Rare Earth Element Abundances in Coal Combustion Byproducts of Saskatchewan

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Abstract

Global demand for rare earth elements and yttrium (REY) is projected to increase drastically in the coming years coincident with a transition to clean energy sources; however, economic ore deposits and global production of REY is concentrated in a small number of locations worldwide. As such, there is interest in developing new sources of REY such as coal combustion byproducts (CCBs) including fly ash and bottom ash. While previous studies have investigated the REY content of CCBs from the United States, Europe, Asia and Africa, CCBs from Saskatchewan have yet to be studied. Accordingly, this work focused on the bulk geochemistry of CCBs from the Poplar River, Boundary Dam and Shand coal-fired powerplants in Saskatchewan, with an emphasis on REY. The results indicate that fly ash from Poplar River has the highest total concentration of REY, while bottom ash from Boundary Dam has the highest concentration of critical REY and an enrichment in the more valuable heavy REY. This work is the first step in assessing the economic potential of CCBs from Saskatchewan, which could provide an economically valuable domestic source of REY.

Keywords: *Williston Basin, rare earth elements (REE), coal combustion byproducts, geochemistry, critical minerals*

1. Introduction

The rare earth elements (REE) are a group of elements comprising the lanthanides (La to Lu), as well as yttrium (Y; collectively REY) and scandium (Sc) due to shared geochemical properties. In non-aqueous geological environments, however, Sc does not behave in a similar manner to the REY due to a smaller ionic radius, and it is not included in this study. The REY are commonly subdivided into light REY (LREY) and heavy REY (HREY), with the mining industry classifying the LREY as La to Nd and HREY as Sm-Lu, while IUPAC classifies LREY as La to Gd and HREY as Tb to Lu due to the filling of the 4f electron orbital. REY have recently been classified as critical minerals by the Canadian government (Natural Resources Canada, 2021) as they are required in clean energy technologies such as wind turbines, photovoltaic cells, nuclear energy and energy storage (Trench and Sykes, 2020). Demand for REY increased approximately 60% between 2015 and 2020 (USGS, 2021) and is projected to further increase throughout the 2020s coincident with a global transition toward clean energy sources (Dushyantha *et al*., 2020). The primary geologic sources of REY are carbonatites, alkaline igneous systems, ion-adsorption clay deposits and monazite-xenotime–bearing placer deposits (Balaram, 2019); however, economic ore deposits only exist in few locations worldwide. Recently, several non-traditional, secondary sources of REY from sedimentary basins have been identified, including coal combustion byproducts (CCBs) and oilfield brines.

CCBs have been recognized as a promising source of REY because they can contain in excess of three times the amount of REY compared to the coals from which they were derived (Seredin and Dai, 2012). Previous studies have noted that the chemical composition of the fly ash depends primarily on the chemistry of the source coal as well as the combustion process (Franus *et al*., 2015). While past studies have investigated the REY potential of CCBs from localities around the world, including the United States (Hower *et al*., 2015; Taggart *et al*., 2016; Kolker *et al*., 2017; Huang *et al*., 2020), China (*e.g*., Pan *et al*., 2018; Wang *et al*., 2019), the United Kingdom (Blissett *et al*., 2014), South Africa (Wagner and Matiane, 2018) and Poland (Blissett *et al*., 2014; Franus *et al*., 2015), CCBs from

Saskatchewan have yet to be investigated. As such, this work presents the REY and trace metal geochemistry of CCBs (*i.e.*, fly ash and bottom ash) from three coal-fired power plants in Saskatchewan.

