

DISTRIBUTION OF MAJOR, MINOR AND TRACE ELEMENTS IN COALS OF THE KOOTENAY GROUP, MOUNT ALLAN, ALBERTA

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ABSTRACT

Medium-volatile bituminous to semi-anthracite coals of the Kootenay Group occur in a 875-m section at Mount Allan, Alberta (NTS 82 J/14). The distribution of 55 elements was studied for 14 selected seams from the section by instrumental neutron-activation analysis. The coals vary in reflectance $R_{o\max}$ from 1.30 to 2.48. Two populations in terms of element distribution appear to be present, divided roughly along rank boundaries. All the medium-volatile and most of the low-volatile bituminous coals show larger concentrations of Cr, Hf, K, Rb, Sc, Th, V and Yb than the samples of higher rank lower in the section, which generally contain more Fe and Mn. Though the changes appear to be rank-related, they may also be related to changes in depositional environments in the original peat swamps. The Na/K ratio, used as an indicator of burial rate, suggests three cycles in the Mount Allan section. The relationship of element concentration to ash content was used to determine organic affinity (e.g., Br and Cl) or inorganic affinity (e.g., Al, Ti). Using 6 and $\frac{1}{6}$ times the Clarke value as thresholds, only Br and Sb are enriched in the Mount Allan coals, whereas Fe, Mg, Mn, Na, K, Co and Ta are depleted in most seams, if the data are evaluated on a whole-coal basis.

Keywords: Kootenay coal, Mount Allan, Alberta, major, minor and trace elements.

SOMMAIRE

Dans une coupe de 875 m dans les roches du groupe Kootenay, au mont Allan, en Alberta (NTS 82 J/14), on trouve des charbons dont la teneur en matières volatiles varie à partir des houilles grasses, moyennement volatiles, jusqu'aux houilles anthraciteuses. On discute de la distribution de 55 éléments (données obtenues par activation neutronique instrumentale) dans 14 couches choisies. La réflectance de ces charbons varie de 1.30 à 2.48 ($R_{o\max}$). Les deux groupes de charbons que l'on distingue par la distribution des éléments correspondent à peu près à leur teneur respective. Tous les charbons à volatilité moyenne, ainsi que les charbons bitumineux, à faible volatilité, possèdent une plus grande concentration de Cr, Hf, K, Rb, Sc, Tb, V et Yb que les échantillons plus anthraciteux, situés plus bas dans la section, et généralement enrichis en Fe et Mn. Quoique ces différences semblent reliées à la teneur en matières volatiles, elles pourraient également refléter des changements dans le milieu de déposition, dans les marais de tourbe. Le rapport des valeurs élémentaires Na/K, indicateur du taux d'enfouissement, fait penser qu'il y a trois cycles de déposition dans la section du mont Allan. On s'est servi de la relation entre la concentration des éléments et

le contenu en cendre de ces charbons pour déterminer leurs affinités organique (e.g., Br et Cl) et inorganique (e.g., Al, Ti). En utilisant comme seuils les facteurs de 6 et de $\frac{1}{6}$ fois le Clarke des éléments, on constate que seuls Br et Sb sont enrichis dans ces charbons, tandis que Fe, Mg, Mn, Na, K, Co et Ta sont appauvris dans la plupart des couches, si l'on considère les données sur une base de charbon total.

Mots-clés: charbon de Kootenay, mont Allan, Alberta, éléments majeurs, éléments traces.

INTRODUCTION

Few systematic studies of mineral matter in Canadian coals, including distribution of trace elements, have been carried out. Trace-element concentrations have been reported by Newmarch (1953), Hawley (1955), Nichols & D'Auria (1981), Landheer *et al.* (1982) and Zodrow (1982). Only Landheer *et al.* (1982) carried out a study of regional scale; most of their samples are representative of commercial coal supplied to power plants and other industrial users.

The Geological Survey of Canada has begun a systematic study of mineral matter and trace elements in major coalfields of the country, in order to define the geological controls on these materials and to determine if significant differences exist among coals of different basins and ages.

The initial phase of the study has concentrated on coals of the Jurassic-Cretaceous Kootenay Group of southeastern British Columbia and southwestern Alberta. Some preliminary results have been published (Goodarzi *et al.* 1985, Goodarzi 1987). The present paper deals with the coals of the Mount Allan area in Alberta and has the following objectives: 1) to identify the vertical variation among seams in a given section, 2) to determine the relationship with environments of deposition, e.g., marine *versus* non-marine, 3) to determine if individual elements have a preferred association with the organic or inorganic (mineral matter) fractions of the coal, and 4) to examine enrichment or depletion of elements as compared to reference data such as Clarke values.

Figure 1 locates the study area and shows a simplified stratigraphic section of the Kootenay Group at this locality, based on studies by Gibson (1985) and Hughes & Cameron (1985). The Kootenay Group at this site is over 1000 metres thick and contains over 30 coal seams. Many of these are too thin

