minerals

Notes on Contributions to the Science of Rare Earth Element Enrichment in Coal and Coal Combustion Byproducts

James C. Hower [1,*], Evan J. Granite [2,†], David B. Mayfield [3,†], Ari S. Lewis [4,†] and Robert B. Finkelman [5,†]

[1]   Center for Applied Energy Research, University of Kentucky, Lexington, KY 40511, USA
[2]   National Energy Technology Laboratory, U.S. Department of Energy, Pittsburgh, PA 15236-0940, USA; evan.granite@netl.doe.gov
[3]   Gradient, 600 Stewart Street, Suite 1900, Seattle, WA 98101, USA; dmayfield@gradientcorp.com
[4]   Gradient, 20 University Road, Cambridge, MA 02138, USA; alewis@gradientcorp.com
[5]   Department of Geosciences, The University of Texas at Dallas, ROC 21, 800 West Campbell Road, Richardson, TX 75080-3021, USA; bobf@utdallas.edu
*   Correspondence: james.hower@uky.edu; Tel.: +1-859-257-0261
†   These authors contributed equally to this work.

Abstract: Coal and coal combustion byproducts can have significant concentrations of lanthanides (rare earth elements). Rare earths are vital in the production of modern electronics and optics, among other uses. Enrichment in coals may have been a function of a number of processes, with contributions from volcanic ash falls being among the most significant mechanisms. In this paper, we discuss some of the important coal-based deposits in China and the US and critique classification systems used to evaluate the relative value of the rare earth concentrations and the distribution of the elements within the coals and coal combustion byproducts.

1. Introduction

Coal is a precious resource, both in the United States and around the world. The United States has a 250-year supply of coal, and generates between 30%–40% of its electricity through coal combustion. Approximately 1 Gt of coal has been mined annually in the US, although the 2015 total will likely be closer to 900 Mt [1]. Most of the coal is burned for power generation, but substantial quantities are also employed in the manufacture of steel, chemicals, and activated carbons. Coal has a positive impact upon many industries, including mining, power, rail transportation, manufacturing, chemical, steel, activated carbon, and fuels. Everything that is in the Earth's crust is also present within coal to some extent, and the challenge is always to utilize abundant domestic coal in clean and environmentally friendly manners. In the case of the rare earth elements, these valuable and extraordinarily useful elements are present within the abundant coal and coal byproducts produced domestically and world-wide. These materials include the coals, as well as the combustion by-products such as ashes, coal preparation wastes, gasification slags, and mining byproducts. All of these materials can be viewed as potential sources of rare earth elements. Most of the common inorganic lanthanide compounds, such as the phosphates found in coal, have very high melting, boiling, and thermal decomposition temperatures, allowing them to concentrate in combustion and gasification by-products. Furthermore, rare earths have been found in interesting concentrations in the strata above and below certain coal seams.

The National Energy Technology Laboratory (NETL) initiated research for the determination and recovery of rare earths from abundant domestic coal by-products in 2014. The NETL Rare Earth EDX Database [2] is a resource for rare earth information as related to coal and byproducts. Many other research organizations have also initiated efforts for the determination and recovery of rare earths from unconventional sources, such as coal byproducts.

Fifty years ago, the rare earth elements (REE) were little more than an interesting diversion from the study of more commercially and environmentally important elements. As stated by Gschneidner [3] "*we know what we know about the Fraternal Fifteen [the rare earth elements, REE] essentially because of scientific curiosity, and this is still one of the most important reasons for studying the rare earths.*" While he did anticipate wider applications of the niche uses at the time of his pamphlet, some applications were still decades away [4].

Today, numerous technologies and devices rely upon rare earth elements. Important commercial uses of REEs include automotive catalytic converters, petroleum refining catalysts, metallurgical additives and alloys, permanent magnets and rechargeable batteries (for hybrid vehicles, wind turbines, and mobile phones), phosphors (for lighting and flat panel displays), glass polishing and ceramics, and medical devices [5]. In short, modern society has become increasingly dependent on the REEs (Figure 1). Due to the growing application of REEs in modern technology (particularly sustainable energy), many countries are developing strategies to obtain or develop additional sources of REE materials [5–7]. While traditional mining has typically provided the majority of REEs, current limitations with developing new mines has resulted in the search for alternative sources, including coal and coal combustion byproducts [8].
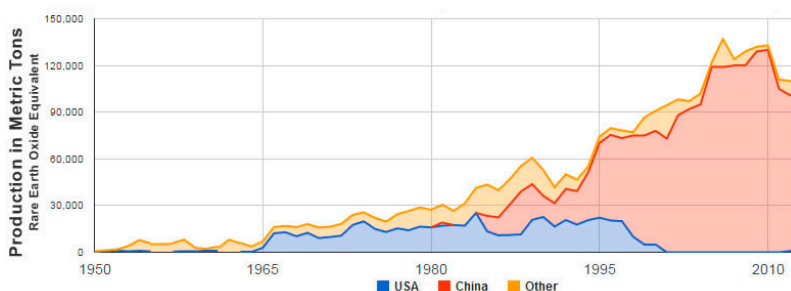

Figure 1. Production of REE oxides from 1950 in USA, China, and other countries.

