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Trace Element Geochemistry of Brackish-Water Coals in the Central Alberta Plains, Canada

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Concentrations of the elements As, B, Br, Cl, Cr, Mn, Na, Sb, Th, U, V, and Zn were determined in ply-by-ply samples from two sections of subbituminous coal from seam 3, Vesta Mine, Alberta Plains. The elemental mean concentrations in section 1 were As 1.0 ppm, B 215 ppm, Br 2.3 ppm, Cl 29 ppm, Cr 7.4 ppm, Co 1.1 ppm, Mn 24.5 ppm, Mo 2.5 ppm, Na 4900 ppm, Sb 0.4 ppm, Se 0.8 ppm, Ti 270 ppm, U 1.4 ppm, Th 2.8 ppm, V 2.9 ppm, and Zn 9.5 ppm. In section 2, the mean concentrations were As 0.7 ppm, B 201 ppm, Br 1.6 ppm, Cl 24 ppm, Cr 20 ppm, Co 1.7 ppm, Mn 30.0 ppm, Mo 2.8 ppm, Na 4200 ppm, Sb 0.3 ppm, Se 0.7 ppm, Ti 340 ppm, U 0.8 ppm, Th 1.8 ppm, V 4.4 ppm, and Zn 68 ppm. Total sulfur content averaged 0.44% in section 1 and 0.48% in section 2. Mean concentrations of these elements are low when compared to western Canadian coals of similar rank, or to world coals (Swaine, 1990). Antimony, barium, and boron are enriched, with the latter being a reflection of the coal-forming environment. Despite the short lateral distance between the sections (~ 100 m), seam 3 in section 1 has slightly higher mean concentrations of As, B, Br, Cl, Na, Sb, Se, U, and Th than in section 2. Seam 3 in section 2 has slightly higher mean concentrations of Cr, Co, Mn, Mo, Ti, V, Zn, and S than in section 1. Elements were differentiated on the basis of their inorganic association, organic association, or intermediate (mixed) association. Thus, As, Ba, Cr, Mo, K, Na, and U in section 1 have a positive correlation with ash and aluminum contents of the coal, while Ca and Co show a weak to moderate relationship with ash content. Iron and Mn do not exhibit a clear relationship to ash in coal from section 1. In section 2, the elements As, Ba, Fe, Mg, Mo, K, Na, Th, U, V, Cr, and Co show a weak to strong relationship with ash content, while Ca and Mn show a moderate relationship. The halogens show a negative relationship with ash content in both sections. An inertinite-rich layer in section 1 has higher concentrations of Ca, Mn, and Fe, when compared to huminite-rich layers above and beneath. It also has the lowest boron concentration (25 ppm), lowest sulfur content (0.19%), and highest fixed carbon value in the section. The high boron concentrations in the Vesta Mine coals (mean is 208 ppm) indicate interaction of the peat with brackish waters during deposition, except for the inertinite-rich layer. The

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study also shows that sulfur content in coal does not always show a correlation to marine influence during coal formation. Perhaps, differences in the paleoenvironmental setting may be responsible for the boron / sulfur relationship in the Vesta Mine coals.

Keywords coal, geochemistry, trace elements

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Trace elements enter the atmosphere as by-products of various processes. One of the major sources of trace element emissions is coal utilization, especially for electrical power generation. Because of the huge quantities of fossil fuels being consumed every year, large amounts of potentially harmful elements are released into the terrestrial, aquatic, and atmospheric environments. In Canada, concern over emissions of trace elements from coal-fired power stations and stricter environmental regulations has resulted in more attention being given to the effects of trace elements on the environment.

Major thermal coal resources are present in the western part of Canada. Geographically, the coals are found in the mountain and inner foothills regions of British Columbia and Alberta, the outer foothills and plains regions of Alberta, the intermontane region of British Columbia, and the plains region of Saskatchewan (Smith, 1989). This study deals with the systematic evaluation of the concentration, vertical and lateral variation, and association of elements in the Vesta Mine coals. Vesta Mine is part of the Battle River coalfield in the eastern plains region of Alberta (Figure 1). A comparison and contrast of the elemental geochemistry in the Vesta Mine coals with that in other coals of similar rank from western Canada has also been attempted. These coals include the Hat Creek coals in intermontane British Columbia, and the Highvale, the Whitewood, and the Obed Mountain thermal coals in the plains and foothills of Alberta.

This study is part of a larger program on the overall quality of Alberta coals currently utilized for electrical power generation. Another study, which deals with the partition of elements during combustion of milled coal at the Battle River power station in bottom ash, fly ash, and flue gas, mineralogical transformations, and dispersion and deposition of elements in the environs of the power station is underway.

Geological Setting

The Battle River coalfield has the greatest resource potential in the east-central region of the Alberta plains, containing in excess of 1000 megatonnes of coal (Dawson et al., 1989). Vesta Mine (Figure 1) is an open-pit mine with production of approximately 3.3 million tonnes of coal in 1991 in combination with the nearby Paintearth mine. The mined coal is utilized solely for electrical power generation at Alberta Power's Limited 735-MW Battle River station.

