minerals

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Petrology and Geochemistry of the Harlan, Kellioka, and Darby Coals from the Louellen 7.5-Minute Quadrangle, Harlan County, Kentucky

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Abstract: The Harlan, Kellioka, and Darby coals in Harlan County, Kentucky, have been among the highest quality coals mined in the Central Appalachians. The Middle Pennsylvanian coals are correlative with the Upper Elkhorn No. 1 to Upper Elkhorn No. 3½ coals to the northwest of the Pine Mountain thrust fault. Much of the mining traditionally was controlled by captive, steel-company-owned mines and the coal was part of the high volatile A bituminous portion of the coking coal blend. Overall, the coals are generally low-ash and low-sulfur, contributing to their desirability as metallurgical coals. We did observe variation both in geochemistry, such as individual lithologies with significant P_2O_5/Ba + Sr/Rare earth concentrations, and in maceral content between the lithotypes in the mine sections.

Keywords: Pennsylvanian; mining history; coking coal; coal quality

1. Introduction

Harlan County, Kentucky, has had a long, colorful, and, at times, violent mining history [1–3]. None of that would have been the case without a base of extensive reserves of high quality coal, much of it directed towards the metallurgical coal market and mined at steel-company-owned mines [4,5].

In this investigation, we examined the petrology and chemistry of coals in Harlan County southeast of Pine Mountain, on the Pine Mountain thrust sheet (Figure 1). In particular, we appraised, in ascending order, the Harlan, Kellioka, and Darby coals of the Pikeville Formation of the Middle Pennsylvanian Breathitt Group (Figure 2). These coals were traditionally some of the better coking coal reserves. The study coals are the approximate correlatives of the Upper Elkhorn No. 1 and Upper Elkhorn No. 2, Upper Elkhorn No. 3 or Van Lear, and the Upper Elkhorn No. 3½ coals, respectively, to the northwest of Pine Mountain [6]. The underlying Path Fork coal, the correlative of the Blue Gem and Pond Creek coals on the northwest side of the Pine Mountain thrust fault, was investigated by Hatton *et al.* [7]. Below the Path Fork, the Grundy Formation Hance coal, correlative of the Manchester and many other coals on the northwest side of the Pine Mountain thrust fault, was studied by Esterle and Ferm [8] as well as Hubbard *et al.* [9]. The study areas for the Path Fork and Hance coals, however, although on the thrust sheet, were to the southwest of the present study area.

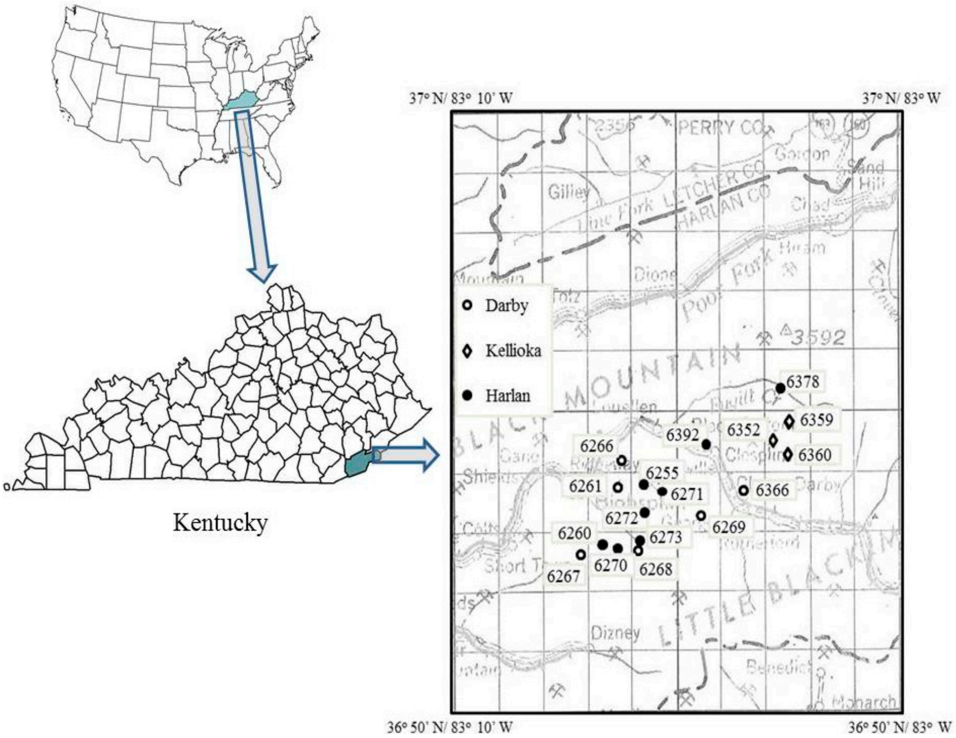


Figure 1. Location of the sample sites in Harlan County, Kentucky. For multiple-bench/multiple-lithotype samples, the site is designated by the sample number of the accompanying whole-coal sample.

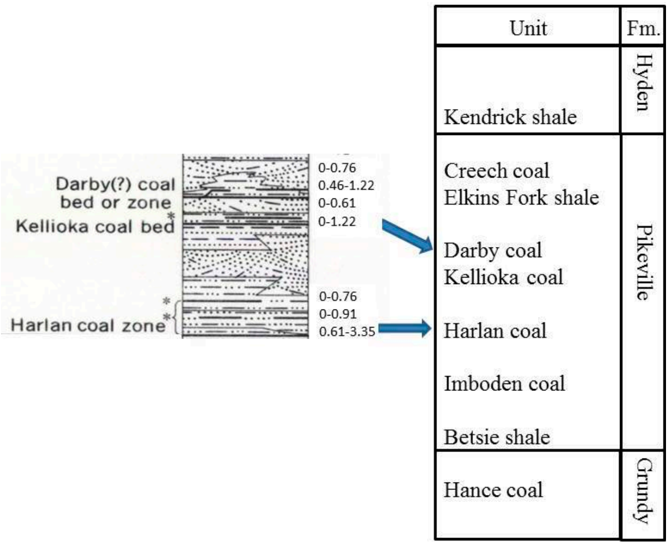


Figure 2. Geologic section of the study interval in the Louellen 7.5-minute quadrangle [10].

The environments of deposition for Kentucky coals have been investigated by the Kentucky Geological Survey and the University of Kentucky Center for Applied Energy Research [7,9,11–14]; John Ferm and his students at various universities, most recently (1980–1999) at the University of Kentucky (for example: Esterle and Ferm [8]); and outside researchers [15,16]. With the exception of Esterle and Ferm [8], Hatton *et al.* [7], and Hubbard *et al.* [9], the studies emphasized settings to the northwest of Pine Mountain. Much of the mining of the coals preceded the 1980s and 1990s studies noted above. As such, the current examination of coals collected in the 1980s represents one of the few detailed studies of Harlan County coals.

2. Methods

Samples were collected both at mines and from company-supplied cores in the 1980s (The samples from the 1980s represent the last widespread availability of mine samples and the serendipitous availability of core samples. Aside from shifts in mining, the CAER sampling interests shifted to other coals) (locations on Figure 1). The coals were collected as whole coal and bench samples, excluding rock partings greater than about 1-cm thick. The proximate and sulfur analyses were conducted at the University of Kentucky Center for Applied Energy Research (CAER) following ASTM procedures. Major oxides were analyzed at the CAER by X-ray fluorescence following procedures outlined by Hower and Bland [17]. All of the latter analyses were done shortly after sampling. Inductively coupled plasma mass spectrometry (X series II ICP-MS, ThermoFisher, Waltham, MA, USA), in pulse counting mode (three points per peak), was used to determine trace elements in the coal ash samples obtained from raw coals at 815 °C. The ICP-MS analyses were conducted at the China University of Mining and Technology (Beijing) on ash samples provided by the CAER. For ICP-MS analysis, samples were digested using an UltraClave Microwave High Pressure Reactor (Milestone, Milano, Italy) [18]. The digestion reagents for each 50-mg coal ash sample are 2-mL 65% HNO_3 and 5-mL 40% HF [18]. The Guaranteed-Reagent HNO_3 and HF for sample digestion were further purified by sub-boiling distillation. Arsenic and Selenium were determined by ICP-MS using collision cell technology (CCT) in order to avoid disturbance of polyatomic ions [19]. Multi-element standards (Inorganic Ventures: CCS-1, CCS-4, CCS-5, and CCS-6; NIST 2685b and Chinese standard reference GBW 07114) were used for calibration of trace element concentrations. The method detection limit (MDL) for each of the trace elements, calculated as three times the standard deviation of the average from the blank samples (n = 10), is listed in Table 1.

Table 1. Method detection limit (MDL, μg/L) of inductively coupled plasma mass spectrometry (ICP-MS) for the Harlan, Kellioka, and Darby coal ashes.

Elements	MDL	Elements	MDL	Elements	MDL
Li	0.0090	Zr	0.0173	Gd	0.0113
Be	0.0103	Nb	0.0567	Tb	0.0071
Sc	0.0067	Mo	0.1052	Dy	0.0198
V	0.0062	Ag	0.0028	Ho	0.0044
Cr	0.0293	Cd	0.0019	Er	0.0089
Co	0.0032	Sn	0.0176	Tm	0.0061
Ni	0.0219	Sb	0.0037	Yb	0.0050
Cu	0.0481	In	0.0028	Lu	0.0042
Zn	0.1547	Cs	0.0088	Hf	0.0129
Ga	0.0016	Ba	0.2019	Ta	0.1194
Ge	0.0015	La	0.0165	W	0.1465
As	0.1799	Ce	0.0071	Tl	0.2137
Se	0.2291	Pr	0.0122	Pb	0.0124
Rb	0.7208	Nd	0.0247	Bi	0.0331
Sr	0.0440	Sm	0.0229	Th	0.0677
Y	0.0144	Eu	0.0049	U	0.88

Maceral analysis, originally done shortly after the sampling, was re-examined for this study following the ICCP nomenclature [20,21]. The petrology was done using Leitz Orthoplan microscopes with oil-immersion, reflected-light, 50-x objectives on particulate pellets prepared to a final 0.05-μm-alumina polish. The reflectance was measured using a 547-nm bandpass filter and a 9-μm-diameter measuring spot with a photomultiplier calibrated against a series of glass reflectance standards in the range of the coal reflectances.

3. Discussion and Results

3.1. Proximate and Sulfur Analysis

The Harlan coal is the thickest of the three coals investigated; with two of the sections exceeding 2.72 m. The Harlan ash yield is higher and more variable than in the Kellioka and Darby coals (Table 2), discussed below. Several samples exceed 20% ash yield, with sample 6400 having 53% ash yield, sufficient to classify it as carbonaceous shale. On the whole-coal basis, the Harlan coal is a low- to medium-S coal, also higher than in the other two coals; exceeding 2% S in the 23.8%-ash-yield sample 6384. With the relative increase in sulfur compared to the other two coals, we can infer that the Harlan peat was subjected to a more significant marine influence. The nature and extent of such an influence is difficult to discern with just three detailed sections. With the exception of this study, the Harlan coal has not been studied in the same detail as some other eastern Kentucky coals (see Introduction). The mined Harlan coal, destined for the metallurgical market, was beneficiated prior to shipment from the facility; therefore, much of the high-ash and high-S coal was not included in those shipments.

Table 2. Thickness (cm), proximate analysis (%), total sulfur and forms of sulfur (%) in the Harlan, Kellioka, and Darby coals. T—total; py—pyritic; org—organic; sulf—sulfate; wc—whole coal; nd—not determined.

Coal	Sample	Bench	Thickness (cm)	Mois	Ash	S (t)	S (py)	S (sulf)	S (org)
Harlan	6255	wc	111.60	2.11	7.64	1.10	0.25	0.00	0.85
	6256	1/4 (top)	16.70	2.41	18.66	1.30	0.37	0.02	0.91
	6257	2/4	9.60	2.29	5.94	1.73	0.67	0.02	1.04
	6258	3/4	28.40	2.20	11.34	1.85	0.84	0.03	0.98
	6259	4/4	57.00	2.20	8.40	1.08	0.26	0.01	0.81
	6260	wc	140.21	1.98	8.88	1.19	0.30	0.01	0.88
	6270	wc	121.92	1.73	13.54	1.07	nd	nd	nd
	6271	wc	126.49	1.59	10.75	1.22	nd	nd	nd
	6272	wc	126.49	1.79	14.54	1.35	nd	nd	nd
	6273	wc	134.11	1.76	35.91	0.91	nd	nd	nd
	6378	wc	272.80	2.08	9.19	0.91	0.20	0.00	0.71
	6379	1/9 (top)	27.43	2.03	9.36	0.89	0.11	0.01	0.77
	6380	2/9	11.58	1.43	29.52	0.53	0.09	0.00	0.44
	6381	3/9	32.92	2.07	8.84	1.34	0.30	0.01	1.03
	6382	4/9	17.68	1.80	4.96	0.79	0.08	0.01	0.70
	6383	5/9	51.51	2.13	5.46	1.51	0.44	0.02	1.05
	6384	6/9	13.41	2.57	23.80	2.06	1.23	0.06	0.77
	6385	7/9	3.35	1.49	16.96	0.49	0.04	0.00	0.45
	6386	8/9	41.15	2.07	3.41	0.64	0.08	0.00	0.56
	6387	9/9	50.29	2.21	7.67	1.19	0.34	0.04	0.81
	6392	wc	292.61	1.88	16.72	1.09	0.29	0.00	0.80
	6393	1/11 (top)	35.05	1.72	7.65	0.71	0.05	0.00	0.66
	6394	2/11	6.71	1.44	8.02	0.73	0.06	0.00	0.67
	6395	3/11	23.77	1.70	5.93	1.27	0.24	0.01	1.02
	6396	4/11	6.40	2.68	25.88	1.09	0.36	0.00	0.73
	6397	5/11	17.98	1.69	4.74	0.98	0.12	0.00	0.86
	6398	6/11	3.05	1.17	5.48	0.80	0.01	0.00	0.79
	6399	7/11	49.38	1.85	4.24	0.95	0.12	0.00	0.83
	6400	8/11	20.42	1.91	53.04	1.37	0.73	0.04	0.60
	6401	9/11	6.71	1.77	23.13	0.58	0.09	0.00	0.49
	6402	10/11	43.89	1.95	4.51	0.77	0.09	0.00	0.68
	6403	11/11	52.12	2.25	5.87	1.25	0.41	0.03	0.81

Table 2. *Cont.*

Coal	Sample	Bench	Thickness (cm)	Mois	Ash	S (t)	S (py)	S (sulf)	S (org)
Kellioka	6352	wc	86.87	2.41	5.44	0.72	0.11	0.00	0.61
	6353	1/6 (top)	18.29	2.60	3.14	0.93	0.21	0.02	0.70
	6354	2/6	16.76	2.60	3.22	1.13	0.39	0.03	0.71
	6355	3/6	8.23	2.32	2.27	0.52	0.05	0.00	0.47
	6356	4/6	11.58	1.99	2.00	0.56	0.05	0.00	0.51
	6357	5/6	19.81	1.79	3.80	0.52	0.03	0.00	0.49
	6358	6/6	12.19	2.06	15.62	0.60	0.09	0.01	0.50
	6359	wc	107.19	2.07	4.19	0.67	0.10	0.00	0.57
	6360	wc	113.03	2.09	4.86	0.97	0.29	0.01	0.67
	6361	1/5 (top)	19.81	2.25	3.75	1.06	0.26	0.03	0.77
	6362	2/5	15.85	2.00	4.50	0.92	0.14	0.02	0.76
	6363	3/5	12.80	2.14	2.93	0.65	0.05	0.00	0.60
	6364	4/5	43.59	1.87	3.98	0.64	0.03	0.01	0.60
	6365	5/5	21.03	2.13	10.26	1.14	0.36	0.04	0.74
Darby	6261	wc	92.05	2.59	2.18	0.56	0.06	0.00	0.50
	6262	1/4 (top)	13.41	2.56	1.77	0.53	0.04	0.01	0.48
	6263	2/4	12.19	5.23	1.93	0.48	0.04	0.01	0.43
	6264	3/4	49.38	3.46	1.29	0.55	0.04	0.00	0.51
	6265	4/4	17.07	3.55	1.80	0.60	0.05	0.01	0.54
	6266	wc	99.06	1.94	2.21	0.54	nd	nd	nd
	6267	wc	164.59	1.96	3.04	0.70	nd	nd	nd
	6268	wc	108.20	2.20	2.67	0.63	nd	nd	nd
	6269	wc	102.11	1.85	4.06	0.53	nd	nd	nd
	6366	wc	76.71	3.03	2.21	0.63	0.04	0.01	0.58
	6367	1/5 (top)	3.35	2.54	7.44	0.56	0.07	0.02	0.47
	6368	2/5	13.41	2.11	2.02	0.53	0.05	0.01	0.47
	6369	3/5	4.57	2.23	3.28	0.53	0.04	0.01	0.48
	6370	4/5	41.45	3.12	1.76	0.54	0.05	0.02	0.47
	6371	5/5	14.33	3.29	2.78	0.59	0.04	0.02	0.53

The ash yield of Harlan coals varies somewhat in our samples depending upon the decisions made about sampling benches. For example, in retrospect, sample 6400 perhaps should not have been included in the whole-coal sample although it would have been part of the mined section along with other partings and portions of the roof and floor. As noted above, coal beneficiation would eliminate many of the higher mineral matter particles, producing a low-ash product.