Within the context of the expanded use of the rare earths and the widening search for economic sources of the elements, Seredin and Dai [9] made a fundamental theory in understanding of the origin and distribution of REEs or REE + yttrium (REY) in coal and, by extension, in coal combustion byproducts such as fly ash and bottom ash. While their paper was developed largely in the context of Chinese and former Soviet deposits, the background was built on knowledge of occurrences in Bulgaria [10–18]; Kentucky [19,20]; Utah [21]; Wyoming [22]; the Russian Far East [23]; China [24–29]; and elsewhere.

2. Rare Earth Elements in Coals

Several studies [30–33] have addressed the origin of rare earth elements in coal. Eskenazy [10–16] discussed the complications of REY enrichment in coals. Dealing primarily with lignites, Eskenazy [11,15] was able to observe organic associations not nearly as evident in the bituminous coals studied elsewhere. The loosely bound REE on clays could be desorbed by acidic waters, with heavy REE (HREE) preferentially desorbed and the subsequent increase in HREE in solution would lead to enrichment in HREE bound to organics [11,13]. As a supplemental or alternative source, the high organic-bound HREE could have resulted from high HREE in the waters feeding the swamp [13]. HREE generally have a stronger organic affinity than light REE (LREE) and HREE complexes are

more stable than LREE complexes. Independent of peat or coal associations, soil studies by Aide and Aide [34] confirmed that HREE-organic complexes are more stable than LREE-organic complexes. Decreases in pH cause a decrease in the stability of the REE-organic complexes [35,36]. In testing of humic acids extracted from a Bulgarian lignite [15], Eskenazy found that Na^+, K^+, Ca^{2+}, and Mg^{2+} bound to –COOH and –OH were replaced by REE cations.

Using a suite of bench samples from a Texas lignite strip mine Finkelman [37] demonstrated that the chondrite-normalized REE distribution pattern changed systematically with the ash yield. The high-ash bench (77 wt % ash) had a REE distribution pattern similar to those of North American shales and high-ash bituminous coals. With lower ash yields (3–51 wt %), the patterns were progressively flatter, indicating a higher proportion of heavier REE elements in the organic-rich benches. He interpreted this trend to indicate that the heavy REE (Eu to Lu) are preferentially complexed with the organics. Finkelman [37] estimated that no more than 10% of the total REE in the lignite had an organic association; the remaining 90% of the REE were associated with REE-bearing minerals.

Finkelman and Palmer (U.S. Geological Survey, unpublished data) used selective leaching on 14 bituminous coals, five subbituminous coals, and one lignite to determine the modes of occurrence of 37 elements including Y, Ce, La, Lu, Nd, Sm, and Yb. Based on the response of the elements to ammonium acetate, hydrochloric acid, hydrofluoric acid, and nitric acid leaches they concluded that in the bituminous samples approximately 70% of the light rare earths (Y, Ce, La, and Nd) were associated with phosphate minerals, about 20% were associated with clays, and about 10% were in carbonate minerals. A smaller proportion was organically associated. The heavier rare earths (Sm, Yb) were primarily associated with phosphates (50%), clays (20%), organics (30%), and carbonates. In contrast, the light rare earth elements in the lower rank coals were associated with clays (60%), phosphates (20%), carbonates (20%), and organics. The heavier rare earths were also associated with clays (50%), phosphates (25%), and carbonates, but had a much larger (25%) proportion associated with organics.

In contrast to Eskenazy's findings of strong HREE-organic associations [11,13,14], Seredin *et al.* [38], in their study of an Eocene subbituminous coal and a Miocene lignite from the Russian Far East, could not universally verify the association. Consequently, they noted that some high HREE concentrations in coal could not be explained by the higher sorption capacity or by higher HREE chelate stability, but rather by elevated HREE in waters which interacted with the organics.

Some Kentucky, Utah, and Wyoming REY occurrences are largely the result of volcanic ash falls. Crowley *et al.* [21] noted three enrichment mechanisms:

(1)   Leaching of volcanic ash with subsequent concentration by organic matter;
(2)   Leaching of volcanic ash with subsequent incorporation into secondary minerals; and
(3)   Incorporation of volcanic minerals into the peat.

