

## VARIATIONS IN THE INORGANIC CHEMISTRY OF COAL

W.S. Fyfe, B.I. Kronberg, Department of Geology, The University of Western Ontario, London, Canada

J. R. Brown, Energy Research Laboratories, Department of Energy, Mines and Resources, Ottawa, Canada

### INTRODUCTION

The composition of coal reflects its complex physical and chemical history. Throughout coal genesis, from accumulation of plant debris and during subsequent coalification, solute species in ground waters are constantly exchanged with the porous and reducing carbonaceous debris. From existing geochemical data (e.g., Wedepohl, 1969; Kronberg et al., 1981), it appears that coal and coal-related materials (peat, lignite, etc.) may incorporate and accumulate a complex array of elements. To some extent coal deposits acts as gigantic carbon filters through which ground waters wash the products of rock leaching. Very little is known concerning the exact siting of trace elements in coal and these elements at times attain ore grade (e.g., U, Mo).

The modern large-scale ( $10^{15}$  g a<sup>-1</sup>) burning of coal may have ramifications not only for the global carbon cycle but contingent on their fates during combustion, also for the global cycle of other elements concentrated in coal. For example the deposition over the past five decades of charcoal as well as several metals (Cr, Fe, Co, Ni, Cu, Zn, Cd, Sn and Pb) in Lake Michigan sediments correlates with variations (oil, coal, wood, installation of control devices) in fuel use (Goldberg et al., 1981). Associated with coal combustion is the accumulation of easily leachable ash. Other recent work (Chapelle, 1980) shows that some metals (Cr, Ni, Zn, Cd, Pb) sorbed onto surfaces of Fe-Al-O phases in ash are easily leached by percolating waters.

Here discussion is confined to the coal chemistry of the transition metals, some of which are known to play catalytic roles in coal combustion and to the coal chemistry of the halogens. The presence of F and Cl at the per cent levels in some coals is significant for combustion technologies (concerned with corrosion problems, etc.) and for problems related to atmospheric emissions.

### EXPERIMENTAL

The analytical data reported here pertain to samples of raw coal, ash from coal, lignite and tar sand, as well as NBS standard reference coals and coal ash. The non-reference coals are bituminous coals from Western Canadian mines, hosted in Cretaceous formations. The lignites are from North Dakota and Ontario, and the tar sand from Fort McMurray, Alberta. The British Columbia coals (samples 2-6, Table 1) are from different seams in the same mine, as are the Alberta coals (samples 7-9). The sample numbers correspond to those appearing in more detailed analytical reports (Kronberg et al., 1981; Brown et al., 1981a, b). The analytical techniques employed in all these studies are spark source mass spectroscopy (SSMS) and electron spectroscopy for chemical analysis (ESCA).

SSMS is useful for surveying the concentrations of 60-70 elements in a single analysis. However, it is necessary to pre-ash or otherwise pre-treat samples containing substantial material of low mass number, which easily forms polyatomic positive ions. Coal, due to its high carbon content exemplifies this difficulty, and an unmanageable number of interferences appear in the mass spectral record of raw coal. In this study the samples of coals, lignites and tar sand were dry ashed for 4-6 hours at 600°C in a muffle furnace. Sample electrodes, prepared by mixing the ash with pure graphite (Taylor, 1965), were sparked in a JEOL mass spectrometer

(JMS-01BM-2). The mass spectra were recorded photographically and interpreted semi-quantitatively using USGS standards (Flanagan, 1973). With regard to the analysis of coals and other geological materials (soils, Mn nodules, rocks, volcanic ash, deep-sea sediments, etc.) the analytical uncertainty is within the variation encountered using normal sampling techniques.

ESCA is a spectroscopic surface sensitive technique by which the concentrations of all elements (except H) can be surveyed semi-quantitatively to a surface depth of 1-5 nm. Detection limits are  $\approx 10^{-9}$  g  $\text{cm}^{-2}$  of surface ( $\approx 0.1$  bulk wt. %). Thus for geological materials, semi-quantitative information can be obtained for major elements and for surface concentrated minor and trace elements (Brown, 1978; Bancroft et al., 1979). There are several advantages of ESCA for coal analysis: (1) ESCA is non-destructive. (2) It is often possible to gather details on the *in situ* chemistry of elements (oxidation state, coordination number, etc.). (3) Both raw coal and coal ash may be analysed. Ashing effectively concentrates the mineral fraction in coal by an order of magnitude, permitting concentration measurement of additional elements. Surface concentration of elements (e.g., F, S) during combustion by surface sorption reactions may be monitored. (4) ESCA multi-element scans may be done quickly ( $\sim 1$  hour) and may be useful in fingerprinting coals.

