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A review of anomalous rare earth elements and yttrium in coal

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ABSTRACT

Coal deposits have attracted much attention in recent years as promising alternative raw sources for rare earth elements and yttrium (REY), not only because the REY concentrations in many coals or coal ashes are equal to or higher than those found in conventional types of REY ores but also because of the world-wide demand for REY in recent years has been greater than supply. In addition to anomalies of enrichment or depletion of light-, medium-, and heavy-REY in coal deposits (normalized to Upper Continental Crust, Post-Archean Australian Shale, or North American Shale Composite), anomalies of redox-sensitive Ce and Eu, and, in some cases, of non-redox-sensitive La, Gd, and Y, could be used as geochemical indicators of the sediment-source region, sedimentary environment, tectonic evolution, and post-depositional history of coal deposits. Factors controlling REY anomalies in coal deposits include the geochemistry of terrigenous source rocks, ingress of hydrothermal fluids, influence of marine environments, percolating natural waters, volcanic ashes, and sedimentary environments of peat formation. Additionally, the smoothness of a normalized REY distribution pattern provides a simple but reliable basis for testing the quality of REY chemical analyses for coal and other sedimentary rocks.

Contents

1. Introduction

The demand for rare earth elements (REE) and yttrium has grown due to their wide applications as metal catalysts, phosphors, light-emitting diodes, permanent magnets, various components for renewable green energy equipment, and batteries (Pecht et al., 2012; Hower et al., 2016). The importance of REE has been universally recognized in the last ten years due to relative changes in supply and demand (Kronholm et al., 2013; Mayfield and Lewis, 2013; Blissett et al., 2014; Scott et al., 2015; Franus et al., 2015). The term REE or REY has been used somewhat inconsistently in the geochemical literature (Loges et al., 2012), but in this study REY (or REE if yttrium is not included) is used to specifically represent the elemental suite La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, and Lu. The ionic radius of Y^{3+} is very

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similar to that of Ho^{3+}, and thus Y^{3+} can be placed between isovalent Dy^{3+} and Ho^{3+} in normalized REY distribution patterns (Bau, 1996; Seredin and Dai, 2012). The oxides of REY in this study are represented by the abbreviation REO. Based on the geochemical classification of Seredin and Dai (2012), the REY in coal are classified into light (LREY - La, Ce, Pr, Nd, and Sm), medium (MREY - Eu, Gd, Tb, Dy, and Y), and heavy (HREY - Ho, Er, Tm, Yb, and Lu) groups. This classification is more convenient than other classifications (e.g., two-fold geochemical classifications) for description of the REY distribution in coals (Seredin and Dai, 2012).

Goldschmidt and Peters (1933) were the first to study the REE in coal in any detail. Coal deposits have since become an important alternative source for REY (Seredin and Dai, 2012; Hower et al., 2015a, 2016), as REY concentrations in some coals and/or coal ashes are equal to or higher than those found in conventional types of REY ores (e.g., carbonatites, alkaline granites, and weathering crusts; Seredin and Dai, 2012; Seredin et al., 2013). In 2015, the U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL) selected 10 projects to receive funding for research in support of their program on recovery of rare earth elements from coal and coal byproducts; the selected research projects were focused on the development of cost-effective and environmentally benign approaches for the recovery of rare earth elements from U.S. domestic coal and coal byproducts (http://www.netl.doe.gov/; Release date, December 02, 2015).

Rare earth elements and yttrium have been widely used for many years as geochemical indicators (Bau et al., 2014) of the sedimentary environment and post-depositional history of coal deposits because of their coherent behavior during different geochemical processes and their predictable patterns of fractionation (Eskenazy, 1987a, 1987b; Kortenski and Bakardjiev, 1993; Van der Flier-Keller, 1993; Hower et al., 1999, 2015a, 2015b; Schatzel and Stewart, 2003; Qi et al., 2007; Seredin, 1996, 1998, 2005; Seredin and Finkelman, 2008; Seredin and Dai, 2012; Dai et al., 2015b), such as anomalies of La, Ce, Eu, Gd, and Y, and the enrichment or depletion of light-, medium-, and heavy-REY.

The smoothness of a normalized (to Upper Continental Crust, UCC; Post-Archean Australian Shale, PAAS, or North American Shale Composite, NASC) REY distribution pattern provides a simple but reliable basis for testing the quality of REY chemical analyses of coal and other sedimentary rocks. For example, although anomalies may exist for redox-sensitive (Ce and Eu) and non-redox-sensitive (La, Gd, and Y) elements, other REY in the distribution patterns would not be expected to have anomalies; otherwise, the quality of the analytical REY data would be questionable. For example, elements Pr, Er, and Tm, which would not be expected to display anomalies, show distinct anomalous patterns in Fig. 1, suggesting questionable determined concentrations in the investigated samples. The anomalies of La, Gd, and Y arise because of subtle differences among the stabilities of REY complexes (Bau et al., 2014). The REY data for coal and host rocks cited from published literature and presented in this paper show smoothness (with exceptions of anomalous REY), suggesting the reliability of analytical procedures; otherwise, the REY data in the literature have been regarded as questionable and have not been used.