Hower *et al.* [19] found that the coal immediately underlying the Fire Clay coal tonstein had 1965–4198 ppm (ash basis) REY, with REE-rich monazite and Y-bearing crandallite as the detectable REY minerals. The 4198-ppm REY lithotype contains thin lenses of the volcanic ash. They noted that, while volcanic glass may not have been stable in organic acids, zircons survived in the lithotype, as indicated by the 4540 ppm Zr (ash basis). Similarly, the Fire Clay-correlative Dean coal section in southern Knox County, Kentucky, has an REY enrichment (based on comparisons to REE levels in other coals in the region) but does not contain a tonstein [20], just as Crowley *et al.* [21] found in their study of Wyoming coals. In the central Eastern Kentucky Fire Clay coal locations, Hower *et al.* [19] noted the following enrichment mechanisms:

(1)   The highest LREE/HREE occurs in the tonstein and in the coal or illitic shale immediately underlying the tonstein;
(2)   The other lithotypes, in particular in the basal and uppermost lithotypes, have a lower LREE/HREE, suggesting concentration in secondary minerals.

Seredin [23] studied a complex assemblage of coals and volcanics in the Russian Far East. The REY entered the peat in a dissolved form. The bulk of the REY in the low-rank coals was sorbed onto

the organics. The mineral assemblages included Eu-rich LREE phosphates with no Th or Y; HREE phosphates deposited on kaolinite; (Ca, Ba, Sr)-bearing aluminophosphates (crandallite) with LREE deposited on kaolinite; LREE-bearing F and Cl carbonates; REE-carbonates, -oxides, and -hydroxides; and other unknown REE mineral species. Based on the high concentrations of REY, he encouraged the recovery of REY from coal combustion by-products, something only considered for U and Ge at that time. Mardon and Hower [20], examining the path of the REY-enriched Dean coal from the mine to the boiler to the ash-collection system at a utility power plant, found that the REY were in concentrations exceeding 1600 ppm in some of the electrostatic-precipitator fly ashes.

The fundamental contributions of Dai and his colleagues [24–26,28,29] were based on deposits in the Jungar and Daqingshan coalfields, Inner Mongolia, and in host rocks in the Late Permian coal-bearing strata from Eastern Yunnan [39].

The interest in the Jungar coals has been driven by the prospects for commercial recovery of gallium, which substitutes for Al in boehmite [24–26], and Al from the coal combustion byproducts [29,40,41]. The REY is low in the partings and relatively high in the coal [25,26], attributed to leaching and incorporation in Al-hydrate minerals, goyazite, and organic matter [25,26]. For example, the REE content of one parting and its underlying coal bench were 231 and 1006 ppm. The LREE are both occur in Sr- and Ba-bearing minerals and have an organic affinity while the HREE are enriched in Sc-, Zr-, and Hf-bearing minerals [26]. The relative organic affinity of LREE *versus* HREE was found to vary between mines within the Jungar coalfield, perhaps indicative of different REE sources [28]. Examining the Light REY (LREY; La, Ce, Pr, Nd, and Sm), Medium REY (MREY; Eu, Gd, Tb, Dy, and Y), and Heavy REY (HREY; Ho, Er, Tm, Yb, and Lu), and the L-type ($La_N/Lu_N > 1$), M-type ($La_N/Sm_N < 1$; $Gd_N/Lu_N > 1$), and H-type ($La_N/Lu_N < 1$) distributions, Dai *et al.* [29] found LREY associations in goyazite and gorceixite, MREY and HREY in boehmite, and some indications of MREY and HREY associations in accessory minerals. L-type REE distributions are found in the upper portion of the Pennsylvanian No. 6 coal, Guanbanwusu mine, due to REE-rich colloidal input from weathered bauxite [29]. The H-type enrichment in the lower portion of the same coal is attributed to natural water influences. In both cases, mixed influences were evident.