With the exception of the lower bench at both of the benched sites, the ash yield of the Kellioka coals is less than 5%; sulfur content is generally low, exceeding 0.9% only in the top two benches at both sites and the basal bench at site 6360. The Darby has a low-ash, low-S content, with the exception of the thin top lithotype (sample 6367) at site 6366 with 7.44% ash yield and 36.4% total vitrinite (ash-free basis).

3.2. Petrology

The petrology of the coals is presented on Table 3. The lithologic profile of the Harlan coal is shown in Figure 3. Despite some similarities between nearby sites, particularly between seam sections 6378 and 6392, the continuity is not as great as we have seen in studies of the Pond Creek and Blue Gem coals [22,23], the Fire Clay coal [12,24,25], although significant short-distance, few-hundred-meter variation is known to occur in other economically important eastern Kentucky coals [23,26].

The total vitrinite in the whole Harlan coals ranges from 58% to 75% (mineral-included basis), the lowest being in sample 6273 owing to the high mineral content. There is a wide variety of maceral distributions among the bench/lithotype samples. This is well illustrated in the low-mineral matter samples 6399 and 6398 of the 6392 sequence. The sample 6399 bright clarain, bench 7 of 11, has 81.6% total vitrinite. In contrast, sample 6398, the thin, 3.05-cm durain directly overlying 6399, has 31.2% vitrinite, 31.6% inertinite, and 36.6% liptinite.

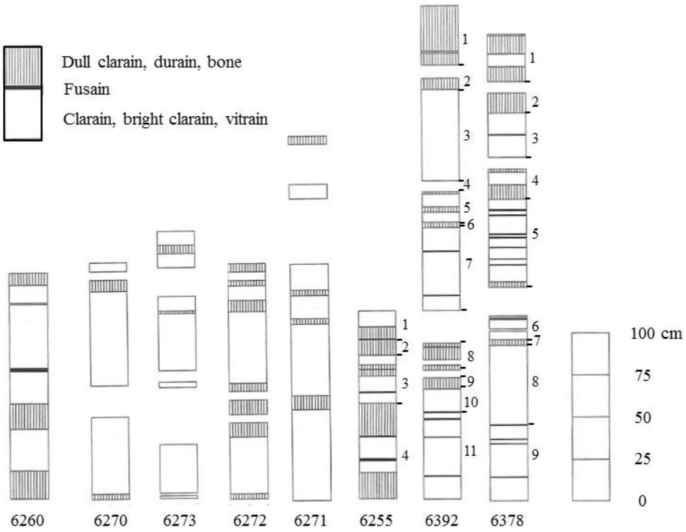


Figure 3. Lithologic sections of the Harlan coal. For the 6255, 6378, and 6392 sequences, the tick marks along the right edge indicate the boundaries of the sampled intervals and the associated numbers represent the bench number. The blank spaces between coal benches indicate non-coal rock intervals. See the tables for the correlation between the bench and sample numbers.

With a few exceptions, such as sample 6357 with less than 41% total vitrinite and sample 6364 with less than 48% total vitrinite, the Kellioka coal samples have over 60% vitrinite. The highest vitrinite is found in the relatively high-S upper benches. The inertinite assemblages in the Kellioka coals are dominated by varying amounts of fusinite, semifusinite, micrinite, and inertodetrinite. Macrinite is most abundant in the low-vitrinite lithologies 6357 and 6364, at 6.4% and 4.6% (mineral-free basis), with 2.2% and 2.4% macrinite found in samples 6355 and 6356, respectively, the lithologies with 63%–65% vitrinite. The liptinite assemblages in the Kellioka coals are dominated by sporinite with lesser amounts of resinite and cutinite.

The whole-coal Darby samples all have at least 68.9% total vitrinite (ash-free basis) and none of the other lithotypes have less than 55% vitrinite. The inertinite is generally a function of varying amounts of fusinite, semifusinite, micrinite, and inertodetrinite. Macrinite exceeds 1.5% only in the whole coal sample 6267 and the lithotype sample 6367. The liptinite assemblages in the Darby samples are dominated by sporinite with lesser amounts of resinite and minor amounts of cutinite.

3.3. Elemental Geochemistry

Table 4 lists the concentrations of major-element oxides and trace elements in the samples from the Harlan, Kellioka, and Darby coals. Compared to average values for world hard coals reported by Ketris and Yudovich [26] and based on the enrichment classification of elements in coal outlined by Dai *et al.* [27], only the averages of Co in the Harlan coals and As in the Kellioka coals are slightly enriched, with CC (CC = ratio of element concentration in investigated coals *vs.* world hard coals) 2.10 and 2.02, respectively. Lithium and Cu in the Harlan coals have CC of 1.60 and 1.84, respectively. The average concentrations of other trace elements in the three coals are either close to or depleted relative to the averages of the same elements for the world hard coals (Figure 4). Particularly, the concentrations of quite a number of trace elements in Kellioka and Darby coals are depleted (Figure 4). According to Dai *et al.* [27], elemental concentrations in coal can be classified as six levels relative to the averages for world coals, unusually enriched (CC > 100), significantly enriched (10 < CC < 100), enriched(5 < CC < 10); slightly enriched (2 < CC < 5); close to the average values for world hard coals (0.5 < CC < 2), and depleted (CC < 0.5).

Table 3. Petrological compositions (volume%) and maximum vitrinite reflectance (%) of coals from Harlan, Kellioka, and Darby.

Coal	Sample	Bench	T	CT	VD	CD	CG	G	T-V	F	SF	Mic	Mac	Sec	Fun	ID	T-I	Sp	Cut	Res	Alg	LD	Sub	Ex	T-L	Sil	Sul	Car	Oth	T-M	$R_{o,max}$
Harlan	6255	wc	3	40.2	3.4	15.2	3	1.2	66	3.2	3.8	3.8	0.2	0.4	0	4.6	16	12.6	1	2.8	0	0.2	0	0	16.6	0.8	0.6	0	0	1.4	0.95
	6256	1/4	3.6	39	7	18.4	1.6	2.6	72.2	2.2	3	1.8	0.2	0.4	0	1.6	9.2	9.2	0.2	2.4	0	0.2	0	0	12	5.8	0.8	0	0	6.6	0.91
	6257	2/4	0.6	26.2	1.2	29.8	0.2	0.4	58.4	4.2	4.4	4.2	2.8	0	0	7.2	22.8	12.4	0	4.8	0	0	0	0	17.2	0	1.6	0	0	1.6	0.96
	6258	3/4	2.2	59.8	1.6	8.4	0.6	1.8	74.4	2.2	1.2	1.2	0.4	0	0	4.8	9.8	7.6	1.2	1.6	0	0	0	0.2	10.6	1.8	3.4	0	0	5.2	0.93
	6259	4/4	2	61	1.2	6.4	0.2	0.4	71.2	7	4.8	1.2	0.6	0.4	0	2.6	16.6	8.8	0.6	1.6	0	0	0	0	11	0.2	1	0	0	1.2	0.93
	WA-H1		2.2	54.4	2.2	10.7	0.5	1.1	71.1	4.8	3.6	1.5	0.7	0.3	0	3.4	14.3	8.9	0.6	2.0	0	0	0	0.1	11.6	1.4	1.6	0.0	0.0	3.1	0.93
	6260	wc	0.4	63.8	1.6	7.4	0.2	1.2	74.6	4.4	3.8	0.6	0.6	0.2	0	4.2	13.8	6.6	1	1.4	0	0	0	0	9	1.4	1.2	0	0	2.6	0.88
	6270	wc	0.6	60	2.8	7	0.4	1.2	72	6	3.4	0.8	0.8	0	0	2.6	13.6	5.4	0.6	1.8	0	0	0	0	7.8	5	1.6	0	0	6.6	0.9
	6271	wc	1	57.6	1.8	10.6	1	1.4	73.4	4	2.4	1.2	1.8	0	0	1.8	11.2	7	0.2	0.8	0	0.4	0	0	8.4	5.8	0.8	0.4	0	7	0.87
	6272	wc	1	52.2	0.8	7.4	2.4	1	64.8	6	2.4	2.4	2.2	0.8	0	3.6	17.4	10	0.2	1.8	0	0	0	0	12	4.4	1.2	0	0.2	5.8	0.9
	6273	wc	3.6	35.2	7	9.4	1.2	1.6	58	4.6	0.2	1.6	0.8	0.4	0	2	9.6	4	1	1.8	0	0.4	0	0.2	7.4	23.4	1.4	0	0.2	25	0.89
	6378	wc	1.2	58.2	1	8	2.4	4	74.8	3.6	2	2.8	1	0.6	0	1.4	11.4	8.8	1.2	0.6	0	0.2	0	0	10.8	2.4	0.4	0	0.2	3	0.95
	6379	1/9	2.8	25	0.6	13	1.4	2.4	45.2	5.8	13.4	4.4	9	0.6	0	7.4	40.6	7.2	1	2.2	0	0	0	0	10.4	3.4	0.2	0	0.2	3.8	0.93
	6380	2/9	2.8	22.2	3.2	9.2	0.6	1.8	39.8	6.8	7.8	5.4	3.8	1.8	0	7.8	33.4	9.8	0	8.4	0	0	0	0	18.2	7.8	0.2	0	0.6	8.6	0.92
	6381	3/9	1	55.6	1.2	7.4	1.6	3.8	70.6	2.4	3.4	3.2	1	0.6	0	3	13.6	8.2	1.6	1.4	0	0	0	0	11.2	2.2	2	0	0.4	4.6	0.91
	6382	4/9	2	46.4	2	11.2	1	2	64.6	2	4.6	2.6	2	0.4	0	4.4	16	14	0.6	3.4	0	0	0	0	18	0.6	0.4	0	0.4	1.4	0.92
	6383	5/9	2.8	57.8	0	10	1.4	1.2	73.2	5.2	3.6	5	0.4	0	0	2.8	17	7.2	0.4	0.6	0.4	0	0	0	8.6	0.6	0.6	0	0	1.2	0.93
	6384	6/9	3.6	38.4	6.4	12.2	1.2	2.2	64	0.4	2.6	2.2	0	0.4	0	3.8	9.4	5.4	0.8	2	0	0	0	0	8.2	13.4	5	0	0	18.4	0.91
	6385	7/9	4.2	13	3.4	13.2	0.6	1.8	36.2	11.6	14.8	1.8	3.2	0.6	0	13	45	14	0.2	2.8	0	0	0	0	17	1.2	0.6	0	0	1.8	0.92
	6386	8/9	1	60	0.2	16.4	1	1	79.6	2	0.2	2.6	0	0	0	1.4	6.2	8	1.2	2.8	0	0	0	0	12	1.8	0.2	0.2	0	2.2	0.95
	6387	9/9	1.2	59.8	1.2	9.2	0.8	0.8	73	3.8	4	3.4	0.2	0	0	2.2	13.6	8.2	0.4	1.6	0	0.4	0	0	10.6	1.8	1	0	0	2.8	0.95
	WA-H2		1.9	50.6	1.2	11.1	1.2	1.7	67.6	3.8	4.5	3.6	1.6	0.3	0	3.5	17.3	8.3	0.8	2.1	0.1	0.1	0	0	11.3	2.6	1.0	0	0.1	3.7	0.93
	6392	wc	4.4	51.8	1	11	1.2	0.8	70.2	3.2	4.6	1.4	1	0	0.2	4	14.4	8	0	1	0	0.4	0	0	9.4	5	1	0	0	6	0.85
	6393	1/11	0.8	22.8	3.4	23.2	0.8	1.4	52.4	3.4	11.2	2.6	5	1.8	0	7.2	31.2	10.4	0	0.8	0	0.6	0	0	11.8	4.6	0	0	0	4.6	0.82
	6394	2/11	1.2	25	1	18.8	0.2	0.2	46.4	4.4	13.8	3.4	1.8	1	0	9.6	34	14	0.4	3.4	0	0	0	0	17.8	1.8	0	0	0	1.8	0.83
	6395	3/11	2.2	57.6	0.8	10.8	1.2	1.4	74	2.6	5	2	0.4	0	0	3.4	13.4	6.4	3	1.2	0	0	0	0.2	10.8	0.8	0.6	0.4	0	1.8	0.82
	6396	4/11	6.4	46.8	7	8.8	2.4	0.4	71.8	4	3.4	1.8	0.2	0	0	1.2	10.6	2.4	1	1.6	0	0	0	0	5	9.4	2.8	0.4	0	12.6	0.78
	6397	5/11	1	51.6	0.2	10.2	0.2	2.2	65.4	3	4.8	1.8	2.2	0.4	0	5.6	17.8	10.4	1	3.2	0.4	0.8	0	0	15.8	0.4	0.2	0.2	0.2	1	0.81
	6398	6/11	0.2	16.2	0.4	12.8	1	0.6	31.2	2.2	7.4	3.4	4.2	0.4	0	14	31.6	29.2	0	7.4	0	0	0	0	36.6	0.2	0.4	0	0	0.6	0.86
	6399	7/11	4	58.6	0	17.6	0.2	1.2	81.6	3.2	3.2	2	0.2	0	0	1.6	10.2	5.2	0.6	0.6	0	0	0	0	6.4	0.8	1	0	0	1.8	0.8
	6400	8/11	5.4	26.2	5.8	10.2	1.6	0.4	49.6	2.6	3.2	0.2	0	0	0	1.6	7.6	2.4	0	0.2	0	0	0	0	2.6	35.4	4.8	0	0	40.2	0.78
	6401	9/11	1.8	47.6	0.8	7.8	0	0.8	58.8	4.4	2.8	0.4	0.4	0	0	9.8	17.8	13	1.2	2	0	0.8	0	0	17	6.4	0	0	0	6.4	0.82
	6402	10/11	2.4	66.2	0.4	5.2	0.2	2.4	76.8	0.6	0.2	1.6	0	0.2	0	1.8	4.4	11	2	1.8	0	1.6	0	0	16.4	2.2	0	0.2	0	2.4	0.87
	6403	11/11	2.4	64.2	0.4	9.8	0	2.2	79	3.8	2.2	2.2	0	0.4	0	1.4	10	7.8	1	1	0	0.6	0	0	10.4	0.2	0.2	0.2	0	0.6	0.86
	WA-H3		2.7	51.4	1.4	12.7	0.5	1.6	70.2	2.8	4.2	1.9	1.0	0.4	0	3.1	13.5	8.1	1.0	1.3	0	0.5	0	0	11.0	4.4	0.8	0.1	0.0	5.3	0.83
	WA-H		2.0	52.3	2.2	10.0	1.3	1.5	69.3	4.2	3.2	2.0	1.1	0.3	0	3.1	13.9	8.0	0.7	1.6	0	0.2	0	0	10.5	5.1	1.0	0.1	0.1	6.3	0.90

