

Lanthanide, yttrium, and zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky

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Abstract

The Fire Clay coal bed in the Central Appalachian basin region contains a laterally-persistent tonstein that is found in the coal throughout most of its areal extent. The tonstein contains an array of minerals, including sanidine, β -quartz, anatase and euhedral zircon, that constitutes strong evidence for a volcanic origin of the parting. For this study, five samples of the tonstein and four sets of coal samples underlying the tonstein were collected from five sites in eastern Kentucky. Inductively coupled plasma-mass spectroscopy (ICP-MS) analysis of the tonstein and underlying coal collected from four sites in eastern Kentucky show that although Zr concentrations are high in the tonstein (570–1820 ppm on a coal-ash basis (cab)), they are highest in the coal directly underlying the tonstein (2870–4540 ppm (cab)). A similar enrichment pattern is observed in the concentration of Y plus the sum of the rare earth elements ($Y + \Sigma\text{REE}$): total $Y + \Sigma\text{REE}$ concentrations in the five tonstein samples range from 511 to 565 ppm (cab). However, $Y + \Sigma\text{REE}$ contents are highest in the coals directly underlying the tonsteins: values range from 1965 to 4198 ppm (cab). Scanning electron microscopy of samples from coal which directly underlies two of the tonstein samples show that REE-rich phosphate, tentatively identified as monazite, commonly infills cracks in clays and cells in clarain and vitrain. Zircon is rare and commonly subhedral. On the basis of coal chemistry and grain morphology, we suggest that volcanic components in the tonstein were leached by ground water. The leachate, rich in Y and REE precipitated as authigenic mineral phases in the underlying coal. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recent studies (Eble et al., 1994; Hower et al., 1994) of the Fire Clay coal bed in eastern Kentucky have demonstrated that the unit was deposited in two distinct stages: the lower split is relatively thin, has high values of sulfur and ash yield, and has maceral and palynomorph associations suggestive of deposition as a planar mire. In places where it was not already terminated by a black, illitic shale, deposition of the lower split was interrupted by a volcanic ash fall preserved as a tonstein. The mineralogy of the tonstein has been documented by Lyons et al. (1992) and Hower et al. (1994) and in previous work cited in these papers. Andrews et al. (1994) provided evidence of volcanic ash layers in the uppermost coal that underlies the tonstein. The mire was re-established above the tonstein and the resulting upper split of the Fire Clay coal bed is generally low in sulfur and ash yield.

Geochemical investigations of the Fire Clay coal bed have followed two approaches. Hower et al. (1997) compared the whole coal geochemistry of the Fire Clay and Pond Creek coal beds, two of the largest producers in eastern Kentucky, with particular emphasis on Pb and As concentrations. Hower et al. (1994, 1997) and Andrews et al. (1994) examined major oxide and minor and trace element chemistry of the coal lithotype samples examined in this study, but REE analyses, as discussed in this paper, were not available until recently.

In this study we will discuss the influence of the volcanic ash on the overall ash geochemistry, particularly as expressed in the trends of the lanthanides, Y, and Zr. The influence of epigenetic sulfides on the As concentration is discussed in Ruppert et al. (1994) for two sites identified by Hower et al. (1997) as having high whole coal As, nearly 1200 ppm (ash basis) in one case.

2. Previous studies of lanthanide enrichment in coal

Numerous studies of the concentration and activity of lanthanide elements in coals have been conducted. In examinations of a Cretaceous bituminous and two Eocene subbituminous coals from Bulgarian coal basins, Eskenazy (1978, 1987a,b,c) observed that leaching of REE and subsequent fixation by organic ligands can occur as pH decreases. Although the most common association of REE in coals is with minerals, primarily clays and phosphates (Eskenazy, 1995), vitrains often have high $Y + \Sigma\text{REE}$ contents, higher than whole coal (Eskenazy et al., 1986; Eskenazy, 1987a). This trend is particularly strong in Pcelarovo basin vitrains overlain by Oligocene pyroclastics (Eskenazy, 1987b). She suggested that the Pcelarovo vitrain REE and associated Zr and Hf enrichments are due to their dissolution from the pyroclastics and their preferential concentration by organic matter.

Vassilev et al. (1995) examined vitrains in a clay lens in an Oligocene subbituminous coal associated with volcanics from the Vulche Pole basin, Bulgaria and found that trace elements comprised 12.7% of the ash yield. They concluded that REE are predominately organically associated, although both monazite and xenotime were identified.