Two major coal beds are found throughout most of the mining area. The beds vary in thickness from 2.0 to 4.0 m and are commonly split into two seams. In the Vesta Mine, there are four seams, numbered 1 to 4 from bottom to top of the succession (Figure 2). Individual seams have thickness ranging from 1.0 to 1.4 m, with the interburden being mudstone. The coal seams are present in the Horseshoe Canyon Formation, which is part of an eastward-thinning wedge of mainly fluvio-

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Figure 1. Battle River coalfield in the Alberta Plains and location of Vesta Mine.

deltaic sediments deposited along the western margin of the Late Cretaceous Bearpaw Sea (Gibson, 1977). The Vesta Mine formation consists mainly of sandstone/siltstone with minor shale, mudstone, and claystone (Figure 2).

The Vesta Mine coal is of subbituminous C rank (%Ro, random = 0.45–0.52) (Gentzis et al., 1990), which is typical of coals in the Alberta plains. The major constituents in the "as-mined" samples are fixed carbon (35%), volatile matter (29%), moisture (26%), and ash (10%). Heating value of the coal is 18,600 kJ/kg. Preliminary data (see Gentzis et al., 1990) show that coal in two sections of seam 3 in Vesta Mine is dominated by huminite group macerals (80.0%, mmf) with humotelinite and humocollinite present in almost equal amounts (~45%) in section 1. There is a predominance of humocollinite over humotelinite in section 2, and liptinite content averages 5.0% but does not exceed 10.0%. Inertinite averages 13.0% in section 1 and 18.0% in section 2, the only exception being a high-inertinite interval (40.0%) in section 1. Total sulfur content in the coals (< 20% ash content) is less than 0.5%, and boron values range from 171 to 265 ppm (Goodarzi & Swaine, 1994a).

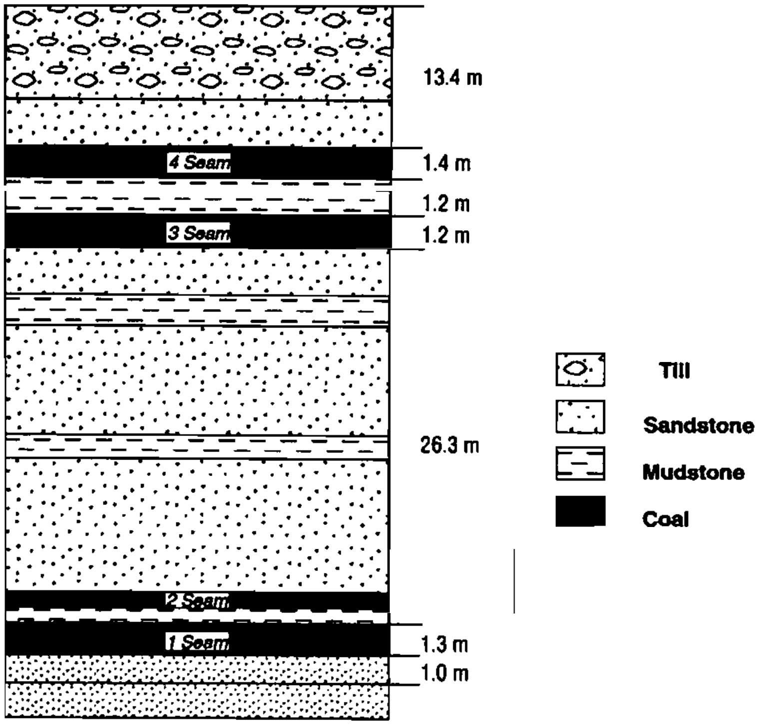

Figure 2. Stratigraphic succession at the Vesta Mine.

Experimental

Twenty samples were taken from seam 3, section 1 in the Vesta Mine, and another 16 samples from the same seam in section 2, approximately 100 m away. Both sections are approximately 160 cm thick. Sampling was performed according to vertical lithotype variations (e.g., inertinite-rich layer in section 1, carbonaceous shale layers near the roof and floor of sections 1 and 2) and not according to intervals of equivalent thickness.

The determination of boron in the coals was achieved by a combination of two methods, inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Pollock, 1975) and prompt gamma-ray spectrometry (Gladney et al., 1976). Concentrations of all other elements were determined by instrumental neutron activation analysis (INAA). Analyses were done on dried, powdered coal. For a detailed description of these methods, the reader is referred to Swaine (1990).

Results and Discussion

Elemental Variation—Seam 3, Section 1

The concentrations of elements are shown in Table 1. Aluminum is less than 6.0% and is higher near the roof and floor of the section. Iron is in the range of 0.3 to 0.5%, with the exception of the 3 uppermost samples, where Fe concentration is up to 1.3%. These three samples also have the highest ash content in the section

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(22–40%). Magnesium follows a pattern similar to that of aluminum, with an increasing trend toward the roof and floor. Potassium and sodium are slightly depleted in sample 1-E, but both elements show an overall increase toward the roof and floor of the seam. Titanium content is low (< 0.1%).

