RELATIONSHIPS BETWEEN INORGANIC CONSTITUENTS AND ORGANIC MATTER IN A NORTHERN ONTARIO LIGNITE

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INTRODUCTION

Coal is a complex substance which is composed of organic material and variable quantities of inorganic matter in the form of minerals and trace elements. The presence of these inorganic constituents normally requires that cleaning or modifying procedures must be implemented prior to or during utilization of the coal, so that problems such as boiler fouling, slagging, corrosion; catalyst poisoning; or environmentally hazardous emission may be avoided. To facilitate this, the location and form, in addition to the concentration, of the inorganic substances must be known and understood. This is particularly important where an intimate relationship exists between the organics and the inorganics, making separation using conventional techniques more difficult. This paper examines the relationship between organic matter and the minerals and trace elements in a northern Ontario lignite.

A large number of minerals have been identified in coal. These include a rapidly increasing number of accessory minerals (1) and ultrafine grains (2) including silicates, sulphides, carbonates, oxides and rare earth minerals. Mineral matter in coal has traditionally been examined by X-Ray Diffraction (XRD) following Low Temperature Ashing (LTA) (3), however this method precludes examination of minerals in situ. More recently Scanning Electron Microscopy (SEM) (4) and Scanning Transmission Electron Microscopy (STEM) (2) coupled with Energy Dispersive X-Ray analysis (EDX) are being utilised to determine the mineral distribution and relationship to the organic matter.

A variety of mineral suites, reflecting the changes in physical and geochemical conditions in the coal during formation, are present in most coals. They commonly include a detrital mineral suite consisting of quartz, feldspar and clay minerals, a syngenetic suite comprising clay minerals and a group of epigenetic minerals including for example carbonates or sulphides. The last two mineral groups are respectively extremely difficult and relatively easy to remove from the coal as a result of their varying modes of occurrence. Epigenetic minerals normally fill cleats and exhibit no relationship to the organic matter, while syngenetic minerals may be intimately associated with the coal macerals.

The concentrations and modes of occurrence of trace elements in coal are extremely variable. Concentrations of most elements are low compared with crustal abundances, however certain elements including U, Ge and V may reach ore grade in some coals. Elements may be associated with the coal macerals, clay minerals, sulphides, rare earth minerals, or they may be present as elemental grains. A variety of geological and hydrological factors, such as depositional environment, depth of burial, chemistry and flow rates of circulating groundwater, rank and other post depositional effects, influence both the concentration and location of the trace elements. Coal rank and clay mineralogy appear to be particularly important influences on the latter (5). Modes of occurrence of trace elements have been examined using a variety of techniques, including analysis of concentrations in float sink fractions (6) or with varying ash content (7); leaching characteristics (8); correlation coefficients (10), and SEM-EDX (1). The latter two techniques are used in this study.

EXPERIMENTAL

The lignite samples discussed below were obtained from the Lower Cretaceous lignite-bearing succession in the Moose River Basin, located in the James Bay Lowlands of northern Ontario. Outcrop exposures and drillcore were sampled. Sampling intervals in the coal seams varied from 1.0 to 0.5 metres, based on lithotype changes in the coal.

Major mineral phases were identified by X-Ray Diffraction. Minor mineral phases and mineral-organic matter relationships were examined using an ISI DS-130 SEM coupled with a PGT System III EDX. Samples for SEM-EDX were prepared from polished sections, broken sample fragments and grain mounts fixed to aluminum studs using silver paint, and carbon or gold coated prior to analysis.

31 major and trace elements were analysed by X-Ray Fluorescence, Atomic Adsorption, and Neutron Activation Analysis. Modes of occurrence of the trace elements were determined using Pearson correlation coefficients and SEM-EDX. Discreet mineral grains were analysed and element windows were run over larger areas to locate elements randomly distributed throughout the organic material. In this way organically bound elements or those associated with extremely fine grained and dispersed mineral matter were identified.