ESCA spectra were recorded using a McPherson 26 spectrometer equipped with an aluminum anode operating at 200 watts. Details of the ESCA procedures used for this study are available elsewhere (Brown et al., 1981a, b).

## RESULTS AND DISCUSSION

The concentrations, obtained by SSMS (Table 1), of transition metals and halogens for some North American coals and coal-related materials are compared (Table 2) to data available for coal from various sources and to crustal abundances. The chaotic concentration patterns for many elements are a reflection of the complexity of chemical and physical processes associated with coal formation. The extreme variation is possibly related to local ground water chemistry and to the local permeability of coal and enclosing strata. With respect to crustal abundances (CA), both the transition metal and halogen concentrations, range from strongly depleted (less than 10-fold CA) to strongly enriched (greater than 10-fold CA). The data from other sources include those from coal deposits on other continents, and the wide concentration ranges may be an expression of the type of Earth processes leading to coal deposition and formation.

Of the transition metals (Table 1) Sc, Y and Zr appear the least mobile. The variations in Nb concentrations are intriguing and Nb may be more mobile or may be hosted in phases distributed more unevenly. The variation in Ti concentrations is noteworthy, and chemical migration of Ti in association with coal diagenesis has been noted (Degens, 1958). Moreover, there is evidence for the chemical coupling of Ti (and Zr) compounds to enzymes and other biologically active macromolecules (Kennedy, 1979). Further, Taylor et al. (1981) have shown that Mg, Ca, Ti, Fe, Cu, Zn species in coal may be extracted by organic solvents.

Our knowledge of the sources of halogens and their mode of concentration in coal is vague. River and ground waters flowing into coal basins would contribute substantial amounts of Cl. It could be introduced by rain and aerosols either directly or transferred via the biosphere. The sources of Br and F are less certain. F could be added during deposition by the influx of fine-grained detrital minerals or volcanic ash. For example, fluorite ( $\text{CaF}_2$ ) is observed in the ESCA scan of coal No. 8 (Table 3).

In the ESCA scans of raw coals (Table 3), the largest peaks correspond to the detection signals for carbon (C 1s) and oxygen (O 1s). Other elements detected included Al, Si, Ca, sometimes S, and in some samples substantial F and Cl. Large

variations, indicated by the number of counts per second during ESCA analysis, are attributed to chemical variations in coal surfaces. The differences in carbon peak positions were of interest especially in sample no. 8, for which the C 1s peak position is indicative of graphitic carbon and this scan also contains the largest F 1s signal.

Recently, an examination of raw coal macerals by XPS indicates that fisinite displays characteristics (C 1s binding energy 284.4 eV) essentially identical to pure graphite. It was also observed that the vitrinite fraction of a western Canadian coal sample was greatly enriched (> 1 wt. percentage) in an organically found fluorine species,  $a(CF_2)_n$  type.

In the ESCA scans of ashed coals (Table 4) many more elements (Na, Mg, Ti and Fe) appeared and the F 1s and S 2s peaks are enhanced. S appearing both as  $SO_4^{2-}$  and  $S^{2-}$  is likely associated with Fe as iron sulphide (pyrite), the outer shell oxidized to sulphate by combustion. The concentrations of Al, Ca, Ti and Fe in NBS reference ash (1633a) measured by ESCA (using the Si 2s peak as a reference) agree well with recommended values. In the ash, F and S surface concentrations are much greater than those observed in the bulk samples, and this could be evidence for preferential siting of these elements on ash surfaces. Cl was not detected on the ash surfaces by ESCA, in contrast to the high signals noted on raw coal surfaces, and Cl may be removed in the volatile phase during combustion.

#### CONCLUSION

The combined use of SSMS and ESCA results was successful in part in overcoming the unique analytical difficulties presented by the heterogeneous chemical and physical distribution of intimately combined inorganic and organic species in coal. These techniques and modifications of them are applicable to the study of the combustion chemistry of coal as well as to the assessment of the environmental impact of coal utilization.