Antimony concentration is 1.5 ppm, being slightly higher in the floor and roof of the section. Arsenic concentration in the coal is extremely low (< 1.7 ppm), with one exception. Sample 1-E has arsenic at 3.1 ppm; petrographic analysis indicates that this sample is enriched in inertinite group macerals and pyrolytic carbon (Gentzis et al., 1990). Barium concentration in the samples ranges from 334 to 1520 ppm; the highest 3 values are found near the bottom of the section. Bromine concentration is less than 3 ppm, except in the topmost sample (1-A) where it is 4.2 ppm. Chlorine is less than 41 ppm, and both halogens have their lowest concentrations in sample 1-E. Molybdenum concentration ranges from 1.4 to 9.2 ppm, being higher in the upper and lower parts of the section. Selenium concentration is low (< 1.5 ppm), but it is slightly higher in the upper part of the section. The same is true for Th, which shows higher concentrations in the ash-rich samples. Thorium ranges from 0.5 to 12.3 ppm, whereas U is in the 0.3–7.1 ppm range. Uranium concentration is low in the middle part of the section and increases toward the top and bottom of the section as well as in "dirt bands," in agreement with results of Goodarzi and van der Flier-Keller (1989). Sample 1-E does not show high concentrations of the radioactive elements Th and U. However, the same is not true for vanadium. Vanadium concentration is in the 1.8–8.3 ppm range, being higher in the ash-rich samples as well as in sample 1-E. The latter has V concentration of 6.5 ppm, whereas the intervals immediately above and below have V concentrations of 1.8 and 2.6 ppm, respectively. Zinc ranges from 4 and 28 ppm; the highest concentrations are associated with the ash-rich samples.

Chromium concentration in the coals ranges from 1.5 to 5.1 ppm. Concentration increases to 18 ppm in sample 1-A1 (a carbominerite having ash content of 36%). Overall, higher Cr concentrations are found in the roof and floor of the section. Sample 1-E has a Cr concentration of 14.4 ppm, which is similar to that in the ash-rich samples. Cobalt ranges from 0.6 to 3 ppm, with the higher concentrations measured near the roof and floor of the seam. Among the coals, Co is slightly elevated in the inertinite-rich layer (1.3 ppm vs. < 0.9 ppm in the other samples). Manganese is present in low concentrations (range is 18–35 ppm), with the exception of sample 1-E where the element is highly enriched (90 ppm). The same is true for scandium (Sc), which has a concentration of 1.2 ppm in sample 1-E but less than 0.9 ppm in the remaining coal samples in section 1.

Boron content in coals having ash content of 5–8% ranges from 171 to 265 ppm, with an exception in sample 1-E (only 25 ppm). This sample has the lowest sulfur content of all samples analyzed (0.19%), the highest fixed carbon (56.8%), and the highest inertinite content (40%) (Gentzis et al., 1990). The low B content of sample 1-E suggests that the coal did not absorb boron from the brackish waters, most likely because the interval represented by this coal sample was formed in an area within the delta complex that was either elevated or isolated from any influence of brackish waters (i.e., away from marine transgressions). This scenario is corroborated by the high inertinite content of this interval and the presence of pyrolytic carbon. The first characteristic indicates either fire or oxidation of the peat surface, and the second points to temperatures of the order of 500°C or even higher (Goodarzi, 1986). Both would be consistent with peat deposition in an area

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Table 1
Mean elemental concentrations, Vesta seam 3, section 1 (data in ppm unless otherwise noted)

Sample	Ash[a]	Al (%)	Sb	As	B	Ba	Br	Ca (%)	Ce	Cl	Cr	Co	Dy	Eu	Hf	Ho	Fe (%)
1-A	36.2	5.94	1.21	1.70	205	755	4.23	0.96	60.2	36	12.8	1.35	3.89	0.56	4.38	0.82	1.33
1-A1	19.5	3.10	1.49	1.50	218	711	2.00	0.89	38.2	26	17.8	2.87	3.53	0.23	3.93	0.78	0.63
1-B	24.6	3.76	0.96	0.94	224	899	2.10	0.85	34.8	33	12.8	0.77	2.51	0.32	3.10	0.63	0.88
1-C	4.5	0.34	0.07	0.91	255	381	2.84	0.89	3.6	32	5.1	0.77	0.87	0.08	0.21	0.15	0.33
1-D	4.7	0.34	0.13	1.02	240	371	3.07	0.86	3.0	38	4.9	0.68	0.54	0.09	0.25	0.08	0.33
1-E	7.8	0.80	0.16	3.05	25	527	0.50	1.70	13.0	16	14.4	1.33	0.99	0.17	0.54	0.15	0.39
1-F	5.1	0.30	0.07	0.90	252	362	2.61	0.90	2.7	26	4.0	0.66	0.49	0.07	0.18	0.09	0.32
1-G	5.0	0.53	0.15	0.78	265	334	2.72	0.92	2.3	27	1.5	0.59	0.47	0.06	0.17	0.08	0.37
1-H	5.5	0.47	0.11	0.65	262	353	2.51	0.87	2.7	29	3.1	0.67	0.47	0.08	0.18	0.10	0.38
1-M	7.5	0.98	0.19	0.84	239	768	1.75	1.04	4.9	41	6.6	0.75	0.73	0.08	0.64	0.08	0.35
1-N	6.0	0.65	0.11	0.56	252	430	1.40	0.96	7.3	30	4.2	0.77	0.63	0.07	0.39	0.14	0.37
1-O	6.2	0.59	0.07	0.79	211	451	2.02	0.96	14.5	19	1.9	0.86	0.71	0.08	0.35	0.13	0.36
1-P	6.5	0.82	0.09	0.72	200	485	1.93	0.96	5.6	35	3.7	0.86	0.63	0.09	0.47	0.15	0.36
1-Q	6.1	0.64	0.13	0.65	227	391	2.21	0.99	14.0	29	2.8	0.83	0.77	0.09	0.41	0.17	0.36
1-R	6.0	0.61	0.14	0.69	261	441	2.74	0.93	16.0	30	1.7	0.74	0.74	0.05	0.35	0.16	0.40
1-T	8.0	0.73	0.09	0.64	171	430	2.45	0.96	4.6	28	3.1	0.83	0.83	0.07	0.55	0.16	0.35
1-U	13.0	1.10	0.15	0.75	229	624	2.76	1.02	3.5	27	4.2	0.81	1.00	0.08	0.55	0.25	0.33
1-W	75.0	1.97	0.97	0.81	<10	1390	2.35	1.08	15.4	21	6.3	1.06	2.06	0.14	2.11	0.45	0.35
1-Y	15.1	2.66	0.85	1.20	177	1520	2.81	0.98	31.8	25	10.6	2.08	3.11	0.21	2.80	0.69	0.43
1-Z	13.5	2.06	0.84	1.00	177	1030	1.40	0.99	31.6	35	11.2	2.63	3.27	0.22	2.02	0.71	0.43