Table 3. *Cont.*

Coal	Sample	Bench	T	CT	VD	CD	CG	G	T-V	F	SF	Mic	Mac	Sec	Fun	ID	T-I	Sp	Cut	Res	Alg	LD	Sub	Ex	T-L	Sil	Sul	Car	Oth	T-M	$R_{o,max}$
Kellioka	6352	wc	1.0	54.4	1.4	15.4	0.6	0.6	73.4	4.0	4.6	2.0	1.2	0.4	0	4.0	16.2	7.4	0.8	0.8	0	0	0	0	9.0	1.4	0	0	0	1.4	0.94
	6353	1/6	0.0	69.4	0.8	10.2	0.6	1.6	82.6	1.4	0.8	3.2	0.0	0.2	0	0.8	6.4	7.0	1.2	0.2	0	0	0	0	8.4	0.8	1.8	0	0	2.6	0.94
	6354	2/6	1.4	57.9	0.8	13.4	0.4	1.4	75.4	3.2	3.8	2.8	0.2	0.0	0	2.6	12.6	7.8	1.0	1.0	0	0	0	0	9.8	0.6	1.6	0	0	2.2	0.94
	6355	3/6	0.6	44.6	0.0	17.2	0.4	0.6	63.4	5.2	11.6	2.0	2.4	0.0	0	4.6	25.8	9.8	0.2	0.6	0	0	0	0	10.6	0.2	0	0	0	0.2	0.93
	6356	4/6	0.8	47.8	0.0	14.2	0.4	1.0	64.2	4.8	6.4	3.6	2.2	0.2	0	6.6	23.8	7.8	1.0	2.2	0	0.6	0	0	11.6	0.2	0	0.2	0	0.4	0.92
	6357	5/6	4.0	22.2	0.8	9.4	0.8	3.4	40.6	7.0	12.8	5.2	6.4	1.6	0	11.6	44.6	9.8	0.0	4.4	0	0.4	0	0	14.6	0.0	0.0	0.0	0.2	0.2	0.96
	6358	6/6	3.2	58.4	2.2	3.8	0.0	1.0	68.6	3.0	2.4	4.6	0.4	0.0	0	2.2	12.6	6.6	1.0	2.4	0	0.2	0	0	10.2	8.2	0.4	0.0	0.0	8.6	0.91
	WA-K1		1.8	49.6	0.8	10.9	0.5	1.7	65.4	4.1	6.1	3.7	2.1	0.4	0	4.9	21.3	8.1	0.7	1.9	0	0.2	0	0	11.0	1.5	0.7	0	0	2.3	0.94
	6359	wc	2.2	50.6	0.6	7.8	0.0	1.6	62.8	3.2	6.6	3.8	2.6	0.0	0	6.0	22.2	10.2	0.0	2.8	0	0.0	0	0	13.0	1.8	0.2	0	0	2.0	0.90
	6360	wc	1.2	55.8	1.6	8.6	0.4	1.2	68.8	6.0	4.2	4.6	2.2	0.2	0	5.2	22.4	6.2	0.2	1.0	0	0.2	0	0.2	7.8	0.8	0.2	0	0	1.0	0.96
	6361	1/5	3.4	65.2	0.8	8.4	0.2	2.0	80.0	2.2	1.2	7.0	0.0	0.2	0	1.0	11.6	3.6	0.6	0.4	0.2	0.4	0	0	5.2	1.6	1.2	0.4	0	3.2	0.95
	6362	2/5	1.2	48.6	1.6	16.2	0.2	2.0	69.8	3.0	4.2	3.4	0.0	0.4	0	4.6	15.6	10.8	0.4	1.0	0	0.6	0	0	12.8	1.6	0.2	0.0	0	1.8	0.94
	6363	3/5	0.6	43.4	0.0	18.2	0.6	0.6	63.4	3.4	8.4	5.6	1.0	0.0	0	6.0	24.4	8.8	0.0	1.4	0	0.6	0	0	10.8	0.4	0.4	0.6	0	1.4	0.96
	6364	4/5	2.6	26.8	0.2	15.2	0.8	2.0	47.6	5.4	16.0	5.0	4.6	0.6	0	10.6	42.2	6.6	0.2	2.0	0	0.8	0	0	9.6	0.6	0	0	0	0.6	0.95
	6365	5/5	4.4	49.8	3.4	12.2	1.4	4.4	75.6	1.6	1.8	4.0	0.2	0.6	0	1.2	9.4	4.8	1.6	1.0	1.2	0.8	0	0	9.4	3.0	2.6	0	0	5.6	0.94
	WA-K2	WA	2.7	42.7	1.1	13.9	0.7	2.3	63.4	3.6	8.3	5.0	1.9	0.4	0	5.8	25.0	6.6	0.5	1.3	0.3	0.7	0	0	9.4	1.3	0.8	0.1	0	2.2	0.95
	WA-K		1.8	50.6	1.1	11.3	0.4	1.5	66.8	4.2	6.0	3.8	2.0	0.3	0	5.2	21.4	7.7	0.5	1.6	0.1	0.2	0	0	10.0	1.4	0.4	0	0	1.8	0.94
Darby	6261	wc	6.8	54.2	0	11.2	1.8	3.8	77.8	4.2	2	2.4	0.2	0	0	3.4	12.2	6.8	1.6	0.8	0	0.2	0	0	9.4	0.2	0.2	0.2	0	0.6	0.93
	6262	1/4	1.6	40.2	0.2	16.6	0.4	1.6	60.6	4.2	8	4	0.2	0.2	0	7	23.6	12	0.6	2.4	0	0.4	0	0	15.4	0	0.4	0	0	0.4	0.86
	6263	2/4	4	55.4	0	11.2	0.4	2.4	73.4	9	2.8	4.8	0	0	0	3.6	20.2	5.6	0	0.6	0	0.2	0	0	6.4	0	0	0	0	0	0.9
	6264	3/4	2.8	57.2	0.4	13.2	0.2	4	77.8	4.2	3	0.4	0	0	0	2.2	9.8	9.2	1	1.8	0	0.2	0	0.2	12.4	0	0	0	0	0	0.93
	6265	4/4	3.6	64.2	0	5.4	0.8	8.8	82.8	2.4	0.4	2.2	0	0	0	0.8	5.8	7.8	1.2	1.2	0	0.8	0	0	11	0	0.4	0	0	0.4	0.92
	WA-D1		2.8	55.8	0.3	12.1	0.4	4.6	76.0	3.8	3.3	1.4	0	0	0	2.7	11.3	9.4	1.0	1.8	0.0	0.4	0	0.1	12.6	0.0	0.2	0	0	0.2	0.92
	6266	wc	1	64.6	0.2	9.2	0	3.2	78.2	1.4	4.4	0.2	1	0	0	3.4	10.4	6	1.8	2.4	0	0.4	0	0	10.6	0.8	0	0	0	0.8	0.93
	6267	wc	2	57.6	0.4	9.2	0.2	2.2	71.6	2.4	5.2	2.2	3.2	0	0	4	17	7	0.8	1	0	0	0	0	8.8	1.8	0.8	0	0	2.6	0.92
	6268	wc	7.6	49.2	0.6	11.8	0.4	2.2	71.8	2.4	9.4	0.8	0.6	0.4	0	4.6	18.2	7	0.4	1.2	0	0	0	0	8.6	1.4	0	0	0	1.4	0.92
	6269	wc	1	55.8	0.6	13.6	0	2.2	73.2	2.6	5.8	0.8	1.4	0	0	2	12.6	9.6	0.8	1.8	0	0.2	0	0	12.4	1.6	0.2	0	0	1.8	0.9
	6366	wc	5.4	48.8	0	11.8	0.2	2.6	68.8	2	10	3	1.2	0.2	0	4	20.4	6.6	0.6	3	0	0.4	0	0	10.6	0.2	0	0	0	0.2	0.99
	6367	1/5	0.4	17.4	1.2	15	0	1.6	35.6	1.6	25.8	2.4	5.6	0	0	4.6	40	14.8	0	7.2	0	0.2	0	0	22.2	2	0	0.2	0	2.2	0.95
	6368	2/5	0.8	41.8	0	18	0	0.4	61	0.2	12.8	1.6	0.6	0.2	0	9	24.4	9.4	0	4.8	0	0.2	0	0	14.4	0.2	0	0	0	0.2	0.95
	6369	3/5	3.8	38	0.6	10.6	0	2.6	55.6	5.4	10.4	1.4	0.8	0.6	0	5.4	24	12.8	0.4	5.4	0	1.6	0	0	20.2	0.2	0	0	0	0.2	0.93
	6370	4/5	4.4	65	0	10	0.4	0	79.8	2.4	2.6	0.4	0	0.4	0	2.8	8.6	7.6	1	1	0	2	0	0	11.6	0	0	0	0	0	1
	6371	5/5	5.6	69	0.6	6.6	0.4	1.4	83.6	2.6	2	3.2	0	0	0	2.6	10.4	2.4	1.2	0.6	0	1	0	0	5.2	0.8	0	0	0	0.8	0.97
	WA-D2		3.8	58.0	0.2	11.0	0.3	0.6	73.9	2.2	5.7	1.3	0.4	0.3	0	4.1	14.0	7.6	0.8	2.1	0	1.4	0	0	11.9	0.3	0	0	0	0.3	0.98
	WA-D		3.8	55.5	0.3	11.2	0.4	2.7	73.9	2.6	5.7	1.5	1.0	0.1	0	3.5	14.5	7.5	1.0	1.8	0	0.4	0	0	10.6	0.8	0.2	0	0	1.0	0.94

T, telinite; CT, collotelinite; VD, vitrodetrinite; CD, collodetrinite; CG, corpogelinite; G, gelinite; T-V, total vitrinite; F, fusinite; SF, semifusinite, Mic, micrinite; Mac, macrinite; Sec, secretinite; Fun, funginite; ID, inertodetrinite; T-I, total inertinite; Sp, sporinite; Cut, cutinite; Res, resinite; Alg, alginate; LD, liptodetrinite; Sub, suberinite; Ex, exsudatinite; T-L, total liptinite; Sil, silicate; Sul, sulfide; Car, carbonate; Oth, others; T-M, total mineral; WA-H1, weighted average based the thickness of bench interval (samples 6256 to 6259); WA-H2, weighted average of samples 6379 to 6387; WA-H3, weighted average of samples 6393 to 6403; WA-H, weighted average of all the Harlan coal samples collected; WA-K1, weighted average of samples 6353 to 6358; WA-K2, weighted average of samples 6361 to 6365; WA-K, weighted average of all Kellioka samples collected; WA-D1, weighted average of samples 6262 to 6265; WA-D2, weighted average of samples 6367 to 6371; WA-D, weighted average of all Darby samples collected.

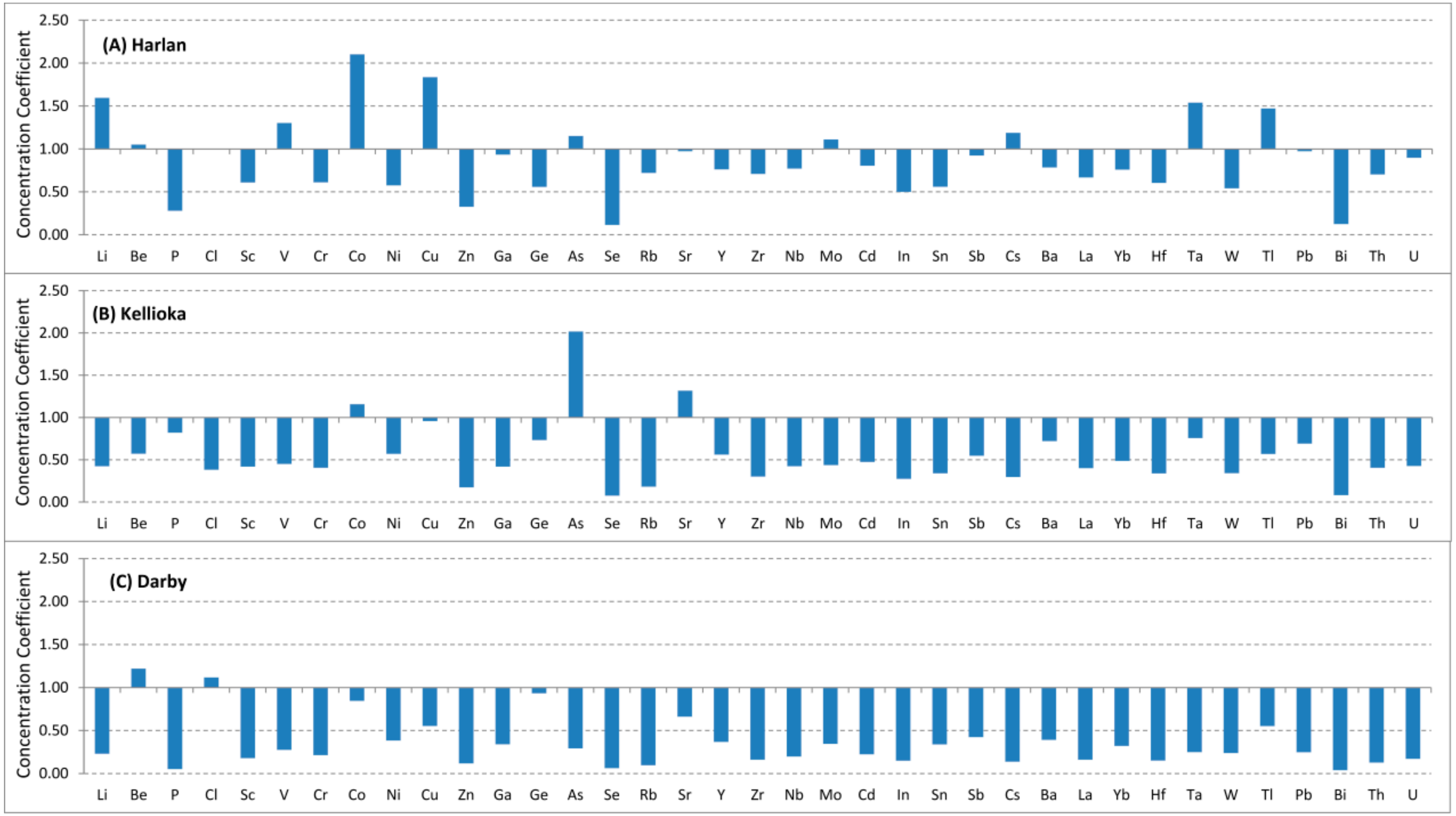


Figure 4. Concentration coefficients of trace elements in the coals studied. (**A**) Harlan; (**B**) Kellioka; (**C**) Darby. Concentration coefficients (CC) are the ratio of the trace-element concentrations in the coal samples *vs.* world hard coals reported by Ketris and Yudovich [26].