Crowley et al. (1989), in a study of tonsteins in the C coal bed in Utah attributed Zr and REE enrichment in coal underlying the tonsteins to three possible factors: (1) leaching of volcanic ash by ground water and subsequent uptake by organic matter, (2) leaching of volcanic ash by ground water and subsequent incorporation in minerals, and (3) incorporation of volcanic ash minerals in peat. They suggested that the primary factor responsible for trace-element enrichment in the coals was tonstein dissolution. Triplehorn and Bohor (1983), Crowley et al. (1993), Ruppert and Moore (1993) and Seredin (1996) reported crandallite and other phosphates, all REE-bearing, as alteration products of volcanic ash. Zielinski (1985), in a study of element enrichment in thin (2 cm) coal horizons below tonsteins, noted that U, Th, and the REE, among other elements were enriched in the coal with Zr and Hf being among the elements resistant to mobilization.

3. Procedure

Complete suites of coal lithotype and parting samples were selected from three localities previously studied Hower et al. (1994) and Andrews et al. (1994) (see Section 1). Two additional tonstein sample sites in the Tilford 7½-min quadrangle, Letcher County, KY were added for this study (Fig. 1): a sample of the underlying coal was available for one of the sites. Major oxide and minor element analyses were done by X-ray fluorescence at the University of Kentucky Center for Applied Energy Research

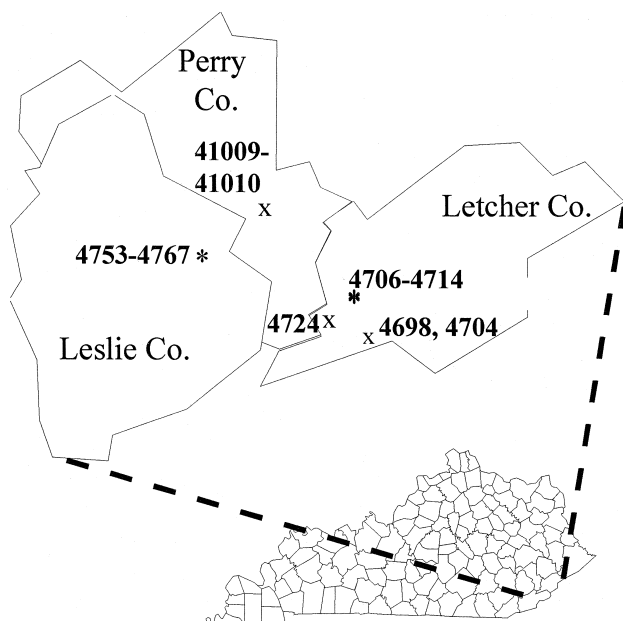
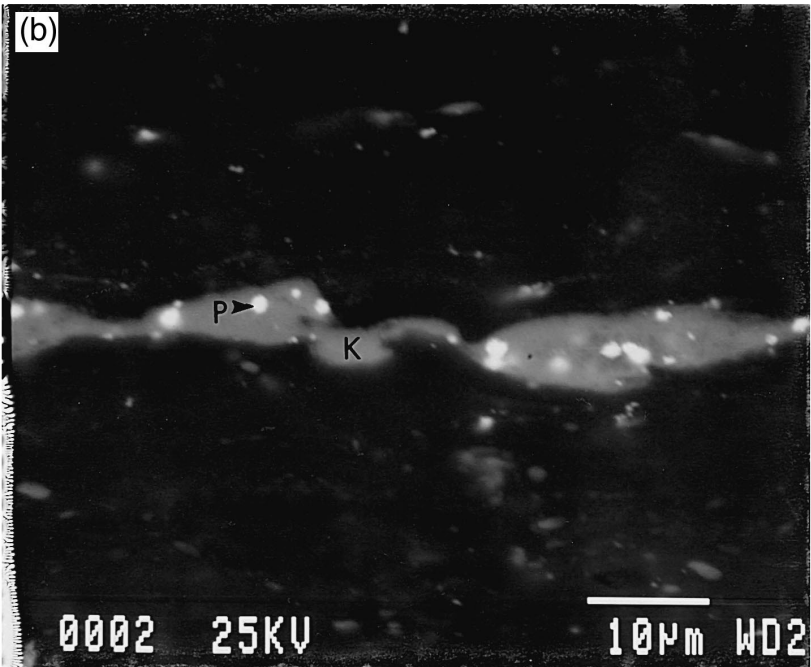
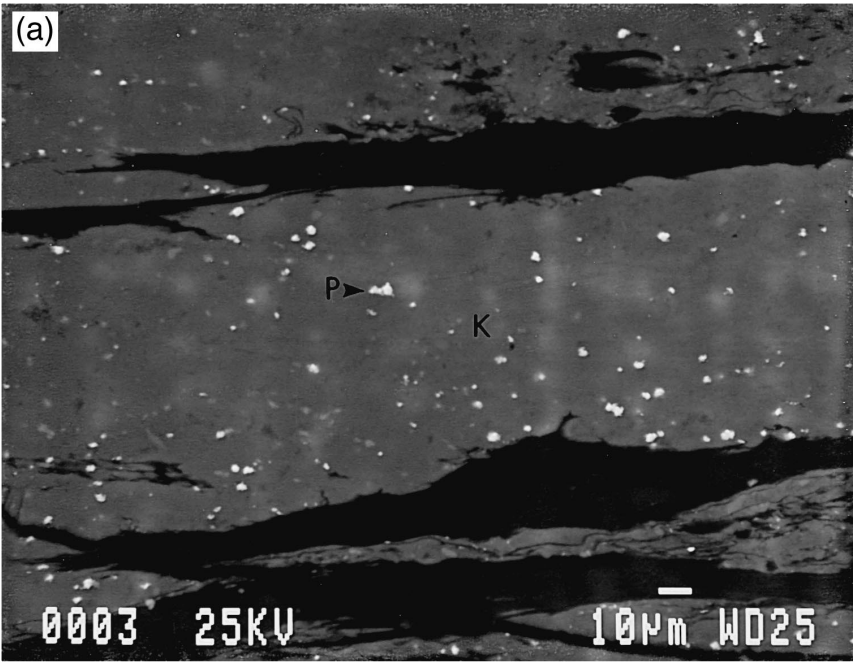