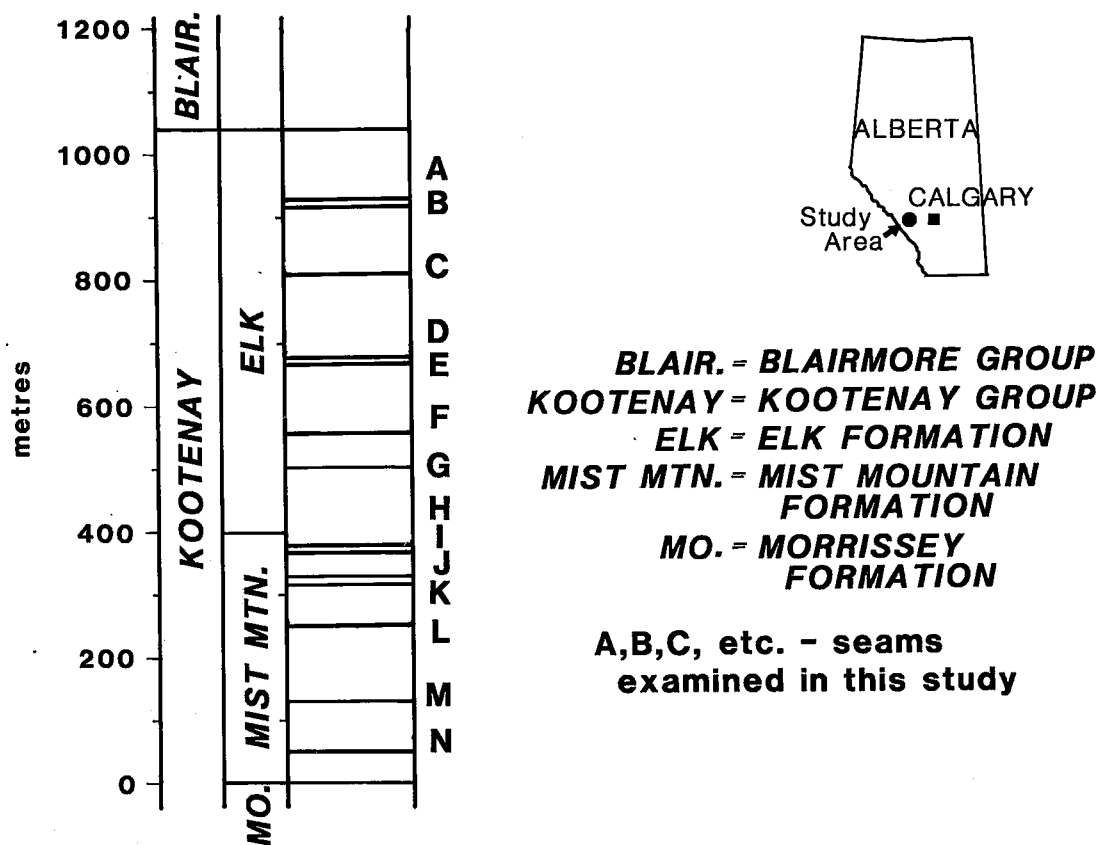


FIG. 1. Locality map and schematic representation of the Mount Allan section.

TABLE 1. CHEMICAL ANALYSES DATA AND REFLECTANCES ON MOUNT ALLAN COALS¹

Seam	Moisture %	Ash %	VM ² %	FC ³ %	C %	H %	N %	S %	O (by diff.) %	Cal. Value MJ/kg	%Ro Max
A	2.50	35.40	18.60	43.50	51.83	3.01	0.72	0.63	5.91	20.3	1.3
B	5.80	19.90	24.00	50.30	59.42	3.65	0.93	0.73	9.57	22.9	1.35
C	2.20	30.00	18.40	49.40	55.95	3.23	1.02	0.71	6.89	22.4	1.43
D	1.20	15.00	17.50	66.30	72.94	3.85	1.36	0.85	4.80	29.3	1.63
E	1.10	7.80	20.00	71.10	80.46	4.38	1.45	0.95	3.86	32.4	1.50
F	2.10	45.00	13.80	39.10	44.46	2.53	0.93	0.64	4.34	16.9	1.63
G	1.60	16.10	17.70	64.60	71.73	3.66	1.36	0.93	4.62	28.4	1.84
H	3.70	9.10	19.10	68.10	74.46	3.82	1.38	0.55	6.99	29.0	1.92
I	3.90	11.70	20.90	63.50	70.63	3.62	1.35	0.37	8.43	27.1	1.99
J	5.20	11.90	20.80	62.10	69.85	3.57	1.21	0.78	7.49	26.7	1.98
K	3.50	16.70	17.30	62.50	67.10	3.36	1.02	0.82	7.50	26.2	2.00
L	1.20	3.30	12.20	83.30	85.12	3.56	1.00	0.82	5.00	33.2	2.19
M	2.00	4.40	14.30	79.30	82.89	3.48	1.01	0.76	5.46	32.0	2.30
N	1.40	6.90	11.20	80.50	82.75	3.49	0.93	0.59	3.94	32.1	2.49

¹ all chemical data and calorific values on as-received basis. ² VM = volatile matter.³ FC = fixed carbon.

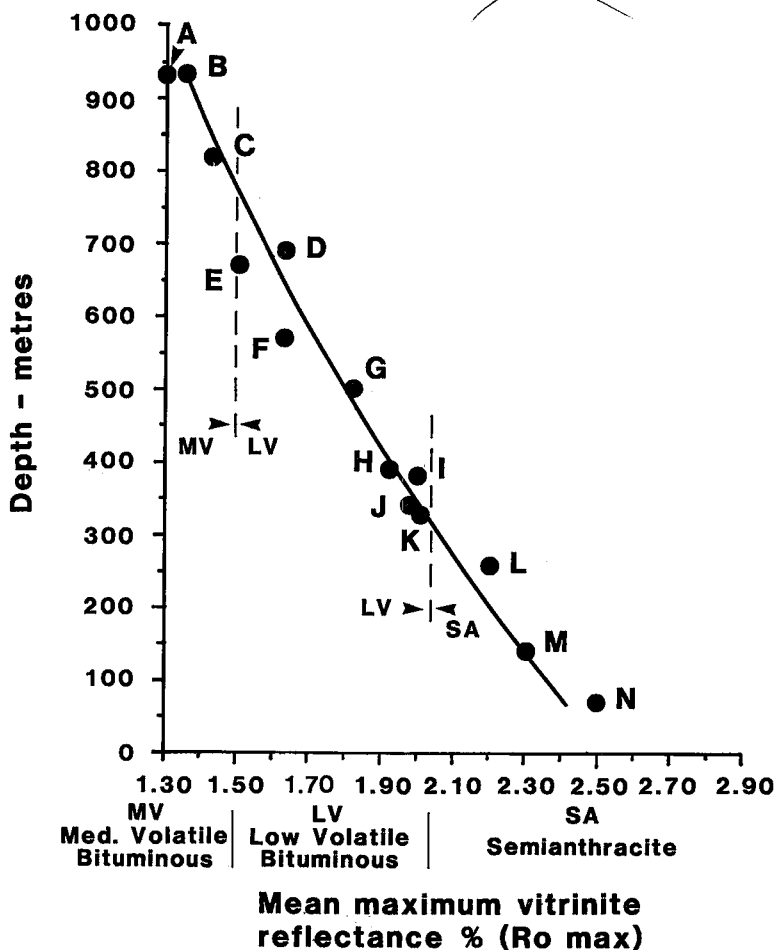


FIG. 2. Depth-reflectance profile for the Mount Allan section (modified after Hughes & Cameron 1985).

to be economically important, although there are also mineable seams, especially toward the base of the section. The lateral equivalents of some of these seams were mined up to the late 1970s at Canmore, a few kilometres from Mount Allan.

Fourteen of the seams present in the Mount Allan section (identified in this paper as seams A through N) were sampled for analysis. These seams cover a stratigraphic interval of some 875 metres. Each seam is represented by one sample, thus preventing examination of lateral variation. Characterization of elemental distribution should be viewed in the light of this constraint.

SAMPLING AND EXPERIMENTAL METHODOLOGY

Whole-seam channel samples of the 14 selected coals were collected from outcrop. Because of

weathering effects, elemental distribution may differ from fresh samples of the same coals. In the initial step of processing, samples were crushed to minus 20 mesh (840 nm). A representative split of the < 20 mesh material from each sample was removed for the preparation of grain mounts or pellets. These were then polished for reflected-light microscopy according to ASTM procedures (standard D 2797-72, ASTM, 1979). The rank of these coals was determined by measuring maximum reflectance with a Leitz Orthoplan microscope equipped with MPV II photometric accessories. The procedure followed is that outlined by the International Committee for Coal Petrology (1971). Reflectance data were related to ASTM rank boundaries according to limiting values proposed by Davis (1978).