Table 4. Percentages of major-element oxides and chlorine (%) and concentrations of trace elements (μg/g) in coals from Harlan, Kellioka, and Darby (on whole coal basis). Bdl—below detection limit; nd—ot determined.

Coal	Sample	Bench	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	Li	Be	Cl	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge
Harlan	6255	wc	3.82	0.123	2.67	0.58	0.073	0.12	0.001	0.254	0.009	17.2	1.58	0.02	1.69	26.2	10.8	6.4	10.8	22.7	7.59	3.79	0.59
	6256	1/4	9.99	0.185	6.09	1.1	0.285	0.08	0.044	0.883	0.019	36.6	2.16	0.02	3	75.7	26.7	8.69	22	43.3	35.5	8.95	1.44
	6257	2/4	2.47	0.096	1.74	1.35	0.036	0.17	bdl	0.082	0.006	8.69	0.65	0.02	0.94	15.5	7.54	2.15	8.25	13.4	4.2	2.14	0.25
	6258	3/4	4.99	0.144	3.79	1.75	0.113	0.1	0.014	0.442	0.013	29.4	0.62	0.03	1.55	37.5	14.7	3.28	12.4	27.5	8.3	5.33	0.42
	6259	4/4	4.15	0.136	3.04	0.56	0.081	0.15	0.012	0.286	0.01	20.6	2.68	bdl	1.75	34.0	12.7	10.7	15.4	30.0	9.7	4.85	1.05
	WA-H1		5.09	0.142	3.575	1.011	0.116	0.13	0.016	0.397	0.012	24.2	1.9	0.02	1.82	39.5	14.8	7.8	15	29.9	12.7	5.35	0.88
	6260	wc	4.34	0.129	3.25	0.59	0.106	0.18	0.028	0.277	0.011	19.8	3.59	bdl	1.88	35.7	13.2	9.06	16.1	23.9	10.7	5.0	2.14
	6270	wc	6.62	0.164	4.61	0.73	0.269	0.57	0.12	0.536	0.017	26.8	4.18	0.02	1.19	43.3	17.8	23.7	25	35.4	19.5	6.85	1.39
	6271	wc	5.02	0.122	3.32	1.36	0.169	0.33	0.07	0.377	0.016	19.1	1.76	bdl	3.11	32.4	16	44.4	45.3	44.9	21.1	5.05	0.89
	6272	wc	7.18	0.172	4.75	1.1	0.276	0.43	0.131	0.552	0.017	27.3	1.59	0.02	3.31	34.1	16.9	19.9	26.3	29.8	18	6.83	1.28
	6273	wc	17.6	0.388	11.4	3.4	0.854	0.51	0.297	1.66	0.037	64.5	4.13	0.02	8.05	112	45.4	16.6	32.7	74.9	61.3	17.5	2.35
	6378	wc	4.63	0.115	2.9	0.77	0.127	0.3	0.052	0.31	0.017	16.7	0.86	bdl	0.38	25.6	10.8	2.91	7.62	19.0	10.1	3.78	1.46
	6379	1/9	5.53	0.183	2.76	0.44	0.068	0.18	bdl	0.16	0.056	16.6	2.26	bdl	3.46	30.7	14.3	5.39	8.4	28.2	9.16	5.58	5.05
	6380	2/9	19.7	0.466	7.46	0.57	0.22	0.01	0.033	1.032	0.051	27.0	1.29	bdl	1.5	51.1	32.3	3.16	7.35	25.7	10.9	10.7	0.85
	6381	3/9	4.03	0.093	3.12	0.91	0.088	0.22	0.063	0.328	0.019	17.0	0.47	bdl	1.11	26.4	11.4	3.18	7.42	22.8	8.46	4.01	0.39
	6382	4/9	2.31	0.094	1.93	0.31	0.039	0.14	0.041	0.08	0.034	10.9	0.47	bdl	1.33	16.6	7.62	1.77	6.04	14.8	3.75	2.41	0.29
	6383	5/9	1.96	0.045	1.67	1.27	0.051	0.35	0.033	0.077	0.042	5.56	1.82	bdl	1.42	14	6.51	1.86	4.41	6.78	7.64	3.55	0.33
	6384	6/9	12.1	0.243	7.58	2.46	0.355	0.08	0.071	0.936	0.015	36.4	2.01	bdl	7.22	63.8	37.0	24.6	83.4	95.8	31.9	9.19	1.43
	6385	7/9	10.3	0.412	5.39	0.38	0.124	0.15	0.017	0.257	0.01	2.25	0.67	bdl	4.42	nd	nd	nd	nd	nd	nd	3.99	0.44
	6386	8/9	1.32	0.03	1.19	0.44	0.069	0.22	0.06	0.077	0.002	6.42	0.32	bdl	0.82	7.21	nd	0.14	nd	0.59	4.03	1.28	0.16
	6387	9/9	3.41	0.084	2.44	1.02	0.12	0.3	0.045	0.273	0.006	19.3	1.38	0.02	1.83	22.8	9.56	3.45	8.49	18.9	11.4	3.49	1.96
	WA-H2		4.32	0.111	2.713	0.895	0.099	0.24	0.043	0.252	0.025	14.2	1.23	bdl	1.94	22.5	10.4	3.71	9.78	18.8	9.16	4.01	1.24
	6392	wc	8.77	0.177	5.3	1.11	0.296	0.23	0.194	0.68	0.012	bdl	bdl	bdl	nd	nd	nd	nd	nd	nd	nd	nd	nd
	6393	1/11	4.03	0.128	2.9	0.24	0.056	0.09	0.068	0.138	0.006	23.2	10.37	bdl	1.29	16.9	9.69	4.83	8.65	20.3	5.2	5.19	5.68
	6394	2/11	4.22	0.068	3.2	0.22	0.042	0.11	0.05	0.115	0.01	24.5	1.05	bdl	1.31	27.2	12.1	3.53	9.59	14.6	2.97	4.91	0.86
	6395	3/11	2.60	0.053	2.14	0.67	0.057	0.2	0.068	0.137	0.007	15.3	0.48	bdl	0.97	23.6	7.19	4.03	9.41	21.4	6.46	3.18	0.49
	6396	4/11	12.1	0.318	9.32	1.06	0.483	0.81	0.405	1.521	0.022	48.6	0.96	bdl	1.81	83.6	35.2	6.02	17.6	62.4	38.7	11.3	0.75
	6397	5/11	2.15	0.038	0.67	1.44	0.048	0.29	0.011	0.101	0.003	2.36	0.25	bdl	0.73	23.7	4.66	1.37	4.32	3.1	9.11	0.94	2.12
	6398	6/11	1.96	0.04	0.65	2.41	0.037	0.32	0.001	0.083	0.002	12.1	0.33	bdl	0.81	18.3	8.64	8.47	7.86	14.1	3.93	2.8	2.06
	6399	7/11	1.27	0.027	0.45	2.04	0.025	0.38	bdl	0.056	0.009	9.79	0.77	bdl	0.71	11.4	6.71	0.4	1.22	7.38	2.85	1.89	1.7
	6400	8/11	21.1	0.37	6.96	21.14	0.408	5.56	0.102	0.892	0.032	29.1	3.03	bdl	6.95	161	56.2	21.5	57.1	112	73.2	10	13.22
	6401	9/11	10.3	0.238	7.7	2.09	0.448	1.42	0.605	0.62	0.018	bdl	bdl	bdl	nd	55.1	23.1	7.4	25	32.4	14.3	nd	nd
	6402	10/11	1.99	0.047	1.35	0.7	0.087	0.12	0.048	0.177	0.004	11.7	0.95	bdl	0.84	14.8	5.7	2.75	6.88	16.2	16.1	2.03	0.27
	6403	11/11	2.59	0.062	1.75	0.92	0.111	0.15	0.064	0.23	0.005	15.3	1.19	bdl	1.02	18.5	7.28	3.38	8.66	20.1	18.8	2.56	0.35
	WA-H3		4.13	0.09	2.174	2.616	0.104	0.64	0.057	0.237	0.008	15.9	2.31	bdl	1.43	30.2	11.735	4.38	10.8	24.1	15.8	3.51	2.51
	WA-H		6.50	0.157	4.24	1.287	0.226	0.33	0.092	0.503	0.016	22.3	2.1	bdl	2.25	36.5	15.245	12.6	18.1	29.4	16.9	5.61	1.34

Table 4. *Cont.*

Coal	Sample	Bench	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	Li	Be	Cl	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge
Kellioka	6352	wc	2.80	0.091	1.54	0.5	0.079	0.23	0.04	0.138	0.043	6.27	1.31	nd	1.7	13.1	7	5.26	9.26	16.3	7.64	2.72	1.58
	6353	1/6	1.42	0.036	0.92	0.54	0.034	0.07	0.02	0.097	0.002	3.32	1.34	0.03	1.29	7.34	3.56	2.12	6.26	7.37	2.7	1.83	0.22
	6354	2/6	1.25	0.036	0.84	0.88	0.031	0.09	0.026	0.07	0.002	2.81	0.22	0.04	0.76	6.51	3.45	1.85	6.85	10.9	1.78	1.11	0.14
	6355	3/6	0.71	0.028	0.58	0.23	0.033	0.67	0.033	0.004	0.002	1.01	0.12	0.03	0.44	2.75	1.93	1.77	6.79	9.11	1.67	0.55	0.08
	6356	4/6	0.83	0.039	0.63	0.26	0.031	0.17	0.033	0.008	0.001	1.61	0.2	0.03	0.75	4.42	3.31	4.37	10.6	18.4	1.88	1.07	0.15
	6357	5/6	1.97	0.092	1.03	0.25	0.061	0.37	0.037	0.005	0.005	4.1	0.44	0.03	1.43	7.67	5.16	5.44	8.47	21.5	3.7	1.09	0.11
	6358	6/6	8.91	0.221	4.76	0.59	0.232	0.08	0.024	0.81	0.01	17.6	7.66	0.04	5.55	50.9	20.2	6.94	15.3	32.7	21.3	13.2	14.7
	WA-K1		2.42	0.074	1.398	0.48	0.067	0.21	0.029	0.15	0.004	4.9	1.54	0.03	1.66	12.5	6.04	3.77	8.77	16.5	5.15	2.9	2.19
	6359	wc	1.97	0.069	1.14	0.6	0.047	0.2	0.028	0.085	0.057	6.72	1.07	nd	0.95	10.4	7.16	2.35	5.77	10.7	3.49	2.07	1.58
	6360	wc	2.27	0.078	1.31	0.73	0.055	0.22	0.033	0.103	0.065	5.51	0.99	nd	1.91	10.6	6.25	15.4	13.9	15.6	4.49	2.28	1.55
	6361	1/5	1.71	0.038	1.01	0.69	0.057	0.1	0.028	0.121	0.004	4.46	0.71	0.03	2.32	10	4.85	19.07	8.47	14.9	3.34	2.16	0.85
	6362	2/5	2.29	0.058	1.29	0.5	0.067	0.11	0.042	0.141	0.006	5.01	0.26	0.03	0.51	9.7	5.06	1.37	4.57	10.7	2.76	1.68	0.18
	6363	3/5	0.75	0.027	0.72	0.57	0.081	0.75	0.038	0.007	0.017	1.07	0.11	0.03	0.23	3.16	1.56	1.15	4.11	8.14	1.64	0.49	0.08
	6364	4/5	1.96	0.093	1.1	0.29	0.038	0.31	0.051	0.004	0.146	3.77	0.35	0.03	1.39	8.54	6.90	3.44	7.03	17.4	2.58	1.47	0.13
	6365	5/5	5.21	0.147	3.3	0.89	0.108	0.12	0.019	0.446	0.043	17.2	2.72	0.04	2.65	52.4	19.4	16.3	29.4	31.5	7.52	7.42	8.94
	WA-K2		2.43	0.081	1.477	0.533	0.063	0.26	0.038	0.126	0.068	6.2	0.81	0.03	1.53	16.5	8.0	8.02	10.8	17.6	3.55	2.62	1.90
	WA-K		2.38	0.079	1.373	0.569	0.062	0.23	0.034	0.12	0.047	5.94	1.14	0.01	1.55	12.6	6.89	6.95	9.7	15.3	4.86	2.52	1.76
Darby	6261	wc	0.90	0.033	0.71	0.24	0.044	0.18	0.026	0.056	0.004	2.71	4.76	0.05	1.06	6.55	3.42	10.5	9.81	10.7	1.79	2.6	4.72
	6262	1/4	0.77	0.052	0.62	0.15	0.023	0.14	0.01	0.008	0.004	2.12	19.67	0.04	1.66	6.32	3.78	16.5	9.87	8.02	1.76	10.7	11.0
	6263	2/4	0.64	0.028	0.68	0.22	0.048	0.26	0.041	0.011	0.003	nd	nd	0.03	nd	nd	nd	nd	nd	nd	nd	nd	nd
	6264	3/4	0.39	0.015	0.49	0.2	0.031	0.13	0.033	0.006	0.002	2.44	0.48	0.04	0.33	2.55	1.5	5.69	7.58	7.51	1.36	0.43	0.11
	6265	4/4	0.77	0.025	0.63	0.21	0.026	0.06	0.014	0.056	0.003	2.57	7.41	0.05	0.09	8.28	3.47	19	12	16.7	1.78	3.21	10.3
	WA-D1		0.54	0.023	0.542	0.19	0.029	0.117	0.025	0.017	0.003	2.41	5.18	0.04	0.5	4.41	2.30	10.3	8.91	9.56	1.52	2.74	4.11
	6266	wc	0.89	0.031	0.73	0.26	0.05	0.14	0.051	0.054	0.004	2.47	0.78	0.04	1.07	5.89	2.57	1.59	5.41	3.86	5.48	1.15	4.70
	6267	wc	1.35	0.04	0.83	0.43	0.06	0.18	0.063	0.082	0.004	3.08	1.23	0.05	0.26	9.21	4.56	2.12	4.79	10.5	3.53	2.42	2.03
	6268	wc	1.20	0.035	0.78	0.3	0.052	0.17	0.059	0.071	0.003	4.83	4.68	0.03	0.66	7.71	3.51	3.63	5.59	9.47	2.78	2.64	0.49
	6269	wc	2.00	0.053	1.18	0.38	0.102	0.15	0.058	0.129	0.005	4.23	2.12	0.04	0.47	13.1	6.71	4.29	8.82	14.1	4.84	2.69	1.44
	6366	wc	1.05	0.034	0.75	0.23	0.024	0.06	0.026	0.038	0.002	3.06	0.5	nd	0.49	6.6	3.14	7.02	5.99	8.13	2.03	1.09	0.21
	6367	1/5	4.38	0.098	2.07	0.5	0.124	0.02	bdl	0.247	0.005	7.75	2.9	0.04	4.59	72.2	15.4	5.69	18.8	14.1	18.5	4.85	1.59
	6368	2/5	1.03	0.046	0.61	0.2	0.018	0.08	0.021	0.008	0.003	2.77	0.12	nd	0.86	6.06	2.45	1.03	2.16	4.09	2.19	0.86	0.3
	6369	3/5	1.89	0.098	0.98	0.18	0.02	0.04	0.043	0.019	0.004	1.42	0.18	nd	1.13	8.27	3.71	1.34	4.1	6.43	3.61	0.71	0.16
	6370	4/5	0.70	0.024	0.64	0.25	0.021	0.06	0.038	0.019	0.002	2.50	0.14	0.04	0.45	5.15	2.04	0.75	1.83	4.26	2.84	0.68	0.11
	6371	5/5	1.35	0.029	0.95	0.29	0.031	0.04	0.013	0.067	0.003	4.35	0.25	0.17	0.65	3.92	2.33	0.83	2.62	2.14	9.08	1.23	0.22
	WA-D2		1.11	0.036	0.77	0.26	0.027	0.06	0.029	0.036	0.003	3.05	0.28	0.055	0.78	8.18	2.85	1.06	2.91	4.39	4.61	1.0	0.23
	WA-D		1.13	0.036	0.79	0.29	0.048	0.13	0.042	0.06	0.003	3.23	2.44	0.038	0.66	7.71	3.63	5.08	6.53	8.84	3.32	2.04	2.24