#### REFERENCES

- Babu, S.P. (Ed.) 1975. Trace elements in fuels. Adv. Chem. Ser. 141. Am. Chem. Soc., Washington, D.C. 214 pp.
- Bancroft, G.M., Brown, J.R., and Fyfe, W.S. 1979. Advances in, and applications of, x-ray photoelectron spectroscopy (ESCA) in mineralogy and geochemistry. Chem. Geol. 25, 227-243.
- Brown, J.R. 1979. Adsorption of metal ions by calcite and iron sulphides: A quantitative XPS study. Ph.D. thesis, University of Western Ontario, London, Ontario, 220 pp.
- Brown, J.R., Kronberg, B.I., and Fyfe, W.S. 1981,a. Semi-quantitative ESCA examination of coal ash surfaces. FUEL 60: 439-446.
- Brown, J.R., Kronberg, B.I., and Fyfe, W.S. 1981,b. An ESCA examination of coal and coal ash surfaces, In: Proceedings "Coal: Phoenix of the '80's" (ed. A.M. Al Taweel), 64th Canadian Chemical Conference, Halifax, N.S.
- Chapelle, F.H. 1980. A proposed model for predicting trace metal composition of fly-ash leachates. Environ. Geol. 3(3): 117-122.
- Degens, E.T. 1958. Geochemische Untersuchungen zur Faziesbestimmung im Ruhrkarbon und im Saarkarbon. Glückauf, Jg. 94, Essen.

Fairbridge, R.W. (ed.) 1972, Encyclopedia of geochemistry and environmental earth sciences series, Vol. IVA, Van Nostrand Reinhold, New York, 1321 pp.

Flanagan, F.J. 1973. 1972 values for international geochemical reference samples. *Geochim. Cosmochim. Acta* 37: 1189-1200.

Goldberg, E.D., Hodge, V.F., Griffin, J.J., Koide, M. and Edgington, D.N. 1981. Impact of fossil fuel combustion on the sediments of Lake Michigan. *Envir. Sci. & Tech.* 15 (4): 466-471.

Goldschmidt, V.M. 1954. *Geochemistry*, Clarendon press, Oxford 730 pp.

Kennedy, J.F., 1979. Transition-metal oxide chelates of carbohydrate-directed macromolecules. *Chem. Soc. Rev.* 8 (2) 221-257.

Kronberg, B.I., Brown, J.R., Fyfe, W.S., Peirce, M. and Winder, C.G. 1981. Distributions of trace elements in western Canadian coal ashes. *FUEL* 6D: 59-63.

Taylor, S.R. 1965. Geochemical analysis by spark source-mass spectrography. *Geochim. Cosmochim. Acta* 29: 1234-1261.

Taylor, L.T., Hausler, D.W. and Squires, A.M. 1981. Organically bound metals in a solvent-refined coal: metallograms for a Wyoming subbituminous coal. *Science*, 213, 644-646.

Wedepohl, K.H. 1969. *Handbook of Geochemistry*. Springer-verlag, Berlin.

TABLE 1 - CONCENTRATIONS ( $\mu\text{g g}^{-1}$ ) OF SOME ELEMENTS IN ASH FROM COAL, LIGNITE AND TAR SAND (SSMS DATA)

