



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.

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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

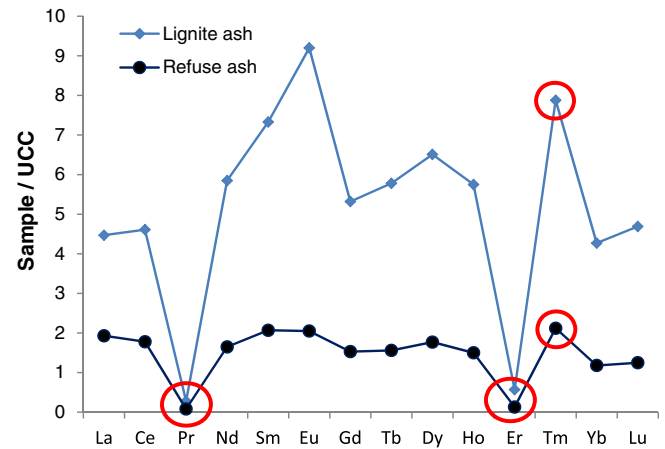


Fig. 1. Profiles showing questionable data for Pr, Er, and Tm in previously-investigated samples.
Data from Singh et al. (2011).

average sum of REY in US coals (62 $\mu\text{g/g}$; Finkelman, 1993) is close to the average for world coals (68 $\mu\text{g/g}$; 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 ($\text{CC} > 100$; CC is Concentration Coefficient, defined as the ratio of trace-element concentrations in the investigated samples compared to averages for world coals), significantly enriched ($10 < \text{CC} < 100$), enriched ($5 < \text{CC} < 10$), slightly enriched ($2 < \text{CC} < 5$), normal ($0.5 < \text{CC} < 2$), and depleted ($\text{CC} < 0.5$). 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 $\geq 1000 \mu\text{g/g}$, or $\geq 800\text{--}900 \mu\text{g/g}$ for a coal seam with thickness $> 5 \text{ m}$ 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 $\mu\text{g/g}$. 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

Table 1Average concentration ($\mu\text{g/g}$) of rare earth elements and yttrium for Chinese coals, US coals, and world coals.

Data of world, US, and Chinese coals are from Ketris and Yudovich (2009); Finkelman (1993), and Dai et al. (2008a), respectively.

Coal	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Sum
World hard coal	11	23	3.4	12	2.2	0.43	2.7	0.31	2.1	8.4	0.57	1	0.3	1	0.2	69
World low-rank coal	10	22	3.5	11	1.9	0.5	2.6	0.32	2	8.6	0.5	0.85	0.31	1	0.19	65
World coal	11	23	3.5	12	2	0.47	2.7	0.32	2.1	8.4	0.54	0.93	0.31	1	0.2	68
US coal	12	21	2.4	9.5	1.7	0.4	1.8	0.3	1.9	8.5	0.35	1	0.15	0.95	0.14	62
China	26	49	5.5	22	4.3	0.9	3.7	0.7	3.1	18	0.7	1.9	0.27	2.1	0.3	138
World coal ash	69	130	20	67	13	2.5	16	2.1	14	51	4	5.5	2	6.2	1.2	404

evaluating some sedimentary rocks, including coal (Haskin et al., 1966; Palmer et al., 1990; Seredin, 1996; Seredin and Dai, 2012).