RESULTS AND DISCUSSION

The Moose River Basin lignite is relatively clean by comparison with United States' and other coals worldwide. Isolated samples show no traces of mineral matter, however most samples contain quartz and kaolinite. Accessory clay minerals are restricted to trace amounts of mixed layer clays, illite and mica. Pyrite occurs in less than half the samples analysed, and gibbsite, gypsum and siderite were noted in isolated samples. Mineral abundance and modes of occurrence are summarised in Table 1.

Much of the mineral matter is detrital, for example quartz, mica and some associated clay minerals (Figure 1). Kaolinite appears to be both detrital and derived from in-situ feldspar degradation. Authigenic (syngenetic) kaolinite is commonly associated with fusinitic lignite (Figure 2). A number of other minerals, including pyrite, are intimately associated with the organic matter. Pyrite occurs as crystals infilling cell hollows (Figures 3 and 4) and replacing cell walls. Pyrite also occurs epigenetically, infilling cracks in the lignite (Figure 5). The soily lignite contains most mineral matter, which is also generally detrital. The woody and fusinitic lignite contain isolated detrital grains, occasional detrital-rich bands, and some authigenic mineralisation.

Trace and major element contents of the lignite are summarised in Table 2. Trace element concentrations are generally low, however Sr, Cd, Mo, Au, and As values are elevated compared with concentrations in the surrounding sediments. Modes of occurrence of the elements, as determined from correlation coefficients (Table 3), vertical distributions in the seams (Figure 6), and SEM-EDX are listed in Table 4. Association with the organic matter is the most common mode of occurrence. Cl, Zn, Mo and possibly Pb occur in this way, while Ni, Sr, W and the platinum group elements are associated to some extent with the organic matter. Cr is associated with the heavy minerals, possibly as chromite grains, while Cu, and in part Co, Ni, Sr, U, and Th are associated with the clay minerals. As, Cd and to some extent Co, Ni, Zr, and W are located in the sulphide minerals.

Humic acids are the main organic sites for trace element adsorption and complexation (11). As coalification proceeds and aromatisation increases, humic acid sites decrease in abundance. Association of trace elements with organic matter in coal therefore appears to be favoured in lower rank coals.

CONCLUSIONS

A strong association between the organic matter and both the minerals and trace elements in the Moose River Basin lignite was established. Minerals are detrital, syngenetic and epigenetic. Detrital and syngenetic minerals are fine grained and occur distributed throughout and intimately associated with the organic matter. Epigenetic pyrite, in contrast, is restricted to crack fills and could be readily removed from the coal.

Trace element concentrations are variable and association with the organic matter is the most common mode of occurrence. Elements are also associated with clay minerals, sulphides and heavy minerals.

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Figure 1 SEM micrograph showing detrital quartz surrounded by clay minerals in woody lignite. Scale bar - 40 microns long.

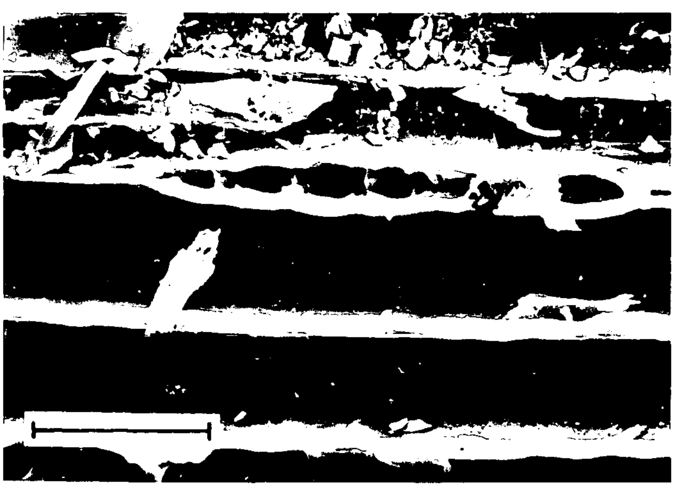

Figure 2 SEM micrograph showing clay minerals in fusinite. Scale bar -40 microns long.

