Distribution of Elements in Coal Macerals and Minerals: Determination by Electron Microprobe

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Systematic study of elemental abundances in coal macerals and minerals is vital to understanding the genetic history and geological significance of particular coal beds, in correlating coal beds for coal mine planning, in assessing the environmental impact of utilization of coal from a particular source, and in evaluating the potential for recovery of waste by-products and for catalytic action in coal conversion. In-situ determinations of elemental concentrations in macerals and in clays, sulfides and other mineral constituents may help to establish the primary vs. secondary emplacement of particular elements, i.e. elements which were fixed when the coal precursors were deposited vs. mobile elements which may have been introduced and/or redistributed by ground water circulation and other diagenetic processes. Furthermore, determination of the distribution of elements between macerals and minerals is essential in evaluating the possibility of removal of contaminants by grinding and washing, because elements in macerals cannot be effectively removed by these procedures.

Application of electron microprobe analysis to coal-related studies is still in the developmental stage (1). We report here preliminary results of intensive study of one columnar coal sample to indicate the nature of the data on elemental distribution that are readily obtainable through use of the electron microprobe. In order to preserve the stratigraphic relationships of the different coal facies, polished blocks (Figure 1) and polished thin sections were prepared to represent the total thickness of the coal bed. These blocks and thin sections were first studied petrographically with the optical microscope, and areas representative of the principal lithologic units (Figure 2) were designated for analysis by the electron microprobe. A 118-cm thick columnar sample of medium volatile bituminous Upper Freeport coal used for this study was collected in the Helen Mine, Indiana County, Pa. Petrographic analysis (E. C. T. Chao et al., unpublished data) indicates that the coal bed is composed of two cycles of organic-matter deposition and five major lithologic coal types (Figure 3). The division between the two cycles of deposition is the base of one major lithologic unit, a carbonaceous shale parting with bands of vitrite between depths 85 and 92.5 cm. This carbonaceous shale, characterized by water-transported depositional features, may be a key stratigraphic marker. Above the shale parting three major lithologic coal types are discernible: one from the top of the coal to 30 cm depth, another from 30 to 50 cm, and a third from 50 to 85 cm. The fifth is the column interval from 92.5 to 118 cm.

The electron microprobe has been used for in-situ determinations of abundances of 23 elements in the macerals and for analyses of discrete mineral grains present at representative depths of the column. The instrument at the Reston laboratories of the U. S. Geological Survey is routinely capable of wavelength dispersive analysis of all elements stable in vacuum and of atomic number 9 (fluorine) and greater. Limit of detectability for most elements is about 100 ppm, and the minimum target area which can be analyzed is approximately 3 x 3μm. Penetration depth of the electron beam into the target is from 1 to 5μm.

Table 1 summarizes the range of abundance of the 23 elements analyzed in macerals of the five major lithologic coal types of the column. At the sites where these elements were detected by probe analysis, discrete minerals were not observed optically down to the limit of resolution (about 0.5μm). Strehlow et al. (2), in a transmission electron microscope study of Illinois No. 6 coal, reported a profusion of mineral particles in vitrinite in the size range from 30nm to approximately 0.2μm. Thus it is probable that some of the elements detected in our electron microprobe maceral analyses are associated with submicron-sized mineral

matter. In particular, silicon and aluminum, which vary in abundance in a parallel manner are probably associated with extremely finely dispersed clay minerals.

Two elements, sulfur and chlorine, clearly seem organically associated in the macerals of this coal. Sulfur appears to be homogeneously distributed throughout a given maceral, implying an association on the molecular level. Furthermore, a comparable amount of iron is not present, as would be true if this were submicron-sized pyrite or marcasite. The amounts of organic sulfur determined by electron microprobe analysis (Table 1) tend to be greater in the lower depositional unit and are in good agreement with analyses of this coal by conventional methods (3,4). The amount of sulfur in inertinite tends to be about half that in vitrinite, while the sulfur content of the exinites analyzed (this coal contains very little exinite (Figure 3)), more closely approaches the level in vitrinite. Harris et al. in a suite of coals they studied (5) found that exinites always have more sulfur than do vitrinites but determinations by Raymond and Gooley (1) generally agree with our results. In the Upper Freeport sample, chlorine like sulfur, seems homogeneously distributed in a given maceral. In addition, comparable levels of cations such as sodium or potassium were not detected (Table 1), as would be expected if the chlorine were associated with mineral inclusions. Gluskoter and Ruch (6) also concluded that in coals from the Illinois Basin weakly bound chlorine in organic combination was a likely mode of occurrence. Chlorine concentrations in the Upper Freeport sample tend to be higher for the upper cycle of deposition (Table 1). X-ray fluorescence data on ash from this coal show a similar trend (3). This trend perhaps implies greater salinity of the swamp water during the period of growth and deposition of the coal precursors of the upper depositional cycle, compared with the lower.