2. Geological Background

Coal in southern Saskatchewan is mined from the Tertiary Ravenscrag Formation at the Poplar River Mine near Coronach, which supplies the Poplar River Power Station, and at the Boundary Dam mine near Estevan, which supplies the Boundary Dam and Shand Power Stations. The Ravenscrag Formation is unconformably overlain by Tertiary- or Quaternary-aged sandstone and gravels, or glacial till (Whitaker *et al*., 1978; Beaton *et al*., 1991) and it conformably overlies the Upper Cretaceous Frenchman Formation, with the contact being interpreted as the Cretaceous–Tertiary boundary in southern Saskatchewan (Whitaker *et al*., 1978; Beaton *et al*., 1991). The Ravenscrag Formation occurs throughout much of southern Saskatchewan on the northern flank of the Williston Basin and consists of interbedded sands, silts, clays and lignite deposited in a low-energy alluvial-plane–fluvial environment (Whitaker *et al*., 1978). It was deposited as part of a continuing sequence of continental-derived sediment associated with uplift of the Laramide orogeny and retreat of the Bearpaw Sea (McCrossan and Glaister, 1964). The Late Cretaceous cratonic subsidence of the Williston Basin, accompanied by local subsidence due to salt dissolution in the underlying Devonian Prairie Evaporite Formation, continued into the early Paleocene, resulting in the deposition of thin, laterally restricted coal beds, with further subsidence leading to an increase in coal seam thickness (Broughton, 1979).

3. Methods

Coal fly ash (FA) and bottom ash (BA) samples were collected from the Boundary Dam (BD), Shand (SND) and Poplar River (PR) coal-fired power plants by employees of each facility. Samples were analyzed for bulk geochemistry, including major oxides, trace metals and REY, utilizing a lithium-borate fusion digestion followed by analysis by inductively coupled-plasma mass spectrometry (ICP-MS) by Bureau Veritas Canada Commodities Ltd., Vancouver, BC (LF200 method).

4. Results and Discussion

Rare earth element data for the three FA and three BA samples are presented as parts per million (ppm; mg/kg) in Table 1, while additional information, including major oxide and trace metal data, is available in Appendix 1, Table 1. Seredin (2010) classified the REY into critical REY (CREY; Nd, Eu, Tb, Dy, Y and Er), uncritical REY (UREY; La, Pr, Sm, and Gd) and excessive REY (EREY; Ce, Ho, Tm, Yb and Lu) based on production, demand and projected economic outlook for each element; however, this is subject to change based on economic conditions. The percentage of critical REY in each sample is calculated as the CREY divided by total REY (TREY). A bar plot representing the proportions of CREY, EREY and UREY is presented in Figure 1. Based on the data, the PR FA has the highest TREY content, followed by the BD BA and the PR BA, while the BD BA contains the highest concentration of CREY at 120 ppm and greatest proportion of CREY at 38.7%. The PR FA contains the second highest amount of CREY at 104 ppm, but it contains the lowest proportion of CREY at 32.5%. Although the SND CCBs contain among the lowest concentrations of TREY and CREY, the BA and FA contain the second and third highest proportions of CREY, respectively.

__Table 1 –__ REY concentrations in ppm for the fly ash and bottom ash samples and sums of the total, critical, uncritical, and excessive REY. The % critical REY is also indicated.

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	TREY	CREY	UREY	EREE	% CREY
Poplar River fly ash	64.5	116.1	12.64	46.3	8.6	1.52	7.96	1.21	6.88	44.2	1.43	4.13	0.6	3.79	0.59	320.45	104.24	93.7	122.51	32.52926
Poplar River bottom ash	59.1	100.8	11.49	41.8	7.7	1.33	6.84	1.09	6.77	41.5	1.33	3.88	0.57	3.78	0.56	288.54	96.37	85.13	107.04	33.39918
Shand fly ash	47.0	87.2	10.14	37.1	7.15	1.36	7.11	1.12	7.00	45.5	1.47	4.43	0.61	4.12	0.63	261.94	96.51	71.4	94.03	36.84432
Shand bottom ash	49.4	88.3	10.43	38.6	7.52	1.35	7.38	1.18	7.39	48.5	1.56	4.82	0.68	4.38	0.65	272.14	101.84	74.73	95.57	37.42192
Boundary Dam fly ash	49.9	91.0	10.47	39.3	6.95	1.43	7.03	1.07	6.32	43.9	1.38	4.03	0.58	3.86	0.59	267.81	96.05	74.35	97.41	35.86498
Boundary Dam bottom ash	53.4	99.8	11.49	43.2	8.29	1.69	8.78	1.41	8.68	59.4	1.95	5.91	0.84	5.31	0.86	311.01	120.29	81.96	108.76	38.67721

