Distribution of rare earth elements in eastern Kentucky coals: Indicators of multiple modes of enrichment?

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ABSTRACT

Four eastern Kentucky Pennsylvanian coals (from oldest to youngest, the Manchester, Pond Creek, Fire Clay, and Hazard coals) were examined for their total rare earth element (REY) concentration and the possible mechanisms for enrichment of the rare earths. Based on previous studies, four possible modes are considered: terrigenous, tuffaceous, infiltrational, and hydrothermal, with the Dean coal, a correlative of the Fire Clay coal, considered to be a typical example of the tuffaceous mode. The Fire Clay owes much of its high REY content to the presence of a volcanic-ash-fall tonstein, with REY-bearing zircon and phosphates in the coal in numerous locations. Some of the original REY elements may have components of the detrital minerals deposited in the peat. Leaching of REY from the tonstein into the surrounding coal and the hydrothermal overprint of mineralizing fluids associated with the northwestwardly movement of the Pine Mountain thrust sheet contributed to the total REY signature in the Fire Clay coal. Not all coals are going to have the complex history of the Fire Clay coal, but it should be considered that the total history of REY enrichment by multiple mechanisms is what gives us both the total REY concentration and the relative distribution of the individual lanthanide elements.

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1. Introduction

Rare earth elements have come to be of increasing interest given their use in a wide array of modern electronics (Greene, 2012; Hatch, 2012; Hower et al., 2016). Enhanced levels of rare earth elements (REE or REY if yttrium is included in the assessment; for this work, REY > 900 ppm on the ash basis will be considered to be an enhanced concentration) are found in many US coals (data from Bragg et al., 1998), with the Central Appalachian coalfield in eastern Kentucky, central and southern West Virginia, and southwestern Virginia having some of the best prospects. In particular, the Middle Pennsylvanian Fire Clay coal and its correlatives are among the most promising resources owing to the presence of a REY-rich volcanic ash-fall parting (tonstein) (Rice et al., 1994; Hower et al., 1999, 2015a) or the presence of high REY concentrations in the absence of the tonstein (Mardon and Hower, 2004). The available resources of the Fire Clay coal were discussed by Thacker et al. (2000).

The light rare earth elements (LREE) have been considered to include La through Sm and the heavy rare earth elements (HREE) span Eu to Lu (Seredin, 1996a, b; Hower et al., 1999; Mardon and Hower, 2004; Dai et al., 2016b; among others). Seredin and Dai (2012) divided the REY into light, medium, and heavy fractions: LREY (La through Sm), MREY — (Eu through Dy plus Y), and HREY — (Ho through Lu). They also noted L-type ($La_N/Lu_N > 1$), M-type ($La_N/Sm_N < 1$, $Gd_N/Lu_N > 1$), and H-type ($La_N/Lu_N < 1$) enrichment patterns. Further, they emphasized that there were four main genetic modes of REY enrichment in coals, as shown in Table 1. In some cases, the enrichment of REY in coal is attributed to mixed mineralization (e.g., mixed tuffaceous-hydrothermal type; Dai et al., 2016a). Notably, for this evaluation, the Dean coal, a Fire Clay correlative, is considered to be a typical example of the tuffaceous mode of accumulation (Seredin and Dai, 2012).

The Fire Clay tonstein contains kaolinite; sanidine; β-quartz; magnetite and magnetite with ilmenite cores; the TiO_2 polymorphs anatase and brookite; sphene; REE and Y-bearing zircon; Y-bearing Ca-phosphates (crandallite); and Y-, La-, Ce-, Nd-, Dy- and Gd-bearing apatite (Fig. 1) and monazite (Lyons et al., 1992; Hower et al., 1994a, 1999).

Table 1
The main genetic types of high REY accumulation in coals.

Type	REO content in ash, %	Associated elements	Typical example
Terrigenous	0.1–0.4	Al, Ga, Ba, Sr,	Jungar, China (Dai et al., 2006; Dai et al., 2008)
Tuffaceous	0.1–0.5	Zr, Hf, Nb, Ta, Ga	Dean, USA (Mardon and Hower, 2004)
Infiltrational	0.1–1.2	U, Mo, Se, Re	Aduunchulun, Mongolia (Arbuzov and Mashen'kin, 2007)
Hydrothermal	0.1–1.5	As, Sb, Hg, Ag, Au, etc.	Rettikhovka, Russia (Seredin, 2004)

REO, oxides of rare earth elements and yttrium.

Recent investigations by Belkin (this paper) found that the LREE-enriched, Ce-bearing monazite contained 60.8 wt.% total rare earth oxides, 4.2 wt.% ThO_2, and 2.1 wt.% Y_2O_3. Zoning in the monazite is due to variations in the Th content. The apatite tends to have a fluorapatite composition and is LREE enriched with about 1 wt.% total rare earth oxides. Zoned HREE-enriched zircons were found to have 0.33 wt.% total rare earth oxides and 0.23 wt.% Y_2O_3.

The coal lithotype underlying the Fire Clay tonstein has 4200 ppm REY and 5700 ppm Zr (both on ash basis) (Andrews et al., 1994; Hower et al., 1999). REY enrichment below tonsteins was also noted by Zielinski (1985); Triplehorn and Bohor (1983); Crowley et al. (1989, 1993), and Ruppert and Moore (1993), as well as cases in other areas (Dai et al., 2016a).

Crowley et al. (1989) noted that secondary enrichment can be a function of (1) ground water leaching of volcanic ash followed by uptake of the REY by organic matter, (2) ground water leaching of the volcanic ash followed by incorporation into minerals, and (3) incorporation of volcanic minerals in the peat. Zielinski (1985) and Crowley et al. (1989), in studies of Wyoming and Utah coals, respectively, noted enrichments of REE in lithotypes immediately below tonsteins. REY in coal are commonly found in clays and phosphates (Eskenazy, 1995); loosely bound REYs may become mobile when associated, in particular, with clays (Eskenazy, 1999). Acidic waters tend to preferentially desorb the heavier REY from the clays. There tends to be an enrichment of HREE in peats and low-rank coals due to the stronger HREE (versus the LREE) affinity for organics and the greater strength of HREE-organic complexes (Eskenazy, 1978, 1987a, b, c, 2015; Eskenazy et al., 1986; Seredin et al., 1999; Pédrot et al., 2010; Davranche et al., 2011; Aide and Aide, 2012). In contrast, for Pennsylvanian coal from Inner Mongolia, China, Dai et al. (2008) found that the LREEs had a
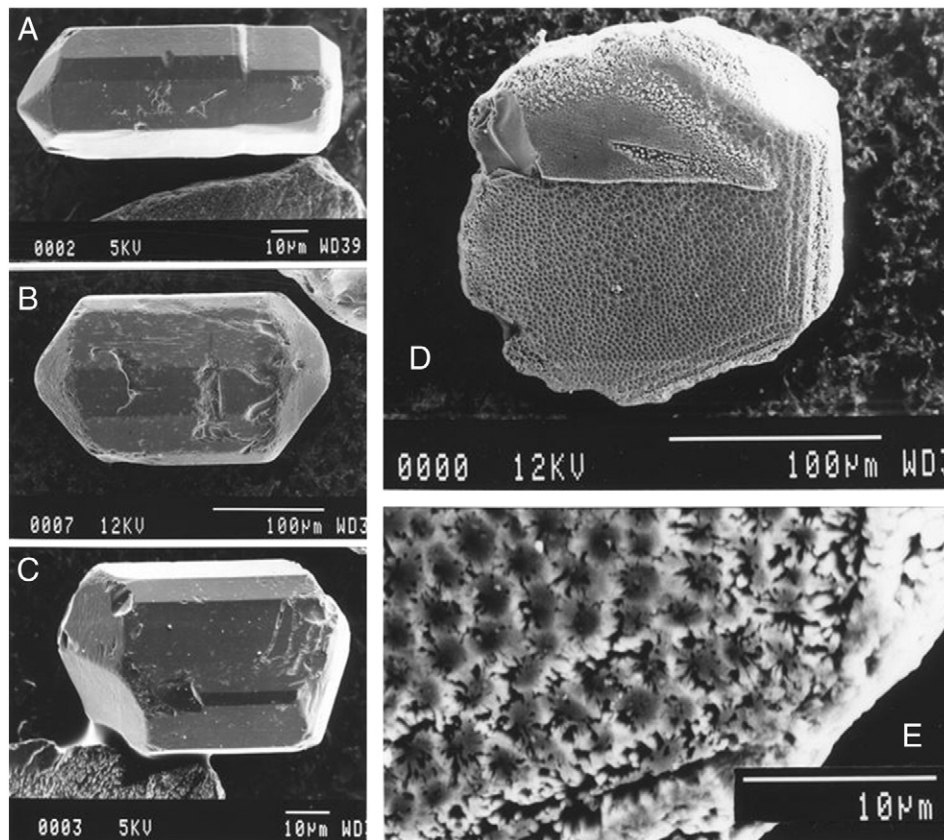