Although the REY concentrations in coal have been normalized to chondrite in some investigations of REY distribution patterns (e.g., Goodarzi et al., 1990; Zhao et al., 2012; Wang and Yang, 2008; Zheng et al., 2007; and others), this is not advisable as the normalization standard should have been affected by similar fractionation processes to the samples being normalized. In order to investigate how REY concentrations in coal are fractionated, the standard materials used for normalization should have a similar genetic origin to coal. In a different context, this is why basaltic rocks are usually normalized to standard basalt values (such as P-MORB and N-MORB). It is therefore advisable that the REY in coal are normalized to an average value for sedimentary rock, such as the Upper Continental Crust (UCC; e.g., Taylor and McLennan, 1985), North American Shale Composite (NASC; e.g., Gromet et al., 1984), Post-Archaean Australian Shale (PAAS; e.g., Taylor and McLennan, 1985), or coal itself (e.g., Finkelman, 1993; Dai et al., 2008a). Pollock et al. (2000) used PAAS rather than NASC for REY normalization of coal because of sampling problems for the NASC as outlined by Gromet et al. (1984). As shown in Fig. 2, the REY distribution patterns of common Chinese and US coals are similar and the REY are not obviously fractionated relative to UCC; however, the REY distribution patterns for both world hard coals and world low-rank coals exhibit a zigzag shape, particularly for medium- and heavy-REY, which is most likely due to analytical problems for the samples collected worldwide (e.g. incomplete dissolution). Thus, if coal is selected as the standard material for REY normalization in the distribution pattern plots, the data for common Chinese and US coals, rather than world coals would be recommended. Nevertheless, the common Chinese and US coals are not from worldwide sources, and thus the UCC, NASC, or PAAS, the normalized patterns for which are similar, are recommended as the standard materials for REY normalization in coal investigations.

In this paper, the REY in coal are normalized to values for the UCC as reported by Taylor and McLennan (1985), not only because the close

relation of the REY values in the UCC and PAAS (Taylor and McLennan, 1985), and thus the similar distribution patterns of UCC- and PAAS-normalized REY in coal, but also because coal by its nature is closer to the UCC than to PAAS (e.g., coal was deposited within the upper continental crust, and contains many detrital UCC contributions mixed within the peat environment). For intra-seam tonstein deposits and some host rocks (e.g., roof and floor strata), which may be at least partly derived from air-borne material of pyroclastic origin, the REY are sometimes normalized to the UCC (e.g., Dai et al., 2014a, 2014b), and in some cases to chondrite (Zhou et al., 2000; Burger et al., 2002; Dai et al., 2011; Zhao and Graham, 2016; Arbuzov et al., 2016), for investigation of the original magmatic material.

In comparison with the UCC (Taylor and McLennan, 1985), three enrichment types of REY in coal are generally identified (Seredin and Dai, 2012): L-type (light-REY; $\text{La}_N/\text{Lu}_N > 1$), M-type (medium-REY; $\text{La}_N/\text{Sm}_N < 1$, $\text{Gd}_N/\text{Lu}_N > 1$), and H-type (heavy REY; $\text{La}_N/\text{Lu}_N < 1$). Additionally, normal type (N-type) of REY distribution patterns represent very weak or no fractionation among the L-, M-, and H-REY. The N-type has rarely been observed in REY-rich coals (e.g., $\text{CC} > 2$), but has commonly been identified in some low-REY coals ($\text{CC} < 0.5$; e.g., Dai et al., 2015a; Jiang et al., 2015; Saikia et al., 2015). The origin of each REY enrichment type in coal was extensively reviewed by Seredin and Dai (2012).

In addition to the enrichment types as described above (L-, M-, H-type), several distinct features of some REY (e.g., Ce and Eu anomalies, and in some cases, La, Gd, and Y anomalies) that develop or change only under specific conditions can be used to reconstruct the geochemical history (Crowley et al., 1989; Hower et al., 1999; Mardon and Hower, 2004), to identify the sediment-source region (Eskenazy, 1987a, 1987b; Van der Flier-Keller, 1993; Dai et al., 2013, 2015c), and to interpret the tectonic evolution of coal deposits (Dai et al., 2016; Zhao and Graham, 2016).

3.1. Cerium anomalies in coal

Cerium is the only member of the REY group that can occur in a tetravalent state within the stability field of water in shallow crustal environments (low-temperature), under highly oxidizing, alkaline pH conditions (Elderfield and Greaves, 1981; Akagi and Masuda, 1998; Braun et al., 1990; Graham et al., 2007; Seto and Akagi, 2008). The ratio of Ce_N to Ce_N^* ($\text{Ce}_N/\text{Ce}_N^*$) provides the simplest basis to quantify redox-related decoupling of Ce from the other REY and produces Ce anomalies (positive or negative) in REY distribution patterns. Ce_N is the ratio of Ce concentration in the investigated sample to the Ce value in the UCC. Ce_N^* can be calculated as:

$$\text{Ce}_N^* = 0.5\text{La}_N + 0.5\text{Pr}_N \quad (1)$$

or, if no Pr data are available (e.g., if the REY are determined by instrumental neutron activation analysis),