An additional portion of each sample was removed for proximate and ultimate analyses, which were per-

TABLE 2. ELEMENTAL DISTRIBUTION IN COAL OF THE MOUNT ALLAN SECTION 1.2

Element ³	Clarke ⁴ value: earth's crust	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Al	81.3K	8.6K	21.8K	34.5K	17.3K	8.3K	45.0K	18.2K	11.6K	10.1K	6.9K	17.3K	6.7K	2.3K	13.9K
Ba	0.4K	0.4K	2.3K	0.4K	0.4K	0.2K	0.8K	0.3K	1.0K	0.3K	0.6K	3.1K	0.8K	0.1K	0.3K
Ca	36.3K	9.9K	25.6K	7.1K	2.7K	3.4K	6.8K	4.0K	12.5K	13.1K	18.5K	12.5K	1.1K	2.2K	1.1K
Fe	50.0K	1.6K	1.6K	5.3K	2.0K	2.8K	5.4K	1.8K	2.1K	20.7K	9.2K	18.5K	0.1K	18.2K	2.3K
Mg	20.9K	1.4K	3.5K	4.0K	1.6K	0.9K	4.0K	1.6K	1.8K	1.9K	3.5K	2.1K	0.4K	0.7K	0.4K
K	25.9K	1.0K	1.7K	8.7K	3.4K	1.3K	12.6K	3.9K	0.5K	0.8K	1.2K	1.7K	<0.2K	0.8K	0.4K
Na	28.3K	0.2K	0.3K	0.2K	0.1K	0.1K	0.3K	0.1K	0.1K	0.1K	0.1K	0.2K	0.2K	0.2K	0.2K
Ti	4.4K	3.0K	1.0K	1.5K	0.8K	0.4K	2.1K	0.8K	0.6K	0.4K	0.3K	1.2K	0.2K	0.2K	0.3K
Sb	0.2	0.9	1.9	3.3	1.8	15.8	5.3	2.5	0.4	0.4	2.2	1.1	0.1	0.3	0.1
As	1.8	2.2	1.5	17.0	1.2	6.8	2.9	1.0	0.7	1.4	8.5	24.3	<0.3	0.8	<0.4
Br	2.5	11.9	10.7	15.8	20.0	23.9	18.5	23.4	42.6	26.6	33.7	17.8	18.0	38.6	32.2
Ce	60.0	33.7	31.1	20.0	17.8	5.4	29.3	11.5	8.2	4.7	4.5	5.0	0.9	16.5	9.6
Cs	3.0	<0.4	0.7	4.0	1.6	0.5	6.2	1.9	<0.2	<0.2	0.4	0.5	<0.1	<1.0	0.4
Cl	130.0	66.8	67.3	93.8	72.8	195.0	88.2	85.0	91.4	91.9	113.0	87.1	75.9	86.3	122.0
Cr	100.0	37.0	28.7	68.8	22.5	19.2	82.1	31.1	8.8	4.9	8.5	11.8	3.4	<1.1	2.1
Co	25.0	0.6	2.8	1.0	3.3	2.3	1.7	2.2	1.2	1.3	2.9	2.4	1.0	0.6	1.7
Eu	1.20	0.01	0.6	0.5	0.7	0.3	0.5	0.4	0.2	0.1	0.3	0.2	0.1	0.3	0.4
Ga	15.0	3.9	<3.77	11.1	5.4	13.5	11.4	6.3	3.0	<4.8	6.2	8.1	<2.2	<5.9	<3.0
Hf	3.0	3.3	1.7	2.0	1.1	0.9	2.2	0.9	0.7	0.6	0.7	0.8	0.2	<0.1	0.7
Ho	1.2	0.7	0.4	0.3	0.4	0.3	0.2	0.3	0.1	1.0	0.4	0.1	<0.1	0.2	1.0
In	0.1	0.02	0.03	0.02	0.01	<0.01	0.04	0.02	0.01	<0.02	<0.01	0.03	<0.01	<0.01	<0.01
I	0.5	0.8	1.4	3.5	1.4	5.9	2.3	0.9	0.4	1.7	1.2	2.3	0.4	<1.0	0.4
La	30.0	21.2	18.5	12.0	11.6	2.3	19.4	7.3	4.4	2.1	2.3	3.1	0.4	10.7	5.2
Lu	0.5	0.6	0.4	0.6	0.4	0.7	0.5	0.5	0.1	0.1	0.5	0.1	<0.03	0.1	0.2
Mn	950.0	9.6	11.4	7.6	10.8	15.8	11.7	9.3	13.7	106.0	140.0	181.0	1.5	184.4	21.0
Mo	1.5	3.8	<1.1	1.3	1.3	3.5	1.2	4.6	0.9	4.9	6.4	3.2	0.6	1.5	<0.8
Nd	28.0	13.0	12.4	7.2	8.6	2.7	9.15	5.1	3.3	2.7	3.9	2.4	<0.9	5.3	6.4
Ni	75.0	<48.5	<41.5	<44.1	<32.0	<49.7	<43.3	<56.0	<22.7	<30.9	<421.4	<39.0	<19.1	<27.0	<23.7
Rb	90.0	5.5	7.8	39.4	16.3	5.5	66.2	16.2	<2.6	<4.2	4.5	12.1	<2.1	<3.7	<2.9
Sm	6.0	2.7	2.3	1.4	2.3	0.8	1.7	1.2	0.6	0.5	0.8	0.5	<0.02	<0.1	1.1
Sc	22.0	13.3	8.0	9.3	4.3	13.7	8.9	7.6	1.8	1.7	7.3	4.8	1.1	1.0	2.1
Se	0.1	<0.7	<0.8	<0.7	<0.1	<0.7	4.0	<1.0	1.3	1.2	2.0	2.1	1.1	0.8	<0.8
Ag	0.1	<1.6	<1.4	<1.4	<1.01	<1.6	<1.4	<1.3	<0.7	<0.8	<1.3	<1.1	<0.6	<0.7	<0.7
Sr	375.0	108.0	746.0	93.5	53.6	<24.6	132.0	45.1	166.0	<43.0	<49.7	503.0	109.0	<53.0	193.0
Ta	2.0	0.9	0.4	0.4	0.2	0.1	0.5	0.2	0.2	0.1	0.11	0.1	0.1	<0.02	0.1
Tb	0.9	0.2	0.3	0.2	0.3	0.3	0.3	0.3	<0.1	<0.1	0.2	0.1	<0.1	0.2	0.2
Th	7.2	4.3	5.6	5.7	2.2	1.6	5.3	2.4	1.5	0.8	0.9	1.2	0.4	0.1	1.3
Tm	0.5	0.3	<0.3	0.3	0.2	0.3	0.3	0.3	<0.2	<0.1	0.3	0.1	<0.1	0.2	<0.2
U	1.8	4.9	3.5	4.0	2.1	1.9	2.1	1.7	1.6	1.1	3.1	1.4	0.6	0.2	0.6
V	135.0	44.7	65.7	146.0	47.7	92.9	198.0	74.9	18.4	14.8	32.0	55.2	4.71	<3.6	6.7
Yb	3.4	1.7	1.1	1.4	1.1	1.9	1.4	1.2	0.3	0.2	1.1	0.3	0.1	0.3	0.6
Zn	70.0	23.1	24.2	18.5	24.5	57.3	50.6	51.9	12.8	21.0	55.9	28.5	5.6	7.3	8.7