A systematic study has also been made of the composition of the clays over the full 118-cm depth fo the column (Table 2). Identification of the clay minerals is based on their chemical compositions. Those with $K_2O>2.5$ wt.% are tentatively designated as illites, those with $Al_2O_3>30$ wt. %, $SiO_2>40$ wt. % and $K_2O\leq1.5$ wt. % are labeled kaolinites, and "mixed layer" clays are those with K_2O between 1.6 and 2.5 wt. %. In the upper unit of deposition, illites are distinctly dominant and kaolinites occur mostly in shale. "Mixed layer" clays are found only below 92.5 cm depth. Clays in the shales are generally lower in silicon and higher in iron than those in the rest of the coal column. Illites tend to be higher in titanium and lower in aluminum than the other two clay types.

Electron microprobe analyses of iron sulfides determined that arsenic is present in pyrite only from depth 5 to 20 cm in this coal column. The mode of arsenic occurrence is discussed by Finkelman et al. (7).

Because much of this sample of Upper Freeport coal is vitrinite-rich (Figure 3), even small amounts of non-volatile elements in the vitrinite (Table 1) will contribute significantly to the coal ash. The clay and quartz optically observed in vitrinite generally is less than 30μm in grain size; thus, the elements shown in the analyses of Table 2 will also probably remain in the coal even after fine grinding and washing.

These preliminary elemental studies using the electron microprobe have documented variations in sulfur and chlorine abundance in macerals, clay compositions, and presence of arsenic in pyrite which clearly indicate differences in the depositional and subsequent environmental characteristics of the upper and lower depositional units of this coal. It is hoped that after refinement of our methods of study, more complete evaluation of the abundance of particular elements in a given coal bed will be possible through correlation of modal analyses of maceral-mineral composition (E. C. T. Chao et al., unpublished data) with in-situ chemical data for macerals and minerals obtained by electron microprobe and proton-induced X-ray emission (the latter for elements at concentrations less than 100 ppm) techniques.

References

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Table 1. Electron Microprobe Determinations of Minor and Trace Element Concentrations (Wt. %) in Macerals of the Five Major Lithologic Coal Types, Upper Freeport Column Sample H2-42P-1.

	0 - 30 cm		30 - 50 cm		50 - 85 cm	
	V	E and I	V	E and I	V	E and I
Al	0-0.11	0-0.14	0.03-0.05	0.09-8.3	0-0.48	0-8.0
Ba	n.d.	n.d.	0	0	0-0.03	0-0.10
Bi	0	0	0-0.07	0-0.06	0	0-0.07
Ca	0.02-0.07	0-0.11	0-0.05	0-2.6	0-0.07	0-6.2
Cl	0.25-0.28	0-0.15	0.24-0.32	0.09-0.48	0.15-0.31	0-2.2
Co	0	0	0-0.05	0-0.08	0-0.04	0-0.04
Cr	0-0.02	0	0-0.05	0-0.05	0-0.03	0-0.08
Cu	0-0.06	0-0.03	0	0	0-0.08	0-0.10
F	0	0-0.08	0	0-0.02	0-0.05	0-0.12
Fe	0-0.05	0-0.41	0-0.04	0-0.20	0	0-0.09
K	0	0-0.36	0	0-0.12	0-0.06	0-0.92 (I) 0-0.05 (E)
Mg	0	0-0.11	0	0-0.04	0	0-0.79 (I) 0-0.06 (E)
Mn	0	0	0	0-0.09	0-0.03	0-0.07
Na	0	0-0.07	0	0-0.07	0-0.03	0-0.35
Ni	0	0	0-0.04	0-0.04	0	0-0.08
P	0	0-0.11	0	0	0	0-0.09
Pb	0	0-0.03	0	0-0.02	0-0.04	0
S	0.46-0.57	0.09-0.40 (I) 0.45-0.48 (E)	0.37-0.49	0.16-0.29 (I) 0.34-0.43 (E)	0.43-0.63	0.13-0.29 (I) 0.23-0.42 (E)
Si	0-0.29	0-0.25	0.04-0.07	0.15-10.9	0-0.30	0-1.80 (I) 0-9.4 (E)
Sr	0	0	0	0	0	0
Ti	0-0.03	0	0.02-0.05	0-0.02	0.02-0.25	0-0.02
V	0-0.02	0-0.03	0	0	0-0.04	0-0.03
Zn	n.d.	n.d.	0	0-0.02	0	0-0.07

