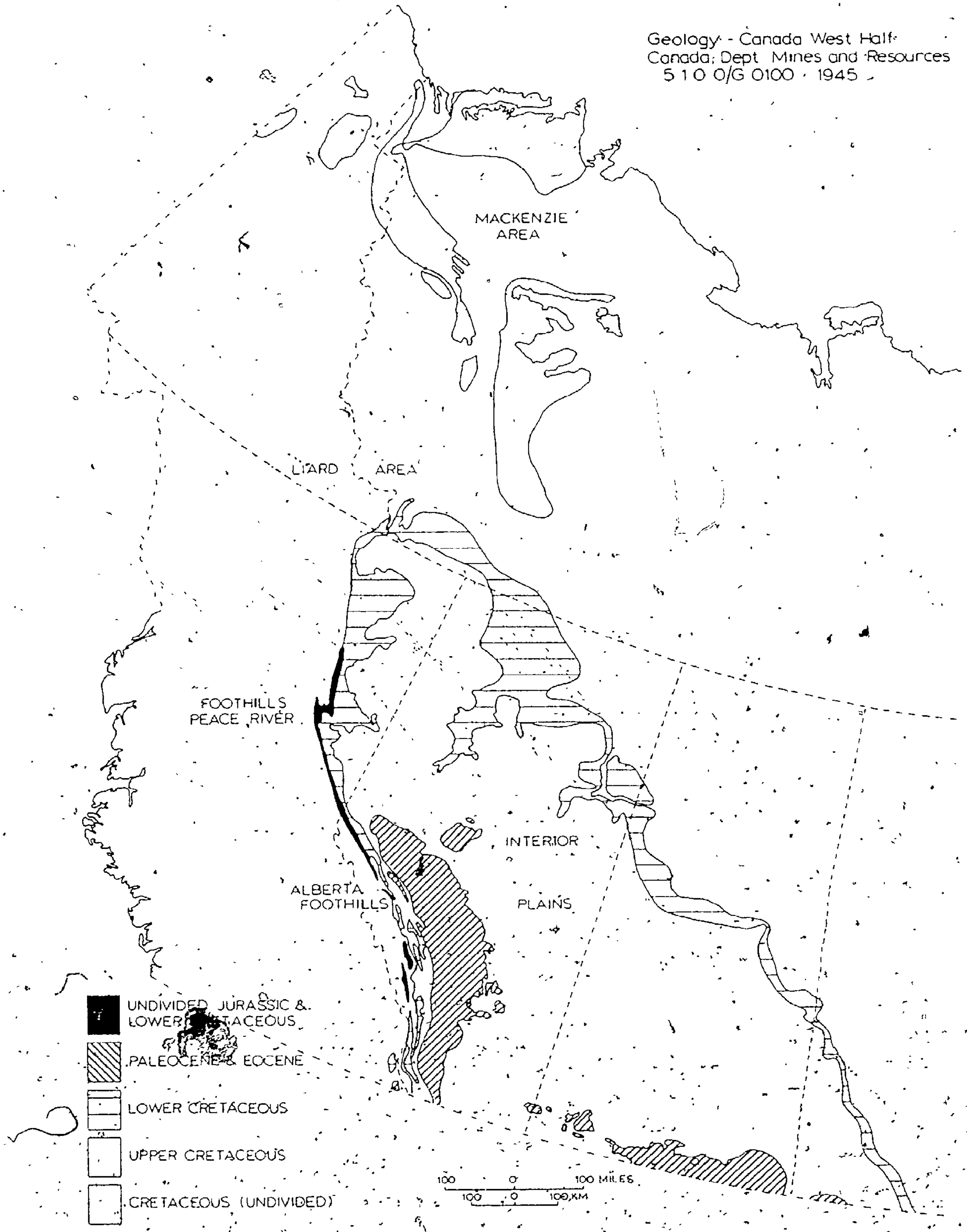
Lignasco drillholes 82-01 and J-1-2 are numbered L-1-x and L-2-x respectively.

The Mattagami Formation in the area examined consists of clean gravels, sands, silts and muds with up to three thin lignite seams. The samples are largely unconsolidated, except for materials in what has been called the Devonian Sextant River Formation (thought however to be of Cretaceous age and laterally equivalent to the Mattagami) and occasional sandstone and gravel outcrops cemented with pyrite and/or carbonate (AC-13-82, RP, RC1). In the unconsolidated material clean sediment was sampled where possible. All samples were transported to the laboratory in sealed light or heavy plastic bags. Adventitious material was removed from the samples by washing with distilled water and those parts of the samples containing much dirt were discarded. The drillcore was split and outer rims of material containing drilling fluid were removed to access the clean sample. The drilled material was on the whole undisturbed, however areas at the base of 82-01 (Lignasco) were highly disturbed and therefore avoided.

2.2 Gates Formation, Northeast British Columbia

The Cretaceous System of northeast British Columbia outcrops along the entire length of the Rocky Mountain Foothills Belt. Cretaceous rocks also occur in the subsurface of the Interior Plains and extend north to the Liard Plateau of the Yukon and to the North West Territories (Figure 2.3). The Cretaceous rocks of northeast British Columbia were deposited along the western margin of the Western Canada Sedimentary Basin and form a major clastic wedge whose thickness decreases eastward below the plains from a maximum of 1,200 metres in the west to 300 metres in the

Figure 2.3 Distribution of Cretaceous rocks in Western Canada



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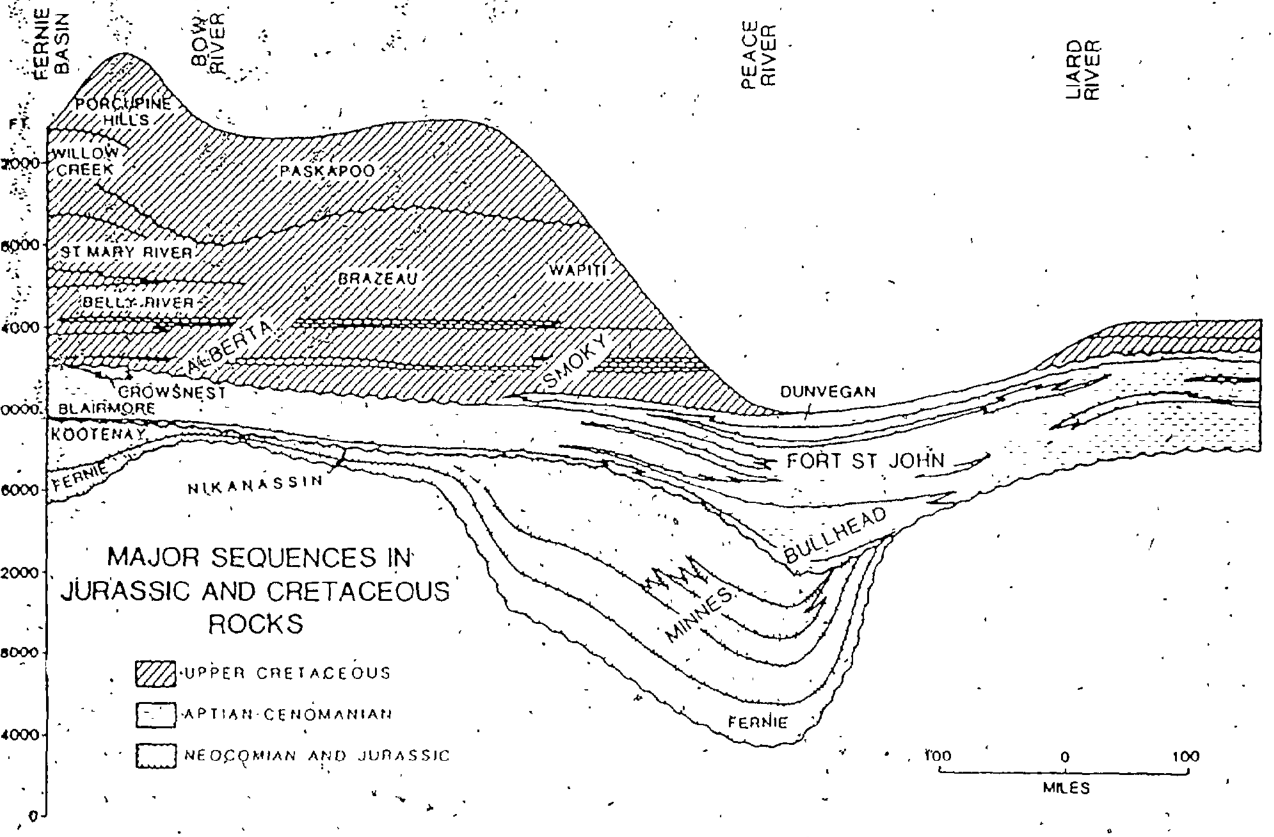
eastern foothills. Due to the southwesterly/southerly derivation of the sediments the present rocks carry a signature of the granites and other metamorphic phases resulting from the Columbian orogeny in the Cordilleran Geosyncline. The western margin of the basin is not preserved and the limit of Cretaceous exposure in this direction is marked by some major faults of the Rocky Mountain System, where Lower Cretaceous rocks are in faulted contact with Devonian and Silurian limestones. The Cretaceous and Upper Jurassic rocks unconformably overly older rocks which become older to the north and east.

Three major clastic sequences are contained in the Cretaceous rocks of northeast British Columbia (Figures 2.4 A and B), each deposited by a major transgressive-regressive cycle. These are related to variations in rates of subsidence in the marine embayment, influx of clastic material, rates of source region uplift and possibly also to global scale eustatic sea level changes. The oldest sequence is represented by marine shales of the Fernie Formation deposited during a late Jurassic transgression of the boreal marine embayment into the northern parts of the Alberta trough. These are overlain by sandstones and mudstones of the Minnes Group which were deposited in the Latest Jurassic to Valanginian when the sea regressed completely from the craton. The middle cycle in the area of study consists of the Bullhead and Fort St. John Groups and the Dunvegan Formation, which were deposited during the late Neocomian and Albian and will be discussed in detail later. The youngest sequence is formed by the Smoky Group and Wapiti Formation, which were deposited during Turonian to Santonian and Campanian to Maastrichtian time respectively (Late Cretaceous). The Smoky Group shales record two marine cycles which were followed by a major regressive event. The Wapiti

Figure 2.4A. The Cretaceous and Upper Jurassic stratigraphy in Northeastern British Columbia (Pine River Region), from Stott 1975. C=continental M=marine

	Group	Formation (thickness in feet)	Member	Description		
Upper Cretaceous		Wapiti (0-1,500)		Conglomerate, fine- to coarse-grained sandstone carbonaceous shale and coal	C	UPPER SEQUENCE
	Smoky Group (1,250-3,900)	Puskwaskau (375-1,200)	Nomad (0-159)	Rusty weathering rubbly shales greenish grey shales and fine-grained thin-bedded sandstones	M	
			Chungo (12-154)	Fine-grained thick-bedded brown weathering sandstones and dark grey siltstone		
			Hanson (115-174)	Dark grey, rusty weathering, blocky to rubbly shales		
			Thistle (100-400)	Dark grey to black, calcareous platy to fissile shales		
			Dowling (50-200?)	Dark grey rubbly to platy shales weathering rust		
		Bad Heart (0-45)		Fine-grained thick- to thin-bedded sandstone weathering brown in some regions includes brackish and non-marine carbonaceous, greyish and greenish shales	C	
		Muskiki (115-381)		Dark grey rubbly to platy shales, weathering rust and having banded appearance	M	
		Cardium (157-225)	Baytree (0-37)	Massive to thick-bedded conglomerate of chert and quartzite pebbles in coarse-grained sandstone matrix	C	
			Moosehound (0-143)	Greyish green to brown carbonaceous rubbly shales fine- to coarse-grained carbonaceous sandstones thin coal beds minor conglomerate		
			Ram (40-44)	Fine-grained thick-bedded sandstone weathering rusty brown		
		Kaskapau (850-2,500)	Opabin (175-325)	Dark grey rusty weathering, blocky to rubbly shales	M	
			Haven (100-620)	Dark grey to black rubbly to platy shales weathering rust, with yellow efflorescence and fetid odour		
			Vimy (250-400)	Dark grey to black, calcareous platy to fissile shales includes much fine-grained thick- to thin-bedded sandstone in northwestern part of region		
			Sunkay (100-1,000)	Dark grey rubbly to platy shales weathering rust sandstone fine-grained thick- to thin-bedded and siltstone argillaceous sideritic concretions		
		Dunvegan (350-1,200)		Fine- to coarse-grained sandstone conglomerate carbonaceous shale and coal	C	MIDDLE SEQUENCE
Lower Cretaceous	Fort St John (2,000-5,000)	Cruiser Fm (350-400)		Dark grey marine shale with sideritic concretions some sandstone	M	
		Goodrich Fm (50-1,350)		Fine-grained, crossbedded sandstone shale and mudstone	C	
		Hasler Fm (500-1,500)		Silty, dark grey marine shale with sideritic concretions siltstone in lower part	M	
		Commotion (1,080-1,500)	Boulder Creek Member (240-560)	Fine-grained well sorted sandstone massive conglomerate non-marine sandstone and mudstone	C	
			Hulcross Member (0-450)	Dark grey marine shale with sideritic concretions	M	
			Gates Member (220-900)	Fine-grained marine and non-marine sandstones conglomerate coal shale and mudstone	C	
		Moosebar (200-1,000)		Dark grey marine shale with sideritic concretions glauconitic sandstone and pebbles at base	M	
	Bullhead (300-2,500)	Gething (75-1,500)		Fine- to coarse-grained brown calcareous carbonaceous sandstone coal carbonaceous shale and conglomerate	C	
		Cadomin (45-700)		Massive conglomerate containing chert and quartzite pebbles		
	Regional erosional unconformity bevels rock of successively older age northward and eastward					
	Minnes (0-4,500)	Unnamed (0-1,400?)		Sandstone, fine-grained and silty shale carbonaceous in part	C	LOWEST MAJOR CYCLIC CLASTIC SEQUENCE
		Monach (0-1,000)		Sandstone, fine-grained argillaceous massive, fine- to coarse-grained quartzose sandstone		
		Beattie Peaks (0-1,300)		Interbedded fine-grained sandstone and silty shales		
		Monteith (0-1,000)		Sandstone, fine grained white, quartzose fine- to coarse-grained sandstone		
Jurassic		Fernie (0-1,500)		Calcareous and phosphatic shales, rusty weathering shales glauconitic siltstone sideritic shales, thinly interbedded sandstone shale and siltstone	M	

Figure 2.4B A schematic cross-section illustrating the three clastic wedges within the Jurassic and Cretaceous rocks between the Fernie Basin and the Liard River, from Stott 1984.



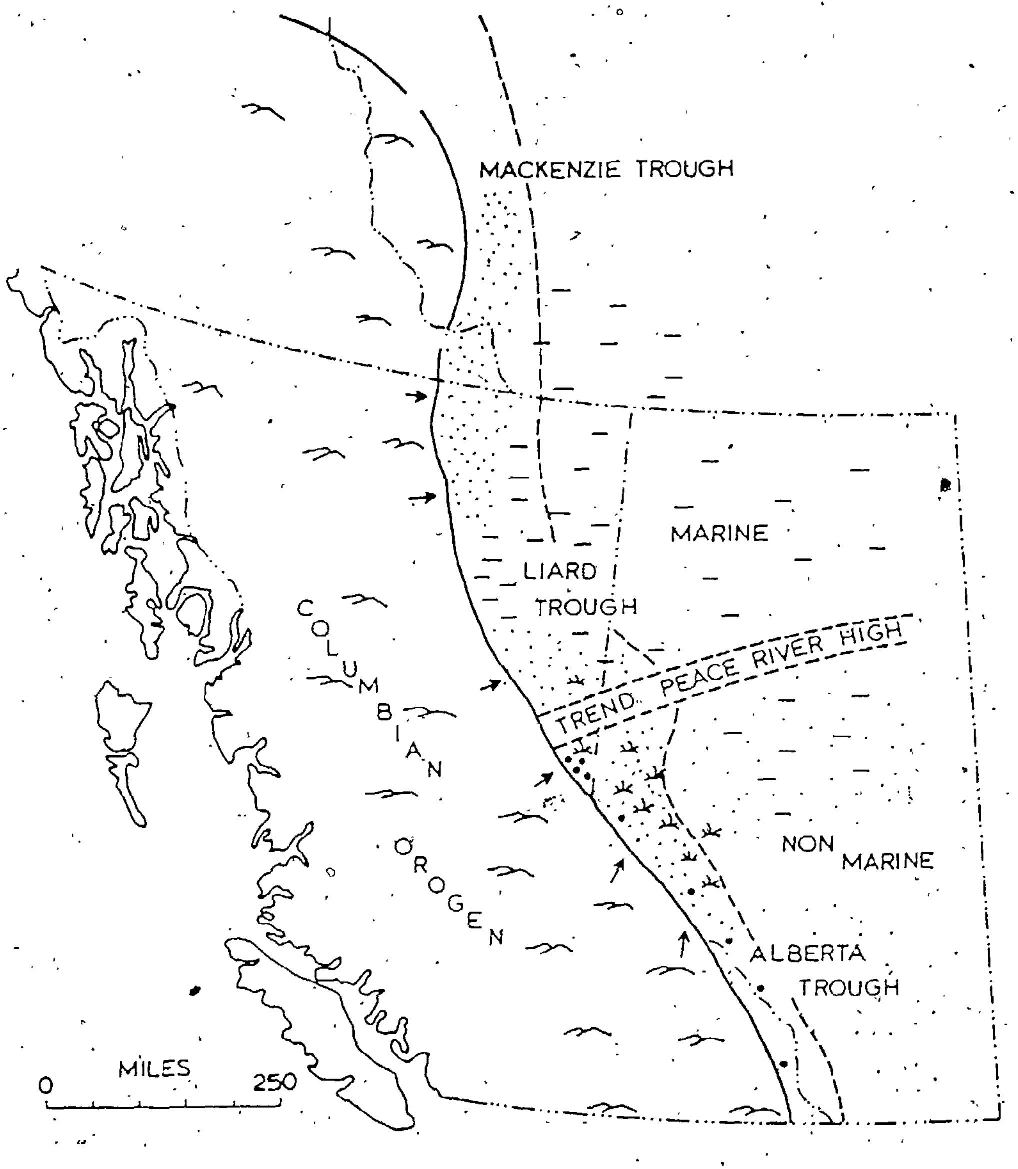
Formation, consisting of dominantly continental sandstones, shale and coal, forms a thick wedge which extends from the foothills across the plains.

2.2.1 Palaeogeography and Description of the Middle Sequence

The palaeogeography during the Albian, when the middle sequence was being deposited, is illustrated in Figure 2.5. Clastic material, derived from the continuing uplift of the Cordilleran region associated with the Columbian orogeny, was deposited towards the north and northeast (Carmichael, 1981 and Leckie, 1981) into the adjacent subsiding Alberta trough. Renewed subsidence in the Alberta trough at the beginning of the Albian allowed the advance of a major Boreal seaway southward toward the Peace River. The seaway was bordered to the south by a broad low lying alluvial plain and to the southwest by several large deltas, from which direction the major sediment supply was derived (material added to the eastern margin of the seaway from the Appalachian highlands was negligible in contrast). Four major transgressions and subsequent regressions occurred in the middle sequence following the initial Bullhead Group transgression. These cycles are represented in the stratigraphy by marine shale succeeding, and laterally equivalent to, nearshore and alluvial deltaic sandstones, shales and coals. Thickest sediment sequences and the major delta depocentres are adjacent to basement highs such as the Peace River Arch (for example see the isopach map of the Fort St. John Group in Stelck, 1975, p455).

The Bullhead Group in the area of study is underlain by a regional erosional unconformity followed by coarse massive Cadomin conglomerate and coarse grained sandstone. The overlying Gething Formation consists of mainly nonmarine calcareous sandstone interbedded with conglomerate,

Figure 2.5. Palaeogeography during the Lower Cretaceous, Early Albian, in Western Canada.



— DEPOSITIONAL LIMIT
•• CONGLOMERATE
∴ SANDSTONE
– SHALE MARINE
⅄ COAL
NON MARINE (UNDIFFERENTIATED)
MOUNTAINOUS LAND
→ DIRECTION OF SEDIMENT TRANSPORT

(from Douglas et al, 1981, and Stott, 1984) siltstone, claystone and coal. Above the Gething Formation are eight units in the Fort St. John Group and Dunvegan Formation which are alternately marine and nonmarine and represent four transgressive-regressive cycles. The Gates Formation is the regressive half of the first of these transgressive-regressive cycles. The first unit in the Fort St. John Group is the Bluesky Formation, a thin poorly developed glauconitic and non glauconitic conglomerate and sandstone unit. This is abruptly overlain by dark grey claystones and siltstones of the Moosebar Formation. Thicknesses of each of the Formations in the Monkman area are shown in Figure 2.6, along with the stratigraphy. The thickness of the succession is controlled by Precambrian basement topographic features such as arches and basins (Stelck, 1975). The Monkman area in Lower Cretaceous time lay towards the north end of the western edge of the Alberta basin, to the south of the Peace River Arch. The proximity to this basement high facilitated the accumulation of a great thickness of sediment in the adjacent trough. This pattern can be observed along the length of the Rocky Mountain Foothills belt.

2.2.2 The First Transgression-Regression of the Fort St. John Formation

The first cycle is represented by the Moosebar and Gates Formations. The Moosebar Formation can be divided into two distinct members in the Monkman area. The lower member, about 75 metres thick, contains a coarsening upward sequence of dark grey claystones containing sideritic concretions. Two thin whitish grey kaolinitic bands occur in the middle of the member and the abundance of silty sandy phases increases above these bands. The member is characterised by heavy bioturbation, pyrite disseminations and minor marcasite blebs. The upper

Figure 2.6 Monkman Area Stratigraphy

Period	Group	Formation	Lithology
Lower Cretaceous	Fort St. John	Shaftesbury 250 m	Dark grey marine claystone; sideritic concretions, some sandstone grading to silty dark grey marine claystone and siltstone in lower part; minor conglomerate at base.
		Boulder Creek 150 m	Fine to coarse nonmarine sandstone; claystone, carbonaceous claystone and conglomerate. Few thin coal seams towards base.
		Hulcross 85 m	Dark grey marine siltstone interlayered with fine sandstone and claystone; gradational change to non-marine mollusc-bearing sandstone and claystone in south.
		Gates 270 m	Fine to coarse non-marine sandstone; conglomerate, major coal seams, siltstone and claystone.
		Moosebar 100 m	Dark grey marine claystone with sideritic concretions in the lower part; gradational increase in sandstone and siltstone at top.
		Bluesky 5 m	Glauconitic fine-grained sandstone, varying locally to glauconitic cobble-conglomerate.
		Gething 130 m	Fine to coarse brown sandstone, coal, carbonaceous claystone and conglomerate.
	Bullhead	Cadomin 60 m	Massive conglomerate containing chert and quartzite pebbles interbedded with quartzose sandstone.
Jura-Cretaceous	Minnes	Nikanassin +2000 m.	Conglomerate, carbonaceous claystone, thin bedded grey and brown sandstone; contains numerous coal seams.

From PetroCanada 1981.

member, 24 metres thick, is coarser and contains interbedded siltstones and claystones, with sandstone beds becoming increasingly dominant towards the top of the member. The upper member is thought to represent a transitional environment between the transgressive marine clays of the lower Moosebar Member and the regressive continental sediments of the Gates Formation.

The Gates Formation consists of a cyclic succession of sandstones, claystones, siltstones, conglomerate and coal. The Formation which is 270 metres thick contains up to twelve coal seams and is the principal coal bearing unit in the area. The Torrens Sandstone, a resistant medium grained massive sandstone forms the base of the Gates Formation. It has a conformable and occasionally gritty contact with the Transition Beds (Carmichael, 1982) which occur between the Moosebar Formation and the Gates Formation. Above the Torrens Sandstone is a carbonaceous claystone/siltstone which underlies the oldest coal seam B1. Overlying the coal bearing part of the member are carbonaceous claystones and siltstones, similar to those which occur interbedded with the coals. A thin pebble conglomerate bed 10-30 cms thick forms the contact between the Gates Formation and the marine Hulcross Formation above. The Hulcross and overlying Boulder Creek Formations represent the second transgressive-regressive cycle in the Fort St. John Group. In the Monkman area the marine Shaftesbury Formation is the youngest stratigraphic unit represented, therefore the regressive half of this cycle and a farther transgressive-regressive cycle are not preserved. The Gates Formation to the north contains non-marine sediments interbedded with three major marine units (Carmichael, 1983), whereas the southern exposures of the Gates are nonmarine.

The Moosebar-Gates cycle lies within the Arcthoplites (=Lemuroceras)-Beudanticeras affine zone of early Albian age (McLearn and Kindle, 1950 and Stott, 1968). The Gates Formation also contains microfauna of Middle Albian age (Stelck et al, 1956) as well as Lower Blairmore-Luscar-Gething flora of Aptian age which must therefore extend up into sediments of Middle Albian age. (More details of the flora and fauna and age determination of the Gates Formation can be found in Stott (1968; 1982).

2.2.3 Previous Work

Coal or "bituminous" substance of Cretaceous age in northeast British Columbia was first noted by Alexander Mackenzie in 1801 in the Peace River Canyon. Early geological reports on the area including Selwyn (1877), Galloway (1924), McLearn and Irish (1944) and Hughes (1964; 1967) were subsequently published. Results of many important early investigations into the Cretaceous stratigraphy by McLearn were compiled by McLearn and Kindle (1950).

Stott (1968) presents a detailed summary of the stratigraphy and occurrences of the Lower Cretaceous Bullhead and Fort St. John Groups and Stott (1975: 1984) provides a regional overview of the Cretaceous system in Northeast British Columbia. Stott (1974: 1982) and McLean (1982) concentrate on the coal-bearing Lower Cretaceous strata in the Foothills of west-central Alberta and northeastern British Columbia and in the Foothills of Alberta respectively.

More specific studies on aspects of the coals such as rank studies, quality and petrographic composition are documented in Hacquebard and Donaldson (1974), Pearson (1980) and Kalkreuth (1982). The mineralogy, degree of diagenesis and sources of the sediments are described in

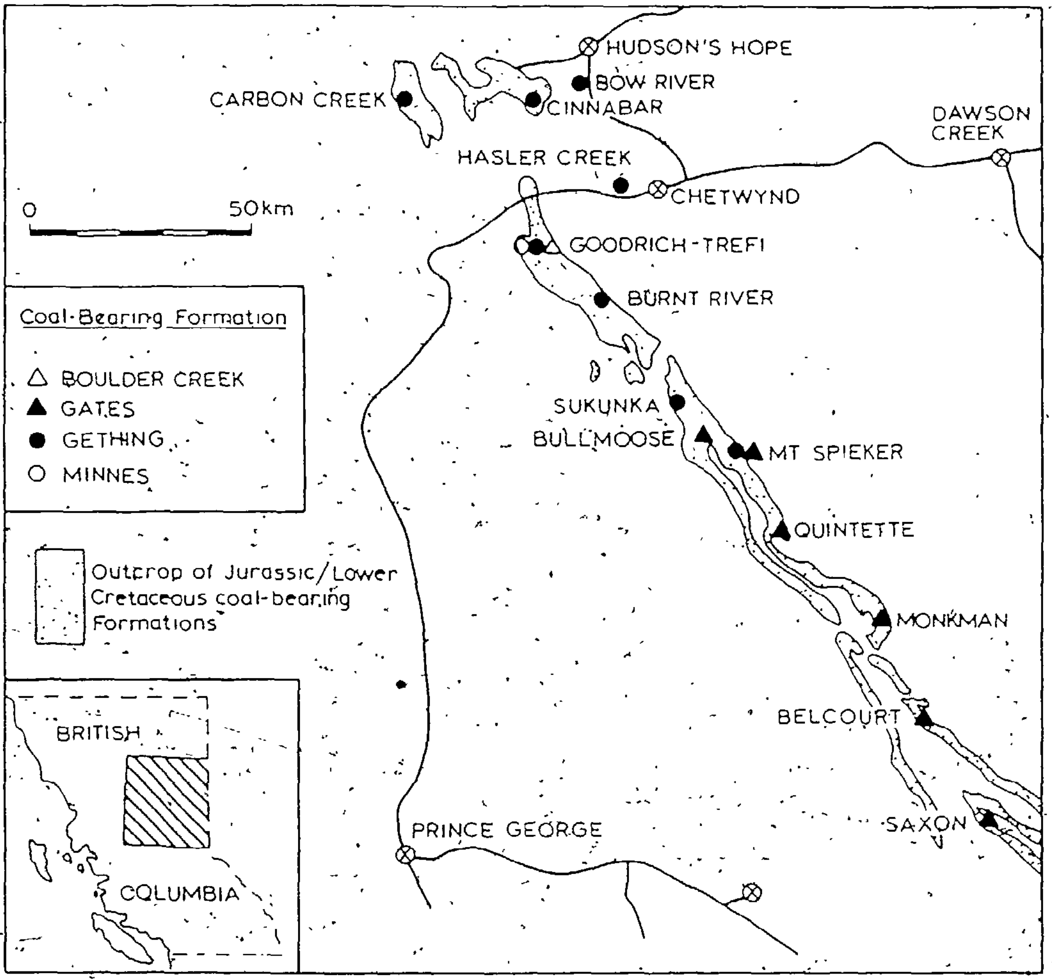
Foscolos and Stott (1975) and Spears and Duff (1984). A detailed sedimentological study of the Moosebar and Gates Formations in the Northeast Coalfields is described in Carmichael (1983).

2.2.4 Regional Coal Geology

The Lower Cretaceous in the Rocky Mountain Foothills belt is an important coal-bearing unit. Economic coal seams are located in the Minnes Group, the southerly equivalent of which, the Kootenay Formation, is the main coal-producing unit in the Kootenay district coalfields, southern Rocky Mountains. The Gething and Gates Formations contain the important coal seams in the Peace River or Northeast Coal Block (Schiller, 1982), to the north. The southerly coalfields in this area contain economic seams in the Gates Formation, while farther north the principal coal-bearing units are the Gething and occasionally the Minnes and Boulder Creek Formations (Figure 2.7).

The main coal seams in the Monkman area are in the Gates Formation, with minor and thin seams occurring in the Gething Formation and the Minnes Group. The coals in the Gates Formation in the Rocky Mountain Foothills Belt appear to lie in four main zones, which are described fully in Stott (1974). These zones can not be correlated other than in areas where extensive drilling has taken place. The coal seams at Monkman appear to lie in the second coal zone (i.e. immediately above a thick unit of fine grained sandstone considered to mark the base of the Gates Formation). Due to progradation of the delta plain on which the coal deposits developed, the seams may not be laterally equivalent but are younger to the north.

Figure 2.7. Locations of developing coal properties in the North East Coal Block, identifying coal-bearing Formations.



(Modified from Schiller, 1982)

2.2.5 Physiography, Structure and Sampling

The Monkman licenses (Figure 2.8) which are held by Monkman Consortium, are located between the Peace and Smoky rivers, approximately 30 km. west of the British Columbia/Alberta border. Dawson Creek is 100 km. to the north and Prince George 100 km. to the southwest.

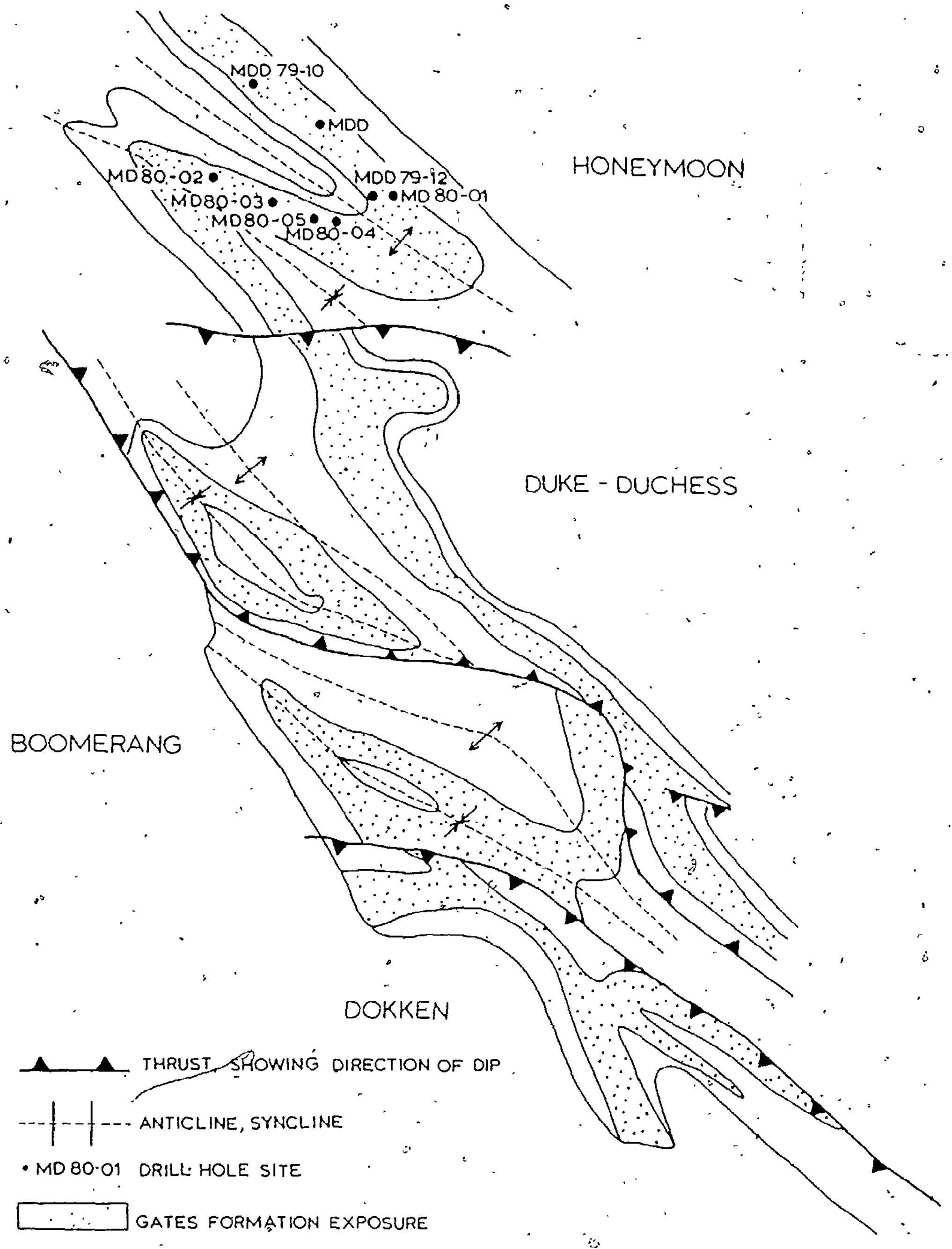
The topography in the Monkman area is typical of the Rocky Mountain Foothills Belt, with rolling hills where good rock exposure can be found at the crests and in river and road cuts. The Cretaceous hills lie in thrust fault contact with higher and steeper Devonian and Silurian limestone ridges which are tightly folded.

The Cretaceous rocks are well consolidated and are allocated to the intermediate middle stage of diagenesis by Foscolos and Stott (1975).

The Monkman area contains four thrust fault-bounded blocks, dividing the area into the Honeymoon, Duke-Duchess, Boomerang and Dokken "pits". The first three blocks contain an anticline-syncline pair, which are arranged en echelon from north to south. The folds trend northwest and are cut by southwest dipping thrust faults. Similar structures arranged en echelon occur throughout the region. Economic coal seams are located in the Honeymoon and Duke Mountain (Duke-Duchess) blocks.

The Honeymoon Pit was chosen for study because of the greatest extent of drilling in this area. The main thicknesses of the coal seams occur on either side of the anticline and six drill holes from both sides were sampled in detail. The general dips are 45° northeast and 48° southwest on the north and south sides of the anticline. The coal from the major seams had been sampled on extraction, so crushed samples only of these coal seams were available. Undisturbed coal was sampled in the

Figure 2.8. Geology of the Monkman area and location of the sampling sites.



from Petro Canada 1981

minor coal seams. No outcrop samples were taken due to the thickness of the oxidised and weathered zone in the area. Samples of 1 kg. were transported to the lab in thick plastic bags.

CHAPTER THREE

SEDIMENTOLOGY

3.1 Introduction

The Mattagami and Gates successions are divided into several lithotypes. A number of lithofacies are identified on the basis of these lithotypes. The depositional conditions for each facies are discussed and from this an overall depositional model is proposed.

The information from the Monkman area comes mainly from drill core data. Gamma and neutron logs provide a measure of the lithology and porosity of the rocks respectively, while density logs indicate the formation density. Drillers logs were also used and farther information was provided by examination of the drill core where possible. Many sedimentary structures and textures visible in outcrop may thus have been overlooked in the drill core material.

The Mattagami Formation data comes from both outcrop and drill core information. The outcrop as mentioned previously has undergone an unknown degree of disturbance and thus reliable palaeocurrent data are not available.

The sedimentology of the Mattagami Formation will be discussed first followed by that of the Gates Formation.

3.2 The Mattagami Formation

The Mattagami Formation consists of a variable sequence of sediments including gravels, sands, silts, clays and lignites. Five lithotypes are present namely gravel and thick sand, thin sands, silts, clays and lignite. These fall into three lithofacies which relate to sedimentation at various sites in the environment of deposition. The lithofacies are a) coarse channel deposits of gravels and sands b) fine grained proximal floodplain deposits consisting of interbedded sand and silt and c) distal floodplain sediments such as clays and swamp deposits.

3.2.1 Lithotypes

Gravel and Thick Sands

The gravels in the section occur interbedded with thick sands in units up to approximately 17 metres thick. The gravels are dominantly clast supported (Plate 2.A), with clasts up to 2 cm in diameter which are angular to well rounded. Large grains tend to be better rounded and exhibit low to high sphericity. Clast composition is variable ranging from white, pink, yellow and grey quartz (93%), black chert (1%), red jasper (1%) and grey tan limestone fragments (1%) to intraformational mud lumps (1%) (approximate percentages are given in parentheses). Organic fragments (3%) are also present in places e.g. the red cemented outcrop on Adam Creek (Location [illegible]), where wood chunks up to 20 cm long are found. The matrix consists either of white kaolinite or greyish brown clay. The percentage of matrix varies from approximately 5 to 15 %. Sorting is generally poor. The proportion of gravel relative to sand is very low in the thick sands and gravels. The sands are coarse to fine grained with similar mineralogical characteristics as the gravels.

Subdivisions of the section have been proposed on the basis of the gravel sand units (Hamblin, 1981 and Telford, 1982). Hamblin used characteristics of the sands such as heavy mineral content, calcite dolomite ratio, sphericity and colour to distinguish an "older, white, calcareous, sorted, angular, spherical, medium, pure

Plate 2.A Gravel outcrop at Location 15, Adam Creek, Moose River Basin showing clast-supported nature of these materials. Lens cap measures 5 cms in diameter.

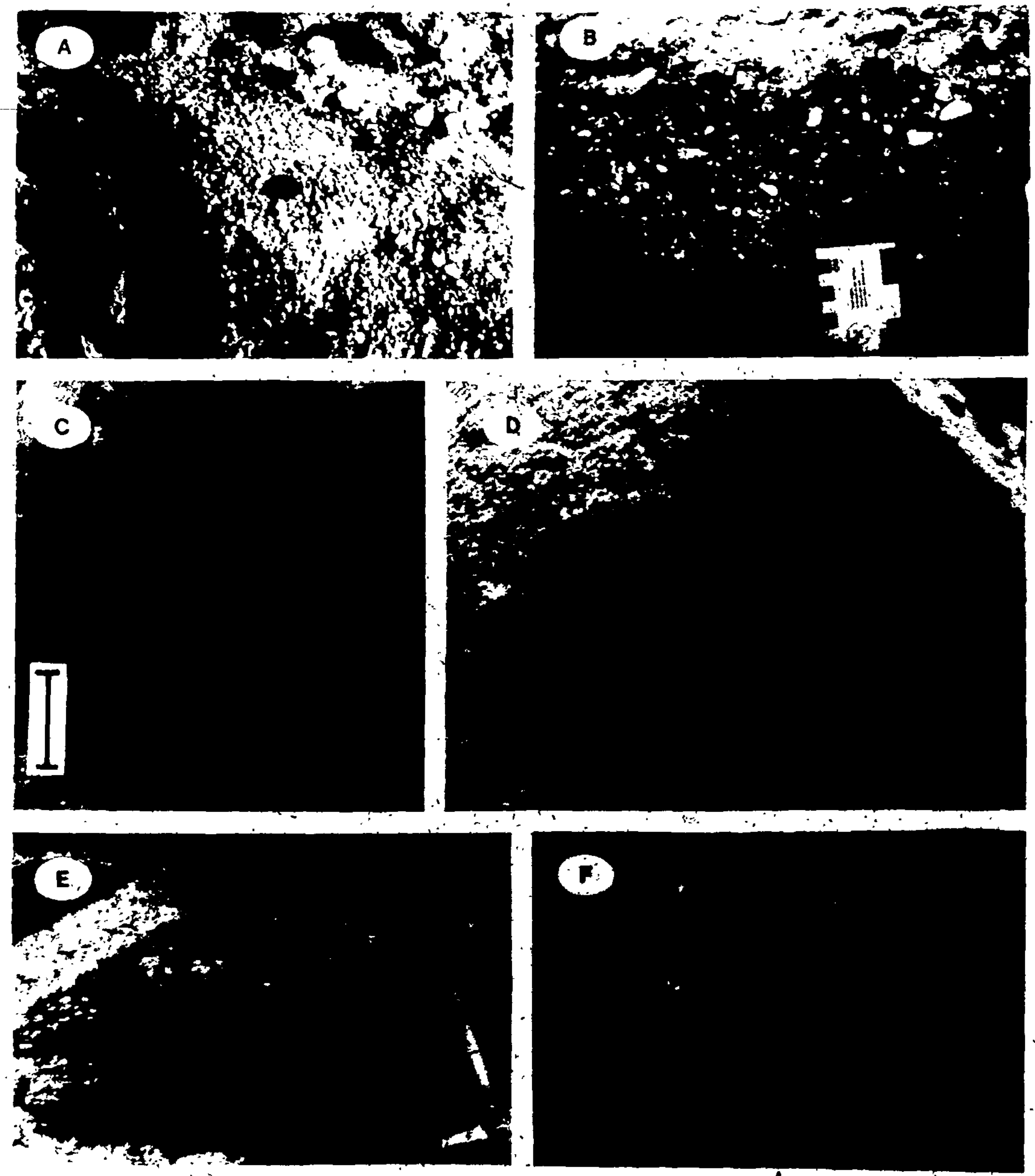
2.B Consolidated sandstone conglomerate outcrop (previously thought to be Devonian Sextant Formation) at Location 1, Adam Creek, Moose River Basin.

2.C Gravel sand outcrop at Location 15, Adam Creek, Moose River Basin showing 0.5 to 0.75 metre thick cross bedded units. Scale bar is 50 cm long.

2.D Millimetre to centimetre scale laminations within the cross bedded units shown in Plate 2.C, outlined by iron staining. Pen is 14 cms long.

2.E Silt laminated with fine sand, Location 12, Adam Creek, Moose River Basin. Note abundant roots. Divisions on large pick are 10 cms.

2.F Clay from Lignasco drillhole J-1-2, Moose River Basin. Note the slickensides, conchoidal fractures and soil textures. Scale is in cms.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sand with abundant lignite fragments and authigenic pyrite and younger, white, sorted, angular, non-spherical, fine, very pure quartz sand with abundant kaolin". Although this seems generally to be the case i.e. the younger sands are cleaner and more kaolinitic, in drill hole J-1-2, white kaolin-rich sands occur toward the base of the section. Telford distinguished two sediment associations, one with thick sections of interbedded sand, oxidised reddish to light brown clays and white kaolinitic clays and the other with dark grey or black silt and clay commonly associated with abundant detrital or in situ carbonaceous material. These associations are given an age connotation by Telford but neither the subdivision nor the stratigraphic sequence were substantiated in this study and will therefore not be used here.

Isolated areas of consolidated conglomerate and sandstone occur in the Mattagami Formation. An example of this occurs at Location 1 in Adam Creek where reddish orange sandstones and conglomerates are found (Plate 2.B). They were originally thought to be Devonian Sextant Formation due to their unusual consolidated nature (Telford, 1982), but the presence of wood fragments up to 20 cm long with similar habit and chemistry as the Mattagami wood material and the presence of kaolinized feldspar grains and quartz grains with embayed edges (Try, 1983) suggest that the outcrop is part of the Mattagami Formation. The cement appears to be iron-rich, and may be sideritic. Try et al (1984) identified limonite and carbonate in the cement. A consolidated sandstone with pure pyrite cement (AC-13-82), was noted at Location 9 on Adam Creek. Isolated areas of cemented material also occur within the gravels and sands e.g. in AC-32-82 where calcite and pyrite cements alternate. Pyrite nodules are common at the base of the gravel/sand outcrops on Adam Creek, for example at Location 12. Iron staining is also common along cross-bedding foresets. Siderite, occurring as a cement, is another common authigenic mineral in the coarse sediments. Some detrital siderite, possibly derived from siderite occurrences in Devonian limestones, may also be present.

The thick units of interbedded gravel and sand contain beds 30 cms to 1.5 metres thick. Large scale (trough) cross bedding is the major structure observed (Plate 2.C). Heights of these features are 1-1.5 metres. Planar cross bedding is also present however due to the lack of three dimensional exposure the exact form of the structures is not known. Centimetre scale laminations occur within the structures described above (Plate 2.D). Graded bedding is present and occurs in a series of fining upward cycles (10-35 cm). Fining upward and coarsening upward sequences both occur in the gravel/sand units e.g. Location 12 and 73-60 feet in drill hole J-1-2 respectively.

Thin Sands

These are fine to medium grained sands occurring in beds less than 1 metre thick. They are characteristically interbedded with silt and in some cases coal. The sand is often muddy and is greyish to tan in colour. Planar and trough cross bedding and flat laminations are present. In the sands interbedded with the silt, centimetre-scale ripples and laminations are common. Both transported and in situ organic materials (including roots and tree trunks) are present and bioturbation is common. These thin sands and interbedded sands and silts commonly grade into clay above and below. Local coarsening and fining upward sequences were observed.

Silt

The silt varies in colour from white and light grey to dark grey with abundant organic material. Structures present range from fine laminations (wavy and flat) to soil textures and conchoidal fractures and slickensides. The silt in the Mattagami Formation has two basic occurrences, 1) Silt associated with clay and silty clay. In these units mica is visible and organic material is common as wood fragments up to 4 cm long, fragmented debris less than 1 cm , finely comminuted organic particles and rootlets. The organics may be concentrated in layers. The silt commonly contains light yellow to orange flecks which are most visible on pseudo-bedding or root slickenside surfaces. Iron rich concretions (siderite and pyrite) are found in well defined horizons in the silty clays, with individual concretions up to 4 cm wide. 2) Silt laminated with fine sand (Plate 2.E). These beds tend to be rippled and laminated and generally contain abundant rootlets which crosscut and distort the laminations vertically and obliquely. This silt is tan in colour and often organic poor except for the rootlets.

Clays

The clays exhibit a large variety of colours including tan, red, green, light and dark grey and black. The colour of the clays is related to the organic matter content and the degree of oxidation, with most organics in the dark grey and black clays and mainly root traces and isolated organic wisps in the tan clays. The red and orange colours reflect oxidation of the iron-bearing phases in the clays and the green reduced iron. The clays are characteristically unstructured and exhibit "crum" soil textures and abundant slickensides. Three main types can be distinguished, a) Tan structureless clays with "crum" soil textures, slickensides, conchoidal fractures and occasional rootlets (Plate 2.F). Flecks of oxidised iron and organic fragments may be present. b) Brown and grey organic rich clays. These also exhibit soil textures and are structureless, however occasional silty lenses are present. The organics occur as finely divided material, rootlets, wood fragments and fusinite fragments. c) Dark and light brown very finely laminated (mm scale) clays and silty clays (Plates 3.A and 3.B). The alternating layers are tan/light brown silty clay and dark brown organic rich clay e.g. AC-06-82.

Ochre coloured clay and a single occurrence of blue grey (podzol-like) clay with tiny spherical sideritic nodules were found at Location 12, Adam Creek (Plate 3.C). Authigenic minerals particularly pyrite and siderite, are common in the clays. Siderite also occurs as bulbous nodules (1 to 15 cm in diameter) which lie in bands parallel to the bedding e.g. AC-31-82. Pyrite is found mainly as cubic crystals in the grey green clays. Where wood fragments are present pyrite may crystallize in and associated with the wood (Plate 3.D).

Lignite

Carbonaceous material in the Mattagami Formation has been classified as lignite, however on the basis of reflectance measurements it appears to be borderline peat/lignite. The lignite contains abundant recognisable plant material including tree stumps, trunks, twigs and branches and resin coatings. Many small twig and branch fragments are completely carbonized with vitreous, black, shiny, conchoidally fracturing, finely banded material making up the interior (Plate 3.E). Other wood fragments have the woody nature and colour preserved and are

Plate 3.A Laminated (mm scale) organic rich clay (AC-04-82) from Adam Creek, Moose River Basin. Penknife is 9 cms long.

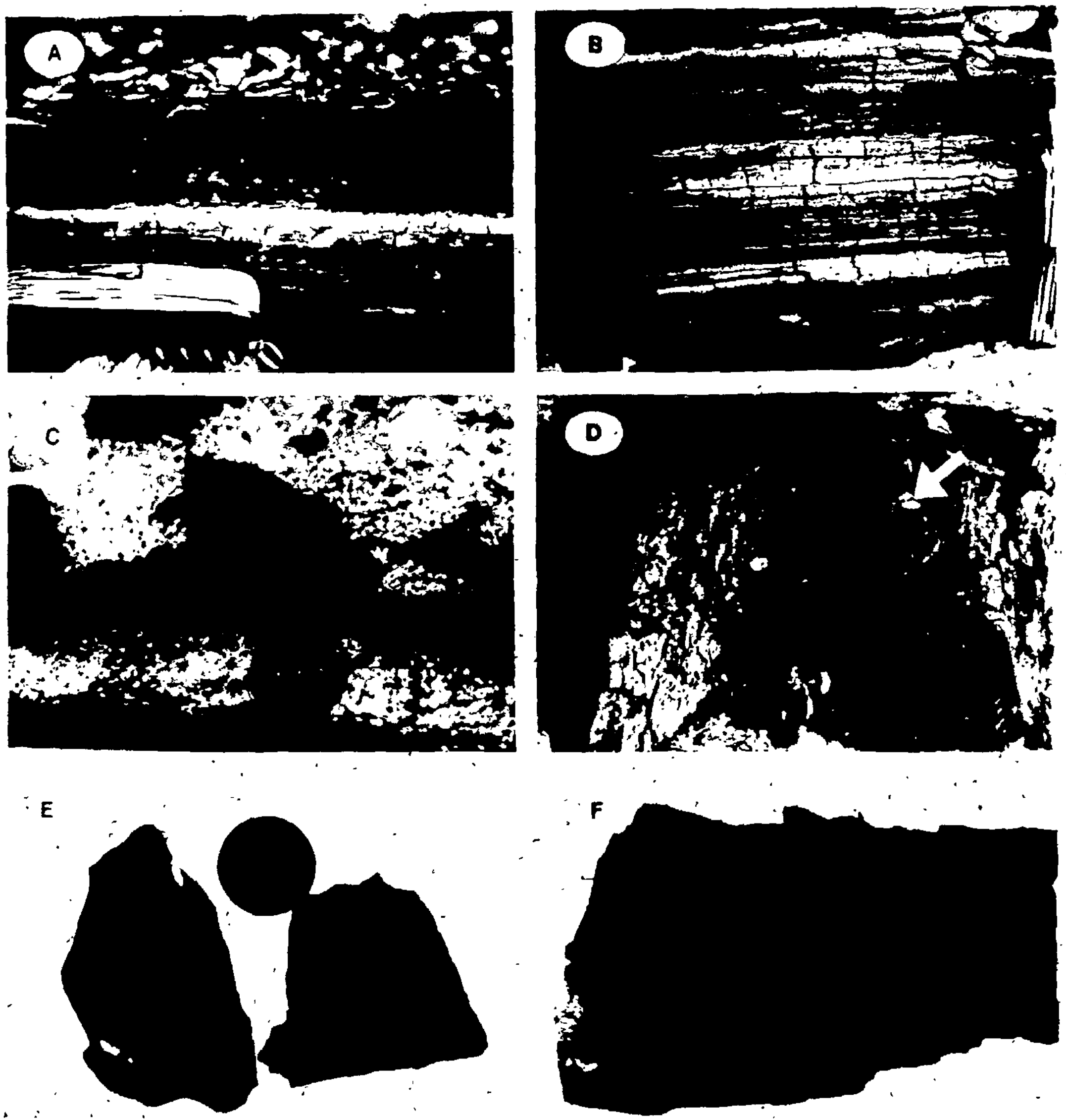
3.B Finely laminated clay and silt (AC-06-82) from Adam Creek, Moose River Basin, representing lake deposition. Penknife is 9 cms long.

3.C Thin ochre coloured clay and clay containing siderite nodules (above lens cap) erosively overlain by sand and gravel. Location 12, Adam Creek, Moose River Basin. Lens cap is 5 cms in diameter.

3.D Tree stump in the Mattagami Formation, Adam Creek, Moose River Basin. Arrow points to an area of pyrite crystallization. Penknife is 9 cms long.

3.E Wood fragments from Mattagami Formation lignite, Moose River Basin. Vitreous, conchoidally fracturing wood at left, fragment retaining woody nature and texture at right. Coin is 1.9 cms in diameter.

3.F Well preserved wood fragment from woody lignite, Mattagami Formation, Moose River Basin. Coin is 1.9 cms in diameter.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not so well carbonized (Plate 3.E and 3.F). These break on drying along the wood grain. Cell structures are preserved in many of the samples (Radforth, 1958) with delicate leaf forms also having been identified (Winder, 1984 pers. comm.). Fusinite fragments are common and appear as bright, black, charcoaly fibrous material. The fragments are often squared to rectangular in shape.