Fig. 1. Location of the study area in eastern Kentucky and location of sample sites within the area. Sites where a full suite of lithotypes and parting samples were analyzed are marked by an asterisk (*).



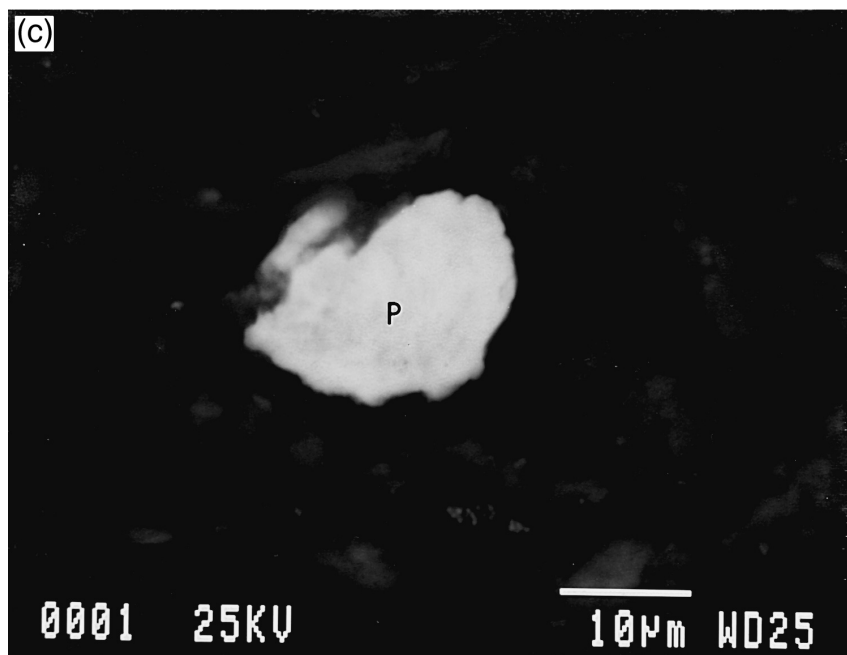


Fig. 2. Scanning electron photomicrographs in back-scatter electron image (BS). BS is sensitive to atomic number—lighter elements appear dark in photomicrographs, heavier elements appear lighter. (A) Ce-, La-, Nd-, Ca-rich phosphate (P), probably monazite (bright spots) in a kaolinite (K) matrix in coal directly underlying the tonstein. (B) Close up of a Ce-, La-rich phosphate (P) in a kaolinite (K) stringer in vitrain in coal directly underlying the Fire Clay tonstein. (C) Ce-, La-, Nd-rich phosphate (P), Fe-oxide, possibly magnetite (Fe), and zircon (Zr) in the tonstein. Sample no. 41009.

following procedures discussed in detail by Hower and Bland (1989). In addition, all five suites of samples were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS) at the U.S. Geological Survey laboratories in Denver, CO following procedures outlined by Meier et al. (1996). Two of the tonstein–coal sample pairs (sample no. 4698 and 4704 and sample no. 41009 and 41010) were examined by scanning electron microscopy (SEM). An attached energy-dispersive X-ray analyzer (EDXA) was used to identify the presence of Zr, Y, and REE in mineral phases.