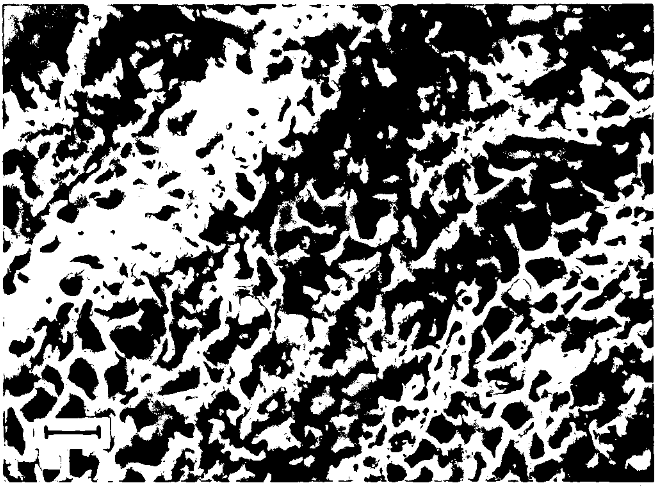

Figure 3 SEM micrograph showing pyrite crystals infilling cells in woody lignite. Scale bar - 40 microns long.

Figure 4 SEM micrograph showing a single pyrite crystal in a cell in woody lignite. Scale bar - 20 microns long.

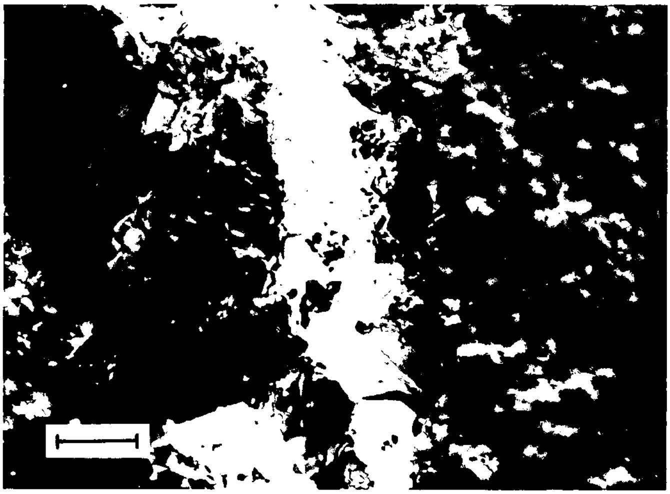

Figure 5 SEM micrograph showing pyrite infilling a crack in woody lignite. Scale bar - 40 microns long.

Table 1: Abundance and Mode of Occurrence of Minerals in the Moose River Basin lignite

	Abundance	Suggested Mode(s) of Occurrence
Quartz	P - ND	detrital infilling cell hollows
Kaolinite	P - ND	detrital authigenic (syngenetic)
Illite	T - ND	detrital
Mica	ND (T)	detrital
Mixed layer clay	T - ND	detrital
Pyrite	T - ND	infilling cell hollows replacing cell walls infilling cracks
Siderite	ND (T)	
Gypsum	ND (T)	recent weathering of pyrite
Gibbsite	ND (T)	authigenic-coating quartz grain surface

P : Major component.
T : Trace component.
ND : Not detected.
() : Mineral present at this level of abundance in only one sample.