Four distinct lignite phases were identified on the basis of appearance and composition in the outcrops and drillcore examined. These correspond to some of the divisions proposed by Dyer (1931), Dyer and Crozier (1933) and Radforth (1958). They are woody, peaty, earthy and fusinitic (Plate 3.F and Plates 4.A, B and C respectively). Although Radforth considered them to be purely structural categories, Ontario Mines Dept and this author consider the four phases to be comparable to the lithotype divisions in bituminous coals and are therefore thought to have a genetic implication.

Woody lignite consists principally of lignitized tree trunks and roots. Peaty lignite consists of many small stems of woody lignite in a matrix of (reddish brown) peaty material. Earthy lignite is crumbly and appears like soil. Fusinitic lignite consists of black fibrous charcoal-like wood material.

Only one in situ outcrop occurrence of a lignite seam was examined, Location 3, Adam Creek. Here the lignite is underlain by brown clay with abundant root remnants. The exposed seam is less than 50 cm thick and consists mainly of finely comminuted earthy and soily material. It is dense and well packed, dull black in colour and contains small fusinitic fragments. It is structureless througnout. The lignite seam becomes woody towards the top of the exposure where wood pieces up to 10 cm long

Plate 4 Lignite varieties identified in the Mattagami Formation, Moose River Basin.

4.A Light coloured peaty lignite. Coin is 1.9 cms in diameter.

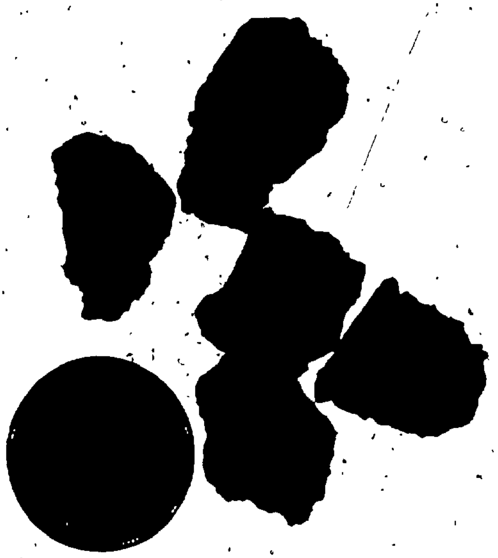
4.B Earthy or soily lignite. Coin is 1.9 cms in diameter.

4.C Fusinitic lignite. Coin is 1.9 cms in diameter.

4.D Weathered woody lignite slab from the stream bed in Adam Creek, showing compressed twigs and other wood fragments in an earthy matrix. Hammer is 30 cms long.

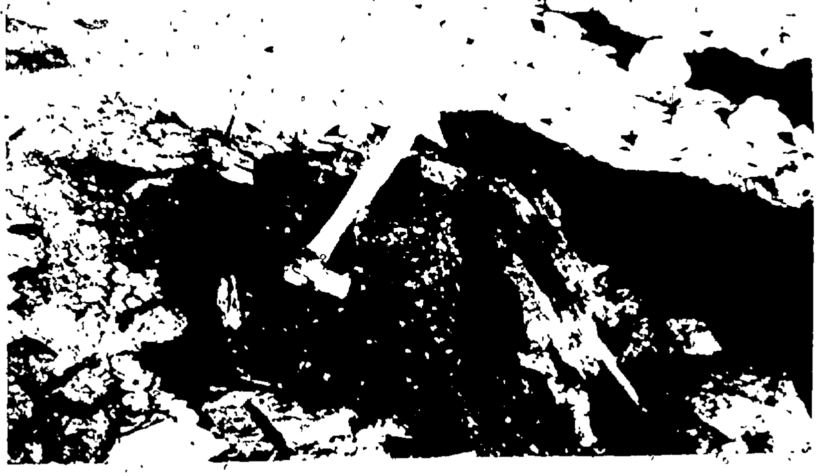
A

B



C

D



occur. The matrix is similar to the earthy lignite below it. Pyrite nodules are common at the top of the exposure. Weathered woody lignite slabs were collected from the stream bed at Adam Creek and these are weakly bedded with abundant small twigs and other compressed wood fragments in an earthy or soily matrix (Plate 4.D).

Good lignite seams were found in some of the recent drill holes, for example J-1-2. Drillhole J-1-2 was drilled using the Vibracore technique and this resulted in excellent recovery of a 16 cm diameter core. For this reason and because four lignite seams occur in this hole, J-1-2 was chosen for detailed sampling and analysis. Samples were taken every foot in the main lignite-bearing zone. A detailed section through this zone is shown in Figure 3.1. Alternating woody and crumbly or earthy lignite occurs interbedded with black organic rich clays and fusinitic zones. The top seam and the majority of the middle seam are made up of woody lignite. The lowermost seam is earthy with some isolated woody areas. Fusinitic bands 2-3 cm wide occur interbedded with the woody and earthy lignite, while peaty lignite is associated with woody lignite.

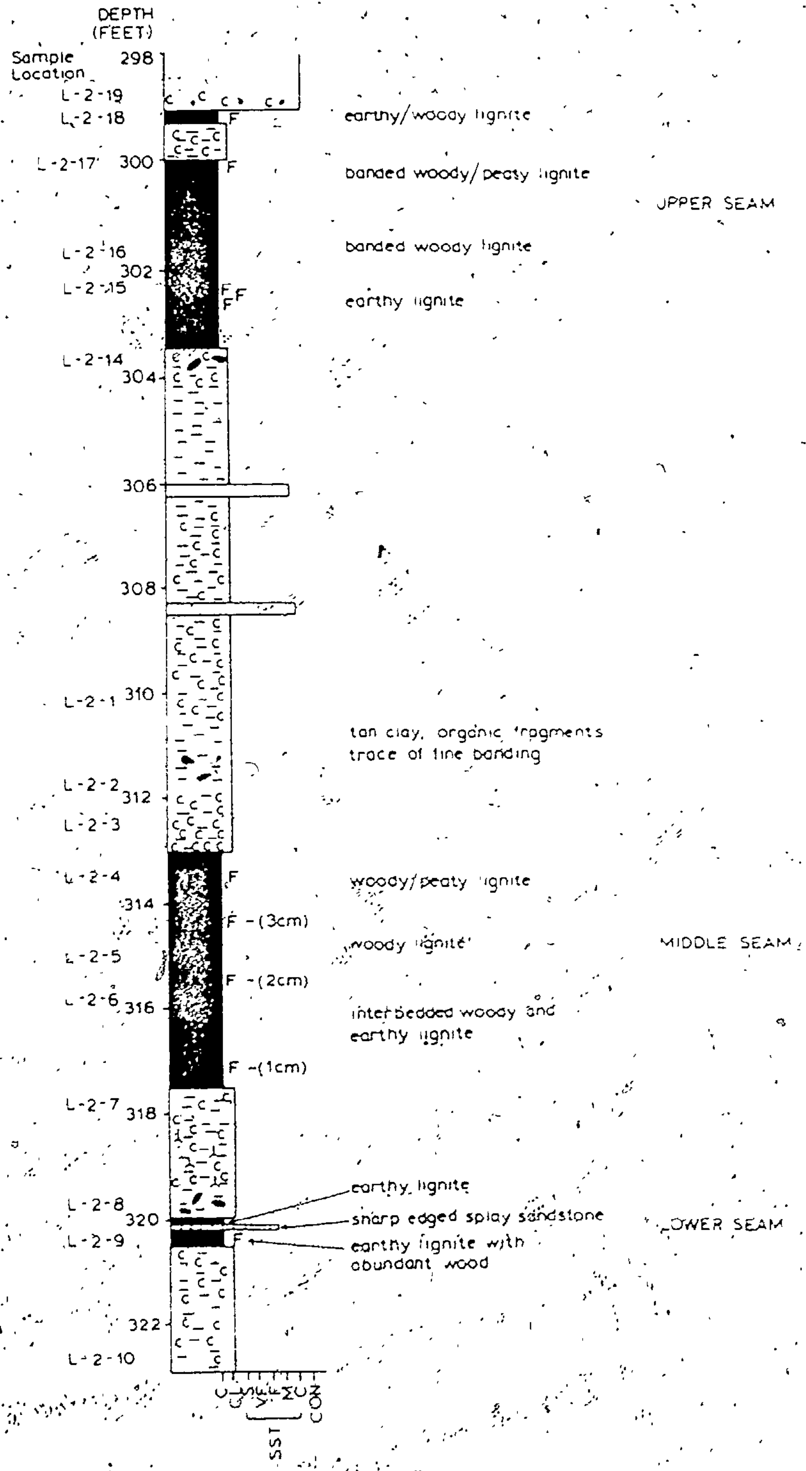
3.2.2 Lithofacies

Three main lithofacies were distinguished in the sediments of the Mattagami Formation, 1) channel deposits, 2) coarse floodplain deposits and 3) fine floodplain deposits.

Channel deposits

A characteristic section through these deposits is illustrated in Figure 3.2. The thick gravel and sands with their erosional bases and intraformational mud chips and stacked series of trough cross beds are

Figure 3.1 Detailed section through the coal-bearing horizon from drill hole J-1-2. For key to this and other lithological sections see page 46



KEY TO LITHOLOGICAL SECTIONS

∘°∘°∘°	gravel/conglomerate
	sand/sandstone
⚋⚋⚋	silt/siltstone
╌╌╌	clay/claystone
■	lignite/coal
C	carbonaceous
F	fusinitic
F-(3cm)	fusinite band 3cm thick
P	pyrite nodules
●	wood/organic fragments
⅄	rootlets
∬	burrows
∂	bioturbated
∿	soft sediment deformation
≣	finely banded
═	laminated
⌒	large scale ripples
⌒	ripples
⋰⋰	cross-bedded

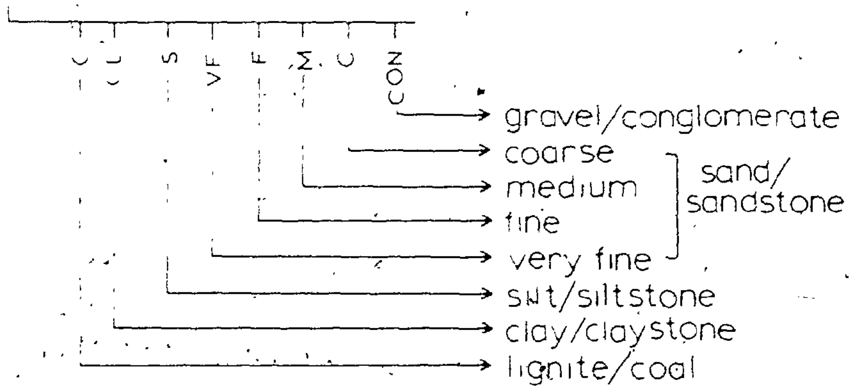
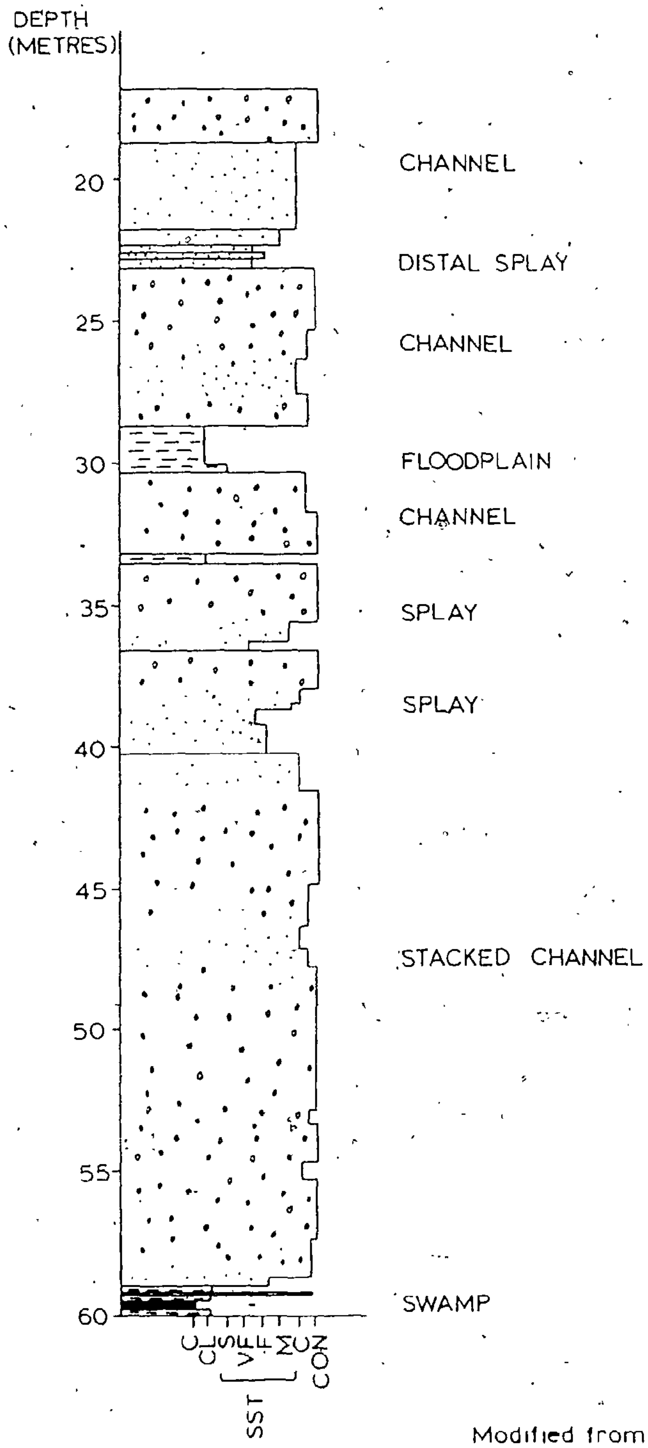


Figure 3.2. Typical section through channel deposits, Mattagami Formation (from drill hole J-1-2).



Modified from Try 1983

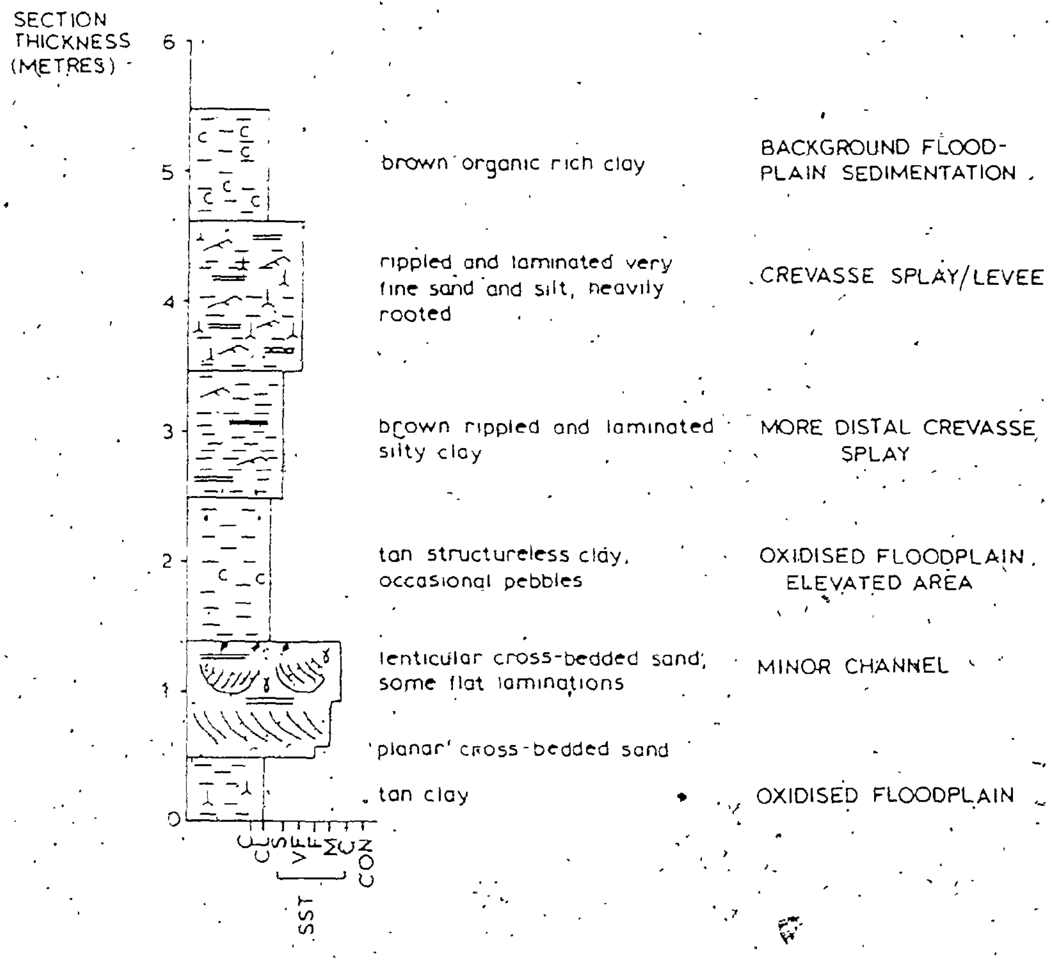
interpreted as channel fill deposits. The channel lag material with mud chips and coarse clasts is overlain by channel bar deposits. The sediments are thought to be derived from the east northeast on the basis of the clast composition and palaeocurrent data (Try, 1983), however the measured crossbeds which were from Adam Creek and a Missinaibi tributary exposure, are considered by the author to be unreliable due to the slumped and disturbed nature of the above.

The sharp bottoms and tops of these units indicate that the channels are largely avulsion controlled (Try et al, 1984).

Coarse floodplain deposits

These were deposited in a lower energy environment than the channel deposits but in close enough proximity to be significantly affected by them. They are made up of thin sands and interbedded sand and silt. A characteristic section through these deposits is shown in Figure 3.3. The thin sands, for example in the centre of the section at Location 11, may represent crevasse channel deposition coarsening up from fine sand levee deposits. The sands are bioturbated and the structures that remain are planar crossbedded sands grading up into flat topped lenticular coarser deposits surrounded by medium sands with some flat laminations. At Location 12, Adam Creek, sample AC-25-82 represents levee deposition with rippled and laminated fine sand and silt which is extensively rooted. These units may also represent rooted splay surfaces. The presence of fining and coarsening upward cycles in the finer grained sands and silts may represent splay abandonment and progradation events (Elliot, 1974 and Try et al, 1984).

Figure 3.3 Typical section containing coarse floodplain deposits, Mattagami Formation, Moose River Basin (Location 11, Adams Creek).



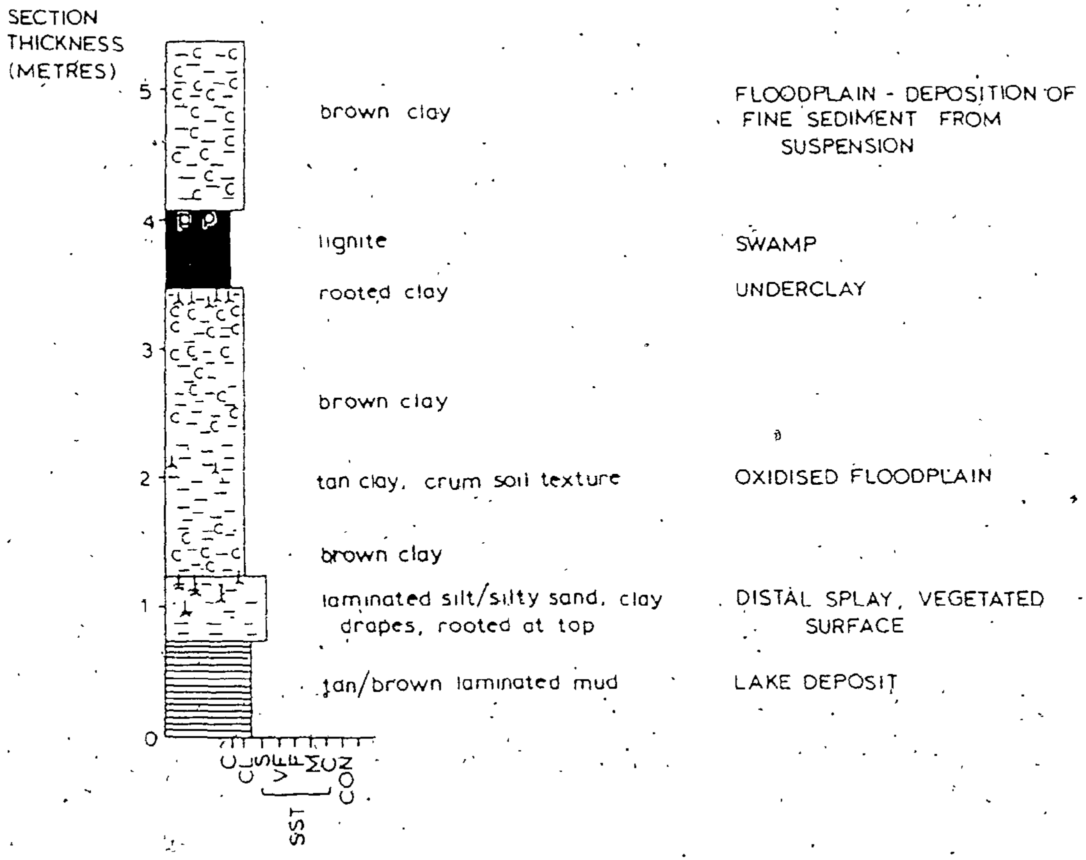
Fine floodplain deposits

The fine floodplain deposits consist of clay, silt and lignite (Figure 3.4), which were deposited in quiet water environments with relatively little sediment input. Deposition was mainly from suspension with occasional sediment influxes from minor channels and distal splays. Thus suspension-deposited clays are the most abundant sediments. Their colour varies depending on the degree of exposure and therefore oxidation. Tan clays formed on slightly elevated, more exposed areas on the floodplain, while the darker clays accumulated in wetter, more depressed zones. The reducing conditions in the latter areas are evidenced by the preservation of the organic materials in these sediments. Finely laminated clays and silty clays were deposited in shallow lakes on the floodplain. Silty clays and silts represent distal splay material formed from spatially concentrated flood episodes which carry coarser material into the distal floodplain. Minor channel deposits also occur, for example in J-1-2 at 320.1 feet where a thin fine to medium sand, with sharp upper and lower boundaries, occurs within a lignite seam.

The lignite formed as a result of accumulation of swamp, tree and shrub vegetation on the floodplain, often in zones parallel to the major channels or on a larger scale in troughs in the Devonian subsurface where the Cretaceous succession is thicker. Channel-margin lignite deposits tend to be thin while lignites that formed in isolated floodplain areas where accumulation was uninterrupted are thicker.

The lignite types represent different local environments of accumulation (Teichmuller, 1975 and Hacquebard and Donaldson, 1969). The woody lignite formed from coniferous vegetation (Radforth, 1958) which

Figure 3.4 Typical section containing fine floodplain deposits, Mattagami Formation, Moose River Basin (from locations 5, 12 and 3)



grows on slightly drier and more elevated areas (forest moor) than the other lignite-forming vegetation. Proximity to the major river channels is indicated by the presence of occasional thin sandy interbeds in this lignite type. The peaty lignite formed from decomposed wood, bark, woody shrubs, grasses and mosses (forest peat litter/detritus) which degraded to a humic detritus. The earthy lignite which consists of finely comminuted material, formed in deeper water where limited flow allowed the breakdown of the plants. The vegetation which formed the earthy lignite is thought to have been composed of reeds and more aquatic vegetation (swamp moor) or of lowland reed moor with limited tree and shrub growth (Try et al, 1984). The fusinitic lignite accumulated from burnt vegetation which was growing in a periodically wet and dry environment. The fusinitic lignite thus represents the driest phase of the source vegetation. These four phases can be equated with vitrain, clarain, durain and fusain lithotypes of bituminous coals for comparative purposes.

Little or no transport of the organic material took place, except in the earthy lignites where locally high concentrations of clay and the occasionally broken up nature of the organic material indicate frequent inundation of the wetland by mud-rich floodwaters. Fragments of fusinitic material in the earthy lignite may indicate some transport of the former locally.

The thick sections of woody lignite (and possibly peaty lignite) which occur adjacent to topographic highs, for example at Onakawana, may represent raised bog accumulation at the margins of the depositional basin (Hopkins and Sweet, 1975). The lack of significant detrital inorganic matter in these lignites supports this hypothesis. A similar facies has been described in the Cologne brown coal (Thompson 1956). It is characterised by light bands with finely detrital groundmass and well preserved wood.

In raised bog environments where pH is low and bacterial activity reduced, plant remains are well preserved.

The Mattagami Formation was deposited under warm temperate to subtropical conditions as indicated by palynological studies of the lignite (Hopkins and Sweet, 1976).

3.2.3 Environment of Deposition

Figures 3.5 A to D show the general distribution of lithofacies of the Mattagami Formation, the thickness of the Cretaceous section, the topography of the upper surface of the Devonian and the Pleistocene and drift thickness respectively in the Moose River Basin. The thickness of the Mattagami Formation appears to be strongly influenced by the underlying Devonian surface, for example Devonian highs are overlain by thin Cretaceous sections or by Pleistocene deposits. Similarly the thickest Pleistocene sections are thought to fill deep glacial or fluvioglacial channels which eroded into the Cretaceous (and the Devonian) leaving very thin or nonexistant Cretaceous sections.

Figure 3.5 A shows a northwest trending zone, through the centre of the Moose River Basin, where the Mattagami Formation contains predominantly channel deposits. The surrounding areas contain mostly floodplain deposits or varying proportions of channel and coarse and fine floodplain sediments. Thick lignite-bearing sections occur north of the Grand Rapids Devonian high and adjacent to the Precambrian basin margin. Fyfe et al (1983) termed the northwest trending zone the Esoom river (Moose spelled backwards) and proposed that flow was towards the

Figure 3.5A Palaeogeographic map of the Mattagami Formation based on proportions of lithofacies present in drill holes

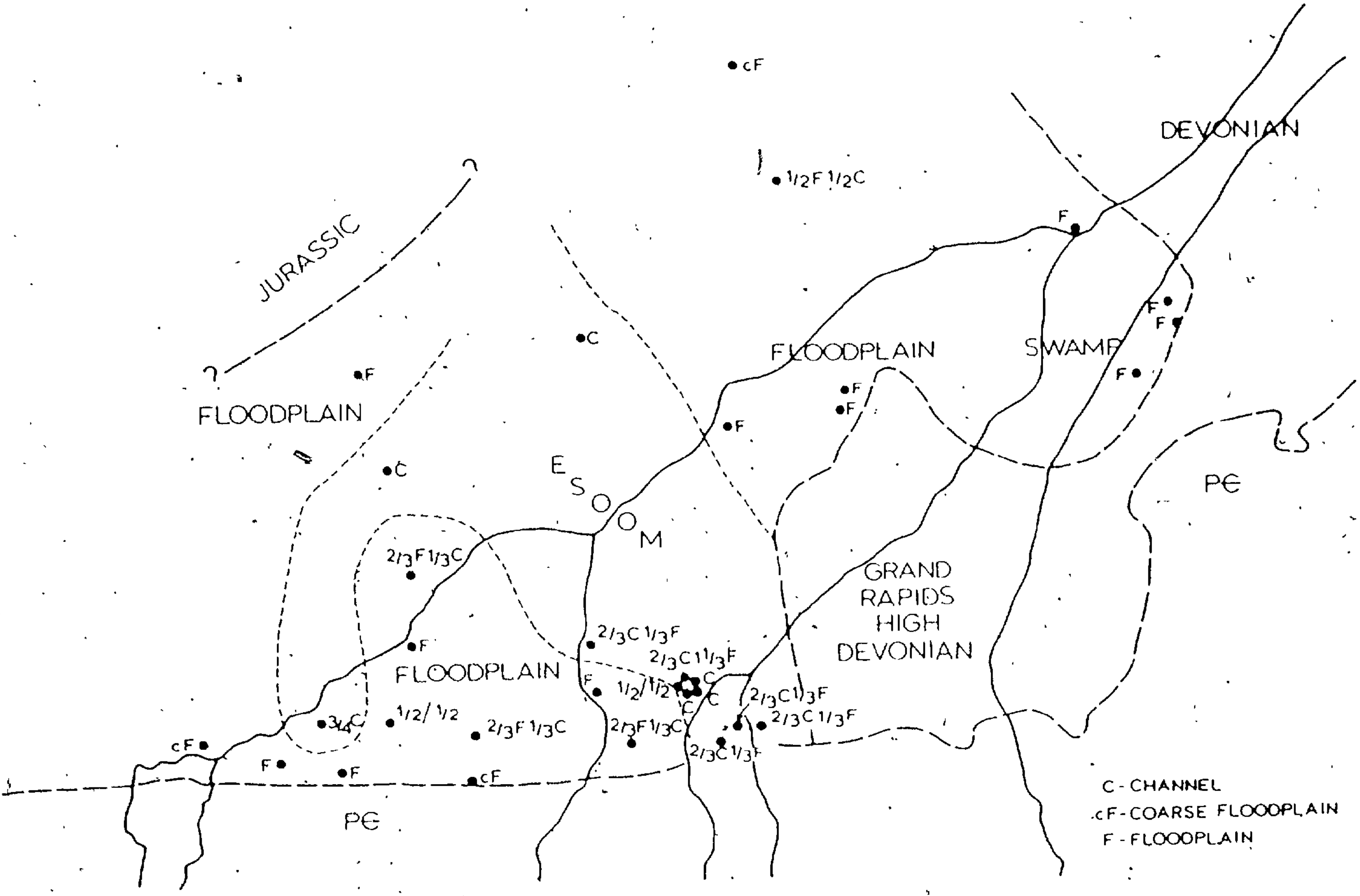


Figure 3.5B Map showing thickness of the Cretaceous in the Moose River Basin (metres).

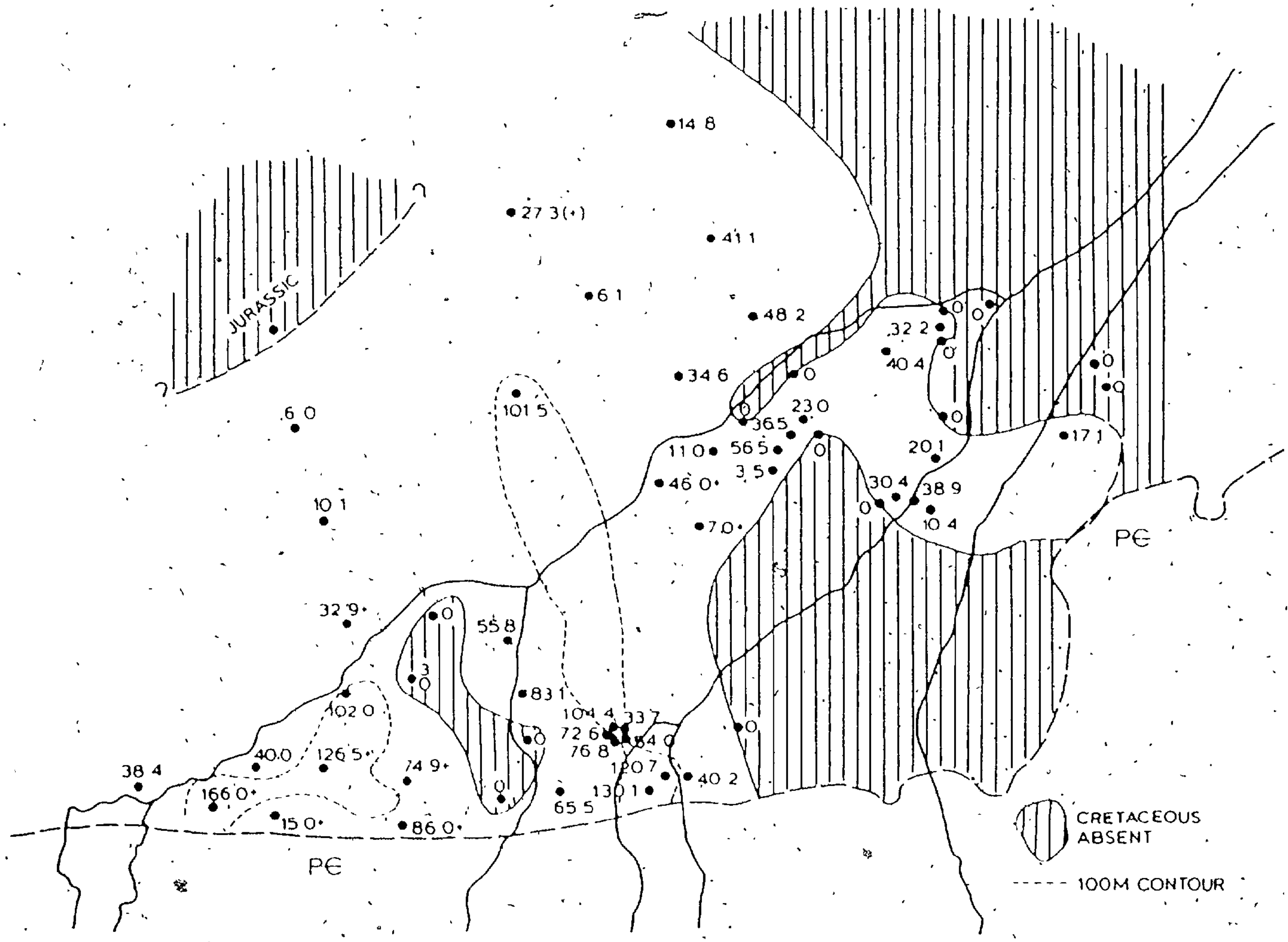


Figure 3.5C. Palaeotopography of the upper surface of the Devonian in the Moose River Basin (in metres relative to sea level).

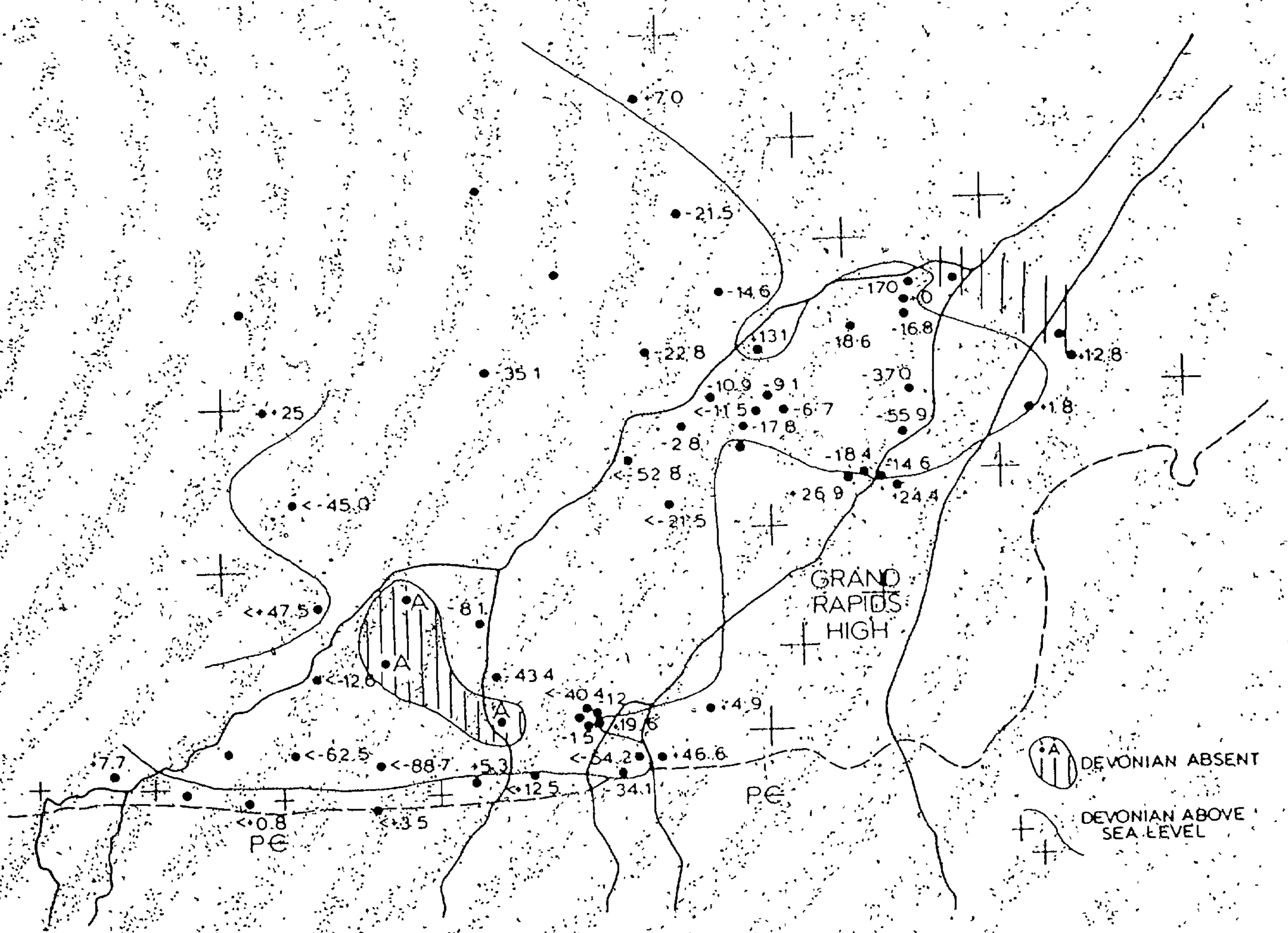
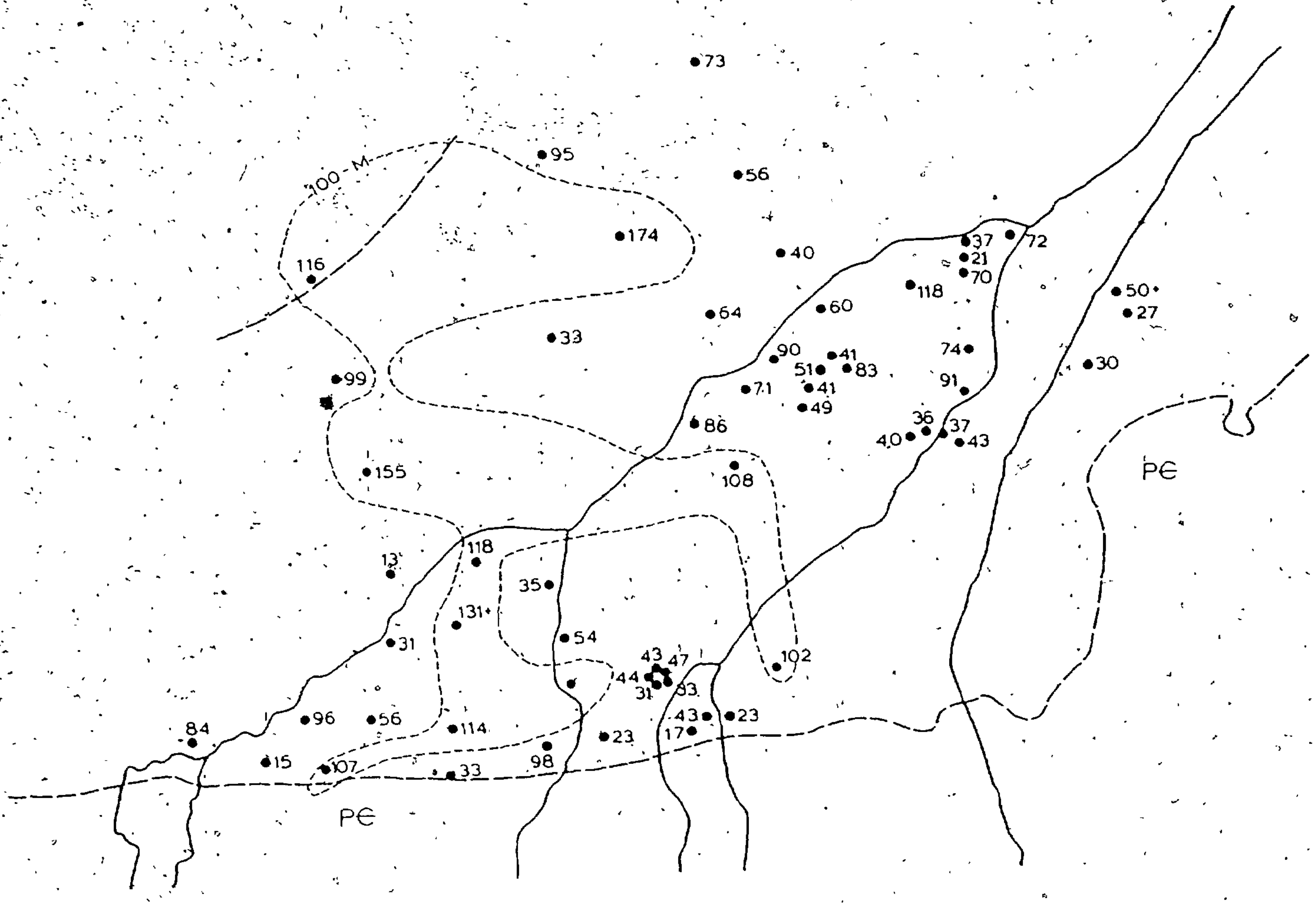


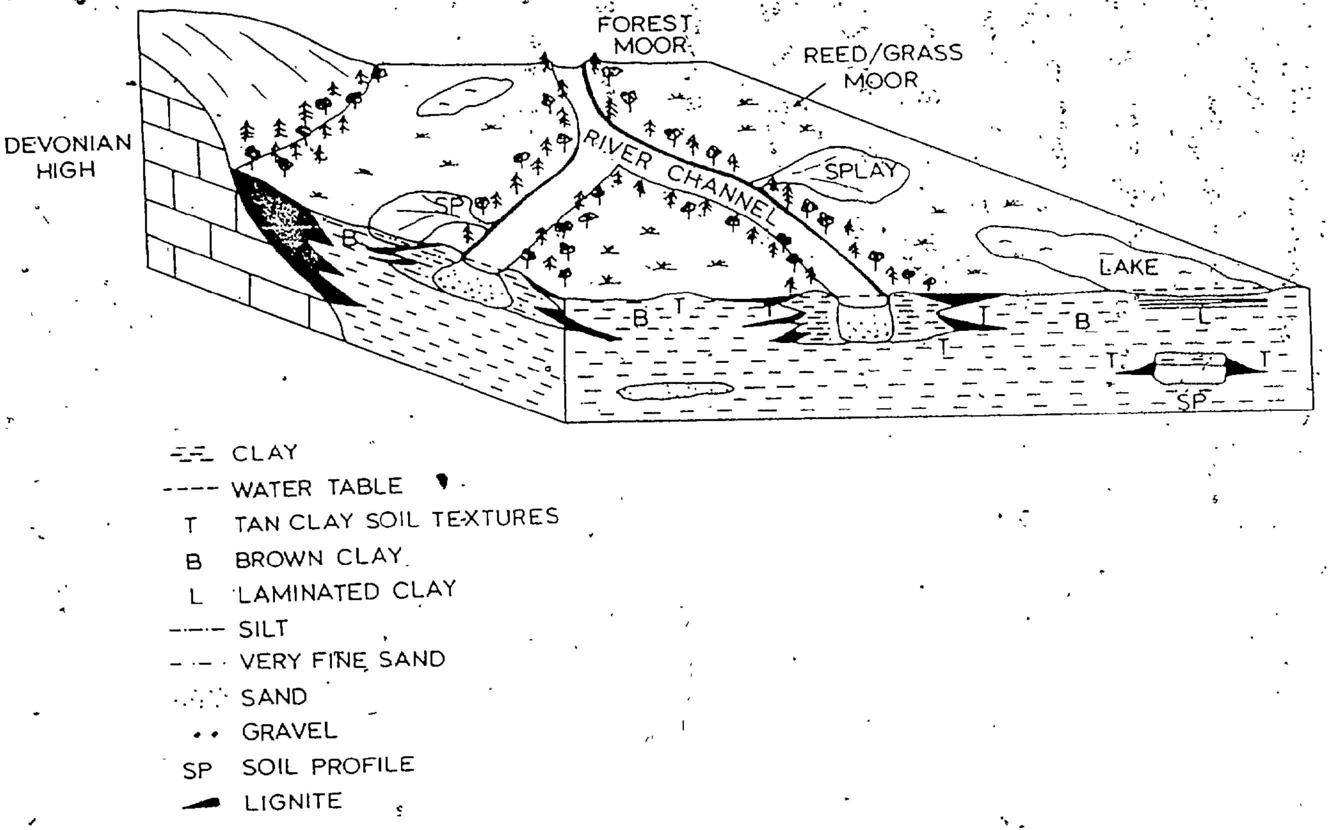
Figure 3.5D Pleistocene and drift thickness in the Moose River Basin (metres).



northwest or west on the basis of the palaeocurrent data and nature of the clasts present in the sediments. Thus throughout the depositional history of the Mattagami Formation a large scale river channel system flowed towards the west northwest with the locus of deposition predominantly within a well defined zone. The areas of increased sand deposition in the floodplain zone may represent tributaries of the major river system. The majority of the area contains mainly floodplain sediments, with major peat/lignite accumulation being limited to the area around Onakawana and the southerly margin of the basin. A depositional model for the Mattagami Formation is illustrated in Figure 3.6.

Few studies on the Mattagami Formation have concentrated on the environment of deposition of the sediments. Fyfe et al (1983) concluded that deposition was from a major stream system draining from the Canadian Shield. The high proportion of clays relative to sands indicates a high-constructive system and the lack of marine fossils or brackish deposits precludes any marine influence on the sedimentation. Try (1983), and Try et al (1984) proposed an anastomosing stream model on the basis of the stacked nature of the channel deposits, the lack of fining upward cycles characteristic of meandering stream deposits, low stream sinuousity and the preservation of a high proportion of overbank deposits in contrast to meandering sequences. Fyfe et al (1983) proposed a channel floodplain/lacustrine situation. It is the feeling of the author that the limited exposure of lateral relationships and undisturbed sections in the slumped river banks make many assumptions on the lateral variability and palaeocurrent and sinuousity values

Figure 3.6. Depositional setting of the Mattagami Formation



questionable, thus limiting speculation on the exact nature of the depositional environment of the Mattagami sediments.

Various deposits of the same age occur throughout North America, with Cretaceous deposits in Western Canada representing sedimentation adjacent to the marine Albian sea which transgressed from the north. The Mattagami sediments are remnants of deposition from a northwest flowing major river system on a continental alluvial plain which merged westward into a deltaic or marine influenced area.

Evidence of farther sedimentation in the Moose River Basin prior to the Pleistocene period has not been found. It appears from the relative lack of coalification of the lignite and the absence of significant diagenetic clay minerals in the sediments, that overburden thicknesses and depth of burial were small. Cenozoic materials have been found elsewhere and it is possible that sediments were eroded from the area during the Pleistocene. However, whereas significant quantities of eroded Mattagami Formation material are included in the Pleistocene tills, Tertiary palynoflora etc. have not been found. It is suggested that the Mattagami Formation was not covered by great thicknesses of sediment and that what material there might have been was eroded off in the Pleistocene along with significant thicknesses of Mattagami Formation sediments. Maximum ice thickness in the area during the Pleistocene is estimated to have been around 2000 metres.

3.3 The Gates Formation

The Gates Formation consists of a complex, rhythmic succession of conglomerate, sandstone, siltstone, claystone and coal of continental origin. These lithologies can be divided into coarse high energy clastics i.e sandstone and conglomerate, fine grained clastics i.e. fine sandstone, siltstone and claystone) and coal. In general the coarse clastics formed as channel deposits, the fine clastics as floodplain interdistributary deposits such as levees, splays and lakes and the coal as swamps. The coarse channel deposits are best developed in the bottom part of the section while the finer clastics are present in both the upper and lower parts of the succession. The coal seams are thickest and most extensive at the base of the section and are thinner and more numerous towards the top. The lower part of the section contains definite cycles while the lithologies in the upper section are randomly interbedded. Although only eight bore holes were examined, a division of the section into two distinct units is proposed on the basis of these sections. The Lower Unit is thought to represent an upper delta plain/fluvial environment while the Upper Unit displays an upper delta plain association.

3.3.1 Lithotypes

Five major lithotypes are present in the Gates Formation, conglomerate, thick and thin sandstones, siltstones, claystones and coal.

Conglomerate

Conglomeratic sediments comprise roughly 5% of the total section. Two main types were recognised based on the clast composition. The most common contain clasts of quartzite, volcanics, chert and argillite which vary in size from 2 cms to coarse sand size and are rounded to subrounded. The matrix varies from coarse and fine sandstone to silt and clay, and although the conglomerates are mainly clast supported, matrix supported bands also occur. Sorting is generally poor but is moderate in the conglomerates at the top of the section. Carbonaceous materials in the form of coaly wisps, lenses, bands and carbonaceous claystone partings are common. The cement is calcite, and pyrite is common where organics are incorporated into the conglomerate. Conglomerate bands tend to be thin i.e. less than 0.78 metres and on average less than 0.20 metres thick. They occur interbedded with and fining up into the medium and coarse sandstones in the thick sandstone channel sequences common in the lower part of the Formation. No structures were identified in the conglomerates.

The other conglomerates (intraformational) contain angular to subrounded clasts of locally derived claystone, siltstone and wood fragments in a medium to fine grained sandstone or silt/clay matrix. They are also on average less than 0.20m thick and occur predominantly as lag deposits at the bases of fining upwards distributary sandstone sequences.

Conglomerates are absent in the middle and upper parts of the section, except in drillholes MDD 79-11, 79-10, 79-14 and MD80-01 where the Gates Formation is terminated by an abrupt erosional surface overlain by a moderately sorted pebble conglomerate or coarse sandstone with granular and conglomeratic phases at the base. These units fine upwards into the Hulcross Formation.

Sandstone

Two main types of sandstone are identified in the Gates Formation. Some are coarse and medium grained and occur interbedded with conglomerate in thick sequences (up to 52 metres) mainly in the lower part of the Formation, Others are fine grained and are found interbedded with siltstone in beds less than 5.5 metres thick, mainly in the upper part of the Formation. Transitional sandstones will be briefly discussed.

The "Thick" Sandstones

The thick sandstones (Plate 5.A) vary from pebbly ~~and~~ coarse to fine grained. They occur stacked with conglomerate and occasional siltstone or claystone interbeds in coarsening and fining upward cycles, the total thickness of which reaches up to 52 metres in places (average greater than 10 metres). The sandstones are poorly to moderately sorted with subrounded to angular grains of chert, volcanics, quartz, claystone and carbonate-altered carbonaceous siltstone. Rip-up clasts of claystone and siltstone are present in layers and/or dispersed within the sandstones towards the bases of the sandstone units. Coaly material and debris is abundant (Plate 5.B) and occurs as stringers, wisps, clasts, bands and lenses (up to 1 cm thick) or as flattened coal rootlets which appear as bright veinlets oblique to the bedding. The sandstones can be very carbonaceous to very clean and the colour varies accordingly from black to light grey (salt and pepper). The coarse sandstones are crossbedded and the medium and fine sandstones contain laminations and small and medium-scale ripple cross stratification. Bioturbated and burrowed zones occur in places throughout the sandstones. The interbeds of silt and conglomerate are generally less than 20 cms thick with some conglomerate bands up to 78 cms thick. The sandstone units have abrupt basal contacts and gradational upper contacts, and consist of many stacked fining up and/or coarsening up sequences as opposed to a single

Plate 5.A Thick cross bedded coarse to medium sandstone, Gates Formation, Monkman. (Drillhole MDD 79-14, 347-349.5 m). Scale bar is 25 cms. long.

5.B Medium to fine grained rippled (large scale) and laminated sandstone containing coaly wisps and stringers, Gates Formation, Monkman. (Drillhole MDD 79-14, 146.5-149 m). Scale bar is 25 cms long.


A
3493


B

thick sandstone fining upward unit. In many of the thick sandstones, a coarsening upward sequence of variable thickness is followed by a series of fining upward sequences or another coarsening upward unit.

The "Thin" Sandstones

The thin sandstones (Plate 6.A) are very fine to medium grained with occasional coarse bands. They are most common interbedded with siltstone and claystone in the upper part of the Formation, where the proportion of sandstone to siltstone and claystone is much less than in the lower part of the Formation. The sandstone units are generally less than 5 metres thick and usually contain thin (less than 3 cms thick) siltstone or claystone interbeds. The sandstones are characteristically laminated (mm scale) and may exhibit small to medium scale ripple cross-bedding. Convolute bedding at siltstone-sandstone contacts especially in the interlaminated sandstone/siltstone beds is often accompanied by soft sediment deformation features such as load casts, ball and pillow structures, flame structures and small scale slumping. These are also common in the fining and coarsening upward minor cycles and are indicative of rapid deposition. Bioturbation is very common and worm burrows from 2 or 3.0-3.5 cms wide were observed. Colour varying from light to dark grey indicates variable quantities of carbonaceous material. Thin coal bands, coaly rootlets and carbonaceous debris are common, with the coaly rootlets often occurring at the base of the sandstones.

The thin sandstone units occur with a variety of internal sequences such as 1) laminated and interbedded with siltstone (Plate 6.B), 2) sharp based fining upward cycles and 3) coarsening upward cycles. 1)

Plate 6.A Thinly bedded very fine to medium grained thin (less than 5 m) sandstone, Gates Formation, outcropping in the Honeymoon area, Monkman. Scale bar is 50 cms long.

6.B Thin sandstone laminated and interbedded with siltstone, Gates Formation, Monkman. (Drillhole MDD 79-14). Scale bar is 25 cms long.


A
B

These units are thinly (3 cm) interbedded, bioturbated, burrowed, and contain coaly rootlets throughout. Both sandstone and siltstone are finely laminated (mm-scale) and small-scale cross bedding is common in the sandstones. Fine or medium sandstone is also found interbedded with coal and coaly laminations. Contacts tend to be sharp. 2) In these cycles fine to medium grained sandstone with coarse lenses at the base fines up into fine grained sandstone which becomes silty and carbonaceous at the top. Rip up clasts are common overlying the erosional basal contact. The units which are less than 6 metres thick, contain small to medium scale cross bedding throughout. 3) In the coarsening upward cycles silty sandstone overlying a gradational or erosional base grades up into fine sandstone with minor coaly claystone laminations. Average thicknesses are 5 metres and the units are laminated and small scale cross bedded.