[a] As received.

above any water influence. The high temperatures experienced by this inertinite-rich interval would also be responsible for the low concentrations of the volatile elements Br, Cl, and Se measured in sample 1-E (Table 1). These elements are expected to volatilize completely at 800°C (Gentzis & Goodarzi, 1995a).

In the carbonaceous shale samples 1-W and 1-X of section 1 (ash content of 81 and 87%, respectively), boron concentrations are very low (< 10 ppm). Although the breakdown of boron into organic and inorganic components was not attempted here, it is expected that boron in these coals would have an organic association. Boron could possibly be associated with ester groups or be chelated with hydroxyl groups (phenolic hydroxyls) in the Vesta Mine subbituminous coals (Goodarzi & Swaine, 1994a). The variance ratio of boron (maximum/minimum value) ranges from 1.2 in section 1 (excluding the carbonaceous shale and the inertinite-rich intervals) to 1.9 in section 2. Such low ratios indicate relatively stable depositional environment conditions with no major fluctuations in water levels for a long period of time.

Seam 3, Section 2

The concentrations of elements are shown in Table 2. Aluminum ranges from 1.0% to 4.3% and increases toward the top of the section. Iron concentration is less than 1.0%, similar to that of seam 3 coal in section 1. Calcium is less than 1.0%; so is magnesium, whereas Mo concentration ranges from 1.0 and 8.6 ppm. Potassium is less than 0.55% and Ti is less than 0.1%. Antimony concentration is less than 1.1 ppm, which is slightly lower than in seam 3, section 1. The range of arsenic is 0.3–2 ppm, with the highest concentration being in the uppermost sample (25% ash

Table 1
Mean elemental concentrations, Vesta seam 3, section 1 (data in ppm unless otherwise noted) (*Continued*)