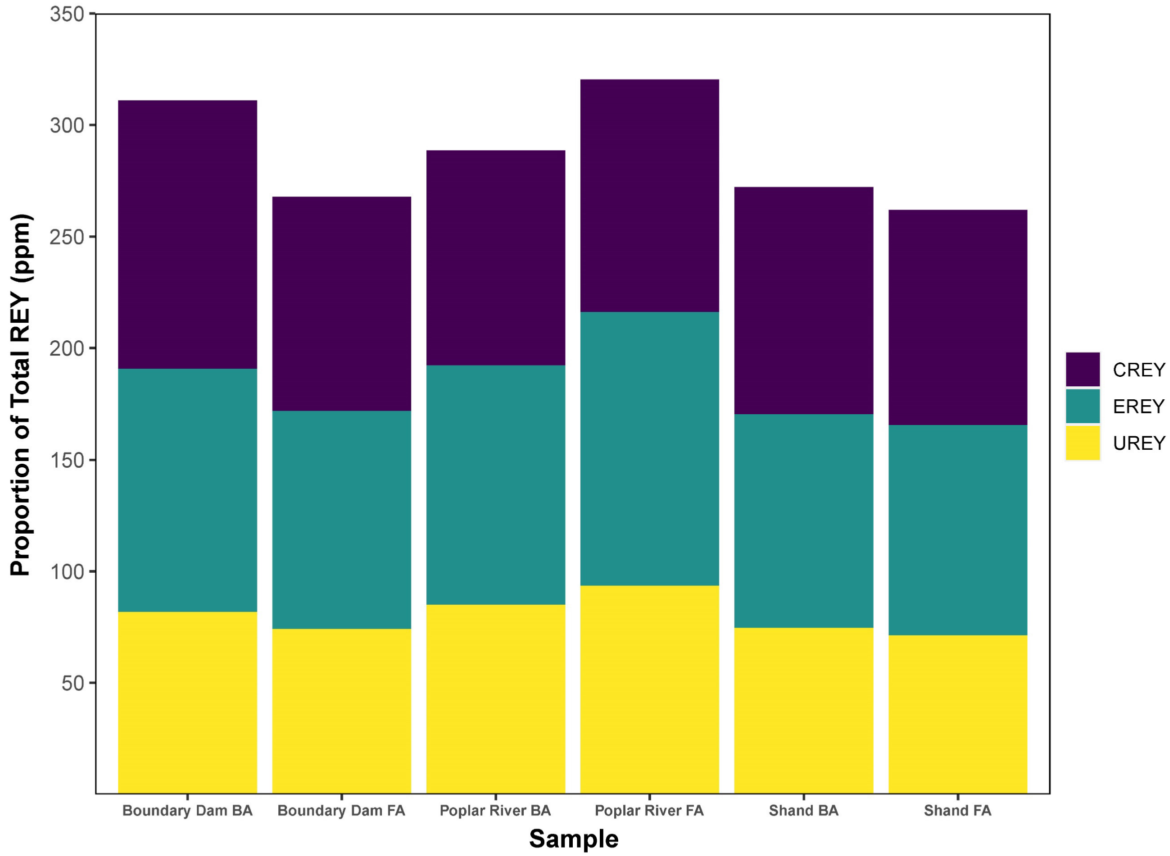

__Figure 1 –__ Bar plot displaying the proportions of critical REY (CREY), uncritical REY (UREY) and excessive REY (EREY) relative to the total concentration of REY in each sample.

REY have been widely used as geochemical indicators of the sedimentary environment and post-depositional history of coal deposits due to their predictable behaviour and fractionation during geochemical processes (Dai *et al*., 2016). Normalization of REY relative to a well-characterized reservoir can be performed to compare REY concentrations between samples in addition to identifying anomalous behaviour of REY. Such normalization can reveal enrichment or depletion of LREY and HREY, as well as La, Ce, Eu, Gd and Ho anomalies which can be indicative of the REY source (Henderson, 1984). Coal and CCBs are typically normalized relative to the upper continental crust (UCC) based on Taylor and McLennan (1985; Dai *et al*., 2016; Table A1-2). A spider plot displaying the normalization patterns of the six samples relative to the UCC is presented in Figure 2, while the La, Ce, Eu and Gd anomalies, Y/Ho ratios, and LREY/HREY ratios are presented in Table 2. REY anomalies were calculated based on Bolhar *et al.* (2004) for La as $La_N/La_N^* = La_N/(3\ Pr_N - 2\ Nd_N)$, Ce as $Ce_N/Ce_N^* = Ce_N/(2\ Pr_N - 1\ Nd_N)$ and Gd as $Gd_N/Gd_N^* = Gd_N/(2\ Tb_N - 1\ Dy_N)$, where the subscript N is the normalized value for each element. Eu anomalies were calculated as $Eu_N/Eu_N^* = Eu_N/(0.67Sm_N + 0.33Tb_N)$ following Bau and Dulski (1996). The Y-anomaly was calculated as the Y_N/Ho_N ratio, while LREY depletion was calculated using the Pr_N/Yb_N ratio (Bolhar *et al*., 2004).