"Transitional" Sandstones

Thicker fine grained sandstones (up to 16.6 metres thick) are present in the transitional zone. They consist of fine sandstone with coarse intervals which generally fine upward into silt. They are laminated and cross bedded with siltstone rip-up clasts and claystone interbeds and have sharp basal and gradational upper contacts.

Siltstone

This lithotype occurs predominantly in the upper part of the Formation. Siltstone is medium grey to dark grey in colour and may be either massive (structures obliterated by bioturbation) or finely laminated and often interlaminated with carbonaceous claystone and/or very fine to fine grained sandstone. The siltstone is characteristically bioturbated and commonly contains abundant carbonaceous material such as coal bands, rootlets and finely divided plant and other coaly debris.

Claystone

Claystones (Plate 7.A) are very common in the upper part of the Formation. They underly and overly coal seams, are interbedded with thin coal bands and grade up into siltstone units. Claystone beds up to 23 metres thick are recorded however thicknesses are on average less than 11 metres and commonly around 5 metres. Thinnest beds occur above and below coal seams in the lower part of the sequence. Claystones are generally black, extremely carbonaceous and interlaminated with thin coal bands and stringers. Massive, hard, dark grey and silty claystones are also present. One light brown claystone was found. Plant fragments are common on bedding planes and bright coaly rootlets, stringers, lenses and bands (4.0-0.5 mms) as well as finely comminuted debris are very common within the claystone. Occasionally silty and sandy lenses and bands (Plate 7.B) are also present. The bedding appears very irregular due to the uneven shapes of the wood and bark fragments and roots. Abundant slickensiding is characteristic of the carbonaceous claystones.

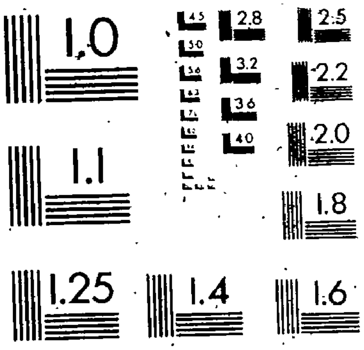
Coal

Up to twelve coal seams, numbered B1 to B12 stratigraphically from the base of the section are present in the Gates Formation. These range in thickness from 8m in B4 (Plate 8.A) to a few tens of centimetres in B11. The seams B1 to B9 and especially B1, B3 and B4 are considered to be economic. The latter are thick, relatively mineral (clastic parting)

Plate 7.A Laminated, carbonaceous claystone, Gates Formation, Monkman. (Drillhole 79-14, 278.3-277.8 m). Scale bar is 25 cms long.

7.B Claystone interbedded with silt and fine sandstone, outcropping in the Honeymoon area, Monkman. Scale bar 25 cms long.

2



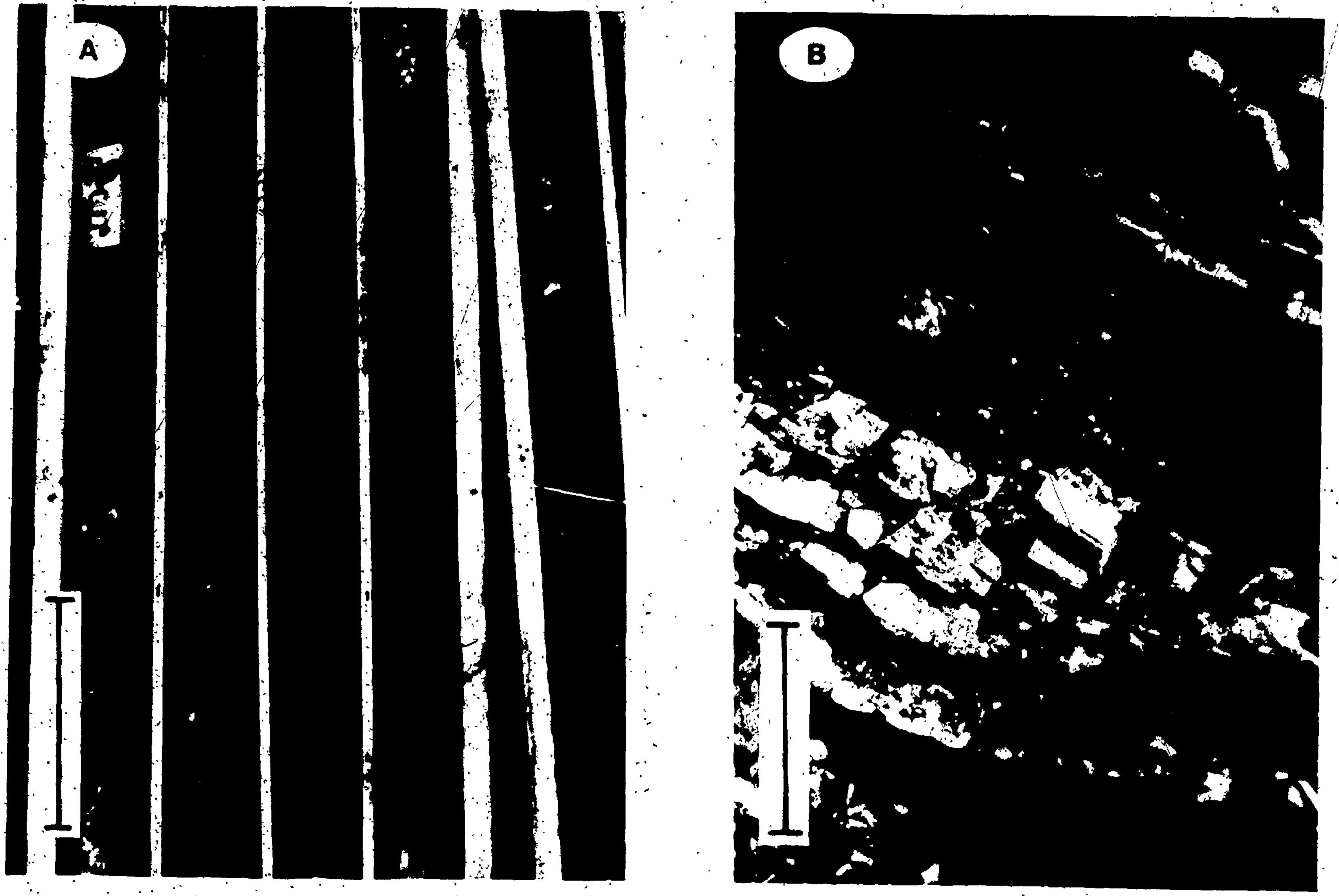

A
1 cm
B

Plate 8.A Top of coal seam B4, Gates Formation, outcropping in the Honeymoon area, Monkman. Lens cap is 5 cms in diameter.

8.B Typical section from the Upper Unit, Gates Formation, Monkman, showing a thin conglomerate at the base (bottom right) and interbedded, rippled and laminated claystone, siltstone and very fine sandstone above it. Note soft sediment deformation and slumping in middle and top left. (drillhole MDD 79-14). Scale bar is 25 cms long.


A
B

free and laterally continuous, while the seams towards the top of the section are more numerous but thinner and dirtier. Carbonaceous claystone, bone coal and stoney coal partings are found in most of the seams but are more frequent in the upper seams.

The lithotypes identified in this study are fusain, bright, bright banded, dull banded, dull and bone coal and carbonaceous claystone. The percentage of each lithotype varies from seam to seam and also within a single seam between adjacent drillholes (Table 3.1). The extent of this variation becomes evident in the following discussion.

B 1, which is on average 2.6 metres thick is overlain by sandstone and is most probably a channel-margin coal deposit. It consists predominantly of dull coal with lesser amounts of dull banded and bright banded material, however it is mainly bright banded in drillhole MDD 79-11.

B 3 is also variable in thickness, but averages 5 metres. It consists mainly of bright banded coal in MDD 79-14, 79-11 and 79-10(repeat), dull banded in MDD 79-10 and dull and dull banded in MD 80-01, 80-02, 80-03, 80-04 and 80-05.

B 4 is the thickest seam in the area, averaging 8.3 metres thick. It consists mainly of alternating bands of dull banded, dull and bright banded lithotypes. The proportions vary from predominantly dull and dull banded in MDD 79-10, MD 80-01, 80-03 and 80-05 to mainly bright banded in MDD 79-14 and 79-11. Quantities of included bone coal and carbonaceous claystone vary from 0.66% to 24.6% of the total seam thickness.

B 5 is on average 2.6 metres thick and contains variable proportions of lithotypes. It consists mainly of dull banded in MDD79-10

Table 3.1 **Summary of lithotype distribution in the Monkman coal seams**

Lithotype Range and (mean) %	B1 *(7)	B3 (8)	B4 (6)	B5 (4)	B6 (3)	B7 (3)	B8 (1)	B9 (1)	B10 (1)	B11 (1)
Dull	77.3 -0.0 (50.2)	55.8 -0.0 (29.9)	37.7 -0.0 (21.7)	47.4 -0.0 (13.4)	58.5 -0.0 (19.5)	37.5 -0.0 (12.5)	31.3	16.5	14.8	32.7
Dull banded	36.0 -11.0 (24.1)	63.5 -8.5 (27.5)	65.6 -14.2 (36.7)	64.2 -0.0 (27.8)	30.4 -0.0 (15.3)	19.0 -0.0 (10.8)	33.1	73.9	41.0	29.2
Bright banded	62.6 -0.0 (18.1)	39.3 -6.6 (21.4)	53.0 -4.2 (21.3)	74.6 -7.2 (37.3)	36.2 -20.0 (28.4)	49.7 -14.4 (35.4)	30.5	-	44.3	31.0
Bright	19.6 -0.0 (4.3)	32.1 -0.0 (10.0)	13.5 -0.8 (5.2)	7.1 -1.4 (3.7)	-	57.9 -6.1 (29.0)	-	-	-	-
Bone coal	12.4 -0.0 (2.9)	13.0 -0.0 (4.7)	14.5 -0.0 (8.2)	12.0 -0.0 (3.0)	18.8 -0.0 (8.3)	1.1 -0.0 (0.4)	2.2	-	-	-
Carbon-aceous mudstone	7.6 -0.0 (1.7)	46.9 -0.0 (6.9)	15.8 -0.1 (7.0)	32.1 -0.0 (13.1)	63.8 -0.0 (28.5)	24.0 -0.0 (11.8)	2.9	9.6	-	7.1

* number of drillholes in which the seam occurs

\- lithotype not encountered in the drillhole and 79-14(lower), bright banded in MDD 79-14(upper) and 79-11 and mainly dull coal in MD 80-01. In this borehole the seam contains a significant proportion of carbonaceous claystone and stoney coal (44%).

B 6 is exposed only in MDD 79-14, 79-11 and 79-10, where it averages 0.79 metres in thickness and is of poor quality in the latter two, alternating between bright banded and carbonaceous claystone and dull and bright banded and carbonaceous claystone respectively. In MDD 79-14 it consists mainly of dull coal.

B 7 is thin, 1.3 metres thick and contains mainly bright and bright banded coal in the recovered core of MDD 79-11 and 79-10. Equal amounts of dull and bright material are present in B 7 in MDD 79-14.

B 8 averages 2.9 metres thick in the area and is exposed in only one drill hole in the study area (MDD 79-14). Here it consists of dull, dull banded and bright banded lithotypes in equal quantities.

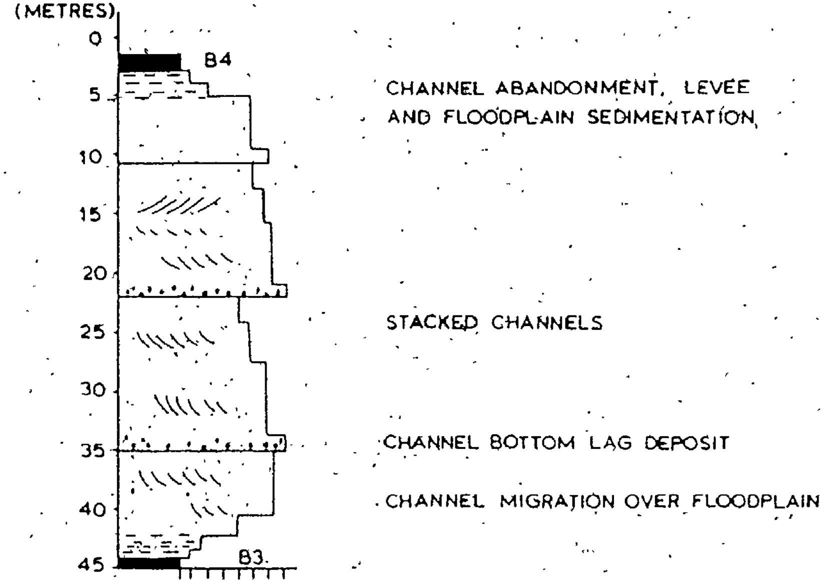
The coal therefore varies from bright banded to dull banded and dull lustrous but is predominantly interbedded dull and bright banded (bands 0.40m -0.01m thick). The individual laminations are less than 3mm thick. Fusinitic zones are relatively rare.

3.3.2 Associations of Lithotypes and their Interpretation

Three main lithofacies are recognised, 1) conglomerate and coarse and medium grained thick sandstones, 2) thin fine sandstones and siltstones and 3) claystone and coal. These are interpreted respectively as representing major distributary channel deposits, coarse floodplain deposits i.e. levee and splay deposits, and fine floodplain deposits i.e. distal crevasse splay, background floodplain (deposition of fine sediment from suspension), lakes and swamp/marsh. These lithofacies and their specific interpretations are illustrated in Figures 3.7, A to D.

Figure 3.7 Summary of Gates Formation lithofacies and their interpretation.

A. Channel deposits.



B. Coarse floodplain deposits (MDD 79-11)

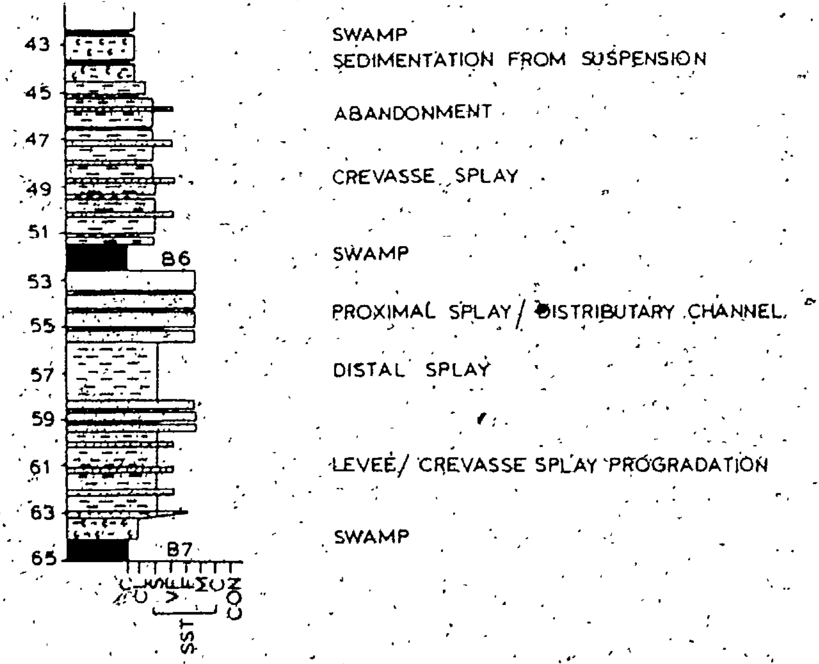
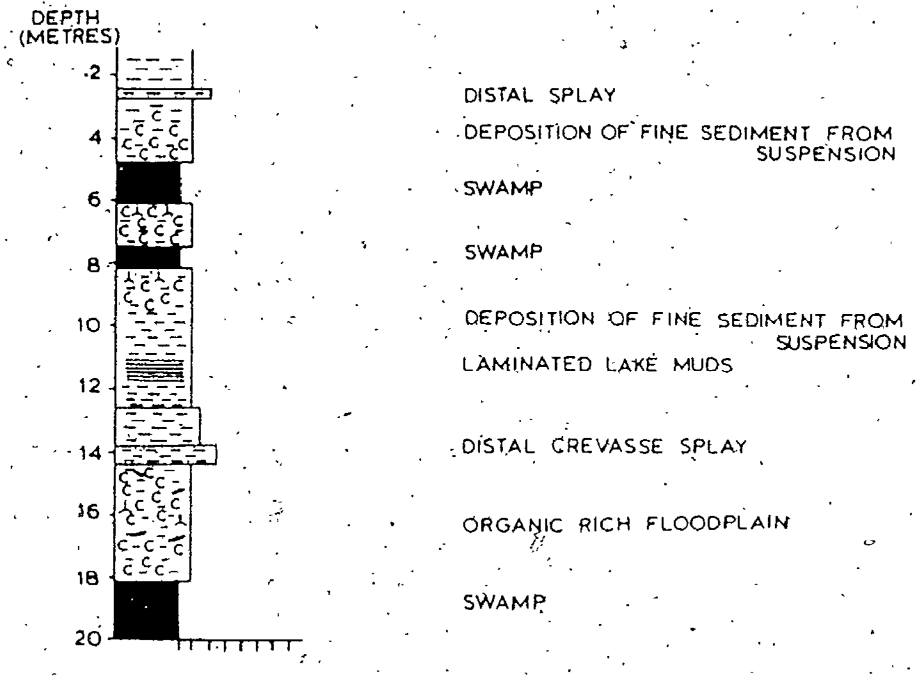
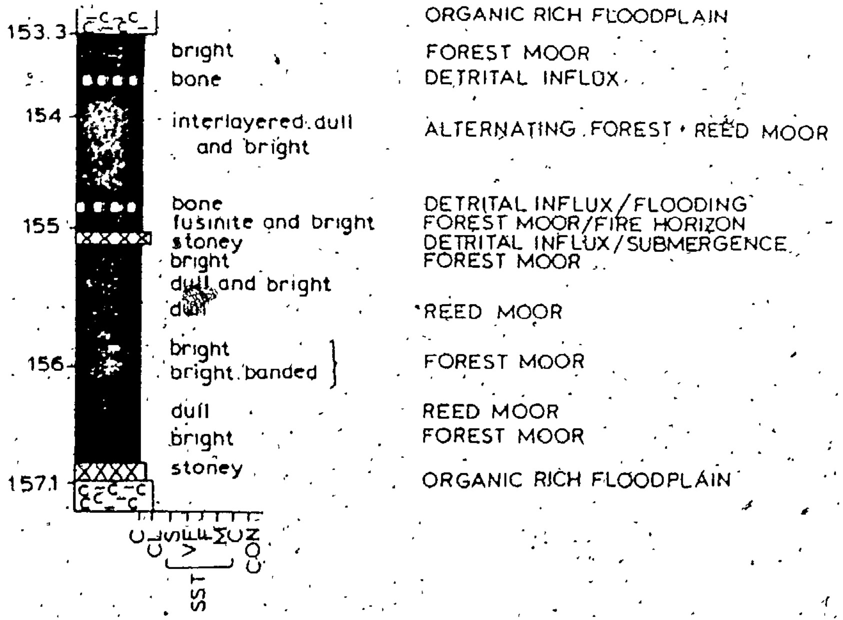


Figure 3.7 continued

C. Fine floodplain deposits



D Swamp types (MD 80-01)



(Interpretations after Elliot 1974 and Teichmuller 1950)

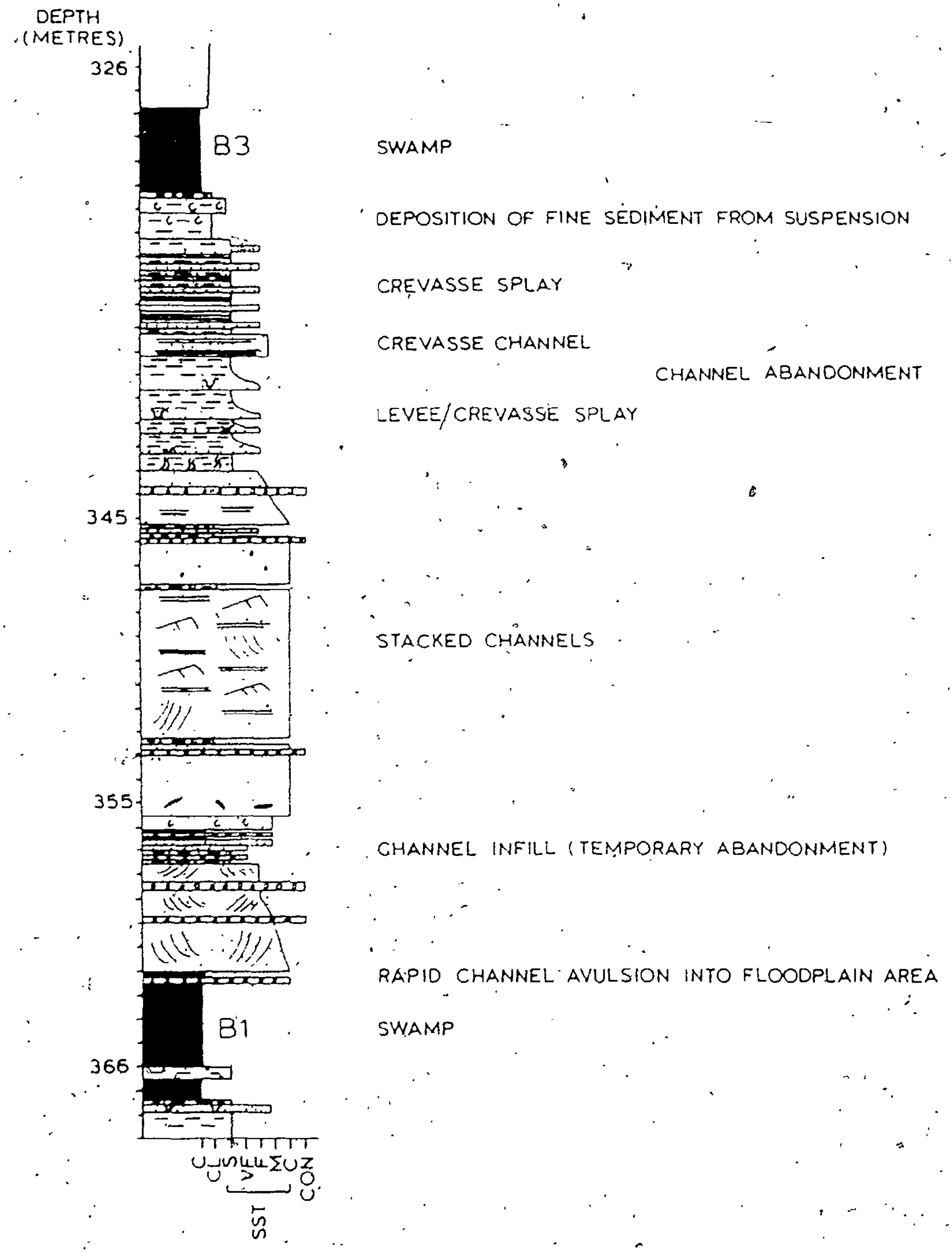
3.3.3. Subdivision of the Gates Formation

As in many coal bearing successions (Murchison and Westoll, 1968) a cyclicity is evident in parts of the Gates Formation. A well developed cycle recurs in the lower part of the Formation in all the boreholes. The upper part of the Formation contains irregular alternations of rock types in no obvious sequence. Based on this and several other differences a division of the Gates into an Upper and Lower unit is proposed.

3.3.3.1 Lower Unit

The Lower unit is characterized by the occurrence of thick channel sandstones and conglomerates, a well developed cyclicity, thick laterally persistent coal seams and a high proportion of coarse clastics relative to fine clastics. The contact with the Upper unit is transitional and occurs between coal seams B4 and B5. A typical Lower unit cycle is illustrated in Figure 3.8. A thin black carbonaceous claystone overlying a coal seam, coarsens up through siltstone and fine sandstone into medium and coarse sandstone and conglomerate. An erosive contact between the coal and coarse sandstone or conglomerate may also occur, for example seam B1 is erosively overlain by coarse sandstone in drillhole MD 80-05. The fine to coarse sandstones and interbedded conglomerates form the bulk of the cycle. They are laterally continuous across the pit area and occur stacked in fining upward cycles or in farther coarsening upward units. This stacked channel sequence grades up into thinly interbedded very fine to fine grained sandstone, siltstone and claystone representing levee, crevasse splay and quieter floodplain environments. The carbonaceous claystones grade into a thick coal seam which completes the cycle.

Figure 3.8. A typical cycle in the lower unit of the Gates Formation, Monkman (from drill hole MDD 79-14).



The cycle therefore represents the avulsion or gradual migration of a distributary channel into a floodplain area, progressively overlying floodplain, then levee deposits in the initial coarsening upward unit. A stacked channel sequence follows representing either repeated cut and fill or minor changes in situation of the channel. Abandonment of the channel and subsequent infilling with successively lower energy and finer grained deposits capped by a swamp/marsh deposit end the cycle.

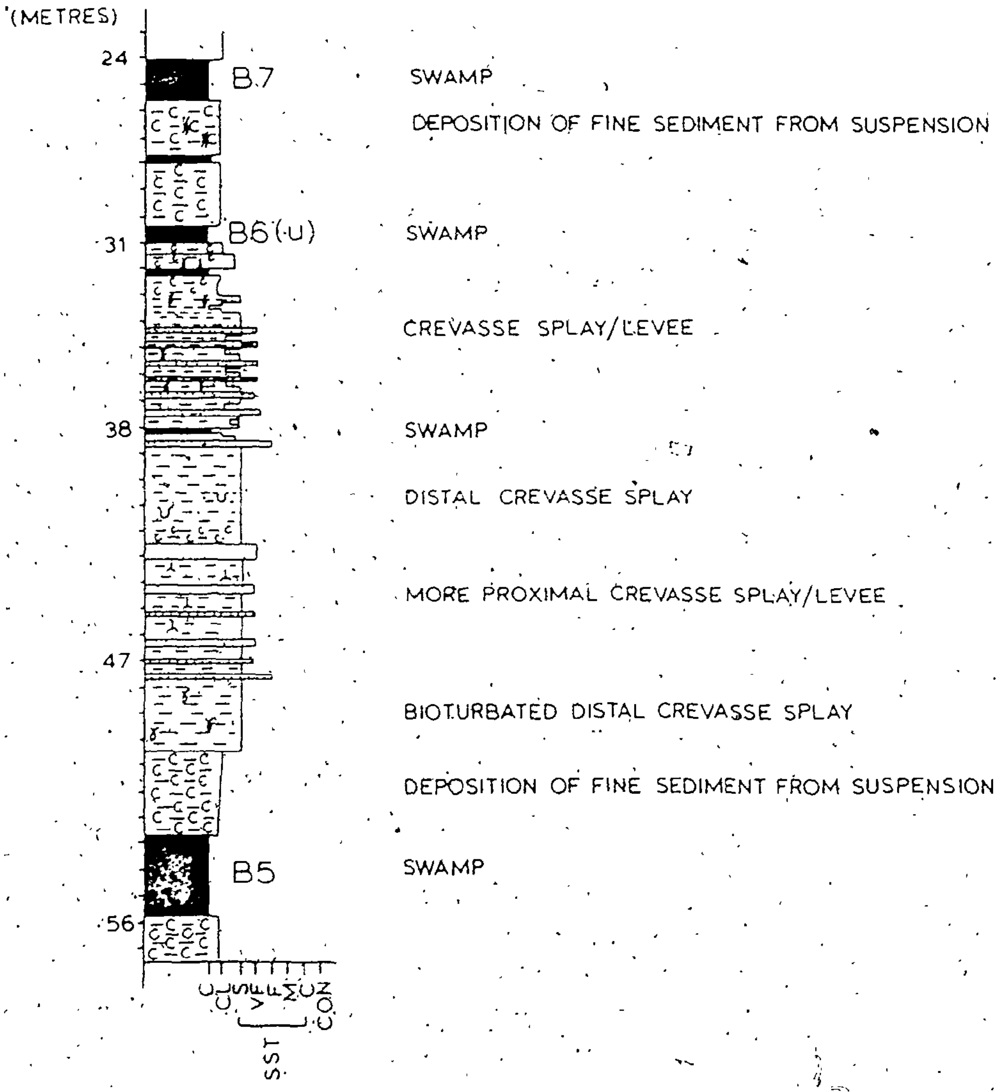
3.3.3.2 Upper Unit

The upper unit (Plate 8.B) is characterised by the absence or minor occurrence of coarse clastics, the predominance of fine grained lithotypes i.e. fine to very fine sandstone, siltstone, claystone and coal, a relative absence of cyclicity and many thin, dirty coal seams. Figure 3.9 illustrates a section characteristic of the upper unit. This consists of an alternating sequence of coarse and fine grained floodplain deposits associated with many thin and laterally not very continuous coals seams.

3.3.4 Depositional Environments of the Upper and Lower Units

To establish the depositional environments of the above successions comparisons were made with the Mississippi delta system (Coleman and Gagliano, 1965; 1964; Frazier and Osanik, 1969 and Coleman, 1981), the Niger delta (Oomkens, 1974) and the Fraser River delta (Styan and Bustin, 1983). The succession was also compared with some ancient deltaic successions (Elliot, 1974; 1975; 1978; Horne and Ferm, 1979; Fielding, 1984 and Haszeldine, 1984) and with some ancient fluvial sequences (Miall, 1977 and Smith, 1980). Marine sediments were not

Figure 3.9. A characteristic section in the upper unit of the Gates Formation, Monkman (from drill hole MDD 79-10)



encountered in the Gates Formation at Monkman, however possible brackish deposits were found in MDD 79-14.

The upper unit is thought to represent sedimentation in enclosed shallow interdistributary lakes or bays on the upper portions of a delta plain. The abundance of swamp deposits and lake-deposited carbonaceous claystones indicates a slow rate of sedimentation, substantial subsidence and distal nature relative to the distributaries for these lithologies. The coarser lithologies in the upper unit represent levee, crevasse splay and minor distributary channel deposits indicating closer proximity to the major distributary channels (Elliot, 1974). Structures such as convolute bedding and the abundance of soft sediment deformation indicate the rapid nature of the sedimentation. The alternations between the fine and coarse floodplain deposits represent the infilling and abandonment of the shallow interdistributary bays and lakes by the flooding of the distributary channels.

The lower unit was deposited in a higher energy environment, as evidenced by the abundance of medium and coarse sandstones and conglomerates, which represent major distributary channel deposits. This together with the relative paucity of floodplain deposits and the occurrence of thicker coal seams, indicates a position higher up the delta plain i.e. upper delta plain/fluvial, for the lower ~~unit.~~ The presence of coarsening upward cycles at the bases of the channel sandstones, representing gradual infilling of the channel-side depressions and subsequent channel migration onto this newly elevated land is characteristic of delta distributary channels and not so much of fluvial channel deposits.

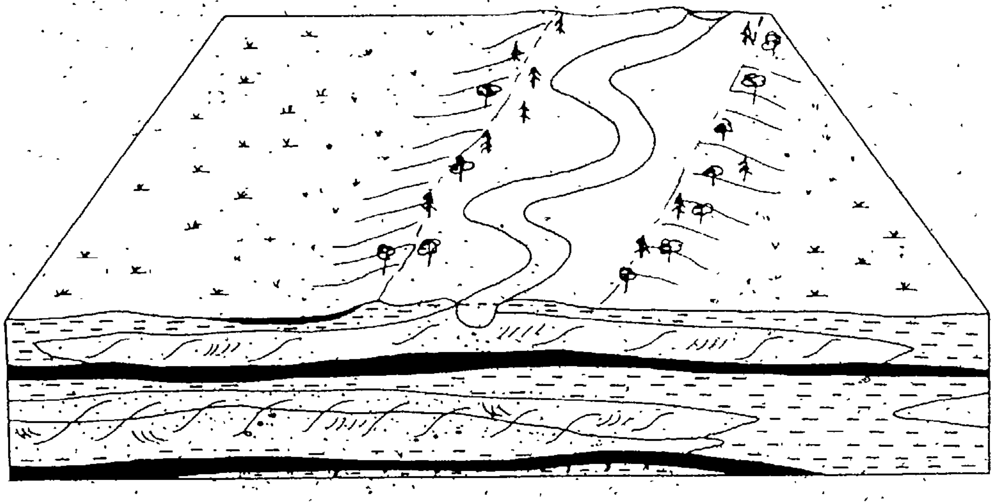
The stacked nature of the channel deposits on a broad scale and their lateral extent may result from the abundance of sediments and the high rate of subsidence in the area. This would enable the river/distributary system to continue to flow in the same area resulting in the stacking of cycles.

The coal bearing section of the Gates Formation therefore was deposited in an upper delta plain/fluvial environment which fines up into an upper delta plain environment. The base and top of the Gates Formation contain brackish claystones and barrier beach sandstones which represent the onset of regression and transgression respectively. A model for the depositional environment is illustrated in Figure 3.10. Carmichael (1983; 1982) carried out a regional study of the Moosebar and Gates Formations in northeastern British Columbia and the model proposed herein agrees with his regional model. He proposes that the river channels are mainly braided with some meandering and anastomosing or straight river reaches also present.

Figure 3.10 shows the lower unit as being deposited by a meandering river system. Although the deposits lack typical fining-upward cycles, the small percentage of conglomerates, the lateral continuity of the sandstones and the relatively low proportions of floodplain deposits support the hypothesis that meandering rivers were important in the deposition of the lower unit sediments. Braided rivers may also have been present. Table 3.2 summarises the sedimentology of the two areas.

Figure 3.10. Depositional model for the Gates Formation, in the study area. Key as in Figure 3.6.

LOWER UNIT



UPPER UNIT

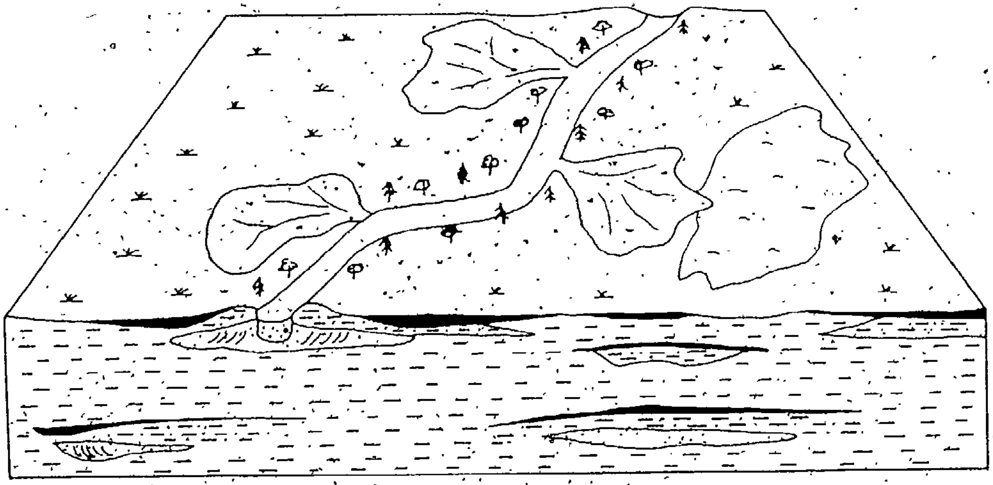


Table 3.2 Summary of general features of the sedimentology of the Mattagami and Gates Formations

Mattagami Formation	Gates Formation
entirely continental	possible brackish unit and marine transgressive intervals above and below
fluvial channel/floodplain environment may be anastomosing	fluvial to upper delta plain environment (lower and upper units respectively)
low gradient alluvial plain	high gradient alluvial/delta plain
gravel and sand in fining and coarsening upward cycles	conglomerates and sandstones in fining and coarsening upward cycles
high proportion of floodplain deposits	high proportion of floodplain deposits in upper unit, low in lower unit
lignite mostly woody, high proportion of forest moor, some raised bog deposits	coal variable proportions of lithotypes, dull and dull banded more common than bright, i.e. more wetter lithotypes
lignite and coal autochthonous, rooted horizons common	
both have channel, coarse and fine floodplain lithofacies	
sedimentation in both areas influenced by basement topography	
sediments unconsolidated	sediments consolidated

CHAPTER FOUR

MINERALOGY

4.1 Introduction and Methods Used

The mineralogy of the Moose River Basin and Monkman sediments and coals are discussed. Relationships between the macerals and minerals are analysed and possible explanations for the associations observed are given. The conditions required for formation of the minerals in both the coals and sediments are outlined and genetic sequences for both areas are proposed.

Characterization of the mineral matter in the sediments and coals was accomplished by optical identification, X-Ray Diffraction, Scanning Electron Microscopy coupled with Energy Dispersive X-Ray analysis and Microprobe analysis.

4.1.1 X-Ray Diffraction

X-Ray Diffraction (XRD) was used to determine the whole sample mineralogy and to characterize the clay minerals. Samples were run on either a Phillips Norelco or Rigaku X-Ray diffractometer. In both cases CuK wavelength was used in conjunction with a graphite or quartz crystal monochromator respectively. Whole rock powders were obtained by crushing with pestle and mortar or the Blueller (to approximately -200 mesh) and were smeared onto the depressed centre of a plastic sample holder. Thus orientation of the clay minerals was produced. To separate the clay minerals in the Moose River Basin samples, dispersion was followed by pouring off the light clay fraction (approximately less than 2 microns). This fraction was allowed to settle and a paste was smeared onto a glass slide. Samples were analysed untreated and glycolated. The Monkman clay minerals were separated, "sieved" through a ceramic tile giving good mineral orientation and analysed untreated, glycolated and heated to 600°C.

4.1.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) and Optical Microscopy are the prime methods for observation of in-situ mineral matter in coals (Mackowsky, 1982 and Finkelman, 1980). Much work has been done on minerals in coal by various other methods such as float sink density separations (Gluskoter et al, 1977), often coupled with dissolutions by various agents to remove carbonates followed by organically held elements (Miller and Given, 1978). Low temperature ashing is also a commonly used means for separating minerals from coal for subsequent analysis by XRD or SEM-EDX. These lines of investigation prove useful in identifying the minerals present and in the case of selective dissolution in determining their mode of occurrence.

In order to examine the minerals in situ and therefore to gain an insight into the exact location of the minerals and their relationship with the coal macerals, a technique that allows examination of an undisturbed sample is required. SEM and Optical Microscopy are such techniques. Optical Microscopy is limited in resolution and can not be successfully used for fine grained mineral matter in coals. SEM is therefore used to examine the mineral particles in coal.

An I.S.I. D.S.-130 Scanning Electron Microscope was run at 30 kV, 25 mm working distance and utilised the wide range of magnifications available. Coupled with the SEM is an Energy Dispersive X-Ray Analyser (P.G.T. System III), which is capable of detecting all elements with atomic numbers of 11 and greater at concentrations above approximately 100 ppm. The EDX, although semi quantitative, was used in this study primarily to list the component elements in mineral grains. The relative peak heights are used as a qualitative indicator of the relative proportions of the elements present, thus allowing mineral particles to be identified. The EDX is also capable of running element windows, and the dot maps produced are useful in showing the distribution of various elements relative to each other. Average run time for each analysis is 100 seconds at 2000 counts per second. The advantage of the SEM is that various sample preparations are acceptable such as thin sections, polished sections, grain mounts, polished blocks and broken fragments from a sample. Samples were fixed to Al stud sample holders with silver paint and Au or C coated prior to analysis.

4.2 Moose River Basin

A summary of the results of the Moose River Basin whole sample XRD analysis is shown in Table 4.1 (Raw data are listed in Appendix 1). Quartz and Kaolinite are present and are the major constituents in nearly all the samples. Trace to very rare amounts of illite/muscovite and some undifferentiated mixed layer clays are present in most samples. Trace to very rare occurrences of feldspar, hematite, gypsum, dolomite, ilmenite, calcite, and galena were recorded in some samples. In other samples major amounts of siderite, pyrite or goethite were observed. Millerite was detected in one sample, AC-10-82. The iron sulphide in some samples is in the form of marcasite and gypsum is commonly associated with both marcasite and pyrite. Traces of gibbsite were detected by XRD in only one sample (AC-18-82).

Table 4.1 **Summary of whole sample mineralogy of the Moose River Basin samples, as determined by XRD**

Mineral	Lignite *(14)	Clay (37)	Silt (13)	Gravel/Sand (13)
Quartz	P-ND	P-L	P-T	P-L
Kaolinite	P-ND	P-ND	P	P-ND
Muscovite /illite	VVL-ND (T)	T-ND	T-ND	VL-ND
Mica	ND (VL)	T-L-ND	ND	ND
Mixed layer clay	VVL-ND	VL-ND (T-VL)	VL-ND (T)	VL-ND
Feldspar	ND	VL-ND	VL-ND	VL-ND (T)
Pyrite	T-ND	ND (T)	ND	ND (P)
Siderite	ND (VVL)	P-ND	T-ND	ND (T)
Gypsum	ND (T)	T-ND	ND	VL-ND
Hematite	ND	T-ND	ND (T-VL)	ND
Dolomite	ND	ND	ND (VL)	ND (VL)
Geothite	ND	ND (P)	ND	ND
Gibbsite	ND	ND (VL)	ND	ND
Ilmenite	ND	ND (VL)	ND	ND
Millerite	(T) in pyrite nodule	ND	ND	ND

* number of samples analysed

P	major component
L	minor component
T	trace component
VL	very little present
VVL	almost negligible
ND	not detected

(X) mineral present at this level of abundance in only one sample

The kaolinite appears to be relatively ordered with strong 7Å reflections. Two sets of well defined triplets indicating d spacings between 2.6Å and 2.3Å are also recorded. The 4.4Å peaks however are often diffuse.

The mixed layer clays are thought to be smectites. They are characterised by diffuse peaks close to 5^{O} (2θ) which expand on glycolation.

The muscovite is made up of detrital muscovite and illite/muscovite (clay grade mica) which can be recognised (in the oriented sample) by the lack of the 4.44Å reflection which characterizes the detrital mica in these samples. This mica tends to occur at the base of hole 82-01 only and towards the middle of the section is replaced by kaolinite and illite.

The basal peaks of kaolinite and illite/muscovite in the coal and sediment samples occur at d values of 7Å and 10Å and are low and broad. The hkl reflections on some of the diffractometer traces have pronounced tails towards lower d values. This suggests that the clay minerals in these samples are of a very small grain size and may be of a poorly crystallised type. Quartz reflections are characteristically strong and well defined.

Heavy mineral analysis was performed by Hamblin (1982), on sand samples from Adam Creek and Ontario Geological Survey drillholes 75-02, 75-03, 75-05 and 75-06. The results of this study are listed in Table 4.2. He notes generally low contents of heavy minerals with varying quantities of hornblende, garnet, magnetite, ilmenite, pyrite, siderite, twinned staurolite, rutile, biotite, dolomite, spinel, pyroxene, topaz and traces of indicolite.

4.2.1 Gravels and Sands

The gravels consist of a clastic framework of white, yellow and grey quartz, red jasper, black chert, minor feldspar, zircon, rutile and organic accessories. The kaolinite matrix is ubiquitous in the upper sands and gravels and kaolinite also occurs in lenses and bands. The gravels contain mud lumps in the bases of palaeochannels e.g. AC-22-82. No other clays are present in the gravels but the sandstones and interbedded sands and silts have VL-VVL of both illite/muscovite and mixed layer clays. Pyrite occurs in the gravels as nodules (Location 15 Adam Creek) and as a cement (AC-13-82) in one case alternating with calcite cement (AC-32a-82). In some of the Adam Creek outcrops iron staining due to the weathering of pyrite outlines the cross-bedding (Plate 3.4), indicating the presence of sulfide minerals on channel dune and ripple foresets. Siderite and hematite also occur as cements in certain gravels e.g. AC-22-82.

Hamblin (1982), observed generally low contents of heavy minerals in the Mattagami Formation sands (see above) and identified two distinct sandstone phases on the basis of heavy mineral contents as well as grain size, composition and texture characteristics, (Table 4.2). Hamblin also noted a distinct relationship between the occurrence of hornblende and pyrite in the sands. In the lower parts of the section pyrite is abundant at the expense of hornblende. He attributes this to the alteration of iron rich hornblende, causing high metal contents in the water. He proposed that this is followed by generation of sulphide ions by sulfate-reducing bacteria which combine with the metal ions forming pyrite. A byproduct of this reaction is an increase in carbonate content

Table 4.2 Heavy mineral contents of the Mattagami Formation sands, from Hamblin 1982

PHASE II		
	Low Content-	
	in south	high- blue green hornblende, pink garnet, magnetite and ilmenite, pyrite, siderite, twinned staurolite, rutile, biotite, dolomite and spinel.
		low- pyroxene
	in north	high- green brown hornblende, pink garnet, hypersthene, clinopyroxene, gold, staurolite.
		low- siderite, twinned staurolite.
PHASE I (exposed only in southern part of the basin)		high- green brown hornblende, pyroxene, topaz.
		low- blue green hornblende, altered pyroxene, enstatite, rutile, traces of indicolite.

(due to the increase in pH) in the lower part of the sequence. Hamblin's two phases of sands are distinguished by matrix contents and composition, with the older phase having little matrix which is dominantly calcareous while the younger phase has abundant dominantly kaolinitic matrix.

4.2.2 Clays

The clay-rich sediments have the most diverse mineralogy. They consist of kaolinite and quartz with varying amounts of illite/muscovite and mixed layer clays. Illite/muscovite is present in all the clays from Adam Creek and borehole 82-01, (T-VL), and is distinctly absent particularly towards the base of borehole J-1-2. Carbonaceous clays tend to contain much less illite/muscovite than the organic poor clays. Mica is present in the basal clays of 82-01 and is absent in all the rest of the samples from the Moose River Basin (excluding sample L-2-1). Mixed layer clays are present (VVL-T) in almost all the clay samples. Pyrite was identified by XRD in only one clay (L-1-2, Jurassic), however isolated pyrite crystals/nodules were observed in several samples including L-3-1, L-2-24 and L-1-17. Gypsum occurs in some clays many of which are organic rich. Siderite is common in clays from 82-01 and Adam Creek but is absent in drillhole J-1-2. Siderite occurs as large nodules (up to 10 cm wide) parallel to the bedding e.g. AC-31-82, as smaller concretions e.g. in AC-17-82, AC-16-82 (Plate 9.A) and AC-21-82., and also finely disseminated e.g. in L-1-12 and L-1-17. Small amounts of feldspar are present in some of the clays. Hematite is also occasionally present and dolomite and goethite are found in L-1-14 and AC-20-82 respectively. Calcite occurs in sample AC-18-82 only and, gibbsite was detected in the above and also in AC-21-82 by SEM-EDX.

Plate 9.A Thin section photomicrograph of siderite concretions (and finely disseminated siderite) in a tan coloured clay, AC-16-82, Location 11, Adam Creek, Moose River Basin. Scale bar is 0.5 mms long. (Plane polarised light).

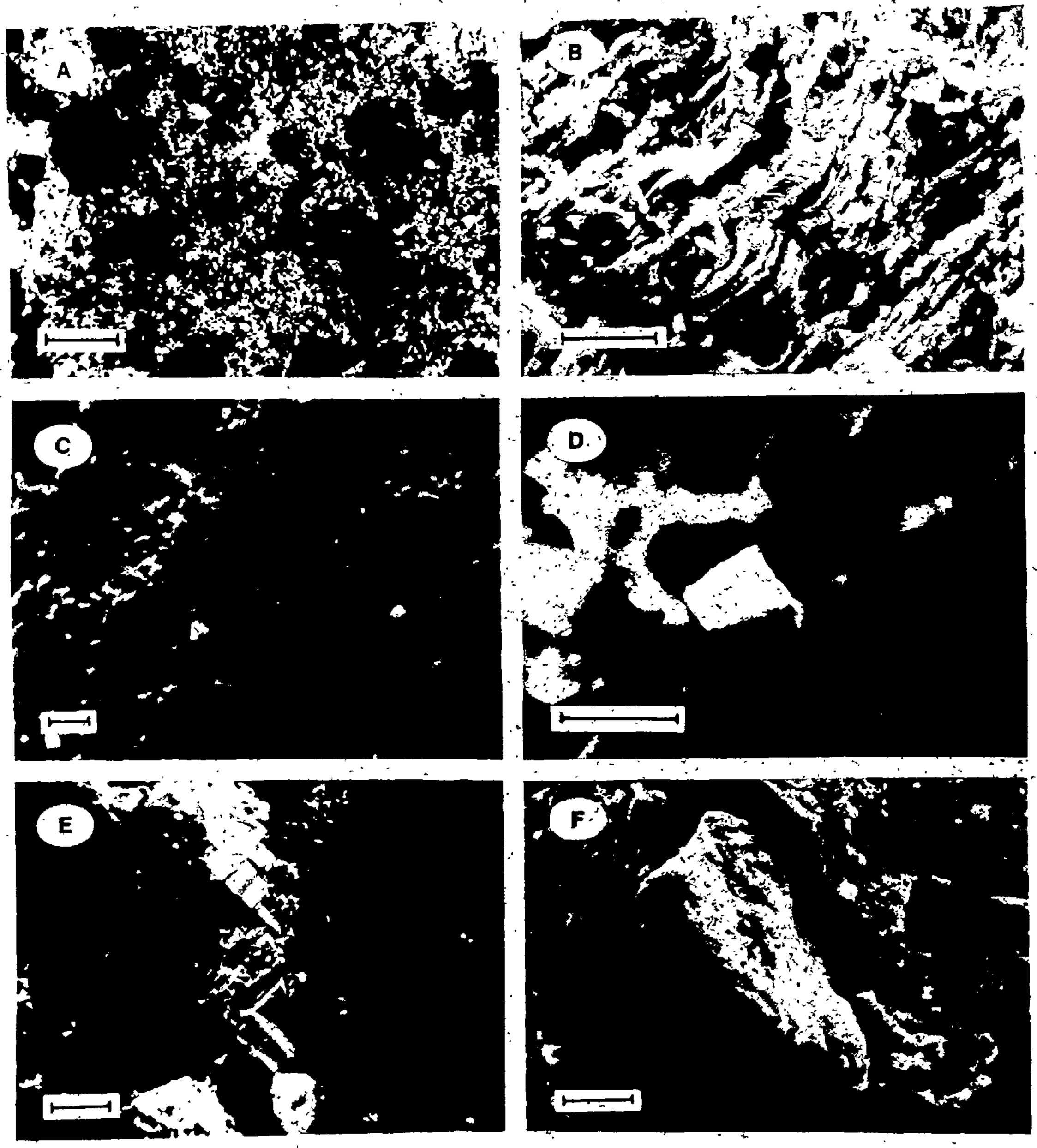
9.B SEM micrograph of pyrite rich Mattagami Formation lignite, showing replacement of woody structure by pyrite, (from Fyfe et al, 1983). Scale bar is 40 microns long (Magnification 506 X).

9.C SEM micrograph of Mattagami Formation lignite, showing pyrite crystals infilling cells in wood, (from Fyfe et al, 1983). Scale bar is 40 microns long (Magnification 241 X).

9.D SEM micrograph enlargement of Plate 9.C, showing a single pyrite crystal in a wood cell, (from Fyfe et al, 1983). Scale bar is 20 microns long (Magnification 20K X).

9.E SEM micrograph of pyrite infilling a crack in Mattagami Formation woody lignite, (from Fyfe et al, 1983). Scale bar is 40 microns long (Magnification 313 X).

9.F SEM micrograph of a detrital quartz grain surrounded by clay minerals in wood, Mattagami Formation lignite. Scale bar is 40 microns long (Magnification 377 X).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4.2.3 Lignites

The occurrence and distribution of the minerals in the lignite were examined using XRD, Optical and Scanning Electron Microscopy. The lignites are generally clean with some showing no traces of mineral matter (L-2-4). Most of the samples however contain some quartz and kaolinite scattered throughout the organic fraction. Quantities vary from none to abundant depending on the detrital input i.e. proximity to a major channel with splays, and the amount of chemical precipitation. The lignites are different from the sediments in that the accessory clays are restricted to very minor amounts of mixed layer clays with no (or VVL) muscovite/illite. Kaolinite varies from absent to abundant and occurs in the clastic horizons in the lignite as well as associated with the organic material. Other minerals present are gypsum and pyrite and these occur in less than half of the samples analysed. Pyrite has several modes of occurrence. In the pyrite rich lignite/ wood samples pyrite may replace the whole wood structure (Plate 9.B); infill the pore spaces (Plates 9.C and D) or occur as crystal coatings on the organic surfaces or in cracks (Plate 9.E). Sulphides are also present as nodules e.g. AC-10-82. Gypsum and pyrite are commonly associated with each other indicating some oxidation of the pyrite. Modes of occurrence and distribution of minerals in the lignites are summarised in Table 4.3. High Al:Si ratios on the order of 8:1 were found by ESCA in some lignite samples. This may indicate the presence of gibbsite in these samples.