Fig. 1. SEM backscattered electron images of unaltered apatite (A–C) and altered apatite (D–E) from the Fire Clay tonstein in eastern Kentucky. The apatite contains 0.08% La_2O_3, 0.51% Ce_2O_3, 0.36% Nd_2O_3, 0.12% Dy_2O_3, and 0.36% Y_2O_3. Quadrangle (7 ½-minute) locations: A & C/Ivydell, Tennessee; B/Hoskinston, Kentucky; and D & E/Sylvester, West Virginia. Specimens and analyses from studies by Harvey Belkin.

greater organic affinity than the HREE. As coal rank increases, the potential for chelation diminishes with the loss of functional groups (Given, 1984; Hatcher and Clifford, 1996). The REY released upon the loss of the ligands could be then bound to clays (for example: Eskenazy, 1995; Seredin, 1996a, b) or form carbonate (such as bastnäsite) or phosphate (such as xenotime) minerals. Extensive lists of REE-bearing minerals can be referenced through webmineral.com.

Dai et al. (2008) noted that preferential leaching of the LREE from partings could lead to a high LREE/HREE in the underlying coal. In this case, LREEs were enriched in Sr and Ba minerals (see also Dai et al., 2006) and HREE were enriched in Sc, Zr, and Hf minerals. Hower et al. (1999) found similar LREE/HREE in lithotypes immediately above and below the REE-rich tonstein (6.31 and 6.69, respectively, versus 9.08 in the tonstein). While the latter coal lithotype values represent a decrease in LREE/HREE from the tonstein, the REE ratio immediately below the coal is higher than in the three HREE-enriched basal lithotypes (3.67–5.30 LREE/HREE). As another measure of the distinct differences in the tonstein vs. coal rare earth chemistry, we note that Ce/Yb, a parameter used by Eskenazy (1987b), is 50 in the tonstein vs. 20.8 in the underlying coal and 10.6–15.4 in the three basal lithotypes (data from Hower et al., 1999).

Dai et al. (2010, 2011, 2012a, b, c, 2013a, b, 2014a, b, 2014c, d, 2015a, b, c) investigated REY occurrences in numerous Chinese coals, finding that both terrigenous and hydrothermal influences account for the distribution of REY among the studied coals. In certain cases, there was evidence for hydrothermal destruction of quartz, kaolinite, and detrital REE-bearing minerals. The latter were redeposited as HREE-depleted REY phosphates and possibly as HREE- and Y-enriched organic compounds (Dai et al., 2013a).

Given suites of samples from several individual coal seams spread across a coal field, is it possible to discern distinct single or multiple modes of accumulation of rare earth and other elements? Based on compilations of previously published data (see Section 2), in this investigation, we are considering aspects of the overall minor and trace element chemistry and the REY chemistry of four of the more heavily mined coals in eastern Kentucky. Each was selected because (1) their lateral extent and quality means that there has been historical production over wide areas of the coal field and (2) they are each generally prominent enough and devoid of multiple splits such that correlation across the coal field is as assured as possible. With respect to point 1, widespread mining does not mean that, despite the reference here to just one coal name, the same name is used throughout the region. On the contrary, at least 21 names have been used for the Manchester coal and its correlatives in Kentucky and Virginia, with at least an additional five names in use when the entire coal zone is considered (based on unpublished Kentucky Geological Survey, University of Kentucky Center for Applied Energy Research, and Kentucky Department of Mines and Minerals compilations in the 1980s; see also Rice and Hiett, 1994). With respect to point 2, while avoiding some widely mined coal zones, such as the Upper Elkhorn No. 1 and Upper Elkhorn No. 2 coals and the Peach Orchard/Coalburg correlatives and splits, even the coals considered here exhibit some interesting configurations. For example, the high-S portion of the Manchester-correlative River Gem coal (Hower and Pollock, 1989; Hower et al., 1996) is actually a rider coal, which merges with the main coal bed within a small area in one mine.

2. Methods

Chemical data for eastern Kentucky coals was obtained from Bragg et al. (1998); procedures in Currens et al. (1987) with added data from Hower et al. (1996, 1999) (Appendix A). In general, all of the coal samples partings >1-cm thick would have been excluded from the sample. The Fire Clay tonstein is generally at least 15-cm thick, although some thin lenses of the tonstein have been observed in an underlying coal lithotype (Andrews et al., 1994). All of the

coal samples listed in Appendix A would be subject to the exclusion of >1-cm partings. The impact on the reported Fire Clay REY chemistry would potentially be significant since the tonstein can account for >20% of the REY in the floor-to-roof seam sections (Hower et al., 2015a).

3. Results and discussion

3.1. Other coals: Gray Hawk and Harlan County coals

Prior to discussing the four coals being emphasized, two other REY occurrences are notable. A three-bench suite of the Langsettian-age Gray Hawk coal (Jackson County, Kentucky) was studied by Hower et al. (2015b). They found that the upper two benches had a tendency towards a medium- and heavy-REY enrichment and the lower bench had a marked heavy-REY enrichment. The bottom and middle benches had 925 and 1168 ppm REY (ash basis), respectively. They speculated that the REY enrichment patterns were the consequence of the influx of acidic waters and/or epithermal processes. Among the Harlan County coals studied by Johnston et al. (2015), Darby coal benches with high REY, TiO_2, and P_2O_5 suggest a TiO_2-mineral, phosphate, and zircon detrital influx as the source of the REY enrichment. The Harlan coal had an M-type REY distribution in contrast to the H-type distribution found in most of the Darby coal lithotypes.

3.2. Manchester, Pond Creek, Fire Clay, and Hazard coals

On average, the Fire Clay coal and its correlatives have the highest REY among the four coals considered for this discussion (Fig. 2; Table 2). Subject to the caveats noted in the Introduction and the consideration of the inclusion, or not, of partings in the whole-seam sample, the relative scatter in the data (all of the individual coal seam averages are less than three-times the standard deviation) should not be surprising. All of the coal seam averages take in samples from across the coal field. The nature of the coals can vary considerably. For example, the Pond Creek and it correlatives vary from a relatively thick coal in Pike and Martin counties (Hower and Bland, 1989) to the thinner
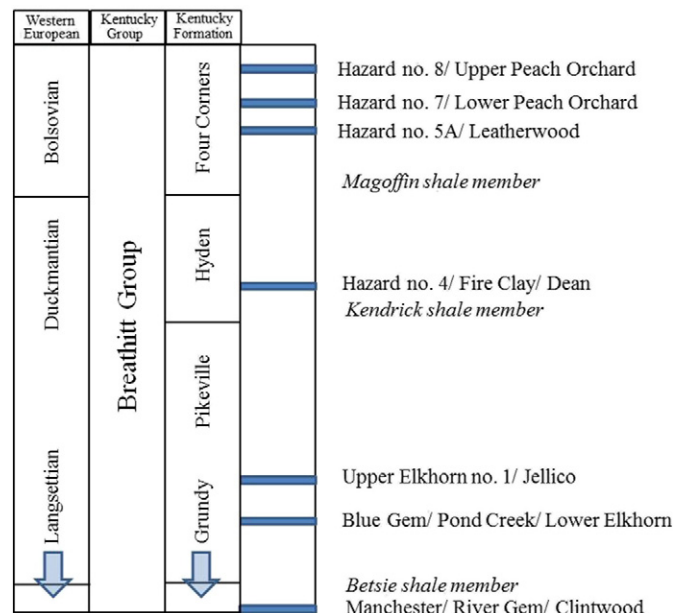

Fig. 2. Generalized coal column after formation and group assignments by Kentucky Geological Survey. Stage and substage boundaries after Eble et al. (2009).