S (%)	La	Lu	Mg (%)	Mn	Mo	K (%)	Sm	Sc	Se	Na (%)	Th	Ti (%)	U	V	Yb	Zn
0.31	32	0.36	0.61	35.4	4.90	0.33	4.69	6.35	1.50	1.02	10.20	0.11	3.93	8.28	1.99	27.0
0.36	18	0.30	0.27	19.4	9.18	0.21	3.76	2.70	1.10	0.65	12.30	0.08	7.06	4.59	1.92	14.0
0.36	18	0.28	0.43	17.1	3.20	0.15	2.85	4.15	1.30	0.81	7.62	0.06	2.78	2.50	1.44	28.0
0.51	1.7	0.07	0.06	22.9	2.40	0.03	0.58	0.89	0.47	0.40	0.42	0.01	0.34	2.62	0.47	5.1
0.50	1.2	0.03	0.06	24.9	1.40	0.03	0.44	0.60	0.59	0.40	0.45	0.01	0.26	1.80	0.22	5.6
0.18	6.2	0.07	0.12	90.1	1.60	0.03	1.07	1.16	0.46	0.03	1.35	0.03	0.53	6.46	0.42	6.7
0.49	1.3	0.03	0.07	22.1	1.40	0.03	0.43	0.56	0.71	0.41	0.46	0.01	0.25	2.60	0.24	3.8
0.45	1.1	0.04	0.08	20.4	1.50	0.03	0.40	0.69	0.38	0.43	0.46	0.01	0.55	2.70	0.21	5.5
0.45	1.0	0.04	0.07	19.8	2.00	0.03	0.40	0.63	0.45	0.44	0.77	0.01	0.36	2.73	0.22	6.7
0.43	2.0	0.05	0.07	21.2	1.50	0.04	0.71	0.90	1.40	0.46	2.35	0.03	0.46	3.04	0.27	8.8
0.45	5.4	0.06	0.05	18.1	1.50	0.04	0.54	0.74	0.88	0.45	1.04	0.01	0.59	1.80	0.32	5.6
0.40	10	0.05	0.07	20.3	1.60	0.04	0.69	0.79	0.90	0.45	0.54	0.02	0.87	2.00	0.40	5.4
0.38	4.1	0.05	0.08	19.6	1.70	0.04	0.58	0.85	1.10	0.45	1.43	0.02	0.50	1.70	0.35	8.6
0.46	13	0.07	0.11	19.5	2.00	0.04	0.69	0.83	0.40	0.45	0.69	0.02	0.60	2.50	0.38	8.7
0.44	13	0.05	0.06	18.6	1.60	0.04	0.66	0.75	0.76	0.45	0.61	0.01	0.75	1.80	0.43	5.7
0.45	3.5	0.07	0.09	20.3	2.20	0.05	0.55	0.91	0.39	0.43	0.99	0.02	0.72	2.37	0.40	5.5
0.49	1.9	0.10	0.07	21.0	1.80	0.04	0.74	1.55	1.10	0.45	1.45	0.02	0.60	2.13	0.57	13.0
—	7.3	0.16	0.08	20.0	2.10	0.13	1.73	2.11	1.10	0.55	5.05	0.04	2.16	2.20	1.00	7.6
0.43	15	0.28	0.13	20.0	3.80	0.06	3.12	2.99	0.60	0.63	5.29	0.03	3.07	2.92	1.68	10.0
0.43	15	0.30	0.13	19.0	3.70	0.07	3.08	2.90	0.81	0.55	3.15	0.02	2.66	2.41	1.83	8.6

content). Barium concentration ranges from 365 to 3150 ppm but the majority of samples have less than 829 ppm. Bromine is extremely low (< 3.2 ppm) and similar to that in section 1. The same is true for chlorine, which ranges between 18 and 33 ppm. Cobalt has a range of 0.5 to 7.3 ppm; its concentration generally increases with increasing ash content. Chromium concentration is low (< 5 ppm) but reaches 124 ppm in an ash-rich (24%) sample at the top of the section.

Manganese has a range from 19 to 48 ppm, with the exception of the uppermost sample (2-A1), which has a concentration of 127 ppm. Uranium is also similar to section 1, having a range from 0.3 to 3 ppm. Thorium has a higher concentration in sample 2-D (12.1 ppm), with most samples having < 1 ppm. Vanadium is in the 1.8–5.3 ppm range, with the exception of the two uppermost samples, which have a concentration of 29.3 and 11.5 ppm. Zinc concentration ranges from 4.9 to 15 ppm; two samples (2-F and 2-J) have considerably higher concentrations (440 and 600 ppm, respectively). This slight enrichment may be due to epigenetic precipitation; this has yet to be substantiated by XRD/SEM analyses. The high concentrations of zinc do not correspond with high concentrations of iron, sulfur, or mineral matter in the two samples. Therefore, the vertical variation of Zn is independent of any variations in the above phases in the coal.

Comparison of Elements in Seam 3, Sections 1 and 2

Despite the short lateral distance (approximately 100 m) between the two sections, there are some differences in the elemental concentrations of seam 3 coal. Thus, seam 3 in section 1 has slightly higher mean concentrations of Sb, As, B, Br, Cl, Na, Se, U, and Th. Chromium, Co, Mn, Mo, Ti, V, Zn, and S are slightly higher in

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Table 2

Mean elemental concentrations, Vesta seam 3, section 2 (data in ppm unless otherwise noted)