4.2.3.1 Minerals Associated with the Different Lithotypes

Woody lignite is generally very clean and contains isolated detrital quartz grains and areas of clay minerals (Plate 9.F). The cell walls are in rare cases altered to pyrite and occasional pyrite infills

Table 4.3 Results of SEM-EDX analyses of mineral matter in selected Monkman and Moose River Basin coal and sediment samples

	Moose River Basin samples						
	AC-22-82	Onakawana clay and wood	Resin from lignite	AC-32-82	AC-21-82	AC-08-82	AC-10-82
pyrite	–	–	–	–	–	–	replacing wood structure
kaolinite	altering from feldspar	authigenic	authigenic? matrix	altering from feldspar	sediment matrix	mineral clumps associated with fusinite	–
feldspar	detrital	–	–	detrital altering to kaolinite	–	in mineral clump	–
other	–	gypsum recent sulfate	–	–	siderite nodules, quartz large detrital grains, gibbsite authigenic crystals on quartz grain	quartz large detrital grain in wood	gypsum weathering product of pyrite

(Table 4.3, continued)

	Monkman samples						
Mineral	S2-5	S2-4	62-6	S1-4	S1-2	S14-1	SS17
pyrite	cell fills crack fills overgrowing matrix	-	-	associated with the coal	-	inertinite cell fills framboids large crystals	inertinite, cell fills framboids large crystals
illite	inertinite cell fills; associated with macerals	-	in the sediments	-	detrital or authigenic grain	inertinite cell fills	-
quartz	-	detrital in silt in crack-like features	detrital in sediment and coaly material	detrital in mineral rich bands	detrital	(inertinite) cell fills	-
feldspar	-	detrital	detrital in sediment	isolated grains (detrital)	-	-	-
kaolinite	-	-	-	authigenic cell fills and broken fragments in coal	-	authigenic in cell fills	-
Other	galena associated with pyrite	zircon detrital in silt, Cl, Na, Ca, Si grain in coaly mtl.	zircon detrital, sphalerite authigenic in coal and sediments	-	linnaeite inertinite cell fill	ankerite cell fills	Sphalerite inertinite cell fills, P (apatite) with calcite in cell fill associated with sphalerite

of the cells have been observed. Fusinitic material contains mineral clumps made up of clay minerals and some quartz and feldspar e.g. AC-08-82 (Plate 10.A). However it is generally also quite clean and still contains a great proportion of unfilled primary porosity. The soily lignite consists of comminuted organics and mineral matter with isolated wood fragments. The broken up nature of this material indicates the important influence of flowing water on its formation. As would be expected soily lignite contains abundant detrital minerals which are dominated by quartz, clay minerals and minor amounts of feldspar or mica. Pyrite is common and is seen weathering to gypsum. The isolated wood fragments are in rare cases pyritised.

A sample of laminated fine sandstone and fusinitic coal (AC-12-82) (Plate 10.B), was found to contain abundant authigenic quartz and calcite (Plates 10.C and D). These minerals (quartz followed by calcite) infill the fusinite porosity and cracks in other organic fragments including leaf sections.

Compared to the abundant authigenic and detrital mineral matter in the macerals of the Monkman coals, the Moose River Basin lignites are very clean. In particular very little authigenic mineral matter (with the exception of pyrite and some kaolinite, and quartz and illite in AC-12-82) intimately associated with the lignite was observed. Thus the porosity in the lignites is high and largely unfilled, while that in the Monkman coals is much less.

Plate 10.A SEM micrograph of fusinite, showing clay mineral rich area (top of photo). In AC-08-82, Mattagami Formation, Adam Creek. Scale bar is 40 microns long (Magnification 0.74K X).

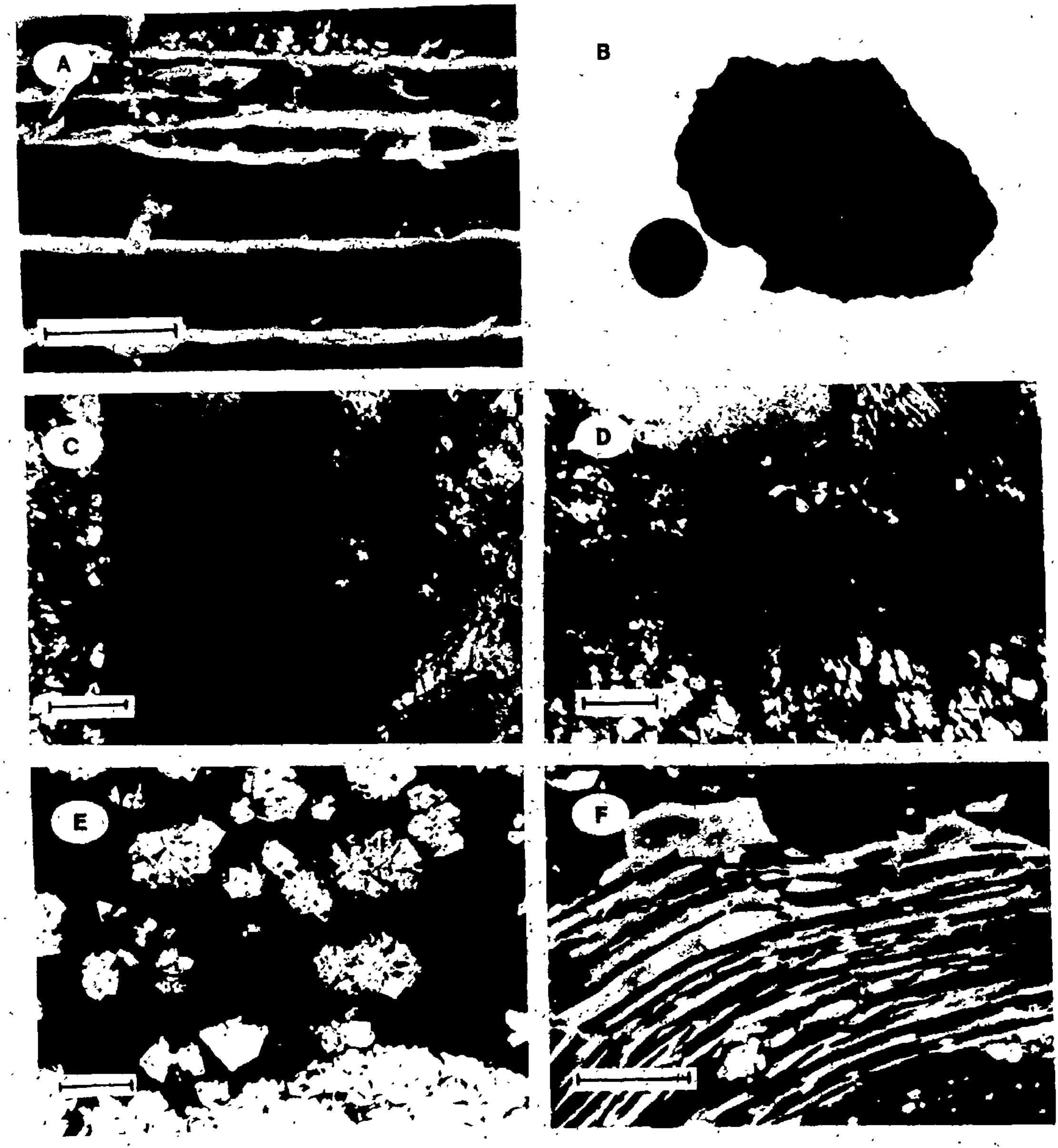
10.B Laminated fusinitic lignite and fine sandstone, AC-12-82, Adam Creek, Mattagami Formation. Coin is 1.9 cms in diameter.

10.C Photomicrograph of fusinitic material in AC-12-82, showing infilling of porosity (cell lumens) by quartz (grey) and lesser calcite (bright). Scale bar is 2.0 mms long. (Crossed nicols).

10.D Photomicrograph of fusinitic material in AC-12-82, showing quartz (grey) cell fills overgrown by calcite (bright). Scale bar is 0.5 mms long. (Crossed nicols)

10.E Photomicrograph (reflected light) showing single and coalescing pyrite crystals in fusinitic material, S14-1, Gates Formation, Monkman. Scale bar is 0.5 mms long.

10.F SEM micrograph of S2-5, Gates Formation, Monkman, showing illite (light grey) and pyrite (bright) infilling cells in fusinite. Pyrite overgrows (and therefore represents a later stage than) illite. Scale bar is 40 microns long (Magnification 599 X).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4.3 Monkman Area

4.3.1 Minerals in the Sediment Samples

A summary of the results of XRD analysis of the Monkman sediments and coal is given in Table 4.4 (Raw data are given in Appendix 1). Quartz is present as a major constituent in most sediment samples. Illite is a common minor to trace or rare phase. Two types have been identified, namely mica and a less well ordered illite/muscovite. The illite is likely the 1Md variety which is the most common illite polymorph. They are distinguished by the sharpness of the peaks and an extra peak at 4.44Å in the case of mica. The mica was found in approximately 25% of the sediment samples as a minor or trace constituent. Illite/muscovite occurs in most samples. Kaolinite ranges from a minor constituent to very rare and absent in some samples. Mixed layer clays were detected by XRD as a very rare component in approximately 62% of the samples.

Of the other minerals present ankerite, siderite, pyrite, calcite, feldspar and galena are the most common. They are present in variable quantities in the samples ranging from major constituents (e.g. ankerite in S3-6) to very rare mineral phases. Trace galena occurs in 1281 and 5292 (both coaly claystones) while VL-VVL was detected in many of the other samples. Ankerite is present mainly in crack fills and on slickenside surfaces, while pyrite tends to occur associated with the detrital organic fragments in the sediments. This produces a rough alignment of pyrite nodules and crystals parallel to the bedding e.g. S14-1. Gypsum, marcasite, sphalerite and barite occur in fewer of the samples. Zircons are present in most of the sediments as accessory

Table 4.4 Summary of whole sample mineralogy of selected Monkman samples, as determined by XRD

Mineral	Coal *(18)	Sediment (22)
Quartz	P-T (ND)	P-L
Kaolinite	T-ND	T-VL (ND)
Muscovite/ illite	T-ND	L-VL
Mica	ND (L and VL)	L-ND
Mixed layer clay	VL-ND	VL-ND
Feldspar	T-ND	VL-ND (T)
Pyrite	VL-ND	VL-ND
Siderite	T-ND	T-ND (L)
Ankerite	T-ND	L-ND (P)
Galena	VVL-ND (VL)	T-ND
Calcite	VL-ND (T)	T-ND
Barite	VVL-ND	VVL-ND
Marcasite	ND	ND (T and VVL)
Gypsum	ND	ND (VL and VVL)

* number of samples analysed

P	major component
L	minor component
T	trace component
VL	very little present
VVL	almost negligible
ND	not detected

(X) mineral present at this level of abundance in only one sample minerals. All three carbonate phases may be present in one sample indicating variable depositional and/or post depositional conditions in the Gates Formation materials.

4.3.2 Minerals in the Coals

XRD analyses indicate that quartz, kaolinite and ankerite are the most common and most abundant minerals associated with the coal samples. Illite, calcite, siderite, pyrite and feldspar are also common but occur in lesser and very variable quantities for example illite ranges from a trace constituent in 1270 to absent in 5305. Mica is detected in only one sample 1296 as a very rare constituent. Other minerals identified in the coals are galena (VVL-VL in approximately 10% of the samples) and barite (VVL-VL in approximately 20% of the samples). In the clay rich areas in the Monkman coals zircons are also found. It is likely that many other accessory minerals are present and could be identified using LTA (Low Temperature Ashing) followed by XRD, or SEM-EDX. Results of SEM-EDX analyses of mineral matter in selected coal samples from Monkman and the Moose River Basin are shown in Table 4.3. Typical modes of occurrence of the minerals are as follows. The most frequent mode of occurrence of pyrite is as coalescing euhedral crystals (Plate 10.E) or as framboids. These are both commonly associated with the inertinite macerals and coaly claystones however crystals (in the same sample) are larger when associated with the organics. Pyrite precipitated in cell lumens (Plate 10.F) and microfissures caused by shrinkage in the macerals, was also observed. Quartz is present both as detrital rounded grains in the mineral rich areas and as authigenic cell fills. Similar modes of occurrence are noted for the clay minerals. Plate 10.F shows authigenic illite cell fills. The carbonates also occur infilling fusinite cells (Plate 11.A) and as epigenetic crack fills (Plate 11.B).

4.3.3 Association of Minerals with Macerals

Most accounts of the mineral matter in coal because of the methods used in analysis, offer no information on the relationship of the minerals to the macerals. Such methods are discussed above. With the more recent application of SEM-EDX and Electron Microprobe techniques to this field, in situ mineral matter can now be analysed. The use of the optical microscope is also very important, however as mentioned above it is hindered by difficulty of identification of very small mineral grains in the coal.

A survey of the literature indicates that no group of minerals is consistently associated with a particular maceral type. Davis et al (1984), have found no clear correlation between the macerals in a coal and their inorganic contents. Finkelman (1980) noted different mineral suites associated with the various macerals. For example illite appears exclusively in the carbominerite bands, while siderite, calcite, silica and several accessory minerals are most common in the inertinite macerals. Minerals such as pyrite and kaolinite occur in both the vitrinite and inertinite macerals. The liptinites contain only barite, chalcopyrite and sphalerite. He also found the greatest variety and highest concentrations of minerals occurring in the carbominerite bands. Lesser amounts occur in the fusinite and semifusinite macerals and least in the vitrinite.

Cecil et al (1981) identified two main suites of minerals and macerals in Upper Freeport coal (Illinois) on the basis of parametric associations. Quartz, illite and kaolinite are associated with

Plate 11.A SEM micrograph of fusinite in S14-1, Gates Formation, Monkman, showing ankerite (grey) and pyrite (bright) infilling cell hollows. Note pyrite overgrowing ankerite (e.g. at left of photo). Scale bar is 40 microns long (Magnification 569 X).

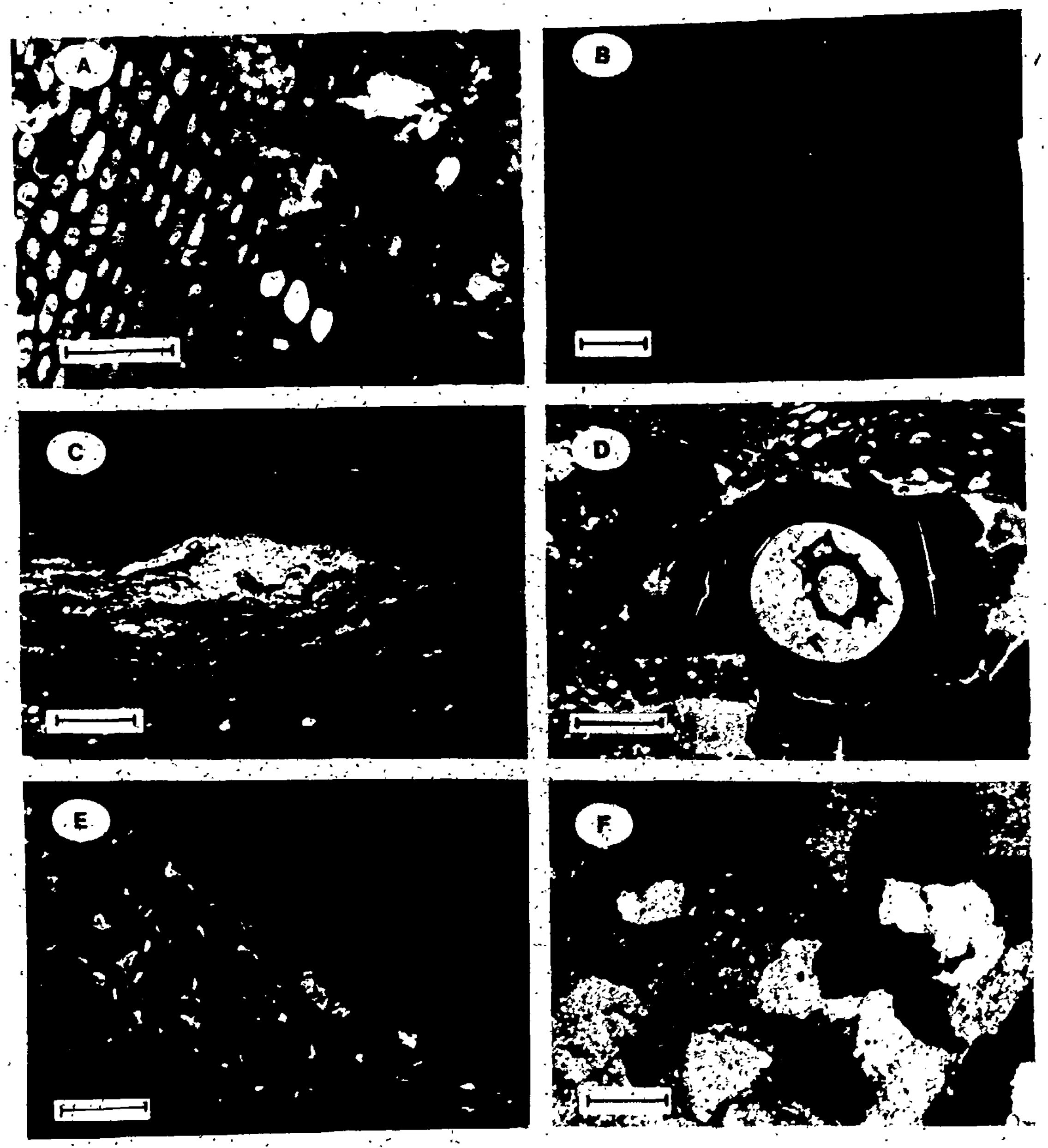
11.B SEM micrograph of S2-5, Gates Formation, Monkman, showing an epigenetic ankerite crack fill. Scale bar is 80 microns long (Magnification 164 X).

11.C Photomicrograph of S5-10, Gates Formation, Monkman, showing a mineral rich lens (starved ripple) in coal. Scale bar is 2.0 mms long. (Plane polarised light).

11.D SEM micrograph of S2-5, Gates Formation, Monkman, showing a sclerotinite grain (centre) infilled with illite and pyrite. Pyrite overgrows illite and also infills cracks (shrinkage) in the surrounding maceral. Scale bar is 80 microns long (Magnification 226 X).

11.E SEM micrograph of S1-4, Gates Formation, Monkman, showing a mineral rich band (parallel to the bedding) in otherwise 'clean' vitrinite. Scale bar is 80 microns long (Mag 226 X).

11.F Photomicrograph of S10-8, Gates Formation, Monkman, showing variety of clast types including chert, quartzite, Fe-rich and carbonate altered clasts in sandstone. Scale bar is 2.0 mms long. (Crossed nicols).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vitrinite, fusinite and semifusinite while pyrite and calcite tend to occur with sporinite and micrinite. Chandra and Taylor (1982) note that clay minerals are mainly associated with vitrinite and inertodetrinite and less with semifusinite, micrinite and other macerals in Gondwana coals. They also note that siderite is found mostly in vitrite or clay layers while calcite and ankerite occur in cell cavities in fusinite and semifusinite. Siderite in these samples is thought to be syngenetic (Smyth 1966), while the calcite and ankerite are epigenetic. This indicates that fusinite porosity was high at a late stage in the coal-forming process. Porosity appears not to be the only factor of importance as pyrite has been observed in the same coals, filling cell cavities and replacing cell walls in vitrinite and rarely in fusinite. This may be related to the oxidising conditions necessary to form fusinite, however the timing of the influx of iron-rich groundwaters may also be of importance.

In the Monkman coals apart from the mineral bands and lenses (Plate 11.C) which are occasionally associated with the coal, fusinite contains the highest proportion of mineral matter. Detrinite bands in the clean coals also contain a significant amount of mineral matter however these are relatively uncommon. Vitrinite contains few minerals and they are in general detrital as opposed to the authigenic type found in fusinite.

Fusinite

Minerals found in the fusinites occur mostly infilling cell hollows. Illite, silica and pyrite are the most common while ankerite and kaolinite are less common. Sphalerite was found in S1-14 infilling some cell lumens and was associated with a phosphorous phase and calcite. In S2-5 galena is associated with pyrite where it occurs overgrowing illite cell fills and the maceral in general. Illite and silica and to a lesser extent calcite, are the primary authigenic minerals in the cell hollows in most of the fusinites examined and pyrite is observed overgrowing these phases (for example see Plate 10.F). It is not clear why illite should form in some coals in preference to silica and vica versa.

One sclerotinite grain containing illite and pyrite was analysed in S2-5 (Plate 11.D). The first mineral to infill the structure was illite and this was subsequently overgrown by pyrite. In this sample the late nature of the pyrite is clearly visible as it is also found infilling cracks in the organic matter surrounding the sclerotinite.

Vitrinite

Vitrinite is clean compared to fusinite and contains rare isolated mineral grains scattered throughout the maceral. Occasional concentration of the minerals in bands parallel to the bedding of the coal, for example in S1-4 (Plate 11.E), may indicate deposition of a greater concentration of minerals at that time or the breakup and compression of a band of vitrinite (precursor) concentrating the small amounts of authigenic and/or detrital mineral matter present. These bands were not observed to be continuous. Minerals found in the vitrinite are dominantly kaolinite and silica, however occasional pyrite, illite and feldspar or mica grains were also observed. The minerals are generally smaller than in the fusinites and are rounded to irregular in shape. Minerals in the mineral rich bands occasionally appear to be broken pore fills as their shapes match those found in crushed fusinite grains. The minerals are therefore both detrital and authigenic.

Liptinite

No liptinite macerals were analysed in the Monkman samples.

In the coal in general there appears to be a clear relationship between the amount of clay bands and layers of clay-rich coal present and the proportion of illite compared to kaolinite in the clay mineral suite. Increased proportions of illite relative to kaolinite are accompanied by increased quantities of clay-rich and stoney/boney bands in the coal. Illite/kaolinite ratios may be a useful factor in assessing the quality of a given coal without the expense of an in-depth survey of the mineral rich bands in that deposit.

4.3.4 Mineral Suites Related to the Coal

Two suites of minerals can be recognised in the samples on the basis of surface texture, form and association of the minerals. These correspond generally to the detrital and authigenic suites recognised by Finkelman (1980). He found quartz, illite and other clay minerals to be detrital and pyrite, sphalerite, galena, quartz and the carbonates to be authigenic. The authigenic minerals tend to exhibit crystal faces, are intimately intergrown with each other and occur most commonly associated with the coaly material. Detrital minerals are rounded to subangular, associated with mineral-rich bands in the coal consisting of intermixed macerals and minerals and occur randomly isolated within the macerals.

In the Monkman samples quartz, zircon, mica, feldspar and perhaps some illite are detrital while the carbonates, kaolinite, illite, barite, some quartz and the sulphides are thought to be authigenic. Epigenetic minerals are those formed after the coalification process is completed. They include mainly ankerite and some pyrite and are found infilling cracks or crystallised on slickenside surfaces. These minerals are by nature not associated preferentially with any particular maceral.

4.3.5 Causes of Maceral Mineral Relationships and Mineral Suites

These maceral mineral associations may be related to different modes of formation and different physical characteristics of the macerals as well as factors such as situation in the peat swamp, progenitor plants etc.

An important control on the unequal distribution of the minerals in the different macerals as mentioned above, may be the porosity variations in these materials. A Transmission Electron Microscope (TEM) study by Harris <u>et al</u> (1981) of the ultrafine structures of two Eastern United States coals (E. Kentucky and Illinois No.6) determined that inertinite is the most porous maceral, containing a broad range of pore sizes from 5 to 50 nm in diameter. Vitrinite exhibited the finest porosity, 2 to 20 nm, with the majority of the pores being at the smaller end of the size range. Liptinite is least porous but exhibits some secondary irregular and tabular pores due either to in situ growth of carbonates or to the catalytic action of minerals. They found granular inertinite to host numerous minerals including calcite, pyrite, gypsum, clay minerals and quartz while in liptinite and vitrinite, S was the only detectable element.

Many of the minerals intimately associated with the macerals are syngenetic in origin. The mode and conditions of formation of the macerals are therefore very important as these determine the minerals that can precipitate. Lithotypes with decreasing proportions of fusinite and vitrinite are formed in environments with progressively higher water tables (Hacquebard and Donaldson, 1969 and Teichmuller, 1975). Eh and pH conditions during the formation of each maceral type are therefore different as are the precursor vegetation types. Vegetation in areas where the water table is highest consists mainly of reeds and aquatic vegetation, while on the more elevated and drier areas (periodically/seasonally below the water table due to flooding) trees are more common (Marchioni, 1980 and Stach et al, 1982). Inertinite macerals form by the alternate partial oxidation and submersion in water of the precursor plants. This process appears to harden the cell walls (and increase the proportion of Carbon) so that while other plants decompose and lose their form the inertinite precursors retain their cell structure. This process may be enhanced by early infilling of the cell hollows which also provides the structure with support. The inertinite porosity in some samples appears not to have been filled until a later stage when for example conditions were favourable for carbonate minerals to precipitate. Cecil et al (1981) found that the burning process thought necessary to produce fusinite would concentrate alkali and alkaline earth metals. Hydrolysis of these elements could produce a neutral to slightly alkaline microenvironment which would favour the formation of pyrite.

4.4 Sediment Source

4.4.1 Moose River Basin

The Moose River Basin sediments are derived from a dominantly granitic source. The abundance of quartz, feldspar, mica and zircon and the relative lack of other detrital minerals confirms this. Minor amounts of heavy minerals such as garnet, staurolite and others identified by Hamblin (1982) indicate some contribution from a metamorphic source while the presence of jasper and other resistant chert clasts in the gravels may confirm a contribution from a greenstone terrain to the south.

4.4.2 Monkman

The Monkman sandstones contain abundant lithic fragments (Plate 11.F), which allow for specific identification of the source materials. The fragments include chert, shale, siltstone, sandstone, carbonate, phosphate and bituminous material, quartzite and minor amounts of volcanic fragments. Although the major source is obviously sedimentary, Rapson (1965) identified four distinct sources on the basis of four suites of lithics. These range from the Selkirk metamorphic province, reworked Palaeozoic and possibly pre-Palaeozoic sedimentary rocks, Pennsylvanian-Permian volcanic province, to the Lowermost Mesozoic to uppermost Palaeozoic sedimentary sequence. Carmichael (1983) interpreted the Mesozoic to Cambrian sedimentary rocks of the Rocky Mountain Front and Main Ranges as being the principal source of the detrital components. The mineralogy is therefore more complicated than in the Moose River Basin succession.

Detrital minerals present other than the lithics include quartz, mica and feldspars.

The Monkman sediments compared to the Moose River Basin sediments are immature. The other major difference is that due to the variability of the Monkman source rocks many different minerals were present in the sediments. Many of the Monkman lithics have since been altered to carbonate, however during this process the ground waters were possibly rich in a variety of cations and anions derived from the lithic fragments.

4.5 Modes of Occurrence and Genesis of the Minerals

Quartz

The most common form of quartz is as a detrital mineral associated with mineral rich coal bands and macerals but it is also present isolated within the other macerals. The mineral rich coal types often contain much fragmented organic material, indicating conditions within the swamp capable of breaking down coal material and carrying detritals into the swamp. These conditions are common at swamp margins or near elevated areas within the swamp (Davis et al, 1984). Mixing with the swamp floor may also result in higher mineral matter contents especially of quartz and clay minerals. Flood waters flowing through the swamp are capable of transporting isolated quartz grains into the organic rich areas.

Davis et al (1984) reported abundant biogenic silica in the Okefenokee peats in the form of sponge spicules, phytoliths and diatoms. These forms are not present in coals. Siever (1957) proposed that biogenic silica dissolves and reprecipitates from supersatuarated solutions at low temperatures to form amorphous silica. Mizutani (1977) proposed a reaction path for the continuation of this process as follows:

amorphous silica → opal CT(disordered crystobalite) → quartz.

The lack of typical authigenic quartz in coals i.e. as void or cell fillings or cements and overgrowths (Davis et al, 1984), means that most of the biogenic silica from peats is carried out of the swamp in the through-flowing waters or contributes to the formation of other authigenic phases such as clay minerals. Although this is true for the Moose River Basin lignites (with the exception of AC-12-82), authigenic quartz occurs in the Monkman coals infilling inertinite cell lumens. This may mean that leaching was not a very active process in these coal-forming environments or that quartz precipitated in the fusinite cells at a later stage in the process, perhaps during sandstone diagenesis when silica-rich solutions were percolating through the coals. The presence of quartz in fusinite in AC-12-82, a consolidated sandstone, can be explained by this process.

Clay Minerals

Millot (1970) in his work on clay minerals in coal attributed their occurrence to mechanical inheritance (detrital input), transformation and neo formation (authigenesis). Following Yoder and Eugster (1955), Levinson (1955), Velde and Hower (1963), Bailey (1966), and Maxwell and Hower (1967), the 1md illite (illite/muscovite) detected in the Moose River Basin and Monkman (Plate 12.A) sediments and coals is thought to be diagenetic while the mica may be detrital. The diagenetic illite may have formed within the coal from the alteration of detrital muscovites (Weaver, 1985 and Velde and Hower, 1966).

Kaolinite in the Moose River Basin sediments and coals is also thought to be derived from the weathering products of other less stable minerals, for example K-feldspar of the microcline type. Evidence for this is found in gravels from the coal-bearing sequence. In thin section feldspars including microcline, with ragged and indented edges are seen

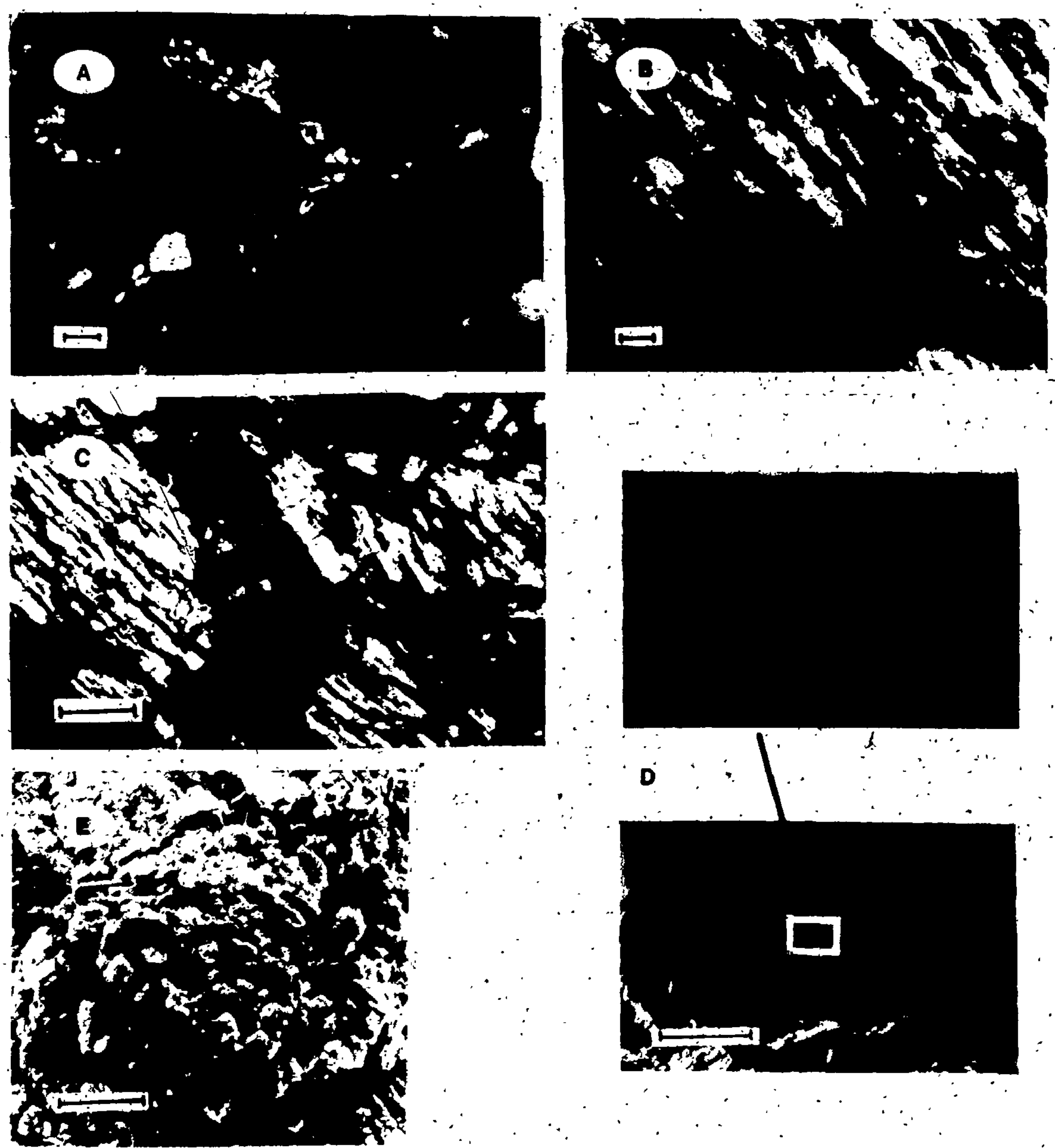
Plate 12.A Photomicrograph of S14-5, Gates Formation, Monkman, showing clay mineral (illite) habit. Scale bar is 0.1 mms long. (Crossed nicols).

12.B Photomicrograph of AC-22-82, Mattagami Formation, Moose River Basin, showing feldspar with ragged and indented edges and surfaces altering to kaolinite. Scale bar is 0.1 mms long.

12.C Photomicrograph of AC-22-82, showing a larger area of feldspar altering to kaolinite. Scale bar is 0.5 mms long.

12.D SEM micrograph of AC-21-82, Mattagami Formation, Moose River Basin, showing gibbsite crystals on the surface of a quartz grain. Scale bar is 80 microns long (Magnification 238 X). Enlargement of central rectangle 6 X.

12.E SEM micrograph of clay from the Mattagami Formation, showing recent sulfate (gypsum) growth. Scale bar is 40 microns long (Magnification 442 X).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surrounded by and laterally equivalent to kaolinite clay (Plates 12 B and C). Kaolinite is the stable mineral in peat-forming areas of low pH (4.8-6.5 in low moor peats and 3.3-4.6 in high moor peats, Stach et al (1982)) where organic acids which are capable of leaching cations (Staub and Cohen, 1978) are present. These conditions were present during peat formation in the Lower Cretaceous of the Moose River Basin. In addition to the low pH and organic acids, the elevated levee areas adjacent to the channels had a high water flow-through rate (wet climate and occasional flooding) which could promote kaolinite formation by leaching Si and K and other cations from the system. This may account for the very clean coals observed by Brown (1982 pers. comm.).

Swamps are neutral to slightly alkaline in pH in contrast to bogs which are acidic. This variation is due to groundwater influence in the former and is particularly evident if the surrounding rocks are carbonate rich. In a swamp situation as the peat-forming process continues and peat accumulates, groundwater influence diminishes and thus the pH decreases (see above). Feldspar in this situation alters to kaolinite.

In the thicker woody lignites of the Moose River Basin, which may have formed in raised bog situations, pH was acidic and thus kaolinite was stable throughout the process of vegetation accumulation and peat formation. The kaolinite in the Monkman coals is thought to have a similar origin to that in the Moose River Basin lignites supporting the conclusion that these coals were also deposited in freshwater conditions.

Carbonates

Mackowsky (1968; 1982) related the occurrences of minerals in coal to the two phases of coalification which she felt were significant identifiable time units. Minerals forming in the first stage of coalification are syngenetic and/or early diagenetic and are generally fine grained and intimately intergrown with the coal. Minerals identified with the second phase of coalification formed after consolidation of the coal. These were precipitated by ascending or descending solutions in cracks, fissures or cavities or by alteration of primarily deposited minerals.

Carbonates in coal belong to both of these genetic groups. Siderite and dolomite are regarded as syngenetic while calcite and ankerite are often epigenetic (Mackowsky, 1982). Cecil et al (1981) consider calcite and siderite to be syngenetically formed minerals in the coals of the Appalachian region. They propose that ions which are held on the organics by ion exchange or as salts are released during coalification. These together with ions set free by the alteration of smectites and mixed layer clays to illite react with dissolved CO_2 from organic decomposition (Stach et al 1982), forming calcite or siderite (provided no reducible sulfate is present). Cecil et al (1983) on the basis of C and O isotope data proposed several additional sources for the carbonates including, 1) resulted from bacteria sulfate reduction, 2) resulted from the action of methanogenic bacteria as indicated by ^{13}C enrichment and 3) from chemical coalification. They conclude that carbonates derived from methanogenesis dominate.

Siderite is the only common carbonate in the Moose River Basin sediments. Trace amounts of dolomite and calcite are found in samples

AC-15-82 and L-1-14, and AC-18-82 respectively. In the lignites carbonates are rare with only very tiny amounts of siderite detected. Pyrite is however common indicating that the ions were taken up by the reducible sulfate in the system rather than forming carbonates. The siderite in the sediments occurs predominantly as nodules in carbonaceous and non-carbonaceous clays, and to a lesser extent in the sands. The nodules tend to lie in bands parallel to the bedding with significant visible lateral continuity indicating a syngenetic origin (Mackowsky, 1982). No compaction around the nodules was observed in the Moose River Basin samples. Another common mode of occurrence is as disseminated crystals overgrowing the matrix of the sediments. These occur singly or in aggregates and where abundant they coalesce forming a massive structure.

Foscolos and Stott (1975) described several reactions to explain the occurrence of siderite in a sediment. They attribute control of sediment pH to the presence or absence of pyrite and calcite, with the oxidation of pyrite producing free hydrogen ions, and calcite counteracting this effect. They suggest that siderite forms when $Fe(OH)_3$ and H_2CO_3 react.

The Monkman sediments and coals contain ankerite, calcite and siderite ranging from major constituents to very tiny amounts. Ankerite was determined by microprobe to be the major constituent in the crack fillings and is therefore thought to be epigenetic. Calcite was found in one sample to be intergrown with sphalerite in a cell filling. Siderite is found as small clusters of crystals overgrowing the matrix.

Kemezys and Taylor (1964), have found that siderite is abundant in seams overlain by freshwater rocks while calcite and ankerite occur in coal overlain by both freshwater and marine rocks.

Sulfides

Sulfides are present in both the Moose River Basin sediments and the Monkman materials in a variety of forms. Replacement of cell walls and complete pieces of wood is a common phenomenon in the Onakawana sediments. Pyrite nodules are also common both in the lignite and in the gravels, while framboids have been found in the lignite (Winder 1985, pers. comm.). Crystals of pyrite in the clays occur infrequently. In the Monkman materials the most frequent occurrence of pyrite is in framboids, as coalescing euhedral crystals or as cell infills. These are commonly associated with the organic material in coaly claystones as well as in the fusinite macerals in the coal. Fillings of microfissures caused by shrinkage in the macerals were also observed. Marcasite is present in some Monkman samples.

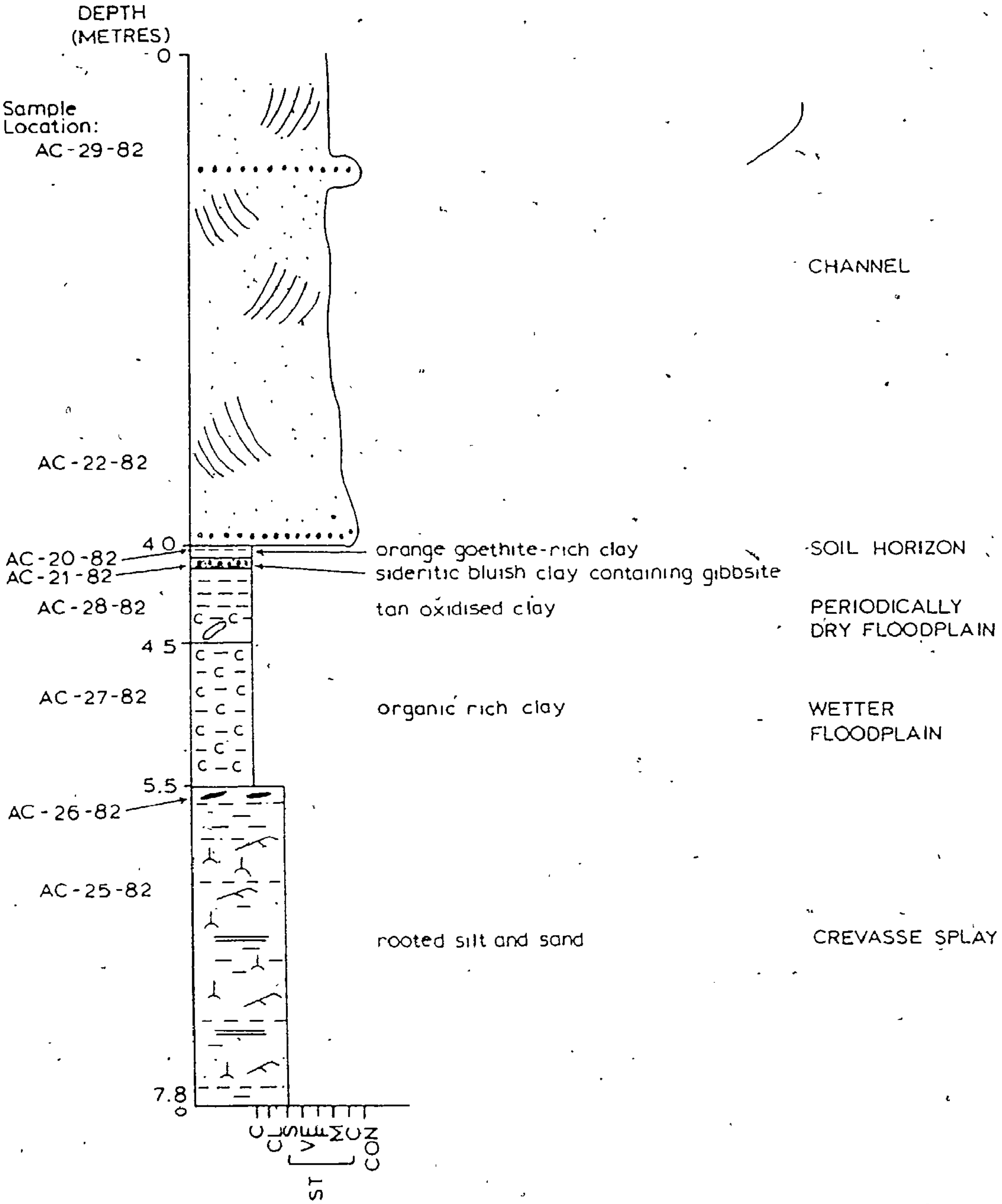
The predominant association of pyrite with coaly material in all the sediment types indicates the dependance on a reducing environment caused by decomposition of the organics and may also be due to the presence of significant S in the plants/organics. The acidic conditions during the early stages of coal accumulation mean that pyrite formed later on during the coalification process in the coals. Less acidic conditions occurred in the surrounding sediments explaining the abundance of pyrite replacing and associated with the organic matter in these materials.

Oxides

Gibbsite is usually found associated with depleted mineral assemblages which contain only quartz and kaolinite. Trace occurrence of gibbsite in some of the Moose River Basin samples therefore indicates element depletion and emphasises the weathered nature of these sediments. Gibbsite in AC-21-82 was observed by the SEM occurring on the surface of a 2mm diameter quartz grain (Plate 12.D). A similar occurrence of gibbsite was noted by Clarke and Keller (1984). The sample is a clay which contains increasing concentrations of siderite nodules towards the top of the sample. The lithology directly above AC-21-82 in the section is a goethite-rich, thin clay. This is erosively overlain by a coarse channel deposit (Figure 4.1 and Plate 3.C). The rock types because of their distinctive mineralogy and structure may represent an original soil profile developed on a levee/crevasse splay surface or a drier elevated area on the floodplain (predominantly above the ground water table). The goethite may be an original product of mineralization rather than a recent weathering product. Situations such as this can develop in localised weathering-prone areas such as levee banks or other elevated areas which experience alternating wetting and drying and these situations are therefore not contiguous over the entire depositional surface.

The goethite represents oxidised pyrite or another Fe-rich phase. Hematite occurs as a late cement in some sands e.g. AC-22-82. It may be directly precipitated or a later weathering product of siderite (or pyrite, magnetite).

Figure 4.1. Location 12 Adam Creek, showing goethite and siderite rich horizons.



Sulfates

The sulfate present in the Moose River Basin sediments is gypsum and as it often occurs together with pyrite is thought to form as a result of pyrite weathering. A distinctive mode of occurrence of gypsum in the clays is illustrated in Plate 12.E. Foscolos and Stott (1975) suggest that gypsum forms from the oxidation of pyrite in the presence of carbonate. Solutions rich in H_2SO_4 from this process react with cations present in solution thus forming sulfate minerals.

4.6. Summary of Mineral Genesis

Tables 4.5 and 4.6 illustrate and summarize the history of mineral genesis in the two areas examined. The minerals have been classified as detrital, syngenetic and epigenetic, however the exact timing of formation of these groups can not be determined. The relative sequence of mineral formation is derived from the interrelationships of the various minerals as well as their form and habit.

The mineralogy of the Moose River Basin sediments is relatively simple compared with that of the Monkman materials and will therefore be discussed first.

4.6.1 Moose River Basin

The detrital minerals introduced into the basin include quartz, feldspar and muscovite, as shown in Table 4.5. Although other detrital minerals are also present, these represent the bulk of the material introduced. Exceptions occurred where bedrock highs consisting of Devonian carbonate were elevated above the general level in the basin and thus supplied carbonate detritus to the surrounding area.

Table 4.5 Mineral genesis in the Moose River Basin, Mattagami Formation

Detrital	Early Syngenetic	Later Syngenetic	Recent
Quartz			Gypsum
Feldspar → ↘	Kaolinite →	Gibbsite	
Muscovite →	Illite →	Kaolinite	
	Siderite		
	Pyrite ———	Pyrite	
	Goethite		
		Hematite	

Table 4.6 Mineral genesis in the Monkman samples, Gates Formation

Detrital		Syngenetic				Epigenetic
Quartz	→	Quartz				
Feldspar		Kaolinite				
Mica	→	Muscovite/illite				
Lithics						
		Pyrite galena	—	—	—	Pyrite
		Sphalerite/ calcite				
				Ankerite	—	Ankerite
Plagioclase	→	Smectite (Montmor- illonite)	→	Illite		
			↘	Kaolinite		

Unlike quartz, feldspar is unstable at low temperatures and pressures and readily alters to various clay minerals, in this case to kaolinite. It is not known if the weathering process was restricted to the basin of deposition or if it began prior to the deposition of the sediments, however feldspar grains in the gravels can be seen altering to kaolinite in situ. The presence of kaolinite with lesser amounts of illite as syngenetic minerals confirms that the coal formed in a freshwater environment (Cecil et al, 1981 and Styan and Bustin, 1983). If the syngenetic minerals are plotted on an activity diagram such as that shown in Figure 4.2, it becomes clear that the pH of the waters to form kaolinite must have been acidic. Samples which contain gibbsite will plot more to the left of the diagram (at lower SiO_2 activities). Low pH in the coal forming environment a) reduces bacterial activity thus inhibiting the degradation of plant material and b) favours the dissolution of the mineral phases present. The depleted nature of the assemblage is emphasised where gibbsite is present with kaolinite.

Cecil et al (1981), suggest an alternative source for the kaolinite in coal from a study of several peats. They propose that in the initial stages of plant degradation the amorphous inorganic plant material which is predominantly of aluminosilicate composition (Table 4.7), will be released. In freshwater conditions kaolinite and smectite subsequently form. The smectite in the peats is thought to alter to illite on burial and loss of interlayer water.

Authigenic silica which may be present can also be derived from plant material (Cecil et al, 1981), see Table 4.7.

Conditions vary considerably in the coal-forming environment and although the areas where peat accumulates are acidic (Stach et al 1982),

Figure 4.2 Activity diagram illustrating the general relationships between aqueous solutions and the given solids, from Garrels 1984.

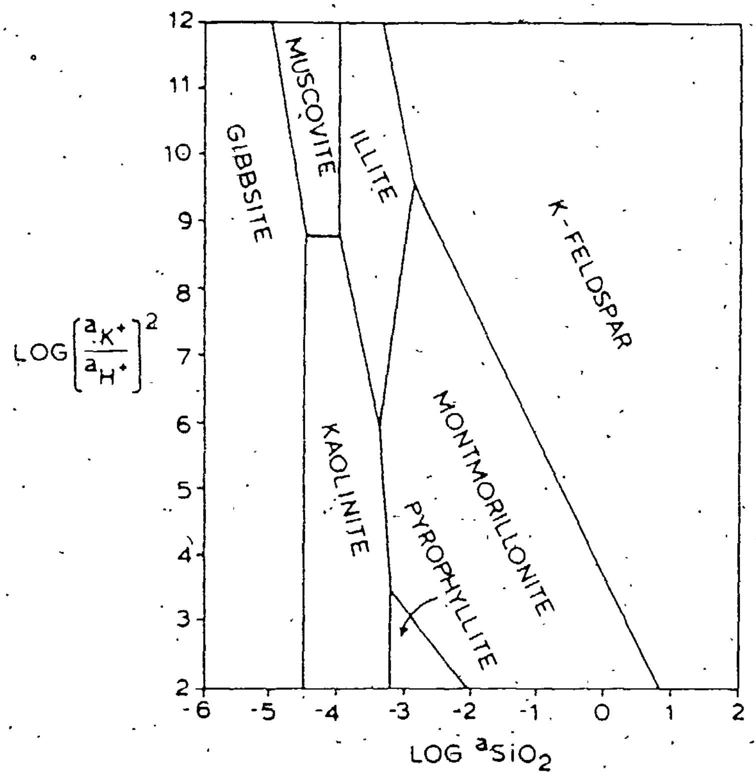


Table 4.7 **Major and trace element contents of algae, ferns, alfalfa grass, grass roots, woody angiosperms and Cypress wood and bark**

Element	Freshwater Algae, Beauty Creek Alberta I	Ferns II	Alfalfa Grass III	Grass Roots, Mississippi area IIII	Woody Angio-sperms II	Cypress wood, bark Mississippi IIII
Si	44,300	5,500	93	55	420	6.5
Al	2,503	230	25	11.3	90-200	1.7
Ca	45,800	.37K	5,800	9.0	3K-14K	28.7
Mg	15,222	1.8K	810	1.9	1.3K-9K	5.1
Na		1,400	200	0.8	34-950	3.6
K	21,887	18K	1,700	2.0	4K-15K	8.1
Fe	2,223	320-700	27	8.1	70-180	1.7
Mn	81.7	700	4	0.3	17-600	0.2
Ti	6.5	5.3	1		1.5-6.4	0.1
P	284	2K	7,010		120-2K	
Cr	946ppb	1.9			0.03-10	
S		1,000	1,037		2000-8700	
Rb		17.5	5		3.4-10	
Sr	265	13		0.02	12-88	0.13
Zr		2.3			0.48	
Cd		0.13			0.02-2.4	
Co		0.66	0.02		0.01-1	
Cu	4,100ppb	15	25		6-14	
Pb	7,052ppb	2.3	0.5		1-8	
Mo		0.8-2.5	1		0.06-3	
Ni	14,620ppb	1.5	0.5		1.4	
Zn	58.9		4	0.04	34-68	0.05
U	92ppb				0.01-0.04	
Th	4,300ppb	0.42			0.14-1.3	
Nb					0.4	
Y		0.77			0.15	
Ba		8			140	
V	1,290ppb	0.13	0.2		0.44-0.69	
Ga		0.23			0.01-0.1	

I Mann 1984, ppm
II Bowen 1979, mg X/kg Dried Matter K= X 1000
III Fairbridge 1972, ppm in Medicago sativa
IIII Renton et. al 1980, percent oxide in ashed (high temp.) sample

higher pH conditions may occur simultaneously elsewhere in the depositional environment. Some sediments where kaolinite is abundant (for example levee/crevasse splay deposits or elevated floodplain areas) are characterised by seasonal wetting and drying, and periodically high water flow-through conditions, thus those elements released by the alteration of feldspar and not taken up by the kaolinite are flushed out. In surrounding areas where conditions are generally wetter (i.e. below the water table) and less acidic, the abundance of K^+ ions from microcline degradation favours the precipitation of illite.

Illite which was found from the XRD plots to be almost indistinguishable from detrital muscovite is thought to have formed from alteration of the latter. The fact that illite is rare in the lignites and common in the clays can then be explained by the corresponding abundances of detrital muscovite in the coal and clay as well as the unfavourable pH conditions in the former. Areas overlain by marine rocks contain illite and montmorillonite whereas coals overlain by continental rocks where no HCO_3^- or CO_3^{2-} are present to neutralise the low pH, form kaolinite (Cecil et al, 1981 and Styan and Bustin, 1983). The presence of increased amounts of muscovite and illite and the virtual absence of kaolinite in the clays towards the base of drillhole 82-01 may be explained by the presence directly below of a basement (Devonian) carbonate high. Dissolved $CaCO_3$ species in groundwaters would buffer pH and allow illite to form in preference to kaolinite, due to decreased amount of leaching (which also results in greater quantities of detrital muscovite remaining) and increased bacterial degradation. As regards the timing of formation of illite and kaolinite the possibilities are as follows ;

a) formed at the same time with variable local conditions, where mineral matter leached from the areas of kaolinite formation with lower pH, was precipitated in areas of higher pH as illite etc.,
b) formed at different times when groundwater conditions were different or c) illite is an intermediate product of kaolinite formation (see Figure 4.2.

Other syngenetic minerals in these sediments and coals include siderite and pyrite. Siderite occurs mainly as nodules in the clays while most pyrite is found in the coals and gravels. These minerals formed after the early stages of deposition of the sediments. According to Baas Becking et al (1960), the pH during the formation of fusain is less than 4; while to form vitrain, clarain and durain normal waterlogged conditions, with a pH of approximately 5, are required. The pH needed to form siderite is higher, approximately 7, thus either the pH in the sediments was significantly higher than in the swamps or the siderite formed later in the coalification process. Siderite may also have been precipitated from cations leached from detrital feldspar, mica or Fe-biotite. Siderite forms in more oxidising and higher pH conditions than pyrite and this may give a further insight into the conditions in the sediments during the early stages of deposition. Siderite also occurs as single crystals or groups of small crystals which have coalesced. In some samples siderite is very abundant and forms a cement.

The pyrite and siderite occur in different samples thus the relative timing of their formation can not be determined, however they may have formed in different locations and environments in the area at the same time. Pyrite formation requires conditions which are reducing with respect to Fe^{3+} and SO_4^{2-}. Such conditions were available in the sediments where enclosed organic fragments were decomposing, and at a later stage pyrite could also form within the coal itself.

Hematite is present as authigenic crystals coalescing in places to form a cement. This represents a later stage of crystallization than siderite, which it follows.

4.6.2. Monkman

In the Monkman sediments the original detrital minerals introduced into the basin are considerably more diverse than those in the Moose River basin due to the abundance of lithic clasts. The lithics are in many cases overgrown by carbonate so that the extent of degradation and weathering prior to alteration is unknown.