Table 2
Average and standard deviation for ash yield; light rare earth elements (LREE), heavy REE (HREE), LREE/HREE, and REE + yttrium (REY) (all whole coal basis); and REY, light REY (LREY), medium REY (MREY), and heavy REY (HREY). The Hazard, Fire Clay, Pond Creek, and Manchester coals and their correlatives are considered (after Hower et al., 1996, 1999; Bragg et al., 1998). The number of samples for each coal is given below the coal name.

| Coal | | Ash | Whole coal basis | | | | Ash basis | | | |
			LREE	HREE	LREE/HREE	REY	REY	LREY	MREY	HREY
Hazard (x = 41)	Avg.	10.86	62	8	8.11	81	834	609	182	42
	St. dev.	6.25	35	4	4.71	41	312	188	123	26
Fire Clay (x = 40)	Avg.	11.21	80	11	8.02	103	944	724	179	42
	St. dev.	5.53	48	6	2.55	60	331	276	94	16
Pond Creek (x = 45)	Avg.	7.05	30	5	5.87	40	569	403	134	33
	St. dev.	4.12	25	3	2.34	30	226	175	74	12
Manchester (x = 40)	Avg.	6.61	32	5	7.25	43	702	519	149	34
	St. dev.	3.82	18	3	3.57	22	277	223	83	16

(± 0.6 m) thick, extremely low-ash (typically <2.0%, dry basis) Blue Gem coal in the southwestern part of eastern Kentucky (Hower et al., 1991a, b).

Another way to examine the REY content of the individual coals is to look at the maps of the distribution of the REY for the four coals (Figs. 3–6). Among the coals emphasized here, none has the wide distribution of REY highs matching the Fire Clay (Fig. 4). Some of the distributions mapped are skewed by the distribution of mining; for example, the Blue Gem coal, one of the Pond Creek correlatives, was mined in Knox County, to the southwest of one of the most intensive areas of Manchester coal mining in Clay County. This alone accounts for some of the differences in the mapped contour patterns.
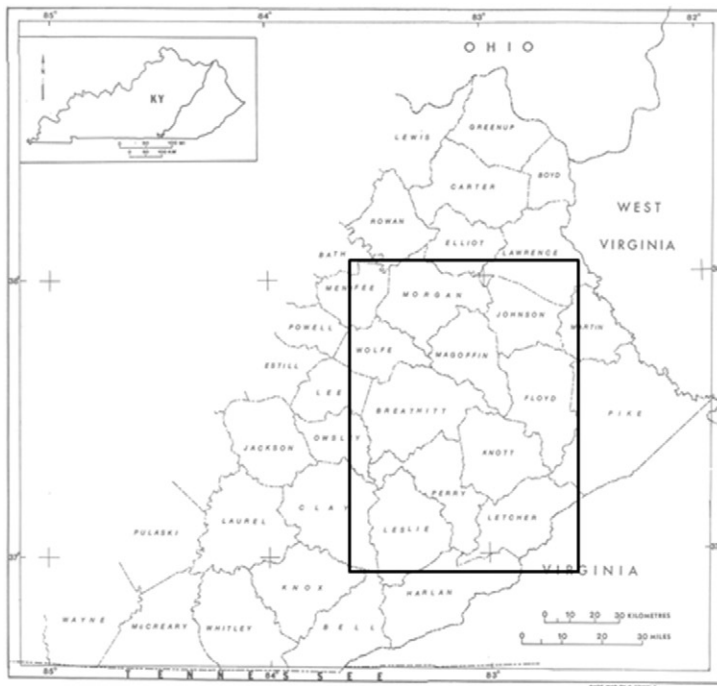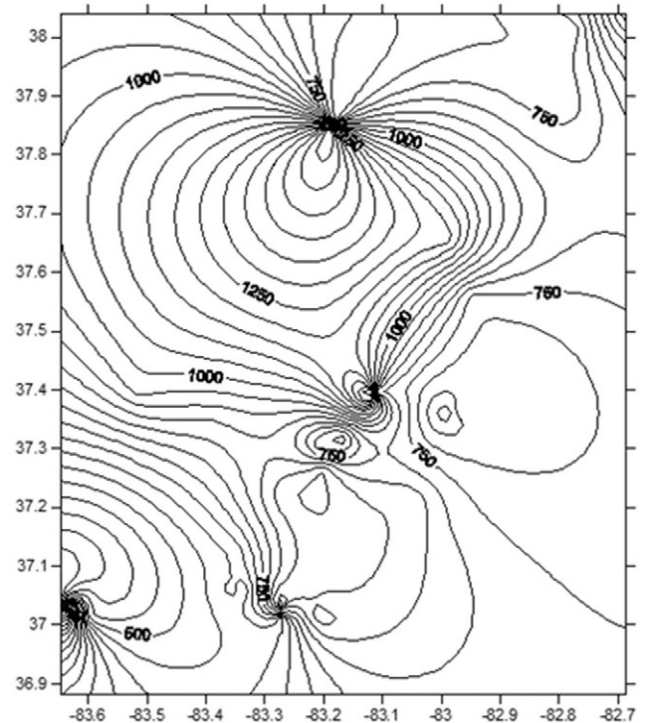