Table 2 – *Calculated REY anomalies relative to the UCC.*

Sample	La_N/La_N^*	Ce_N/Ce_N^*	Eu_N/Eu_N^*	Gd_N/Gd_N^*	Y_N/Ho_N	Pr_N/Yb_N
Poplar River fly ash	1.21	1.02	0.91	1.15	1.12	1.03
Poplar River bottom ash	1.20	0.97	0.88	1.22	1.13	0.94
Shand fly ash	1.10	0.95	0.94	1.25	1.13	0.76
Shand bottom ash	1.15	0.95	0.89	1.23	1.13	0.74
Boundary Dam fly ash	1.19	0.99	1.02	1.20	1.16	0.84
Boundary Dam bottom ash	1.16	0.99	0.98	1.20	1.11	0.67

Positive La and Gd anomalies were present in all samples (La_N/La_N^* = 1.10 to 1.21; Gd_N/Gd_N^* = 1.15 to 1.25), while no substantial Ce anomalies were observed (Ce_N/Ce_N^* = 0.95 to 1.02). Minor negative Eu anomalies were found in all samples except for the Boundary Dam fly ash, and normalized Y/Ho ratios indicated a positive Y anomaly ranging from 1.11 to 1.16. With the exception of the Poplar River fly ash, all samples displayed a slight HREY enrichment, with the Boundary Dam bottom ash exhibiting the largest HREY enrichment based on Pr_N/Yb_N ratios.

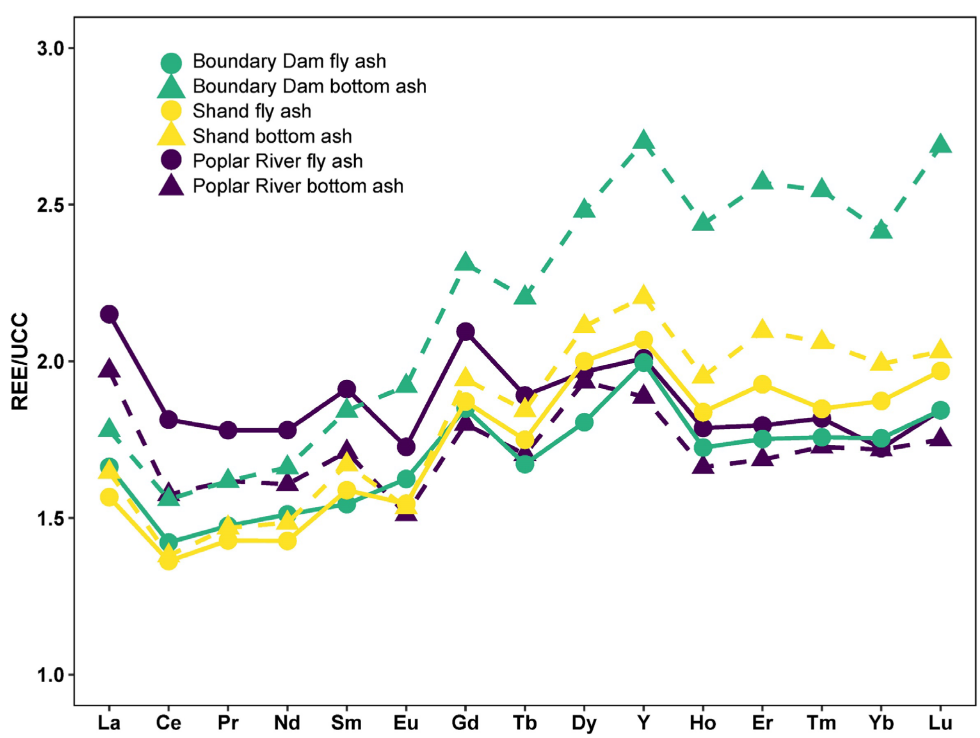

Figure 2 – *Spider plot displaying the REY normalization of each sample relative to the UCC (Taylor and McLennan, 1985). Circles with solid lines represent fly ash samples and triangles with dashed lines represent bottom ash samples.*