The syngenetic minerals which formed early on in the coalification process include kaolinite, illite and silica. The earliest mineral to form in the coals is kaolinite, as broken fragments of kaolinite cell fills are present intimately associated with the coal material in some samples. The situation is thought to have been similar to that in the Moose River Basin. Illite formed at a later stage in the coals and may have formed in the sediments by alteration of mica or precipitation from solution at an earlier stage, simultaneously to kaolinite formation in the coals. Syngenetic mineral matter intimately intergrown with the coal substance is often difficult to distinguish from detrital material e.g. clay minerals (see Plate 12.A), especially when in the case of illite it may have formed from alteration of the detrital minerals. Pyrite is seen overgrowing illite in the macerals. Although pyrite formed later than illite in many of the samples, some of the pyrite nodules in the Monkman samples associated with the organic material are oriented parallel to the bedding planes and are thought to be early syngenetic. Pyrite also occurs associated with fractures in the macerals (e.g. S2-5). The selective distribution of pyrite in the samples may be explained by the availability and circulation of Fe-rich fluids combined with variability in geochemical conditions in different materials.

The carbonate represents the latest stage of mineralization in the Monkman samples, however as in the case of pyrite, carbonate minerals may have formed both syngenetically and epigenetically i.e infilling cell porosity, overgrowing the matrix and in late-stage cracks and slickensides. Ankerite is the most common carbonate phase however lesser amounts of siderite and calcite are present. Where ankerite overgrows a sediment, euhedral crystals occur overgrowing clasts (particularly chert) while the matrix and other clasts contain irregular small crystals. $FeSO_4$ in late high Fe^{2+} solutions caused by the oxidation of pyrite, may have reacted with calcite already present in the sediments, forming ankerite.

The Monkman coals contain a greater number of detrital bands than the Moose River Basin lignites. This may be a result of the lesser degree of compaction and thus concentration of the mineral matter in the latter. The Monkman coals also are different from the Moose River Basin lignites in that they contain an abundance of authigenic minerals infilling the porosity in particular in the fusinites. This may be related to the rank of the coal or the amount of circulating ground water, which in turn could be associated with the depth of burial of the succession.

CHAPTER FIVE

CHEMICAL ANALYSIS AND DISCUSSION

5.1 Methods of Analysis

The methods used to analyse the coal and sediment samples are listed in Table 5.1. The study is concerned primarily with the inorganic components of the materials (SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, TiO_2, P_2O_5, S, L.O.I., Cr, Rb, Sr, Zr, Cd, Co, Cu, Pb, Mo, Ni, Zn, U, Th, Nb, Y, Ba, Ga, Au, P.G.E., As and W), however limited organic analyses were carried out on selected samples. Results from trace element analyses are discussed in detail with emphasis on siting and interrelationships of the elements. Comparisons are drawn with other studies.

5.1.1 Organic Analyses

Moisture, ash, volatiles, fixed carbon, sulphur, and calorific value were determined on an air dried basis on composite coal seam samples from various drill holes in Monkman. The same samples cleaned were analysed for all of the above and P_2O_5. Similarly proximate and ultimate analyses were carried out on a bulk Moose River Basin lignite sample giving values for moisture, ash, carbon, hydrogen, sulphur, nitrogen and oxygen on the as received and air dried (107°C) sample.

For the majority of samples the Loss On Ignition (LOI) was taken as an estimate of the organic matter content. Contribution of CO_2 and H_2O from the inorganic materials in the sample must however be taken into account. The ash percentage (as determined from the LOI) is therefore less than the true mineral matter content and consequently the organic

Table 5.1 Analytical methods used in the study

Element	Method	Detection Limit	
Moose River Basin samples			
Major elements	X-Ray Fluorescence (XRF)	0.010%	X-Ray Assay Ltd., Toronto
S		0.002%	
Cr, Rb, Sr, Zr		10.000ppm	
Cu, Ag,	Atomic Absorption (AA)	1.000ppm	Barringer Magenta Ltd., Toronto
Co, Pb, Mo, Ni, Zn		5.000ppm	
Cd		0.500ppm	
Monkman samples			
Major and trace elements	X-Ray Fluorescence		U.W.O.
Moose River Basin and Monkman samples			
U	Delayed Neutron Counting (DNC)	0.010ppm	Nuclear Activation Services Ltd., Toronto
Th	Induced Neutron Activation Analysis (NAA)	0.300ppm	Ditto
Au, Rh, Re	Fire Assay Neutron Activation (FANA)	1.000ppb	Ditto
Ru, Pt		5.000 (20.000)ppb	
Os, Ir, Pd		3.000, 0.100, 5.000 (10.000)ppb	
30 element scan	Emission Spectroscopy DC-Arc	variable	X-Ray Assay Ltd., Toronto
Mo, Cr, Co	Plasma Emission Spectrometry (DCP)	0.500, 2.000, 0.500ppm	Ditto
As, W	Neutron Activation (NA)	1.000, 0.500ppm	Ditto
Sn	Emission Spectroscopy (EMS)	3.000ppm	Ditto
Si, Al, Fe, Ca Cl, S, C, O, N	Electron Spectroscopy for Chemical Analysis (ESCA)		Dr.J. Brown, Energy Mines and Resources Canmet, Ottawa

content is overestimated. Correlation coefficients between organically associated elements such as Ni and LOI will be lower than would be the case if corrected organic contents were used.

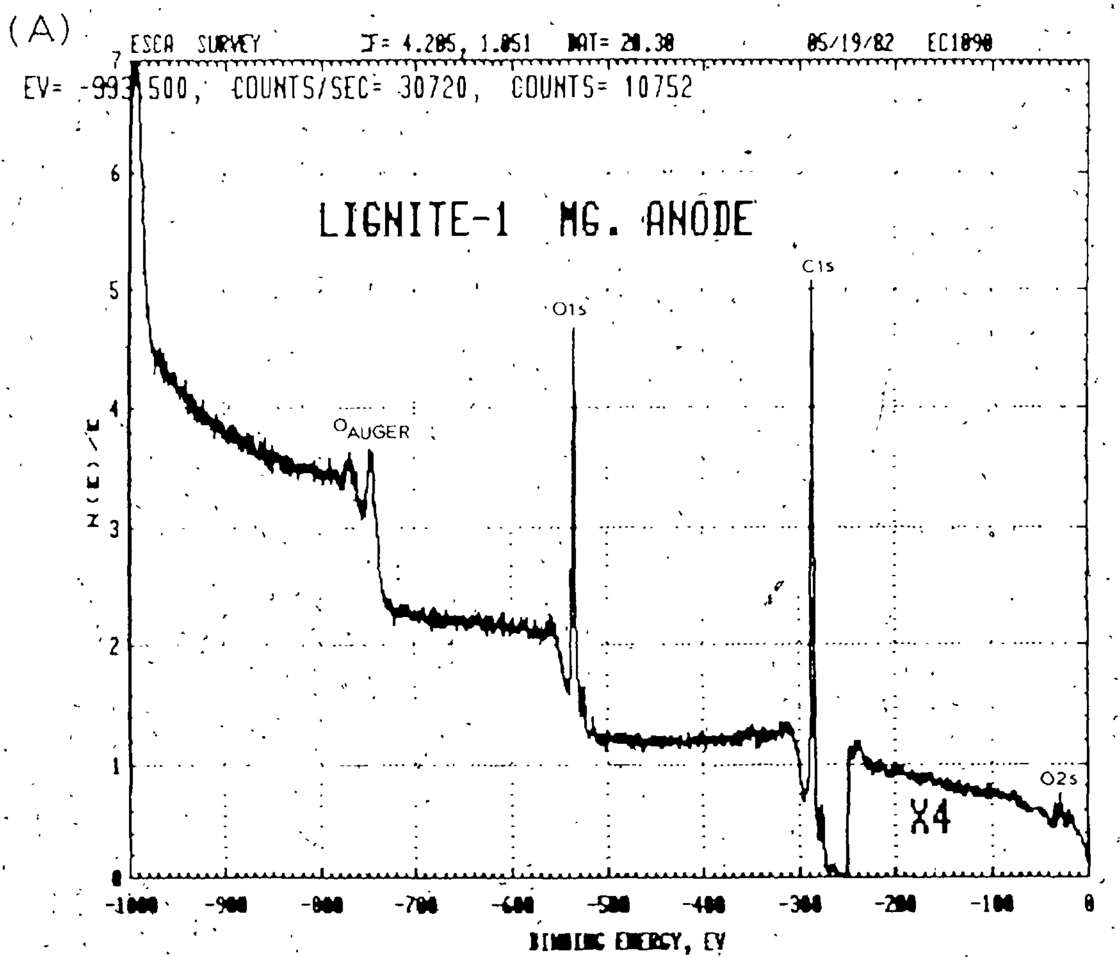
5.1.1.1 Electron Spectroscopy for Chemical Analysis, ESCA

Surface analyses of selected coal and wood lignite particles were run using ESCA (J.R.Brown, Energy Mines and Resources, Canmet, Ottawa, 1982). Characteristic spectra from Moose River Basin lignite and Monkman coal are shown in Figures 5.1 A to D. In addition to determining qualitative weight percentages of Si, Al, S, C, O, Ti, Ca, Fe and Ba (Table 5.2), the method allows analysis of the coordination states of the elements present (Table 5.3). Bond types for the elements may be proposed. In most cases results concur with the conclusions of Chapter 4. Si is found to be present as SiO_2 and in clay minerals. Al occurs as Al_2O_3 and in clay minerals in the Moose River Basin lignites analysed and as clay minerals and elemental Al in the Monkman samples. S also occurs in the elemental state and/or in SO_4^{2-} in all the samples. Carbon bonds present in both the Monkman and Moose River Basin coals are C--C and C--O. In the Monkman ash C--O--O was also noted. Halogens such as F and Cl were not detected or were present in very low concentrations.

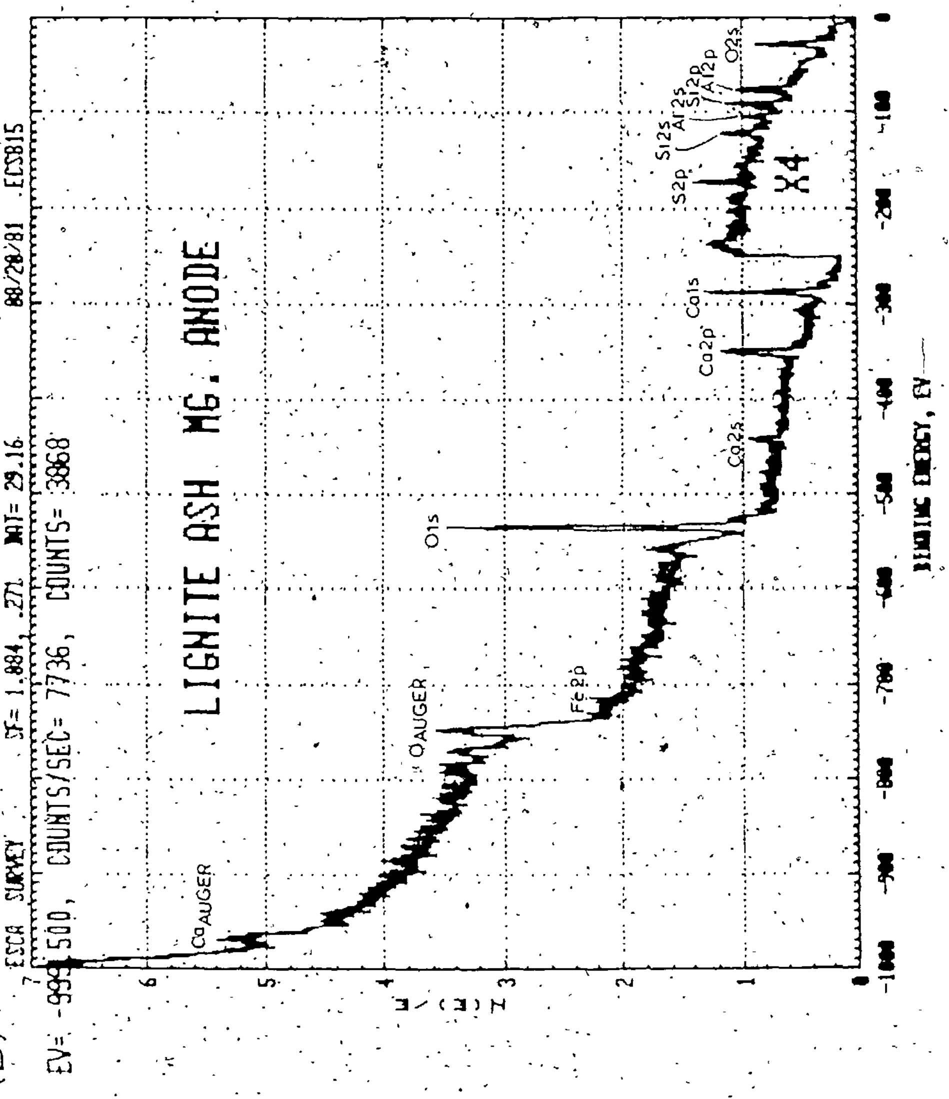
5.1.2 Inorganic Analyses

Methods used to analyse the inorganic components of the samples as listed in Table 5.1, include X.R.F., A.A., D.C.P., D.N.C., I.N.A.A., F.A.N.A. and E.M.S. The X-Ray Fluorescence on the Monkman samples was carried out at UWO using a Phillips PW 1450 Automatic Sequential Spectrometer. Where possible a coal standard, National Bureau of Standards 1635a, was run with the coal samples, while the sediments were

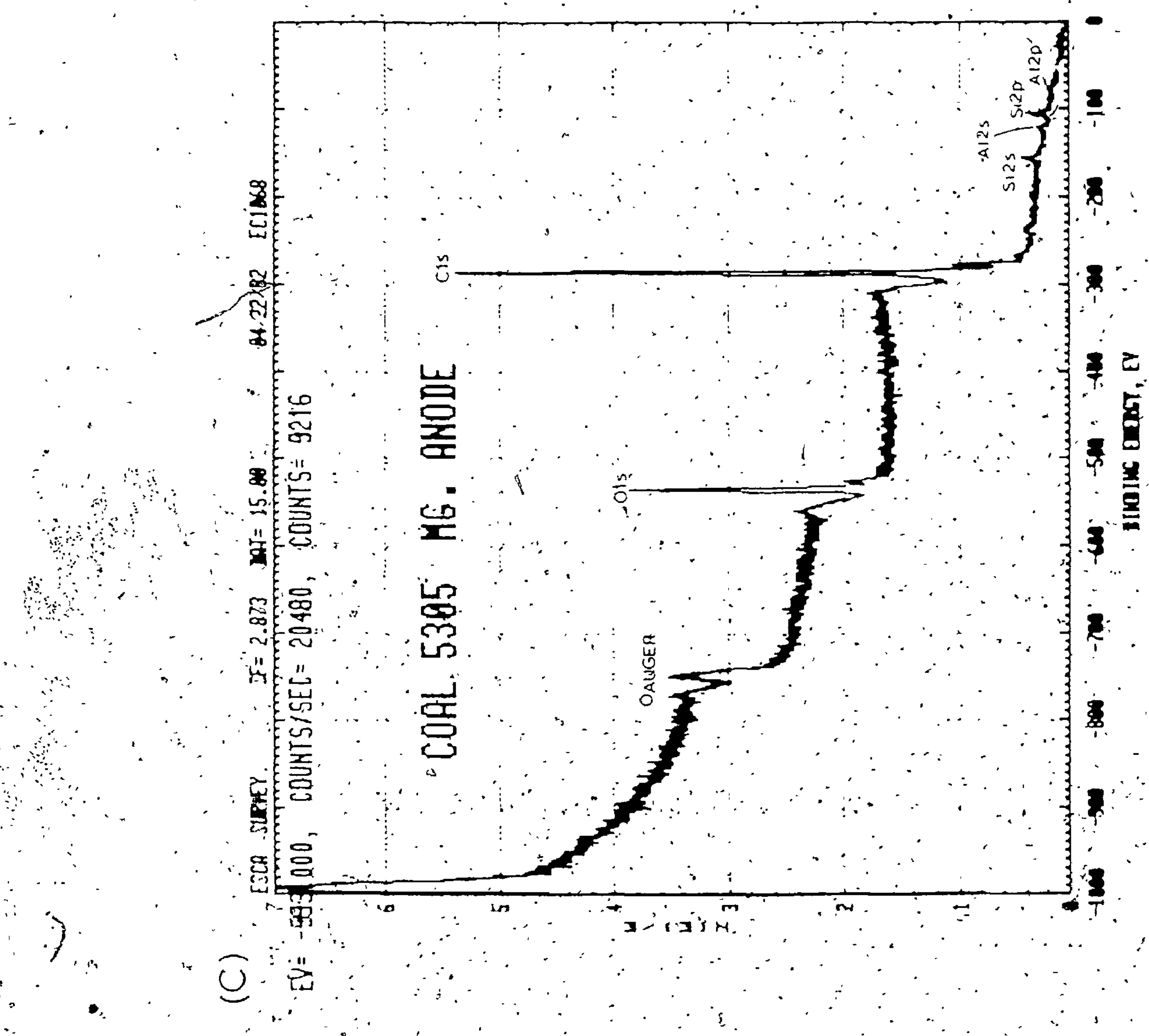
Figure 5.1 Characteristic E S C A spectra for a Moose River Basin lignite (A), lignite ash (B), Monkman coal 5305 (C), and coal ash 5356 (D) (J Brown, Canmet, Ottawa)



(B)


ESCA SURVEY SF= 1.884, .271 MAT= 29.16 08/28/81 ECSB15
EV= -999.500, COUNTS/SEC= 7736, COUNTS= 3868
LIGNITE ASH MG. ANODE
N(E)/E
7
6
5
4
3
2
1
0
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
0
BINDING ENERGY, EV
Ca_{AUGER}
O_{AUGER}
Fe2p
O1s
Ca2s
Ca2p
C1s
S2p
Si2s
Ar2s
Si2p
Al2p
O2s
X4

(C)


ESCA SURVEY
EV= -33.000, COUNTS/SEC= 20480, COUNTS= 9216
DF= 2.873
DT= 15.00
04.22.82
EC1868
COAL 5305 MG. ANODE
C1s
O1s
OAUGER
Si2s
Al2s
Si2p
Al2p
N(E)/E
0
1
2
3
4
5
6
7
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
0
BINDING ENERGY, EV

(D)

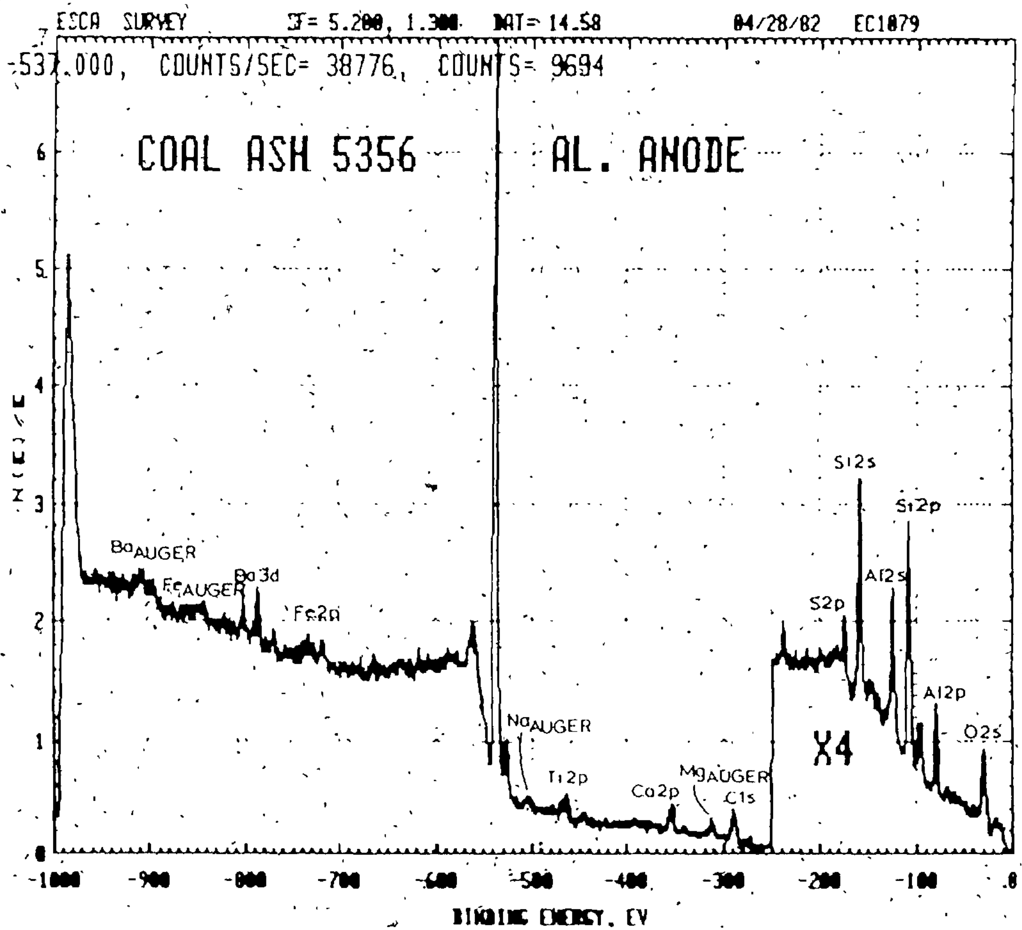

ESCA SURVEY
SF= 5.200, 1.300 DAT= 14.58
04/28/82 EC1079
EV= -537.000, COUNTS/SEC= 38776, COUNTS= 9694
COAL ASH 5356
AL. ANODE
N(E)/E
0
1
2
3
4
5
6
7
Ba AUGER
Fe AUGER
Ba 3d
Fe2p
Na AUGER
Ti2p
Ca2p
Mg AUGER
C1s
X4
S2p
Si2s
Al2s
Si2p
Al2p
O2s
-1000
-900
-800
-700
-600
-500
-400
-300
-200
-100
0
BINDING ENERGY, EV

Table 5.2 Qualitative weight percentages of Si, Al, S, C, O, Ti, Ca, Fe and Ba for some surface analyses of Monkman and Moose River Basin coals, as determined by ESCA

Element	Moose River Basin lignite logs		Monkman coals			
	1	2	5352	5305(I)	5305(II)	5305(etched)
Si	0.6	0.29	13.4	8.2	7.3	10.2
Al	-	0.4	10.2	4.0	7.7	7.2
Fe			1.4		-	-
Ca	0.3	-			-	-
Cl	-	0.3			-	-
S	0.5		0.8	1.2		-
C	73.7	75.6	39.7	71.0	66.6	58.1
O	21.1	22.8	32.8	15.6	18.3	24.3
N		-	1.7	-	-	-

Table 5.3 Summary of Coordination states of the elements analysed by ESCA in the surfaces of some Monkman and Moose River Basin coals

Element	Moose River Basin lignite logs	Monkman coal	Monkman ash
Si	SiO_2, Al-silicate	SiO_2, clay	SiO_2, silicate
Al	clay, (Al_2O_3)	clay, Al^o	Al_2O_3
Fe			Fe_3O_4, $FeSO_4$, FeOOH
Ca			$CaSO_4$, CaO, ($CaTiO_3$)
S	SO_4^{2-}, S^o/organic	SO_4^{2-}, S^o/organic	SO_4^{2-}
C	C-O, (C-C)	C-C, C-O	C-C, C-O, $\mathrm{C}\begin{array}{l}=\mathrm{O}\\ \diagdown \mathrm{O}\end{array}$
O	OH, C-O, Si-O	OH, C-O, Si-O, S-O	SO_4, Al_2O_3, SiO_2

run with United States Geological Survey (USGS) sediment and igneous rock standards. Many of the totals are greater than 100% or less than 90%, however it was considered unwise to standardise the results as the proportion of error contributed by various elements was not fully understood and thus the data may have been distorted. Duplicate standards and samples were run and the average percentage variation from the mean determined from these analyses was less than 5% for most elements and generally less than 15% for Na_2O (15%), CaO (12.7%), MgO (9%), Nb (19.9%), Pb (10.7%), Zn (6.7%), Ni (5.8%) and Ga (7.8%).

Other analyses were carried out by X-Ray Assay Labs, Barringer-Magenta Ltd. and Nuclear Activation Services Ltd.. A number of internal, NBS and USGS standards were used in these analyses. The accuracy of XRF for normal silicates is expected to be within 1% where the concentration of an oxide is greater than 1% (Norrish and Hutton, 1969). Accuracy for the other methods is assumed to be good on the basis of the standards used etc.. Duplicates were sent out with each group of samples analysed and the average percentage variation about the mean is less than 1% for all elements except Na_2O (11.5%), Rb (1.3%); Sr (2.9%), Zr (2.2%), Cu (4.2%), Ni (9.1%), Zn (1.4%), U (1.2%) and Th (3.5%). Results of the analyses are summarized in Tables 5.4 and 5.5. The samples from the Monkman area are subdivided into coal and non coal samples on the basis of LOI greater than or less than 55%. Four sample groups were assembled from the Moose River Basin samples. The lignites contain greater than 55% LOI, and the sediments were distinguished by lithology. Statistics determined for the data (using the Statistical Package for the Social Sciences, S.P.S.S.) include mean, standard deviation, standard error, variance, kurtosis and skewness. Of these only the mean is reported

Table 5.4 Summary of major and trace element data for the Moose River Basin lignites, clays, gravels and silts

	Moose River Basin lignites (17 samples)		Moose River Basin clays (40 samples)	
Element	Mean	Range	Mean	Range
%				
SiO_2	8.57	0.34-30.20	48.72	28.60-67.10
Al_2O_3	3.18	0.19-10.30	22.38	9.32-36.00
CaO	1.44	0.57- 3.41	0.96	0.19- 7.41
MgO	0.30	0.11- 0.73	0.62	0.03- 3.44
Na_2O	0.02	0.00- 0.07	0.09	0.00- 1.19
K_2O	0.06	0.01- 0.21	0.80	0.04- 2.59
Fe_2O_3	1.77	0.24- 6.18	5.04	0.24-30.20
MnO	0.01	0.00- 0.09	0.03	0.00- 0.45
TiO_2	0.17	0.01- 0.80	1.07	0.47- 3.24
P_2O_5	0.03	0.00- 0.25	0.08	0.00- 0.40
Cr_2O_3	0.02	0.00- 0.08	0.002	0.000- 0.020
LOI	83.59	55.50-97.40	20.83	8.31-54.08
S*	1.44	0.45- 2.47	0.106	0.008-0.790
ppm				
Cr	65.6	0.0 - 497.5	132.0	0.0 - 320.0
Rb	5.9	0.0 - 20.0	54.1	0.0 - 200.0
Sr	108.7	0.0 -1000.0	77.4	10.0 - 920.0
Zr	93.5	0.0 - 530.0	266.6	110.0 - 870.0
Cd	0.76	0.59- 4.77	0.50	0.50- 0.50
Co	35.9	5.0 - 197.5	17.1	5.0 - 35.0
Cu	20.0	2.0 - 44.0	55.4	18.0 - 108.0
Pb	25.1	5.0 - 155.0	34.4	5.0 - 90.0
Mo	5.9	5.0 - 15.0	5.9	5.0 - 35.0
Ni	47.4	4.2 - 190.7	48.3	15.0 - 165.0
Zn	159.2	5.2 -1311.2	51.1	7.0 - 160.0
U	1.60	0.14- 7.20	4.81	0.40- 8.43
Th	2.74	0.14- 6.50	11.49	6.80- 16.00
Th/U	1.98	0.02- 3.63	2.56	1.15- 4.84

* 9 and 26 samples of lignite and clay respectively

Table 5.4 continued

	Moose River Basin gravels (15 samples)		Moose River Basin silts (9 samples)	
Element	Mean	Range	Mean	Range
%				
SiO_2	78.62	31.90-95.00	55.00	44.10-64.50
Al_2O_3	6.53	1.40-14.70	25.20	20.90-29.20
CaO	0.30	0.04- 2.59	0.27	0.09- 0.49
MgO	0.11	0.00- 0.35	0.50	0.22- 0.98
Na_2O	0.03	0.00- 0.08	0.05	0.00- 0.10
K_2O	0.31	0.11- 0.66	0.61	0.34- 0.96
Fe_2O_3	6.68	0.15-40.60	3.11	1.10- 7.18
MnO	0.05	0.00- 0.48	0.03	0.00- 0.06
TiO_2	0.41	0.03- 1.95	1.15	0.89- 1.38
P_2O_5	0.03	0.01- 0.06	0.05	0.04- 0.06
Cr_2O_3	0.00	0.00- 0.00	0.00	0.00- 0.00
LOI	6.22	1.23-21.20	14.10	9.77-23.50
S*	0.26	0.008-1.60	0.093	0.028-0.280
ppm				
Cr	220.0	50.0 -1720.0	187.3	140.0 - 230.0
Rb	9.0	0.0 - 20.0	35.5	10.0 - 60.0
Sr	11.5	0.0 - 40.0	27.3	10.0 - 50.0
Zr	240.0	0.0 -1270.0	478.2	220.0 - 860.0
Cd	0.50	0.50- 0.50	0.50	0.50- 0.50
Co	63.0	5.0 - 140.0	33.6	5.0 - 65.0
Cu	25.5	4.0 - 82.0	56.1	30.0 - 83.0
Pb	14.0	5.0 - 40.0	29.5	5.0 - 60.0
Mo	5.7	5.0 - 10.0	5.0	5.0 - 5.0
Ni	34.7	5.0 - 200.0	70.0	30.0 - 150.0
Zn	22.3	5.0 - 55.0	242.2	26.0 -1480.0
U	1.46	0.15- 6.51	4.76	3.46- 7.23
Th	6.85	1.20- 35.60	9.11	6.20- 11.00
Th/U	5.42	1.78- 9.78	1.95	1.52- 2.40

* 8 and 9 samples of gravel/ sand and silt respectively

Table 5.5 **Summary of major and trace element data for the Monkman sediments and coal.**

Element	Monkman coal (43 samples) Mean	Monkman coal (43 samples) Range	Monkman sediments (84 samples) Mean	Monkman sediments (84 samples) Range
%				
SiO_2	17.39	9.06-45.83	57.84	30.02-90.43
Al_2O_3	4.96	0.77-13.89	17.84	5.96-27.78
CaO	2.77	0.12-28.51	4.93	0.00-23.90
MgO	0.08	0.00- 1.03	1.01	0.00- 4.86
Na_2O	0.32	0.00- 0.61	0.33	0.00- 0.71
K_2O	0.41	0.00- 2.43	2.50	0.00- 4.76
Fe_2O_3	1.42	0.00-11.02	2.03	0.15- 3.58
MnO	0.001	0.00- 0.02	0.15	0.00- 0.14
TiO_2	0.50	0.01- 1.23	0.77	0.23- 1.04
P_2O_5	0.14	0.03- 0.89	0.13	0.04- 0.51
LOI	82.79	57.30-96.98	26.71	6.10-54.00
S	0.94	0.30- 3.38	0.65	0.04- 3.58
ppm				
Nb	40.0	10.1 - 128.8	32.8	0.0 - 78.3
Zr	60.9	23.4 - 100.5	104.8	30.9 - 450.7
Y	7.3	3.2 - 17.0	7.2	0.1 - 12.4
Sr	151.4	19.8 - 701.3	103.0	25.2 - 350.3
Rb	33.1	10.5 - 83.7	70.0	2.2 - 124.7
Pb	15.4	8.0 - 22.4	10.1	1.8 - 62.8
Zn	30.6	16.6 - 110.0	83.4	9.7 - 383.3
Cu	12.9	9.8 - 16.7	13.9	8.0 - 24.7
Ni	25.0	13.7 - 94.0	28.3	5.9 - 86.4
Co	9.1	1.9 - 20.5	10.0	3.0 - 32.2
Cr	29.6	10.3 - 82.3	77.2	21.9 - 139.8
Ba	1092	262 - 3105	822	174 - 2334
V	57.6	15.1 - 399.4	122.9	30.0 - 240.8
Ga	14.5	6.3 - 57.8	10.6	1.9 - 76.6
U*	2.11	0.34- 5.96	4.64	1.63- 11.30
Th*	3.0	0.7 - 7.3	6.8	0.3 - 12.0
Th/U	1.50	0.43- 2.08	9.31	0.08- 164.0

* 14 coal and 21 sediment samples analysed for these elements

here. Pearson correlation coefficients and significance values were run using SPSS PEARSON CORR (Nie et al, 1975). Values of r (Pearson's product-moment coefficient of linear correlation) greater than 0.6 (where values of r close to 1.00 indicate a nearly perfect fit to a linear regression line and negative values of r indicate inverse correlation) with a level of significance of 0.001 are considered to be significant for small sample sets (smallest sample set in these analyses is 15), however values between 0.5 and 0.6 are also included in the tables to document less well developed trends. Correlation matrices for the sample groups are shown in Tables 5.6 to 5.11. Platinum group elements, Au, As, Mo and W were analysed only in selected samples and are therefore not included in the general correlation matrices.

5.2 Major Elements

Major elements including SiO_2, Al_2O_3, K_2O, TiO_2, Fe_2O_3, MnO, MgO, CaO, P_2O_5, Na_2O and S were analysed in all the samples. Although this study deals mainly with the behaviour and distribution of the trace elements, a brief survey of the distribution and siting of the major elements will also be presented. Major element contents and correlation coefficients are listed in Tables 5.4, 5.5 and 5.6 to 5.11 respectively. Summary tables of the minerals present identified by XRD and SEM can be found in Tables 4.1, 4.3 and 4.4.

5.2.1 Moose River Basin

Four main groups of major elements were identified by statistical methods in most of the sample sets. CaO and MgO occur together and are found in carbonate minerals such as calcite and siderite, and gypsum. Fe_2O_3, MnO and S are located mainly in pyrite or marcasite, Fe_2O_3 may

Table 5.6 Pearson correlation matrix for major and trace elements analysed in the Moose River Basin lignites

	SiO_2	Al_2O_3	CaO	MgO	K_2O	Fe_2O_3	MnO	TiO_2	P_2O_5	LOI	Cr	Rb	Sr	Zr	U	Th	Co	Pb	Mo
SiO_2																			
Al_2O_3	.79																		
CaO																			
MgO			.95																
Na_2O																			
K_2O																			
Fe_2O_3																			
MnO						.83													
TiO_2	.83	.78	.53	.51															
P_2O_5																			
LOI	-.75	-.68																	
Cr						.54													
Rb		.66						.72											
Sr								.78				.57							
Zr						.68	.75				.57								
U																			
Th	.60	.75						.69											
Th/U					.54										-.60				
Cd																			
Co						.51					.94			-.53					
Cu	.52	.79						.60				.61				.85			
Pb																			
Mo																			
Ni											.65						.57		.55
Zn																			
S		-.64						-.57	-.75	.50			-.50		-.65	-.69		.54	

Table 5.7 Pearson correlation matrix for major and trace elements analysed in the Moose River Basin clays

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	P_2O_5	LOI	Cr	Rb	U	Mo
SiO_2														
Al_2O_3														
CaO		-.58												
MgO		-.56	.84											
Na_2O			.94	.83										
K_2O				.82	.50									
Fe_2O_3														
MnO							.83							
TiO_2														
P_2O_5														
LOI	-.67													
Cr		.57								-.67				
Rb				.62		.89								
Sr									.84					
Zr	.71							.78						
U				-.53		-.58								
Th														
Th/U				.53		.64						.66	-.63	
Cd														
Co														
Cu		.56											.66	
Pb														
Mo														
Ni													.53	.71
Zn														
S	-.67							-.51		.84	-.56			

Table 5.8 Pearson correlation matrix for major and trace elements analysed in the Moose River Basin gravels

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	MnO	TiO_2	P_2O_5	LOI	Cr	Zr	U	Th/U	Co	Cu	Pb	Ni
SiO_2																			
Al_2O_3																			
CaO																			
MgO		.75																	
Na_2O																			
K_2O				.54															
Fe_2O_3	-.96																		
MnO	-.73						.74												
TiO_2		.60																	
P_2O_5		.59	.77																
LOI	-.99						.98	.67											
Cr									.89										
Rb				.53	.50	.77	.53				-.52								
Sr			.79																
Zr		.54							.98			.91							
U		.81							.76				.73						
Th									.96			.96	.98	.64					
Th/U		-.51																	
Cd															.71				
Co				-.55	-.65										-.52				
Cu		.77							.50					.86		-.50	.60		
Pb		.51		.54					.50				.54	.64			.61		
Mo														.55					
Ni	-.79						.85				.86								
Zn		.81		.65						.74				.51	-.61		.62		
S							.93											.63	.73

Table 5.9 Pearson correlation matrix for major and trace elements analysed in the Moose River Basin silts

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	MnO	TiO_2	P_2O_5	LOI	Cr	Rb	U	Th	Th/U	Co	Ni
SiO_2																		
Al_2O_3	-.68																	
CaO	-.50																	
MgO																		
Na_2O																		
K_2O				.90														
Fe_2O_3				.57		.71												
MnO				.70		.85	.96											
TiO_2				.56														
P_2O_5	-.57					.50	.68	.65										
LOI	-.80		.82															
Cr									.72									
Rb				.60	.65	.86	.54	.69										
Sr			.73							.58		.70						
Zr				.80		.60			.81			.53						
U		.73																
Th				.59										.78				
Th/U		-.69												-.67				
Cd																		
Co																		
Cu	-.52	.64		-.58							.63							
Pb	-.86	.67			.60						.67			.58	.63			
Mo																		
Ni																.60	.80	
Zn												.58						
S				-.65		-.76		-.50	-.51				-.67	.70	.79			-.58

Table 5.10 Pearson correlation matrix for major and trace elements analysed in the Monkman sediments

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	P_2O_5	Nb	Y	Sr	Rb	Pb	Cu	Ni	Cr
SiO_2																	
Al_2O_3																	
CaO																	
MgO			.80														
Na_2O																	
K_2O		.69			-.59												
Fe_2O_3					-.54												
MnO							.86										
TiO_2		.72	-.57	-.52		.54											
P_2O_5																	
LOI	-.89			-.58													
Nb																	
Zr																	
Y		.54				.62				.87							
Sr									.59								
Rb		.72				.84		.66		.55	.76						
Pb																	
Cu		.60				.65					.56						
Ni														.62			
Co			.55	.61												.71	
Cr		.71				.76		.66			.60		.76		.65		
Ba												.67					
V		.59						.63					.66				.77
Ga																	
U																	
S																	

Table 5.11 Pearson correlation matrix for major and trace elements analysed in the Monkman coals

	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Fe_2O_3	MnO	TiO_2	P_2O_5	LOI	Nb	Zr	Y	Sr	Rb	Pb	Zn	Cu	Ni	Cr	V
SiO_2																						
Al_2O_3	.89																					
CaO																						
MgO			.71																			
Na_2O																						
K_2O	.85	.83																				
Fe_2O_3																						
MnO			.75	.74																		
TiO_2	.77	.76	-.57	-.52		.51																
P_2O_5																						
LOI	-.90	-.82				-.82			-.69													
Nb			.69	.65				.63														
Zr									.57			.69										
Y			.55	.64				.60				.96	.70									
Sr			.80					.54				.53										
Rb	.53	.53		.57		.69		.54			-.50	.71	.53	.84								
Pb												.60		.59								
Zn	.58	.63				.78					-.52					.73						
Cu												.83	.56	.88		.71	.70					
Ni		.54				.66										.57		.87				
Co								.51									.53		.54	.60		
Cr	.69	.70				.77			.54		-.68							.66		.68		
Ba			.52							.52					.78							
V																					.74	
Ga																						
U	.72	.77				.65			.74		-.67										.78	.64
S					-.57		.64															

also be present in carbonates such as ankerite and siderite as well as in clay minerals. Al_2O_3, K_2O, MgO and TiO_2 occur in the clay minerals and detrital muscovite. Where Fe_2O_3, MnO and TiO_2 are present with this group feldspars or muscovite may be the host mineral. SiO_2 is not strongly correlated with this group because it's concentration is distributed between quartz and the aluminosilicates. TiO_2 is occasionally associated with the detrital heavy mineral fraction as rutile and P is correlated with Sr in the clays indicating the presence of phosphates.

As would be expected SiO_2 is most common in the gravels and is present predominantly as quartz. Fe_2O_3 and MnO are similarly most abundant in the gravels indicating greatest pyrite concentrations in these samples. The clay samples also contain significant pyrite while sulfides are not so common in the lignites. Highest S contents are however found in the lignites indicating the presence of S in another form, possibly associated with the organic material. As mentioned previously ESCA confirms the presence of some organically bound S. SEM-EDX analysis of the coaly substance shows S to be homogenously distributed indicating an association on the molecular level. SEM analyses have also shown some TiO_2, CaO, SiO_2 and Fe_2O_3 intimately associated with the organic matter (this may represent inherent plant inorganic matter, see Table 4.7).

Calcite is most abundant in the lignites with lesser concentrations in the clays and least in the gravels. The clays are most enriched in Al_2O_3, MgO, K_2O, TiO_2, Na_2O and P_2O_5 indicating highest concentrations of clay minerals, muscovite, feldspar and phosphates in these samples. Quantities are less in the gravels and least in the lignites.

5.2.2 Monkman

Similar major element groups are present in the Monkman sediments and coals. SiO_2 is again mostly present in quartz. SiO_2, Al_2O_3, TiO_2 and K_2O are found in clay minerals, mica, and feldspar. Where only clay minerals are present Al_2O_3 and K_2O are correlated, however if mica or feldspar occur MgO, CaO, K_2O and TiO_2 are also correlated with this group. The carbonate group in the Monkman samples consists mostly of ankerite, thus as expected MgO, CaO and occasionally MnO are correlated. MnO occurs in solid solution with calcite (Deer, Howie and Zussman, 1976). Fe_2O_3 is also present in pyrite so correlations with the carbonate group are not high.

Phosphate and the carbonate minerals are most abundant in the coals while the other mineral phases are more concentrated in the sediments. Na_2O concentrations are equal in both sample groups.

5.3 Trace Elements

In the following section results for individual trace elements will be examined. Comparisons will be made with other studies and where possible siting of the elements in the coal and the sediments will be proposed. This is done on the basis of correlations between elements, and relative concentrations in different sediment groups. The results are confirmed where possible with SEM-EDX analyses. Methods used by other authors to determine siting of the elements in coal include float sink separations and analysis of different specific gravity fractions (Horton and Aubrey, 1950; Otte, 1953; Zubovic <u>et al</u>, 1960; 1961; Bogdanov, 1965; Gluskoter <u>et al</u>, 1977 and Kuhn <u>et al</u>, 1978), determination of the variation of trace element concentration with ash content (Nicholls, 1968 and Szilagyi, 1971), leaching characteristics (Filby *et al*, 1977; Kuhn *et al*, 1978 and Miller and Given, 1978), correlation coefficients (Gluskoter *et al*, 1977; Kuhn *et al*, 1978 and Cecil *et al*, 1979) and SEM-EDX (Finkelman, 1980). There are limitations and disadvantages to many of these methods. For example, the float sink method, which is the most commonly used, assumes perfect separation of the organic and inorganic components of the coal. In practise, fine grained mineral matter (which behaves differently to the bulk of the coal) is often entrained in the light floating organic material. This method also assumes negligible variations in the relationship between total mineral matter and ash contents throughout the density fractions. The second method assumes that "the concentration of every element is uniform in each increment of ash content" (Finkelman, 1980). Considering the extreme mobility of some elements in coal as evidenced by the large numbers of authigenic minerals present in most coals, this assumption must be carefully examined before use. The leaching method of determination of trace element associations in coal involves the assumption that solvents leach throughout the coal. This has been disproved by Greer (1977).

Finkelman (1980) states that elements which exhibit high correlation coefficients in coal do not necessarily have similar modes of occurrence, but that they are derived from similar sources. However different relative mobilities of the elements within the coal deposit must be taken into account. The method is best applied to a single deposit where samples of all the sediment types are analysed in conjunction with the coal, thus providing a certain amount of control.

Many of the results derived from the use of correlation coefficients in this study have been confirmed by SEM-EDX analyses.

Table 5.12 lists the maximum trace element concentrations found in coal, as reported in the literature. This is useful for comparative purposes.

Phosphorous

The mean P content of United States coals as determined by Abernethy and Gibson (1963) is 185 ppm with a range of 20-1430 ppm. Average P values for some coals and peats are listed in Wedepohl (1978, Table 15-L-10) and range from less than 0.01% in a mineral coal from Central England to 0.57% in fusite (microlithotype with greater than 95% fusinite) from Central England. Mean P_2O_5 concentrations for the Monkman and Moose River Basin coals are 0.14% and 0.03% respectively. The Monkman sediments average 0.13% P_2O_5 while the Moose River Basin clays, silts and gravels contain averages of 0.08, 0.05 and 0.03% P_2O_5 respectively.

Phosphorus has been documented as occurring in several forms in coal, however the best defined modes of occurrence are in mineral phases. This may be due in part to the bias in study techniques, for example SEM detects minerals in coal more readily than dispersed elements. Brown and Swaine (1964) found P to occur mainly in apatite minerals in Australian coals and found no evidence of organic affinity. Rao <u>et al</u> (1951) concluded that most of the P in the coals they examined was in inorganic form, probably as the mineral fluorapatite. In the low ash fractions, P, which was present in higher quantities than warranted by the ash contents is postulated to be organically bound. Several P-bearing minerals were found by Finkelman (1980) in his study of a

Table 5.12 **Maximum trace element contents in coal ash compared with average crustal abundances (ppm)**

Element	Maximum content in coal ash	Average in earth's crust
Li	960	65
Be	2,800	6
B	8,600	10
Sc	400	5
Ti	20,000	4,400
V	11,000	150
Cr	1,200	200
Mn	22,000	1,000
Co	2,000	40
Ni	16,000	100
Cu	4,000	70
Zn	10,000	40
Ga	6,000	19
Ge	90,000	7
As	8,000	5
Rb	33	280
Y	800	28
Zr	5,000	220
Nb	2	20
Mo	2,000	2.3
Ag	5-10	0.02
Cd	80	0.18
In	2	0.1
Sn	6,000	40
Sb	3,000	1
I	950	3
Cs	4	3.2
La	31	18
Ta	0.1	2.1
Pt	0.7	0.005
Au	0.2-0.5	0.001
Hg	50	0.5
Tl	25	1.3
Pb	1,000	16
Bi	200	0.2
U	600	4

Source Fairbridge 1972
(Note: high values due to secondary enrichment were not excluded.)

variety of different coals. The minerals most commonly identified include rare earth phosphates and apatites, however Finkelman states that when the accessory minerals were quantified only half the 100 ppm of P present in a Waynesburg coal was accounted for. Trudinger and Swaine (1979) found P in soils to replace Si in micas and clay minerals giving rise to crystalline hydrous Al phosphates of Na, NH_4 and K. Phosphorous and Ca minerals also occur (Murray et al; 1983 noted apatite formation on calcite) as well as phosphates of Fe and Al with colloidal characteristics.

Several authors (Rao et al., 1951; Bogdanov, 1965; Kuhn et al, 1978 and Wedepohl, 1978) found P to have organic affinities in coals. This is not surprising since P is a biologically essential element. Intermediate affinities are recorded by Francis (1961) and Gluskoter et al (1977).

P_2O_5 is strongly correlated with Sr in the Moose River Basin clays and with CaO and Zn and to a lesser extent with Al_2O_3 in the Moose River Basin gravels. P is weakly correlated with Ba and Sr in the Monkman coals and sediments respectively and negatively with S in the Moose River Basin coals. In a Monkman coal sample P was determined in a carbonate grain associated with sphalerite. This may indicate the presence of apatite in association with calcite (Murray et al, 1983). The correlation of P with CaO and Zn in the Moose River Basin gravels and clays may indicate a similar association in these sediments. The weak correlation with Al_2O_3 may also indicate some association with the clay minerals. The correlation with Ba and Sr in the Monkman samples may indicate substitution of these elements in apatite or substitution of Ba, Sr and P (for the Ca ion) in calcite. No separate phosphate minerals were observed in any of the samples. The negative correlation with S in the Moose River Basin lignites may indicate that P is inorganically associated because S is predominantly organically held in these samples. The low correlation coefficients in most of these sample groups indicate that P is present in several forms and is moreover likely to be present in significant quantities associated with the organic material.

In the Monkman sections P is concentrated in the tops and particularly the bottoms of the coal seams and occasionally in the sediments above and below the seams. The latter may be caused by an epigenetic effect.

Chlorine

Average Cl content in United States coal is 580 ppm (Given and Yarzab, 1978). Up to 4% Cl has been reported from the Ferron coal (Minkin cited in Finkelman, 1980). Cl was analysed in several Moose River Basin samples by Spark Source Mass Spectrometry (SSMS) (Murray, 1984). Values are generally less than 50 ppm in the sediments while concentrations of up to 1500 ppm were determined in some lignite ashes. The range of values in the lignite ashes is 17 to 1500 ppm. Cl was not analysed in the Monkman samples however a mineral grain containing Cl and trace Na was observed by SEM-EDX in a coal sample.

Much of the Cl in coals is organically bound (Bethell, 1962; Gluskoter and Ruch, 1971; Finkelman, 1980 and Minkin in Finkelman, 1980). The absence of Na associated with the Cl, the stoichiometry of the Cl extracted from the coals and the strong negative association of Cl with the ash content of coal have been cited to support this conclusion. Some grains of halite, sylvite and bloedite have been identified in coal by Finkelman (1980) and Lee et al (1978), however the quantities are not great enough to accomodate all the Cl present. Bethell (1962) proposed that Cl may be ionically bonded to the N atoms in coal but that if Na and K are available, halides of local significance may occur. Cl rich coals tend to be marine influenced therefore given the availability of Na and K under these conditions halides are the dominant Cl hosts in these coals, for example the Salzkohle facies in the Brown coal deposits of Germany (Bouska, 1981).

The occurrence of maximum Cl values in the lignites of the Moose River Basin samples and particularly in the low ash lignites supports the conclusion that Cl is organically bound in these materials. Cl may also be present in other forms particularly in the sediments, for example as inorganic chlorides, however the relative importance of these forms is not known. Cl was not analysed in the Monkman samples, however in one sample the presence of a Cl-rich mineral grain was determined by SEM-EDX, indicating that at least some Cl occurs in this form.

Titanium

Average Ti concentrations in the samples are greatest in the clays and silts of the Moose River Basin (1.07 and 1.15% TiO_2 respectively). Lowest values occur in the Moose River Basin lignites (0.17%). The average for Moose River Basin gravels is 0.41%. In the Monkman samples the coals contain on average 0.50% and the sediments 0.77% TiO_2. This compares with 180 and 400 ppm Ti respectively in brown and hard coals worldwide (Yudovich et al, 1972) and 0.08% in United States coals (Swanson et al, 1976).

Various reports on the occurrence of Ti in the literature yield very complex solutions however organic tendencies have been noted by the following, (Horton and Aubrey, 1950; Otte, 1953; Zubovic et al, 1961;

Brown and Swaine, 1964; Miller and Given, 1978 and Minkin, Chao and Thompson, 1979). Wedepohl (1978) suggests that Ti concentration in coal can be explained by biological enrichment of living plants.

Ti is most strongly correlated with Zr and to some extent SiO_2, Cr, U and Th in the Moose River Basin gravels, clays and silts. This indicates the association of Ti with the detrital heavy minerals. The presence of rutile in quartz and in the heavy mineral fraction of the sediments was substantiated by examination of thin sections. Highest average values in these samples indicate that association with the heavy minerals is the most important mode of occurrence.

Ti is strongly correlated with Al_2O_3 and other clay mineral components in the Monkman sediments and coals, the Moose River Basin lignites and to a lesser extent in the Moose River Basin gravels, indicating an association with the clay minerals in these samples. Ti partly replaces Al^{3+}, Fe^{3+}, Nb^{5+} and Mn^{3+} in many minerals such as feldspars and clay minerals and may therefore have been deposited in the basin in a detrital mineral phase. Weathering of the feldspar would have caused the dissolution of Ti followed by either transformation into aqueous Ti oxide and then anatase or rutile (Wedepohl, 1980) or incorporation into newly formed clay minerals, such as kaolinite (Weiss and Range, 1966 and Dolcater, 1970) or organic matter (Correns, 1971).

Ti is weakly correlated with CaO and MgO in the Moose River Basin lignites and silts and in the Monkman coals. Some association with the carbonate mineral phase must therefore exist. Ti in this form may represent a later stage of introduction into the system.

Most of the Ti in the Monkman and Moose River Basin samples is controlled by the detrital heavy mineral contents, clay minerals and to some extent by the carbonates, however EDX analysis of the organic material in the coals yields peaks for several elements including Ti. This may indicate that some of the Ti is also organically bound, or occurs in very small mineral grains associated with the organics. Ti concentrations in the sections are lithologically dependant and as such are of detrital or of syngenetic origin.

Vanadium

Vanadium is a commonly occurring trace element in organic-rich sediments. However the concentrations are highly variable as indicated by the following examples; 0.15-2 ppm in all living organisms, up to 0.65% in the dried matter of certain land plants, from 0.03 ppm in coal up to 0.31-4.92% in the ashes of some coals (Valkovic, 1983), around 50-75% V_2O_5 in asphalts, bitumens and some crude oils (Goldschmidt, 1954) and 38.22% V_2O_5 in 0.63% ash from an Argentinian asphaltite (Valkovic, 1983).

The mean V concentration in United States coals is 20 ppm (Swanson et al, 1976). Average V values in the Monkman coals and sediments are 57.6 and 122.9 ppm respectively. The Moose River basin samples were not analysed for V.