Fig. 3. Rare earth + yttrium (REY) distribution for the Hazard coal (ppm, on ash basis). Each contour line represents 50 ppm YEY.
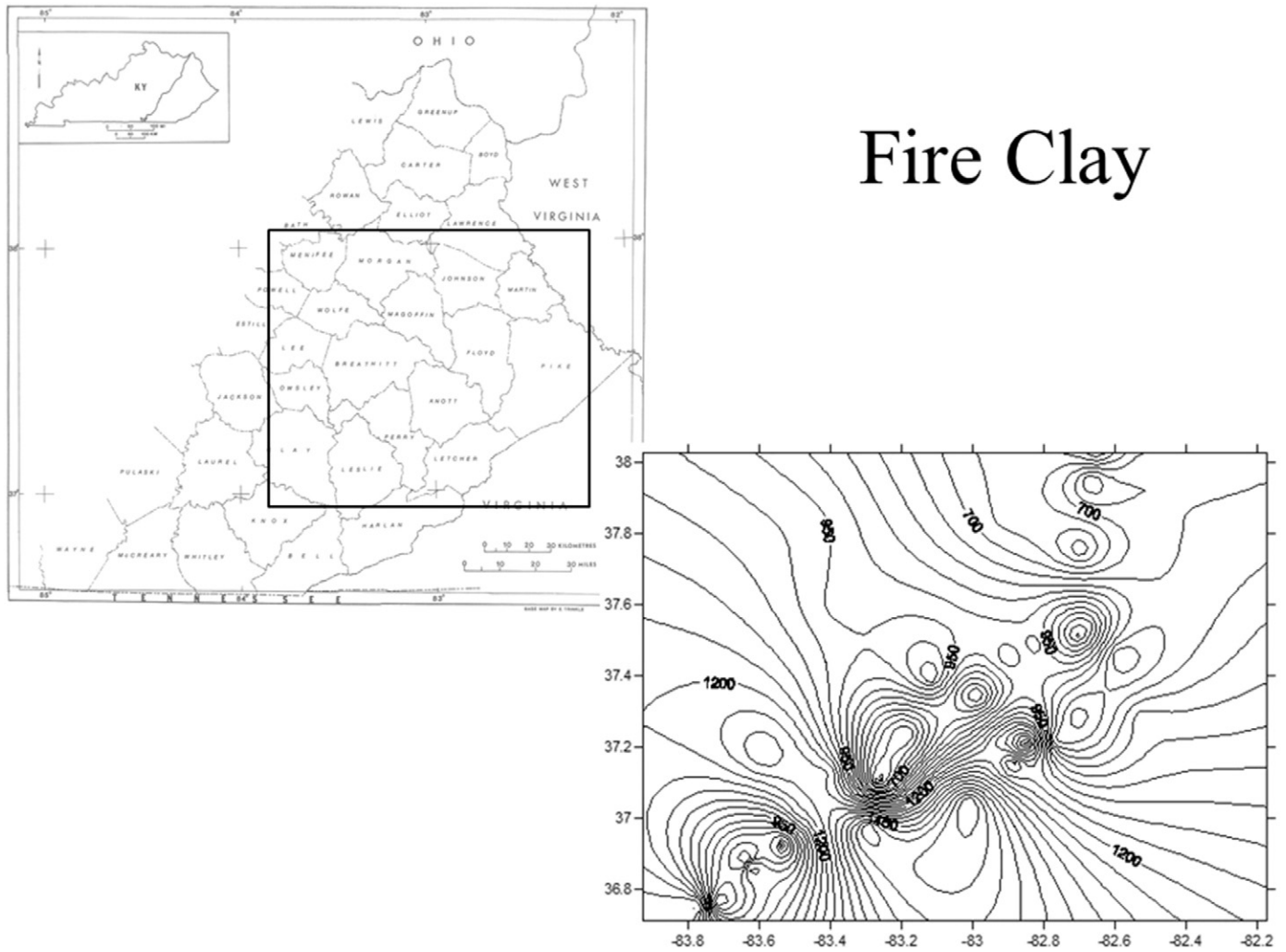
Fig. 4. Rare earth + yttrium (REY) distribution for the Fire Clay coal (ppm, on ash basis). Each contour line represents 50 ppm YEY.

Figs. 7 and 8 show the total REY vs. LREE/HREE for all four coals and for the Fire Clay and Manchester coals, respectively. In general, the Hazard, Pond Creek, and Manchester trends overlap the broader Fire Clay trends (Fig. 7). Isolating the Manchester and Fire Clay coals (Fig. 8) emphasizes that the Manchester REY and light REE/heavy REE occupy a much smaller range than the Fire Clay coal. This shows both the significant influence of the REY-rich tonstein on the Fire Clay geochemistry and the possibility that some of the Fire Clay REY distribution could be due to more diverse sources than just the tuffaceous input.

The relationship between Al_2O_3 and TiO_2 can be used to discriminate between modes of origin of elements in coals (Dai et al., 2015a, b). Specifically, Dai et al. (2011, 2014c) used the Al_2O_3/TiO_2 ratio to distinguish alkali, mafic and felsic tonsteins. With respect to all four of the coals emphasized here, the whole coal Al_2O_3 vs. TiO_2 tends to be higher in the Hazard and Fire Clay coals than for the Pond Creek and Manchester coals (Fig. 9). Looking specifically at lithologies within the Fire Clay coal (Fig. 10), while there is overlap between the fields, the tonstein has a higher Al_2O_3 content than the coal immediately underlying the tonstein. An even sharper demarcation exists between the tonstein and the basal lithotype, with the latter lithology having <33% Al_2O_3 and the tonstein generally having >33% Al_2O_3. The basal lithotype has a wider range of TiO_2 than the tonstein or the underlying coal, including some of the highest TiO_2 concentrations. This is not surprising as the

basal lithotype in many eastern Kentucky coals has been noted to have high concentrations of TiO_2, suggesting the presence of detrital rutile or anatase (Hower and Bland, 1989; Hower and Pollock, 1989; Hower et al., 1991a, b, 1994a, b, 1996; Hatton et al., 1992; Andrews et al., 1994; Mardon and Hower, 2004).

Hydrothermal saline fluids were directed to the northwest with the emplacement of the Pine Mountain thrust fault to the southeast of much of the study area under discussion (Fig. 11). This is seen in high levels of chlorine in coals to the northwest of the fault versus negligible Cl in the same coals on the thrust sheet (Hower et al., 1991a, b). Relatively high levels of trace metals in the coals (Collins, 1993; Sakulpitakphon et al., 2004) and the higher coal rank (Hower and Rimmer, 1991) to the northwest of the fault are also observed. Movement of REY-enriched hydrothermal deep-seated basinal fluids coincident with the thrust emplacement of Pine Mountain has not been investigated as of this time but other studies may provide insight into the setting. Johannesson et al. (1996) noted that the Ln^{3+} state of the lanthanides would be the dominant form in acidic, hypersaline waters. Eskenazy (1999) noted that acidic waters would tend to preferentially desorb the HREE with the HREE subsequently bound by organics. In the case of REE enrichment in Russian Far East coals, but not necessarily restricted to that geologic time and that location, Seredin (1996a, b) believed that the REEs were transported in a dissolved form.
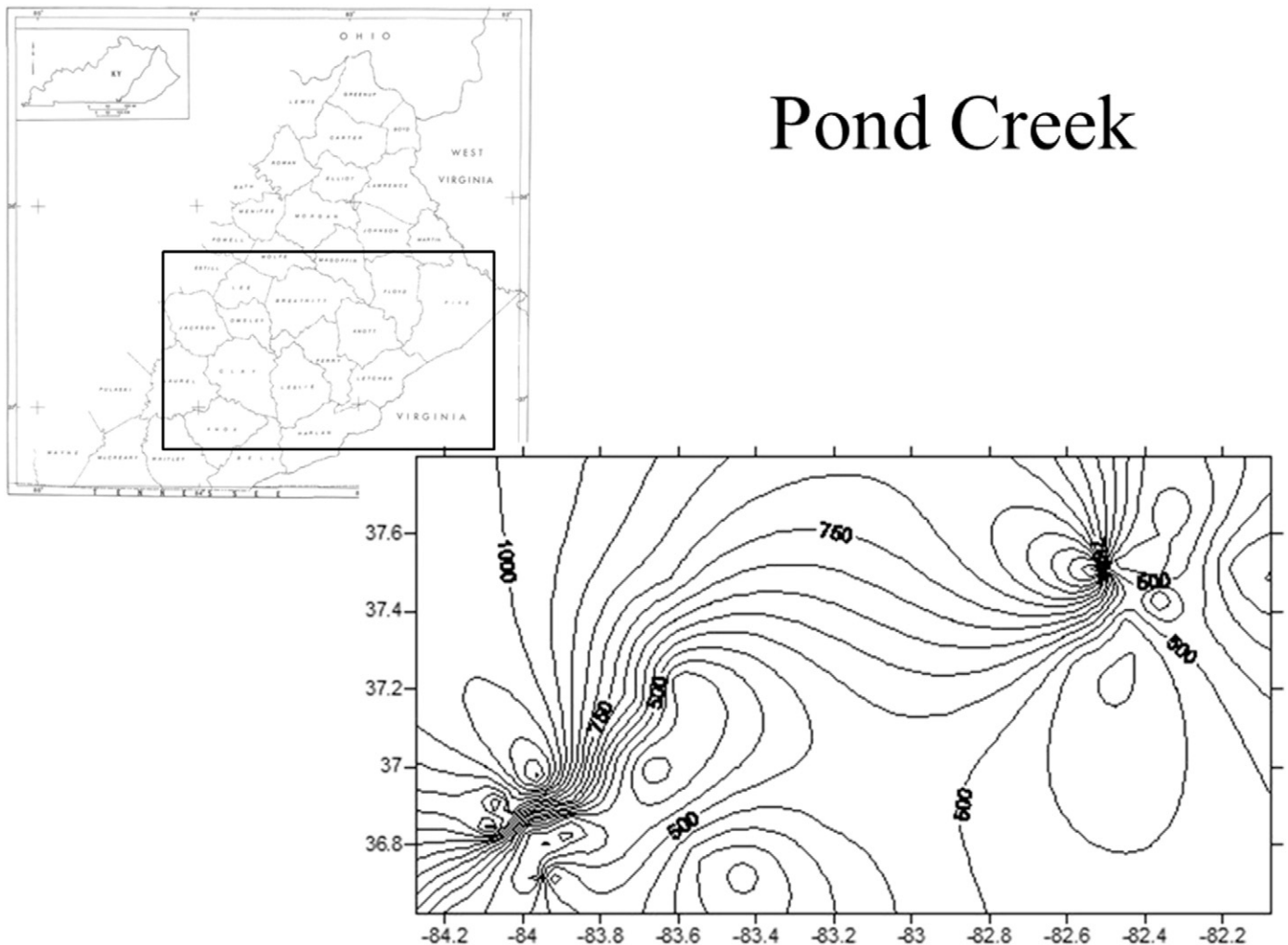
Fig. 5. Rare earth + yttrium (REY) distribution for the Pond Creek coal (ppm, on ash basis). Each contour line represents 50 ppm YEY.