¹ data on whole-coal basis. ² determinations were made on Cd, Cu, Dy, Er, Ge, Au, Ir, Nb, Pr, Sn, W, Y, and Zr but are not included in Table because standard deviations > 20. ³ values in ppm except for Al, Ba, Ca, Fe, Mg, K, Na and Ti for which data are ppm x 1000 - (k). ⁴ Clarke values from Mason and Moore (1982).

formed according to ASTM specifications (standards D 3172-73 and D 3176-74, ASTM, 1979). A third split of each sample was ground to < 100 mesh (149 nm) for elemental studies.

Trace-element determinations were made by instrumental neutron-activation analysis (INAA) on unashed coal. Statistical treatment of the data included cluster analysis of elemental distribution using a method described by Labonté & Goodarzi (1985).

RESULTS AND DISCUSSION

The rank of the subject coals ranges from medium-volatile bituminous to semi-anthracite. Reflectance data are presented in Table 1 along with chemical data. Reflectivities are also shown graphically on a reflectance-depth profile (Fig. 2).

Data on elemental distribution are presented in Tables 2 and 3 on a whole-coal and ashed basis, respectively. Determinations were carried out on 55 elements. For a number of elements, data on some samples are reported as "less than" values. If any element showed more than one such value, it was not included in the cluster analysis nor in some of the other statistical calculations performed on the data. Also, the calculated values (Table 3) are limited to the more restricted group of elements. However, all elements have been included in Table 2.

Variation among seams

Within the context of this study, only the vertical variation in the section can be examined. The lateral variation within any one of these seams has not been studied. The vertical distribution of elements among

TABLE 3. ELEMENTAL DISTRIBUTION IN SEAMS OF MOUNT ALLAN SECTION CALCULATED TO ASH BASIS

	Seams													
	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Concentration in percent														
Al	2.4	10.3	11.2	11.4	10.5	9.8	11.1	12.3	8.3	5.5	10.0	19.9	5.1	19.9
Ba	0.1	1.1	0.1	0.3	0.3	0.2	0.2	1.1	0.3	0.5	1.8	2.4	0.1	0.4
Ca	2.7	12.1	2.3	1.8	4.2	1.5	2.5	13.2	10.8	14.7	7.2	3.3	4.9	1.6
Fe	0.4	0.7	1.7	1.3	1.5	1.2	1.1	2.2	17.0	7.3	10.7	0.3	40.5	3.2
Mg	0.4	1.7	1.3	1.0	1.1	0.9	1.0	1.9	1.5	2.8	1.2	1.1	1.6	0.5
K	0.3	0.8	2.8	2.2	1.7	2.7	2.4	0.5	0.6	0.9	0.1	0.7	1.7	0.6
Na	0.5	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.7	0.4	0.3
Ti	0.8	0.5	0.5	0.5	0.5	0.5	0.5	0.7	0.3	0.3	0.7	0.7	0.5	0.4
Concentration in ppm														
Sb	2.6	9.0	10.7	11.5	200.3	11.5	15.5	4.3	3.0	17.7	6.5	1.5	6.0	1.6
Br	32.8	50.6	51.5	131.7	302.9	40.3	143.0	450.8	218.4	268.5	102.9	538.9	860.0	460.0
Ce	92.8	147.2	65.2	117.2	68.2	63.8	70.3	87.1	38.4	36.0	29.1	28.1	367.5	137.0
Cl	184.0	318.5	305.7	479.3	2472.0	191.9	519.6	967.2	754.5	900.4	503.5	2272.0	1922.0	1743.0
Cr	101.9	135.8	224.3	148.1	243.4	178.6	190.1	93.3	40.5	67.7	68.2	101.5	<24.5	29.6
Co	1.7	13.0	3.2	21.5	28.9	3.7	13.3	12.2	10.8	23.2	14.0	29.0	12.7	24.0
Eu	0.02	2.8	1.6	4.6	3.9	1.1	2.3	1.9	1.2	2.4	1.2	1.8	6.0	5.0
Hf	9.0	8.2	6.5	7.5	11.9	4.7	5.6	7.6	5.3	5.4	4.7	6.9	<2.7	9.6
Ho	1.8	2.0	0.9	2.7	4.1	0.5	1.7	1.2	0.7	3.1	0.8	<1.5	4.0	1.3
I	2.1	6.8	11.5	9.1	74.4	4.9	5.2	4.6	14.1	9.9	13.5	11.4	<20.5	6.0
La	58.4	87.6	39.1	76.4	28.9	42.2	44.7	46.7	16.9	18.7	17.7	12.6	238.3	74.7
Lu	1.8	2.1	1.8	2.6	9.0	1.2	2.8	1.2	0.9	3.8	0.6	<0.9	2.5	2.4
Mn	26.5	53.6	24.8	71.1	200.3	25.5	57.0	145.0	870.3	1116.0	1046.0	45.8	4098.0	230.0
Nd	35.8	58.7	23.5	56.8	34.1	19.7	30.9	34.7	22.2	31.3	13.9	<27.0	118.0	90.9
Sc	36.6	37.8	30.3	28.4	117.6	14.4	46.3	19.3	13.6	58.3	27.5	33.2	21.4	30.4
Ta	2.5	1.9	1.3	1.3	0.9	1.1	1.1	1.4	0.7	0.6	0.8	2.1	0.5	0.9
Th	11.8	26.6	18.6	14.2	13.4	11.5	14.4	15.9	6.4	7.1	7.1	11.1	2.2	18.9
U	13.6	16.3	13.0	13.6	24.6	4.6	10.1	16.8	8.7	24.9	7.8	17.1	5.4	8.6
V	123.1	310.9	478.9	314.0	1177.0	430.8	457.8	194.7	121.5	255.0	319.1	141.0	<80.9	95.3
Yb	4.8	5.4	4.4	7.1	24.2	3.0	7.2	3.6	1.7	8.9	1.5	3.3	6.7	9.0
Zn	63.6	114.5	60.3	161.3	726.2	110.1	317.2	135.4	172.4	445.4	164.7	166.8	162.1	124.9