Vanadium is commonly reported occurring in organic combination in coal (Horton and Aubrey, 1950; Otte, 1953; Almassey and Szalay, 1956; Zubovic, 1960; 1966; Gluskoter et al, 1977; Swaine, 1977 and Gindy et al, 1978). Zubovic (1966) suggests the presence of V^{4+} chelates or V^{3+} Nitrogen porphyrins incorporating V in coals. V porphyrins are common in oil shales as reported by Riley and Saxby (1982). They also indicate that these small organic structures are quite readily attacked on weathering with subsequent release of the V as oxides or vanadates. The V may then be adsorbed onto the clay minerals. Leutwein and Rosler (1956), Bogdanov (1965), Szilagyi (1971) and Miller and Given (1978) report V as occurring both in organic and inorganic combination in coals while Nazarenko (1937), Nicholls and Loring (1962), Nicholls (1968) and Miller (1974) have found V to be inorganically associated. Krauskopf (1956) and Nicholls (1968) found sorption on clay minerals to be the dominant mechanism for V accumulation in coal and this has been substantiated by Finkelman (1980) with microprobe analysis of an Upper Freeport coal sample. V minerals and V-bearing minerals found in coal are fully described in Finkelman (1980). Maylotte _et al._ (1981) found the V in a V-rich coal to occur mostly as V_2O_3 or roscoelite in the heavy fraction and in the light fraction predominantly as V^{4+} in oxygen coordination with one short bond.

Vanadium which is most abundant in the Monkmah shales exhibits a high positive correlation coefficient with Al_2O_3 indicating that V is associated with the clay minerals. V in the coals is related to ash contents, increasing proportionately with greater amounts of detrital matter and clay partings. Low V in iron rich and Al_2O_3 poor samples precludes the occurrence of V in pyrite as suggested by Krauskopf (1956). Channel samples through the coal seams indicate marginal enrichments i.e. in the coaly clays above and below the seam and also in the claystone partings within the coal again substantiating the association of V with the clay mineral fraction. This also may indicate epigenetic accumulation of V from circulating ground waters.

Chromium

The average Cr content of United States coals is 15 ppm (Swanson et al, 1976). Average Cr contents of the Monkman sediments and coals are 77.2 and 29.6 ppm respectively. Values are higher in the Moose River Basin materials with the maximum average concentration of 220.0 ppm occurring in the gravels, 187.3 ppm in the silts, 132.0 ppm in the clays and the lowest average value 65.6 ppm occurring in the coals. Ranges of values are high in each group.

Cr has been found occurring in many different forms in coal. Otte (1953), Hawley (1955), Leutwein and Rosler (1956) and Miller and Given (1978) found Cr associated predominantly with the organic substance. Gluskoter et al (1977) and Horton and Aubrey (1950) cite a wide range of affinities from organic to inorganic, while Zubovic et al (1961) reported an intermediate affinity. Bogdanov (1965), Schultz et al (1975), Filby et al (1977), and Ford (1977) found Cr to be inorganically bound. Szilagy (1971) and Finkelman (1980) suggest that epigenetically precipitated chromites (irregularly distributed and finely disseminated) account for the distribution of Cr in coals and explain the wide range of float sink data.

Cr correlates with Al_2O_3, K_2O and other clay mineral-forming elements in the Monkman sediments and coals. This indicates that the Cr is bound by clay minerals, probably by illite which is the common K_2O-bearing sheet silicate in these materials. Frolich (1960) supports this conclusion suggesting that Cr is mostly concentrated in the micas and illite in sediments. Nicholls and Loring (1962) found much of the Cr in the sediments and coals of the Bersham section to be strictly detrital.

while the remaining Cr was adsorbed onto clay minerals from the overlying waters.

The elements associated with Cr in the Moose River Basin gravels are TiO_2, Zr and Th, which are present in these sediments in rutile/ilmenite and zircons. Cr is therefore associated with the heavy minerals perhaps as detrital chromite. Cr correlates with the ash content of the Moose River Basin clays and to a lesser extent with Al_2O_3 and negatively with S. This indicates at least partial incorporation of Cr in the clay minerals in these samples. Cr contents in most of the Moose River Basin coal samples are below detection limits (10ppm) however high values are found in the remaining samples. Table 5.13 shows the results of selected analyses of five unashed Moose River Basin lignite and clay samples. Cr is variable in the bulk lignite sample perhaps indicating that Cr occurs in locally concentrated phases such as in detrital zircons. A high detrital input into the lignites and coals would then account for the high concentrations of elements such as Cr and Ti in these materials relative to United States coals.

Cr is relatively enriched in the shales above and often below the Monkman coal seams. Nicholls (1968) attributes the marginal enrichment of Cr in coal seams to post-burial sorption onto finely divided clay minerals intimately mixed with the organic matter. Syngenetic accumulation in detritals as well as post-burial accumulation of Cr from circulating ground waters onto clay minerals is suggested for the successions studied here.

Cobalt

Mean Co values for the Monkman materials are 9.1 ppm and 10.0 ppm in the coals and sediments respectively. Contents are higher in the

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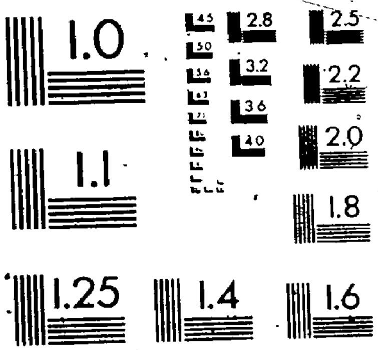


Table 5.13 Au, Mo, Cr, Co, As and W contents of some unashed Moose River Basin lignites and clays.

Sample Number	Au ppb	Mo ppm	Cr ppm	Co ppm	As ppm	W ppm	Sample Description
P5	1	9.0	66	0.5	6	3	wood with pyrite
P6	53	9.5	76	3.0	3	1	Onakawana bulk sample
P7	80	9.0	44	3.0	3	1	Onakawana bulk sample
P8	6	1.0	67	7.0	5	2	OEC green clay (103.5-106.5m)
P9	7	6.0	160	2.0	1	5	OEC black clay (45.5 m)

Moose River Basin succession with a maximum average of 63 ppm in the gravels. Mean contents decrease from 35.9 ppm in the coals and 33.6 ppm in the silts to 20.3 ppm in the clays. The mean value for United States coals is 7 ppm (Swanson et al, 1976) while worldwide averages vary from 4 ppm in hard coals to 3 ppm in brown coals (Yudovich et al, 1972).

Co and Ni are alike in many of their physical and chemical properties (Wedepohl 1978). Both are siderophilic and the distribution of Co in sediments and sedimentary rocks mimics that of Fe.

Co correlates with Ni and MgO in the Monkman sediments and with Ni and to a lesser extent MnO, Pb and Cu in the Monkman coals. In the Moose River Basin samples Co is not strongly correlated with any element except with Ni in the silts, however weak correlations are present with MnO and Fe_2O_3 in Moose River Basin clays and coals respectively. This trend also occurs in the five unashed samples of clay and lignite from the Moose River basin which were analysed with lower detection limits (Table 5.13). Maximum Co concentrations occur in the samples with highest Fe contents. Co was not found to correlate with S, however its association with Fe_2O_3 and other sulphide-forming elements suggests that Co may be present in sulphide phases in the Monkman coals, Moose River Basin coals and possibly in part in the Moose River Basin clays. An example of this occurs in AC-10-82 where Ni and Co are both enriched in pyrite nodules from the top of a lignite seam. The Moose River Basin gravels, in which Co is most concentrated, show strong correlations between Co and Th/U ratios. This may indicate immobility and an association with the detrital heavy mineral phase as an important mode of occurrence of Co in these samples.

It is evident from the low correlation coefficients that Co occurs in several forms in many of the samples. These may include adsorption onto the organics or association with the clay minerals. Co is commonly cited in the literature as occurring in partial organic combination in both clays and coals, for example Nicholls and Loring (1962) found that montmorillonite, illite and freshly precipitated iron hydroxide adsorbed 90-96% of the Co present in distilled water.

Co in the Monkman sections appears to be enriched towards the bottoms of the coal seams and occasionally in the sediments above and below the coal seams. In the Moose River Basin samples Co is enriched in coaly clays above the lignite seams and in wood samples isolated in the sediments (e.g. AC-03-82 and AC-26-82). This indicates a post depositional mode of accumulation from circulating ground waters.

Nickel

Average Ni contents in hard and brown coals worldwide are 69 and 28 ppm respectively (Yudovich et al, 1972). Swanson et al (1976) cite 15 ppm as the mean value for United States coals. Nickel values in the Monkman coals and sediments (25.0 and 28.3 ppm respectively) are lower than values in the Moose River Basin materials. This may reflect the generally high Ni contents in Archaean Greenstones from which Ni in the Moose River Basin materials may be derived. Moose River Basin silts, 70.0 ppm, have highest average concentrations, with values decreasing from 56.3 ppm in the clays and 47.4 ppm in the coals to 34.7 ppm in the gravels.

Ni occurs as a trace element in all organisms, with contents of 1.4, 1.5 and 2.1-5.3 mg/kg dried matter in woody angiosperms, ferns and woody gymnosperms respectively (Bowen, 1979). The Moose River Basin coals contain more Ni than would be expected if the Ni were derived from plants assuming a concentration factor of 3-10 from plants to coals. In the literature Ni is cited as having inorganic; (Goldschmidt (1954) and Finkelman (1980) found Ni associated with pyrite, and millerite and linnaeite respectively in the mineral substance of coal), intermediate and organic affinities in coal. Zubovic (1966) found organically bound Ni in coal to be held as chelated complexes and Filby *et al* (1977) identified Ni porphyrins in coals. Reynolds (1948) and Swaine (1980) cite the propensity for Ni to form organometallic complexes as a reason for its enrichment in carbonaceous sediments. Nicholls (1968) states that Ni in coals with a substantially greater Ni concentration than 3 ppm is inorganically associated. He emphasises the importance of sulfides as Ni is often coprecipitated with Fe and Mn oxides and sulfides (Wedepohl, 1978). In low-sulfide coals Ni can be sorbed by clay minerals or can be coprecipitated with Fe-bearing carbonates (Nicholls, 1968).

Ni in the Monkman sediments correlates with Co and Pb and in the Monkman coals with Co, K_2O, Zn, Cr and to a lesser extent with Al_2O_3 and Rb. Ni is probably associated with galena and other sulfides in the sediments while an association with the clay minerals is likely in the coals. The negative slope of plots of Ni/Al_2O_3 ratios versus % Al_2O_3 indicate that Ni is not entirely associated with the clay minerals in these samples.

Ni in the Moose River Basin gravels correlates with Fe_2O_3, S and LOI indicating an association with pyrite and the organic material. Correlations with Co occur in the Moose River Basin silts and to a lesser extent in the Moose River Basin coals. In these samples both Co and Ni may be organically associated and/or occur adsorbed onto clay minerals. Correlations with Ni in the Moose River Basin clays do not occur. Millerite was detected by XRD in a pyrite-rich zone in the Adam Creek lignite outcrop. Ni is also observed to increase in gravels with a pyrite matrix. It seems likely given the correlation coefficients of Ni in the gravels that it is associated primarily with pyrite in these samples. In the pyrite rich coal samples Ni is incorporated in or coprecipitates with pyrite but in the coals with lower Ni contents, Ni is probably in organic combination or associated with the clay minerals as stated previously.

Ni is often concentrated in the sediments above and below coal seams in the Monkman sections, however concentrations also appear to be lithologically dependant. This indicates both syngenetic and epigenetic origin.

Copper

The average value for Cu in the United States coals is 19 ppm (Swanson et al, 1966). Average Cu values are 12.9 and 13.9 ppm in the Monkman coals and sediments respectively. Moose River Basin average values are higher with 55.4 ppm in the clays, 56.1 in the silts, 25.5 in the gravels and 20.0 ppm in the lignites.

Cu behaves similarly to Pb in that it has restricted mobility in the weathering environment. High concentrations are adsorbed from weathering solutions onto clay minerals, iron oxides and organic matter. Fraser (1961) reported up to several % Cu in the dry weight of peat from New Brunswick. Cu fixation in peats is by complexing with living and dead organic matter and partly by adsorption (Wedepohl, 1978). Reduction of Cu^{2+} and precipitation as sulphides may also be important. Wedepohl (1978) also states that bituminous clays contain greater concentrations of Cu than non-bituminous clays and that the organic fraction of black shales is often locally enriched in Cu. Several authors report Cu in organic association in coal (Reynolds, 1948; Otte, 1953 and Leutwein and Rosler, 1956). Miller and Given (1978) state that most Cu in coal occurs in ion exchangeable and chelate complexes. Horton and Aubrey (1960), Zubovic (1961) and Schultz et al (1975) favour an inorganic association for Cu in coal; while Bogdanov (1965), Nicholls (1968) and Gluskoter et al (1977) report intermediate affinities. Bethell (1962) and Finkelman (1980) found Cu occurring mostly in chalcopyrite but Finkelman (1980) states that some is organically bound in low rank coals.

Cu correlates highly with Al_2O_3 and other clay mineral constituents in the Monkman sediments and in the Moose River Basin silts, coals and gravels. In the Monkman coals Cu correlates with Nb, Y, Rb and Pb. It is thought that in the former sample groups Cu is adsorbed or otherwise associated with the clay minerals. In the Moose River Basin clays Cu is correlated with U and to a lesser extent with Al_2O_3. Cu and U in these samples are also thought to be adsorbed on clay minerals (Van der Flier and Fyfe, 1985). The mode of occurrence of Cu in the Monkman coals may vary from sulfide minerals, adsorption on clay minerals to intimately associated with the organic matter. SEM dot maps run on sections of Monkman coal samples show Cu to be dispersed, thus favouring association with the organic matter or finely dispersed sulphide or aluminosilicate grains in association with the coaly substance.

Cu is often slightly enriched towards the base of Monkman coal seams or in the basal sediments.

Zinc

Average Zn values are 30.6 and 83.4 ppm for Monkman coals and sediments respectively. Moose River Basin coals contain an average of 159.2 ppm Zn while the clays and gravels contain averages of 51.1 and 22.3 ppm respectively. Silts from the Moose River Basin contain anomalous values for the sediments with a mean of 242.2 ppm.

Bethell (1962) summarized the literature on Zn in coals and concluded that up to 50 ppm can be associated with the organic material and higher concentrations occur in cleat-type sphalerite. The exact type of organic association has not been specified in many studies (for example Leutwein and Rosler, 1956 and Bogdanov, 1965). Miller and Given (1978) attribute the 1 ppm of Zn in the acid soluble fraction of the North Dakota lignite to ion exchangeable complexes or chelate complexes. The high adsorption of Zn by peat was proposed from a study by infrared to be a chelating reaction (De Mumbrum and Jackson, 1956a; b). In some cases closer examination of the organic matter-Zn association may reveal small sphalerite grains intimately associated with and dispersed throughout the organic material.

Some terrestrial plants accumulate Zn by more than a factor of ten relative to the rocks and soils they grow on and it's level of toxic concentration is higher than for other metals, for example Cd, Cu, Pb and Hg (Wedepohl, 1978). There are also several hundred enzyme systems which require Zn. Degradation of possible Zn-bearing organic complexes during coalification and the subsequent release of the Zn may provide a source for the secondary crystalline sphalerite associated with the coal substance. Calculations in Wedepohl (1978) based on a concentration factor of 3 to 10 from the plant material to the coal indicate that given the range of Zn values (50-150ppm) in coal, the original plants must contain at most 15-50 ppm Zn. This is in accordance with values listed for plants in Wedepohl (1978).

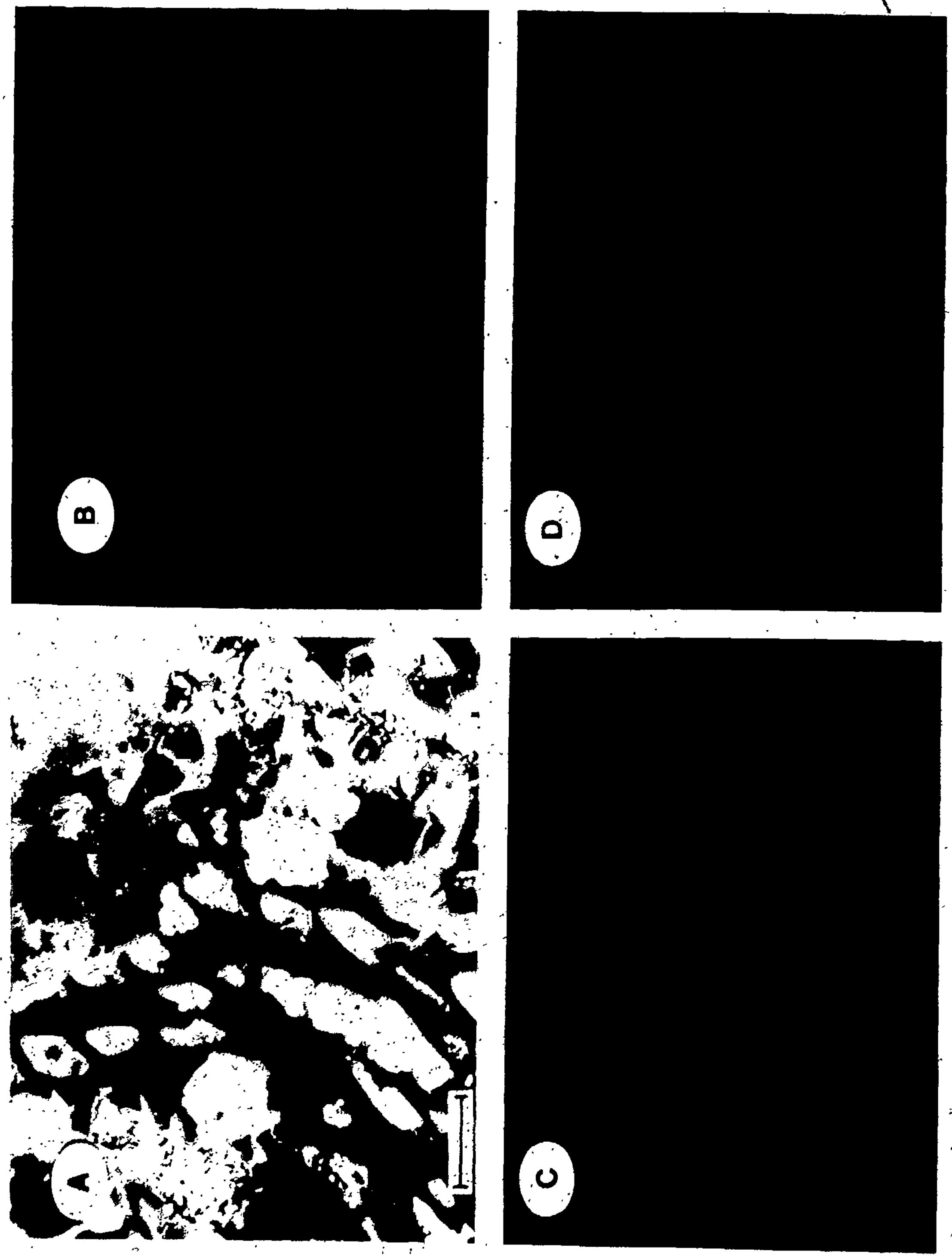
The strong Zn concentration in the lignites of the Moose River Basin may indicate adsorption onto the organic material. In the gravels a correlation exists between Zn and Al_2O_3, MgO, P_2O_5, Cu and to a lesser degree with U. These elements are commonly found in clay minerals and it is thought that the Zn may be adsorbed onto the clay minerals in these samples. A similar association between Zn and clay mineral-forming elements occurs in the Monkman coals. Wedepohl (1978) cites the low mobility of Zn in weathering solutions and attributes this to adsorption on clay minerals, ferric iron oxide and organic substances. Zn does not correlate with any other element in the Monkman sediments, Moose River Basin clays and Moose River Basin coal sample sets. SEM analysis of Monkman coaly clays and coals revealed the presence of small sphalerite grains intimately associated with the coal macerals and the clay-rich zones. Finkelman (1980) observed the same relationship in the Waynesburg coal. Element windows of Zn in pyrite-rich zones in coals from both study areas revealed no relationship between the pyrite and Zn (Plate 13). Sphalerite was found in a cell fill/grain associated with a P-rich carbonate in Monkman sample S14-23. This pyrite and organic rich sandstone is abnormally Zn-rich compared to the other samples studied and some association with pyrite was evident in this sample. The lack of correlation with other elements and the high concentrations of Zn in the Moose River Basin coals and silts indicate many modes of occurrence, the most important of which is probably the association with the organic matter. Zn in the Moose River Basin clays (again on account of the lack

Plate 13.A SEM micrograph of S2-5, Gates Formation, Monkman, showing illite (grey) and pyrite (bright) infilling fusinite cells. Pyrite overgrows illite. Scale bar is 20 microns (Magnification 0.75K X).

13.B SEM-EDX dot map showing distribution of Fe in the area illustrated in Plate 13.A.

13.C SEM-EDX dot map showing distribution of Pb in the area illustrated in Plate 13.A. Note that Pb is distributed similarly to Fe, which occurs in the pyrite infills.

13.D SEM-EDX dot map showing distribution of Zn in the area illustrated in Plate 13.A. Note that no relationship exists between Fe (pyrite) and Zn.


A
B
C
D

of significant correlations) is thought to be associated with several phases including sphalerite, clay minerals and organic matter.

In the Monkman sections Zn is enriched in the sediments above and often below the coal seams, indicating an epigenetic mode of occurrence. The situation in the Moose River Basin samples where Zn concentrations are related to lithology indicates a syngenetic origin. The reason for high Zn contents in the Moose River Basin silts is not known.

Gallium

Average Ga values in coal ranging from 45 ppm in Nigerian subbituminous coal (Simpson, 1954) to 5.5 ppm in British coals (Dalton and Pringle, 1962) have been reported in the literature. Monkman coals and sediments have average Ga contents of 14.5 and 10.6 ppm respectively. Ga was not analysed in the Moose River Basin samples.

Both organic and inorganic associations have been reported for Ga in the literature. Horton and Aubrey (1950), Otte (1953), Ryczek (1959) and Zubovic (1961; 1966) found Ga to be organically associated. Ga is one of four elements organically associated in all of Zubovic's analyses. Zubovic (1966) also describes a near source enrichment for Ga in the Illinois Basin which he accounts for by the strong chelating properties of the Ga ion with degraded lignin. Widawska-Kusmierska (1981) found Ga occurring in coals as colloidal inorganic compounds primarily concentrated in fusinite with lesser amounts in micrinite and vitrinite.

Ratynskiy and Glushnev (1967) found Ga to occur in both the organic fraction of the coal and in the inorganic fraction where it appeared to be concentrated in the clay minerals. Nicholls (1968) also suggests both forms of occurrence, but states that an organic association occurs in the Ga-rich coals.

Dalton and Pringle (1962) favour association of Ga with the dispersed aluminosilicates but note that between 9 and 46% may be organically associated or in the fixed adventitious inorganic matter. Zhou and Ren (1981) identified three genetic types of Ga distribution in coals and their paper provides an excellent summary of the systematics of Ga in coals. The residuum type are characterised by Ga/Al ratios slightly higher than those in the surrounding sediments. Gallium contents are low and the Ga substitutes for Al in and is adsorbed onto the clay minerals. In the synsedimentary Ga-rich and Ga-poor types, Ga and Al are differentiated strongly and the Ga/Al ratios are extremely variable. Organic acids which give rise to low pH's in the centres of the bogs (where there are fewer bases available to consume the H^+ produced) dissolve clay minerals releasing both camouflaged and adsorbed Ga. As the pH increases Ga hydroxides precipitate at lower pH's than Al hydroxides (Borisenok, 1971 and Vologdin, 1975 both cited in Zhou and Ren, 1981) producing Ga rich areas with high Ga/Al ratios. The Ga here has a strong organic affinity.

Ga in the Monkman samples does not correlate with any other elements. Ga/Al ratios were calculated and while the ratios in the sediments were constant (and close to ratios found in normal resistate sediments i.e. 0.41-0.61) there was a great increase in the coals, up to 11.37 (Table 5.14). The Ga in the sediments is probably associated with the clay minerals. This is not unexpected as the trivalent Ga cation is similar in size to the Al ion and may substitute for the latter in the clay mineral lattice. Ga is also readily adsorbed onto clay minerals

Table 5.14 Ga/Al ratios, Ga concentration and LOI in Monkman samples from drillhole MD 80-03

Sample Number	Ga/Al	Ga ppm	LOI %
Drillhole MD80-03			
S3-12	0.61	6.0	6.4
S3-11	0.34	4.3	8.2
S3-10	0.36	6.4	9.4
S3-9	0.50	10.0	33.7
5348	1.14	9.9	65.2
5349	0.50	8.9	37.1
5350	1.12	9.1	66.7
5351	0.38	7.6	16.1
5352	2.42	17.6	80.0
5353	3.67	13.7	84.6
5354	8.67	21.6	92.5
S3-8 top coal	0.73	9.7	41.5
S3-8 mid+ base	0.43	10.2	10.9
S3-7	0.65	11.9	28.1
5355	11.37	25.7	84.2
5356	2.56	10.0	82.7
5357	6.51	18.5	93.7
S3-6	0.56	10.8	28.3
S3-5	0.19	1.9	8.3
S3-4	0.32	4.8	14.1
5359	1.74	11.3	86.5
5360	5.67	12.7	96.5
S3-3	0.42	9.5	6.5
S3-1	0.64	10.5	23.1

Note that Ga/Al ratios increase in samples which have most Ga and highest LOI.

(Hirst, 1962; Nicholls and Loring, 1962; Liu, 1965 and Zhou and Ren, 1981). In the coal samples the concentration of Ga usually increases in the samples with high Ga/Al ratios indicating that much of the Ga in these samples is held in another form than in the clay minerals. The preferential enrichment in the coals and the high Ga/Al ratios suggests that the Ga may be organically associated. Lack of correlation with LOI may be due to incorporation of CO_2 and H_2O lost from inorganic phases in this value. Conditions such as those cited for the synsedimentary Ga-rich coals in Zhou and Ren (1981) (see above) may explain the Ga enrichment and the differentiation of Ga and Al in the coals.

Ga was found to be preferentially enriched towards the tops and bottoms of the coal seams in the Monkman sections. This may result from varying pH conditions within the coal forming swamp or may indicate variable quantities of Ga present in the ground waters at different times during the deposition of the coal. Nicholls and Loring (1962) and Zubovic (1966) found Ga concentrations to reflect adsorption and redistribution subsequent to initial formation of the deposits.

Arsenic

The mean As content of United States coals is 15 ppm (Swanson et al, 1976). Arsenic values in six Monkman coals range from 10 to less than 1 ppm with a mean of 3.8 ppm. Arsenic contents of the 5 unashed Moose River Basin coals and sediments (Table 5.13) range from 1 to 6 ppm with a mean of 3.6 ppm.

Arsenic has variable affinities in different coal samples. Goldschmidt (1935), Brown and Swaine (1964), Gluskoter et al (1977), Ford (1977), Swaine (1977), Kuhn (1978), Finkelman (1980), and Harris et al (1981) found As to exhibit inorganic tendencies. Many of these authors (Brown and Swaine, 1964; Minkin in Finkelman, 1980 and Harris and Yust, 1981) report As occurring in pyrite and possibly also in arsenopyrite. Finkelman (1980) also reports trace As in chalcopyrite, linnaeite and a Sr-Al bearing particle. Kirsch <u>et al</u> (1968) indicate that As is associated with the clay minerals in the coals they studied. Hawley (1955) noted As in both light and heavy specific gravity fractions of a Nova Scotian coal. Leutwein and Rosler (1956) and Bogdanov (1965) found that As was associated with the organic coal substance. The consensus from the literature is therefore that As is involved mainly with the sulfides in coals, however other modes of occurrence must also be taken into account.

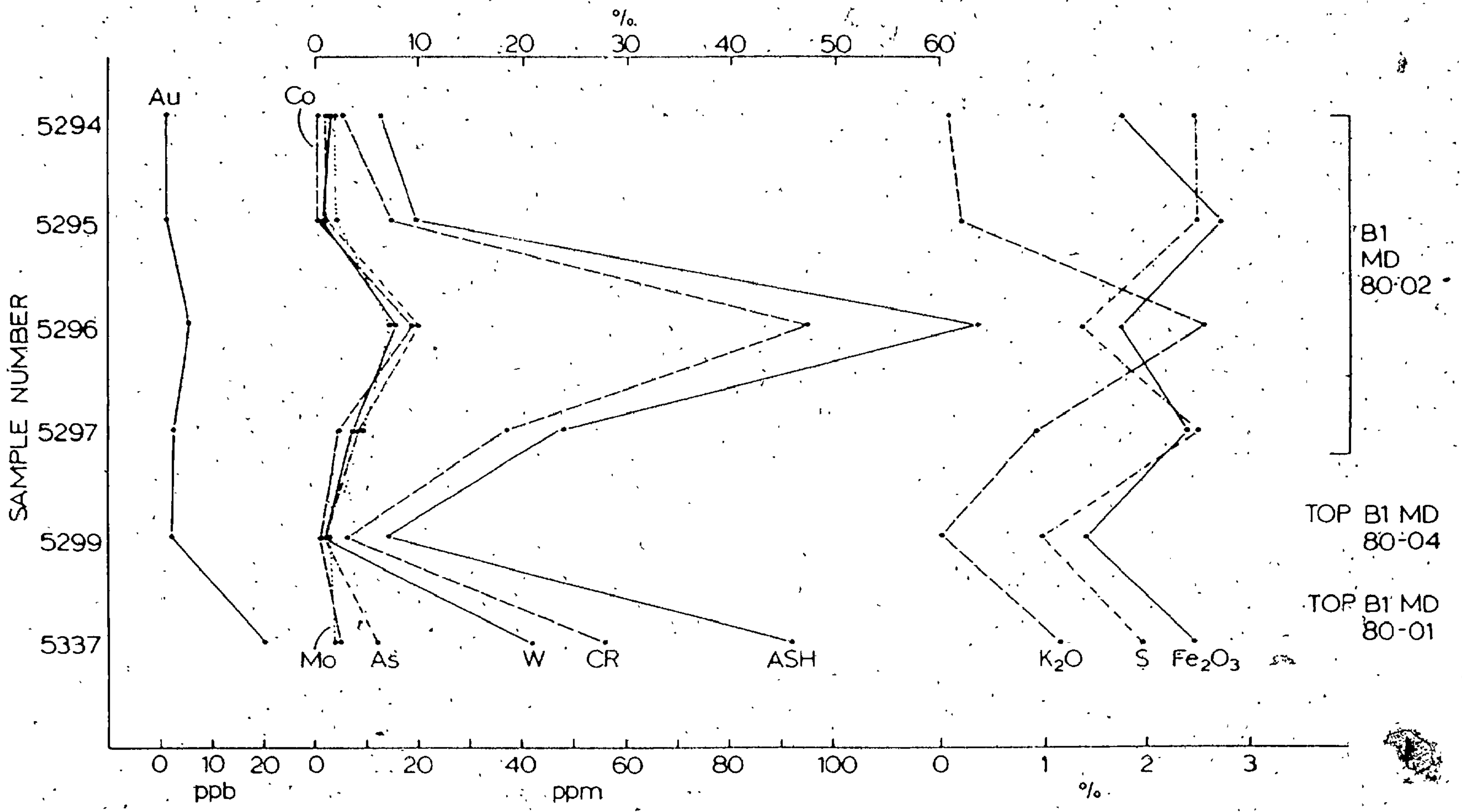
As and ash contents are directly related in the Monkman coal samples. No relationship exists between As and Fe_2O_3 (as would be expected); however As correlates well with Al_2O_3 and K_2O values. A relationship between As and the clay minerals particularly illite is therefore implied. As also correlates with W, Cr, Co and Mo indicating that these elements may also be associated with the clay minerals. These relationships are illustrated in Figure 5.2.

In the Moose River Basin samples highest As contents occur in the pyrite-rich lignite and in the green clay which contains 5-15% Fe. This indicates an association with the sulfides in these samples. The lowest contents are in the organic-rich black clay from higher in the section.

Rubidium

Gluskoter <u>et al</u> (1977) gave the following averages for Rb in Illinois Basin coals, Eastern United States coals and Western United States coals; 19, 22 and 4.6 ppm respectively. Mean contents in clays

Figure 52. Graph showing the concentration of Au (ppb); Co, As, W, Mo, Cr (ppm); and Ash, K_2O, Fe_2O_3 and S (%) in six Monkman coal samples (unashed).



and shales are considerably higher, for example Wedepohl (1978) cites averages of 116 and 164 ppm in recent argillaceous sediments and 253 shale samples respectively.

The Monkman and Moose River Basin shales and clays contain highest Rb values with averages of 70 ppm and 54.1 ppm respectively. Average values are considerably lower in the Moose River Basin coals (5.9 ppm) and gravels (9.0 ppm). Monkman coals average 33.1 ppm Rb.

Rb correlates strongly with K_2O (and other clay mineral constituents including Al_2O_3, TiO_2, MgO, Na_2O and MnO) in all the sample groups except the Moose River Basin coals. Rb and K are closely linked in nature following each other geochemically in rock-forming minerals, weathering processes and in plants and soils (Aidinyan, 1959). It is evident that Rb is associated with the clay minerals and is probably fixed in the interlayer positions. Rb may also be present in microcline in the Moose River Basin samples, particularly in the gravels where there is relatively little illite and significant feldspar. Degens et al (1957) and Finkelman (1980) found Rb to be associated with mixed layer clays as well as illite.

Illite is more common in the Monkman succession than in the Moose River Basin samples explaining the higher concentrations of Rb in the former. Rb was not detected (less than 10ppm) in many of the coal and lignite samples and this may be related to the absence or low concentrations of illite relative to kaolinite in these samples. Authigenic illite which is more common in the coals than detrital illite/mica may also contain less Rb than the latter. In the Moose River Basin lignites Rb correlates with TiO_2, Al_2O_3 and SiO_2 indicating an association with the detrital mineral fraction. Rb was found by

Gluskoter et al (1977), Filby et al (1977) and Kuhn et al (1978) to display a strong inorganic affinity supporting the conclusions cited above.

Rb in the lithological sections (for example MD-80-05) displays a pattern of enrichment in the coaly clays immediately above and below the coal seams. Otherwise Rb concentrations show no net increases or decreases with depth. The enrichment in the coaly clays associated with the coal is mirrored by maximum K_2O concentrations in these samples indicating the enrichment in muscovite/illite, illite and possibly feldspar. The distribution is therefore lithologically controlled.

Strontium

The mean Sr value for United States coals is 100 ppm (Swanson et al, 1976). Mean values in the Monkman and Moose River Basin coals are 151.4 and 108.7 ppm respectively representing the maximum values in the successions. Average Sr values are lowest in the Moose River Basin gravels, 11.5 ppm, and range up to 27.3 ppm and 77.4 ppm in the silts and clays. The mean Sr value in the Monkman sediments is 103.0 ppm.

Sr in the Moose River Basin lignites correlates highly with CaO, MgO and TiO_2. In the Monkman coals it is correlated with CaO and Ba indicating in both cases an association with the inorganic fraction of the coal. Leutwein and Rosler (1956) and Filby et al (1977) also found Sr associated with the inorganics in coal. Nicholls (1968) states that Sr occurs mostly in carbonates, however O'Gorman and Walker (1972), Nicholls and Loring (1962) and Nicholls (1968) suggest that sorption onto clay minerals may also be an important process. Sr and Ca are diadochic (Wedepohl, 1978) and Sr and Ba follow each other in nature, therefore the occurrence of Sr in calcite in both the Moose River Basin and Monkman coals and also in barite in the latter coals is not unexpected. MgO and TiO_2 occur associated with the clay minerals in the Moose River Basin coals indicating on the basis of the correlation coefficients that some Sr also occurs in association with the clay minerals.

In the Monkman sediments Sr correlates only with Ba indicating that most of the Sr is substituting in the barite lattice. In the Moose River Basin gravels and silts Sr and CaO are correlated and probably occur together in calcite, while in the clays Sr correlates only with P_2O_5. Harris et al (1981) found Sr in both freshwater and marine-influenced coals to correlate with P and P and Ca respectively. Although no phosphate minerals were identified, some apatite may be present and the elements are thought to occur either in a carbonate phase or in the apatite.

High Sr values in some of the Sr-enriched coals exceed the amount expected to be incorporated in calcite (given the CaO present). No Sr minerals were detected such as those found in Finkelman (1980). The excess Sr may therefore be organically bound. Brown and Swaine (1964) and Miller and Given (1978) found Sr bound to carboxyl groups in low rank coals. Gluskoter et al (1977) and Kuhn et al (1978) also found Sr occurring mostly in organic combination in coals.

In lithological sections from the Moose River Basin Sr appears to be concentrated in the carbonaceous clays above the coal seams. In contrast to this Sr in the Monkman sections is highest towards the middle and base of the seams following the trend observed for CaO.

Yttrium

Y contents of coals reported in the literature appear to be quite variable. Swanson et al (1976) reported an average value in United States coals of 10 ppm, Goldschmidt and Peters (1933) found Y to average 100 ppm in British and German coals and Swaine (1977) cites 7 ppm Y as the mean content in New South Wales and Queensland bituminous coals. Mean Y contents of the Monkman coals and sediments are 7.2 and 7.3 ppm respectively. The range of values is higher in the coals. Y was not analysed in the Moose River Basin samples.

Several modes of occurrence are cited for Y in the literature, ranging from organically associated (Yershov, 1961; Bogdanov, 1965 and Miller and Given, 1978) to occurrence in mineral phases in the coal. Many workers have found that in a single coal Y occurs in several forms often both organically and inorganically held (Goldschmidt and Peters, 1933; Zubovic, 1960; Schofield and Haskin, 1964; Ratynskiy and Glushnev, 1967 and Singh et al, 1983). The most common inorganic forms are in the heavy rare earth phosphate minerals xenotime and monazite (Swanson et al, 1976 and Finkelman, 1980), and in clay minerals (Bethell, 1962; Wagner et al, 1980 and Singh et al, 1983). The xenotime and monazite grains are often finely dispersed in the organic matter (Finkelman, 1980).

Y in the Monkman coals correlates with Nb, Zr, Rb, Cu, MnO, MgO and to a lesser extent with Pb and CaO. In the sediments Y correlates with Nb, Rb, K_2O, Cr, Al_2O_3 and to a lesser extent with Cu. Several modes of occurrence are possible in the Monkman samples. From the correlation coefficients in the Monkman coals it appears that Y is most commonly present associated with Nb and Zr possibly in heavy rare earth (phosphate) minerals or with detrital heavy minerals such as zircons. The correlation between Y and several clay mineral-forming constituents indicates some association with the clay minerals. Some Y may also be present in the carbonates. Y in the Monkman sediments is also present in association with Nb (possibly in the heavy mineral suite) as well as in the clay minerals.

No definite trends of enrichment in the sediments above or below the coal seams were observed, therefore it appears that Y concentration depends on syngenetic rather than epigenetic processes.

Zirconium

The average crustal abundance of Zr is 165 ppm (Taylor, 1964). The average concentration in sandstone is 220 ppm and in shales this falls to approximately 180 ppm (Wedepohl, 1978). Values in sands often have greater variability due to the irregular distribution of zircons which contain much of the Zr present. Average contents in coals are variable. Yudovich et al (1972) report worldwide averages of 28 ppm and 10 ppm for hard and brown coals respectively. Values from 16-160 ppm occur in coals from the Bersham section (Nicholls and Loring, 1962) and Swanson et al (1976) cite 39 ppm as the mean value for United States coals. Two Appalachian anthracite deposits yielded concentrations ranging from 202-959 and 200-300 ppm respectively (Medlin et al, 1975).

Average Zr concentrations in the Monkman coals and sediments are 61 and 105 ppm respectively. These values are much lower than for the Moose River Basin materials whose averages are 240, 94, 478 and 267 ppm for the gravels, coals, silts and clays respectively.

Zirconium is generally thought to occur in the inorganic fraction of coal (Gluskoter et al, 1977) either as detrital zircon (Butler, 1953 and Swaine, 1977), and/or proxying for Al in the clay minerals (Degenhardt, 1957 and Nicholls and Loring, 1962). However Otte (1953), Leutwein and Rosler (1956), Miller and Given (1978) and Finkelman (1980) find Zr to be associated with the organic fraction of coal. Miller and Given (1978) suggest that a Zr-organic complex may exist and Finkelman observed authigenic zircons in inertinite pores.

SEM studies of the Monkman coal have shown Zr to be present in zircons concentrated in the detrital-rich zones of the coal. Zr contents are highest in the coals with greatest (detrital) ash contents. Zr correlates with Y, Nb and to a lesser extent with TiO_2, Rb and Cu in these coals. The latter elements are commonly found in clay minerals. Zr therefore also occurs associated with clay minerals perhaps proxying for Al in the structure. Zr may also be present associated with the organic fraction. Zr correlates with Fe_2O_3 and MnO in the Moose River Basin coals and therefore appears to be associated with pyrite. The association of pyrite with the organic material may indicate a similar mode of occurrence for Zr.

The suite of elements associated with Zr in the Moose River Basin gravels includes TiO_2, Cr, U and Th. These elements are found in the detrital heavy minerals such as rutile and chromite. The zircon most probably occurs in detrital zircon.

In the Moose River Basin and Monkman clays and claystones Zr is correlated with SiO_2 and TiO_2 and is therefore also associated with the detrital mineral fraction in these samples. The presence of zircons associated with quartz in some Monkman claystones was substantiated using the SEM. Zr may also be present adsorbed onto clay minerals (Nicholls and Loring, 1962).

The Zr which is associated with the muds and organics is thought to be derived from detrital zircons. The variability in the present distribution is therefore probably a reflection of the variability of the source rather than of the present association of the Zr.

Niobium

Average Nb content of United States coals is 3 ppm (Swanson et al, 1976). Mean values in the Monkman sediments and coals are 33 and 40 ppm respectively. Nb was not analysed in the Moose River Basin samples.

Ratynskiy and Glushnev (1967) found that Nb is associated with both organic and inorganic fractions of coal. Finkelman (1980) found Nb in the Waynesburg coal to be concentrated in the lighter specific gravity fractions, but also notes a high correlation between Nb and Zr. This may indicate the presence of some Nb in zircons. The association of Nb with zircons and rutile or ilmenite in coal is commonly reported in the literature (Goldschmidt, 1954 and Finkelman, 1980). Goldschmidt (1954) states that Nb can enter into some zircon types but is more commonly associated with the Ti minerals. Nb follows Zr in igneous rocks with the average amount of Nb being one tenth that of Zr.

Nb in the Monkman coals correlates strongly with Y, Rb, Cu , less with MnO, MgO, CaO, Zr, Pb and to a small extent with Sr. Nb in the Monkman sediments correlates with Y and to a small extent with Rb. It is evident that Nb is present in several forms in the samples and that it shows many similarities to Y (see previous section). The association with Y and Zr in the coals may indicate the presence of Nb in the heavy mineral suite in zircons or Rare Earth minerals in these samples. Nb is also associated with ankerite (MgO, CaO, MnO and Sr) in the coals. Since

Rb is associated to some extent with the clay minerals it follows that another mode of occurrence of Nb in the coal samples may be in this form. Nb in the Monkman sediments may be present in zircons and rare earth minerals as well as to a lesser extent associated with the clay minerals.

No obvious marginal enrichments were found in the Monkman sections, and from the associations of Nb it appears that much of the element may have entered the system in the detrital heavy minerals.

Molybdenum

Mo contents in the 6 Monkman coal samples range from 7.5 to 1.5 ppm with a mean of 3.3 ppm, similar to the mean value of 3 ppm in United States coals (Swanson et al, 1976). Yudovich et al (1972) report means of 24 and 15 ppm in the ashes of hard and brown coals respectively. Most of the Moose River Basin sediments and coals have Mo in concentrations less than the detection limits for the method used (5.00 ppm). Average values (taking the less than 5.00 ppm value to equal 5.00 ppm) are 5.9 ppm in the clays, 5.0 ppm in the silts, 5.9 ppm in the coals and 5.7 ppm in the gravels. Where Mo is greater than the detection limits the samples are either fusinitic coals, dirty gravels or clays. Highest values are found in the fusinitic woody lignites (L-2-18 and L-2-17). In these two samples Ni is also at its maximum concentration. Five unashed lignite and clay samples from the Moose River Basin were analysed by D.C.P. to a detection limit of 0.500 ppm (Table 5.13). Mo in these samples is higher in the lignites than in the clays, and of these the black organic-rich clay has highest Mo. This may imply an association with the organic matter or that the original Mo accumulation was organically promoted.

Mo has been reported occurring with both organic and inorganic associations in coal. Gluskoter et al (1977) from float sink studies found Mo to be predominantly inorganically associated in Illinois Basin and other coals. Korolev (1957; 1958) concluded that pyrite in the heavy fractions of the coals he examined contained 70-96 and 75-90% of the Mo present in the coal. He also states that remaining Mo may be associated with the organic substance. Golovko (1961) and Petrov (1961) proposed that Mo is retained by the organic matter during the initial coal-forming stages and is subsequently released by diagenetic processes and forms sulfides. Ratynskiy and Glushnev (1967) found Mo associated with both organic and inorganic fractions while Nicholls (1968) found Mo associated with the inorganics in low-Mo coals and with the organics in high-Mo coals. Horton and Aubrey (1950) and Zubovic et al (1961) found Mo to exhibit intermediate organic affinities with slight inorganic tendancies. Kutnetsova and Saukov (1961) noted at least two forms of Mo in coals including metal-organic compounds and dispersed microscopic sulfide inclusions. The majority of workers cite an organic association for Mo in coal (Otte, 1953; Krauskopf, 1955; Leutwein and Rosler, 1956; Bogdanov, 1965; Szilagyi, 1971 and Finkelman, 1980). This however may be due to a certain extent to finely dispersed sulfide grains within the coaly substance. Bethell (1962), in a study of Hungarian coals found Mo to correlate with U and S. In the same coals Almassey and Szalay (1956) determined Mo to be bound to the organic matter.

Mo is insoluble in soils at pH's below 5 (Karlsson, 1961) and can therefore not be taken up by plants in the acidic coal-forming environment. Land plants in general contain little Mo (Table 4.7), on average 0.5 ppm (Vinogradov 1954). Leutwein and Rosler (1956) found the

Mo concentration in wood to be much lower than the contents in coals and concluded that post depositional uptake of the metal from ambient fluids must be an important process in the concentration of that element in coals.

Mo in the Monkman coal is distributed similarly to ash content, Al_2O_3, K_2O, Cr, As, Co and to a lesser extent W (Figure 5.2). It therefore appears to be associated with the mineral matter, and in particular with the clay and sulfide minerals in the coal. No significant correlation exists with S or Fe_2O_3, however this may be due to Fe being present in several forms in the coal, including in pyrite and carbonates. Small quantities of Mo may be present in pyrite or as grains of molybdenite as impurities in the pyrite, however it appears that most of the Mo in the coals is associated with the clay minerals and in particular with illite.

In the Moose River Basin samples, maximum Mo and Ni values occur in fusinitic woody lignite from drillhole J-1-2. This would indicate that they are organically associated in the coal. Fusinite requires fire (very oxidising conditions) for its formation and the particular geochemical conditions produced by this process are conducive to the precipitation of metal rich salts in the organic material. Association of Mo with the organic matter was also noted in the unashed samples as mentioned previously. The appearance of Mo in the dirty sands indicates that Mo may be associated with impurities such as Fe-rich cements in these samples.

Cadmium

Mean Cd content in United States coals is 1.3 ppm (Swanson <u>et al</u>, 1976). Cadmium contents were determined only for the Moose River Basin samples and were found to be below the detection limit of 0.5 ppm in all but some coal ash samples. In these, values range from 80 ppm to less than 0.5 ppm and correspondingly high Zn values are often present. Gluskoter et al (1977) found Cd to have a strong inorganic affinity in coal. Cd was found to occur in sphalerite in Illinois Basin and other coals (Gluskoter and Lindahl, 1973; Hatch et al, 1976; Finkelman, 1980 and Minkin in Finkelman, 1980). Godbeer and Swaine (1979) however found no direct relationship between Cd and Zn in low-Cd Australian coals, and Bogdanov (1965) found Cd and Zn to be associated with the organic substance. It seems probable that the Cd in Cd and Zn-rich coals occurs in the form of sphalerite and that other modes of occurrence are more important in Cd-poor coals. No direct relationship between Cd and Zn is apparent in the Moose River Basin coal ash.

Barium

Yudovich et al (1972) and Swanson et al (1976) reported the mean Ba contents in coals worldwide and in the United States to be 120 and 150 ppm respectively. Average values in the Monkman coals and sediments are 1092 and 822 ppm respectively. The range of values is also high, 262-3105 ppm in the coals and 174-2334 ppm in the sediments. Ba contents of selected Moose River Basin samples are reported in Murray (1984). Values are generally lower than in the Monkman samples, with contents ranging from 6-1900 ppm in the lignite ash and from 22-675 ppm in the sediments. Mean values are 980 (in ash) and 223 ppm respectively.

In the literature the consensus of opinion is that Ba is associated with the inorganic material in coal. Leutwein and Rosler (1956), Leutwein (1966), O'Gorman and Walker (1972), Miller and Given (1978) and

Singh et al (1983) specify an inorganic mode of occurrence for Ba, associated with minerals such as clays, carbonates or other silicates. Other authors including Hawley (1955), Nicholls (1968), and Finkelman (1980) found Ba in barite and/or witherite. O'Gorman and Walker (1971) state that most Ba in coal occurs in the form of finely divided barite or Ba/Sr absorbed on illite. However they also noted that Ba in Ba-rich low rank coals is held by ion exchange with carboxyl groups. Tourtelot (1964) lists the principal sorbents of Ba to be organic matter, clay minerals (especially illite), colloidal iron monosulphide and possibly phosphates.

Intermediate affinities of Ba were found by Bogdanov (1965), Gluskoter et al (1977), and Kuhn et al (1978).

Ba is highly correlated with Sr in both the Monkman coals and sediments and also to a lesser extent with CaO in the coal. Barite was detected by XRD in very tiny quantities in some sandstones and coals. Sr is known to replace Ba in barite but may also occur with Ba replacing Ca ions in calcite (Deer, Howie and Zussman, 1966). No association between Ba and Sr and the clay mineral constituents was determined therefore adsorption on clay minerals is not thought to be an important mode of occurrence. The correlation coefficient with Sr is not very high in the sediments therefore some of the Ba may also be in organic combination in these samples. The higher contents in the organic rich materials supports this conclusion.

Ba concentrations in the vertical sections are frequently higher towards the bottoms of coal seams and often also in the tops and centres. This may be related to ground water flow preferentially in some zones in the coals. The association with carbonates which are epigenetically precipitated in veins and cracks supports the thesis that Ba was epigenetically enriched in many of the samples. Barite is thought to occur as an epigenetic mineral in fractures and cavities in the sediments.

Tungsten

Gluskoter et al (1977), report average W contents of 0.69, 0.82 and 0.75 ppm in Eastern United States coals, Illinois basin coals and Western United States coals respectively. Headlee and Hunter (1953) reported an average of 90 ppm W in West Virginia coal ash (range 40-440 ppm). Block and Dams (1975) found between 0.4 and 1.2 ppm W in Belgian coals, while Dekate (1967) reports an average of 2.7 ppm in Indian lignites and carbonaceous shales. Anthracite ash from Pennsylvania contains 8-90 ppm W (Nunn et al, 1953). The average W values in sedimentary rocks (1-2 ppm) are similar to those found in igneous rocks (Wedepohl, 1978). Values in the six Monkman coals examined range from 1.5 to 42 ppm with a mean of 12 ppm. Mean contents in the 5 unashed Moose River Basin lignites are 2.4 ppm with values ranging from less than 1 to 5 ppm (Table 5.13).

Dekate (1967) reports up to 2-18 times concentration of W in some plants relative to the background level of 2.7 ppm. Doucet (1966) found organic matter to complex W at pH's between 6 and 7, however Gannett (1919) found peat to have no effect on the solubility of W compounds. Many authors (including Ratynskiy and Glushnev, 1967; Gluskoter et al, 1977 and Kuhn et al, 1978) have found W to be organically associated in coals. Zubovic (1976) notes that the strong organic affinity of W is consistent with it's ionic potential of 5.5. Eskenazy (1977; 1982) concluded from adsorption, desorption and other studies that W is bonded in covalent organometallic complexes in coal. He further notes that W may be carried in solution by organic complexes (formed in acid solutions containing organic ligands) via which it may be fixed in coal. In phyllites W correlates strongly with C and is stratigraphically controlled. From this Wedepohl (1978) concludes that W was originally concentrated by organic processes and is of syngenetic origin.

Inorganic Mo phases have also been identified in coal. W and Mo are chemically very similar and both form insoluble compounds with Pb, Cu and Fe. Tungsten also makes very stable complexes with Si, P and Sb in acid solutions. Very reducing conditions are needed to form W disulfide but W can be adsorbed onto oxides of Fe and Mn from solution.

W contents in the Monkman coals mirror the ash contents and appear to follow the Al_2O_3 and K_2O trends as do Co, As, Cr and Mo (Figure 5.2). An association with the clay minerals appears likely. W contents are high in sample 5337 relative to ash contents. The excess may be located in sulfides or occur in association with the organic matter. No association of W with Fe or Mn was documented in the Monkman samples.

Highest W values in the Moose River Basin samples occur in the black clay and pyritic lignite samples. A link with pyrite formed in association with decomposing organic matter is implied. The W may occur in the pyrite as an impurity or together with the pyrite as a separate phase. No evidence was found to support either mode of occurrence.

Platinum Group Elements

Results of the Platinum Group Element (PGE) analyses for both ashed and unashed Monkman and Moose River Basin samples are listed in Table 5.15.