4. Summary

Four eastern Kentucky Pennsylvanian coals were considered with respect to their total rare earth element concentration and the possible modes of origin of the rare earths. Four possible modes are considered: terrigenous, tuffaceous, infiltrational, and hydrothermal. Among the coals studied, the Dean coal, a correlative of the Fire Clay coal, was considered to be a typical example of the tuffaceous mode by Seredin and Dai (2012); after data from Mardon and Hower (2004). The Fire Clay owes much of its high REY content to the presence of a tonstein in the coal in many locations, although it is not present at the mine studied by Mardon and Hower (2004). The Fire Clay tonstein contains REY-bearing zircon, crandallite, apatite, and monazite. Leaching of the tonstein, an infiltrational input, albeit within the coal seam, contributed to the enhanced REY concentrations in the surrounding coal lithotypes, particularly the coal underlying the tonstein (Hower et al., 1999). Considering that zircons and the phosphate minerals (crandallite, apatite, and monazite) can be part of the detrital mineral input to any peat, not just the Fire Clay peat, it is possible that terrigenous REY input is a common feature in many coals, including the eastern Kentucky coals studied here. In addition, it is known that there were subtle hydrothermal influences associated with the northwestward-directed emplacement of the Pine Mountain thrust sheet. The coals to the northwest of the thrust fault, including all of the locations considered here, experienced the emplacement of higher concentrations of Cl and trace metals (Hower et al., 1991a, b; Collins, 1993; Sakulpitakphon et al., 2004) with an enhanced metamorphism (Hower and Rimmer, 1991; Hower et al., 1991a, b) than in the correlative coals on the thrust sheet.

The Fire Clay coal might be considered to be an extreme example, perhaps not typical of any other coal in the Central Appalachians. But, any coal may have experienced multiple types of REY accumulation and the Fire Clay coal, in particular, may have been influenced by all four modes of REY accumulation noted by Seredin and Dai (2012). The observed concentrations of REY and the relative distributions of the lanthanide elements are the products of the entire geologic history of the coal. Separating the individual events, such as the differentiation between the terrigenous and tuffaceous input, the hydrothermal metamorphic overprint, and the leaching and redistribution of the elements with the coal, requires more detailed studies.
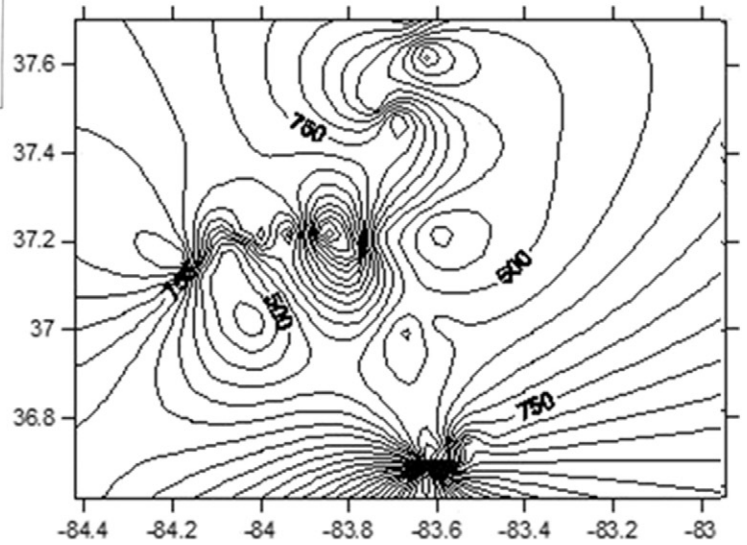
Acknowledgements

Manchester

Fig. 6. Rare earth + yttrium (REY) distribution for the Manchester coal (ppm, on ash basis). Each contour line represents 50 ppm YEY.
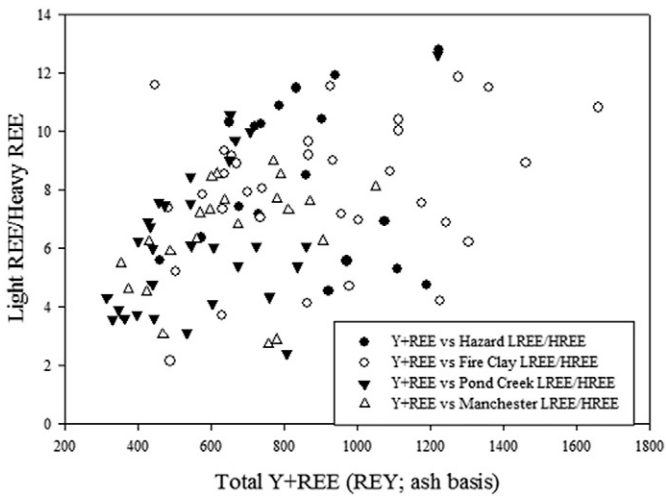

Fig. 7. Total REY (ppm) vs. LREE/HREE for all four coals considered in the discussion. The Hazard coal/Blaine quadrangle and Manchester coal/Tallega quadrangle have much higher LREE/HREE values than the other samples and, for the sake of showing the detail of the other 102 data points, those points have been excluded from the plot.
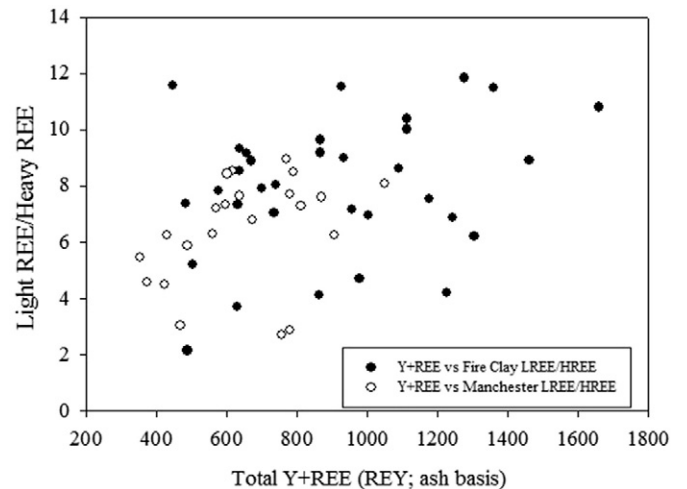