The main purpose of this paper is to provide a critical review on the current state of knowledge on anomalous REE + Y concentrations within coal basins. There is a bias towards coals from China, Far East Russia, and the eastern USA, as coals in these regions contain anomalous concentrations of REE + Y and have been studied by a number of people. The most important areas which require further detailed studies include the mechanisms of REE incorporation into coal-forming peat mires, how REE become mobilized during and after the coalification process, and the relative importance of primary versus secondary REE concentration mechanisms.

2. Concentration anomalies of REY in coal

The average concentrations of REY for world low-rank and hard coals, as well as those for Chinese and US coals, are presented in Table 1. The

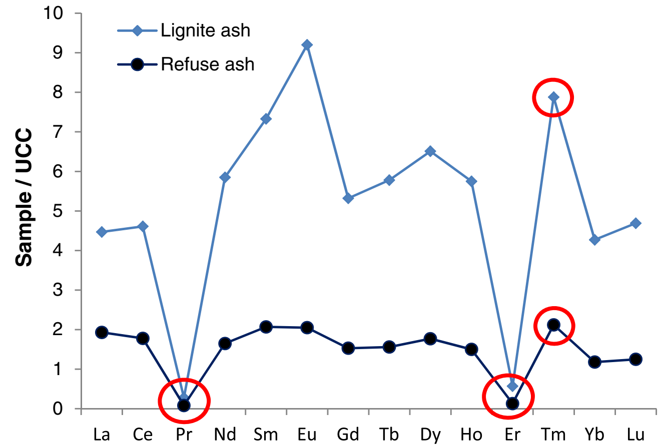

Fig. 1. Profiles showing questionable data for Pr, Er, and Tm in previously-investigated samples.
Data from Singh et al. (2011).

average sum of REY in US coals (62 μg/g; Finkelman, 1993) is close to the average for world coals (68 μg/g; Ketris and Yudovich, 2009). However, the estimated average sum of REY in Chinese coals is around twice that for world and US coals because more coal samples of Late Permian age from southwestern China, which contain higher REY concentrations (e.g., Zhuang et al., 2012; Dai et al., 2014a, 2015a) than those from northern China (e.g., Huang et al., 2000) and northwestern China (e.g., Li et al., 2012; Li et al., 2014; Jiang et al., 2015; Dai et al., 2015d), were included in the analyzed dataset.

Based on the relative enrichment of trace elements (Dai et al., 2015a), concentrations of trace elements in coal can be classified into six categories: unusually enriched ($CC > 100$; CC is Concentration Coefficient, defined as the ratio of trace-element concentrations in the investigated samples compared to averages for world coals), significantly enriched ($10 < CC < 100$), enriched ($5 < CC < 10$), slightly enriched ($2 < CC < 5$), normal ($0.5 < CC < 2$), and depleted ($CC < 0.5$). From the industrial and practical points of view, and according to the criterion of Seredin and Dai (2012), the cut-off grade of REY in coal ash, expressed as REO, is ≥1000 μg/g, or ≥800–900 μg/g for a coal seam with thickness > 5 m in which relatively thick coal benches with highly-elevated REY concentrations suitable for selective mining may be found (Seredin and Dai, 2012). Based on estimations by Ketris and Yudovich (2009), the average concentration of REO in world coal ashes is 485 μg/g. Thus, if the REO concentration coefficient (CC) in a coal ash is higher than 2, the REO could be an economically viable by-product from the coal combustion residues. Coal therefore has a great potential for REY recovery, and this is one of the reasons why coal ash is a promising alternative raw REY source that has attracted much attention in recent years. However, other factors, such as the thickness of the coal, the ash yield, other associated valuable metals (e.g., Ge, Ga, Al, Nb, Au, and U), present demand, and extraction methods, also need to be taken into account.

3. Distribution patterns and anomalies of rare earth elements and yttrium in coal

REY distribution patterns (or spidergrams) are presented as plots of the concentration of the REY in the investigated samples normalized to a standard material (e.g., usually average chondrite meteorite materials for igneous rocks) versus their atomic number. REY distribution patterns have been used for many years to determine genesis and differentiation processes of igneous rocks, and have also been extended to