$$\text{Ce}_N^* = 0.67\text{La}_N + 0.33\text{Nd}_N. \quad (2)$$

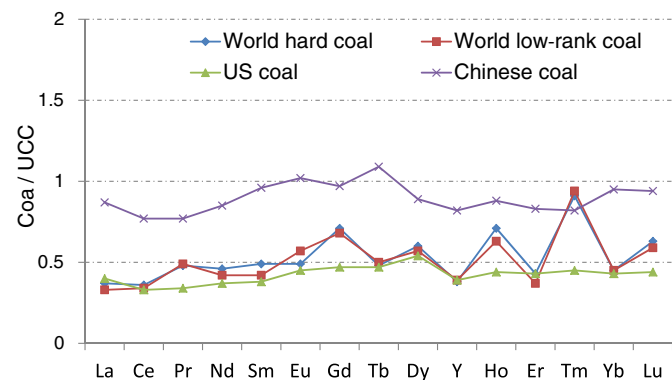


Fig. 2. Distribution patterns of average values of REY in common US coals, Chinese coals, and world low-rank and hard coals, normalized to average REY concentrations in the Upper Continental Crust (Taylor and McLennan, 1985). REY concentrations in Chinese coals, US coals, and world coals are respectively from Dai et al. (2008a); Finkelman (1993), and Ketris and Yudovich (2009).

Cerium in coal mainly exhibits negative, weakly negative, or no anomalies. Strong positive Ce anomalies rarely occur in coal, but have been observed in some intra-seam partings and host rocks of coal

seams. Relative to the UCC, Ce in common Chinese and US coals does not show any anomalies (Fig. 2). Several factors, including the rocks in the sediment-source region, groundwater or hydrothermal leaching, seawater, and Fe–Mn oxyhydroxide mineralization, may control the Ce features in coal and coal-bearing strata. In contrast to anomalies of La, Eu, Gd, and Y in coal, as described below, the mineral and thermal waters that originate from deeper environments generally show no pronounced Ce anomalies (Gob et al., 2013) and consequently those waters generally cannot give rise to Ce anomalies in coal; however, surface waters have negative or strongly negative Ce anomalies (Gob et al., 2013).

The geochemical composition of the sediment-source region is the one of the important factors in controlling the Ce anomaly in coal, although REY mobility during weathering is still an area of debate (Leybourne et al., 2000; Zhang et al., 2012). Sediment source regions dominated by basalts (e.g., high-Ti or low-Ti basaltic lavas; Xu et al., 2001; Xiao et al., 2004) do not show a Ce anomaly (Fig. 3A). Thus coals with input of these terrigenous materials generally do not show distinct Ce anomalies. For example, the Kangdian Upland that is dominantly composed of mafic basaltic lavas is the exclusive sediment source region for the C2 and C3 Coals in the Xinde Mine (Xuanwei, eastern Yunnan, China (Dai et al., 2014b)), which are characterized by no or very weak Ce anomalies (Fig. 3B). A similar situation applies to the late Permian Liuzhi coals from western Guizhou Province (Li et al., 2016).

Sediment source regions dominated by felsic or felsic-intermediate rocks are characterized by weakly negative Ce anomalies (Fig. 3C), and coals with input from these terrigenous materials usually have weak Ce anomalies. For example, the inorganic matter in the No. 25 Coal from the Guxu Coalfield (Sichuan Province, China) was mainly derived from the felsic-intermediate rocks at the top of the Emeishan basalt sequence, rather than from the Emeishan mafic basalts (Dai et al., 2015e), and thus the coal is characterized by negative Ce anomalies (Fig. 3D). The Ge-rich lignite from Lincang (Yunnan Province, China), where biotite- and two-mica granites served as both the basement for the coal-bearing sequence and a source of sediment input, do not show

distinct Ce anomalies (Dai et al., 2015c). The sediment source region for the U-rich coals in the Yili Basin was mainly of felsic and, in some cases, intermediate composition (Min et al., 2005; Wang et al., 2006), and Ce in these coals exhibits negative, weakly negative, or no anomalies (Dai et al., 2015d).