Fig. 8. Total REY (ppm, ash basis) vs. LREE/HREE for the Fire Clay and Manchester coals.
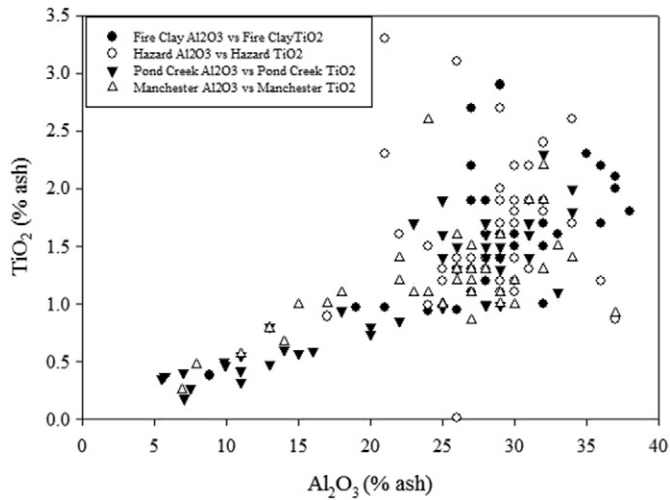
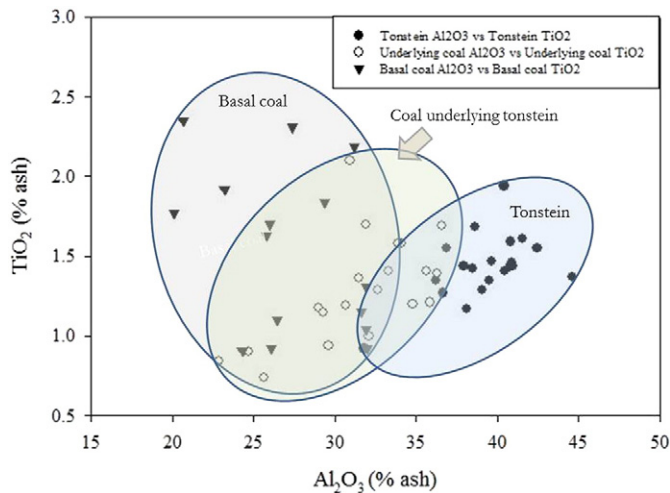Fig. 9. Al₂O₃ vs. TiO₂ for all four coals emphasized in the study.

Fig. 10. Al₂O₃ vs. TiO₂ for the Fire Clay tonstein, the coal lithotype immediately underlying the tonstein, and the basal coal lithotype.
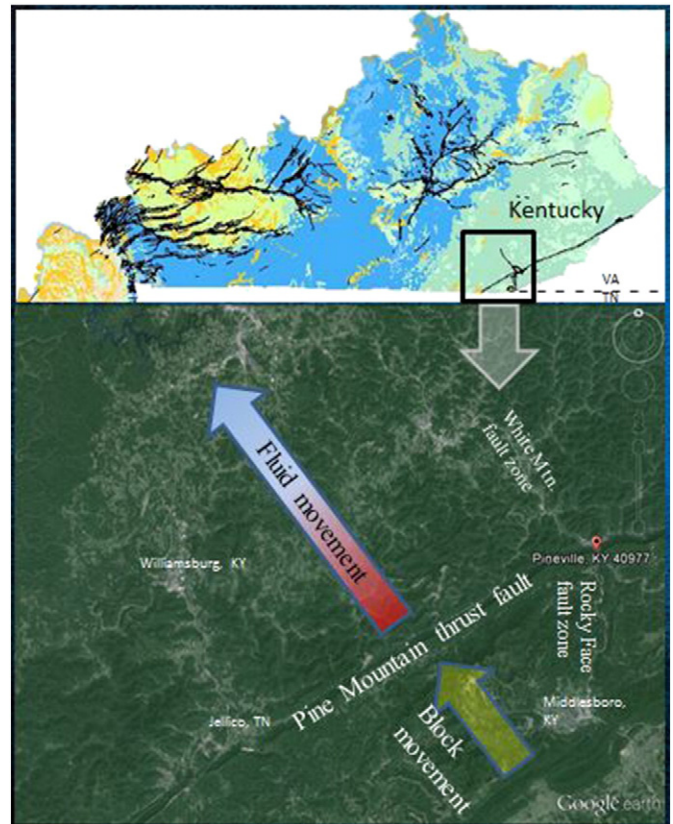

Fig. 11. Google Earth view of southeastern Kentucky and adjacent parts of Virginia and Tennessee. The Pine Mountain thrust fault and the direction of movement of the thrust sheet, the direction of fluid movement in front of the thrust sheet, the Rocky Face fault zone on the thrust sheet, and the White Mountain fault zone southeastern Kentucky in front of the thrust sheet are labeled on the Google Earth map. The locations of Middlesboro and Williamsburg, Kentucky, and Jellico, Tennessee, are also shown on the map. The location of the Google Earth area is indicated by the black square on the Kentucky map above the image. The border between Virginia (VA) and Tennessee (TN) is shown as a dashed line on the latter map.

Appendix A. Supplementary data

Chemical data for eastern Kentucky coals from Bragg et al. (1998) with added data from Hower et al. (1996, 1999). The Manchester, Pond Creek, Fire Clay, and Hazard coals are emphasized in the text discussions. Compilations for the Peach Orchard and Upper Elkhorn No. 1 and No. 2 coals are also included in the Excel file. In the compilations (tab: quad just the average) for the Manchester, Pond Creek, Fire Clay, and Hazard coals, the 7 1/2-minute quadrangle codes (http://kgs.uky.edu/kgsweb/download/topo/TOPOX.html) were added to the tables. Supplementary data associated with this article can be found in the on-line version, at doi: http://dx.doi.org/10.1016/j.coal.2016.04.009.

References

Aide, M.T., Aide, C., 2012. Rare earth elements: their importance in understanding soil genesis. ISRN Soil Sci. http://dx.doi.org/10.5402/2012/783876 (2012, article 783876).

Andrews Jr., W.M., Hower, J.C., Hiett, J.K., 1994. Investigations of the Fire Clay coal bed, southeastern Kentucky, in the vicinity of sandstone washouts. Int. J. Coal Geol. 26, 95–115.

Arbuzov, S.I., Mashen'kin, V.S., 2007. Oxidation Zone of Coalfields as a Promising Source of Noble and Rare Metals: A Case of Coalfields in Central Asia. Problems and Outlook of Development of Mineral Resources and Fuel-Energetic Enterprises of Siberia, Tomsk Polytechnic Univ., Tomsk. pp. 26–31 (in Russian).

Bragg, L.J., Oman, J.K., Tewalt, S.J., Oman, C.L., Rega, N.H., Washington, P.M., Finkelman, R.B., 1998. U.S. Geological Survey coal quality (COALQUAL) database: version 2.0. U.S. Geol. Surv. Open File Rep. 97–134, (CD-ROM).

Collins, S.L., 1993. Statistical Analysis of Coal Quality Parameters for the Pennsylvanian System Bituminous Coals in Eastern Kentucky, USA (Unpublished PhD thesis). Chapel Hill, University of North Carolina, p. 401 pp.

Crowley, S.S., Stanton, R.W., Ryer, T.A., 1989. The effects of volcanic ash on the maceral and chemical composition of the C coal bed, Emery Coalfield, Utah. Org. Geochem. 14, 315–331.

Crowley, S.S., Ruppert, L.F., Belkin, H.F., Stanton, R.W., Moore, T.A., 1993. Factors affecting the geochemistry of a thick, subbituminous coal bed in the Powder River Basin: volcanic, detrital, and peat-forming processes. Org. Geochem. 20, 843–854.

Currens, J.C., Bragg, L.J., Hower, J.C., 1987. Analysis of coal samples from the Hazard District, Kentucky. Kentucky Geological Survey, Series XI, Information Circular 19 (381 pp.).

Dai, S., Ren, D., Chou, C.-L., Li, S., Jiang, Y., 2006. Mineralogy and geochemistry of the no. 6 coal (Pennsylvanian) in the Junger Coalfield, Ordos Basin, China. Int. J. Coal Geol. 66, 253–270.