4. Discussion

The Fire Clay tonstein is dominated by kaolinite, as shown in SEM photomicrographs (Fig. 2A and B) and as reflected in an enrichment of SiO_2 and Al_2O_3 (Tables 1 and 2). Sanidine, commonly altered almost entirely to kaolinite, Y-bearing Ca-phosphates, commonly lacking REE, and euhedral to subhedral zircon which occasionally contain detectable Hf and Y, are the most common accessory minerals in the tonstein samples (Fig. 2C). β -quartz, anatase, and magnetite, accessory minerals that are indicative of a

Table 1

(A) Ash yields, major oxide (percent), and trace elements (ppm) in Fire Clay coal and tonstein samples, as determined by X-ray fluorescence

Location	Sample type	Sample	Ash	S(total)	S(py)	MgO	Na ₂ O	Fe ₂ O ₃	TiO ₂	SiO ₂	CaO	K ₂ O	P ₂ O ₅	Al ₂ O ₃	SO ₃
Hyden East, Leslie	1 of 11 (top)	4754	3.96	0.88	0.15	0.59	0.66	8.23	1.27	54.64	2.10	1.98	0.08	27.43	1.19
	2 of 11	4755	10.46	5.63	5.30	0.14	0.78	77.51	0.16	9.90	1.27	0.18	0.04	7.63	0.87
	3 of 11	4756	3.77	0.81	0.05	0.29	1.19	4.38	1.37	56.79	1.63	0.47	0.07	31.49	0.77
	4 of 11	4757	13.45	0.85	0.17	0.20	0.70	2.93	2.39	70.15	0.76	0.83	0.07	19.50	0.48
	5 of 11	4758	6.74	0.81	0.04	0.16	0.65	2.03	1.43	58.04	0.79	0.55	0.07	33.95	0.42
	6 of 11	4759	4.91	1.10	0.26	0.26	0.78	10.58	0.97	49.87	1.37	0.38	0.08	33.30	0.69
	7 of 11	4760	10.63	2.33	1.50	0.44	0.03	20.86	0.92	39.02	6.21	0.85	0.12	22.44	7.20
	flint clay	4761	86.93	0.04	0.04	0.32	0.52	1.49	1.44	55.24	0.47	0.54	0.15	37.93	0.00
	8 of 11	4762	10.23	0.92	0.03	0.37	0.00	1.94	1.15	60.79	2.19	0.97	0.28	29.30	1.44
	9 of 11	4763	25.69	0.70	0.08	0.37	0.44	1.69	1.87	68.72	0.41	1.76	0.07	23.28	0.09
	10 of 11	4765	25.63	1.00	0.25	0.95	0.64	3.74	0.98	60.77	0.71	3.95	0.07	26.55	0.25
Tilford, Letcher	11 of 11 (base)	4767	9.92	0.98	0.11	0.62	0.43	3.93	0.92	56.47	1.06	2.44	0.11	31.96	0.30
	1 of 7 (top)	4706	2.28	0.81	0.11	1.70	1.80	12.19	1.23	35.13	10.17	1.09	0.10	24.07	11.86
	2 of 7	4707	3.54	0.74	0.06	0.83	1.94	8.06	1.29	48.90	4.52	0.78	0.07	29.59	2.59
	3 of 7	4708	4.89	0.84	0.13	0.61	0.82	7.20	1.47	51.43	3.01	0.65	0.08	30.78	1.84
	4 of 7	4709	5.88	0.88	0.19	0.46	0.79	7.74	1.71	54.27	2.04	1.00	0.08	29.18	1.34
	5 of 7	4710	17.10	0.64	0.04	0.31	0.48	1.48	2.25	67.35	0.87	1.56	0.09	23.30	0.31
	6 of 7	4711	9.97	0.79	0.05	0.49	0.20	2.59	1.37	55.53	1.68	1.30	0.21	34.20	0.83
	flint clay	4712	85.63	0.07	0.06	0.11	0.09	0.91	1.43	54.41	0.71	0.40	0.17	40.71	0.00
	illitic clay	4713	92.71	0.15	0.11	1.70	0.73	5.44	0.90	59.70	0.30	5.03	0.06	24.68	0.00
	7 of 7 (base)	4714	11.29	1.86	0.80	0.90	0.31	14.47	1.10	50.67	1.09	2.70	0.14	26.42	0.45
	flint clay	4698	85.80	0.04	0.04	0.12	0.37	0.76	1.39	53.90	0.54	0.32	0.18	41.09	0.00
	underlying coal	4704	33.94	2.13	1.17	0.76	0.03	7.64	1.02	56.36	0.45	2.70	0.15	30.03	0.08
Tilford, Letcher	flint clay	4724	85.96	1.66	1.29	0.15	0.37	3.04	1.25	52.31	0.49	0.35	0.15	39.98	0.00
Hazard South, Perry	flint clay	41 009	84.93	0.07	n.a.	0.00	0.16	0.70	1.55	57.80	0.46	0.44	0.13	36.84	0.00
	underlying coal	41 010	17.39	0.79	n.a.	0.13	0.00	1.97	1.21	57.00	0.86	0.85	0.17	35.87	0.25