Negative to weakly negative Ce anomalies in coals are also probably due to the in-situ precipitation of Ce^{4+} during the weathering and oxidation of the sediment-source region. Coals with input of felsic terrigenous materials sometimes have a lower La_N/Lu_N than that of the terrigenous rocks in the sediment source region, because weathering of the felsic materials leads to an enrichment of L-REY in the residuum (Braun et al., 1990; Aubert et al., 2001); in consequence, the weathering fluids injected into the peat swamp are expected to be depleted in LREY.

In some cases, groundwater or hydrothermal leaching of partings can cause Ce anomalies both in the partings and in the directly underlying coal benches. During leaching of the partings, if oxygen is available, Ce^{3+} is oxidized to Ce^{4+} , which is usually immobile and is preferentially precipitated in-situ (Braun et al., 1990; De Carlo et al., 1998; Taunton et al., 2000), leading to the generation of Ce-poor REY-rich leachates from the partings to the underlying organic matter. This may cause the partings to be lower in total REE content, but to have a relatively higher Ce content and Ce_N/Ce_N^* values than the underlying coal benches (e.g., the Jungar coals from Inner Mongolia; Dai et al., 2006, 2008a). However, not all leached partings show higher Ce_N/Ce_N^* values than the underlying coal bench (e.g., Hower et al., 1999; Dai et al., 2013). This is probably due to the reducing conditions of the peat swamp; Ce^{3+} cannot be oxidized to Ce^{4+} under these conditions, and Ce^{3+} would have been leached along with other REY from the partings to the underlying organic matter.

The formation of coal on mafic tuff is not a common occurrence; however, a mafic volcanic eruption occurred during the late Permian and volcanic ash fell on to the eroded surface of the middle-Permian Maokou Formation (China Coal Geology Bureau, 1996). Subsequently, the volcanic ashes experienced weathering, leaching, and eluviation, leading to the formation of a residual plain mainly composed of mafic