Dai, S., Li, D., Chou, C.-L., Zhao, L., Zhang, Y., Ren, D., Ma, Y., Sun, Y., 2008. Mineralogy and geochemistry of boehmite-rich coals: new insights from the Haerwusu Surface Mine, Jungar Coalfield, Inner Mongolia, China. Int. J. Coal Geol. 74, 185–202.

Dai, S., Zhao, L., Peng, S., Chou, C.-L., Wang, X., Zhang, Y., Li, D., Sun, Y., 2010. Abundances and distribution of minerals and elements in high-alumina coal fly ash from the Jungar Power Plant, Inner Mongolia, China. Int. J. Coal Geol. 81, 320–332.

Dai, S., Wang, X., Zhou, Y., Hower, J.C., Li, D., Chen, W., Zhu, X., Zou, J., 2011. Chemical and mineralogical compositions of silicic, mafic, and alkali tonsteins in the late Permian coals from the Songzao Coalfield, Chongqing, Southwest China. Chem. Geol. 282, 29–44.

Dai, S., Wang, X., Seredin, V.V., Hower, J.C., Ward, C.R., O'Keefe, J.M.K., Li, T., Li, X., Liu, H., Xue, W., Zhao, L., 2012a. Petrology, mineralogy, and geochemistry of the Ge-rich coal from the Wulantuga Ge ore deposit, Inner Mongolia, China: new data for genetic implications. Int. J. Coal Geol. 90-91, 72–90.

Dai, S., Zou, J., Jiang, Y., Ward, C.R., Wang, X., Li, T., Xue, W., Liu, S., Tian, H., Sun, X., Zhou, D., 2012b. Mineralogical and geochemical compositions of the Pennsylvanian coal in the Adaohai Mine, Daqingshan Coalfield, Inner Mongolia, China: modes of occurrence and origin of diaspore, gorceixite, and ammonian illite. Int. J. Coal Geol. 94, 250–270.

Dai, S., Jiang, Y., Ward, C.R., Gu, L., Seredin, V.V., Liu, H., Zhou, D., Wang, X., Sun, Y., Zou, J., Ren, D., 2012c. Mineralogical and geochemical compositions of the coal in the Guanbanwusu Mine, Inner Mongolia, China: further evidence for the existence of an Al (Ga and REE) ore deposit in the Jungar Coalfield. Int. J. Coal Geol. 98, 10–40.

Dai, S., Zhang, W., Ward, C.R., Seredin, V.V., Hower, J.C., Li, X., Song, W., Kang, H., Zheng, L., Zhou, D., 2013a. Mineralogical and geochemical anomalies of late Permian coals from the Fusui Coalfield, Guangxi Province, southern China: influences of terrigenous materials and hydrothermal fluids. Int. J. Coal Geol. 105, 60–84.

Dai, S., Zhang, W., Seredin, V.V., Ward, C.R., Hower, J.C., Wang, X., Li, X., Song, W., Zhao, L., Kang, H., Zheng, L., Zhou, D., 2013b. Factors controlling geochemical and mineralogical compositions of coals preserved within marine carbonate successions: a case study from the Heshan Coalfield, southern China. Int. J. Coal Geol. 109–110, 77–100.

Dai, S., Li, T., Seredin, V.V., Ward, C.R., Hower, J.C., Zhou, Y., Zhang, M., Song, X., Song, W., Zhao, C., 2014a. Origin of minerals and elements in the late Permian coals, tonsteins, and host rocks of the Xinde Mine, Xuanwei, eastern Yunnan, China. Int. J. Coal Geol. 121, 53–78.

Dai, S., Seredin, V.V., Ward, C.R., Jiang, J., Hower, J.C., Song, X., Jiang, Y., Wang, X., Gornostaeva, T., Li, X., Liu, H., Zhao, L., Zhao, C., 2014b. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. Int. J. Coal Geol. 121, 79–97.

Dai, S., Luo, Y., Seredin, V.V., Ward, C.R., Hower, J.C., Zhao, L., Liu, S., Tian, H., Zou, J., 2014c. Revisiting the late Permian coal from the Huayinshang, Sichuan, southwestern China: enrichment and occurrence modes of minerals and trace elements. Int. J. Coal Geol. 122, 110–128.

Dai, S., Ren, D., Zhou, Y., Seredin, V.V., Li, D., Zhang, M., Hower, J.C., Ward, C.R., Wang, X., Zhao, L., Song, X., 2014d. Coal-hosted rare metal deposits: genetic types, modes of occurrence, and utilization evaluation. J. China Coal Soc. (Meitan Xuebao) 39, 1707–1715 (in Chinese with English abstract).

Dai, S., Li, T., Jiang, Y., Ward, C.R., Hower, J.C., Sun, J., Liu, J., Song, H., Wei, J., Li, Q., Xie, P., Huang, Q., 2015a. Mineralogical and geochemical compositions of the Pennsylvanian coal in the Hailiushu Mine, Daqingshan Coalfield, Inner Mongolia, China: implications of sediment-source region and acid hydrothermal solutions. Int. J. Coal Geol. 137, 92–110.

Dai, S., Hower, J.C., Ward, C.R., Guo, W., Song, H., O'Keefe, J.M.K., Xie, P., Hood, M.M., Yan, X., 2015b. Elements and phosphorus minerals in the middle Jurassic inertinite-rich coals of the Muli Coalfield on the Tibetan Plateau. Int. J. Coal Geol. 144-145, 23–47.

Dai, S., Liu, J., Ward, C.R., Hower, J.C., Xie, P., Jiang, Y., Hood, M.M., O'Keefe, J.M.K., Song, H., 2015c. Petrological, geochemical, and mineralogical compositions of the low-Ge coals from the Shengli Coalfield, China: a comparative study with Ge-rich coals and a formation model for the Wulantuga Ge ore deposit. Ore Geol. Rev. 71, 318–349.

Dai, S., Chekryzhov, I.Y., Seredin, V.V., Nechaev, V.P., Graham, I.T., Hower, J.C., Ward, C.R., Ren, D., Wang, X., 2016a. Metalliferous coal deposits in East Asia (Primorye of Russia and South China): a review of geodynamic controls and styles of mineralization. Gondwana Res. 29, 60–82.

Dai, S., Graham, I.T., Ward, C.R., 2016b. A review of anomalous rare earth elements and yttrium in coal. Int. J. Coal Geol. 159, 82–95.

Davranche, M., Grybos, M., Gruau, G., Pédrot, M., Dia, A., Marsac, R., 2011. Rare earth element patterns: a tool for identifying trace metal sources during wetland soil reduction. Chem. Geol. 284, 127–137.

Eble, C.F., Blake, B.M., Gillespie, W.H., Pfefferkorn, H.W., 2009. Appalachian Basin fossil floras. In: Greb, S.F., Chesnut Jr., D.R. (Eds.), Carboniferous Geology of the Appalachian Basin. Kentucky Geological Survey Special Publication vol. 10, pp. 46–58.

Eskenazy, G., 1978. Rare-earth elements in some coal basins of Bulgaria. Geol. Balc. 8, 81–88.

Eskenazy, G.M., 1987a. Rare earth elements and yttrium in lithotypes of Bulgarian coals. Org. Geochem. 11, 83–89.

Eskenazy, G.M., 1987b. Zirconium and hafnium in Bulgarian coals. Fuel 66, 1652–1657.

Eskenazy, G.M., 1987c. Rare earth elements in a sampled coal from the Pirin deposit, Bulgaria. Int. J. Coal Geol. 7, 301–314.

Eskenazy, G., 1995. Geochemistry of rare earth elements in Bulgarian coals. Annuaire de l'Universite´ de Sofia "St. Kliment Ohridski", Faculte´ de Geologie et Geographie. Livre 1-Geologie 88, pp. 39–65.

Eskenazy, G.M., 1999. Aspects of the geochemistry of rare earth elements in coal: an experimental approach. Int. J. Coal Geol. 38, 285–295.

Eskenazy, G.M., 2015. Sorption of trace elements on xylain: an experimental study. Int. J. Coal Geol. 150-151, 166–169.