V: Vitrinite E: Exinite I: Inertinite "0" = < 0.01 wt. %.
n.d. = not determined

Table 1. continued

	85 - 92.5 cm		92.5 - 118 cm	
	V	E and I	V	E and I
Al	0.09-0.30	0.14-3.3	0-0.47	0-8.9 (I) 0-0.03 (E)
Ba	0	0	0-0.07	0-0.16
Bi	0	0	0-0.08	0-0.07
Ca	0-0.07	0-0.09	0-0.10	0-0.89
Cl	0.02-0.24	0	0.21-0.27	0.02-0.12
Co	0	0	0	0-0.03
Cr	0-0.02	0-0.04	0-0.02	0-0.04
Cu	0	0-0.02	0	0
F	0-0.04	0-0.02	0-0.05	0-0.78
Fe	0.04-0.13	0.05-0.34	0-0.07	0-1.78 (I) 0-0.14 (E)
K	0-0.06	0-0.04	0	0-0.03
Mg	0	0-0.06	0-0.02	0-0.17
Mn	0-0.03	0-0.04	0-0.04	0-0.08
Na	0	0-0.71 (I) 0-0.03 (E)	0-0.02	0-0.34 (I) 0-0.05 (E)
Ni	0-0.05	0	0-0.02	0
P	0	0	0	0-0.30
Pb	0	0	0-0.02	0-0.06
S	0.63-0.66	0.28-0.38 (I) 0.41 (E)	0.59-0.69	0.18-0.42 (I) 0.44-0.56 (E)
Si	0-0.26	0.20-0.48	0.04-0.77	0.03-10.7 (I) 0-0.09 (E)
Sr	0	0	0	0
Ti	0.22-0.39	0-0.02	0.02-0.17	0 (I) 0-0.42 (E)
V	0-0.05	0	0-0.03	0
Zn	0	0-0.03	0-0.03	0-0.05

V: Vitrinite E: Exinite I: Inertinite "0" = < 0.01 wt. %.
n.d. = not determined

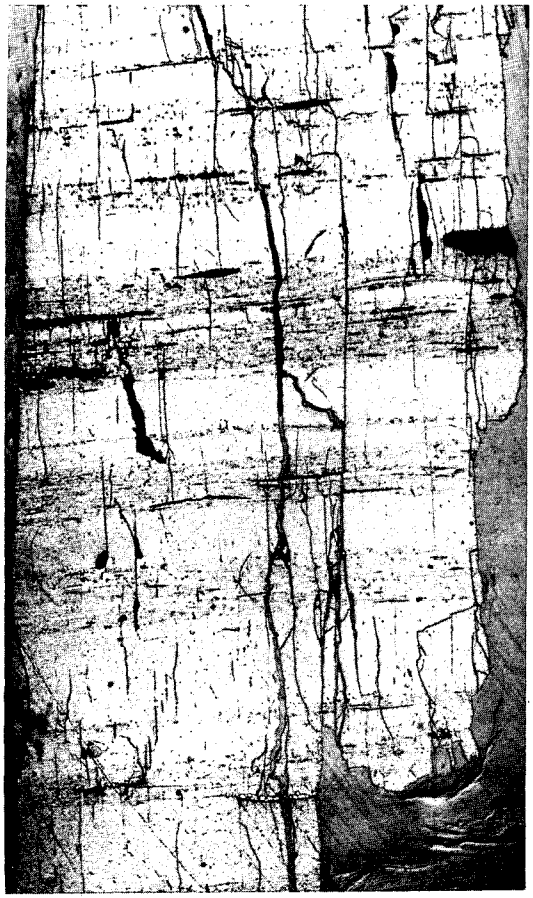
Table 2. Electron Microprobe Analyses of Clay Minerals in Upper Freeport Coal Column Sample H2-42P-1

	ILLITES		KAOLINITES		"MIXED LAYER" CLAYS	
Depth (cm.)	56	88	88	112	96	112
SiO_2	48.9	45.2	44.6	44.6	47.2	47.6
Al_2O_3	32.4	35.4	36.0	38.1	36.9	36.2
FeO*	1.42	2.69	3.2	0.63	1.22	1.73
MgO	1.70	0.43	0.85	0.15	0.60	0.87
CaO	0	0	0	0	0.05	0.05
K_2O	6.6	8.2	0.16	0.10	1.71	1.83
Na_2O	0.23	0.69	0.09	0.07	0.18	0.55
TiO_2	0.49	0.18	0.03	0	0.07	0.03
MnO	0	0	0	0	n.d.	0
Total Oxide Wt. %	91.7	92.8	84.9	83.6	87.9	88.9

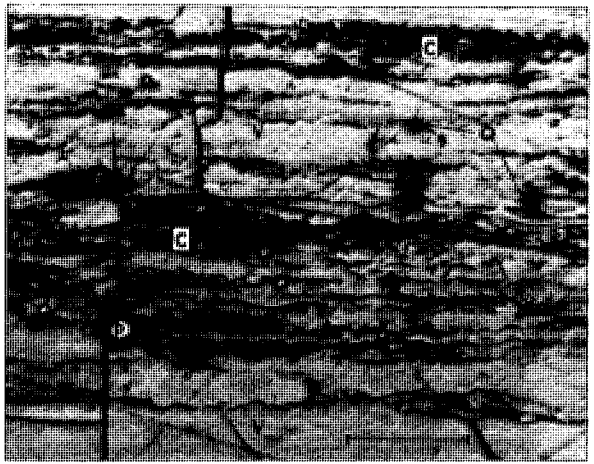
"0" = < 0.01 wt. %.

n.d. = not determined.