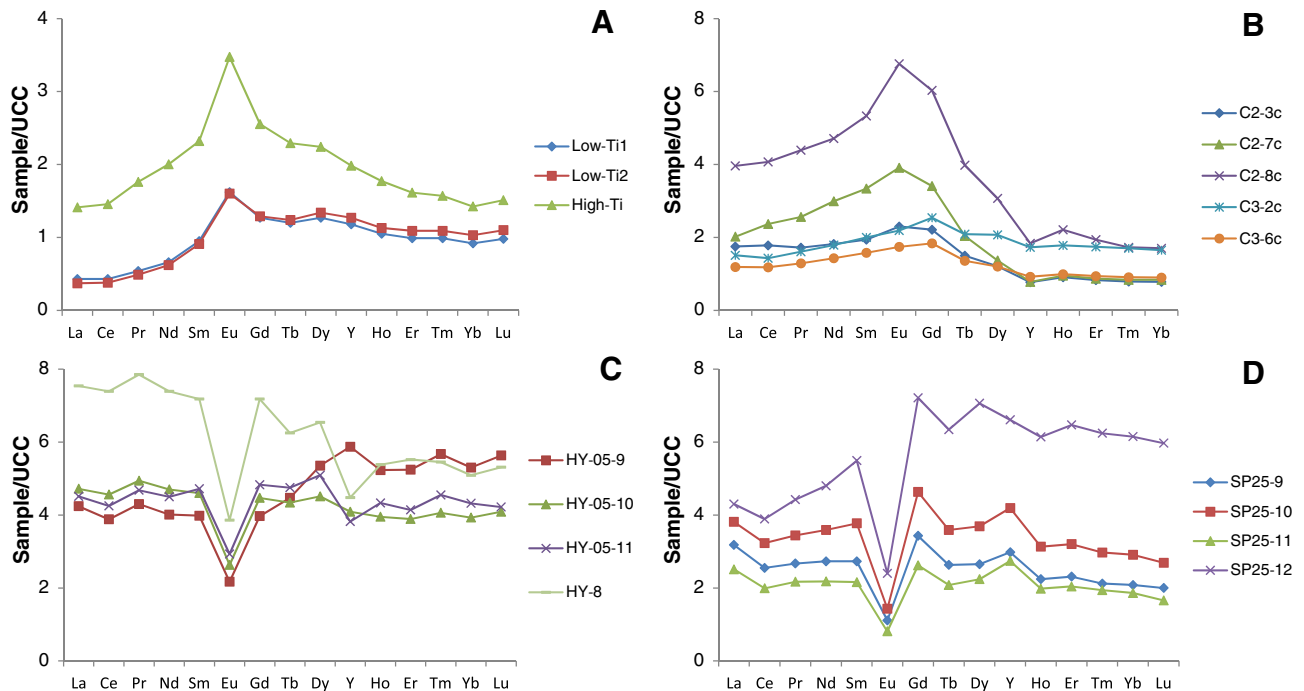


Fig. 3. REY distribution patterns of rocks in the sediment source region and coals partially derived from those terrigenous materials. (A), High- and low-Ti mafic basalts of the Kangdian Upland (data from Xiao et al., 2004); (B), Coals from the Xinde Mine (Yunnan Province, China) with terrigenous materials of high-Ti mafic basalts (data from Dai et al., 2014b); (C), Felsic-intermediate rocks at the top of the Kangdian Upland (data from Shao et al., 2007); (D), The No. 25 Coal in the Guxu Coalfield (Sichuan Province, China) with terrigenous felsic-intermediate rocks (data from Dai et al., 2015e). All plots normalized to the UCC (Taylor and McLennan, 1985).

tuffs. As described by Zhang (1993) and the China Coal Geology Bureau (1996), a widespread coal covering a total area of ~70,000 km² was deposited in a peat swamp that developed on the mafic tuffs in a continental environment (China Coal Geology Bureau, 1996). The mafic tuff generally exhibits positive Ce anomalies (Fig. 4A). Similar cases are found in the immediate floor strata of the C2 and C3 coal seams at the Xinde Coal Mine (eastern Yunnan, China), which are made up of completely argillized high-Ti basaltic volcanic ash (Dai et al., 2014b). Owing to the in-situ precipitation of Ce⁴⁺, the REY distribution patterns of the floor strata display positive Ce anomalies, not only relative to the UCC, but also to the high-Ti basalts (Fig. 4B,C).

Some studies have shown that coals formed in a marine-influenced environment have negative Ce anomalies (Wang et al., 2008), although the REY concentrations in seawater are low and the combination mechanism of REY from seawater into peat is unknown. Negative Ce anomalies are considered as an indication of a marine depositional environment (Murray et al., 1990; Alibo and Nozaki, 1999). Typical Ce_N/Ce_N^{*} values are <0.5 in oxic marine water, ~0.6–0.9 in suboxic marine water, and ~0.9–1.0 in anoxic marine water (Chen et al., 2015a). Coals preserved within carbonate successions, and also the associated carbonate roof strata, may thus have negative or very weak Ce anomalies (Fig. 4D); these weak negative Ce anomalies were probably due to the combined influence of seawater and a basaltic sediment source region (Kangdian Upland).

Large positive Ce anomalies have been observed in high-REY Fe-Mn oxyhydroxide ores in the Cenozoic coal-bearing sequences of the Pavlovka deposit of Far East Russia (Seredin and Dai, 2012). The Fe-Mn oxyhydroxide ores (e.g., goethite, hematite, Al-lithiophorite, cryptomelane, hollandite, and vernadite), contain 5–44% MnO₂, 2–65% Fe₂O₃, and 0.1–4.0% REO (averaging 0.5%). These ores are selectively enriched in Ce (average Ce/La ratio is 30, about 15 times higher than that of the UCC) and are characterized by M-REY type enrichment, suggesting that the hydroxide ores formed during neutralization of acid reduced solutions (Seredin, 1998; Ferenczi, 2001). Unlike oceanic Fe–Mn

concretions and crusts that contain Ce as adsorbed ions (Hein et al., 1999) and because Ce⁴⁺ is preferentially adsorbed to Mn oxides compared to REY³⁺ (De Carlo et al., 1998), these high-REY Fe-Mn oxyhydroxides in coal-bearing strata contain a number of Ce-bearing minerals.