Location	Sample type	Sample	Ash	Mo	Zn	Cu	Ni	Co	Cr	Ba	V	Mn	Rb	Sr	Zr
Hyden East, Leslie	1 of 11 (top)	4754	3.96	4	105	312	193	39	417	3690	560	236	103	2740	491
	2 of 11	4755	10.46	0	0	341	107	0	144	1030	121	0	0	540	117
	3 of 11	4756	3.77	24	87	167	119	27	348	3640	453	16	43	3430	590
	4 of 11	4757	13.45	0	30	124	40	11	431	1760	408	214	64	860	690
	5 of 11	4758	6.74	12	37	140	108	20	495	2720	630	161	17	1680	610
	6 of 11	4759	4.91	16	61	278	191	35	352	2790	472	149	20	2440	590
	7 of 11	4760	10.63	0	149	258	147	36	241	1330	348	337	62	1240	1170
	flint clay	4761	86.93	0	52	59	28	7	142	1540	98	191	16	530	700
	8 of 11	4762	10.23	0	312	102	176	44	403	1420	630	187	35	1330	2870
	9 of 11	4763	25.69	13	92	117	64	19	429	1050	444	199	132	400	540
	10 of 11	4765	25.63	0	590	105	174	42	485	2170	1060	240	332	810	312
	11 of 11 (base)	4767	9.92	14	660	302	388	81	750	2370	1900	193	177	1620	396
Tilford, Letcher	1 of 7 (top)	4706	2.28	0	183	362	486	116	438	6820	700	198	57	5600	671
	2 of 7	4707	3.54	18	48	221	164	43	331	6950	409	229	51	4700	606
	3 of 7	4708	4.89	18	109	211	122	32	403	6100	460	181	44	2600	510
	4 of 7	4709	5.88	10	110	203	113	30	429	4250	510	187	65	2300	535
	5 of 7	4710	17.10	3	85	99	36	10	455	2210	483	222	112	581	502
	6 of 7	4711	9.97	0	144	125	79	28	331	2360	471	80	111	1200	1300
	flint clay	4712	85.63	0	57	62	23	5	173	1930	176	201	8	200	614
	illitic clay	4713	92.71	0	188	87	66	25	336	2170	365	444	325	185	271
Tilford, Letcher	7 of 7 (base)	4714	11.29	16	620	399	424	72	497	2360	840	283	172	970	500
	flint clay	4698	85.80	0	45	60	25	5	172	1440	171	215	5	300	570
	underlying coal	4704	33.94	0	840	198	326	60	431	1870	820	223	269	442	3200
Tilford, Letcher	flint clay	4724	85.96	0	46	51	30	11	128	1730	170	164	6	328	630
Hazard South, Perry	flint clay	41009	84.93	4	46	32	12	0	0	620	63	19	0	1050	1830
	underlying coal	41010	17.39	6	246	109	108	29	75	850	218	85	6	2610	4540

All elemental values are on an ash basis.

Table 2

(B) Trace elements (ppm) in the Fire Clay coal and tonstein samples, as determined by inductively-coupled plasma mass spectroscopy