the seams shows a variety of patterns. With some elements, *e.g.*, chlorine and cobalt, there is no discernible trend across the section (Fig. 3). Other elements, *e.g.*, uranium, hafnium and the rare earths, show a uniform decrease in concentration downward in the section, whereas other elements, such as bromine, decrease upward in the section (Fig. 4). Two other kinds of distribution patterns are illustrated (Fig. 5). Potassium, chromium and vanadium show low and uniform concentrations in seams of the basal part of the section, whereas seams in the upper part show a much more erratic though generally higher concentration. Concentrations of iron and manganese (Fig. 5) are higher toward the base of the section.

Differences in elemental distribution among seams may be relatively small, as for chlorine, or high, as for antimony. The former shows a range from 195.0 to 66.8 ppm (seams E and A, respectively) compared to antimony, in which the range is from 15.8 to 0.05 ppm (seams E and L, respectively).

The highest values for individual elements on the whole-coal (unashed) basis are not uniformly spread among the seams studied. Some seams have a pronounced concentration of such values (Table 4); individual elements are listed according to the seams in which their highest values occur. Seams A, E and F (Table 4) are characterized by concentrations of

high values. To a large extent these concentrations reflect the high content of ash in some coals, *e.g.*, seams A and F (see Table 1 for ash contents).

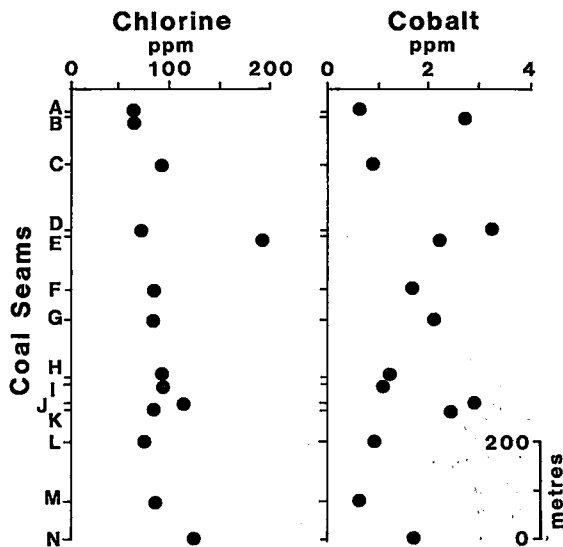


FIG. 3. Variation in concentration of chlorine and cobalt with increasing depth.

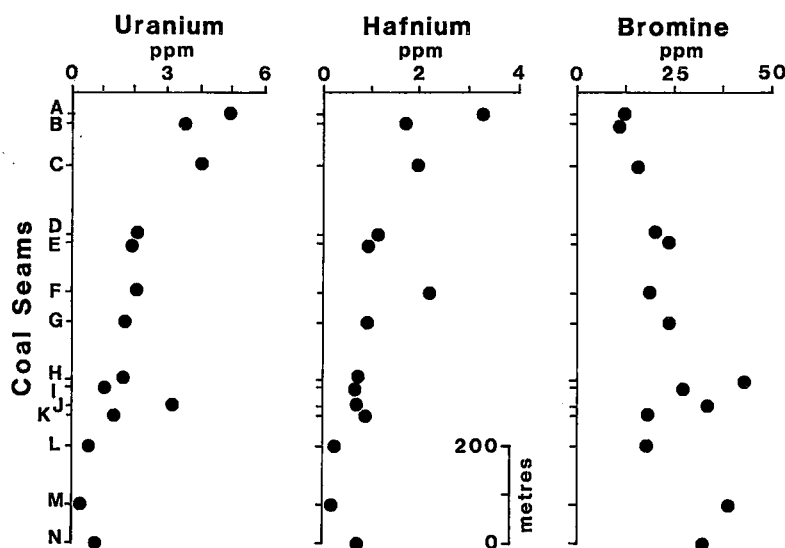


FIG. 4. Variation in concentration of bromine, hafnium and uranium with increasing depth.

However, seam C also has a high content of ash but only two "highs" for particular elements, whereas seam E, relatively low in ash, shows highest values for 7 elements. Clearly, the distribution of elements in seam E is not only a function of ash content, but represents factors in the geochemical environment during deposition of this seam that were rather different from those for the other seams. Differences in element assemblages and relative concentrations among seams could be useful in seam correlation, provided lateral variation is not great. More samples are needed to verify this for Mount Allan coals.

Relationship with environment of deposition

Elemental distributions in coals of the Mount Allan section reflect the local geochemistry of the peat-swamp environment and differences in the floral populations of these swamps. Also important were the lithologies of the provenance areas supplying sediment to the swamps. These factors cannot be evaluated in detail for Mount Allan, but some appreciation of changes in environmental conditions can be gained by examination of the general depositional environment in which the Kootenay Group was laid down. According to Gibson (1985), the depositional environment was that of a prograding delta, and the sandstones of the Morrissey Formation were likely beach-ridge, coastal-dune sediments with coal-forming swamps on the landward side. Thus the lower seams of the Kootenay Group accumulated in environments relatively close to

marine conditions. In any given section, seams at successively higher stratigraphic levels would have been formed under conditions farther and farther removed from marine influence. Corresponding to such a progression of environments, different geochemical and floral populations might be expected.

Metamorphic and igneous rocks apparently contributed little to Kootenay sedimentation. According to Gibson (1985), sources were likely carbonate and clastic sequences of Early Mesozoic and Paleozoic age lying in uplifted areas to the west.

An important paleoenvironmental consideration in the deposition of the Kootenay Group may have been the varying influence of marine or brackish conditions, especially for the seams in the bottom part of the section. The upward decrease in concentration of elements such as bromine may be a reflection of upwardly waning marine influences. Goodarzi (1987) found a similar pattern of distribution in another section in the Kootenay Group.