Sample Element	Yukon coal	British Columbia coals					Alberta coals					North Dakota lignite					NBS Reference Materials								
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	
F	50	>500	>500	150	5	>500	500	500	30	>500	>500	500	500	30	>500	>500	500	500	30	>500	>500	500	500	30	>500
Cl	5	5	5	2	5	15	>50	50	10	1	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Sc	30	100	100	100	30	30	30	30	3	15	10	30	100(40) <sup>a</sup>	30	10	30	100(40) <sup>a</sup>	30	10	30	100(40) <sup>a</sup>	30	10	30	10
Ti	1,000				1,000		300			3,000															
V	15	40	150	150	15	40	40	40	10	1,250	13	130	400(300)	130	40	130	400(300)	130	40	130	400(300)	130	40	130	40
Cr	15	15	15	5	5	15	15	5	0.3	15	18	3	18(196)	18	6	3	18(196)	18	6	3	18(196)	18	6	3	6
Mn																									
Fe	100,000				10,000		1000			200,000															
Co	40	13	13	13	130	40	40	13	3	130	1	10	12(46)	12	360	1	10	12(46)	12	360	1	10	12(46)	12	360
Ni	150	15	15	15	450	150	50	50	5	60	1	15	5(127)	5	5	1	15	5(127)	5	5	1	15	5(127)	5	5
Cu	180	60	180	60	180	180	60	60	60	180	2	20	50(118)	18	18	2	20	50(118)	18	18	2	20	50(118)	18	18
Zn	40	400	40	12	120	40	40	120	3	85	4	4	35(220)	35	12	4	4	35(220)	35	12	4	4	35(220)	35	12
Br	0.5	0.5	0.5	0.2	0.2	0.5	0.5	0.5	0.2	0.2	0.05	1	0.2	0.2	0.2	0.05	1	0.2	0.2	0.2	0.05	1	0.2	0.2	0.2
Y	40	40	40	40	120	120	120	120	5	60	1	35	35	35	35	1	35	35	35	35	1	35	35	35	35
Zr	200	200	200	200	200	200	200	200	60	200	5	20	60	60	200	5	20	60	60	200	5	20	60	60	200
Nb	4	40	13	40	40	40	40	13	2	13	1	5	13	13	1	5	13	13	13	1	5	13	13	13	13
Mo	3	3	3	3	30	30	3	3	5	200	1	4	10(30)	4	1	1	4	10(30)	4	1	1	4	10(30)	4	1
I	1	0.3	1	<0.3	1	0.3	<0.3	3	30	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1

a NBS reference values

b raw coal analysis

TABLE 2

ELEMENT	RANGE <sup>a</sup>	DATA FROM VARIOUS SOURCES <sup>b,c,d,e</sup>		CRUSTAL ABUNDANCE <sup>f</sup>
		coal	ash	
F	30->500	71-175		544
Cl	1->50	6-1000	186-3,000	126
Sc	3-100	3	10-1,000	25
Ti	300-8000	180-960	~30,000	10,500
V	10-1250	4-50	0.2-24,600	136
Cr	0.3-15	< 2-27	116-800	122
Mn		70-130	250-280	
Fe				
Co	3-130	3-25	10-39	29
Ni	5-450	4-100	5-80,000	99
Cu	60-180	3-180	15->500	68
Zn	3-400	20-200	160-10,000	76
Br	0.2-0.5	0.1-23	7-12	2.5
Y	5-120	3-25	100	31
Zr	60-200	10-300	115-5000	162
Nb	2-40	5-41		20
Mo	3-200	trace-3000	8-500	1.2
I	<0.3-30		142-587	0.46

<sup>a</sup>this study    <sup>b</sup>Babu, 1975    <sup>c</sup>Goldscmidt, 1954    <sup>d</sup>Wedepohl, 1969    <sup>e</sup>Yudovich et al., 1972

<sup>f</sup>Fairbridge, 1972.

TABLE 3 - ESCA Chemical Analysis of Raw Coal Surfaces

Element (wt %)	Raw Coal Samples <sup>a</sup>													
	NBS Standards				North American Coals									
	1632a		1635		1		5		8		10		12	
ESCA	bulk <sup>b</sup>	ESCA	bulk <sup>b</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	
Si	7.7	5.8	1.3	0.52	10.5	6.0	1.0	1.0	2.7	1.0	N.D.	2.0	4.1	N.A.
Al	5.20	3.1	0.8	0.30	10.6	2.0	2.5	2.0	7.4	1.0	1.2	2.0	3.4	N.A.
Fe	N.D. <sup>d</sup>	1.1	N.D.	0.22	N.D.	2.0	0.4	0.1	N.D.	0.50	0.9	1.0	1.0	N.A.
Ca	N.D.	0.24	1.5	0.54	N.D.	5.0	1.7	2.0	2.4	0.30	N.D.	0.5	1.7	N.A.
Ti	N.D.	0.15	N.D.	0.02	N.D.	0.1	N.D.	0.5	N.D.	0.1	0.9	0.3	N.D.	N.A.
S	N.D.	1.59	0.8	0.32	N.D.	2.0	N.D.	3.0	N.D.	2.0	3.1	3.0	N.D.	N.A.
F	1.25	N.A. <sup>e</sup>	1.4	N.A.	N.D.	N.A.	1.9	N.A.	3.8	N.A.	N.D.	N.A.	N.D.	N.A.
Cl	N.D.	0.08	N.D.	0.003	0.8	N.A.	1.1	N.A.	0.9	N.A.	1.5	N.A.	2.2	N.A.
N	1.2	1.27	1.5	1.0	0.3	N.A.	2.0	N.A.	1.4	N.A.	N.D.	N.A.	62.0	N.A.
C <sup>f</sup>	59.3	{86.7	73.8	{97.1	48.1	{82.9	74.0	{91.4	60.0	{95.1	71.8	{91.2	25.6	N.A.
O <sup>g</sup>	25.3		18.9		29.7		15.3		21.4		20.6			