5. Conclusions and Future Work

The goal of this study was to present the REY content of CCBs from southern Saskatchewan since CCBs have been identified as potential sources of critical minerals. The PR FA contained the highest concentration of REY, while the BD BA were found to have the highest abundance and proportion of CREY. The PR CCBs were LREY-enriched and the BD and SND CCBs were enriched in HREY. Future work should investigate the sources of REY in the coals, their subsequent enrichment in the CCBs, and potential extraction technologies suitable for CCBs from Saskatchewan. This may involve studying the microscale bonding environment of REY using synchrotron techniques such as X-ray adsorption spectroscopy (XAS) including X-ray adsorption fine structure (XAFS) or X-ray adsorption near edge structure (XANES; *e.g.*, Stuckman *et al*.; 2018, Liu *et al*., 2019), or aqueous geochemical methods such as sequential extractions (*e.g.*, Pan *et al*., 2019; Park *et al*., 2021), acid leaching (Cao *et al*., 2018) or bio-recovery (*e.g.*, Park and Liang, 2019). A review of a number of potential REY extraction techniques is provided in Zhang *et al*. (2020). Future work should also examine the heterogeneity of REY in CCBs over extended periods to assess how the geochemistry and REY content of the CCBs vary over the course of a mine's life cycle.

A transition to cleaner energy sources has been indicated to be a solution to combatting climate change (IPCC, 2018); however, these technologies will require new source of critical minerals, specifically REY (Sovacool *et al*., 2020). CCBs are a promising alternative source since they contain elevated REY concentrations relative to the source coals and have the potential to turn a waste stream into an economic asset while simultaneously reducing environmental liability. Furthermore, with the impending closure of coal-fired power plants by 2030, the recovery of critical minerals from coal products has the potential to extend the life cycle of coal mines in the south of the province by both providing potential employment opportunities and positioning Saskatchewan as a leader in the energy transition.

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Appendix 1: Analytical Results **[also see separate Microsoft® Excel® file]**

Table A1-1 – *Results of the ICP-MS analysis as provided by Bureau Veritas.*

	Analyte	**SiO2**	**Al2O3**	**Fe2O3**	**MgO**	**CaO**	**Na2O**	**K2O**	**TiO2**	**P2O5**	**MnO**	**Cr2O3**	**Ba**	**Ni**	**Sc**	**LOI**	**Sum**	**Be**	**Co**	**Cs**	**Ga**	**Hf**	**Nb**	**Rb**	**Sn**
	Unit	%	%	%	%	%	%	%	%	%	%	%	PPM	PPM	PPM	%	%	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
	MDL	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.002	1	20	1	-5.1	0.01	1	0.2	0.1	0.5	0.1	0.1	0.1	1
Sample	**Type**																								
Poplar River Fly Ash	Coal	39.58	26.64	4.76	5.82	18.58	0.35	0.97	0.69	0.06	0.07	0.008	3708	<20	14	1.7	99.64	6	5.1	3.7	65.5	7.5	20.4	35.8	10
Poplar River Bottom Ash	Coal	39.41	22.88	10.95	5.77	17.2	0.21	0.61	0.73	0.03	0.06	0.004	3824	<20	12	1.4	99.68	5	4.7	1.8	20.4	9.9	23.8	20.6	3
Shand Fly Ash	Coal	53.65	19.26	4.21	2.8	8.16	5.89	1.89	0.76	0.34	0.02	0.009	5169	33	15	2	99.55	7	13.2	6.9	29.7	7	19.9	75.3	4
Shand Bottom Ash	Coal	53.57	18.77	4.82	2.83	9.05	3.93	1.76	0.78	0.35	0.02	0.009	5687	35	16	3	99.52	10	13.9	6.2	18.6	8.3	20.8	71.5	2
Boundary Dam Fly Ash	Coal	54.28	18.91	4.85	3.28	8.35	5.28	2.09	0.67	0.36	0.02	0.011	5047	34	15	0.9	99.53	7	11.7	8.9	30.2	5.9	18.1	91.5	4
Boundary Dam Bottom Ash	Coal	53.09	18.7	4.89	3.06	11.4	4.56	1.3	0.8	0.4	0.02	0.008	6174	42	17	0.5	99.44	7	13.2	4.5	19.2	8.9	23.4	53.1	2