Table 5.15 Gold and Platinum Group Element contents of selected Moose River Basin and Monkman sediments and coals (in ppb)

	Moose River Basin					
Sample Number	Au	Pt	Pd	Rh	Ir	Sample Description
L-2-1	3	10	-	-	0.4	clay
L-2-2	3	5	-	-	-	clay
L-2-3	5	15	30	-	-	black clay
L-2-4	1	-	-	-	-	lignite (ash)
L-2-5	2	-	-	-	-	lignite (ash)
L-2-5B	8	5	7	-	-	lignite (ash)
L-2-6	1	-	-	-	-	lignite (ash)
L-2-7	10	-	30	-	0.2	grey clay
L-2-8	2	-	-	-	0.1	clay
L-2-9	7	-	-	-	-	black clay
L-2-10	8	-	<50	2	-	Black clay
L-2-11	3	-	-	-	-	black woody clay
L-2-12	4	-	-	-	-	banded clay
L-2-14	3	-	-	-	-	white clay
L-2-15	5	-	-	-	-	lignite (ash)
L-2-16	1	-	-	-	-	lignite (ash)
L-2-17	1	-	-	-	-	lignite (ash)
L-2-18	2	5	-	-	0.1	lignite (ash)
L-2-19	2	-	-	-	-	sand
L-2-20	1	-	-	-	0.2	sand
L-2-21	15	-	-	-	0.1	grey clay
L-2-22	3	40	-	-	0.1	lignite (ash)
L-2-23	6	-	-	-	0.1	gravel
L-2-24	6	-	-	-	0.1	silt
L-2-25	3	110	<10	<10	-	sand
L-2-26	2	-	-	-	0.1	clay and sand
L-2-27	20	25	-	-	0.2	sand and clay
L-2-28	2	20	7	<1	<3	white clay

(Table 5.15, continued)

L-1-6	15	75	-	-	-	clay
L-1-16	5	-	-	-	0.3	silty clay
L-1-21	1	-	-	-	-	gravel
L-1-24	2	-	-	-	-	sand
L-1-23	5	-	-	-	-	lignite (ash)
L-1-25	3	-	37	-	-	clay
AC-07-82	8	15	-	-	-	clay
AC-08-82	5	-	-	-	-	lignite (ash)
AC-09-82	5	15	17	-	-	wood (ash)
AC-12-82	3	-	10	-	0.2	sandstone and coal
AC-13-82	2	-	-	-	0.2	sandstone
AC-20-82	6	-	6	-	0.1	clay
AC-21-82	2	-	-	-	-	clay
AC-23-82	3	-	-	-	-	brown clay and silt
AC-23B-82	4	-	-	-	0.1	clay
AC-25-82	5	-	-	-	-	silt and sand
AC-26-82	3	-	5	-	0.1	wood (ash)
AC-27-82	3	-	-	-	-	clay
AC-28-82	4	5	-	-	-	clay
AC-29-82	17	-	-	-	-	gravel
AC-30-82	4	10	-	-	0.1	wood (ash)
Detection Limits	<1	<5	<5	<1	<0.1	
FM-1	41	80	-	-	0.1	soily lignite (ash) Onak.
FM-4	31	50	10	1	0.3	woody and soily lignite (ash) Onak.
P-1	32	-	-	-	0.5	lignite (ash)
P-2	96	35	250	2	-	lignite (ash)
P-3	55	-	10	1	0.1	OEC black clay (ash)
P-4	8	-	-	-	0.3	OEC green clay (ash)
RC1	17	-	-	-	0.1	red sandstone with wood pieces (ash)
RP	6	-	-	-	0.1	red sandstone with pyrite (ash)
PY	36	-	10	-	0.1	pyrite nodule from gravel (ash)
Detection Limits	<1	<20	<10	<1	<0.1	

(Table 5.15, continued)

Monkman

						Au unashed	
5294	800	<400	35	1	1.0	<1	coal (ash)
5299	41	20	20	-	0.8	2	coal (ash)
5337	5	-	-	-	0.2	20	coal (ash)

- below detection limits

Monkman samples analysed are 5294, 5299 and 5337, three coals from the tops of seam B4 in three different boreholes. Pt contents are less than 400, 20 and less than 20 ppb (parts per billion) respectively. (The high Au concentration in sample 5294 has interfered with the Pt peak preventing accurate determination of Pt in this sample). Pd values are 35, 20 and less than 20 ppb respectively, while Ir contents follow a similar trend, with 1.0, 0.8 and 0.2 ppb in the same samples. Os contents are less than 3, 5 and 5 ppb respectively, Rh is below detection limits except in 5294 where it's concentration is 1 ppb. No Re or Ru were detected in the samples. Gold values are 800, 41 and 5 ppb respectively, however the same samples unashed contained less than 1, 2 and 20 ppb respectively. Ash contents of the samples are 7.81, 11.19 and 46.00% respectively indicating that maximum Au, Pd and Ir are in the samples with lowest ash contents. The opposite is true for Au in the unashed samples.

Over fifty lignite (ashed) and sediment samples from the Moose River Basin were analysed for Au and the PGE. Ru, Os, Re and Rh were detected in only four samples in total. Pt, Pd and Ir were below detection limits in many of the samples however concentrations well above the average crustal abundance (Goldschmidt, 1935; 1954) were determined in several of the samples. Highest Pt concentration was found in the sand L-2-25, with high values also occurring in red, black and a white clay and in several of the ashed wood and lignite samples. Pd contents were highest in the clays with 37 ppb in a lignite underclay and 30 ppb in a black and grey clay. Ashed wood from the lignite seam exposed in Adam Creek contains 17 ppb Pd, and AC-12-82, a banded coal and sand contains 10 ppb. Ir contents are also highest in the clays with the maximum value of 0.4 ppb occurring in L-2-1. Where Ir is detected in the sands, concentrations are 0.2 ppb, while in the lignites values are 0.1 ppb. The average Au contents in the samples are 5 ppb (range 2-15 ppb) in the clays, 4 ppb (range 1-8 ppb) in the lignites and 6 ppb (range 1-20 ppb) in the gravels and sands. In the lignite ash samples Au values up to 96 ppb were observed. Relative to the crustal abundance data in Wedepohl (1978), the samples with detectable Pt and Pd and many of the Au contents, show enrichment.

From the lack of correlation of the PGE, with any other element or with the ash or LOI of the samples, it appears that they occur in more than one form in the samples. Chyi (1982) found Pt to correlate with Ga in the Kentucky coals he sampled. Negative correlations existed for low temperature ash content (LTA), Au, Fe and Tb. Widawska-Kusmierska (1975; 1981) found Ga occurring in coals as colloidal inorganic complexes associated primarily with fusinite and to a lesser extent with micrinite and vitrinite. The correlation with Ga may suggest that Pt occurs in a similar fashion. Goldschmidt (1954) suggests that soluble or complex ions of the PGE could be precipitated by organic matter in the soil as in the case of Au. Cousins and Kinloch (1976) found that on weathering the PGE are oxidised and dissociate releasing colloidal platinoid metal of near molecular dimensions. These particles may then coalesce and accrete to form larger particles. Ong and Swanson (1969) state that a change in pH towards a more acidic situation (such as that found in a bog or coal environment) would prompt Au and Pt to mix with organic acids present and form colloidal precipitates. This might lead to an association of PGE with the organic material in coals. Finkelman (1980) detected no minerals containing PGE in the coals he examined, but he suggests that PGE may have a similar mode of occurrence to Au. As mentioned previously Finkelman (1980) attributes Au in coal to discreet grains of native Au or Au alloys. These would have been incorporated as detrital grains in the coal. He finds the low values in coal consistent with a detrital source.

Pt in the samples from drill hole J-1-2 (Moose River Basin) shows a weak positive correlation with Zr. No other correlation exists in the samples either indicating variable modes of occurrence of the PGE, or the presence of detrital flakes containing PGE unrelated to either the organic or mineral phase as suggested by Finkelman (1980). Association with organic matter may also be important. Shotyk et al (1982) indicate that PGE in waters from peat-forming areas may be complexed by simple organic compounds and as such may contribute to the concentration of PGE in coals. Os metal is very volatile even at 25°C therefore if the Os is held in organic complexes in the coal and the coal is exposed at the surface and oxidised, the hydrocarbon structure may change leading to loss of the Os to the environment (J.H. Crocket- pers. comm., 1982). Os is detected in the Monkman coals after ashing up to 600°C therefore the Os must be held in a very stable and resistant form, for example in detrital mineral phases.

Gold

Gold was analysed in six Monkman coals and in the ash of three of these. Over 50 samples of Moose River Basin coal, ash, silt, clay and gravel from drill hole J-1-2, Adam Creek and elsewhere were also analysed for Au.

Goldschmidt and Peters (1933) report 0.5-1 ppm Au in the ashes of ten low ash coals. Block and Dams (1975) found Au contents ranging from

10-40 ppb in Belgian coals. Compared with the crustal abundances 1.8 and 1.1 ppb cited by Shaw et al (1976) and Crocket and Kuo (1979) respectively, these coals are enriched in Au. Values in the Monkman coal ash range from 5 to 800 ppb and from less than 1 to 20 ppb in the coals. 5.1, 5.7 and 3.6 ppb are average Au contents in the unashed Moose River Basin clays, gravels/silts and lignites respectively. Values ranging from 6 to 96 ppb were found in the bulk ashed lignite samples.

Gold may be concentrated in plants (Chyi, 1982) and organic matter (Ong and Swanson, 1969), however it appears that in the Monkman and Moose River Basin samples Au values are related to the ash contents or the mineral fraction rather than the organics (Figure 5.2). Chyi (1982) documents associations of Au with Co, Sb, Sc and R.E.E. in coals. All of these elements are ash-forming constituents and Chyi concludes that Au is absorbed or trapped in minerals growing in situ. Au is also associated with Br, K and Na and this is attributed to introduction of the metal in halogen complexes. Bogdanov (1965) also found Au to have an inorganic affinity. Finkelman (1980) attributes Au in the Waynesburg and other coals he studied to detrital elemental gold particles. Some workers (for example Bethell, 1962) suggest that Au is associated with the pyrite, however Wedepohl (1978) states that Au content in sulfides depends largely on the environment and suggests that authigenic pyrites from coal-bearing environments would not be rich in Au.

Gold can be both insoluble and soluble in groundwater, for example, Ong and Swanson (1969) found Au in negative colloids of metallic Au, formed in the presence of organic acids, to be slightly mobile, whereas Curtin et al (1970) report adsorption of Au ionic species on Fe and Al-hydroxides and kaolinite, inhibiting its removal in groundwater. They also state that Au can be transported as organically protected colloids in waters of pH 4-9. The solubility of Au in humic acids is suggested by Manskaya and Drozdova (1968) to account for its concentration in coals.

The Au values in the Monkman coals are related to the ash content and follow Al_2O_3 and K_2O as do Mo, Cr, As and Co. Au is most similarly distributed with W, being enriched above that expected according to its ash content in sample 5337. Au appears to be associated with the clay minerals and particularly with illite. The high variability in the ashed samples may indicate the presence of detrital isolated flakes of Au.

In the Moose River Basin samples the highest Au values are in the clays with occasional high values occurring in the gravels. Au contents of the lignite ashes are low, generally less than 8 ppb. Pyrite samples contain less Au than the lignite samples. Some Au may be associated with the clay minerals, however the higher values are probably related to detrital gold flakes in the samples giving occasional isolated high concentrations. This is especially applicable to the gravels where detrital gold may occur together with the heavy minerals.

Lead

The mean Pb value for United States coals is 16 ppm (Swanson et al, 1977). Average values in the Monkman and Moose River Basin coals are 15.4 and 25.1 ppm respectively. The mean concentration in the Monkman sediments is 10.1 ppm. The Moose River Basin clays contain greatest average Pb values (34.4 ppm) and values are 29.5 and 14.0 ppm in the Moose River Basin silts and gravels respectively. The range of values is high especially in the Moose River Basin coals (5.0 to 155.0 ppm).

Previous studies on Pb in coals (for example Breger et al, 1955; Bethell, 1962; Brown and Swaine, 1964; Nicholls, 1968; Gluskoter, 1977 and Finkelman, 1980) have shown that Pb is predominantly inorganically associated. Finkelman summarizes the Pb-bearing mineral phases found in coals and concludes that it is variable with geographic location. Lead selenides are common in the Appalachian coals while galena is a more common constituent in coals from other areas. In sulphide-poor coals Pb was found to occur substituting for Ba (similar charge and size) in authigenic sulfates, carbonates, phosphates and silicates (Finkelman, 1980).

Pb follows K in igneous rocks and significant concentrations of Pb occur in feldspars and micas. Weathering of these minerals would release Pb into solution and the low concentrations in surface waters means that Pb is readily adsorbed on clay minerals (Correns, 1924; Krauskopf, 1956 and Lagerwerff and Brower, 1973), ferric oxides (Krauskopf, 1956) and organics (Krauskopf, 1956 and Swanson et al, 1966). Adsorption of Pb on clay minerals in freshwater deposits and weathering profiles is very common (Wedepohl, 1978). Koster (1966) found 400-1500 ppm Pb in kaolinite derived from the weathering of arkoses. Bogdanov (1965) found Pb associated with the "organic substance" of coal.

In the Monkman coals Pb correlates with Nb, Cu and to a lesser extent with Y and Co. In the sediments Pb correlates only with Ni. Dot maps produced by the SEM for a pyrite-rich section of S2-5, a coaly shale, showed Pb to have the same distribution as Fe (Plate 13) and it is therefore thought to either substitute for Fe in pyrite or occur as intergrowths of galena as contaminants in the pyrite. The correlations with Nb and Cu in the Monkman coals indicate association with the clay minerals and possibly the organic matter.

In the Moose River Basin clays and coals Pb correlates with no other elements. In the silts Pb correlates with Al_2O_3, Na_2O, L.O.I., Th and negatively with SiO_2. Pb in the gravels is highly correlated with U and to a lesser extent with Al_2O_3, MgO, TiO_2 and Zr. Pb in these samples is therefore more probably associated with the clay minerals (detrital fraction) and possibly also with the organics and heavy minerals. The lack of a significant correlation with any element in the Moose River Basin clays and coals may indicate several forms of occurrence in these samples, for example associated with pyrite or the organic matter.

Pb exhibits a slight basal enrichment both within the coal seams and in the sediments below the coal. This favours a syngenetic mode of deposition of the Pb.

Uranium

Average U content in coals worldwide is 1 ppm (Bertine and Goldberg, 1971), however anomolously high values are commonly reported in the literature (for example King and Young, 1956 and Lamb, 1982). Average contents in the Monkman and Moose River Basin coals are 2.11 and 1.60 ppm respectively. The value for the Monkman sediments is higher averaging 4.64 ppm. In the Moose River Basin highest average values are found in the clays (4.81 ppm) and the silts (4.76 ppm) with lowest average contents in the gravels (1.46 ppm).

High U values in sediments and coals are commonly associated with the presence of organic matter. A simple experiment run on crushed and uncrushed Moose River Basin lignite revealed that the U from a 100 ppm U solution was adsorbed by the lignite within the first few hours of contact. U is therefore readily adsorbed by coal. U occurs in many forms in coals and coaly substances, however there appears to be a strong association with the organic material and particularly with the humic acid fraction of coals (Breger et al, 1955; Szalay, 1964: 1974; Gluskoter et al, 1977; Kuhn et al, 1978; Cecil et al, 1979; Borovec et al, 1979; Halbach et al, 1980 and Hurst, 1981).

U in coal is thought to be derived from the fluids circulating through the system. In these waters U may be carried as chloride complexes or as suggested in Van der Flier and Fyfe (1985) (Appendix II) as simple organic complexes. U may be introduced syngenetically in which case it will be uniformly distributed throughout the coal, or epigenetically. Epigenetic U tends to be concentrated in the upper levels of coal seams (Denson and Gill, 1956 and Vine, 1962), and generally occurs in mineral phases such as uraninite or coffinite (Breger, 1974). Ackers et al (1978) list fifteen U-bearing minerals from low rank Western United States coals, however Finkelman (1980) states that this mode of occurrence is of relatively little importance in non-uraniferous coals. Finkelman (1980) used the Lexan technique to determine the mode of occurrence of U in coals. His results suggest that most of the U occurs dispersed probably in organic combination in the coal. Approximately 20% was found in zircons (see also Hurlay and Fairbain, 1957). Finkelman also reports significant amounts of U occurring in a number of R.E. phosphates.

U in the Monkman coals correlates with SiO_2, TiO_2, Al_2O_3, K_2O, Cr, V and negatively with LOI. These major elements are important components of clay minerals particularly illite and U is thought to occur as with V and Cr adsorbed onto the clay minerals. The negative association with

LOI or organic matter substantiates the conclusion that U is associated with the mineral fraction of the coal. In the undifferentiated Monkman sediments U exhibits no correlations with any other elements. This may imply that U is associated in different ways in the various sediment types (as is found in the Moose River Basin samples) or that U occurs in many forms in each group, for example associated with both the clay minerals, heavy minerals and with the organic matter.

In the Moose River Basin lignite U is correlated most highly with Th (which is correlated with Al_2O_3) and also with TiO_2, Sr, to a small extent with Cu and negatively with S. No mineral phases of U have been detected with the SEM-EDX and U is thought to occur associated with the clay minerals, possibly kaolinite and also perhaps with a carbonate phase.

The U in the gravels is associated with the detrital heavy minerals such as zircon, rutile and chromite and also with the clay minerals (correlation coefficients are high with Al_2O_3, TiO_2, Zr, Th, Cu, Pb and to a lesser extent with Zn). Halbach <u>et al</u> (1980) found U to be associated with zircon etc. in the Brocken granite. The Moose River Basin sediments are derived from granitic material and the heavy mineral phases are proposed as the source of the U. Loss of U relative to Th in these materials is evidenced by the high Th/U ratios. If we assume that the U in solution, derived from the weathering of the heavy minerals, is adsorbed onto the clay minerals and partly onto the organic matter in the surrounding sediments, then this explains the low Th/U ratios found in these materials.

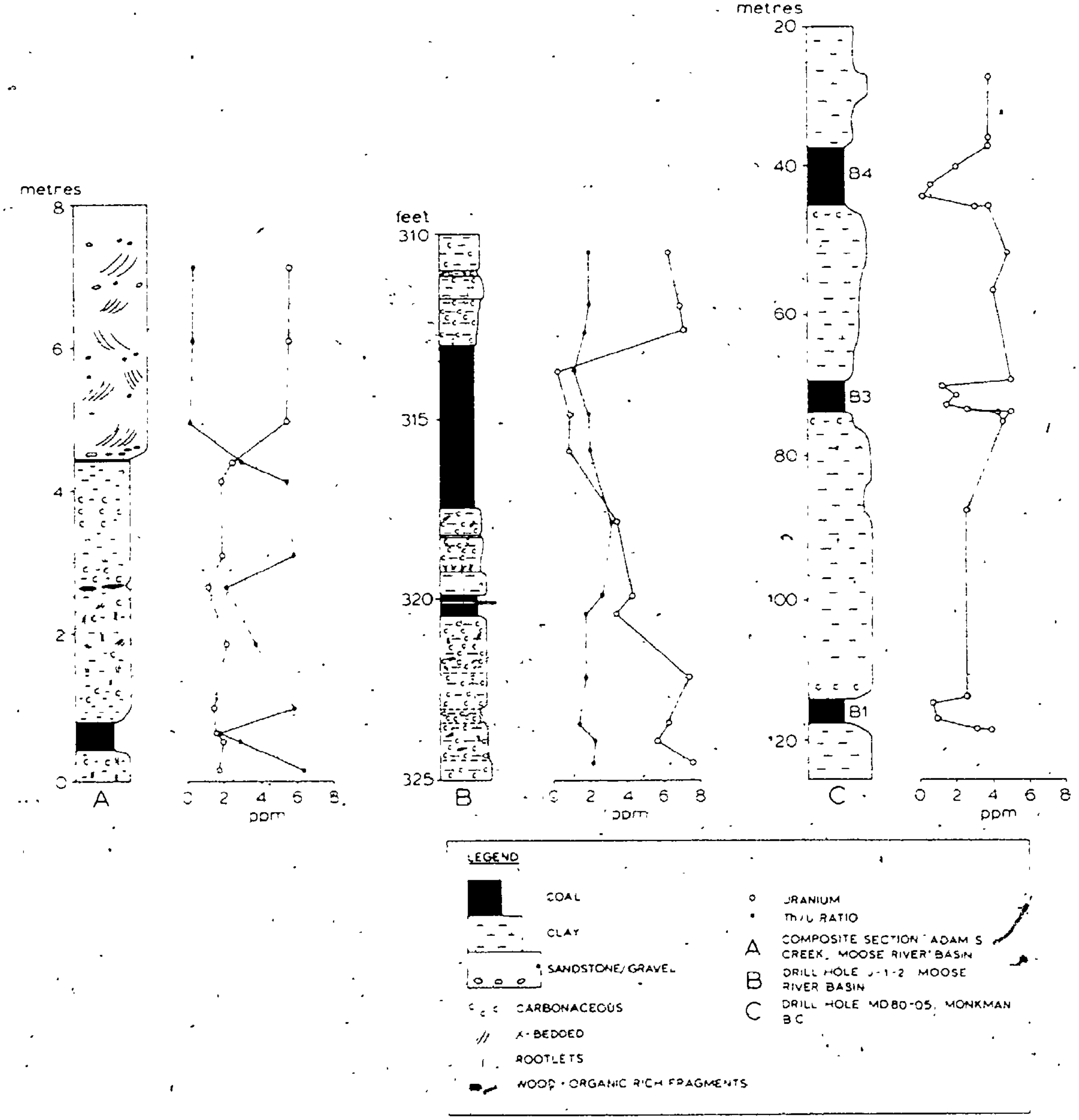
U in the Moose River Basin clays correlates with Cu and to a lesser extent with Ni. Low negative correlations exist for MgO and K_2O. Cu is associated at least in part with the clay minerals in these samples but the lower coefficients indicate that adsorption onto clay minerals is not the only mode of occurrence of the U and the Cu. The increased U contents in the coaly or carbonaceous clays indicates that U may also be associated with the organic matter in these samples. In Van der Flier and Fyfe (1985) it was suggested that organic complexes transporting U may be adsorbed onto the clay minerals and/or bonded onto the organics resulting in highest U concentrations in the organic-rich clays and shales.

In representative vertical profiles (Figure 5.3) from the Moose River Basin and Monkman areas, it is evident that U is depleted in the coal seams relative to the other sediments. If the U is predominantly associated with the clay minerals and the detrital heavy minerals it follows that since these phases are less abundant in the coals U will also be depleted. U may have been adsorbed to a greater extent onto the organic material at some stage in the history of the coal but the high porosity of this lithotype coupled with high rates of water flow through the system may have leached the U from the coals. Clays tend to be less porous and thus the U remains concentrated in these sediments. There is no net increase or decrease in U content in the sections, therefore the U must have been introduced during the early stages of deposition and coalification of the materials rather than epigenetically.

Thorium

Average Th content for United States coals as determined by Swanson <u>et al</u> (1976) is 4.7 ppm. Average values in the Monkman and Moose River Basin coals are 3.0 and 2.7 ppm respectively. The contents in the

Figure 5.3 Representative vertical profiles from Monkman and the Moose River Basin, showing U and Th/U distribution with depth and lithology



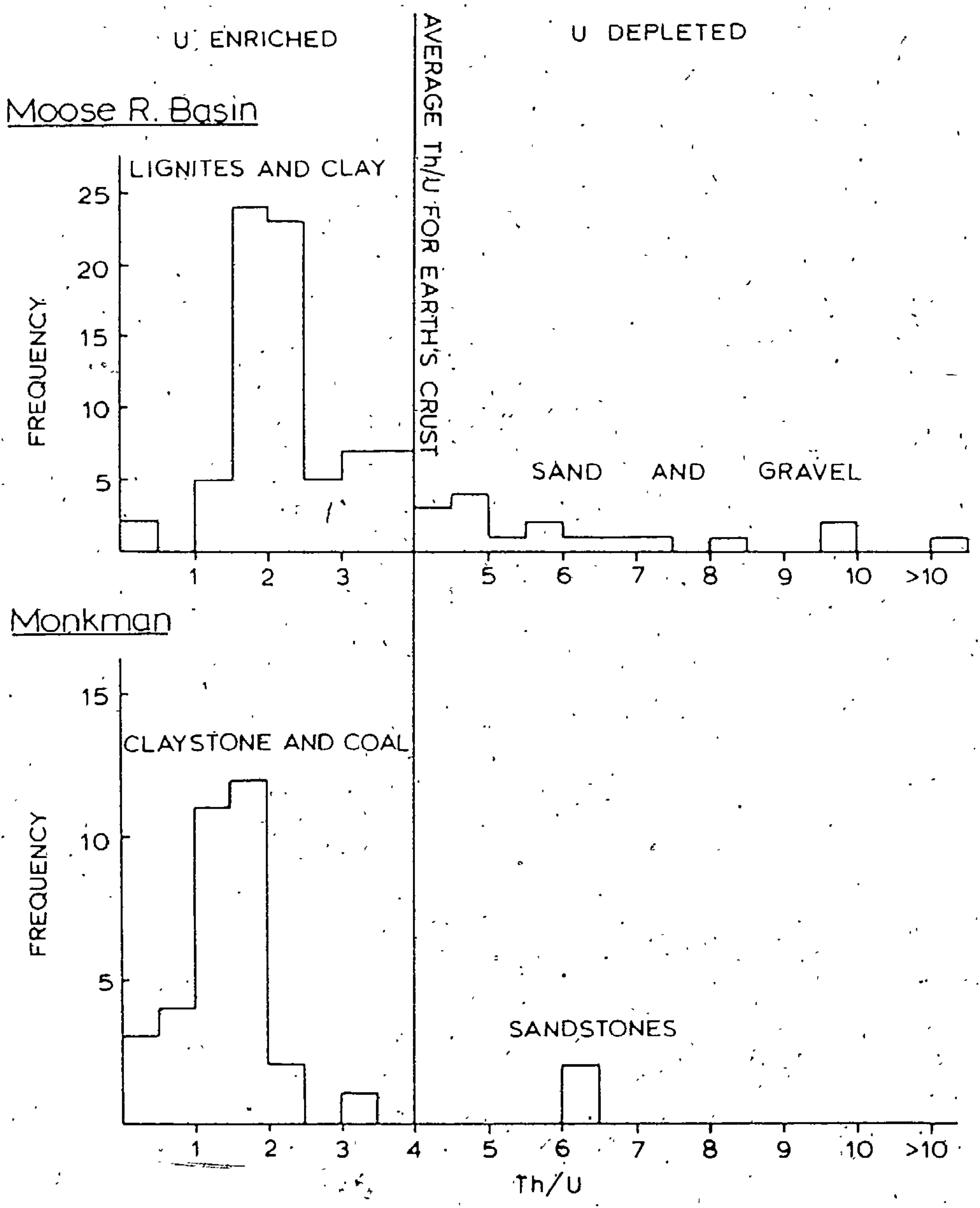
sediments are significantly higher with averages of 6.8 ppm in the Monkman sediments and 11.5, 9.1 and 6.9 ppm in the Moose River Basin clays, silts and gravels respectively.

Th/U ratios for all the samples analysed were calculated and their distribution is shown in Figure 5.4. Values range from 16.15 to 0.02 and are less than average crustal ratios in all but the Moose River Basin gravels and some of the coarser Monkman sediments. This indicates that Th is enriched relative to U in the gravels while in all the other samples U is enriched relative to Th. Th is known to be relatively immobile in the weathering process and the source of the Th is thought to be (as with U), zircons and detrital heavy minerals. Th is found in the Moose River Basin gravels to be highly correlated with TiO_2, Zr, Cr and to a lesser extent with U, confirming an association with the heavy mineral suite. The high Th content in the clays may be explained by the common occurrence of zircons in these sediments or by some mobilization of Th in the system (Langmuir and Herman, 1980). Th correlates with U in many of the sediments and may therefore follow U in being adsorbed onto clay minerals and possibly organic matter in the coaly clays.

In the Moose River Basin lignites Th correlates with Al_2O_3, TiO_2, SiO_2, Cu, U and negatively with S and therefore occurs adsorbed onto the clay minerals and perhaps to some extent associated with the detritals such as quartz and rutile. Th in the Moose River Basin clays is not correlated with any other element indicating several modes of occurrence possibly including association with the clay minerals, the organic matter or with the remaining detrital heavy minerals.

Gluskoter et al (1977) found Th in coals to exhibit a strong inorganic affinity. This conclusion is supported by Filby et al (1977)

Figure 5.4. Distribution of Th/U ratios in the Moose River Basin and Monkman samples.



and Finkelman (1980). In his study of the Waynesburg coal Finkelman (1980) found Th to occur predominantly in monazite grains. In addition the Th/Zr ratio, which he found to be equal to that cited by Taylor (1964) for the crustal average serves as evidence for the predominant detrital source for the Th. Baranov and Titayeva (1961) found that in the organic-rich sediments they studied Th was introduced in detrital and colloidal materials. Finkelman (1980) found Th in some coals occurring in zircons, xenotime grains and one RE phosphate. In addition he states that Th may also be associated with the clay minerals. Kuhn *et al* (1978) found Th to have organic tendencies.

CHAPTER SIX

DISCUSSION

In this study trace element associations in the coals and sediments of the Moose River Basin and Monkman are examined. Table 6.1 provides a summary of the results obtained for each element in each sample group. Table 6.2 shows the element suites (or groups of elements which are strongly correlated) identified in each sample set.

Differences in the sedimentology and mineralogy of each area are discussed in chapters three and four. Aspects of these and other factors thought to have influenced the concentration and association of the trace elements in the two deposits will be discussed. Comparisons will also be drawn with other areas.

Tables 6.1 and 6.2 show that many elements including Ti, Ni and Mo are variably associated in different sediment types and also in the different areas. Major variations in element concentrations were also observed between the sample groups.

Of the elements examined V, Ti, Rb, Cd, Y, Nb, Cr, As and Au appear to be associated entirely with the inorganic fraction in the samples. Of the other elements Sr, Zr, Ga, Pb, Cu, Zn, Ba, Ni, Co, Mo, W, Cl, U and Th may be in part associated with the organic matter in some of the sample groups. Clay minerals are important element sites in both the Monkman and Moose River Basin samples. Cu, Rb, Cr, Au and U are associated with clay minerals in almost all the sample sets. Elements such as Rb can substitute for ions in the clay mineral lattice while Cu and U may occur adsorbed onto the clay mineral surface. Heavy minerals appear to contribute elements such as Zr, Ti, Cr and in some cases U and

Table 6.1 Summary of the element associations in the Moose River Basin and Monkman samples

	MOOSE RIVER BASIN			MONKMAN	
	LIGNITE	CLAY	GRAVEL	COAL	SEDIMENTS
P		carbonate	carbonate clay minerals	calcite barite	calcite
Cl	organics	inorganics chlorides	NA	NA	NA
Ti	clay minerals	heavy minerals	heavy minerals clays minerals	clay minerals	clay minerals
V	NA	NA	NA	clay minerals	clay minerals
Cr	heavy minerals	partly in clay minerals	heavy minerals	clay minerals (illite)	clay minerals (illite)
Co	sulfides clay minerals	sulfides organics clay minerals	sulfides?	sulfides	sulfides
Ni	organics clay minerals pyrite		organics pyrite	clay minerals	sulfides galena
Cu	clay minerals	clay minerals	clay minerals	clay minerals sulfides organics	clay minerals
Zn	organics	organics clay minerals sphalerite	clay minerals	clay minerals sphalerite	sphalerite
Ga	NA	NA	NA	organics	clay minerals
As	sulfides	sulfides	NA	clay minerals sulfides	NA
Rb	detritals	illite feldspar	illite feldspar	illite	illite
Sr	carbonate clay minerals organics	carbonate phosphate	carbonate	carbonate barite	barite

(Table 6.1, continued)

Y	NA	NA	NA	heavy minerals clay minerals carbonate	heavy minerals clay minerals
Zr	pyrite organics	zircons clay minerals?	zircons	zircons clay minerals organics?	zircons clay minerals
Nb	NA	NA	NA	heavy minerals ankerite clay minerals	heavy minerals clay minerals
Mo	organics	organics	Fe-rich cements	clay minerals sulfides	NA
Cd	sphalerite	ND	ND	NA	NA
Ba	NA	NA	NA	barite calcite	barite calcite organics
W	sulfides organics	sulfides organics	NA	clay minerals sulfides	NA
PGE	detrital organics	detrital organics	detrital organics	NA	NA
Au	?	clay minerals	detrital	clay minerals	NA
Pb	organics?	organics?	clay minerals organics? heavy minerals	clay minerals organics pyrite?	pyrite
U	clay minerals carbonate	organics clay minerals	heavy minerals clay minerals	clay minerals	clay minerals organics heavy minerals
Th	clay minerals heavy minerals rutile	clays minerals organics heavy minerals	heavy minerals		

NA Not Analysed
ND Not Detected

Table 6.2 Element suites identified in the sample sets from Pearson correlation coefficients

Moose River Basin	Monkman
Clays	Sediments
SiO_2, Zr, -LOI, -S	SiO_2, -LOI
Al_2O_3, (Cr, Cu, -CaO, MgO)	TiO_2, Al_2O_3, Rb, Cr, (K_2O, Y, Cu, V)
CaO, MgO, Na_2O, K_2O, Rb	MgO, CaO
Fe_2O_3, MnO	Fe_2O_3, MnO, (-Na_2O)
TiO_2, Zr	
LOI, S, -Cr, (Mo)	
U, Cu, (Ni)	Ni, Co, Pb, MgO
Mo, Ni	Ba, Sr, (P_2O_5)
P_2O_5, Sr	

Lignite	Coal
SiO_2, Al_2O_3, TiO_2, Th Cu, Rb, -LOI	SiO_2, TiO_2, Al_2O_3, U, -LOI, (K_2O, Cr, Rb, Ni, Zn)
CaO, MgO, Sr, (TiO_2)	MnO, MgO, CaO, Nb, Y, Sr
Fe_2O_3, MnO, Zr, (Cr, Co)	Sr, Ba, (CaO)
TiO_2, U, Sr, Th, (Cu, -S)	Nb, Zr, Y, Rb, Cu, (Pb)
Cu, Th	

Table 6.2 continued

Gravel

SiO_2, $-Fe_2O_3$, -MnO, -LOI, -Ni

Al_2O_3, TiO_2, U, Cu, Zn

CaO, P_2O_5, Sr

Fe_2O_3, MnO, LOI, Ni, (S)

TiO_2, Cr, Zr, U, Th

K_2O, Rb

Zn, MgO, P_2O_5, Cu, -Th/U

Pb, S

Cu, Pb, Mo, Zn

Silts

SiO_2, $-Al_2O_3$, -LOI, -Pb

Al_2O_3, U, Pb, Cu

CaO, LOI, Sr

Fe_2O_3, MgO, K_2O, MnO, P_2O_5, Rb, Zr

TiO_2, Cr, Zr

Cr, Sr

U, Th, S

Co, Ni

Th to the samples. Elements such as Pb, Ni and Co do not have high correlation coefficients with any elements and are thus thought to occur in several forms. Association with the clay minerals, organics, sulphides, carbonates and/or the heavy minerals are examples of some of these.

Variations in concentrations of elements in the sample sets appear to support these relationships, for example Zn which is organically associated in the Moose River Basin lignites exhibits highest concentrations in this sample group. Rb, U, Th, Cu and Pb are most concentrated in the Moose River Basin clays, Co is highest in the gravels, Sr and Ni are high in both clays and lignites while Zr is equally concentrated in the clays and gravels. In the Monkman samples Zr, Rb, Zn, Cr, V, U and Th are more concentrated in the sediments while in the coals Nb, Sr, Pb, Ba and Ga are relatively enriched. Equal concentrations of Y, Cu, Ni and Co are found in the sediments and coals. The higher concentrations in either the sediments or the coals may be due to different detrital inputs, more favourable geochemical conditions for the precipitation or adsorption of that element, or the higher number of favourable sites in either of these groups. Competition for certain elements which are not very abundant in the ground waters may also be intense. For example U in the Monkman sediments can be adsorbed onto organics as well as clay minerals, and as U is low in these samples, sediments which contain both organics and clay minerals i.e. the carbonaceous clays are most enriched in U.

The element suites identified from the correlation matrices further emphasise these relationships as can be seen from Table 6.2. Clay mineral-forming major elements are associated with Cu, Rb, Th and others while carbonate-forming major elements are associated with Sr and occasionally Nb and Y. Similarly Zr and often Th and U are linked to the detrital heavy mineral suite which includes TiO_2 and is associated with SiO_2 representing the detrital matter.

Detrital input in the form of heavy minerals, clay minerals, feldspar etc., can be important in the concentration of trace elements in a coal. However due to the remobilization of trace elements in coal-forming environments element sources are often difficult to distinguish. Determination of the contribution of for example clay minerals to the trace element contents of a coal is facilitated by examination of the related sediments. Thus zircons can be identified as a source for the U in the Moose River Basin samples and systematics of U distribution can be derived.

Adsorption of trace elements onto clay minerals and organic matter from circulating ground waters is another important process in trace element accumulation in coals and sediments. Elements accumulated in this way tend to be preferentially distributed close to areas of increased permeability and porosity such as boundaries between different sediment types etc. Increased flow of circulating ground waters along coal/clay boundaries leads to marked marginal concentrations of elements such as V, Cr, Zn and Ni.

Plants contain significant inorganic material as shown in Table 4.7. Some of this may have contributed to the mineral and trace element contents of the coal and lignite. Organic associations of trace elements decrease as coal rank increases indicating that fewer sites are available and that trace element redistribution is taking place.

6.1 Element associations in the coal samples

Results shown in columns one and four in Table 6.1 can be compared with those of Table 6.3. This lists the results of studies on organic and inorganic affinities of trace elements in various coals. The variability of modes of occurrence of trace elements in coal is apparent. It is notable that many elements not only show variations between coals but also within a single deposit or seam. Thus organic and inorganic affinities have been noted for a single element in one coal deposit. This was also observed in the Monkman and Moose River Basin coals, for example Ni is associated with the organic matter or the clay minerals in Ni-poor lignites and with pyrite in lignites with higher Ni contents.

Finkelman (1980) attributes much of the variability to the occurrence of intimately dispersed accessory minerals in coal. Concentration of a particular trace element in a coal may also be important, for example where little U is present in a coal it may be associated with the organic matter or the clay minerals, whereas when present at higher concentrations separate U minerals such as uranocircite or uraninite tend to form. The same has been noted for Zn.

Generally the trace elements in the Moose River Basin and Monkman coals appear to be more commonly associated with the inorganics than is the case for the deposits listed in Table 6.3. This may be due to the higher inorganic content and detrital input of the Monkman and Moose River Basin coals. Also as mentioned previously the commonly used float sink method of determining organic and inorganic affinities incorporates a bias in favour of organic affinity of the elements.

Table 6.3 Summary of organic/inorganic affinities of trace elements in coal as determined by Goldschmidt, Zubovic, Nicholls, Gluskoter, Finkelman and Fairbridge

Element	Goldschmidt 1935	Zubovic 1966	Nicholls 1968	Gluskoter 1974	Finkelman 1980	Fairbridge 1972
P					I/O	I/O
Cl					O	
Ti		O			I/O	O/I
V			I		I	I/O
Cr		O/I	I	O/I	I	O
Co		O/I	I	O/I	I	I/O
Ni		O/I	O/I	O/I	I/O	O/I
Cu	I/	I/O	O/I	O/I	I	I/O
Zn	I/	I		I	I	I/O
Ga		O	O/I		I/O	I/O
As	I/		O/I	I	I	O/I
Rb					I	
Sr			I		I/O	
Y	I/	O/I			I	O/I
Zr					I	O
Nb					I	
Mo		I/O	O/I	I	I/O	O/I
Ba			I		I	I
W					O	
Pt					I	
Au					I	
Pb	I/		I		I	I/O
U					I/O	
Th					I	

O organically associated
I inorganically associated
I/O inorganically associated > organically associated
O/I organically associated > inorganically associated

6.2 Factors which affect mineral and trace element associations

Coal has a complex geochemical history. Many of the trace element characteristics observed in samples from present day swamps and in peat profiles (Manskaya et al, 1960; Erametsa et al, 1969; Sillanpaa, 1972 and Casagrande and Erchull, 1976) are overwritten by later geochemical events which the organic material undergoes. Thus trace element profiles characteristic of peat bogs are not observed in coal sequences. Redistribution of the trace elements and extreme mobility is the basis for the observed trends and patterns. The organic structure of the coal alters continuously throughout the depositional and coalification processes and thus original trace element associations and particularly organic associations may be destroyed. Changes in organic structure are also reflected in significant porosity variations which may influence water flow-through rates and thus mineralogy and trace element concentrations in the coals.

6.2.1 Depositional Environments

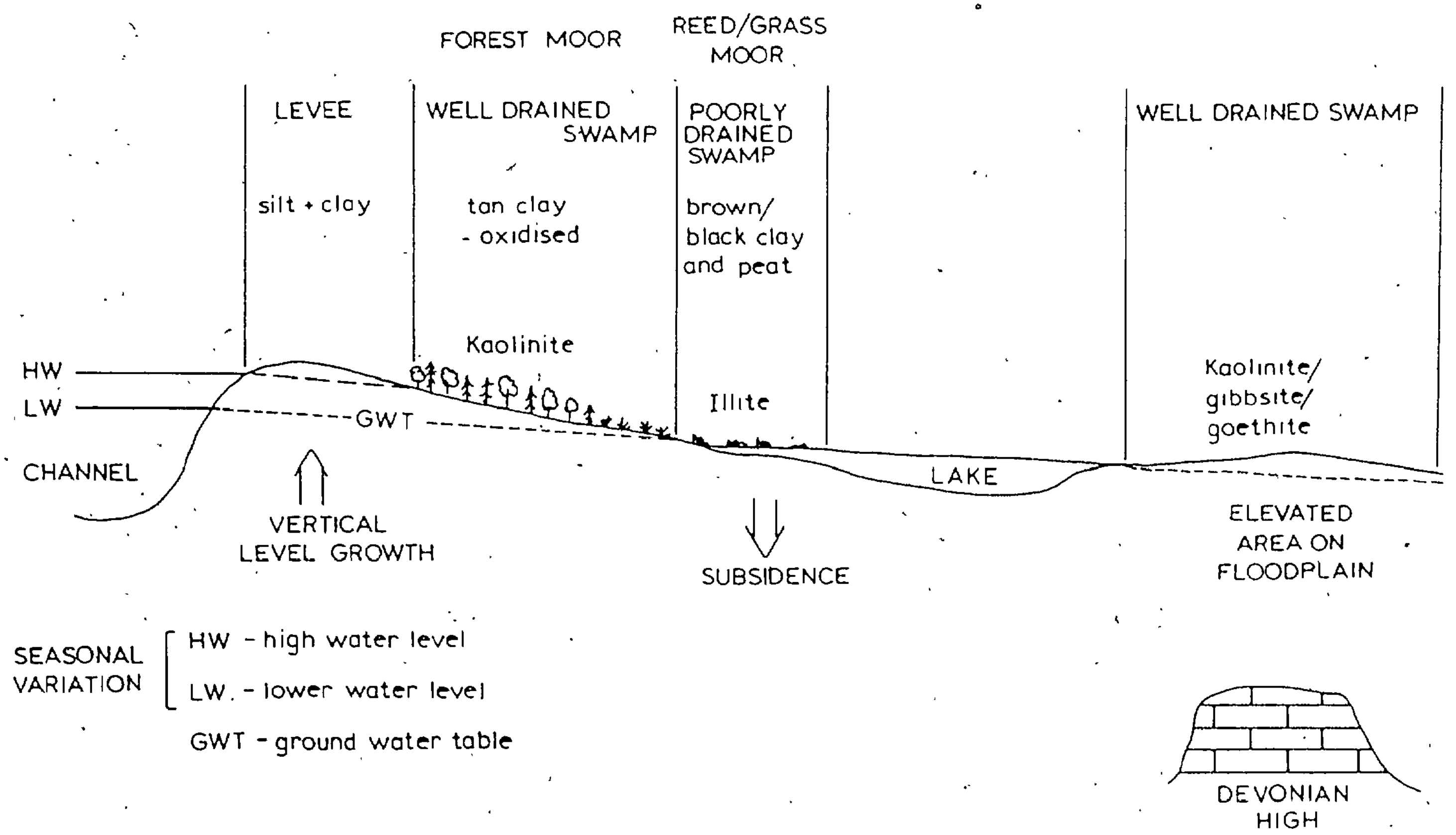
The effects of the geochemical conditions during the depositional and early diagenetic stages of coal formation can readily be identified from the mineral content and distribution in the sediments and coal. As mentioned in chapter four certain areas in the depositional environment are wetter and more oxidising or reducing than others. For example the levee sediments and crevasse splay surfaces have a mineralogy characteristic of acidic situations with periodically high water flow-through rates (alternating wet and dry). Minerals such as kaolinite and gibbsite occur in these sediments in the Moose River Basin. Illite forms in higher pH situations (where the water table is at or above the sediment surface) where the leaching of mineral matter is not so great.

Kaolinite and illite are thought to form in the sequences at approximately the same times (i.e. syngenetically) and a situation such as that shown in Figure 6.1 is proposed. On the elevated areas in the depositional environment kaolinite forms in preference to illite, while in the depressions and wetter zones illite forms. Where illite occurs, trace elements which may have flowed through or been leached from the kaolinite-forming zones may be adsorbed onto the illite and other minerals for example muscovite or siderite.

Marine influence can greatly affect the coal mineralogy and trace element content (Mansfield and Spackman, 1965; Horne et al, 1978; Cecil et al, 1981 and Styan and Bustin, 1983b). Clay minerals such as montmorillonite, smectites and illite are more common in marine influenced than freshwater coals (the same is also true for sediments, Olorunfemi 1983 and Olorunfemi and Fyfe, 1984). Williams and Keith (1963) and Horne et al (1978) have demonstrated that coals having marine roof rocks contain more S and pyrite than coals with roof rocks of freshwater origin. Although trace elements in these coals have not been analysed, it is thought that elements such as U, Mo, Cl and Na will also be enriched. This is due to the greater availability of these elements and the more alkaline conditions associated with brackish or saline waters.

The sub-environments of formation of the coal lithotypes also affect the element and mineral concentrations in these materials. Bone or stoney coal in the Gates Formation coal seams and soily lignite in the Moose River Basin, formed when the swamp was flooded and fine grained detrital material was deposited. Such sediments are rich in detrital components whereas the coal itself generally contains very

Figure 6.1. Some characteristics of channel-margin and floodplain sediments controlled by position and seasonal variation of the ground-water table.



(modified from Weimer and Land 1975)

little detrital material. The bright and bright banded lithotypes formed in relatively dry situations while the dull and dull banded lithotypes formed under progressively wetter conditions. Certain elements such as U are more likely to precipitate in the higher pH conditions of the wetter lithotypes than the more oxidised and acidic. Fusinitic material as mentioned previously requires extreme oxidising conditions to form and as a result of this, specific minerals and trace elements are concentrated in the cell cavities of the fusinitic material. In coal /lignite seams with predominantly dull or earthy lithotypes, the detrital input is great and this will be reflected in the trace element contents. Lithotype characteristics such as the porosity and nature of the organic matter (i.e. the types of organic molecules) will also influence the subsequent trace element distribution and concentration. Precursor vegetation which is different for each lithotype will contribute varying amounts of inorganic material to the system (see Table 4.7)

6.2.2 Groundwater

Coal is a porous and absorbent medium thus factors such as the groundwater composition must be of great importance. Groundwaters flowing through different rock types in each area will contain different elements in varying concentrations. Metal-rich peat deposits (such as the Cu-rich peat in New Brunswick, Canada, Fraser, 1961) can often reflect anomalies in the surrounding rocks. Marine influenced surface waters affect the geochemistry differently than nonmarine (Horne et al, 1978). This factor as well as rising groundwaters near the marine interface can be invoked to explain the high Mo and U concentrations observed in some Brazilian sulphide rich coals (Lamb, 1982; Forman and Waring, 1980 and Ayres, 1981).

The porosity and permeability characteristics of the sediments and coal will influence the quantities and rates of flow of the groundwaters through these materials. High porosity coupled with high rates of water flow through silts or clays will, given low SiO_2 activity and pH, lead to the formation of gibbsite rather than kaolinite or illite due to removal of leached cations. Also high permeability zones such as cleats in the bituminous coal are often the sites for precipitation of epigenetic minerals. As noted above, several trace elements concentrate towards the upper and lower boundaries of coal seams. This has been explained by higher groundwater flow along the coal sediment boundaries leading to greater interaction between the trace elements in solution and possible adsorption sites in the sediments and coal.

6.3 Comparison of the two deposits

The geological histories of the two coal bearing successions although they are of similar ages are very different. The Cretaceous sediments of the Moose River Basin are flat lying to gently warped while the Monkman sediments have been folded, thrust faulted and have undergone more compaction and diagenesis. Resulting from this, the rank of the coal, degree of diagenesis and subsequently the mineralogies are different in each area.

If percentage Al_2O_3 is used as a measure of the clay minerals present and percentage K_2O of the illite (feldspar is assumed to be equal in both areas), it is evident that illite is more common in the Monkman samples. Studies such as Farrah and Pickering (1979), have shown that on the illite clay mineral lattice there are more adsorption sites than on the more simple kaolinite lattice. Fewer elements are associated with the clay minerals in the Moose River Basin samples (Cu, Cr and occasionally U) while due to the higher number of adsorption and substitution sites available in the Monkman samples more elements occur in this way (Y, Rb, Cu, V and Cr) in these samples.

The trace elements introduced into the coal-forming swamp in the detrital heavy minerals will also differ as the source rocks differ. As shown in chapter four the mineralogy of the Monkman sediment is more complex than that of the Moose River Basin, however trace elements in the coal and clay thought to be derived from or associated with the heavy minerals are quite similar. A higher number of epigenetic minerals are present in the Monkman samples, thus ankerite in the coals is associated with some trace elements including Nb, Y and Sr.

The carbonaceous deposits of the Monkman area are more highly compacted and "coalified" than the Moose River Basin lignites. A significant number of elements are thought to occur in organic combination in the lignites while fewer elements are directly associated with the organic matter in the coal. It is thought that elements such as Zn which have high organic affinities may have at one time been associated with the organic matter in the Monkman coals, however during coalification the organic structure changes altering the Zn-organic bonds. Also studies by Moore (1950) and Cameron and LeClair (1975) have shown that lignites and lower rank coals adsorb higher proportions of U from aqueous fluids than do higher rank coals.

Stach et al (1982) note that humic acids which are present in peats and lignites do not occur in bituminous coals. Humic acids are thought to be important accumulators and adsorbers of trace elements (Manskaya et al; Szalay and Szilagyi, 1967; Szilagyi, 1971; Szalay, 1964; 1974; Schnitzer and Khan, 1972; Rashid, 1974; Nissenbaum and Swaine, 1976; Kerndorff and Schnitzer, 1980 and Scholkovitz and Copland, 1981) and thus the loss of these during coalification may release significant amounts of trace elements previously held in their structures. Elements subsequently released may be taken up by clay minerals or in the case of Zn may form epigenetic minerals such as sphalerite. Shotyk et al (1983) proposed that some elements, for example the platinum group elements and U, may have been transported into the swamp environment as organometallic complexes. These complexes might easily be incorporated into the decomposing plant matter leading to an organic association in the coal. Such associations, which may be evident in the lignite have an increased liklihood of being destroyed in the more advanced coalification stages required to produce bituminous coal.

The exact nature of the association of trace elements such as Zn, Mo and Ga with the organic matter is not known. The presence of humic acids is obviously very important in lower rank coals, while adsorption onto other organic molecules or complexation with the organics and the formation of chelate complexes may also be of significance (Reuter and Perdue, 1977; Swanson et al, 1966 and Vuceta and Morgan, 1978).

During the process of coalification from lignite to bituminous coal, the organic structure changes considerably. This is reflected in substantial porosity changes. Randomly oriented organic molecules in the lignite polymerise and become oriented in bituminous coals thus reducing the porosity. Through-flowing groundwaters will be less in the higher rank coals than in the lignites.

As mentioned above porosity and permeability characteristics are extremely important. This is particularly evident in the light of the almost catastrophic washing which the Moose River Basin sediments and lignite have undergone. These materials probably were flushed with great quantities of dilute water during each ice sheet retreat throughout the Pleistocene.

CHAPTER SEVEN

CONCLUSIONS

A detailed study of the Moose River Basin and Monkman sediments and coal has shown that trace element concentrations and associations are extremely variable. Elements which exhibit organic affinities in some of the sample groups are Sr, Zr, Ga, Pb, Cu, Zn, Ba, Ni, Co, Mo, W, Cl, U and Th. Of these Cl, Zn, Mo and Pb are associated entirely with the organics in the Moose River Basin lignites. Ga is the only element entirely organically associated in the Monkman coals.

The most common trace element occurrence is in association with the clay minerals, and in particular with illite in the Monkman samples. Less illite is present in the Moose River Basin samples and consequently fewer elements are associated with the clays. Kaolinite which is more common in these samples contains fewer adsorption sites and as it is syngenetically precipitated is cleaner than might be the case for detrital clay minerals.

Detrital heavy minerals such as zircons, chromite, rutile and rare earth phosphates host elements such as Zr, Cr, Ti, U, Th, Y and Nb. Some elements, for example U and Th are thought to have originally been present only in heavy minerals from which they were released and redistributed in the clays and coals.

Elements can exhibit several modes of occurrence in one sample group. Due to the mobility of trace elements in the coals and sediments, trace element sites may have been quite variable through time. For example an organically associated element such as Ni in the Moose River Basin lignites is also present in pyrite in more Ni-rich samples. This may reflect diagenetic concentration and redistribution. A similar situation was noted for Zn in the Monkman coals where it occurs associated with the organics as well as in sphalerite.

Association with the carbonates was noted for P, Sr, Y, Ba, and U in some of the sample groups. As the carbonate minerals are commonly epigenetic, these elements may have been introduced into the sediments at this late stage when the water composition was likely different or were redistributed from other sites and incorporated into the carbonates.

Several factors influencing the mineral and trace element characteristics of the sediments and coal have been proposed. These include variations between and within depositional environments, original vegetation type, composition of the groundwater and flow patterns, nature of the surrounding rocks, diagenetic factors including depth of burial etc., coal rank and postdepositional effects. The interrelationships of some of the above in the Monkman and Moose River Basin areas have been examined.

These coal deposits exhibit no anomalous trace element concentrations relative to values for other coals and sediments and as such are regarded as "normal" coals. Few studies have examined both sediments and coals from a single area. An important aspect of this study has been to trace the associations of elements in several sediment types as well as coal and thus to improve the understanding of the trace element systematics in a coal-bearing sequence.