Sample	Ash (%)[a]	Al (%)	Sb	As	B	Ba	Br	Ca (%)	Ce	Cl	Cr	Co	Dy	Eu	Hf	Ho	Fe (%)
2-A1	23.7	1.90	0.3	2.04	153	477	0.47	0.71	15.4	19	124.0	5.53	1.00	0.17	1.17	0.21	4.74
2-C	15.2	1.01	0.2	1.12	175	469	1.20	0.81	18.9	25	96.3	7.28	1.37	0.14	0.81	0.27	0.27
2-C2	14.2	3.06	0.6	0.90	154	1870	1.10	0.90	35.9	30	14.9	1.79	2.79	0.19	2.56	0.49	0.27
2-D	22.5	4.31	1.1	0.74	150	3150	0.70	0.99	14.8	32	36.9	0.76	1.86	0.13	3.81	0.29	0.31
2-E	6.8	1.01	0.4	0.53	187	829	1.70	1.13	9.1	31	4.6	0.59	0.98	0.10	0.90	0.11	0.31
2-F	5.3	0.58	0.1	0.60	205	543	2.10	1.00	2.0	30	3.0	0.46	0.43	0.05	0.34	0.10	0.31
2-G	5.2	0.68	0.1	0.74	198	675	1.50	0.85	12.7	15	38.9	6.05	1.46	0.16	0.46	0.23	0.25
2-H	4.9	0.45	0.1	0.64	221	430	1.60	1.02	0.7	22	2.6	0.59	0.35	0.03	0.27	0.10	0.29
2-I	4.4	0.37	0.1	0.50	295	365	1.00	0.88	2.4	20	3.4	0.68	0.38	0.08	0.26	0.07	0.32
2-J	7.1	0.85	0.1	0.32	215	756	1.10	0.96	11.9	18	4.4	0.54	0.58	0.13	0.48	0.06	0.30
2-L	6.3	0.80	0.1	0.71	192	543	2.20	1.02	17.3	27	2.6	0.60	0.56	0.16	0.39	0.06	0.30
2-M	4.6	0.45	0.1	0.72	223	392	2.65	1.00	0.9	29	3.3	0.63	0.47	0.07	0.17	0.08	0.31
2-N	4.1	0.27	0.1	0.80	217	395	2.07	0.95	1.3	32	3.1	0.72	5.32	0.06	0.30	0.10	0.37
2-O	4.3	0.34	0.6	0.60	225	385	2.52	0.95	2.7	33	3.2	0.80	1.00	0.07	0.18	0.23	0.33
2-P	5.0	0.39	0.4	1.00	222	365	3.19	0.91	8.6	27	3.7	0.98	1.35	0.09	0.35	0.34	0.33
2-S	6.4	0.63	0.1	0.80	198	411	2.44	0.98	7.8	24	3.0	0.88	0.72	0.05	0.51	0.12	0.36

[a] As received.

section 2. Coals often show lateral variations in trace element concentrations over short distances, even within the same seam and mine site. These variations are attributed mostly to paleoenvironmental and postdepositional processes (Clarke & Sloss, 1992; Goodarzi & Swaine, 1994b). The vertical variation of elemental concentration is dependent on the specific location of the coal sample within the section. For example, aluminum concentration is low in the middle part of section 1 and increases toward the top and bottom of the section. This coincides with an increase in the ash content of the coal and, presumably, the aluminosilicate clay mineral content. The same is true in coal seam 3, section 2, where aluminum increases toward the high-ash intervals near the top of the section. Trace-element enrichment at the top and bottom of coal seams has been attributed to epigenetic and syngenetic processes (Gluskoter et al., 1977). The high mineral matter content at the top of the Vesta Mine coal seams is responsible for the high concentrations observed.

Certain similarities become apparent in the vertical variation of the elements As, Ba, Cr, Co, K, Mg, Na, U, Ti, Zn, and all the rare earth elements (REEs) in section 1. These elements follow the vertical variation of aluminum, showing that they have a positive relationship with the coal's ash content. It is well known that the major elements Al, K, Mg, Na, and Ti, as well as Ba, Cr, U, and the REEs, are associated with the structure of clay minerals and feldspars; hence they have an inorganic association in coals (Gentzis & Goodarzi, 1995b; Querol et al., 1995). On the other hand, the elements As, Co, and Zn are usually found in association with sulfide minerals. Calcium is the only major element not showing a clear association with aluminum. Calcium is most likely associated with finely dispersed minerals within the coal matrix, probably carbonates and sulfates. Calcium in the Vesta Mine coals has the same vertical variation as in the Highvale Mine coals in the Alberta plains (Gentzis & Goodarzi, 1995b). Iron exhibits a vertical variation similar to that of sulfur, an indication that it is present as sulfide(s). Manganese

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Table 2
Mean elemental concentrations, Vesta seam 3, section 2 (data in ppm unless otherwise noted) (*Continued*)

S (%)	La	Lu	Mg (%)	Mn	Mo	K (%)	Sm	Sc	Se	Na (%)	Th	Ti (%)	U	V	Yb	Zn
0.41	9.0	0.14	0.08	127.0	8.62	0.55	1.09	2.56	1.40	0.44	1.74	0.10	0.34	29.30	0.8	15.0
0.42	10.2	0.16	0.04	28.9	0.20	1.39	1.39	1.98	0.93	0.38	1.12	0.09	0.39	11.50	0.9	11.0
0.42	17.9	0.19	0.07	19.9	3.60	0.11	3.47	2.30	1.00	0.57	5.90	0.04	3.04	3.00	1.2	13.0
0.40	7.3	0.12	0.11	25.0	7.69	0.33	1.69	3.03	1.10	0.72	12.40	0.07	2.77	2.90	0.8	8.5
0.44	6.0	0.52	0.05	25.6	2.80	0.04	0.93	1.10	0.61	0.46	2.11	0.02	1.69	2.20	0.4	6.1
0.40	1.5	0.39	0.06	25.1	2.50	0.03	0.25	0.53	0.90	0.44	0.76	0.09	1.01	1.80	0.2	440.0
0.42	7.3	0.16	0.05	23.4	4.20	0.06	1.17	1.59	0.46	0.42	0.70	0.03	0.77	5.29	0.9	4.9
0.41	0.2	0.02	0.05	24.7	1.30	0.03	0.22	0.52	0.61	0.41	0.60	0.02	0.58	1.90	0.2	6.5
0.41	1.5	0.02	0.03	19.0	1.00	0.03	0.34	0.65	0.71	0.42	0.49	0.02	0.35	1.80	0.1	14.0
0.44	6.2	0.05	0.05	21.6	1.10	0.04	0.88	1.21	0.92	0.44	1.14	0.04	0.36	2.60	0.2	600.0
0.48	11.4	0.03	0.06	22.8	2.20	0.03	0.71	1.07	1.50	0.41	1.10	0.02	0.52	2.20	0.3	5.8
0.52	0.6	0.04	0.07	24.3	1.40	0.04	0.33	0.59	0.55	0.41	0.52	0.01	0.39	2.39	0.2	6.1
0.49	0.8	0.05	0.06	47.6	1.30	0.04	0.38	0.50	0.36	0.41	0.44	0.01	0.37	2.00	0.3	6.0
0.52	1.4	0.09	0.05	31.7	1.00	0.04	0.50	1.06	0.77	0.40	0.29	0.01	0.44	2.20	0.6	5.7
0.49	9.1	0.21	0.05	21.3	1.10	0.04	0.56	1.67	0.68	0.42	0.39	0.01	0.71	2.30	1.1	6.3
0.51	6.4	0.06	0.06	19.2	1.50	0.04	0.59	0.86	0.38	0.44	0.73	0.02	0.79	1.80	0.5	11.0