Location	Sample type	Sample	Be	Li	Sc	Th	Ag	As	Au	Bi	Cd	Cs	Ga	Ge	Nb	Pb	Rb	Sb	Sn	Te	Tl	U
Hyden East, Leslie	1 of 11 (top)	4754	280	140	110	33	2	750	10	2	0.8	3	250	360	44	130	66	130	20	2	17	70
	2 of 11	4755	31	48	9	15	2	4000	10	2	0.8	0.4	22	4.3	8	20	9.5	2	10	2	97	3
	3 of 11	4756	30	210	43	36	2	84	10	2	0.8	0.7	68	9	30	110	9.5	4	20	2	3	20
	4 of 11	4757	9	71	29	35	2	30	10	2	0.8	3	38	4	40	64	36	2	20	2	2	11
	5 of 11	4758	26	170	52	56	2	30	10	3	0.8	1	56	7.4	30	120	14	3	10	2	14	21
	6 of 11	4759	52	190	44	64	2	190	10	2	0.8	0.7	71	9.7	30	96	11	2	10	2	12	21
	7 of 11	4760	21	83	28	83	2	420	10	2	0.8	4	120	23	54	84	45	2	20	2	29	50
	flint clay	4761	2	95	9	66	2	4	10	2	0.8	1	48	2	30	110	31	2	20	2	2	17
	8 of 11	4762	46	96	71	200	3	6	10	2	1	2	150	31	140	130	30	8.9	30	2	2	85
	9 of 11	4763	25	83	47	54	2	10	10	2	0.8	6.5	44	8	30	140	87	5.4	10	2	2	23
	10 of 11	4765	20	120	55	35	2	40	10	2	2	13	81	18	30	160	190	20	10	2	4	52
Tilford, Letcher	11 of 11 (base)	4767	67	270	120	63	2	60	10	3	2	6.4	190	130	44	220	81	57	10	2	6.1	84
	1 of 7 (top)	4706	670	110	130	33	4.3	480	10	2	0.8	4.3	710	600	89	79	70	51	40	2	2	24
	2 of 7	4707	41	120	35	38	2	47	10	2	0.8	3	56	8.2	30	88	53	2	20	2	3	15
	3 of 7	4708	20	180	37	46	2	71	10	2	0.8	3	61	7	40	100	45	3	20	2	7.8	18
	4 of 7	4709	25	140	47	47	2	110	10	2	0.8	5.1	63	11	44	92	74	4	20	2	11	22
	5 of 7	4710	23	67	38	44	2	8	10	2	0.8	11	44	7.2	44	75	120	2	20	2	2	11
	6 of 7	4711	40	120	44	130	2	10	10	2	0.8	12	180	37	88	130	150	8.4	30	2	2	87
	flint clay	4712	2	140	7	48	2	10	10	2	0.8	0.8	58	2	40	150	23	2	20	2	2	17
	illitic clay	4713	4	55	23	17	2	9	10	2	0.8	17	56	3	20	40	370	2	10	2	2	5.9
	7 of 7 (base)	4714	52	74	72	75	2	190	10	2	0.8	18	150	48	45	170	230	59	20	2	16	79
	flint clay	4698	2	110	9	76	2	4	10	2	0.8	0.6	41	2	30	120	14	2	20	2	2	18
Tilford, Letcher	underlying coal	4704	7	84	32	120	10	84	10	2	1	22	64	13	150	170	330	5.3	40	2	13	59
	flint clay	4724	2	130	10	72	2	48	10	2	0.8	0.6	41	2	30	140	17	2	20	2	2	21
Hazard South, Perry	flint clay	41009	2	150	9	77	2	4	10	2	0.8	0.7	47	2	30	120	18	2	20	2	2	24
	underlying coal	41010	23	150	39	110	4	5	10	2	0.8	3	120	24	76	110	45	2	43	2	2	40

Location	Sample type	Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Hf	Ta	Y + REE	W
Hyden East, Leslie	1 of 11 (top)	4754	390	140	270	33	130	36	8	40	9	58	12	36	5	33	9	2	1211	30
	2 of 11	4755	67	60	110	12	50	10	2	10	2	10	2	6	0.8	5	2	1	350	10
	3 of 11	4756	190	250	470	54	190	42	5	40	6	37	7	20	3	18	10	3	1345	40
	4 of 11	4757	79	140	240	28	90	20	3	20	3	18	4	11	2	10	10	4	682	8
	5 of 11	4758	210	180	370	44	160	36	4	30	6	35	6	19	3	17	10	2	1132	10
	6 of 11	4759	340	240	470	57	210	49	5	50	8	51	10	30	4	27	10	2	1563	20
	7 of 11	4760	200	270	500	58	200	44	4	40	7	46	9	30	5	29	30	3	1475	20
	flint clay	4761	49	110	200	24	90	19	1	20	2	13	2	6	0.8	4	20	3	564	2
	8 of 11	4762	430	790	1500	190	660	150	13	130	22	130	25	75	11	72	50	3	4251	10
	9 of 11	4763	110	110	210	25	90	22	4	20	4	28	6	18	3	17	10	3	680	7
	10 of 11	4763	120	110	200	26	100	26	6	20	4	24	5	15	2	13	7	2	680	10
	11 of 11 (base)	4767	320	160	360	47	190	51	12	50	10	61	12	36	5	34	8	2	1358	30
Tilford, Letcher	1 of 7 (top)	4706	630	220	390	47	190	46	10	60	10	78	17	55	8	54	10	2	1827	20
	2 of 7	4707	210	240	460	53	200	40	5	40	5	33	6	19	3	17	10	2	1343	20
	3 of 7	4708	210	200	400	49	180	40	5	40	6	36	7	20	3	17	10	2	1225	20
	4 of 7	4709	230	190	360	44	170	38	4	40	6	38	7	22	3	19	10	3	1184	10
	5 of 7	4710	120	170	310	36	130	26	3	20	4	25	7	14	2	13	10	3	891	4
	6 of 7	4711	330	430	820	96	350	71	6	70	10	67	13	40	6	38	30	3	2380	20
	flint clay	4712	47	90	190	24	90	19	1	20	2	14	2	6	0.8	5	20	4	535	3
	illitic clay	4713	15	70	120	14	50	11	2	9	1	8	2	4	0.7	4	5	2	318	2
	7 of 7 (base)	4714	320	240	500	60	240	53	9	50	9	64	13	43	7	43	10	2	1663	20
Tilford, Letcher	flint clay	4698	51	100	190	24	90	1	20	2	13	13	2	6	0.7	4	20	3	546	2
	underlying coal	4704	160	360	740	89	340	72	7	60	9	57	10	30	4	27	50	3	2018	2
Tilford, Letcher	flint clay	4724	55	100	210	25	100	20	1	20	3	15	2	7	1	6	20	3	588	2
Hazard South, Perry	flint clay	41 009	49	100	200	25	90	20	1	20	2	13	2	5	0.7	4	20	3	555	2
	underlying coal	41 010	280	390	770	94	350	73	6	70	10	66	13	40	6	37	30	3	2238	7