	Analyte	**Sr**	**Ta**	**Th**	**U**	**V**	**W**	**Zr**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**TOT/C**	**TOT/S**
	Unit	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	%
	MDL	0.5	0.1	0.2	0.1	8	0.5	0.1	0.1	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.02	0.03	0.01	0.05	0.01	0.02	0.02
Sample	**Type**																								
Poplar River Fly Ash	Coal	1167.5	1.9	29	19.6	76	8.6	257	44.2	64.5	116.1	12.64	46.3	8.6	1.52	7.96	1.21	6.88	1.43	4.13	0.6	3.79	0.59	0.19	0.47
Poplar River Bottom Ash	Coal	981	1.9	24.1	13.4	49	6.5	353.6	41.5	59.1	100.8	11.49	41.8	7.7	1.33	6.84	1.09	6.77	1.33	3.88	0.57	3.78	0.56	0.19	0.08
Shand Fly Ash	Coal	2376.9	1.4	20.7	9.7	118	4.5	272.2	45.5	47	87.2	10.14	37.1	7.15	1.36	7.11	1.12	7	1.47	4.43	0.61	4.12	0.63	0.26	0.53
Shand Bottom Ash	Coal	2651.1	1.5	20.6	11.1	120	3.9	303.5	48.5	49.4	88.3	10.43	38.6	7.52	1.35	7.38	1.18	7.39	1.56	4.82	0.68	4.38	0.65	1.58	0.2
Boundary Dam Fly Ash	Coal	2411.6	1.2	17.8	12.5	143	5	228.8	43.9	49.9	91	10.47	39.3	6.95	1.43	7.03	1.07	6.32	1.38	4.03	0.58	3.86	0.59	0.09	0.2
Boundary Dam Bottom Ash	Coal	3262.5	1.7	22.2	12.8	111	5.5	356.2	59.4	53.4	99.8	11.49	43.2	8.29	1.69	8.78	1.41	8.68	1.95	5.91	0.84	5.31	0.86	0.19	0.08

Table A1-2 – *REY values normalized to upper continental crust.*

Sample	La_N	Ce_N	Pr_N	Nd_N	Sm_N	Eu_N	Gd_N	Tb_N	Dy_N	Y_N	Ho_N	Er_N	Tm_N	Yb_N	Lu_N
Poplar River fly ash	2.15	1.81	1.78	1.78	1.91	1.73	2.09	1.89	1.97	2.01	1.79	1.80	1.82	1.72	1.84
Poplar River bottom ash	1.97	1.58	1.62	1.61	1.71	1.51	1.80	1.70	1.93	1.89	1.66	1.69	1.73	1.72	1.75
Shand fly ash	1.57	1.36	1.43	1.43	1.59	1.55	1.87	1.75	2.00	2.07	1.84	1.93	1.85	1.87	1.97
Shand bottom ash	1.65	1.38	1.47	1.48	1.67	1.53	1.94	1.84	2.11	2.20	1.95	2.10	2.06	1.99	2.03
Boundary Dam fly ash	1.66	1.42	1.47	1.51	1.54	1.63	1.85	1.67	1.81	2.00	1.73	1.75	1.76	1.75	1.84
Boundary Dam bottom ash	1.78	1.56	1.62	1.66	1.84	1.92	2.31	2.20	2.48	2.70	2.44	2.57	2.55	2.41	2.69
UCC[1] (ppm)	30.00	64.00	7.10	26.00	4.50	0.88	3.80	0.64	3.50	22.00	0.80	2.30	0.33	2.20	0.32

[1] Upper Continental Crust. Samples were normalized against the UCC based on Taylor and McLennan (1985).