shows a mixed organic/inorganic association, pointing to its presence in more than one association (with clay minerals/iron sulfides and/or coal macerals). The halogens Br and Cl do not show a clear association. Bromine is predominantly associated with the organic matter in coal, but in sample 1-A (39.6% ash content) it could be associated with clays. Chlorine also follows the trend of bromine, that is, mainly having an organic association in these subbituminous coals.

There is an overall decrease in boron concentration of Vesta coal seam 3 from floor to roof in section 2. There is also an increase in chromium concentration in the same direction. These features suggest a decrease in marine influence in that direction (Goodarzi & van der Flier-Keller, 1988). This is more evident in section 2 than in section 1 of seam 3. In the two sections analyzed, roof and floor samples as well as carbonaceous layers (partings) interbedded with coal have lower boron content than the coal samples immediately above or below the partings. This is in agreement with the results of Goodarzi and van der Flier-Keller (1989) and Goodarzi and Swaine (1994b) on coals from British Columbia and Alberta. However, the opposite trend has also been observed in coals from Australia and western Canada, pointing to the fact that it is not possible to predict the distribution of boron in coaly and carbonaceous layers even in the same coal-bearing succession.

The relative enrichment of boron in coal beneath carbonaceous shale or carbominerite partings could be explained by the solubilization of the element in percolating waters and subsequent mobilization and deposition from the sedimentary partings to the coal beneath. This is particularly evident in section 1, where B concentration increases from < 10 ppm to 177 ppm in the transition from carbonaceous shale to coal and from 205–224 ppm to 255 ppm in the transition from the roof sediments to coal beneath. The same pattern is observed in section 2, with B concentration increasing from the 153–175 ppm range in the roof to 190 ppm in coal beneath and from 150 ppm to 187 ppm in the transition from

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carbonaceous shale to coal. This happens in the early stages of coalification when coal is highly porous and can assimilate boron much more easily than sedimentary partings. A similar explanation is given for the REEs Ce, Dy, Eu, and La, whose concentrations are considerably higher in the coal beneath the carbonaceous shale represented by sample 1-W in section 1. However, it does not appear that any mobilization of hydrolyzable REEs has taken place from the roof sediments to coal beneath in section 1. Such a process is strongly suggested in section 2, where a considerable increase in the concentrations of Ce, Dy, Ho, La, Sm, and Yb from the roof sediments to coal beneath was noted.

Comparison with Other Western Canadian Coals—Possible Effects of Elements

Table 3 shows the mean trace element concentrations of coals from the Vesta Mine, compared to the average elemental concentrations of subbituminous coals from the Whitewood and Highvale mines in the Alberta plains as well as to those of the Obed Mountain high-volatile bituminous coals in the outer Alberta foothills. A comparison is also made with the Hat Creek lignite to subbituminous coals in south-central British Columbia. The coals are of slightly different rank based on reflectance (0.38% to 0.50% Ro, random) and age. The Vesta Mine coals are Upper Cretaceous to Paleocene in age, the Whitewood, Highvale and Obed Mountain coals are Paleocene, and the Hat Creek coals are Eocene to Oligocene. There are also differences in the depositional environment. The Hat Creek coals formed in an intermontane graben under freshwater conditions. The Whitewood,

Table 3
Comparison of mean concentrations of selected elements in Vesta Mine coal with coals from western Canada and the world

Element	Whitewood	Highvale	Obed Mountain	Hat Creek	Vesta	World[a]
As	4.7	3.8	4.0	12.7	0.9	10
Ba	450	700	490	171	450	200
Br	15.1	286	7.5	11.8	2.0	20
B	~50	~50	~50	~40	208	50
Cl	21.5	72.3	80.6	60.8	27.0	1000
Co	3.3	3.2	2.1	9.1	1.4	5
Cr	7.0	11.5	7.1	30.0	13.8	20
Mo	4.8	5.0	3.3	3.5	2.7	3
Mn	110	100	31.8	28.8	27.0	70
Th	6.0	5.6	1.9	2.4	1.8	4
U	2.5	2.6	1.5	1.4	1.1	2
V	19.3	17.1	n.a.	122	3.7	40
Sb	0.7	0.7	1.2	0.5	3.3	1
Se	1.0	1.7	1.1	1.1	0.8	1
S	0.6	0.5	0.4	0.45	0.45	n.a.