The change in elemental distributions near the point in the section (seam H) where the rank changes from bituminous to semi-anthracite suggests that some of the variation may be rank-related (Figs. 2, 5). The environments of deposition were likely changing upwardly with successive seams, but this change presumably was rather gradual, whereas the change in distribution of some elements (as shown in Fig. 5) is rather abrupt; hence rank is possibly an important factor. The Mount Allan samples fall into two populations (Fig. 6), one consisting of seams of semi-anthracitic rank and the upper end of the low-

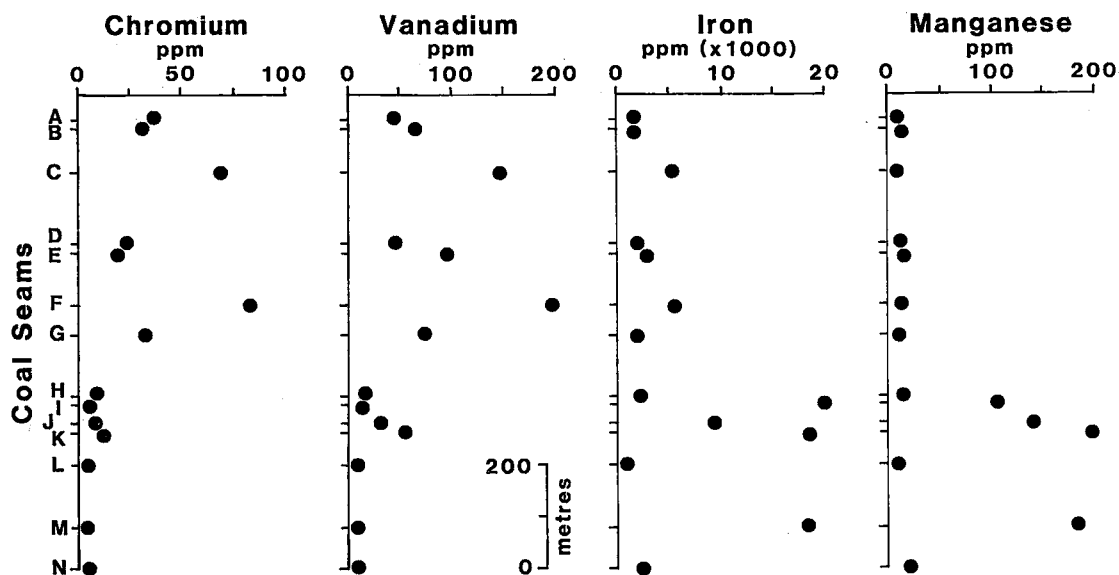


FIG. 5. Variation in concentration of chromium, vanadium, iron and manganese with increasing depth.

TABLE 4. ELEMENT DISTRIBUTION LISTED BY SEAM IN WHICH HIGHEST CONTENT OCCURS*

SEAM	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Elements	Ce	Ca	Mg	Co	Cl	Al	Tm	Br	Fe	Mo	As	-	Mn	-
	Dy	Na	Th	Eu	Ga	Cs					Ba			
	Hf	Sr			I	Cr					Cu			
	Ho				Lu	In								
	La				Sb	K								
	Nd				Sc	Rb								
	Sa				Zn	Se								
	Ta					Tb								
	Ti					V								
	W													
	U													
	Yb													

* (data on whole-coal basis)

volatile bituminous range, whereas the other is comprised of the remainder of the low-volatile coals along with those of medium-volatile bituminous rank.

The value of the Na/K ratio is an indicator of rate of sedimentation (Nicholls & Loring 1960). Although the values for the Mount Allan samples were determined on coal, they appear to agree with the results of the Nicholls & Loring study, which was carried out on clays. The results of the Mount Allan coals relative to sedimentological rates agree in general with the field studies of Gibson (1985).

The premise underlying the use of this ratio involves the degradation of illite, so that slow burial is reflected in a high Na/K value, and rapid burial by a lower value. These values for the Mount Allan coals show evidence of three major cycles with less apparent subcycles (Fig. 7). The relatively high values of the Na/K ratio at the base of the Mist Mountain Formation indicate relatively slow sedimentation, whereas lower values in the upper part of the Mist Mountain Formation and into the Elk Formation suggest more rapid burial. A third cycle appears to be present toward the top of the Elk Formation

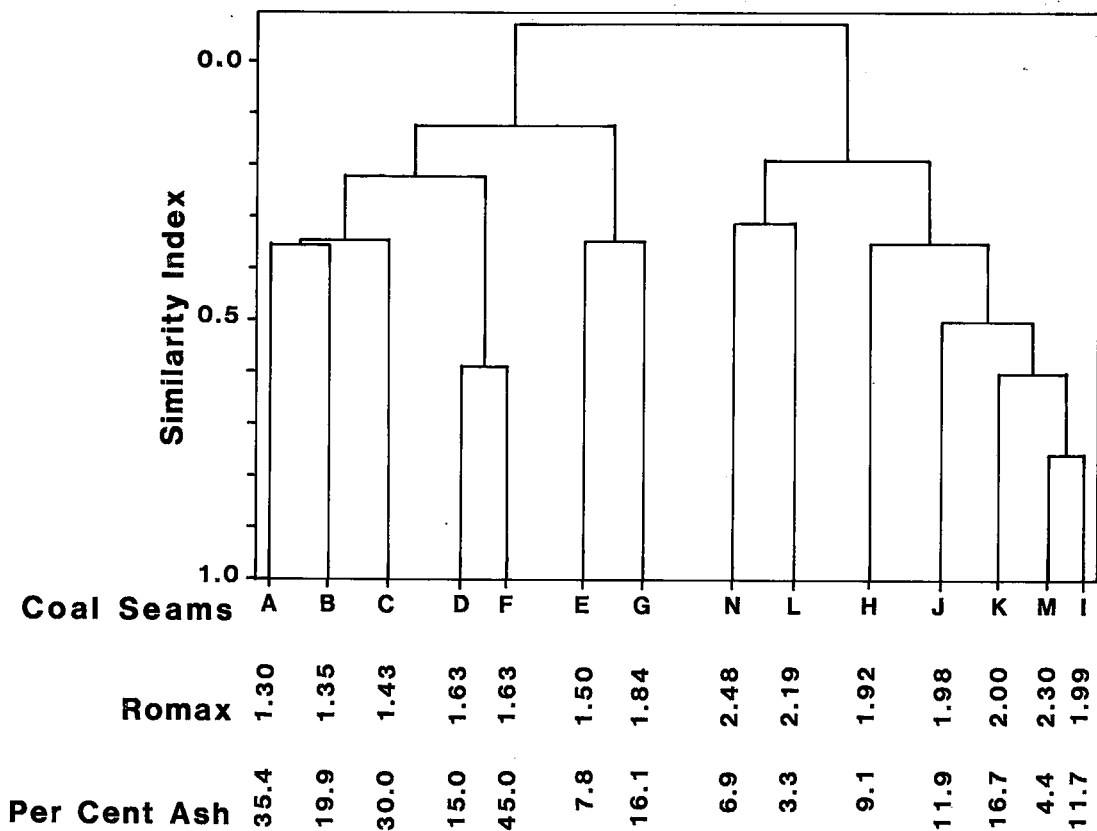


FIG. 6. Dendrograph showing similarity indices among the coal samples based on the elements in coals. Also shown are the reflectivities and ash contents of the samples.