Table 4. *Cont.*

Coal	Sample	Bench	As	Se	Rb	Sr	Zr	Nb	Mo	Cd	In	Sn	Sb	Cs	Ba	Hf	Ta	W	Tl	Pb	Bi	Th	U
Harlan	6255	wc	10	0.1	10.2	54.1	22.7	2.79	2.09	0.11	0.017	0.66	0.78	0.86	67.4	0.65	1.31	0.5	0.94	6.43	0.13	1.75	1.11
	6256	1/4	5.23	0.15	31.8	44.9	31.6	4.16	3.08	0.17	0.031	1.17	2.36	3.31	109	0.98	0.32	0.92	0.81	13.32	0.14	2.77	2.62
	6257	2/4	37.8	0.17	1.37	45.3	17.2	1.95	3.24	0.09	0.013	0.56	0.37	0.21	33.4	0.51	0.19	0.33	2.43	4.43	0.11	1.17	0.79
	6258	3/4	22.6	0.13	14.1	45.9	27.3	2.89	3.96	0.12	0.021	0.88	1.11	1.46	64.8	0.8	0.27	0.42	1.51	9.34	0.17	1.89	2.77
	6259	4/4	6.33	0.1	7.09	47.9	23.4	2.75	2.05	0.13	0.016	0.62	1.31	0.75	60.5	0.65	0.5	0.64	0.42	7.19	0.1	2.05	1.57
	WA-H1		13	0.12	12.1	46.7	25.1	2.93	2.79	0.13	0.019	0.76	1.34	1.27	66.6	0.73	0.39	0.6	0.93	8.42	0.12	2.04	1.97
	6260	wc	9.54	0.05	8.41	64.9	23.8	2.79	2.34	0.13	0.017	0.67	0.97	1.02	66.7	0.66	0.38	0.58	0.74	6.39	0.13	2.16	1.7
	6270	wc	9.44	0.15	10	350	30.2	3.69	2.74	0.18	0.024	0.92	1	1.79	307	0.88	0.57	0.83	0.72	6.86	0.16	0.69	2.23
	6271	wc	10.6	0.27	6.59	46.4	23.1	2.82	3.08	0.18	0.017	0.71	1.1	1.02	66.6	0.67	0.36	0.6	0.68	10.54	0.1	3.08	1.79
	6272	wc	20	0.24	23.1	108	31.3	3.98	2.39	0.15	0.025	0.91	1.19	1.62	144	0.9	0.46	0.7	1.24	9	0.17	3.46	2.36
	6273	wc	7.96	0.32	52.9	170	67.9	8.54	2.38	0.53	0.062	2.04	1.43	4.51	307	1.86	0.95	1.04	1.49	25.38	0.38	8.16	4.32
	6378	wc	4.2	0.17	3.74	75.8	20.5	2.15	1.7	0.1	0.014	0.55	0.7	0.74	64.7	0.59	0.17	0.27	0.3	5.35	0.11	0.42	0.99
	6379	1/9	6.2	0.18	4.81	131	38.3	4.47	1.21	0.09	0.025	0.92	1.05	0.52	85.3	1.04	0.39	0.54	0.19	7.84	0.2	2.88	1.55
	6380	2/9	2.08	0.21	21.2	122	99.7	9.14	0.76	0.2	0.039	1.9	0.41	2.58	140	2.74	0.72	0.62	0.16	11.47	0.25	1.43	1.74
	6381	3/9	11.1	0.08	5.82	84.3	15.6	1.71	2.82	0.1	0.019	0.57	0.8	0.79	119	0.46	0.15	0.29	0.6	6.23	0.12	1.09	0.68
	6382	4/9	1.76	0.04	1.25	128	17	1.86	1.59	0.11	0.013	0.42	0.54	0.18	96.7	0.49	0.17	0.21	0.07	4.59	0.11	1.06	0.52
	6383	5/9	22.3	0.15	12.5	23.2	9.36	1.17	3.36	0.04	0.011	0.35	0.5	0.9	51.4	0.25	0.13	0.3	0.12	3.74	0.06	1.26	0.74
	6384	6/9	14.5	0.14	14.8	618	40.9	5.52	3.38	0.41	0.035	1.22	1.92	1.01	499	1.06	0.53	0.93	1.33	30.58	0.28	6.17	4.2
	6385	7/9	0.91	0.27	39.3	6.6	70.2	8.78	0.82	0	0.012	1.34	0.36	0.55	84.8	1.89	1.65	0.65	−0.06	0	0.01	4.07	1.3
	6386	8/9	1.35	0.07	1.6	25	5.46	0.76	2.01	0.09	0.007	0.2	0.15	0.14	18.1	0.17	0.32	0.2	0.02	9.12	0.05	0.55	0.27
	6387	9/9	14.1	0.14	8.03	91.3	15.1	1.55	1.62	0.12	0.011	0.49	0.86	1.21	95	0.47	0.14	0.36	1.05	5.47	0.11	1.49	0.81
	WA-H2		10.8	0.13	8.16	101	21.1	2.37	2.2	0.11	0.016	0.58	0.69	0.81	99.1	0.59	0.27	0.37	0.42	7.57	0.12	1.64	0.98
	6392	wc	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	6393	1/11	1.5	0.08	3.05	27.3	25.1	2.8	0.8	0.07	0.014	0.55	0.67	0.3	75.5	0.67	0.26	0.31	0.11	6.84	0.15	1.37	0.75
	6394	2/11	2	0.07	2.04	23.1	13.1	2.01	0.63	0.03	0.012	0.36	0.55	0.25	34.1	0.4	0.15	0.17	0.06	7.83	0.08	0.9	0.71
	6395	3/11	11.8	0.08	1.98	79.3	9.36	1.1	3.46	0.09	0.011	0.36	1.48	0.23	78.9	0.29	0.15	0.44	0.82	7.18	0.09	1.13	0.9
	6396	4/11	5.12	0.61	23.3	96.7	56.8	6.04	3.68	0.32	0.049	1.74	1.75	3.11	191	1.73	0.5	0.4	0.41	20.85	0.6	0.83	1.98
	6397	5/11	2.47	0.06	4.88	10.5	6.98	0.73	1.33	0.06	0.003	0.19	0.24	0.33	110	0.18	0.06	0.12	0.33	9.07	0.01	0.38	0.35
	6398	6/11	3.6	0.03	11.2	60	7.92	0.91	3.04	0.04	0.009	0.17	0.8	0.73	54.4	0.18	0.09	0.2	0.14	6.66	0.05	0.6	0.89
	6399	7/11	1.85	0.04	2.87	36.8	5.68	0.66	4.01	0.04	0.007	0.21	0.08	0.58	42.5	0.16	0.21	0.12	0.01	3.24	0.06	0.36	0.25
	6400	8/11	35.6	0.32	42.3	115	61.3	7.89	25.97	0.89	0.041	1.53	4.6	3.11	519	1.5	0.82	1.98	19.36	53.6	0.17	5.17	7.97
	6401	9/11	nd	nd	36.1	794	87.2	6.25	nd	nd	nd	nd	nd	nd	665	nd	nd	nd	nd	nd	nd	nd	nd
	6402	10/11	10.8	0.09	5.34	57	5.84	0.91	1.12	0.06	0.011	0.83	0.67	0.54	58.2	0.26	0.08	0.3	0.62	6.66	0.04	1.12	0.82
	6403	11/11	14.4	0.08	5.34	67.5	9.64	1.17	1.44	0.12	0.014	1.64	0.81	0.65	70.2	0.34	0.18	0.37	0.87	7.71	0.08	1.51	1.09
	WA-H3		9.58	0.1	7.56	54.8	15.4	1.88	3.96	0.15	0.014	0.81	0.97	0.76	104	0.45	0.23	0.41	1.94	10.54	0.09	1.34	1.32
	WA-H		9.56	0.15	13	97.4	25.5	3.09	2.33	0.16	0.02	0.78	0.92	1.31	118	0.73	0.46	0.54	0.85	8.77	0.14	2.25	1.71

Table 4. *Cont.*

Coal	Sample	Bench	As	Se	Rb	Sr	Zr	Nb	Mo	Cd	In	Sn	Sb	Cs	Ba	Hf	Ta	W	Tl	Pb	Bi	Th	U
Kellioka	6352	wc	3.12	0.09	6.12	106	10.5	1.49	0.91	0.08	0.012	0.46	0.53	0.69	85.5	0.38	0.14	0.36	0.26	4.46	0.11	1.4	0.77
	6353	1/6	16.2	0.06	4.85	67.9	5.64	0.72	1.21	0.04	0.005	0.21	0.45	0.44	63.5	0.17	0.07	0.54	0.51	3.37	0.05	0.76	0.5
	6354	2/6	39.7	0.05	3.2	85.7	3.7	0.72	0.94	0.05	0.006	0.17	0.15	0.23	73.8	0.17	0.13	0.11	0.89	2.9	0.07	0.72	0.49
	6355	3/6	0.74	0.03	0.05	117	3.29	0.56	0.6	0.02	0.004	0.15	0.05	0.01	91.9	0.15	0.06	0.08	0.08	1.62	0.02	0.33	0.15
	6356	4/6	0.47	0.04	0.3	116	6.96	0.84	0.56	0.03	0.006	0.25	0.08	0.03	102	0.19	0.08	0.13	0.12	1.72	0.05	0.51	0.26
	6357	5/6	0.68	0.06	0.06	198	−0.01	2.06	0.32	0.05	0.015	0.91	0.1	0.02	104	0.49	0.29	0.14	0.12	3.1	0.1	1.56	0.62
	6358	6/6	2.12	0.13	3.55	587	38.2	4.96	0.79	0.16	0.046	1.18	2.71	0.25	543	0.94	0.43	0.64	1.39	13.78	0.31	3.5	1.91
	WA-K1		11.6	0.06	2.2	185	8.5	1.62	0.75	0.06	0.013	0.5	0.54	0.18	150	0.35	0.18	0.28	0.53	4.29	0.1	1.25	0.66
	6359	wc	7.31	0.12	2.51	72	13	1.6	0.79	0.08	0.008	0.5	0.54	0.24	74	0.41	0.21	0.35	0.16	3.3	0.06	0.72	0.81
	6360	wc	49.8	0.14	2.33	129	14.8	1.94	1.13	0.17	0.011	0.53	0.56	0.25	107	0.46	0.43	0.38	0.45	14.55	0.09	1.9	1.05
	6361	1/5	37.3	0.08	3.98	102	6.34	1.19	1.63	0.14	0.009	0.22	0.77	0.23	93.2	0.21	0.15	0.76	0.25	2.71	0.06	0.91	1.09
	6362	2/5	23.9	0.07	1.77	69.5	9.2	1.11	1.02	0.04	0.008	0.36	0.16	0.28	64.1	0.27	0.09	0.11	0.44	3.23	0.07	0.29	0.46
	6363	3/5	0.79	0.07	0.11	100	4.73	0.56	0.94	0.03	0.004	0.18	0.1	0.01	67.6	0.14	0.05	0.1	0.08	2.08	0.06	0.14	0.21
	6364	4/5	0.84	0.06	0	276	0	2.01	0.62	0.05	0.012	0.39	0.15	0.01	186	0.53	0.21	0.18	0.09	3.46	0.1	1.87	0.63
	6365	5/5	8.37	0.14	11.9	118	24.9	3.3	1.23	0.17	0.021	0.71	1.83	1	106	0.71	0.26	0.47	0.58	10.68	0.14	1.59	1.29
	WA-K2		11.8	0.08	3.17	167	7.56	1.82	1	0.09	0.012	0.39	0.57	0.27	124	0.43	0.17	0.32	0.26	4.48	0.09	1.23	0.76
	WA-K		16.8	0.1	3.27	132	10.9	1.69	0.92	0.1	0.011	0.48	0.55	0.33	108	0.41	0.23	0.34	0.33	6.22	0.09	1.3	0.81
Darby	6261	wc	1.2	0.09	1.65	82.8	4.93	0.79	0.46	0.03	0.006	0.17	0.66	0.18	58	0.17	0.06	0.27	0.15	2	0.04	0.47	0.28
	6262	1/4	0.74	0.09	0.18	75.9	1.74	1.47	0.17	0.02	0.005	0.29	0.97	0.02	44	0.28	0.1	0.28	0.2	1.94	0.04	0.69	0.24
	6264	3/4	0.63	0.05	0.16	101	1.21	0.29	0.49	0.02	0.004	0.16	0.05	0.02	86.5	0.07	0.03	0.1	0.02	1.02	0.03	0.17	0.05
	6265	4/4	1.24	0.08	0.55	29.8	4.24	0.76	0.46	0.04	0.006	0.21	1.43	0.13	17.3	0.13	0.04	0.45	0.17	1.93	0.04	0.04	0.26
	WA-D1		0.78	0.06	0.25	81.8	1.95	0.59	0.43	0.02	0.005	0.19	0.5	0.04	64.6	0.12	0.04	0.21	0.08	1.37	0.03	0.23	0.13
	6266	wc	1.42	0.1	0.68	31.4	5.53	0.81	0.48	0.04	0.004	0.16	0.6	0.11	21.4	0.16	0.09	0.23	0.61	1.88	0.03	0.66	0.32
	6267	wc	8.64	0.09	4.62	44.6	7.01	1.05	0.78	0.06	0.005	0.21	0.45	0.29	56.5	0.21	0.08	0.36	0.2	2.84	0.03	0.18	0.54
	6268	wc	2.82	0.07	3.37	74.9	5.79	0.8	0.57	0.04	0.006	0.16	0.22	0.25	71.9	0.17	0.09	0.18	0.24	2.26	0.05	0.29	0.25
	6269	wc	1.33	0.11	1.54	99.2	8.74	0.7	0.95	0.07	0.009	0.24	0.34	0.16	83.8	0.26	0.05	0.17	0.9	4.38	0.08	0.45	0.6
	6366	wc	1.51	0.05	0.33	63.4	5.87	0.74	0.98	0.07	0.005	0.2	0.14	0.07	52.9	0.17	0.08	0.21	0.13	1.41	0.05	0.41	0.23
	6367	1/5	3.47	0.32	6.42	29.3	16.9	3.37	0.65	0.09	0.014	0.73	1.69	0.5	39.7	0.48	0.16	0.34	0.29	6.75	0.1	1.1	1.52
	6368	2/5	0.85	0.09	3.83	7.72	8.74	1.03	1.33	0.03	0.003	0.26	0.25	0.25	15.1	0.22	0.1	0.55	0.2	1.71	0.02	0.65	0.22
	6369	3/5	1.07	0.05	2.77	3.01	20.8	2.11	1.18	0.06	0.003	0.38	0.09	0.22	12.5	0.57	0.3	0.31	0.15	2.38	0.01	1.26	0.36
	6370	4/5	1.34	0.05	0.46	41.7	4.07	0.54	1.27	0.03	0.004	4.32	0.63	0.03	54.5	0.13	0.09	0.14	0.24	1.31	0.04	0.42	0.14
	6371	5/5	3.94	0.09	1.07	140	4.66	0.69	0.87	0.06	0.026	0.21	0.13	0.09	141.6	0.16	0.1	0.38	0.34	1.64	0.06	0.6	0.31
	WA-D2		1.81	0.07	1.56	51.3	6.54	0.87	1.17	0.04	0.00829	2.46	0.49	0.11	60.7	0.19	0.11	0.27	0.25	1.74	0.04	0.57	0.26
	WA-D		2.44	0.08	1.75	66.2	5.79	0.79	0.73	0.04	0.006	0.47	0.42	0.15	58.7	0.18	0.08	0.24	0.32	2.23	0.04	0.41	0.33