Scope for Further Research

Fine grained mineral matter in coal is an important repository of trace elements. Methods have been developed to analyse such mineral matter e.g. SEM-EDX; however it is important to quantify the amounts present and more carefully examine their associations. Techniques such as TEM or SIMS may be appropriate.

In addition to this more detailed geochemical analyses of the different macerals, with a view to establishing the trace element contributions from different precursor vegetation would be of great interest.

Factors which influence the trace element concentrations in coals and sediments such as groundwater composition have been discussed. A detailed study of a single coal deposit and associated groundwaters (taking into account water composition and flow-through rates) would assist in unraveling the processes involved in this system. In this way minerals which are in equilibrium with the groundwaters can be identified.

More detailed geochemical studies of coals from different depositional environments (from back-barrier to lacustrine) preferably in a single deposit would be useful.

APPENDIX A: Table A.1 Whole sample mineralogy of Moose River Basin samples, as determined by X-ray diffraction

Sample Number	Quartz	Kaol-inite	Musc-ovite/illite	Mixed layer clay	Sid-erite	Gyp-sum	Feld-spar	Other
Drillhole 82-01								
L-1-22	P	L	-	-	-	-	-	
L-1-21	P	L-T	-	-	-	-	-	
L-1-19	P	P	VL	VVL	-	-	VL	
L-1-18	P	P	VL	VL	-	-	VL	
L-1-24	P	L	-	-	-	-	T	
L-1-23	-	VVL	-	-	-	L	-	L-pyrite
L-1-25	P	P	T	VL	-	-	-	
L-1-20	P	P	L	T	-	-	VL	
L-1-17	P	P	T	VL	T	-	-	T-VL-hematite
L-1-16	L	P	T	VL	-	-	-	
L-1-15	P	P	VL	VL	T	-	VL	
L-1-14	P	P	VVL	VL	T	-	-	VL-dolomite
L-1-13	P	P	VL	VL	T-VL	-	VL	
L-1-12	P	P	VL	VL	T	-	VL	
L-1-11	P	P	-	-	-	-	VL	
L-1-10	P	P-L	T	VL	-	-	VL	
L-1-9	P	L	T	T	VVL	VVL	VL	VVL-hematite
L-1-8	P	L	(VL) T-VL	T	-	-	-	
L-1-7	P	L	(T) T-VL	-	P	-	-	
L-1-5	P	-	(L-T) VL	VL	-	-	-	
L-1-6	P	-	(T) VVL	T	-	-	-	T-hematite
L-1-4	P	L-T	(T-L) -	VL	-	-	-	
L-1-3	P	-	-	VL	-	-	-	VL-hematite
L-1-2	P	-	(L-T) -	VVL	-	-	-	T-pyrite
L-1-1	P	VVL	(VL) T	VL	-	-	-	

(Table A.1 continued)

Drillhole J-1-2

L-2-27	P	P	-	-	-	-	-	T-hematite
L-2-28	P	P	VL	VL	-	-	-	
L-2-26	P	P	VL	VL	-	-	-	
L-2-25	P	L	-	VVL	-	-	-	
L-2-23	P	L	VL	-	-	VL	-	
L-2-24	P	P	VL	VL	-	-	-	
L-2-20	P	T	-	-	-	-	VL	
L-2-19	P	L	VVL	VL	-	-	-	
L-2-18	P	P-L	-	VL	-	-	-	
L-2-17	L	L	-	VL	-	-	-	
L-2-16	P	-	-	-	-	-	-	
L-2-15	L	L	-	VL	-	-	-	
L-2-14	P	P	VVL	VL	-	-	-	
L-2-1	L	P	VL (VL)	VVL	-	-	-	
L-2-2	L	P	T	-	-	-	-	
L-2-3	P	L	-	VL	-	VL	-	
L-2-4	-	-	-	-	-	-	-	
L-2-5	-	-	-	VVL	-	-	-	
L-2-6	L	P	-	VL	-	VL	-	T-pyrite
L-2-7	P	P	VL	VL	-	T	-	
L-2-8	P	P	-	VL	-	VVL	-	
L-2-9	P	P	-	VVL	-	-	-	
L-2-10	P	P	-	VVL	-	T-VL	-	
L-2-13	P	P	-	VL	-	-	VL	
L-2-11	L	L	-	-	-	-	-	
L-2-12	P	P	-	VL	-	-	-	
L-2-21	P	P	-	T-VL	-	-	-	
L-2-22	P	L	-	VVL	-	T	-	

(Table A.1 continued)

Location 12 Adam Creek

AC-29-82	P	T	-	-	-	-	-	
AC-22-82	P	L	VL	VVL	-	-	-	
AC-20-82	P	P	VL	-	-	-	VVL	P-geothite
AC-21-82	L	P	L	VL	P	VVL	VVL	(gibbsite-SEM)
AC-28-82	P	P	T-VL	VL	-	-	-	
AC-27-82	P	P	VL	VL	-	-	-	
AC-26-82	P-L	P	T-VL	VL	-	T-L	-	
AC-25-82	T	P	VL	VL	-	-	-	
AC-24-82	P	L	VL	VL	-	-	VL	
AC-23-82	P	P	T-VL	VL	T-VL	VVL	-	
AC-30-82	L	P	VVL	VVL	-	VVL	-	T-pyrite
AC-31-82	VL	L	-	-	P	-	-	T-rutile

Location 11 Adam Creek

AC-14-82	P-L	P	T-VL	VVL	-	-	-	
AC-17-82	P	P	VL	VVL	L-P	-	VL	
AC-15-82	P	-	-	-	T	-	-	P-pyrite near top VVL-dolomite
AC-16-82	L	P	T	VL	L	-	-	
AC-19-82	T	L	-	VVL	-	VVL	-	
AC-18-82	VL	P	VL	VVL	-	-	-	VL-gibbsite VVL-calcite

Location 3 Adam, Creek

AC-10-82	VL	-	-	VVL	-	-	-	P-pyrite T-millerite
AC-09-82	VL	L	VVL	-	-	-	-	
AC-08-82	P	L	-	VVL	-	-	-	
AC-07-82	P	P	-	VL	-	-	VL	VL-ilmenite

(Table A.1 continued)

Location 15 Adam Creek							
AC-32-82	P	T	-	-	-	VL	VL
AC-33-82	P	T	-	-	-	-	-
AC-34-82	P	P	T	-	-	-	-
AC-35-82	P	P	VL	VVL	-	VL	-

P major component
L minor component
T trace component
VL very little present
VVL almost negligible

(X) Mica

Table A.2 **Whole sample mineralogy of selected Monkman samples, as determined by XRD**

Sample Number	Quartz	Kaolinite	Muscovite illite	Mixed layer clay	Ankerite	Other
Drillhole MDD79-14						
S14-1	P	T	VL	-	L	VL-pyrite
1270	P	T	T-VL	VVL	-	VL-siderite, galena VVL-pyrite
S14-6	P	T	T	VL	-	VL-siderite, pyrite VVL-galena
S14-5	P	L	T	VVL	L	L-siderite
S14-9	P	T	T	VL	VVL	VVL-siderite, pyrite galena
S14-13 coal	L	T	VL	-	VL	VL-pyrite VVL-barite
1281	P	L	T	VL	-	T-galena
S14-18	P	T	T	VVL	VL	VL-galena siderite feldspar
1283	P	T-VL	T-VL	VVL	T-VL	VL-pyrite
1294	L	VL	L	-	T	T-calcite VL-siderite barite feld
1296	T	-	VVL VL	-	T-VL	VVL-barite feldspar
S14-19	P	T	T	-	-	VVL-siderite gypsum galena
S14-20	P	VL	T-VL	VL	L	T-calcite VL-siderite hematite
Drillhole MD 80-05						
S5-5	P	T-VL	L-T L	-	-	VL-siderite galena, feldspar VVL-pyrite
5307	L	T	T-VL	VL	VL	VL-siderite, calcite
5308	L	VL	-	VL	-	VVL-pyrite galena ankerite siderite
5309*	-	-	-	-	-	
5310	P	T	VL	VL	-	
S5-7 coal	P	T-VL	T	VVL	-	VL-galena siderite
S5-2	P	T	T	VL	-	VL-pyrite, galena calcite siderite barite
5305	L	VL	-	VL	T-VL	T-feldspar T-VL-siderite
5306	T	VL	VVL	VVL	-	VL-siderite
S5-1	P	VL	T L	-	-	VL-gypsum, galena VVL-calcite, marcasite, barite, feldspar
S5-1*	L	T	L	-	-	

*clay only

(Table A.2 continued)

Drillhole MD 80-02						
S2-7	P	T	VL	-	T	T-calcite VL-pyrite, siderite
5290	P	VL	T (L-T)	VVL	VL	T-feldspar, siderite VL-galena
5291	P	T	T	VL	-	T-siderite, feldspar VL-calcite
5292	P	T	L (L)	-	VL	T-siderite, galena VL-calcite, feldspar
S2-6	P	-	T-L (L)	VVL		T-VL-siderite, galena VL-calcite VVL-feldspar, pyrite
S2-2	P	VL	T (L)	VL	VL	VL-siderite, calcite, galena VVL-feldspar, barite, pyrite
Drillhole MD 80-01						
S1-1	P	T	T	VL	-	
(coal)	P	VL	T (L)	VL	VVL	VVL-galena
5361	P	T	VL	-	-	VL-siderite
5343	T	VL	VL	VL	-	
5341	P	VL	-	-	T	VL-siderite
5337	P	T	VL	-	-	VL-pyrite
5338	T	VL	VVL	VVL	VVL	VVL-pyrite, calcite, feldspar /barite
Drillhole MD 80-03						
5354	L	-	VL	VL	T	VL-calcite, VVL-siderite
5355	L	T	VVL	VL	VL	VL-feldspar, siderite
S3-6	P	VL	T (T)	VL	P	T-marcasite, VL-calcite

P major component
L minor component
T trace component
VL very little present
VVL almost negligible

(X) Mica

URANIUM THORIUM SYSTEMATICS OF TWO CANADIAN COALS

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ABSTRACT

A detailed study of U-Th distribution in two Lower Cretaceous coals in Canada shows that for these coals formed in a continental fluvial and deltaic environment with no marine influence, the U contents are in the range 0.07-7.5 ppm with Th in the range 0.3-11.0 ppm. Average Th/U ratios are near 2 which indicates slight uranium enrichment. The environments of the two coals show different degrees of weathering (montmorillonite-illite and kaolin-gibbsite) and U values are lowest in the more weathered environment. In sedimentary profiles associated with the coals, the maximum uranium values are not in the coals but in carbonaceous clay sediments above and below coal seams. Uranium distribution patterns can be correlated with Ni, Cu, Rb, Pb, Sr, and Zr, indicating contributions from heavy minerals plus more mobile species (possibly simple organic compounds) which are adsorbed or bonded onto clays or organic matter.

INTRODUCTION

High uranium values have been observed in coals from various parts of the world, e.g. S. Dakota, S. Brazil, Warwickshire, G.B., etc. The average concentration of uranium in coals world-wide is 1.0 ppm (Bertine and Goldberg, 1971 and U.S. Env. Prot. Agency, 1975) but values as high as 10% have been reported in coal material (King and Young, 1956). This large range is attributable to a variety of factors including coal rank, chemistry of the groundwater, local hydrology, enclosing lithologies, rate of weathering of the surrounding rocks, and depositional environment.

Two coals were examined in this study. A Cretaceous bituminous coal from the Peace River Basin in N.E. British Columbia and a Cretaceous lignite from the Moose River Basin in N. Ontario. The coals and a variety of sediments were analysed for uranium, thorium, major and ten additional trace elements. Mineralogy was determined by X-ray diffraction.

The objective of this study was to establish

a) the concentrations of U in the coal and associated sediments

b) the siting of the U in the coals

c) any associated trace elements or trace element suites

d) the characteristics of the Th/U distribution relative to the general stratigraphy in both areas

e) possible relationships to the depositional environments.

The association of U with coal has long been known (Berthoud, 1935). Moore (1954) established experimentally the ability of carbonaceous materials to extract U from solutions, and showed that more than 98% of the U from a solution of uranyl sulfate (UO_2SO_4), containing 200 ppm uranium at a pH of 2.45 was taken up by peat, lignite and sub-bituminous coal. Proposed sources for uranium in coal have included the original plant material. Although enhanced concentrations of uranium have been found in plants growing in regions of uranium mineralization, e.g. 160 ppm U in the ash of oak leaves (Dean, 1966), 1.5-1000 ppm U in ashes of New Zealand shrub Copromosa Australis

(Whitehead and Brooks, 1969), uranium is generally considered an abiogenic element. Average uranium values in terrestrial plants are characteristically low, 0.58-0.20 ppm U in ash (Dean, 1966), 0.6 ppm U in ash (Cannon, 1960) and 0.005-0.06 ppm U in plant dry matter (Bowen, 1979).

Most peats also show low average U values, for example Shotyk (1984) calculated an average of 0.2 ppm U for samples from several peat deposits. U in peat tends to concentrate at a definite level near the bottom of the bogs (Erameta et al., 1969). Preferential accumulation at this level may be attributed to U sorption from very dilute solutions in natural waters moving upward due to summer evaporation (Taylor, G. H., 1979; Erameta et al., 1969). Peat bogs do not exhibit the near surface U concentrations that would be related to enrichment by living plants.

Following the trend of low U contents in plants and peats, most coals are also uranium poor, however, higher U values are found in coals affected by U-rich waters during and/or after coal deposition.

Most workers now agree that U in coal is derived from circulating-ground waters, where it may travel as the Uranyl ion UO^{2+} (Breger and Duel, 1956), as an alkali uranyl carbonate (Breger, 1974) or as various organo-uranyl complexes (Germanov and Panteleyev, 1968).

Heavy liquid, acid leaching experiments, etc., have demonstrated that U is associated with the organic material and particularly with the humic acid fraction in coals (Hurst, 1981;

Halbach et al., 1980; Borovec et al., 1979; Breger, Duel and Rubinstein, 1955; Zubovic, 1976, 1961). Breger and Duel (1956) proposed three ways in which this may occur. Where

1) the organics act as reducing agents converting soluble UO^{2+} to the insoluble uranous form,
2) the coal decomposition products, e.g. H_2S act as a reducing agents,
3) the carbonaceous material adsorbs U from the ground waters resulting in organo uranium complex formation.

Szalay (1964, 74) found the cation exchange properties of humic acids to be responsible for U accumulation. As this is a reversible process Kochenov et al. (1965) proposed that cation exchange in a continuous reducing environment could lead to the observed U contents in peats. Breger, Duel and Rubinstein (1955) found U in the S. Dakota lignite to be held in organo uranium complexes. Davidson and Ponsford (1954) found the U in coal to cumulate predominantly by sorption which then results in organo uranium complexes. Such complexes have been reported intact from Precambrian carbonaceous material from Cluff, Saskatchewan (Bonnamy, Olerin and Richet, 1982). Gruner (1956) described colloidal size coffinite and uraninite in the Fort Union lignite. These colloids form when U bearing solutions are introduced into the coal along fractures and shrinkage cracks, and adsorption of the U on the coal leads to the formation of complex U compounds which may later be reduced to U minerals (Breger, 1974; Kononova, 1966). Clearly several stages and processes may be involved in U accumulation in coal. Initial adsorption may be followed by formation of organo uranium complexes or colloids.

GENERAL GEOLOGY

The Moose River Coal Basin is situated in the Cochrane District of N. Ontario, about 50 miles south of Moosonee, between 82° and 83°W longitude, and 51° and 51°30'N latitude. The sediments are from the L. Cretaceous Mattagami formation and include lignite, clays, silt, sandstone and gravel. The section examined at Adam's Creek, can be subdivided into an upper kaolinitic quartz gravel unit overlying a finer grained sequence of silts, clays and lignite. The depositional environments are fluvial channel and floodplain/swamp respectively possibly in an anastomosing river situation (Fyfe et al., 1983; Try, 1984 and Try et al., 1983).

The Monkman coal deposit lies in the Rocky Mountain Foothills belt, approximately 60 miles W. of the B.C./Alberta border, and S. of Dawson Creek, at approximately 120°44' longitude and 54°48' latitude. Samples are from the L. Cretaceous Gates Member which at Monkman contains twelve bituminous coal seams together with clay, coaly clay, silt, carbonaceous sandstone, and rare conglomerate. The materials were deposited in a lower to upper delta plain environment (Carmichael, 1982).

METHODOLOGY

Samples were obtained from recently exposed outcrop and drill core at Moose River and from drill core at Monkman. The samples were airdried and crushed to a -200 mesh size fraction, some relatively undegraded wood samples were ashed in open porcelain crucibles over a bunsen burner and subsequently ground.

Approximately 200 samples were analysed for U by Delayed Neutron Counting. Th was analysed in 85 of these by Induced Neutron Activation Analysis. This work was carried out by Nuclear Activation Services, Hamilton, Ontario. Detection levels were 0.01 and 0.3 ppm for U and Th respectively. Major and trace elements were analysed by X.R.F. The Monkman samples were analysed at the University of Western Ontario and the Moose River samples at X-Ray Assay Labs, Don Mills, Ontario. Mineralogy was determined using X.R.D. accompanied by some S.E.M. and thin section work.

MINERALOGY

The dominant minerals in the Moose River Basin sediments are quartz and kaolinite. Trace gibbsite was detected in one sample (AC-18-82). This mineralogy indicates a highly weathered continental situation. Secondary minerals such as pyrite, calcite and siderite are also abundant in some of the samples. The lignites and sediments are relatively unconsolidated and flat-lying.

The Monkman materials contain predominantly quartz, illite and montmorillonite with minor secondary calcite, ankerite and pyrite. Illite occurs in less weathered environments or as an alteration product of kaolinite and/or montmorillonite with increasing depth of burial. The Monkman sandstones often contain coaly stringers and wisps, which contrasts strongly with the organic free Moose River Basin gravels and sandstones. These sediments are well consolidated and are structurally deformed. No discrete U minerals were found in any of the samples.

RESULTS AND DISCUSSION

The results of the U and Th analyses are listed in Tables 1, 2 and 3. Tables 1 and 2 give lithology, U and Th and Th/U where available for each sample from the Moose River basin and Monkman respectively. In Table 3 the samples have been divided by lithology into coal/wood, clay/silt and sand/gravel, with averages and ranges given for each group.

The range in U contents for all the samples is 11.3 to 0.05 ppm. Clays and silts contain the highest average U, i.e. 4.89 and 4.84 ppm in the Moose River and Monkman samples respectively. Within the clays highest values occur in the most organic rich samples (where the organics are either disseminated or occur as discrete fragments/rootlets). The average U content in the coals/woods is much lower, 1.63 and 2.45 ppm for Moose River and Monkman respectively. This decrease in U content in the coal is also evident in vertical logs drawn from both study areas (Fig. 1). 1.08 and 2.76 ppm are the average U values for the Moose River and Monkman sands and gravels. The Th/U ratios are higher than for the coals or the clays, 5.41 and 5.19 in the Moose River and Monkman sands and gravels respectively. The average Th/U

TABLE 1 - U, Th and Th/U values by sample

Moose River basin lignites and sediments

	U ppm	Th ppm	Th/U	
AC-03-82	1.13	2.8	2.48	Wood from red sst
AC-04-82	2.65	6.9	2.60	Laminated mud silt, org-rich
05	(2.15)	(5.6)	2.60	Wood
06	1.88	7.1	3.78	Laminated mud/silt, org-rich
07	6.35	11.6	1.83	Clay with roots, brown
08	2.97	6.1	2.05	Lignite
09	1.88	3.2	1.70	Wood from lignite
10	0.13	2.1	16.15	Pyrite + wood
11	(0.35)	(1.27)	3.63	Wood
12	0.87	1.8	2.07	Laminated sst + coal
13	0.15	1.2	8.00	Pebbly sst
14	3.46	6.2	1.79	Banded silt and sand, + roots
15	0.97	2.2	2.27	Sandstone
16	5.29	9.4	1.78	Clay (tan)
17	4.13	9.6	2.32	Clay (tan)
18	6.83	15.2	2.23	Clay (light-brown)
19	8.43	12.7	1.51	Brown clay
20	3.15	10.0	3.17	Orange clay
21	4.81	11.0	2.29	Browny/blue clay
22	0.52	3.5	6.73	Gravel
23	5.39	9.9	1.84	Brown clay + roots
24	5.95	9.2	1.55	Brown clay
25	3.80	9.2	2.16	Silt + sst with roots
26	(2.23)	(2.86)	1.28	Wood
27	5.95	12.4	2.08	Brown clay
28	5.57	11.4	2.05	Clay (White)
29A	1.04	5.9	5.67	Gravel with clay
30	(0.43)	(0.66)	1.54	Wood
31	0.42	1.6	3.81	Clay (White)
32B	0.67	5.0	7.46	Gravel
32C	1.57	2.8	1.78	Iron-stained gravel
33	3.05	11.3	3.70	Clay (White)
34	6.72	8.3	1.24	Brown clay
35	(7.2)	(0.14)	0.02	Wood
Py	0.88	NA	- -	Pyrite nodule from gravel
RCI	0.59	NA	-	Red sst/gravel + wood
RP	0.24	NA	- -	Red sst/gravel with pyrite
OE1	2.56	7.3	2.85	Weathered lignite
OE2	0.07	< 0.3	4.29	Wood stump
OE3	0.29	0.7	2.41	Bark lignite
OE4A	0.33	0.3	0.91	Wood - inside
OE4B	1.10	2.5	2.27	Wood - outer portion
OE6	1.03	2.3	2.23	Wood
OE7	1.21	NA	-	Green clay
29 clay	2.39	10.9	4.56	Clay (White)
29 gravel	3.64	35.6	9.78	White gravel

NOTE: (   ) = values extrapolated from U. ppm in ash, assuming no U. loss on ashing.

Hole J-1-2

Sample No.	Depth Feet	U	Th	Th/U	clay
L-2-27	94.0	4.27	12.0	2.81	White+red+green+sst
L-2-28	94.8-95.1	4.31-0.00	9.8		White-yellow clay
L-2-26	226.8	10.4	12.0	1.15	Brown clay + silty sst
L-2-25	228.6	6.41	14.0	2.15	Med. sst (clay + org rich)
L-2-23	254.85	0.97	5.6	5.77	qtz. gravel
L-2-24	255.1	7.23	11.0	1.52	tan silt + orgs
L-2-20	297.8	0.34	2.1	6.18	white silica sst
L-2-19	298.8	0.85	3.0	3.53	tan-grey org rich sst
L-2-18	299.0-299.3	5.96	11.0	1.85	black earthy lignite + woody
L-2-17	300.0	0.80	1.3	1.63	woody lignite
L-2-16	301.8	0.52	1.2	2.31	v. woody lignite
L-2-15	302.4	2.29	6.3	2.75	earthy lignite
L-2-14	303.9	6.56	13.0	1.98	white (+ brown) clay
L-2-1	310.3	6.65	14.0	2.11	med. dk brown clay + few orgs
L-2-2	311.7	7.25	16.0	2.21	lt. grey. tan clay + orgs
L-2-3	312.5	7.49	14.0	1.87	black v. org. rich clay
L-2-4	313.6	0.51	0.7	1.37	woody + peaty lignite
L-2-5	314.8	1.18	2.5	2.12	woody + peaty lignite
L-2-6	315.8	1.09	2.4	2.20	woody + soily lignite
L-2-7	317.8	3.59	12.0	3.34	dk. grey clay + orgs
L-2-8	319.85	4.40	12.0	2.73	dk. grey original clay
L-2-9	320.35	3.54	6.5	1.84	black clay
L-2-10	322.15	7.43	14.0	1.88	org rich black clay + silt lens
L-2-13	322.85	NA	NA	NA	med. dark grey clay
L-2-11	323.4	6.28	9.1	1.45	dk. grey+black clay, much wood
L-2-12	323.9	5.73	13.0	2.27	dk. + lt. grey banded clay + wood
L-2-21	324.5	7.59	16.0	2.11	med. grey clay
L-2-22	343.0	1.30	2.5	1.92	lignite earthy + silt lenses

Hole 82-01

Sample No.	Depth Feet	U	Th	Th/U	
L-1-22	172.5	1.54	5.0	3.25	quartz gravel
L-1-21	200-185	0.77	7.4	9.61	sandy gravel
L-1-19	237.1	5.34	10.0	1.87	dark grey silt (banded v.f.)
L-1-18	238.9	4.73	9.7	2.05	dark grey silt + org. mtl.
L-1-24	245.1-244.9	0.53	2.9	5.47	sandstone
L-1-23	245.6	0.14	<0.3	<2.14	lignite
L-1-25	247.1	5.25	8.2	1.56	lignite underclay
L-1-20	255.0	4.77	9.1	1.91	banded silt + orgs.
L-1-17	258.3	5.07	9.1	1.79	med.-dark grey silty clay + orgs.
L-1-16	260.0	6.36	12.0	1.89	dark grey silty clay
L-1-15	274.0	4.49	9.8	2.18	light grey silt
L-1-14	276.0	4.86	8.9	1.83	light grey silt
L-1-13	278.8	4.64	8.8	1.90	med. grey silt
L-1-12	285.5	3.91	9.4	2.40	v.f. sst (mainly silt)
L-1-11	303.5	1.82	6.6	3.63	med./fine sst + silty sst poorly sorted
L-1-10	323.5	4.15	13.0	3.13	red + green clay
L-1-9	327.9	2.85	13.0	4.56	red + green clay
L-1-8	333.1	2.08	8.1	3.89	green + yellow clay
L-1-7	342.0	3.34	6.8	2.04	yellow + green clay
L-1-5	348.2	2.32	10.0	4.31	green grey clay + orgs.
L-1-6	358.05	3.20	11.0	3.44	red + lt. green clay
L-1-4	359.1	3.83	13.0	3.39	green grey clay (little orgs.)
L-1-3	366.0	3.79	13.0	3.43	yellow/grey clay
L-1-2	373.8	3.23	15.0	4.64	orange red clay
L-1-1	382.5	2.89	14.0	4.84	red + grey green clay

TABLE 2 - U, Th and Th/U values by sample
Monkman, B.C.

MD 80-01

Depth (metres)	Sample Number	U	Th	Th/U	
42.70- 42.73	S1-8	2.64			coal in v.c. sst
48.65- 48.75	S1-7	4.62	2.7	0.58	coal + coarse sst
57.22- 57.30	S1-6	7.40			coal + clay
70.20- 70.35	S1-5	4.17			ground coal + clay
79.35- 79.55	S1-4 coal	4.33			stoney coal
	clay	5.85			clay
86.59- 86.64	S1-3	6.41	7.8	1.22	coaly silt
88.90- 89.19	5344	5.96	7.2	1.21	B5 repeat
90.11- 91.92	5347	3.27	5.5	1.68	
92.90- 92.97	S1-1	3.69			clay + coal stringers
93.07- 93.28	S1-2	4.41			clay + coal
124.41-124.65	5361	4.62	9.0	1.95	B5
127.33-130.18	4343	0.81	1.7(1.5)	1.98	
153.61-155.02	5340	1.24	2.1	1.69	B3
155.02-156.91	5341	1.44			
193.78-194.24	5337	1.76			B1
194.24-195.80	5338	0.83			

MD 80-02

30.25- 30.35	S2-7	2.74			coal + clay
31.30- 31.55	5290	4.92			B3
31.55- 32.05	5291	3.10(3.03)			
32.05- 32.70	5292	4.93			
32.70- 32.85	2-6	5.52			clay
76.49- 76.50	S2-5	2.67			dull coal + v.f. sst
76.72- 76.80	S2-4	1.70	5.7	3.35	stoney coal + clay
76.80- 78.10	5294(A)	0.65	1.2	1.85	B1
78.10- 79.87	5295	0.96	2.0	2.08	
79.97- 80.30	5296	4.90	8.7	1.78	
80.30- 81.79	5297	2.20	3.8	1.73	
81.79- 81.83	S2-3	3.99	<0.3	0.075	coal + coaly clay
86.32- 86.37	S2-2	4.96			clay, coal + M. sst
97.60- 97.67	S2-1	2.33			coal + coarse sst

MD 80-04

4.95- 5.66	5303	2.44			B3
5.66- 6.20	5304	1.99			
56.45- 57.09	5299	0.88			B1
59.06- 60.77	5301	0.48			

Hole MD 80-03

Depth (metres)	Sample Number	U	Th	Th/U	
26.32- 26.20	S3-12^{T}	2.04			fine sandstone
	$_{B}$	2.87	3 2	1.11	coal
29.82- 29.76	S3-11	3 36			fine sst + coal
37 05- 37.15	S3-10	4 20			clay + silt
39.14- 39.34	S3-9	9.98	10.6	1.06	clay + coal
39.61- 42.07	5348	2.77			
42.55- 43.03	5349	4 09			
43 03- 43.70	5350	3.49			B4 seam
43.90- 44.34	5351	5 29			
44.34- 46.52	5352	2 66			
46.60- 48.01	5353	2.21			
48.01- 50.90	5354	0.47			
51.28- 51.43	S3-8^{T}	3.67			coal
	$_{M+B}$	4.52			clay
72.22- 72.32	S3-7	5.40	10.3	1 91	clay + coal
73.64- 74 99	5356	1.48	2.8	1 89	
74.99- 76.37	5357	1.06			B3 seam
76.81- 77.01	S3-6	11.3	9.0	0.80	clay + coal
108.81-108 98	S3-5	2.08	2.6	1.25	v.f. sst + dirty coal
111.27-111.32	S3-4	3.36			coal + carby. silt
113.75-114.10	5360	0.56	1.0	1.79	B1 seam bese
114.91-115.10	S3-3	4.22			clay + coal
121.42-121.50	S3-2	0.05	8 2	1.64	fine sst + dirty coal
122.23-122.04	S3-1	5.71	1.9	0.33	clay + coal

Hole MD 80-05

27.38- 27.50	S5-11		3.95	clay + coal
35.92- 36.10	S5-10		3.84	clay + coal
36.91- 36.80	S5-9		3.87	clay + coal
38.71- 41.12	5311		2.12	
41.53- 42.88	5312		0.72	B4 seam
42.88- 45.05	5313		0.34	
45.15- 45.30	S5-8	coal	1.11	coal
		clay	3.44	clay
51.92- 52.00	S5-12		4.94	clay + coal
56.94- 57.00	S5-6		4.17	silt + v.f. sst
69.36- 69.50	S5-5		5.10	coal + clay
69.50- 71.11	5307		1.24	
71.17- 72.23	5308		2.02	B3 seam
72.45- 73.40	5309		1.45	
73.40- 73.80	5310		2.68	
73.80- 73.94	S5-7		5.12	silt
		coal	4.37	coal
75.29- 75.19	S5-4		4.60	claystone
87.48- 87.55	S5-3		2.67	v.f. sst + grey silt
113.80-113.86	S5-2		2.65	fine sst + coaly partings
113.86-115.52	5305		0.71	
116.34-117.40	5306		0.96	B1
117.96-118.03	S5-1	coal	3.16	coal
		clay	3.92	clay + silt

MOD 79-14

	Sample Number	U	Th	Th/U	
113.02-112 91	S14-22	4.73			sst lenses in black silt
117 21-117.26	S14-1	2.57			Bone coal + sst
134 88-136.04	1270	2.83	3 8	1.34	coal
136.15-136.30	S14-2	4 83			clay + coaly partings
144.10-144.45	S14-6	4.80			coal + clay
155.40-155.51	S14-3	8.23	9.3	1.13	clay + coaly str.
167 95-167.98	S14-4	5.37			dirty coal + clay
172.28-172.39	S14-5	3.11			fine sst + clay
177.56-177.61	S14-7	6.21			coal + clay
191.30-191.40	S14-8	4.61			clay + coal
206.04-206.08	S14-9	4.27			carby. mud + coal
212.14-212.21	S14-10	4.29			clay + coal
215.50-215.68	S14-11	7.02	7.9	1.13	coal in clay
217.95-218.60	S14-12	3.96			clay + coal
220.29-220.34	S14-13	clay 3.79 coal	8.2 5.15	2.16 0.43	coal + clay
222.80-223.10	S14-14	2.58			clay + coal
243.90-244.36	1281	7.48			coal
244 36-244.46	S14-15	6.13			coaly clay + clay
247.75-249.86	S14-16	2.40			coal + clay
250.85-250.93	S14-17	6.27			coal + clay
253.23-253.39	S14-20	1.63	2.3	1.41	coal + v.f. sst
284.70-284.88	S14-18	5.22			coal + clay
286.51-287.35	1283	4.52			
287.35-287.54	1284	6.63	10.8	1.63	
287.54-288.38	1285	2.69	0.7	1.25	
291.65-293.31	1291	3.09			
293.31-294.69	1292	1.41			B4 seam
294.69-295.77	1293	2.82			
295.77-297.08	1294	0.96			
297.09-298.12	1295	0.50			
298.12-298.90	1296	0.62			
327.70-329.25	1297	?			
330.52-331.20	1298	?			B3 seam
331.24-331.40	S14-19	5.23(5.13)			coal + clay
356.99-357.03	S14-21	1.62			v.f. sst + coal
371.48-371.60	S14-23	3.13			silt + v.f. sst

MDD 79-10

	Sample Number		U	Th	Th/U	
20.12- 20.38	S10-1		4.19			dirty coal + clay
22.58- 22.75	S10-2		3.44			clay + coal
32.11- 32.31	S10-3		3.38			dirty coal + clay
35.58- 35.70	S10-4		5.06	7.3	1.44	coal bands in clay
39.00- 39.11	S10-5		1.18	0.8	0.68	coal
50.88- 51.00	S10-6		5.04			silt + clay
53.64- 53.79	S10-15		4.00			coal + clay
57.43- 57.69	S10-7		6.03			clay + coal frags.
79.25- 79.35	S10-8	coal	3.98	2.5	0.63	
		clay	1.44(1.48)	9.1	6.32	f. sst + coal
93.30- 93.40	S10-9		3.08			clay + coal
93.50- 93.68	S10-10		3.69			coaly clay + coal
94.90- 94.98	S10-11		4.42			coal + clay
120.58-120.70	S10-12		4.94			clay
122.30-122.56	S10-14		4.17(4.20)			coal + clay
135.50-135.80	S10-13		7.36	12.0	1.63	clay + coal
165.51-165.45	S10-16		3.78			carby clay + calcite veins
173.08-173.28	S10-17		4.67			coal + clay
180.10-180.23	S10-18		4.47			clay + coal str.
224.20-224.40	S10-19		4.05			clay + coal partings

TABLE 3 Ranges and Averages of U, Th & Th/U for Various Lithological Groups

	U			Th			Th/U		
	No. of Samples	Range	Average	No. of Samples	Range	Average	No. of Samples	Range	Average
M.R.B. COAL	23	7.2-0.07	1.63	23	11.0-<0.3	2.79	23	4.39-0.02	2.11
M.R.B. CLAYS/SILT	54	10.4-1.88	4.89	54	16.0-6.2	10.95	53	4.56-1.15	2.47
M.R.B. GRAVEL/SAND.	15	3.64-0.15	1.08	15	35.6-1.2	6.04	15	9.78-1.78	5.41
B.C. COAL	60	7.48-0.34	2.45	18	10.8-0.7	3.83	18	2.10-0.43	1.47
B.C. CLAYS/SILT	60	11.3-1.70	4.84	12	12.0-0.3	7.53	12	3.35-0.08	1.35
B.C. GRAVEL/SAND.	19	4.96-0.05	2.76	5	9.1-2.3	4.98	5	16.4-0.58	5.19

value for the continental crust is in range of 3 to 4 (Wedepohl 69-78), therefore the sands and gravels are depleted in U while the coals and clays with ratios <4 are relatively enriched in U.

The higher average U values in the Monkman coals may be a function of coal rank (Breger and Moore, 1955; Cameron and LeClair, 1975), or result from the less weathered environment. The higher average U values in the Monkman sands and gravels may be explained by the abundance of coaly stringers, wisps and detritus within them compared to the relatively clean Moose River gravels and sands. The organics may provide sites for U complexing and adsorption as well as a reducing environment that could enhance U precipitation.

Fig. 1 shows U, Th/U ratio variations with depth and lithology. U values show no net increase or decrease with depth, which indicates that origin is syngenetic rather than by later introduction.

Lithology has an important effect on U distribution, with clay rich sediments having highest U concentrations. This is also the case for clay partings within a coal seam. This could be explained by the presence of a greater number of potential sites in the organic rich clays, i.e. both clay minerals and humic acids whereas only humic acid sites are present in coals.

Several other elements (Cu, Ni, Pb, Zr, Sr) exhibit the same trend relative to lithology as U (Fig. 2). Major elements Al_2O_3, SiO_2, TiO_2 and Fe_2O_3 are similarly distributed. Grain size with its effect on porosity and permeability may have some effect on U

Fig. 1. Variations in the contents of U and Th/U with depth and lithology in a composite section from Adam's Creek, Moose River basin, drill hole J-1-2, Moose River basin and drill hole MD80-05, Monkman, B.C.

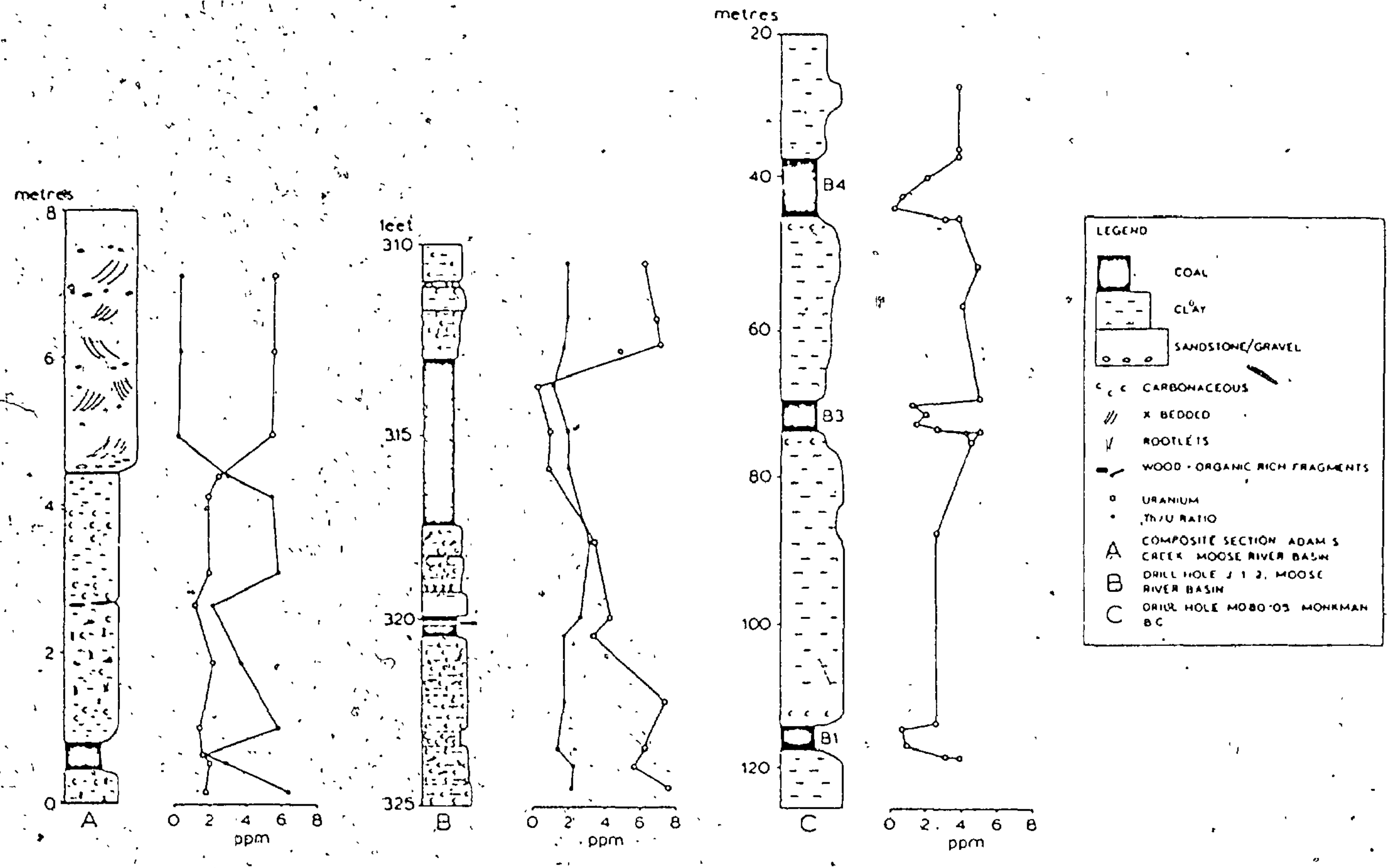
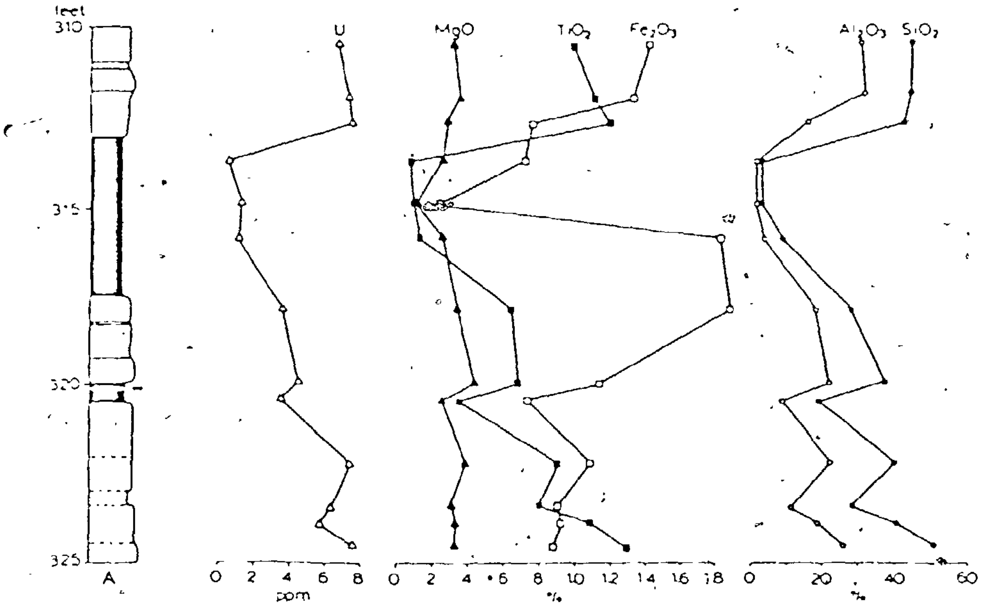
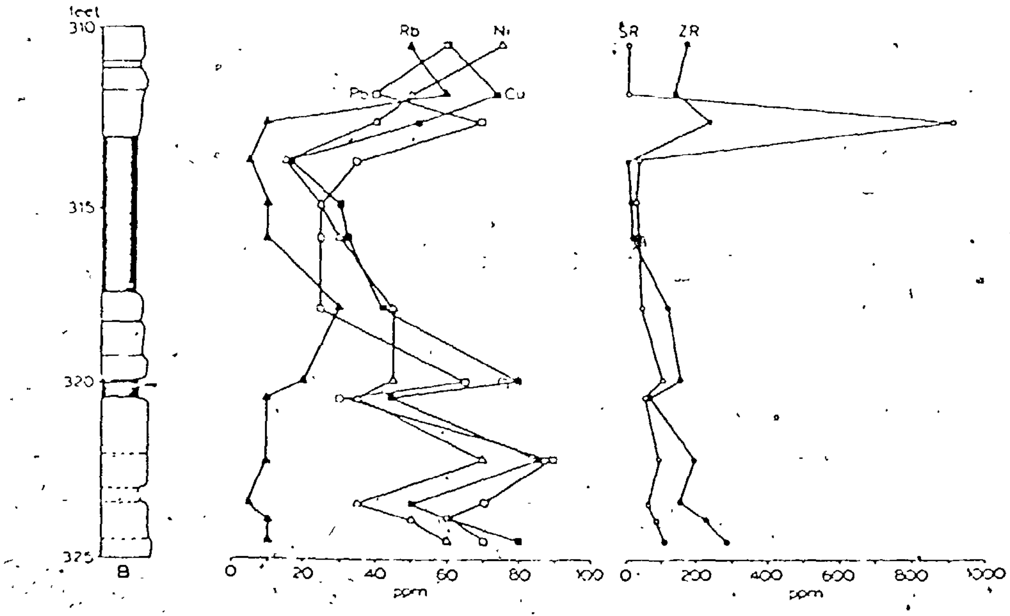
metres
8
6
4
2
0
A
0 2 4 6 8
ppm
feet
310
315
320
325
B
0 2 4 6 8
ppm
metres
20
40
60
80
100
120
B4
B3
B1
C
0 2 4 6 8
ppm
LEGEND
COAL
CLAY
SANDSTONE/GRAVEL
CARBONACEOUS
X BEDDED
ROOTLETS
WOOD - ORGANIC RICH FRAGMENTS
URANIUM
Th/U RATIO
A COMPOSITE SECTION ADAMS CREEK MOOSE RIVER BASIN
B DRILL HOLE J 1 2, MOOSE RIVER BASIN
C DRILL HOLE MO80-05 MONKMAN B.C.

Fig. 2. A. Variations in the contents of U, MgO, TiO_2, Fe_2O_3, Al_2O_3 and SiO_2 with depth and lithology in a lignite bearing section of J-1-2.

B. Variations in the contents of Pb, Rb, Ni, Cu and Zr in the same section.


feet
310
315
320
325
A
U
MgO
TiO2
Fe2O3
Al2O3
SiO2
0 2 4 6 8
ppm
0 2 4 6 8 10 12 14 16 18
%
0 20 40 60
%


feet
310
315
320
325
B
Rb
Ni
Pb
Cu
SR
ZR
0 20 40 60 80 100
ppm
0 200 400 600 800 1000
ppm

concentration in the sediments. For example an organic rich silty sandstone contains less U than an organic rich clay (3.80 ppm U in AC-25-82 vs 6.35 ppm U in AC-07-82).

DISCUSSION

Pearson correlation coefficients were determined from analyses of both sample sets (Table 4) in order to establish elements or suites of elements associated with U. In the Moose River Basin lignites a correlation exists between U and Ni. The clay sediments exhibit a correlation between U and Cu and to a lesser extent with Al_2O_3. This association of U and Cu is also evident in samples from peat profiles (Shotyk, 1984), where the elements are similarly correlated and appear to behave in a similar fashion. However the correlation is greatest in the algal calcareous oozes directly below the peat ($r = .92566$ for U and Cu) where U and Cu values are also at maximum concentration. U in the gravels is associated with TiO_2, Zr, Th, Cr and less strongly with Al_2O_3, MgO, P_2O_5 and Cu. Organic C was not analysed but it is clear that U is more concentrated in the organic-rich clays and gravels.

Most of the U in the gravels is probably detrital, associated with zircon or other heavy minerals. U in the lignite and the clays appears to have been introduced later into the system. Nickel and in some cases copper are commonly associated with the humic acids in coal (Nicholls and Loring, 1960; Swaine, 1977; Zubovic, 1976; Zubovic et al., 1961). Their correlation with U

TABLE 4 Significant Pearson Correlation Coefficients (r) - with Uranium

	Moose River coal	Moose River clay	Moose River gravel	Monkman-all
Al_2O_3	NS	.6708	.6909	.8775
TiO_2	NS	NS	.9415	.8142
K_2O	NS	NS	NS	.9463*
MgO	NS	NS	.6983	.7211
SiO_2	NS	NS	NS	.6460
P_2O_5	NS	NS	.5321	NS
Y	NS	NS	NS	.8617
Pb	NS	NS	NS	.8884
Zn	NS	NS	NS	.6990
Sr	NS	NS	NS	.7703
Ba	NS	NS	NS	.8608
Ni	.7305	NS	NS	NS
Zr	NS	NS	.9396	.5037
Th	NS	NS	.9267	NA
Cr	NS	NS	.9266	.8847
Cu	NS	.8262	.6304	.6115

* NS means not significant.

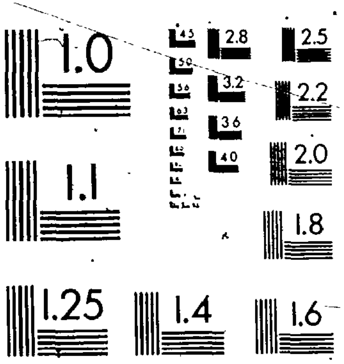
may indicate that the U is organically bound. This is also indicated by the obvious increase in U in organic rich clays and gravels. In the clays, U is also inorganically held, probably on the mineral kaolinite, where it may be adsorbed on the outer surface directly or indirectly on adsorbed humic acids (Rashid, 1974; Greenland, 1971; Brookins and Lee, 1974; Borovec, 1981). Copper is also readily adsorbed onto clays. At pH's > 6 U and Cu adsorption onto clays may be important, with the reducing environment produced by the organic material providing further incentive for the precipitation of U (Farrah and Pickering, 1979). It is probable that both organic and inorganic sites exist for the U and that adsorption can occur directly or indirectly.

The Monkman material was not subdivided for this analysis, however the same general trends may be recognized. U shows significant correlations with Al_2O_3, K_2O, MgO and TiO_2 which are important constituents of illite. U is also correlated with Cr, Y, Pb, Zn, Sr and Ba, of which Cr and Y are generally organically associated in coal. Pb, Zn and Sr, Ba are found in sulphides, and barite or clay minerals respectively.

Transporting Mechanism for Uranium

The association of U and organic matter has up till now been explained by the reduction of the Uranyl ion by the organic matter and/or the sorption and formation of organouranyl complexes (Szalay, 1974; Doi et al., 1975; Muto et al., 1968; Blundell

4 OF/DE 4



and Jenkins, 1977). The possibility exists that U may also be transported in natural water by simple organic compounds and U accumulation occurs by polymerization or bonding of the simple organic compounds to the coal network.

Langmuir (1978), Dongarra and Langmuir (1980) have shown that U in natural waters is usually complexed. Langmuir indicates that fluoride and hydroxy complexes are important in anoxic freshwaters at pH 3-4 and higher pH's respectively. In oxidized waters fluoride and UO_2 are found at low pH's, while at medium (5-7) and high (>7) pH's, $UO_2(HPO_4)$ and uranyl di- and tri-carbonates dominate respectively (see Fig. 11 in Langmuir, 1978). Most authors consider carbonate complexes to be the most important transporting mechanism for U in both marine and freshwater environments.

Depositional Environments

The environments of deposition of the Monkman and Moose River coals are lower to upper delta plain and fluvial respectively. Their chemistries may be compared to that of a back-barrier swamp type coal from S. Brazil, to examine the effect of different depositional environments on U contents in coals. The Middle Permian age Figueira deposit of S. Brazil (Ayres, 1981; Forman and Waring, 1980) is U rich (up to 0.05-0.5% U) and has correspondingly high Mo and S values (up to 0.1-1.0% Mo and up to 27.38% S) (Lamb, 1982). The U in the coal occurs in the form of uranocircite (Forman and Waring, 1980). The continental coals contain much less U and Mo and are low in S (<3.7%). This may be explained in part by looking at the chemistry of the circulating waters.

Sea water contains more dissolved U, Mo, and S and is more oxidising than continental waters (Table 5). Periodic inundation by sea water and contact with more saline ground waters would lead to elevated U, Mo and S contents in coals affected by marine waters. Other factors influenced by the depositional environment should also be taken into account. For example, porosity variations between an adjacent barrier sandstone and a fluvial channel sandstone may affect ground water flow rates through a coal. Different coal lithotypes also exhibit variable porosities and Schopf and Gray (1954) found the more porous layers in a U-rich Dakota lignite to be preferentially enriched in uranium. Also chemistry of lithologies overlying the coals will vary from marine to fluvial environments. Position relative to sea level must also influence the quantity and type of ground water flow through a given coal deposit. It is evident that depositional environment plays a role in determining U content in coals. Post depositional and diagenetic processes may also be important for U accumulation. For example King and Young (1956) found proximity to aquifers and permeability (jointing) to be important controlling factors on mineralization in S. Dakota uraniferous lignites. Also Denson and Gill (1956) and Vine (1962) have shown that the stratigraphically highest coal beds below the volcanic tuff U source rocks in E. Montana and N. and S. Dakota are most

TABLE 5. Sea water and continental water chemistry.

	Sea H_2O	fresh water	brines	
S	0.1%	1 ppm sulphate		Casagrande 1977
U ppb	1-4 ppb	0.040×10^{-9} g/cc*		from Wedepohl
Mo g/l	11.0 g/l	0.5 g/l	1.7 g/l	from Wedepohl
peat pH Seawater and freshwater influenced	neutral	4		from Casagrande 1977

*In the Mississippi River (Rona and Urry, 1952).

enriched in uranium.

CONCLUSIONS

The conclusions of the study are as follows.

1. Highest U values are found in the organic rich clays with low U in the coals and gravels. Th/U ratios were less than 4 in the clays and coal with lowest values in the lignites/coal and the organic rich clays indicating greatest U enrichment relative to Th.
2. Highest average U values are found in the coals of higher rank.
3. The U in the coal may be held in organo uranyl complexes, and in the clays is probably adsorbed on the clay minerals directly or indirectly via humic acid U complexes.
4. Grain size may have some effect on U concentration especially when related to mineralogy and hence adsorption sites.
5. Depositional environments especially marine vs non marine effect U concentration in coals. Coals with high U may show influence of marine waters.

Two examples of normal coals have been studied here. Normal coals are trace element poor relative to mean sediment values (Bowen, 1966, p. 42-45) and crustal abundances (Taylor and McLennan, 1981 and Bowen, 1966, p. 44-45), have originated from plants and peat that are inherently depleted in many trace elements and have been influenced by normal groundwaters.

There has been a tendancy in the geochemical literature to focus attention on coals that have abnormal and above average metal contents. Such enrichment may have occured through contact with metal rich circulating groundwaters, for example marine, deep groundwaters or groundwaters influenced by mineral deposits. Coals such as these are therefore the exception and more normal coals should be studied to obtain better average trace element data for coals.

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