Table 2: Summary of major and trace element data for the Moose River Basin lignites

Moose River Basin lignites (17 samples)

Element %	Mean	Range			
			ppm		
SiO_2	8.57	0.34-30.20	Cr	65.6	0.0 - 497.5
Al_2O_3	3.18	0.19-10.30	Rb	5.9	0.0 - 20.0
CaO	1.44	0.57- 3.41	Sr	108.7	0.0 - 1000.0
MgO	0.30	0.11- 0.73	Zr	93.5	0.0 - 530.0
Na_2O	0.02	0.00- 0.07	Cd	0.76	0.0 - 4.77
K_2O	0.06	0.01- 0.21	Co	35.9	5.0 - 197.5
Fe_2O_3	1.77	0.24- 6.18	Cu	20.0	2.0 - 44.0
MnO	0.01	0.00- 0.09	Pb	25.1	5.0 - 155.0
TiO_2	0.17	0.01- 0.80	Mo	5.9	5.0 - 15.0
P_2O_5	0.03	0.00- 0.25	Ni	47.4	4.2 - 190.7
LOI	83.59	55.50-97.40	Zn	159.2	5.2 - 1311.2
S	1.44	0.45- 2.47	U	1.60	0.14 - 7.20
ppb (18 ashed samples)			Th	2.74	0.14 - 6.50
Au	13.6	1-96	Mo	9.1	9.0 - 9.5
Pt	13.3	0-80	As	4.0	3.0 - 6.0
Pd	16.1	0-250	W	1.7	1.0 - 3.0
Ir	0.07	0-0.05			

Table 3: 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								
Th	.60	.75						.69											
Th/U					.54										-.60				
Cd																			
Co						.51					.94			-.53					
Cu	.52	.79						.60				.61				.85			
Mo																			
Ni											.65						.57		.55
Zn																			
S		-.64						-.57	-.75	.50			-.50		-.65	-.69		.54	

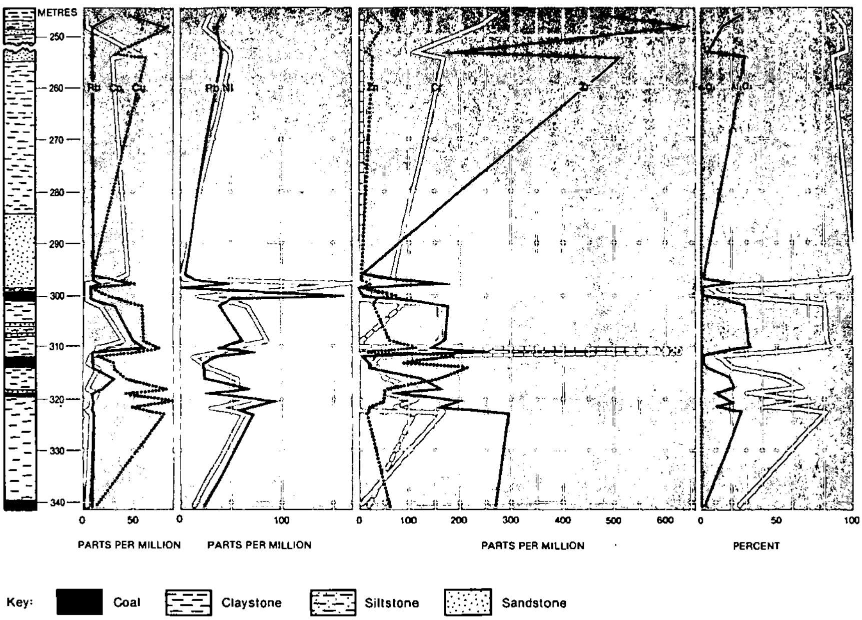

Figure 6 Vertical distributions of trace and major elements in samples from a drill hole (J-1-2) in the Moose River Basin

Table 4: Associations of trace elements in the Moose River Basin lignite

Element	Mode of Occurrence	Element	Mode of Occurrence
Cl	organics	Zr	pyrite
Cr	heavy minerals	Mo	organics
Co	sulphides	Cd	sphalerite
	clay minerals	W	sulphides
Ni	organics		carbonates
	clay minerals	PGE	detrital
	pyrite		organics
Cu	clay minerals	Pb	organics?
Zn	organics	U	clay minerals
As	supphides		carbonate
Rb	detritals	Th	clay minerals
Sr	carbonates		heavy minerals
	clay minerals		
	organics		