The coal-bearing strata of Late Permian Xuanwei Formation in eastern Yunnan (Southwestern China) have (Nb, Ta)$_2$O$_5$–(Zr, Hf)O$_2$–(REY)$_2$O$_3$–Ga in 1–10-m-thick alkalic ore beds of pyroclastic origin [39]. Dai *et al.* [39] identified four types of ore lithologies: clay altered volcanic ash, tuffaceous clay, tuff, and volcanic breccia. The minerals associated with the above elevated concentrations of rare metals (e.g., the most common REY-bearing minerals monazite and xenotime) are rare, suggesting that the rare elements occur as adsorbed ions. Although the mineralization of (Nb, Ta)$_2$O$_5$–(Zr, Hf)O$_2$–(REY)$_2$O$_3$–Ga assemblage has been identified in felsic and alkalic tonsteins in many coal deposits for many years [19,21,42–47], this mineralization anomaly has never caused particular interest as raw materials for rare metals, owing to the low thickness (from 1–20 cm, mostly 3–6 cm) of the tonsteins. However, the occurrence of such thin tonsteins provides a basis for predicting the possibility of thick horizons of Nb–Zr–REY-bearing tuffs outside of coal seams [44]. This forecast has been successfully realized in China by discovery of such thick alkalic ore beds in Yunnan Province by Dai *et al.* [39], and thus, previous skeptical views in relation to this mineralization in coal-bearing strata should be reconsidered. As pointed out by Spears [46], *"Linked to the tonstein studies, Dai et al. (2010) found a new rare metal deposit comprised of several Nb–Zr–REE–Ga bearing tuffaceous horizons with thicknesses up to 10 m in Yunnan province,"* and to the best of our knowledge, this the first successful case of the application from the tonstein academic theory to discovery of rare-metal ore deposits.

3. Seredin and Dai Synthesis

Seredin and Dai [9] reinforced some of the basic principles outlined above, as shown in Table 1 (Table 2 as cited in [9]). The introduction of REY into a peat or coal falls into four basic paths. As we saw above, few coals are likely to have one dominant source of REY. Indeed, the Jungar coals were noted to have multiple modes of REY emplacement [25,26]. Similarly, while the Dean (Fire Clay) coal

REY is dominated by the REY-rich tonstein and the enrichment of adjacent coal lithologies through the leaching of REY from the tonstein, the coal bed had a depositional history prior to and following the ash fall [19]. In particular, Eastern Kentucky coals typically have TiO_2- and Zr-enriched basal lithologies which can also have REY enrichment [19,20]. For example, a section of the Fire Clay coal has 1358-ppm-REY (ash basis) basal lithotype, significantly less than the 4251-ppm-REY (ash basis) lithotype immediately underlying the tonstein, but double the 680-ppm-REY (ash basis) concentration in the lithotypes between those two portions of the coal [19]. Basically, on a whole-seam basis, and probably also for most lithotypes, mixed modes of REY emplacement are to be expected but it is also important to understand the end members in order to fully understand the continuum.

Table 1. The main genetic types of high REY accumulation in coals. After Seredin and Dai [9].

Type	REO Content in Ash, %	Associated Elements	Typical Example
Terrigenous	0.1–0.4	Al, Ga, Ba, Sr,	Jungar, China [25,26]
Tuffaceous	0.1–0.5	Zr, Hf, Nb, Ta, Ga	Dean, USA [20]
Infiltrational	0.1–1.2	U, Mo, Se, Re	Aduunchulun, Mongolia [48]
Hydrothermal	0.1–1.5	As, Sb, Hg, Ag, Au, *etc.*	Rettikhovka, Russia [49]

REO, oxides of rare earth elements and yttrium.

In addition to the classification of light-, medium-, and heavy-REY, as well as the corresponding enrichment types (L-, M-, and H-types), Seredin and Dai [9] set a criterion of REY concentration evaluation of REO content ⩾ 1000 ppm in coal ash, or 800–900 ppm in coal ash for coal seams with thicknesses of > 5 m, as the cut-off grade or beneficial recovery of the REY. The second criterion they set in their work for the evaluation of coal ash as REY raw materials is the individual composition of the elements. Seredin and Dai's [9] Figure 6 (Figure 2 in this paper) is a synthesis of the REY concentration in coal ashes and non-coal REY-enriched deposits compared to an expression of the current commercial need as weighted by the availability of the individual elements. The *x* axis, the outlook coefficient, is calculated as [9,50]:

$$C_{outl} = ((Nd + Eu + Tb + Dy + Er + Y/\Sigma REY)/((Ce + Ho + Tm + Yb + Lu)/\Sigma REY)$$
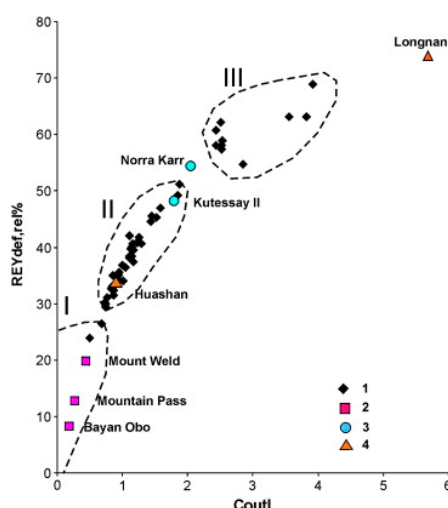
Figure 2. Classification of REY-rich coal ashes by outlook for individual REY composition in comparison with selected deposits of conventional types. 1, REE-rich coal ashes; 2, carbonatite deposits; 3, hydrothermal deposits; and 4, weathered crust elution-deposited (ion-adsorbed) deposits. Clusters of REE-rich coal ashes distinguished by outlook for REY composition (numerals in figure): I, unpromising; II, promising; and III, highly promising. From Seredin and Dai [9].