<sup>a</sup>Surface concentrations are calculated from equation 1 using ESCA peak intensity ratios normalized to Si 2s except Sample No. 10, where Al 2s had to be used. Note the surface compositions have been calculated on a hydrogen free basis as hydrogen cannot be detected by ESCA.

<sup>b</sup>Accepted values from US NBS certificate of analysis (14) and/or reference (15).

<sup>c</sup>Bulk analysis by XRF and/or SSMS (4); note carbon and oxygen (a combined value) are determined by difference; coal 12 not analyzed.

<sup>d</sup>N.D. not detected.

<sup>e</sup>N.A. not analyzed.

<sup>f</sup>Carbon content measured by ESCA includes a small sorbed portion (hydrocarbons) derived from the UHV system.

<sup>g</sup>Oxygen content measured includes a small portion of adsorbed oxygen due to handling in air prior to analysis.

TABLE 4 - ESCA Chemical Analysis of Coal Ash Surfaces

Element (wt %)	Ashed Samples <sup>a</sup>												
	NBS Standard		North American Coal Ash										
	1633a	b	1		5		8		10		12		
ESCA	bulk	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>	ESCA	bulk <sup>c</sup>
Si	16.9	22.8	10.9	10.0	21.5	25.0	2.8	3.0	5.1	10.0	4.6	5.3	
Al	10.0	(14.0)	8.2	7.0	10.0	10.0	6.4	3.0	11.3	9.0	9.5	6.6	
Fe	2.7	9.4	1.4	6.1	N.D.	1.0	1.1	0.1	4.2	10.0	8.0	5.4	
Ca	2.2	1.1	5.8	10.0	0.9	0.5	2.9	0.1	5.1	4.0	9.8	25.7	
Ti	1.3	(0.8)	1.5	0.1	2.5	1.0	0.6	0.03	0.6	0.3	N.D.	0.2	
S <sup>d</sup>	4.2	[≥0.05]	1.87	N.D.	N.D.	N.D.	1.6	N.D.	3.74	N.D.	3.9	4.9	
F	2.0	[=0.05]	0.9	0.05	N.D.	N.D.	1.0	0.05	N.D.	0.05	N.D.	N.A.	
Ba	N.D.	(0.15)	0.8	0.2	N.D.	0.06	1.5	0.6	N.D.	0.3	N.D.	N.A.	
Mg	N.D.	0.50	0.9	5.0	N.D.	0.10	N.D.	N.D.	6.7	10.0	14.5	5.8	
Na	N.D.	N.A.	N.D.	N.A.	N.D.	N.A.	N.D.	N.A.	3.2	N.A.	N.D.	0.7	
C <sup>e</sup>	14.1	(51.14)	40.5	(61.55)	31.4	(62.34)	66.5	(93.12)	34.4	(56.35)	28.1	(45.4)	
O <sup>f</sup>	46.6		27.3		33.7		14.0		25.7		21.7		

<sup>a</sup>Surface concentrations are calculated from equation 1 using XPS peak intensity ratios normalized to Si 2s.

<sup>b</sup>Accepted values from US NBS certificate of analysis (14); values in brackets listed but not certified, values in square brackets determined in concomitant SSMS study (4).

<sup>c</sup>Analysis by XRF and/or SSMS (4).

<sup>d</sup>Sulphur is present as the sulphate species (S<sup>6+</sup>) except for ashed sample No. 8 where sulphide (S<sup>2-</sup>) was also detected.

<sup>e</sup>As per Table 1; note some of this carbon is probably carbonaceous surface sited residue deposited during the coal ashing step.

<sup>f</sup>As per Table 1; some of this oxygen will be from oxygen species such as CO, CO<sub>2</sub>, etc., associated with the carbonaceous coating (see e).