3.2. Europium anomalies in coal

Apart from cerium, europium is the only other redox-sensitive REY. Eu³⁺ can be reduced to Eu²⁺ in reducing settings, resulting in a distinct Eu anomaly relative to the other REY (Elderfield, 1988). However, this redox transformation requires both extremely reducing conditions and high-temperature (Sverjensky, 1984; Bau, 1991), a combination most commonly found in magmatic processes (Rard, 1985) rather than in earth-surface environments (Bau, 1991). Reduction of Eu³⁺ to Eu²⁺ increases with increasing temperature (Uysal and Golding, 2003). The ratio of Eu_N to Eu_N^{*} (Eu_N/Eu_N^{*}), where Eu_N is the ratio of the Eu concentration in the investigated samples vs. the Eu concentration in the UCC, is commonly used to quantify decoupling of Eu from the other REY, and produces Eu anomalies (positive or negative) in REY distribution patterns. Eu_N/Ce_N^{*} can be calculated as:

$$\text{Eu}_N/\text{Eu}_N^* = \text{Eu}_N / (0.5\text{Sm}_N + 0.5\text{Gd}_N). \quad (3)$$

In order to avoid interference of the Gd anomaly with the Eu anomaly, Eu/Eu_N^{*} can be calculated as (Bau and Dulski, 1996):

$$\text{Eu}_N/\text{Eu}_N^* = \text{Eu}_N / [(\text{Sm}_N \times 0.67) + (\text{Tb}_N \times 0.33)]. \quad (4)$$

3.2.1. Factors for Eu anomalies in coal

Europium in coal may exhibit positive, negative, or no anomalies in REY distribution patterns. Relative to the UCC, the Eu in common Chinese and US coals does not show distinct anomalies (Fig. 2). Because