Because the three coals have relatively low ash yields and most of the trace elements in the coals have inorganic affinity, the concentration of trace elements in ashes of the three coals were compared to the averages of the same elements for the world coal ash reported by Ketris and Yudovich [26]. Elements including Li, Co, Cu, As, and Ta in the Harlan coal ashes, elements P, Co, Cu, As, Sr, Ba, Ta, and Pb in the Kellika coal ashes, and elements Be, Co, Ni, Cu, Ga, Ge, Sr, Y, Mo, Sn, Sb, Ba, and Tl in the Darby coal ashes are relatively enriched (Figure 5).

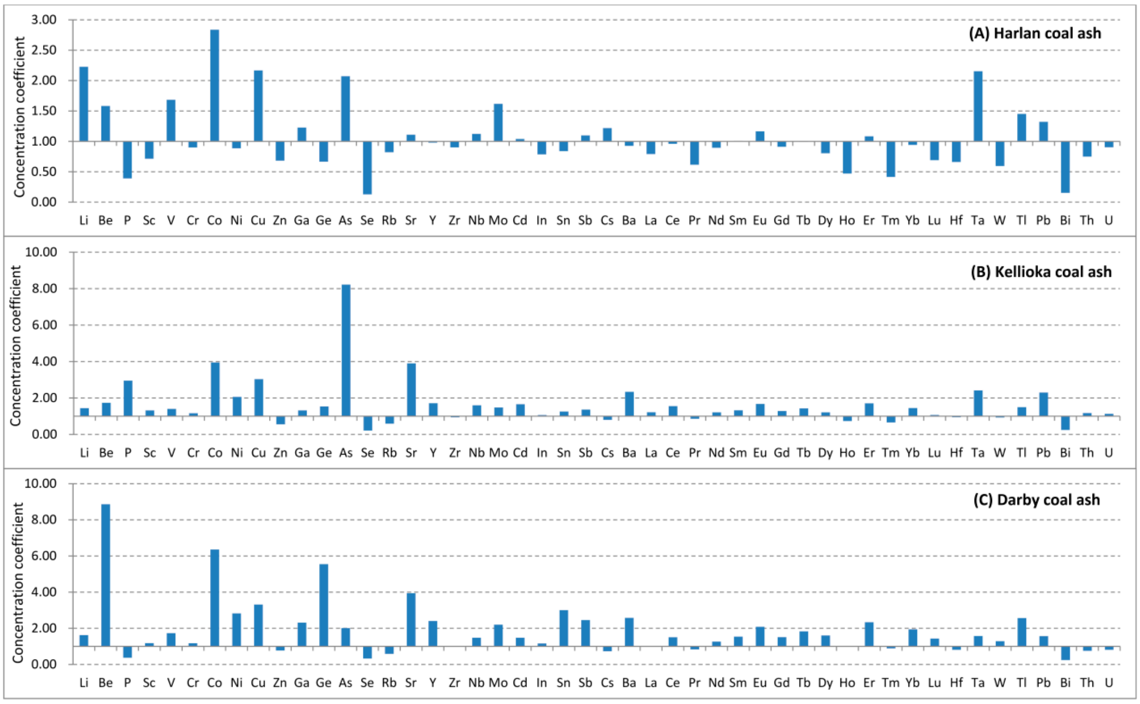


Figure 5. Concentration coefficients of trace elements in the coal ashes studied. (**A**) Harlan; (**B**) Kellioka; (**C**) Darby. Concentration coefficients (CC) are the ratio of the trace-element concentrations in the coal ash samples *vs.* world coal ash reported by Ketris and Yudovich [26].

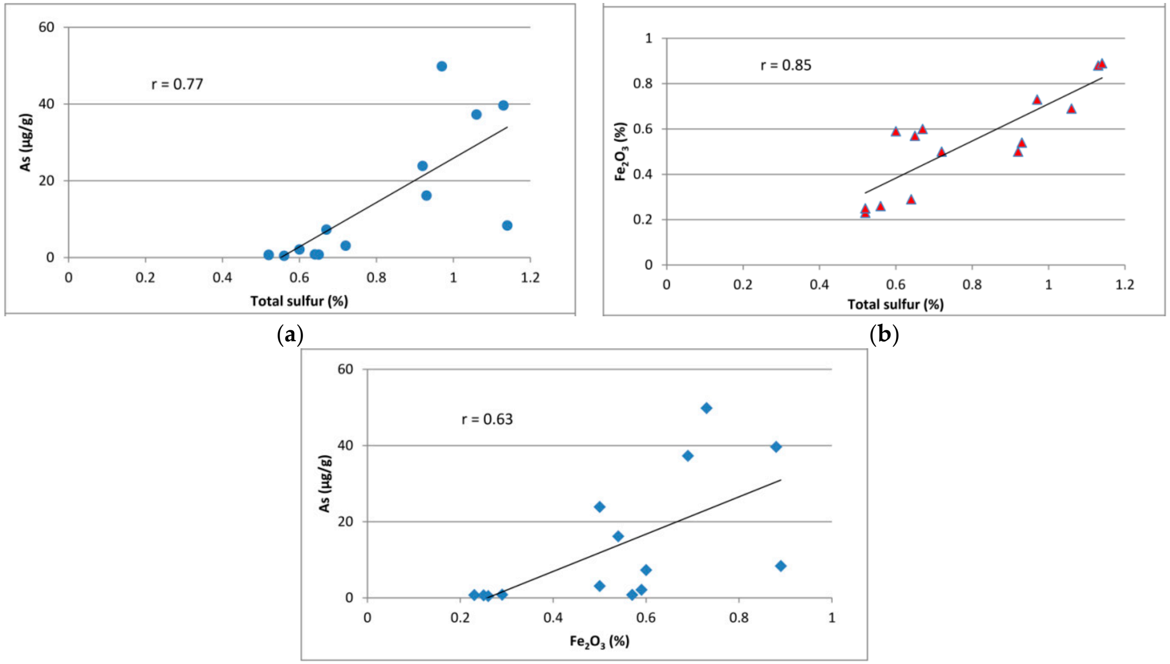
The correlation coefficient (r = 0.59) of Li and ash yield in the Harlan coals indicates an inorganic affinity. Further, lithium positively correlated to Mg (r = 0.74), SiO_2 (r = 0.61), Al_2O_3 (r = 0.740), and K_2O (r = 0.84), indicatingit is mainly associated with clay minerals (e.g., kaolinite, mixed-layer illite/smectite, or illite).

The Cu in the Harlan coals is positively correlated to Ash (r = 0.87), Al_2O_3 (r = 0.77), SiO_2 (r = 0.80), and K_2O (r = 0.76), but has a weak correlation coefficient with total sulfur (r = 0.37), indicating Cu mainly occurs in clay minerals. The correlation coefficient of Co and ash is 0.41, indicating that Co has a dominant inorganic association and a small proportion may be associated with organic matter.

The concentrations of As in Kellioka coals and coal ashes are 16.8 and 378 μg/g respectively, much higher than their averages for world hard coals and coal ashes (9 and 46 μg/g, respectively [26]. The adverse effects on environment of arsenic in Kellioka coals should be of concern. The correlation coefficient of As-St (r = 0.77) and As-Fe_2O_3 (r = 0.63), and Fe-St (r = 0.85) (Figure 6) of the Kellioka coals indicate that As is mainly associated with pyrite.

With exceptions of Li, Cu, and Co in the Harlan coals, and As in the Kellioka coals, the remaining elements in the three coals are either close to or lower than the averages for world hard coals [26], and most of them have an inorganic affinity (Figure 7). However, some elements including Be, Ga, Ge, Sr, Mo, Sn, and W have different modes of occurrence in the three coals. For example:

The correlation coefficient of Be and ash yield in the Harlan and Darby coals (r = 0.17, and r = −0.14, respectively) show an organic-inorganic mixed affinity (also see Figure 8). Be in the Kellioka coals, however, showed inorganic affinity (r = 0.95; Figure 8).



(**a**) (**b**)

(**c**)

Figure 6. Relation of (**a**) Arsenic-total sulfur, (**b**) Fe_2O_3-total sulfur, and (**c**) arsenic-Fe_2O_3 in Kellioka coals.

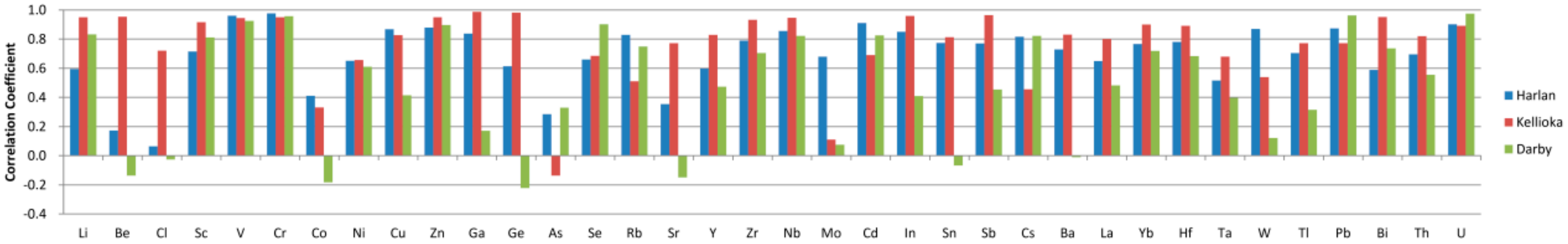


Figure 7. Correlation coefficient of trace elements and ash yield of the coals in Harlan, Kellioka, and Darby.