The *y* axis (REY$_{def, rel\%}$) is the percentage of critical REY (Figure 3) in the total REY. Cluster I, which includes some of the mined REE ores, is not as promising as Cluster II. Seredin and Dai [9] noted that mining of Cluster I "*will neither mitigate the crisis in REY resources nor eliminate the shortage of the most critical REY, but will only result in overproduction of excessive Ce (p. 75).*" Cluster II, with a variety of L-, M-, and H-type distributions, contains many of the known coal ashes, including the Dean (Fire Clay) ash. Given concentrations exceeding the economic threshold, a variable, coal ashes in the Cluster II concentration and C$_{outl}$ range would be promising resources. Cluster III contains H-type REY's with hydrothermal origins. Seredin-Dai's classification and evaluation criteria of REY in coal deposits have been adopted and used by a number of researchers ([51–58], among others).
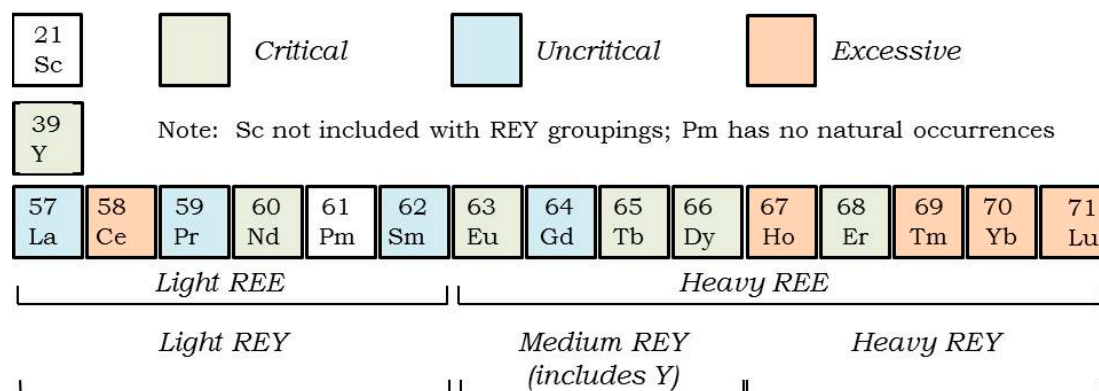
Figure 3. Divisions of lanthanides and yttrium into light, medium, and heavy REY; light and heavy REE; and critical, uncritical, and excessive groups (after Seredin [50] and Seredin and Dai [9]).

Coal scientists have identified coals that were successfully utilized as raw materials for rare-metal recovery during periods of raw material crises [41]. The first time the coal deposits were used as the major source of uranium was for the incipient nuclear industries in the former USSR and the United States following World War II. The second time was that the coal deposits are one of the major Ge sources for world industry. The third time, Al and Ga extraction was expanded from Jungar coal ashes of Northern China [41]. It is now time to address the coal-hosted rare earth elements and yttrium from coal deposits as a byproduct not only because of the REY supply crisis in recent years, but also because the distinct benefits of REY extraction from coal ash, such as the relatively low cost for the necessary infrastructure as compared to developing new mining projects, as well as the benefits associated with recycling of a waste product.

4. Conclusions

Much of the recent research on coal utilization in the United States has focused upon the capture of pollutants such as acid gases, particulates, and mercury, and the greenhouse gas carbon dioxide. The possible recovery of rare earth elements from abundant coal and byproducts is an exciting new research area. Additional data is needed on the rare earth contents of coals and byproducts in order to determine the most promising potential feed materials for extraction processes. Future work will likely focus on the characterization of coals and byproducts, as well as on separation methods for rare earth recovery.