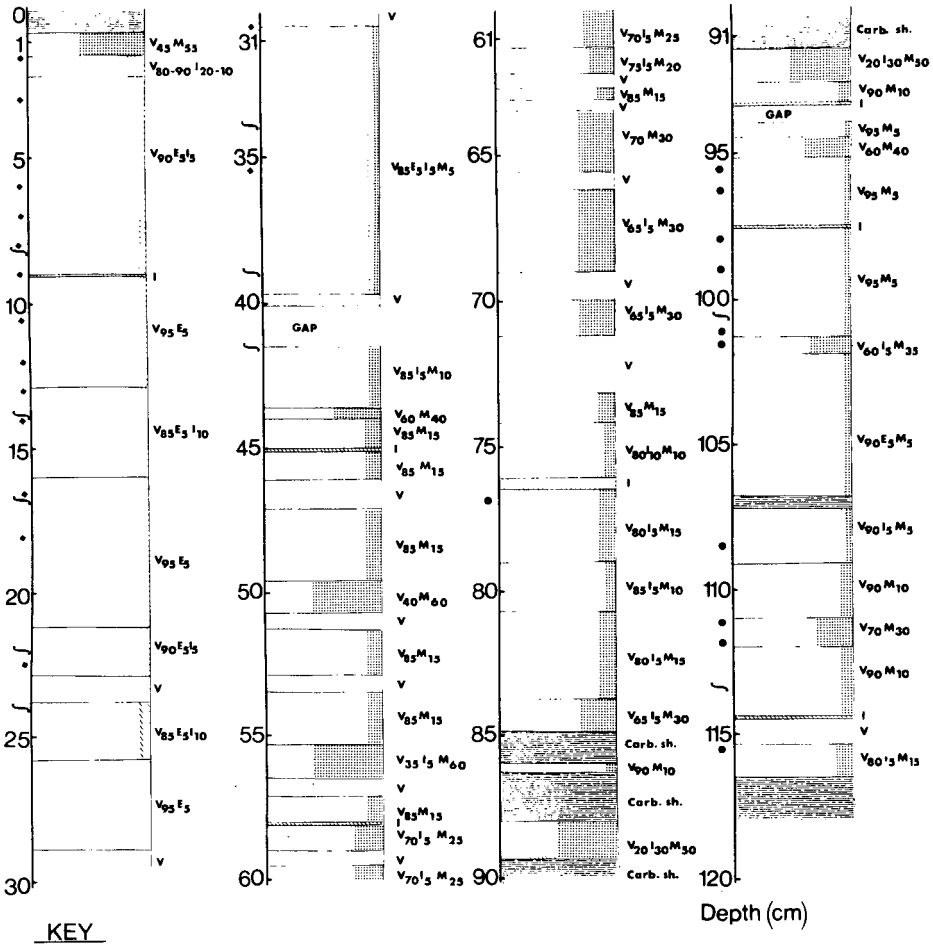
*Total Fe as FeO.



(Left) Figure 1. Vertical-illumination photograph of a polished block from depths 27-30.5 cm, Upper Freeport column sample H2-42P-1. Light gray bands are vitrinite; darker bands are assemblages containing 90-95 volume % vitrinite, 5% exinite and lesser amounts of inertinite and mineral matter. Very dark lenses at depth 28-28.5 cm are inertinites (fusinite and semifusinite). Bar scale 0.5 cm.



(Above) Figure 2. Photomicrograph of an area at depth 96.5 cm, same column, showing mineral matter dispersed in vitrinite. Vitrinite is labelled V, quartz Q, clay C, pyrite P, and inertinite I. Taken in reflected light using an oil-immersion contrast objective lens. Bar scale 0.1 mm.



KEY

- Vitrinite
- Exinite
- Inertinite
- Mineral matter
- Shale and Carbonaceous shale
- massive & granular sulfide
- framboidal sulfide
- location of thin fusinite bands

Figure 3. Generalized columnar profile of H2-42P-1. Volume percentages of macerals and mineral matter are plotted across the column according to the amount of each present, and indicated numerically by the label at the right side of the column for a particular depth interval.