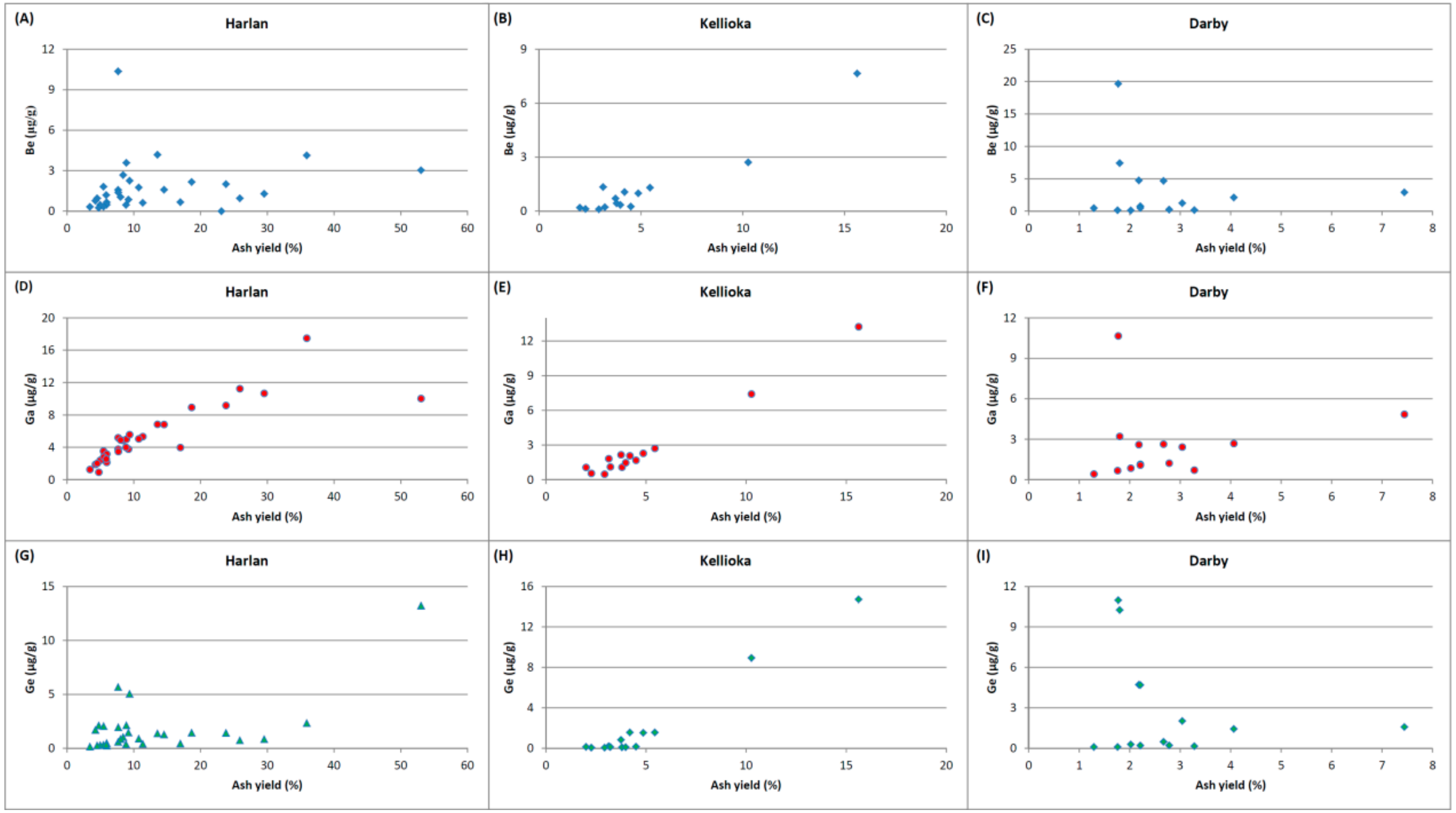


Figure 8. *Cont.*

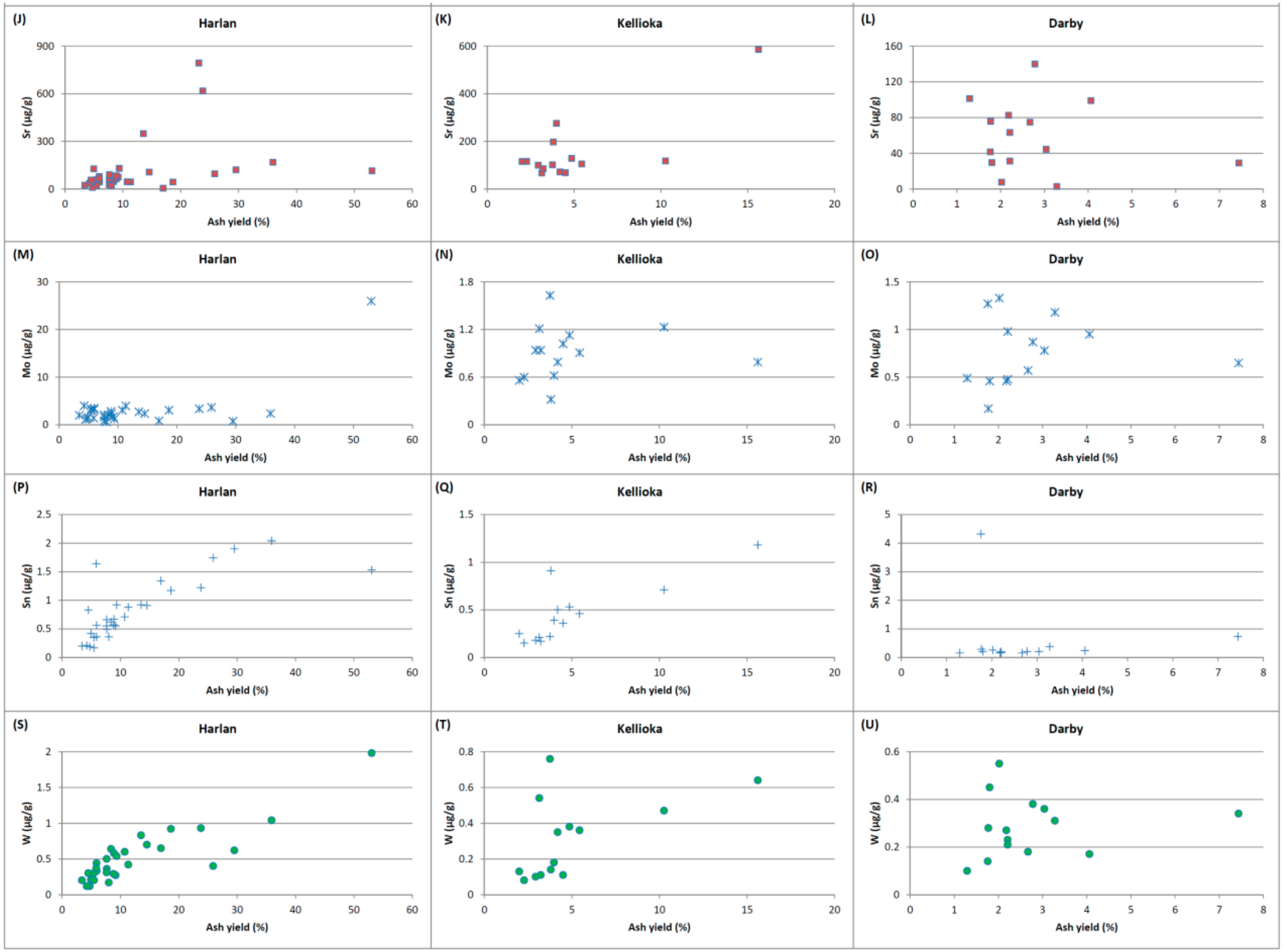


Figure 8. Relations of ash yield and some selected trace elements in the coals in Harlan, Kellioka, and Darby.

Gallium in the Harlan and Kellioka coals shows an inorganic affinity (r = 0.84 and r = 0.99 respectively; Figure 8D,E), but in the Darby coals it has an organic-inorganic mixed affinity (r = 0.17; Figure 8F).

Germanium, Sr, and Mo in the three coals show an organic-inorganic mixed affinity (Figure 8). Although the correlation coefficient of Ge and ash yield in Kellioka coals is high (r = 0.98; Figure 8H), there are only two points fall in the area with Ge concentration higher than 8 μg/g. However, twelve scattered points fall in the area of Ge concentration of less than 1.6μg/g, showing an organic-inorganic mixed affinity. The correlation coefficient of Sr and ash yield in the Kellioka is also high (r = 0.77), the scattered points in the Figure 8K (only one point with high Sr concentration, 587μg/g) also indicate a mixed affinity.

Tin and W show an inorganic affinity in the Harlan and Kellioka coals but have an inorganic-organic mixed affinity in the Darby coals (Figure 8).

Although the average concentrations of most of trace elements in the three coals are not enriched relative to the averages of the world coals, some trace elements are relatively enriched in some benches of each coal seam. For example, see Sections 3.3.1–3.3.3 below.

3.3.1. The Harlan coals

The Harlan geochemistry has hints of the high values of certain minor element associations noted in other coals, such as TiO_2 + Zr, V + Cr, and Ba + Sr (such as the Darby for the latter association, see below). The TiO_2 + Zr has been found to be associated with detrital minerals in the basal benches of some coals [17,28]; V + Cr, possibly in association with clay minerals, can be enriched in the top bench; and Ba and Sr can be associated with phosphates and carbonates [28,29]. The fourth benches in both sections 6378 and 6392, bench 6 of 9 of section 6378, and bench 8 of 11 of section 6392 have some of the higher Cr and V values. In all cases, these benches underlie a parting, an event nearly as significant as the final demise of the coal [13], therefore, also an event likely to be marked by the same geochemical indicators as the top of the coal.

The Ba + Sr content exceeds 6000 ppm in sample 6401, but this is considerably lower than the high values encountered in the Darby coal (see below). Certain benches in the 6378 section also have >1000 ppm (ash basis) Ba and/or Sr, in some cases corresponding with P_2O_5 > 0.5% (ash basis). The Rare earth elements + Y (REY) content is not high by what might be considered to be potential commercial standards (perhaps 900 ppm on the ash basis) [30]. We note, however, that the samples with REY >600 ppm correspond to the samples with P_2O_5 >0.5%, not surprising since the REY are often found in phosphate minerals.

3.3.2. The Kellioka coals

The high-Fe_2O_3 content generally occurs in the top two benches, the higher pyritic S lithologies. These are also the benches with the highest As concentrations, up to 1231 ppm As and 0.39% S_{py} (both on ash basis) in sample 6354. The third benches from the top at both sites, samples 6355 and 6363, are the highest CaO samples. Very little mineral matter is evident in microscopic examination and carbonates are not among the microscopic minerals. The concentrations of Sr, Ba, and REY are generally highest in the same samples, for example >11000 ppm Sr + Ba and 929 ppm REY in sample 6364, corresponding to a phosphate concentration of 3.50% (all on the ash basis).

3.3.3. The Darby coals

The samples generally have a relatively high amount of Ba + Sr, with sample 6264 (sample 3 of 4 from the 6261 series) exceeding 14560 ppm and sample 6370 (sample 4 of 5 from the 6366 series) having >11000 ppm Ba + Sr (both on the ash basis). Such levels of Ba + Sr might be attributable to associations with carbonates or phosphates. Neither sample has the highest REY content of the Darby samples, nearly 1700 ppm in sample 6262 (bench 1 or 4 from the 6261 series). Without further microbeam-based mineralogy studies, we cannot be certain about the association.

Vanadium and Cr, known in other coals to be associated with clays and frequently observed in the uppermost lithotype of many coal beds [31,32], are highest in the top lithology of both bench suites. Germanium and Ga are relatively high in the upper and lower benches of the 6261 series. Germanium is known to be enriched in coal lithotypes bordering the roof, floor, or partings [33].

3.4. Rare Earth Elements and Yttrium

The classification of rare earth elements and yttrium (REY, or REE if yttrium is not included) used in the present study is based on Seredin and Dai [30] and includes light (LREY: La, Ce, Pr, Nd, and Sm), medium (MREY: Eu, Gd, Tb, Dy, and Y), and heavy (HREY: Ho, Er, Tm, Yb, and Lu) REY. Accordingly, normalized to the upper continental crust (UCC; Taylor and McLennan [34]), three enrichment types are identified [30]: L-type (light-REY; $La_N/Lu_N > 1$), M-type (medium-REY; $La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type (heavy REY; $La_N/Lu_N < 1$).

The concentrations of rare earth elements (Table 5) in the three coals are lower than the averages for the world coals [26]; Figure 4), but their concentrations in coal ashes are close to the average for the world coal ash (Ketris and Yudovich [26]; Figure 5). The three coal seams have different REY distribution patterns:

(1) With the exceptions of some samples (samples 6387, 6386, and 6383 in Figure 9C; samples in Figure 9D; samples 6397 and 6398 in Figure 9E; samples 6399, 6402, and 6403 in Figure 9F), the REY in the Harlan coals are characterized by M-type enrichment.

(2) The Kellioka coal samples do not show much fractionation among the L-, M-, and H-REY, with the exception of sample 6358, which has a distinct H-REY enrichment type (Figure 10).

(3) With a few exceptions of samples 6264, 6370, 6371, and 6369, which a slight M-REY enrichment, the Darby coal samples are enriched in heavy REY relative to the upper continental crust [35] (Figure 11).

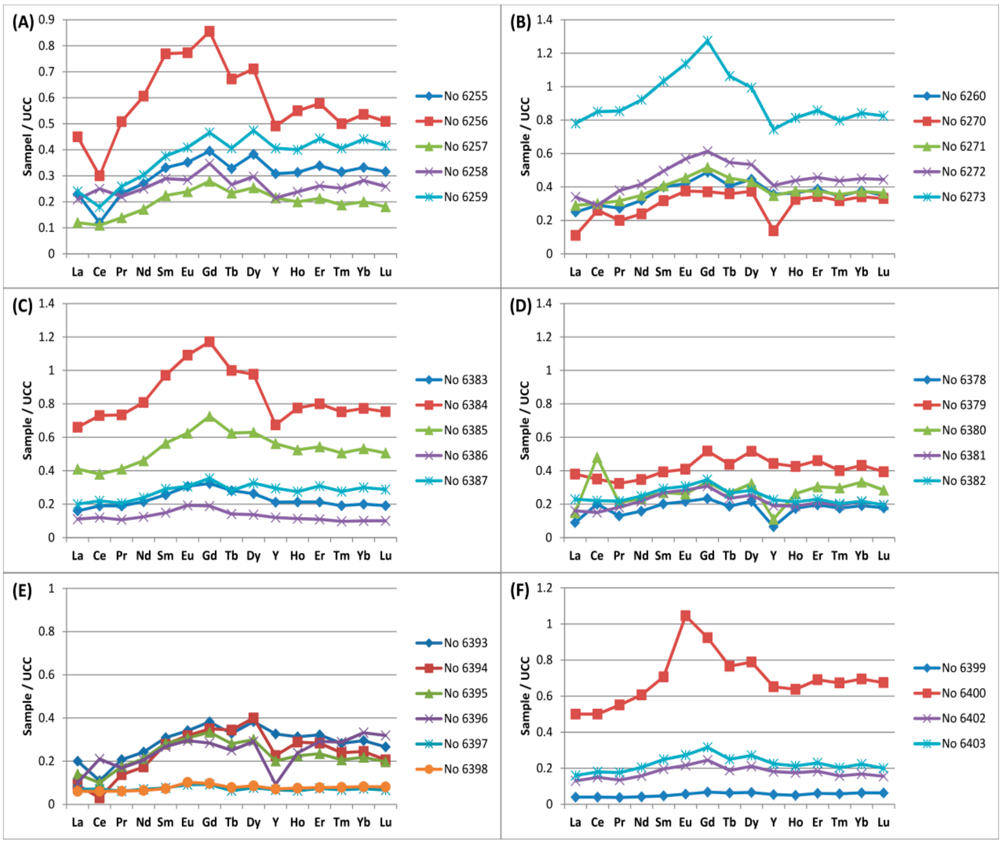


Figure 9. Distribution patterns of REY in Harlan coals. REY concentrations are normalized by those in the Upper Continental Crust [35].

Table 5. Concentrations of rare earth elements and yttrium (μg/g) in coals from Harlan, Kellioka, and Darby (on whole coal basis).