Conflicts of Interest: This paper/information was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents

that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References

1. US Department of Energy Coal Production Statistics. Available online: http://www.eia.gov/coal/production/quarterly/ (accessed on 29 January 2016).
2. US Department of Energy Rare Earth EDX Database. Available online: https://edx.netl.doe.gov/ree/ (accessed on 29 January 2016).
3. Gschneidner, K.A., Jr. *Rare Earths: The Fraternal Fifteen*; United States Atomic Energy Commission. Division of Technical Information: Washington, DC, USA, 1964; p. 46.
4. Dent, P.C. Rare Earth Future. Available online: http://www.magneticsmagazine.com/main/channels/materials-channels/rare-earth-future/ (accessed on 25 March 2016).
5. Pecht, M.G.; Kaczmarek, R.E.; Song, X.; Hazelwood, D.A.; Kavetsky, R.A.; Anand, D.K. *Rare Earth Materials: Insights and Concerns*; CALCE EPSC Press: College Park, MD, USA, 2012; p. 194.
6. U.S. Department of Energy. *Critical Materials Strategy*; U.S. Department of Energy: Washington, DC, USA, 2011; p. 197. Available online: http://energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf (accessed on 25 March 2016).
7. European Commission. Report on Critical Raw Materials for the EU. In *Report of the Ad Hoc Working Group on Defining Critical Raw Materials*; European Commission: Bruxelles, Belgium, 2014; p. 41. Available online: http://ec.europa.eu/DocsRoom/documents/10010/attachments/1/translations/en/renditions/native (accessed on 25 March 2016).
8. Mayfield, D.B.; Lewis, A.S. Environmental review of coal ash as a resource for rare earth and strategic elements. In Proceedings of the 2013 World of Coal Ash (WOCA) Conference, Lexington, KY, USA, 22–25 April 2013; pp. 22–25. Available online: http://www.flyash.info/2013/051-mayfield-2013.pdf (accessed on 25 March 2016).
9. Seredin, V.V.; Dai, S. Coal deposits as a potential alternative source for lanthanides and yttrium. *Int. J. Coal Geol.* **2012**, *94*, 67–93. [CrossRef]
10. Eskenazy, G. Rare-earth elements in some coal basins of Bulgaria. *Geol. Balc.* **1978**, *8*, 81–88.
11. Eskenazy, G.M. Rare earth elements and yttrium in lithotypes of Bulgarian coals. *Org. Geochem.* **1987**, *11*, 83–89. [CrossRef]
12. Eskenazy, G.M. Zirconium and hafnium in Bulgarian coals. *Fuel* **1987**, *66*, 1652–1657. [CrossRef]
13. Eskenazy, G.M. Rare earth elements in a sampled coal from the Pirin Deposit, Bulgaria. *Int. J. Coal Geol.* **1987**, *7*, 301–314. [CrossRef]
14. Eskenazy, G. 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* **1995**, *88*, 39–65.
15. Eskenazy, G.M. Aspects of the geochemistry of rare earth elements in coal: An experimental approach. *Int. J. Coal Geol.* **1999**, *38*, 285–295. [CrossRef]
16. Eskenazy, G.M. Sorption of trace elements on xylain: An experimental study. *Int. J. Coal Geol.* **2015**, *150–151*, 166–169.
17. Eskenazy, G.M.; Mincheva, E.I.; Rousseva, D.P. Trace elements in lignite lithotypes from the Elhovo coal basin. *Comptes rendus del'Académie bulgare des Sciences* **1986**, *39*, 99–101.
18. Eskenazy, G.M.; Brinkin, K. Trace elements in the Karlovo coal deposit. *Comptes rendus del'Académie bulgare des Sciences* **1991**, *44*, 67–70.
19. Hower, J.C.; Ruppert, L.F.; Eble, C.F. Lanthanide, Yttrium, and Zirconium anomalies in the Fire Clay coal bed, Eastern Kentucky. *Int. J. Coal Geol.* **1999**, *39*, 141–153. [CrossRef]
20. Mardon, S.M.; Hower, J.C. Impact of coal properties on coal combustion by-product quality: Examples from a Kentucky power plant. *Int. J. Coal Geol.* **2004**, *59*, 153–169. [CrossRef]
21. Crowley, S.S.; Stanton, R.W.; Ryer, T.A. The effects of volcanic ash on the maceral and chemical composition of the C coal bed, Emery Coal Field, Utah. *Org. Geochem.* **1989**, *14*, 315–331. [CrossRef]

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

23. Seredin, V.V. Rare earth element-bearing coals from the Russian Far East deposits. *Int. J. Coal Geol.* **1996**, *30*, 101–129. [CrossRef]

24. Dai, S.; Ren, D.; Li, S. Discovery of the superlarge gallium ore deposit in Junger, Inner Mongolia, North China. *Chin. Sci. Bull.* **2006**, *51*, 2243–2252. [CrossRef]