All elemental values are on an ash basis.

volcanic origin, have also been documented in the Fire Clay tonstein (Lyons et al., 1992; Hower et al., 1994).

Considering the presence of abundant zircon, we should expect to find significant concentrations of Zr in the tonstein samples. Zirconium contents of the Fire Clay tonstein, as well as in a larger sample set investigated by Hower et al. (1994), are indeed higher than the Zr contents of most of the coal lithotype ashes (Table 3). However, Zr concentrations in tonstein, which range from 570 to 1830 ppm (ash basis), are dwarfed by the concentrations in ashes from the coal lithotype immediately underlying the tonstein, for example, compare tonstein–coal pairs: no. 4761 and 4762 (700 vs. 2870 ppm), no. 4698 and 4704 (570 vs. 3200 ppm), and no. 41009 and 41010 (1830 vs. 4540 ppm). In contrast, coal lithotype sample no. 4714, separated from the tonstein by an intervening black, illitic clay, is not enriched in Zr (500 ppm cab). For the two complete sample suites (Hyden and Tilford $7\frac{1}{2}$ -min quadrangle sites), the coal lithotype immediately overlying the tonstein also has an elevated Zr concentration, although not as high as in the lithotype underlying the tonstein.

Notable is the Zr concentration of 4540 ppm (ash basis) in coal sample no. 41010 from the Hazard South $7\frac{1}{2}$ -min quadrangle site studied by Andrews et al. (1994) and re-examined for this study. They suggested that plant roots reworked zircons from the tonstein into the underlying coal, but in our SEM-EDXA examinations, zircons are most abundant in tonstein samples (Fig. 2B): small ($< 5 \mu\text{m}$), subhedral zircons are present in the underlying coal sample, in some cases in kaolinite lens that may be volcanic (Andrews et al., 1994), but not as common as they are in tonstein samples. Eskenazy (1978) suggested that Zr in coal may be organically-associated, but we have no evidence to support this interpretation, other than the lack of abundant zircon grains. Some of the Zr may be incorporated in REE-phosphates (Finkelman, R.B., 1997, personal communication), and indeed, one of the analyzed REE-phosphates contains trace amounts of Zr. However, additional study is needed to document all of the modes of occurrence of Zr in these samples.

Both U and Th follow the trends noted above for Zr (Table 1), consistent with substitution of U for Zr in zircon, but U was not detected in any of the mineral phases in any of the samples analyzed with SEM. Hf, noted by Crowley et al. (1989) as a trace element in zircon, also tends to follow the Zr trend (Table 2) and Hf was detected as a trace element in some of the zircons from the tonsteins and the coal samples.

Table 3

Average concentrations (in ppm) on an ash basis of selected lanthanides, Y and Zr in the Fire Clay coal bed and three other eastern Kentucky coal beds

Coal	Number (REE)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Y (no. analyses)	Zr (no. analyses)
Coalburg	57	103	189	10	95	17	4	13	3	3	<1	4	10	76 (57)	252 (97)
Fire Clay	28	155	290	23	138	25	3	11	4	12	2	10	14	843 (43)	536 (85)
Pond Creek	32	83	164	15	37	15	4	4	3	6	<1	2	13	451 (58)	290 (185)
Clintwood	21	90	165	10	74	17	4	17 ^a	4	12	<1	7	11	92 (22)	238 (52)

^aIncludes one value of 173 ppm.

Hower et al. (1997) found higher concentrations of Y in the Fire Clay coal bed compared to the Pond Creek, Coalburg, and Clintwood coal beds of eastern Kentucky (Table 3). Yttrium has similar associations as the REE, but in the samples that we examined with SEM, Y most commonly occurs as an accessory element in Ca-phosphates.