Coal	Sample	Bench	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
Harlan	6255	wc	6.82	7.82	1.65	7.01	1.49	0.31	1.5	0.21	1.34	6.77	0.25	0.78	0.1	0.73	0.1
	6256	1/4	13.6	19	3.61	15.76	3.46	0.68	3.25	0.43	2.49	10.8	0.44	1.33	0.17	1.18	0.16
	6257	2/4	3.63	7.25	0.99	4.44	1.01	0.21	1.06	0.15	0.89	4.72	0.16	0.49	0.06	0.44	0.06
	6258	3/4	6.38	16	1.56	6.53	1.3	0.25	1.32	0.17	1.04	4.72	0.19	0.6	0.08	0.62	0.08
	6259	4/4	7.06	11.4	1.84	7.88	1.69	0.36	1.77	0.26	1.66	8.94	0.32	1.02	0.13	0.97	0.13
	WA-H1		7.58	13.4	1.96	8.42	1.8	0.37	1.82	0.25	1.56	7.78	0.29	0.91	0.12	0.87	0.12
	6260	wc	7.55	18.3	1.94	8.33	1.8	0.37	1.86	0.26	1.56	7.86	0.29	0.89	0.11	0.83	0.11
	6270	wc	3.24	16.6	1.42	6.21	1.43	0.33	1.41	0.23	1.31	3.04	0.26	0.79	0.11	0.75	0.11
	6271	wc	8.55	19.3	2.25	9.09	1.83	0.4	1.96	0.29	1.51	7.67	0.3	0.86	0.12	0.82	0.12
	6272	wc	10.1	18.5	2.69	10.8	2.23	0.5	2.33	0.35	1.87	8.99	0.35	1.05	0.14	0.99	0.14
	6273	wc	23.3	54.1	6.06	24	4.65	1	4.84	0.68	3.48	16.39	0.65	1.97	0.26	1.85	0.26
	6378	wc	2.59	12.7	0.92	4.12	0.91	0.19	0.89	0.12	0.76	1.43	0.14	0.45	0.06	0.42	0.06
	6379	1/9	11.4	22.4	2.3	9.02	1.77	0.36	1.97	0.28	1.81	9.74	0.34	1.06	0.13	0.95	0.13
	6380	2/9	4.41	30.5	1.48	6.11	1.21	0.23	1.26	0.17	1.13	2.42	0.21	0.7	0.1	0.73	0.09
	6381	3/9	4.7	9.47	1.29	5.68	1.21	0.25	1.17	0.15	0.89	4.2	0.15	0.48	0.06	0.47	0.06
	6382	4/9	6.85	14.3	1.55	6.45	1.32	0.27	1.32	0.17	0.99	4.99	0.17	0.53	0.07	0.48	0.06
	6383	5/9	4.9	12.2	1.34	5.6	1.15	0.27	1.23	0.18	0.92	4.66	0.17	0.49	0.06	0.44	0.06
	6384	6/9	19.7	46.8	5.21	21.01	4.37	0.96	4.45	0.64	3.42	14.8	0.62	1.84	0.25	1.7	0.24
	6385	7/9	12.2	24	2.91	11.95	2.54	0.55	2.76	0.4	2.2	12.4	0.42	1.25	0.17	1.17	0.16
	6386	8/9	3.34	7.42	0.76	3.23	0.67	0.17	0.72	0.09	0.48	2.63	0.09	0.25	0.03	0.22	0.03
	6387	9/9	5.97	14.2	1.46	6.22	1.31	0.27	1.35	0.18	1.14	6.49	0.22	0.71	0.09	0.66	0.09
	WA-H2		6.56	15.6	1.62	6.72	1.39	0.3	1.45	0.2	1.15	5.76	0.21	0.65	0.08	0.6	0.08
	6393	1/11	5.87	7.06	1.47	6.28	1.39	0.3	1.45	0.21	1.34	7.17	0.25	0.74	0.09	0.65	0.09
	6394	2/11	2.8	2.23	0.97	4.49	1.25	0.28	1.33	0.22	1.4	4.97	0.23	0.65	0.08	0.54	0.07
	6395	3/11	4.22	6.68	1.24	5.48	1.27	0.27	1.27	0.18	1.05	4.43	0.18	0.54	0.07	0.48	0.06
	6396	4/11	3.02	13.5	1.19	5.33	1.2	0.26	1.08	0.16	1.02	2.05	0.19	0.67	0.1	0.73	0.1
	6397	5/11	2	4.32	0.44	1.81	0.34	0.08	0.35	0.04	0.27	1.48	0.05	0.17	0.02	0.16	0.02
	6398	6/11	1.66	3.53	0.43	1.67	0.33	0.09	0.37	0.05	0.3	1.57	0.06	0.18	0.03	0.18	0.03
	6399	7/11	1.25	2.39	0.27	1.1	0.21	0.05	0.26	0.04	0.23	1.19	0.04	0.14	0.02	0.14	0.02
	6400	8/11	15.1	31.9	3.91	15.78	3.18	0.92	3.51	0.49	2.76	14.34	0.51	1.59	0.22	1.53	0.22
	6402	10/11	3.86	9.64	0.96	4.1	0.88	0.19	0.93	0.12	0.74	3.99	0.14	0.42	0.05	0.37	0.05
	6403	11/11	4.93	11.6	1.25	5.34	1.12	0.24	1.2	0.16	0.95	4.95	0.17	0.53	0.07	0.49	0.06
	WA-H3		4.56	9.26	1.18	4.97	1.06	0.25	1.13	0.16	0.94	4.71	0.17	0.53	0.07	0.49	0.07
	WA-H		7.35	16.9	1.97	8.15	1.69	0.37	1.74	0.25	1.41	6.4	0.26	0.81	0.11	0.76	0.11

Table 5. *Cont.*

Coal	Sample	Bench	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu
Kellioka	6352	wc	4.22	9.87	1.01	4.22	0.9	0.2	1	0.14	0.96	5.68	0.18	0.59	0.08	0.55	0.07
	6353	1/6	2.29	5.52	0.63	2.85	0.7	0.17	0.88	0.14	0.95	6.49	0.19	0.62	0.08	0.55	0.08
	6354	2/6	2.54	6.01	0.63	2.68	0.55	0.12	0.59	0.07	0.43	2.1	0.08	0.23	0.03	0.2	0.03
	6355	3/6	1.95	4.11	0.41	1.7	0.33	0.08	0.35	0.04	0.27	1.34	0.05	0.14	0.02	0.13	0.02
	6356	4/6	2.81	6.09	0.55	2.23	0.42	0.1	0.47	0.06	0.36	1.89	0.07	0.2	0.03	0.17	0.02
	6357	5/6	4.99	10.8	0.97	3.86	0.74	0.16	0.82	0.11	0.65	3.53	0.12	0.37	0.05	0.34	0.05
	6358	6/6	9.41	19.4	2.32	8.89	1.61	0.39	1.92	0.31	2.03	12.37	0.43	1.4	0.19	1.36	0.2
	WA-K1		3.99	8.7	0.91	3.7	0.74	0.17	0.85	0.12	0.79	4.69	0.16	0.5	0.06	0.46	0.06
	6359	wc	2.93	8.56	0.87	3.5	0.71	0.18	0.78	0.12	0.68	2.69	0.13	0.41	0.06	0.37	0.05
	6360	wc	5.67	12.5	1.37	5.42	1.08	0.26	1.2	0.18	1.01	5.47	0.2	0.6	0.08	0.56	0.08
	6361	1/5	2.52	6.07	0.77	3.34	0.81	0.21	0.93	0.18	1.17	7.46	0.24	0.76	0.1	0.69	0.1
	6362	2/5	1.56	6.14	0.52	2.28	0.49	0.11	0.48	0.06	0.38	1.2	0.07	0.21	0.03	0.21	0.03
	6363	3/5	0.39	2.32	0.1	0.44	0.09	0.03	0.12	0.01	0.08	0.4	0.01	0.04	0.01	0.04	0.01
	6364	4/5	7.08	13.8	1.38	5.56	1.05	0.23	1.12	0.15	0.87	4.57	0.16	0.48	0.06	0.42	0.06
	6365	5/5	9.8	22.7	2.2	8.9	1.78	0.36	1.89	0.26	1.67	9.46	0.32	1.03	0.13	0.96	0.14
	WA-K2		5.26	11.7	1.16	4.75	0.96	0.21	1.03	0.15	0.91	5.04	0.17	0.54	0.07	0.5	0.07
	WA-K		4.41	10.3	1.06	4.32	0.88	0.2	0.97	0.14	0.87	4.71	0.17	0.53	0.07	0.49	0.07
Darby	6261	wc	2.08	5.4	0.52	2.32	0.55	0.13	0.67	0.1	0.7	5.13	0.14	0.46	0.06	0.42	0.06
	6262	1/4	3.4	6.99	0.71	3.15	0.75	0.19	0.98	0.16	1.24	10.23	0.26	0.84	0.11	0.76	0.1
	6264	3/4	1.43	3.99	0.36	1.64	0.36	0.09	0.4	0.05	0.31	1.9	0.06	0.17	0.02	0.14	0.02
	6265	4/4	0.56	3.09	0.24	1.19	0.34	0.08	0.43	0.08	0.64	1.41	0.14	0.46	0.06	0.41	0.06
	WA-D1		1.57	4.3	0.39	1.8	0.42	0.1	0.5	0.07	0.54	3.19	0.11	0.34	0.04	0.3	0.04
	6266	wc	2.02	5.13	0.57	2.45	0.57	0.15	0.62	0.11	0.68	4.41	0.14	0.42	0.06	0.38	0.06
	6267	wc	1.61	5.51	0.53	2.25	0.49	0.13	0.54	0.09	0.57	1.37	0.12	0.36	0.05	0.31	0.04
	6268	wc	1.38	4.76	0.45	1.93	0.43	0.11	0.47	0.08	0.45	2.06	0.09	0.27	0.04	0.25	0.04
	6269	wc	1.77	6	0.6	2.59	0.59	0.14	0.61	0.1	0.63	2.27	0.12	0.39	0.05	0.36	0.05
	6366	wc	1.57	3.68	0.45	2.04	0.47	0.11	0.52	0.08	0.48	2.83	0.09	0.29	0.04	0.26	0.04
	6367	1/5	3.89	12.47	1.18	5.51	1.5	0.35	1.77	0.29	1.99	11.8	0.39	1.26	0.17	1.23	0.16
	6368	2/5	3.15	7.52	0.77	3.26	0.71	0.18	0.86	0.14	0.84	7.77	0.18	0.54	0.07	0.46	0.07
	6369	3/5	4.18	8.95	0.85	3.33	0.64	0.15	0.72	0.09	0.5	2.82	0.09	0.29	0.04	0.27	0.04
	6370	4/5	1.67	4.02	0.47	2	0.42	0.12	0.43	0.06	0.32	1.65	0.06	0.18	0.02	0.16	0.02
	6371	5/5	1.85	3.82	0.59	2.61	0.62	0.16	0.63	0.1	0.57	3.02	0.11	0.31	0.04	0.27	0.04
	WA-D2		2.21	5.25	0.6	2.56	0.57	0.15	0.62	0.09	0.54	3.48	0.11	0.32	0.04	0.29	0.04
	WA-D		1.78	5	0.51	2.24	0.51	0.13	0.57	0.09	0.57	3.09	0.11	0.36	0.05	0.32	0.04

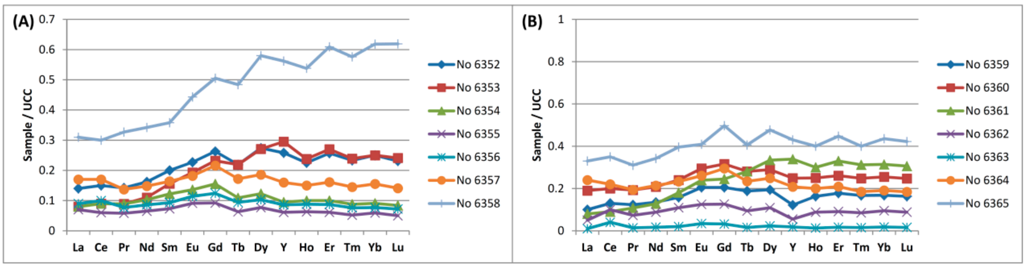


Figure 10. Distribution patterns of REY in Kellioka coals. REY concentrations are normalized by those in the Upper Continental Crust [35].

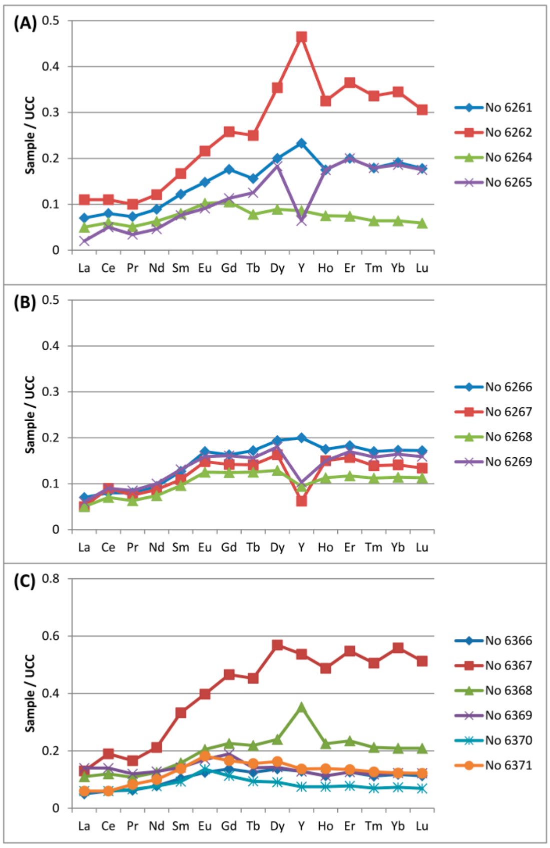


Figure 11. Distribution patterns of REY in Darby coals. REY concentrationsare normalized by those in the Upper Continental Crust [35].

Geochemical influences were likely to have been complex. Aside from the expected terrigenous influx at the time of deposition, the region was subject to the influence of hydrothermal fluids during diagenesis. This is most notable on the footwall side of the Pine Mountain thrust fault where an enhanced coal rank compared to correlative coals on the thrust sheet (as we are studying here), albeit all within the high volatile A bituminous rank range, are accompanied by enhanced levels of Cl and Hg and other trace metals [34]. While not previously demonstrated, it is possible that the coals on the Pine Mountain thrust sheet could have been similarly influenced, if not from fluids squeezed out in advance of the Pine Mountain thrust sheet, then by fluid flow influenced by thrust faults to the southeast in Virginia. Examination of the Al_2O_3 *vs.* TiO_2 plot (Figure 12) provides a view of another aspect of mineral influx. The Harlan benches have a much wider distribution than the Kellioka or Darby benches, having both higher and lower Al_2O_3 and lower TiO_2 than the other coals. Among the Darby samples with the highest TiO_2, bench samples 6262 and 6368 have strikingly different REY distributions than any of the other benches among the three coals. In particular, the Y concentration *versus* the UCC baseline value is high. Relative to other Darby benches, the P_2O_5 is also high, suggesting that an influx of Y- (and REY) bearing phosphates could have accompanied the TiO_2 influx. TiO_2-mineral/Phosphate/Zircon sediments are common in detrital (often the basal coal) lithotypes [17,25,26,36–43].

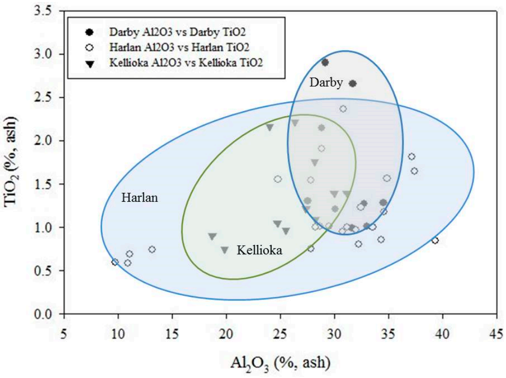


Figure 12. Distribution of Al_2O_3-TiO_2 in the coals from in Harlan, Kellioka, and Darby.

4. Summary

The Harlan, Kellioka, and Darby coals have traditionally been among the more important coal resources in Harlan County, Kentucky.

The Harlan coal is the thickest and has the highest ash and sulfur content of the three coals in the study. In practice, the ash and sulfur content could be reduced by beneficiation. An enrichment of TiO_2 + Zr in the basal lithotype and V + Cr in the top lithotype and in lithologies immediately below partings is similar to occurrences seen in other eastern Kentucky coals. The lithotypes with REY >600 ppm correspond to concentrations of P_2O_5 > 0.5%. Much of the Harlan coal has an M-type REY distribution pattern (after Seredin and Dai [30]).

The Kellioka coal generally has less than 5% ash yield and a sulfur content <0.9% in most lithotypes. Pyritic S is highest in the uppermost two lithotypes and, in the 6360 section, in the basal lithotype. Concentrations of Sr + Ba > 11000 ppm, accompanied by 929 ppm REY, occur in a lithotype with 3.50% P_2O_5. The Kellioka samples generally do not have REY patterns corresponding to the Seredin and Dai [30] distributions.

The Darby coal is generally low-ash and low-sulfur. The Ba + Sr content exceeds 14,560 ppm (ash basis) in one sample and has relatively high values in other lithotypes. While a carbonate or phosphate association might be the source of the elements, there is no direct mineral evidence for such an association in this coal. The highest REY content, nearly 1700 ppm, does not correspond to the highest Sr + Ba. A few of the Darby samples show an M-type distribution, with most samples enriched in heavy REY elements. As with the Harlan coal, the V + Cr is highest in the uppermost lithotype in both benched sections.

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