Note. All values in ppm; n.a., not available.
[a] After Clarke and Sloss (1992).

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Highvale, and Obed Marsh coals formed in fluvial settings, also under freshwater conditions. Only the Vesta Mine coals represent coal formation under the influence of marine (brackish) waters in a lower delta plain depositional environment.

Table 3 shows that, with the exception of barium, boron, and antimony, the Vesta Mine coals have lower mean concentrations of elements compared to world coals. The enrichment in boron is due to depositional environment conditions, as interpreted by geological evidence, and not due to differences in rank or age. This is in agreement with Goodarzi and Swaine (1994b), who found no relationship between boron content and rank or between boron concentration and age of a large suite of coals from Canada and Australia. Most world coals have a boron range of 5–400 ppm with a probable mean in the range of 30–60 ppm. The present study coals, although they have a higher mean, fall within the range for the majority of coals. However, very high concentrations of boron may be harmful to plants, causing retardation to their growth (Swaine, 1990). Fly ash resulting from the utilization of feedcoal from the Vesta Mine in the nearby Battle River power station may be enriched in boron. This would be useful in agriculture, because fly ash could be used as soil amendment material.

Antimony in coal may have a wide range of association, from inorganic to organic (Finkelman, 1994). As a chalcophile element, Sb has been found in solid solution in pyrite but has also been detected in finely dispersed form in the coal's organic matrix. Previous studies (Meij, 1989; Clarke & Sloss, 1992; Helble, 1994; Rizeq et al., 1994) have shown that antimony completely volatilizes during coal combustion, and that the element tends to be highly enriched in the small ash particles following nucleation and condensation. Antimony is not considered a deleterious element during coal utilization (Swaine, 1990). The mean value of Sb in the Vesta Mine coals (3.3 ppm) is slightly higher that the mean value for coals burned in nine European Union countries (2.3 ppm; Sabbioni et al., 1983).

Barium is considerably less volatile than antimony during combustion and is expected to be only slightly enriched in fly ash particles (Rizeq et al., 1994). This element is not considered hazardous during coal utilization (Swaine, 1990). Although most coals have mean values of Ba in the range of 70 to 300 ppm, the mean value of the element in the Vesta Mine coals (450 ppm) should not be of concern because there have been no published reports of untoward effects of Ba during coal mining or utilization (Swaine, 1990).

The Vesta Mine coals have lower Co concentrations (mean is 1.4 ppm) than western Canadian coals deposited under freshwater conditions (mean values range from 2 to 9 ppm). This is in agreement with the observations of Swaine (1990) that Co tends to be higher in freshwater-influenced coals. However, no enrichment of Mo, U, or V in the marine-influenced Vesta coals is apparent compared to the other freshwater coals, as suggested by Chou (1984). To the contrary, the Vesta Mine coals have lower mean concentrations of these elements (Table 3).

Although boron differentiates the Vesta Mine coals from the other coals (see Table 3), total sulfur content in these coals is similar to that in western Canadian coals deposited under freshwater conditions (0.4–0.6%; Table 3). While boron concentrations show a variation in the Vesta coals, sulfur values in the same coals are within a low and narrow range, thus not responding to changes in the depositional environment from marine (brackish) to mildly brackish water conditions. It appears that paleosalinity variations may have affected the concentrations of boron and sulfur in the Vesta Mine coals at different rates. The present study coals would plot in the area of the "Suite 1" coals of the study of Banerjee and Goodarzi (1990), that is, coals formed in stacked shoreline sequences where transgessive marine sediments directly overlying the coals are responsible for the high B concentrations in the coals. Results from this study confirm that the relationship between total sulfur content and marine influence in coals is unclear.

Conclusion

1. The mean concentrations of the elements Br, Cl, Cr, Co, Mn, Mo, Na, Se, Ti, U, Th, V, and Zn are low and within the range for world coals. The Vesta Mine coals are suitable for utilization in power stations.
2. Despite the short distance between the sections (100 m), seam 3 in section 1 has slightly higher concentrations of Sb, As, B, Br, Cl, Na, Se, U, and Th. Section 2 has slightly higher concentrations of Cr, Co, Mn, Mo, Ti, V, Zn, and S than section 1.
3. All elements, with the exception of Br and Cl, have a positive relationship with ash content. Calcium and Mn have an intermediate association with ash.
4. Boron concentration (mean is 208 ppm) indicates peat interaction with brackish waters, whereas total S content ($<0.50\%$) does not corroborate with boron, indicating a complex sulfur/boron relationship for coals deposited in paralic environments.
5. Intervals rich in inertinite selectively concentrate Ca, Fe, and Mn. No other relationship between elemental enrichment and/or depletion and maceral content was evident.

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