With the exception of the high pyritic sulfur, high-As lithotype discussed by Ruppert et al. (1994), all coal lithotypes have REE concentrations exceeding those of the tonstein samples (Tables 1 and 2). The five tonstein samples, which range in thickness from 10.4 to 14 cm, have a remarkably similar Y + Σ REE content, a range of 535–588 ppm. The three samples of the underlying coal (sample nos. 4762, 4704 and 41010), range in thickness from 2.5–9.5 cm, and exhibit a wider Y + Σ REE range: 2018–4251 ppm. The next highest concentrations are generally in the two lithotypes immediately above the tonstein although the basal and upper lithotypes from the Hyden East $7\frac{1}{2}$ -min quadrangle (sample nos. 4754 and 4767) also has a high Y + Σ REE content. In addition, the complete Tilford $7\frac{1}{2}$ -min quadrangle sequence, which contains an illitic shale immediately below the tonstein, also shows a similar sequence: the highest Y + Σ REE concentration is found in the lithotype above the tonstein (sample no. 4711) with high concentrations in the basal and uppermost lithotypes (sample nos. 4707 and 4714, respectively).

Scanning-electron microscopy show the presence of abundant, small ($< 2 \mu\text{m}$), irregularly-shaped, REE-rich phosphates, tentatively identified as monazite, in the coal samples underlying the tonstein (Fig. 2A and C). Monazite is associated with cracks in kaolinite and illitic clay and cells in clarain and vitrain. In sample no. 41010 from the Hazard South $7\frac{1}{2}$ -min quadrangle site, the presence of monazite is reflected in the chemical analyses (Tables 1 and 2): La-, Ce-, Nd-, and Gd-bearing monazite are the most common REE-rich phosphate (Fig. 2B). Yttrium, while not a rare earth element, has a similar mode of occurrence as the REE: in the coal samples that we examined by SEM-EDXA, Y is most commonly associated with small ($< 10 \mu\text{m}$) Ca-phosphate phases that also infill cracks and fissures in clay. However, most of these Y-bearing Ca-phosphates (crandallite?) lack detectable REE.

In light of the distribution of Zr, Y, and the REE of the coal lithotypes, it is interesting to compare the overall concentrations of the Fire Clay coal bed with other major coal beds in Eastern Kentucky. The average concentrations of the REE, Y, and Zr for the Fire Clay, Coalburg (correlatives include the Peach Orchard, Hazard No. 7, Hazard No. 8, coals, among others), Pond Creek (correlatives include the Imboden, Path Fork, Blue Gem, coals, among others), and Clintwood (correlatives include the Manchester, River Gem, Bingham coals, among others) coal beds are shown in Table 3. With the exception of a very high value of Gd in the Clintwood coal bed which skews the average REE averages, the highest Zr, Y, and REE values are in the Fire Clay coal bed. The Fire Clay coal bed is the only coal bed that contains a recognized, regionally-extensive tonstein.

Overall, the petrography and trace element trends in the Fire Clay coal bed strongly suggest that the volcanic ash influenced the chemical composition of the entire coal bed. The REE enrichments, the morphology and association of the REE-bearing phosphates with cracks, fissures, and vitrain in underlying coal lithotypes suggests that leaching of

the volcanic ash by ground water occurred. Crowley et al. (1989) proposed such a mechanism for REE enrichments observed in the C coal, Utah. Leaching of volcanic minerals and glass may have contributed significant amounts of Y, REE, and P for incorporation in authigenic mineral phases such as monazite and crandallite (?) in the underlying, and perhaps, the overlying coal lithotypes.

5. Summary

The Fire Clay tonstein significantly influenced the geochemistry of the Fire Clay coal bed in eastern Kentucky. The tonstein itself is enriched in Zr (570–1820 ppm, ash basis), compared to most of the coal lithotypes in the coal bed. However, where coal directly overlies the tonstein, Zr contents are extremely high (2870–4540 ppm, ash basis). The primary mechanism for the Zr enrichment in the underlying coal, may be the incorporation of volcanic ash minerals in peat by plant roots as suggested by Crowley et al. (1989) and Andrews et al. (1994), the incorporation of Zr in REE-phosphates, or an organic-association.

Lanthanide elements show a similar enrichment in the coal directly underlying the tonstein, ranging from 1965 to 4198 ppm (ash basis) for Y + Σ REE compared to 511 to 565 ppm in the tonstein samples. We suggest that the mechanism for the enrichment of Y + Σ REE is leaching of volcanic ash by ground water, and the incorporation of those elements into monazite and Y-bearing Ca-phosphates (crandallite?). The trace element distribution the Fire Clay coal bed suggests that the geochemical influence of the ash fall extended throughout the coal.

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