25. Dai, S.; Ren, D.; Chou, C.L.; Li, S.; Jiang, Y. Mineralogy and geochemistry of the No. 6 coal (Pennsylvanian) in the Jungar Coalfield, Ordos Basin, China. *Int. J. Coal Geol.* **2006**, *66*, 253–270. [CrossRef]

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

27. Dai, S.; Wang, X.; Chen, W.; Li, D.; Chou, C.L.; Zhou, Y.; Zhu, C.; Li, H.; Zhu, X.; Xing, Y.; *et al.* A high-pyrite semianthracite of Late Permian age in the Songzao Coalfield, southwestern China: Mineralogical and geochemical relations with underlying mafic tuffs. *Int. J. Coal Geol.* **2010**, *83*, 430–445. [CrossRef]

28. Dai, S.; Zou, J.; Jiang, Y.; Ward, C.R.; Wang, X.; Li, T.; Xue, W.; Liu, S.; Tian, H.; Sun, X.; *et al.* 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.* **2012**, *94*, 250–270. [CrossRef]

29. Dai, S.; Jiang, Y.; Ward, C.R.; Gu, L.; Seredin, V.V.; Liu, H.; Zhou, D.; Wang, X.; Sun, Y.; Zou, J.; *et al.* 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.* **2012**, *98*, 10–40. [CrossRef]

30. Birk, D.; White, J.C. Rare earth elements in bituminous coals and underclays of the Sydney Basin, Nova Scotia: Element sites, distribution, mineralogy. *Int. J. Coal Geol.* **1991**, *19*, 219–251. [CrossRef]

31. Kortenski, J.; Bakardjiev, S. Rare earth and radioactive elements in some coals from the Sofia, Svoge and Pemik Basins, Bulgaria. *Int. J. Coal Geol.* **1993**, *22*, 237–246. [CrossRef]

32. Pollock, S.M.; Goodarzi, F.; Riediger, C.L. Mineralogical and elemental variation of coal from Alberta, Canada: An example from the No.2 seam, Genesee Mine. *Int. J. Coal Geol.* **2000**, *43*, 259–286. [CrossRef]

33. Schatzel, S.J.; Stewart, B.W. Rare earth element sources and modification in the Lower Kittanning coal bed, Pennsylvania: Implications for the origin of coal mineral matter and rare earth element exposure in underground mines. *Int. J. Coal Geol.* **2003**, *54*, 223–251. [CrossRef]

34. Aide, M.T.; Aide, C. Rare earth elements: Their importance in understanding soil genesis. *ISRN Soil Sci.* **2012**, *2012*. [CrossRef]

35. Pédrot, M.; Dia, A.; Davranche, M. Dynamic stricture of humic substances: Rare earth elements as a fingerprint. *J. Colloid Interface Sci.* **2010**, *345*, 206–213. [CrossRef] [PubMed]

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

37. Finkelman, R.B. The origin, occurrence, and distribution of the inorganic constituents in low-rank coals. In Proceedings of the Basic Coal Science Workshop, Houston, TX, USA, 8–9 December 1981; Schobert, H.H., Ed.; Grand Forks Energy Technology Center: Grand Forks, ND, USA, 1981; pp. 70–90.

38. Seredin, V.; Shpirt, M.; Vassyanovich, A. REE contents and distribution in humic matter of REE-rich coals. In *Mineral Deposits: Processes to Processing*; Stanley, C.J., Ed.; A.A. Balkema: Rotterdam, The Netherlands, 1999; pp. 267–269.

39. Dai, S.; Zhou, Y.; Zhang, M.; Wang, X.; Wang, J.; Song, X.; Jiang, Y.; Luo, Y.; Song, Z.; Yang, Z.; *et al.* A new type of Nb (Ta)–Zr(Hf)–REE–Ga polymetallic deposit in the late Permian coal-bearing strata, eastern Yunnan, southwestern China: Possible economic significance and genetic implications. *Int. J. Coal Geol.* **2010**, *83*, 55–63. [CrossRef]

40. Dai, S.; Zhao, L.; Peng, S.; Chou, C.L.; Wang, X.; Zhang, Y.; Li, D.; Sun, Y. 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.* **2010**, *81*, 320–332. [CrossRef]

41. Seredin, V.V. From coal science to metal production and environmental protection: A new story of success. *Int. J. Coal Geol.* **2012**, *90–91*, 1–3. [CrossRef]

42. Arbuzov, S.I.; Ershov, V.V.; Potseluev, A.A.; Rikhvanov, L.P. *Rare Elements in Coals of the Kuznetsk Basin*; Publisher House KPK: Kemerovo, Russia, 2000; p. 248. (In Russian)

43. Arbuzov, S.I.; Mezhibor, A.M.; Spears, D.A.; Ilenok, S.S.; Shaldybin, M.V.; Belaya, E.V. Nature of tonsteins in the Azeisk deposit of the Irkutsk Coal Basin (Siberia, Russia). *Int. J. Coal Geol.* **2016**, *153*, 99–111. [CrossRef]

44. Seredin, V.V. The first data on abnormal Niobium content in Russian coals. *Dokl. Earth Sci.* **1994**, *335*, 634–636.