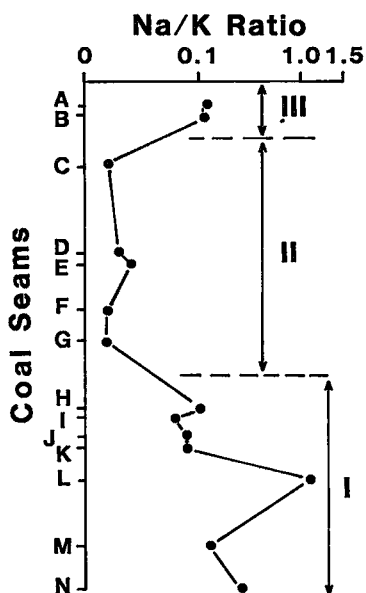


FIG. 7. Plot of values of the sodium/potassium ratio versus depth.

(seams A and B). The contact between the Elk and Mist Mountain Formations occurs at the top of cycle 1.

Organic versus inorganic affinities

Nicholls (1968) demonstrated a method of identification of those elements that are organically bound, as compared to those more related to the mineral matter or inorganic fraction. The method involves plotting concentrations of particular elements against ash content. Those elements that show a positive correlation with ash content are considered to be associated with the mineral fraction. Examples from the Mount Allan section are titanium and aluminum (Fig. 8). Those elements that show a negative correlation with ash are considered to be organically bound. Examples from Mount Allan are bromine (Fig. 8) and, to a lesser extent, chlorine. Most of the elements in the Mount Allan coals seem to be inorganically bound, although some of the elements considered to be organically bound (Gluskoter *et al.* 1977), such as boron and germanium, were not determined in this study. Affinities are also shown

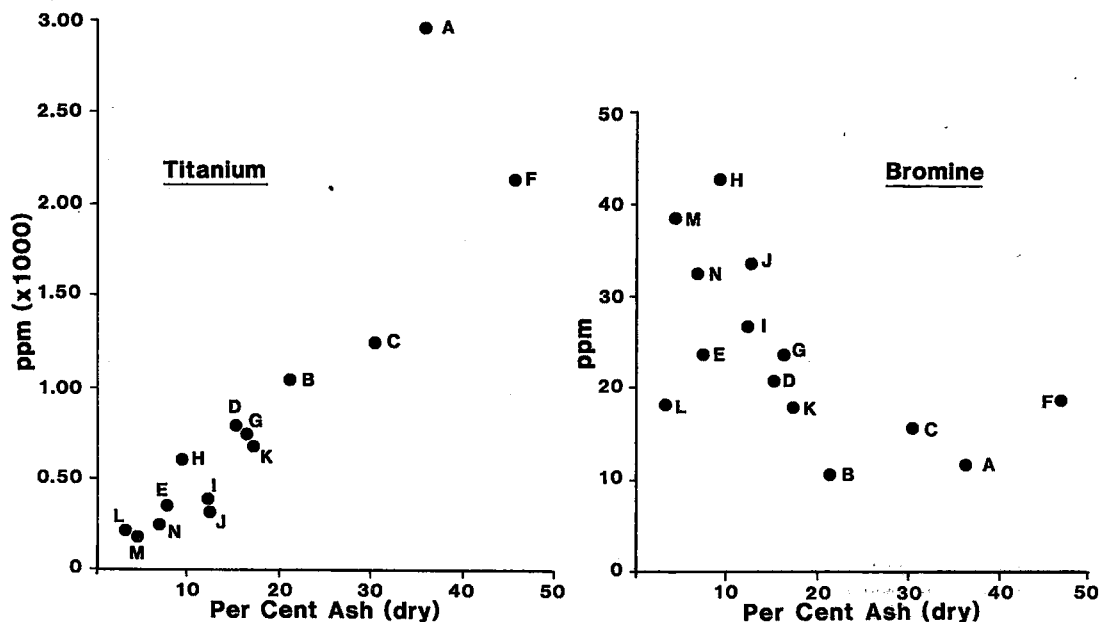


FIG. 8. Correlation of inorganically and organically bound elements in coal with ash content of coal: a) titanium, inorganically bound, positive correlation; b) bromine, organically bound, negative correlation.