Eskenazy, G.M., Mincheva, E.I., Rousseva, D.P., 1986. Trace elements in lignite lithotypes from the Elhovo coal basin. Comptes Rendus del'Académie Bulgare des Sciences 39 (10), pp. 99–101.

Given, P.H., 1984. An essay on the organic geochemistry of coal. Academic press. Coal Sci. 3 (63–251), 339–341.

Greene, J., 2012. Digging for rare earths: the mine where iPhones are born. http://www. cnet.com/news/digging-for-rare-earths-the-mines-where-iphones-are-born/.

Hatch, G.P., 2012. Dynamics in the global market for rare earths. Elements 8, 341–346.

Hatcher, P.G., Clifford, D.J., 1996. The organic geochemistry of coal: from plant materials to coal. Org. Geochem. 27, 251–274.

Hatton, A.R., Hower, J.C., Helfrich, C.T., Pollock, J.D., Wild, G.D., 1992. Lithologic succession in the Path Fork coal bed (Breathitt Formation, Middle Pennsylvanian), southeastern Kentucky. Org. Geochem. 18, 301–311.

Hower, J.C., Bland, A.E., 1989. Geochemistry of the Pond Creek coal bed. East. Ky. Coalfield: Int. J. Coal Geol. 11, 205–226.

Hower, J.C., Pollock, J.D., 1989. Petrology of the River Gem coal bed, Whitley County, Kentucky. Int. J. Coal Geol. 11, 227–245.

Hower, J.C., Rimmer, S.M., 1991. Coal rank trends in the central Appalachian coalfield: Virginia, West Virginia, and Kentucky. Org. Geochem. 17, 161–173.

Hower, J.C., Riley, J.T., Thomas, G.A., Griswold, T.B., 1991a. Chlorine in Kentucky coals. J. Coal Qual. 10, 152–158.

Hower, J.C., Rimmer, S.M., Bland, A.E., 1991b. Geochemistry of the blue gem coal bed, Knox County, Kentucky. Int. J. Coal Geol. 18, 211–231.

Hower, J.C., Andrews Jr., W.M., Wild, G.D., Eble, C.F., Dulong, F.T., Salter, T.L., 1994a. Coal quality trends for the Fire Clay coal bed, southeastern Kentucky. J. Coal Qual. 13, 13–26.

Hower, J.C., Hiett, J.K., Wild, G.D., Eble, C.F., 1994b. Coal resources, production, and quality in the eastern Kentucky coalfield: perspectives on the future of steam coal production. Nonrenewable Resour. 3, 216–236.

Hower, J.C., Ruppert, L.F., Eble, C.F., Graham, U.M., 1996. Geochemical and palynological indicators of the paleoecology of the River Gem coal bed, Whitley County, Kentucky. Int. J. Coal Geol. 31, 135–149.

Hower, J.C., Ruppert, L.F., Eble, C.F., 1999. Lanthanide, yttrium, and zirconium anomalies in the fire clay coal bed, eastern Kentucky. Int. J. Coal Geol. 39, 141–153.

Hower, J.C., Groppo, J.G., Henke, K.R., Hood, M.M., Eble, C.F., Honaker, R.Q., Zhang, W., Qian, D., 2015a. Notes on the potential for the concentration of rare earth elements and yttrium in coal combustion fly ash. Minerals 5, 356–366.

Hower, J.C., Eble, C.F., O'Keefe, J.M.K., Dai, S., Wang, P., Xie, P., Liu, J., Ward, C.R., French, D., 2015b. Petrology, palynology, and geochemistry of the Gray Hawk coal (Early Pennsylvanian, Langsettian) in eastern Kentucky, USA. Minerals 5, 592–622.

Hower, J.C., Granite, E.J., Mayfield, D., Lewis, A., Finkelman, R.B., 2016. Notes on contributions to the science of rare earth element enrichment. Minerals http://dx.doi.org/10. 3390/min6020032.

Johannesson, K.H., Lyons, W.B., Yelken, M.A., Gaudette, H.E., Stetzenbach, K.J., 1996. Geochemistry of the rare-earth elements in hypersaline and dilute acidic natural terrestrial waters: complexation behavior and middle rare-earth element enrichments. Chem. Geol. 133, 125–144.

Johnston, M.N., Hower, J.C., Dai, S., Wang, P., Xie, P., Liu, J., 2015. Petrology and geochemistry of the Harlan, Kellioka, and Darby coals from the Louellen 7.5-minute quadrangle, Harlan County, Kentucky. Minerals 5, 894–918.

Lyons, P.C., Outerbridge, W.F., Triplehorn, D.M., Evans Jr., H.T., Congdon, R.D., Capiro, M., Hess, J.C., Nash, W.P., 1992. An Appalachian isochron: a kaolinized Carboniferous air-fall volcanic-ash deposit (tonstein). Geol. Soc. Am. Bull. 104, 1515–1527.

Mardon, S.M., Hower, J.C., 2004. Impact of coal properties on coal combustion by-product quality: examples from a Kentucky power plant. Int. J. Coal Geol. 59, 153–169.

Pédrot, M., Dia, A., Davranche, M., 2010. Dynamic structure of humic substances: rare earth elements as a fingerprint. J. Colloid Interface Sci. 345, 206–213.

Rice, C.L., Hiett, J.K., 1994. Revised correlation chart of coal beds, coal zones, and key stratigraphic units in the Pennsylvanian rocks of eastern Kentucky, U.S. Geological Survey Miscellaneous Field Studies Map MF-2275.

Rice, C.L., Belkin, H.E., Henry, T.W., Zartman, R.E., Kunk, M.J., 1994. The Pennsylvanian Fire Clay tonstein of the Appalachian Basin — its distribution, biostratigraphy, and mineralogy. In: Pennsylvanian stratigraphy, central Appalachian Basin, (Rice, C.L., Ed.). Geol. Soc. Am. Spec. Pap. 294, 87–104.

Ruppert, L.F., Moore, T.A., 1993. Differentiation of volcanic ash-fall and water-borne detrital layers in the Eocene Senakin coal bed, Tanjung Formation, Indonesia. Org. Geochem. 20, 233–247.

Sakulpitakphon, T., Hower, J.C., Schram, W.H., Ward, C.R., 2004. Tracking mercury from the mine to the power plant: geochemistry of the Manchester coal bed, Clay County, Kentucky. Int. J. Coal Geol. 57, 127–141.

Seredin, V.V., 1996a. Rare earth element-bearing coals from the Russian far east deposits. Int. J. Coal Geol. 30, 101–129.

Seredin, V.V., 1996b. Rare earth element-bearing coals from the Russian far east deposits. Int. J. Coal Geol. 30, 101–129.

Seredin, V.V., 2004. Metalliferous coals: formation conditions and outlooks for development. Geoinformmark, Moscow, Coal Resources of Russia VI, pp. 452–519 (in Russian).

Seredin, V.V., Dai, S., 2012. Coal deposits as potential alternative sources for lanthanides and yttrium. Int. J. Coal Geol. 94, 67–93.

Seredin, V.V., Shpirt, M., Vassyanovich, A., 1999. REE contents and distribution in humic matter of REE-rich coals. In: Stanley, C.J., et al. (Eds.), Mineral Deposits: Processes to Processing, Rotterdam, A.A. Balkema, pp. 267–269.

Thacker, E.E., Weisenfluh, G.A., Esterle, J.A., Greb, S.F., Hiett, J.K., 2000. Coal Resources of the Fire Clay Coal Zone in Eastern Kentucky. KGS Map and Chart Series 1088, 1 Sheet.

Triplehorn, D.M., Bohor, B.F., 1983. Goyazite in kaolinitic altered tuff beds of Cretaceous age near Denver, CO. Clay Clay Miner. 31, 299–304.

Zielinski, R.A., 1985. Element mobility during alteration of silicic ash to kaolinite—a study of tonstein. Sedimentology 32, 567–579.