45. Seredin, V.V.; Finkelman, R.B. Metalliferous coals: A review of the main genetic and geochemical types. *Int. J. Coal Geol.* **2008**, *76*, 253–289. [CrossRef]

46. Spears, D.A. The origin of tonsteins, an overview, and links with seatearths, fireclays and fragmental clay rocks. *Int. J. Coal Geol.* **2012**, *94*, 22–31. [CrossRef]

47. Zhou, Y.; Bohor, B.F.; Ren, Y. Trace element geochemistry of altered volcanic ash layers (tonsteins) in late Permian coal-bearing formations of eastern Yunnan and western Guizhou Provinces, China. *Int. J. Coal Geol.* **2000**, *44*, 305–324. [CrossRef]

48. Arbuzov, S.I.; Mashen'kin, V.S. Oxidation zone of coalfields as a promising source of noble and rare metals: A case of coalfields in Central Asia. In *Problems and Outlook of Development of Mineral Resources and Fuel-Energetic Enterprises of Siberia*; Tomsk Polytechnic University: Tomsk, Russia, 2007; pp. 26–31. (In Russian)

49. Seredin, V.V. Metalliferous coals: Formation conditions and outlooks for development. In *Coal Resources of Russia*; Geoinformmark: Moscow, Russia, 2004; Volume 6, pp. 452–519. (In Russian)

50. Seredin, V.V. A new method for primary evaluation of the outlook for rare earth element ores. *Geol. Ore Depos.* **2010**, *52*, 428–433. [CrossRef]

51. Blissett, R.S.; Smalley, N.; Rowson, N.A. An investigation into six coal fly ashes from the United Kingdom and Poland to evaluate rare earth element content. *Fuel* **2014**, *119*, 236–239. [CrossRef]

52. Saikia, B.K.; Ward, C.R.; Oliveira, M.L.S.; Hower, J.C.; Leao, F.D.; Johnston, M.N.; O'Bryan, A.; Sharma, A.; Baruah, B.P.; Silva, L.F.O. Geochemistry and nano-mineralogy of feed coals, mine overburden, and coal-derived fly ashes from Assam (North-east India): A multi-faceted analytical approach. *Int. J. Coal Geol.* **2015**, *137*, 19–37. [CrossRef]

53. Chen, J.; Chen, P.; Yao, D.; Liu, Z.; Wu, Y.; Liu, W.; Hu, Y. Mineralogy and geochemistry of Late Permian coals from the Donglin Coal Mine in the Nantong coalfield in Chongqing, southwestern China. *Int. J. Coal Geol.* **2015**, *149*, 24–40. [CrossRef]

54. Franus, W.; Wiatros-Motyka, M.M.; Wdowin, M. Coal fly ash as a resource for rare earth elements. *Environ. Sci. Pollut. Res.* **2015**, *22*, 9464–9474. [CrossRef] [PubMed]

55. Zhao, L.; Ward, C.R.; French, D.; Graham, I.T. Major and Trace Element Geochemistry of Coals and Intra-Seam Claystones from the Songzao Coalfield, SW China. *Minerals* **2015**, *5*, 870–893. [CrossRef]

56. Hower, J.C.; Eble, C.F.; O'Keefe, J.M.K.; Dai, S.; Wang, P.; Xie, P.; Liu, J.; Ward, C.R.; French, D. Petrology, Palynology, and Geochemistry of Gray Hawk Coal (Early Pennsylvanian, Langsettian) in Eastern Kentucky, USA. *Minerals* **2015**, *5*, 894–918. [CrossRef]

57. Zhang, W.; Rezaee, M.; Bhagavatula, A.; Li, Y.; Groppo, J.; Honaker, R. A review of the occurrence and promising recovery methods of rare earth elements from coal and coal by-products. *Int. J. Coal Prep. Util.* **2015**, *35*, 295–330. [CrossRef]

58. Li, B.; Zhuang, X.; Li, J.; Querol, X.; Font, O.; Moreno, N. Geological controls on mineralogy and geochemistry of the Late Permian coals in the Liulong Mine of the Liuzhi Coalfield, Guizhou Province, Southwest China. *Int. J. Coal Geol.* **2016**, *154–155*, 1–15. [CrossRef]