TABLE 5. CORRELATION COEFFICIENTS FOR SELECTED ELEMENTS AND ASH CONTENT OF MOUNT ALLAN SAMPLES

	Al	Ba	Ca	Fe	Mg	K	Na	Ti	Sb	Br	Ce	Cr	Cl	Co	Eu	Hf	Ho	I	La	Lu	Mn	Nd	Se	Ta	Th	U	V	Yb	Zn	Ash
Al	1.00	0.19	0.07	-0.18	0.41	0.93	0.41	0.51	0.13	-0.46	0.61	0.89	-0.18	0.12	0.36	0.51	0.08	0.25	0.63	0.37	-0.37	0.49	0.16	0.42	0.78	0.31	0.89	0.38	0.25	0.77
Ba	1.00	0.59	0.17	0.27	0.05	0.36	0.1	-0.16	-0.35	0.19	0.02	-0.28	0.36	0.11	0.04	-0.09	-0.01	0.15	-0.13	0.25	0.33	-0.04	0.04	0.18	0.07	0.06	-0.07	-0.02	0.10	
Ca	1.00	0.16	0.54	-0.11	0.18	0.16	-0.15	-0.16	0.26	0.02	-0.24	0.33	0.17	0.26	0.27	-0.06	0.21	0.12	0.19	0.39	-0.02	0.21	0.33	0.48	0.01	0.11	0.17	0.19		
Fe	1.00	-0.10	-0.12	-0.15	-0.20	-0.21	0.27	-0.45	-0.28	-0.04	-0.12	-0.48	0.33	-0.52	0.07	-0.47	-0.45	0.89	-0.39	-0.53	-0.33	-0.38	-0.34	-0.19	-0.45	-0.08	-0.37			
Mg	1.00	0.33	-0.03	0.20	-0.08	0.21	0.18	0.34	-0.17	0.03	0.01	0.22	-0.02	-0.03	0.16	0.07	-0.14	0.16	-0.15	0.17	0.39	0.33	0.32	0.06	0.09	0.67				
K	1.00	0.30	0.50	0.23	-0.35	0.47	0.93	-0.11	0.02	0.30	0.48	0.06	0.31	0.50	0.44	-0.29	0.34	0.23	0.41	0.66	0.28	0.93	0.42	0.36	0.78					
Na	1.00	0.33	-0.22	-0.49	0.55	0.34	-0.37	-0.15	0.25	0.30	0.10	-0.14	0.55	-0.02	-0.14	0.47	0.21	0.37	0.50	0.17	0.25	-0.03	-0.33	0.40						
Ti	1.00	-0.01	-0.61	0.82	0.72	-0.32	-0.20	0.79	0.94	0.80	0.04	0.82	0.55	-0.28	0.80	0.47	0.96	0.74	0.72	0.55	0.58	0.14	0.91							
Sb	1.00	-0.13	-0.04	0.27	0.82	0.26	0.06	0.13	0.20	0.89	-0.06	0.66	-0.23	-0.08	0.56	-0.02	0.08	0.13	0.50	0.67	0.66	0.08								
Br	1.00	-0.67	-0.54	0.29	-0.15	-0.72	0.63	-0.53	-0.26	-0.05	-0.54	0.38	-0.73	-0.66	-0.63	-0.65	-0.55	-0.47	-0.55	-0.13	-0.58									
Ce	1.00	0.69	0.45	0.04	0.85	0.89	0.68	-0.05	0.96	0.52	-0.53	0.96	0.38	0.87	0.89	0.69	0.51	0.54	0.04	0.77										
Cr	1.00	-0.15	-0.05	0.54	0.74	0.36	0.34	0.69	0.65	-0.44	0.57	0.45	0.68	0.86	0.57	0.94	0.64	0.35	0.91											
Cl	1.00	0.17	0.00	0.23	-0.09	0.71	0.40	0.29	0.00	-0.44	0.22	0.30	-0.39	-0.38	-0.16	0.29	0.11	-0.31												
Co	1.00	0.25	0.09	0.27	0.20	0.03	0.28	0.03	0.21	0.00	-0.24	0.01	0.06	0.12	0.30	0.55	-0.08													
Eu	1.00	0.86	0.88	0.04	0.68	-0.47	0.92	0.52	0.83	0.69	0.77	0.32	0.71	0.20	0.24															
Hf	1.00	0.78	0.15	0.88	0.71	-0.42	0.87	0.53	0.97	0.84	0.85	0.58	0.72	0.21	0.88															
Ho	1.00	0.08	0.66	0.78	-0.42	0.76	0.61	0.72	0.55	0.85	0.52	0.78	0.34	0.60																
I	1.00	-0.09	0.58	-0.04	-0.06	0.45	-0.01	0.16	0.20	0.58	0.59	0.50	0.15																	
La	1.00	0.51	-0.54	0.94	0.37	0.86	0.97	0.65	0.52	0.52	0.04	0.78																		
Lu	1.00	-0.44	0.54	0.80	0.80	0.80	0.77	0.67	0.99	0.70	0.31																			
Mn	1.00	-0.41	-0.48	-0.40	-0.51	-0.32	-0.34	-0.42	-0.02	-0.30																				
Nd	1.00	0.38	0.84	0.83	0.75	0.41	0.56	0.09	0.31																					
Se	1.00	0.53	0.41	0.58	0.46	0.79	0.44	0.60																						
Ta	1.00	0.79	0.81	0.47	0.61	0.05	0.86																							
Th	1.00	0.74	0.73	0.59	0.14	0.85																								
U	1.00	0.42	0.75	0.28	0.67																									
V	1.00	0.66	0.54	0.79																										
Yb	1.00	0.69	0.56																											
Zn	1.00	0.31																												
Ash	1.00																													

by the data presented in Table 5. In this table, correlation coefficients based on linear-regression analyses are shown for each element with all other elements as well as ash. The best correlations with ash con-

tent are shown by titanium, chromium, hafnium, tantalum, thorium and vanadium, in that order, suggesting that these elements are most closely associated with the inorganic fraction. The elements showing

TABLE 6. DEPLETION/ENRICHMENT CHARACTERISTICS FOR ELEMENTS IN COAL SEAMS AT MOUNT ALLAN

	Whole-coal basis													
	A ¹	B ¹	C	D	E	F	G	H	I	J	K	L	M	N
Aluminum	D				D			D	D	D		D	D	
Barium											E		D	
Calcium				D	D							D	D	D
Iron	D	D	D	D	D	D	D	D				D	D	
Magnesium	D			D	D		D	D	D	D	D	D	D	D
Potassium	D	D		D	D		D	D	D	D	D	D	D	D
Sodium	D	D	D	D	D	D	D	D	D	D	D	D	D	D
Titanium					D			D	D	D		D	D	D
Antimony		E	E	E	E	E	E			E				
Bromine			E	E	E	E	E	E	E	E	E	E	E	E
Cerium					D			D	D	D	D	D		D
Chlorine														
Chromium								D	D	D	D	D	D	D
Cobalt	D	D	D	D	D	D	D	D	D	D	D	D	D	E
Dysprosium														
Europium	D							D	D			D		
Hafnium												D	D	
Holmium								D	D		D	D	D	D
Iodine			E		E									
Lanthanum					D			D	D	D	D	D		
Lutetium												D		
Manganese	D	D	D	D	D	D	D	D	D	D		D	D	D
Neodymium					D			D	D	D	D	D		
Scandium								D	D			D	D	D
Tantalum				D	D		D	D	D	D	D	D	D	D
Thorium					D			D	D	D	D	D		
Uranium													D	
Vanadium								D	D			D	D	D
Ytterbium								D	D		D	D	D	D
Zinc												D	D	D

1. A, B, etc. designate coal seams
D = depleted E = enriched

the poorest correlation with ash content (Table 5) are bromine, iron, chlorine and manganese, in that order. These should be the elements with the greatest affinity for the organic fraction. The position of iron and manganese is anomalous in this series because commonly they have been identified with the inorganic fraction (Gluskoter *et al.* 1977, Zubovic 1966).

Enrichment and depletion

Gluskoter *et al.* (1977) suggested that an element in a coal be considered enriched if its content is 6 times its clark value (average abundance in earth's crust) and depleted if it is $\frac{1}{6}$ (or less) of the clark. On this basis, only antimony and bromine are enriched in the Mount Allan coals, whereas iron, magnesium, potassium, sodium, cobalt, manganese and tantalum are depleted in the majority of the seams studied. Table 6 summarizes depletion and enrichment characteristics for various elements based on the criteria of Gluskoter *et al.* (1977).

CONCLUSIONS

The present study suggests that: 1) concentration of certain elements (Cr, Fe, Mn, V) in the coals can be broadly related to the ranks of the coals in this section, 2) based on values of the Na/K ratio, three depositional cycles are present in the section, one characterized by a rapid influx, the other two by slower burial, 3) organic or inorganic affinities of elements in coal may be determined using the concentration of elements *versus* ash content, and 4) bromine and antimony are the only elements enriched in these coals.

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