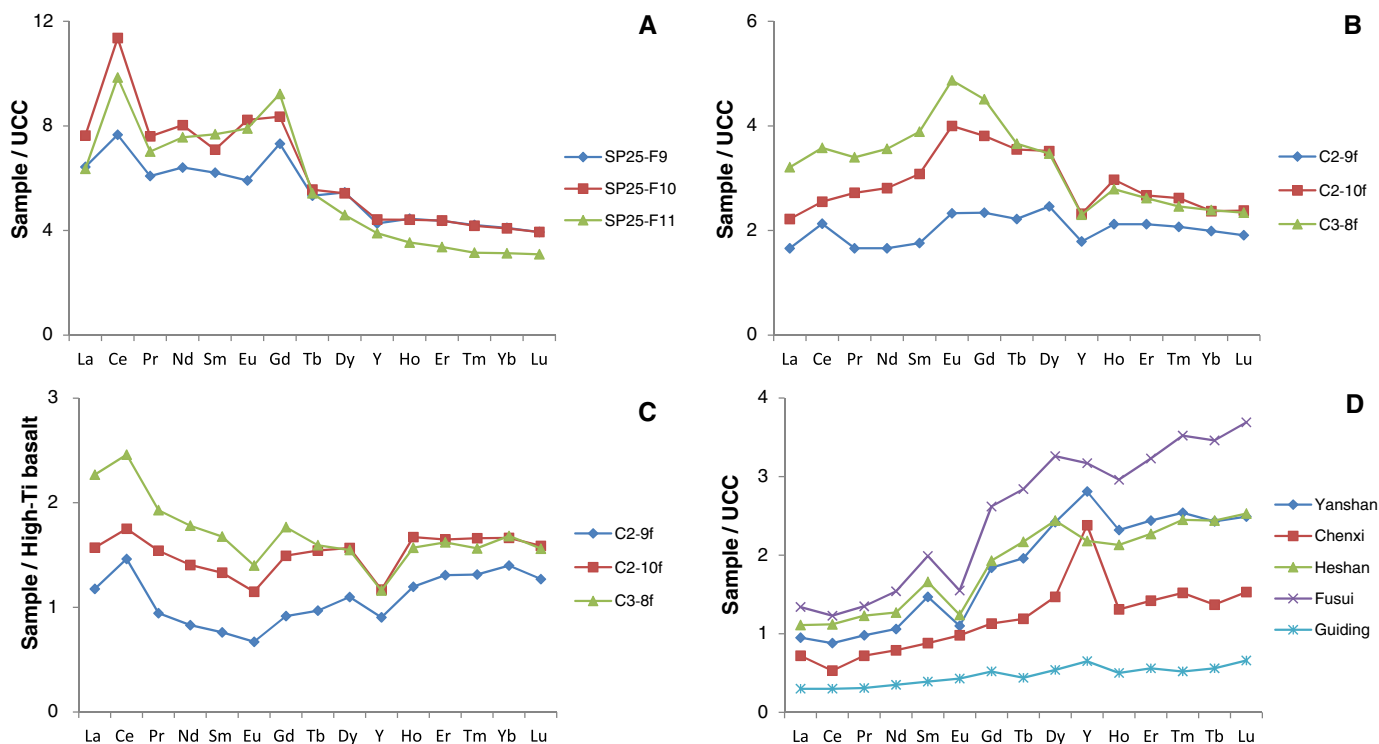


Fig. 4. REY distribution patterns for floor strata mainly composed of mafic tuffs, as well as those for coals preserved within carbonate successions. (A). Floor strata of the No. 25 coal seam in the Guxu Coalfield (Sichuan Province, China); data from Dai et al. (2015e); (B) Floor strata of the No. 2 and No. 3 Coals in the Xinde Mine (Yunnan, China); data from Dai et al. (2014b); (C) Floor strata of the No. 2 and No. 3 Coals in the Xinde Mine (data from Dai et al., 2014b), normalized to high-Ti mafic basalts (data from Xiao et al., 2004); (D) Coals preserved within carbonate successions; data from Dai et al. (2015a). REY in (A), (B), and (D) are normalized to UCC (Taylor and McLennan, 1985).

the reduction of Eu occurs only under extremely reducing conditions and at temperatures $>250\text{ }^{\circ}\text{C}$ (Sverjensky, 1984), which do not exist within natural aquatic systems (Rard, 1985; Bau, 1991), Eu anomalies in coal are generally not thought to have originated from weathering processes in the sediment source region or during metal transportation from the sediment source region to the peat swamp, but are instead inherited from rocks within the sediment source region (e.g., Eskenazy, 1987b; Qi et al., 2007; Yossifova et al., 2011; Dai et al., 2015e) and affected by high-temperature hydrothermal fluids (e.g., positive Eu anomaly, Bau et al., 2014; Michard and Albarède, 1986; Bau, 1991). As with coal, the Eu anomaly in other sedimentary rocks is also usually interpreted as being inherited from the primary igneous source rocks (Taylor and McLennan, 1985; McLennan and Taylor, 1991).

Felsic rocks with large negative Eu anomalies are probably formed by more fractional crystallization of feldspar and/or by smaller degrees of partial melting of source rocks containing feldspar than those with smaller negative Eu anomalies (Cullers, 2000). Coals with input of felsic or felsic-intermediate terrigenous materials (Fig. 3C) usually display

distinct negative Eu anomalies. For example, the Kangdian Upland, mainly comprising mafic basalts, is the sediment source region for most Late Permian coals in southwestern China (China Coal Geology Bureau, 1996); however, the inorganic matter in Late Permian coals from Fusui (Guangxi Province, southern China; Dai et al., 2013) are dominantly derived from the Yunkai Upland, consisting mainly of felsic Permo-Carboniferous rocks. The Fusui coals are characterized by negative Eu anomalies (Fig. 4D), with $\text{Eu}_N/\text{Eu}_N^*$ from 0.54 to 0.82 and an average of 0.67. Based on negative Eu anomalies, Chen et al. (2015b) proposed that the sediment source region for the Late Permian coals from the Nantong Coalfield (Chongqing, China) was the Longmenshan Island and/or Jiangnan Oldland, rather than the basaltic Kangdian Upland as previously suggested by the China Coal Geology Bureau (1996). The upper portion of the floor strata of the No. 25 Coal from the Guxu Coalfield (Sichuan Province, southwestern China) was derived from terrigenous rocks at the top of the Emeishan basalt sequence, which is characterized by felsic-intermediate compositions and strong negative Eu anomalies, with $\text{Eu}_N/\text{Eu}_N^*$ from 0.38 to 0.41 and an average of 0.40 (Fig. 5A; Dai et al., 2015e). The No. 25 Coal is also characterized

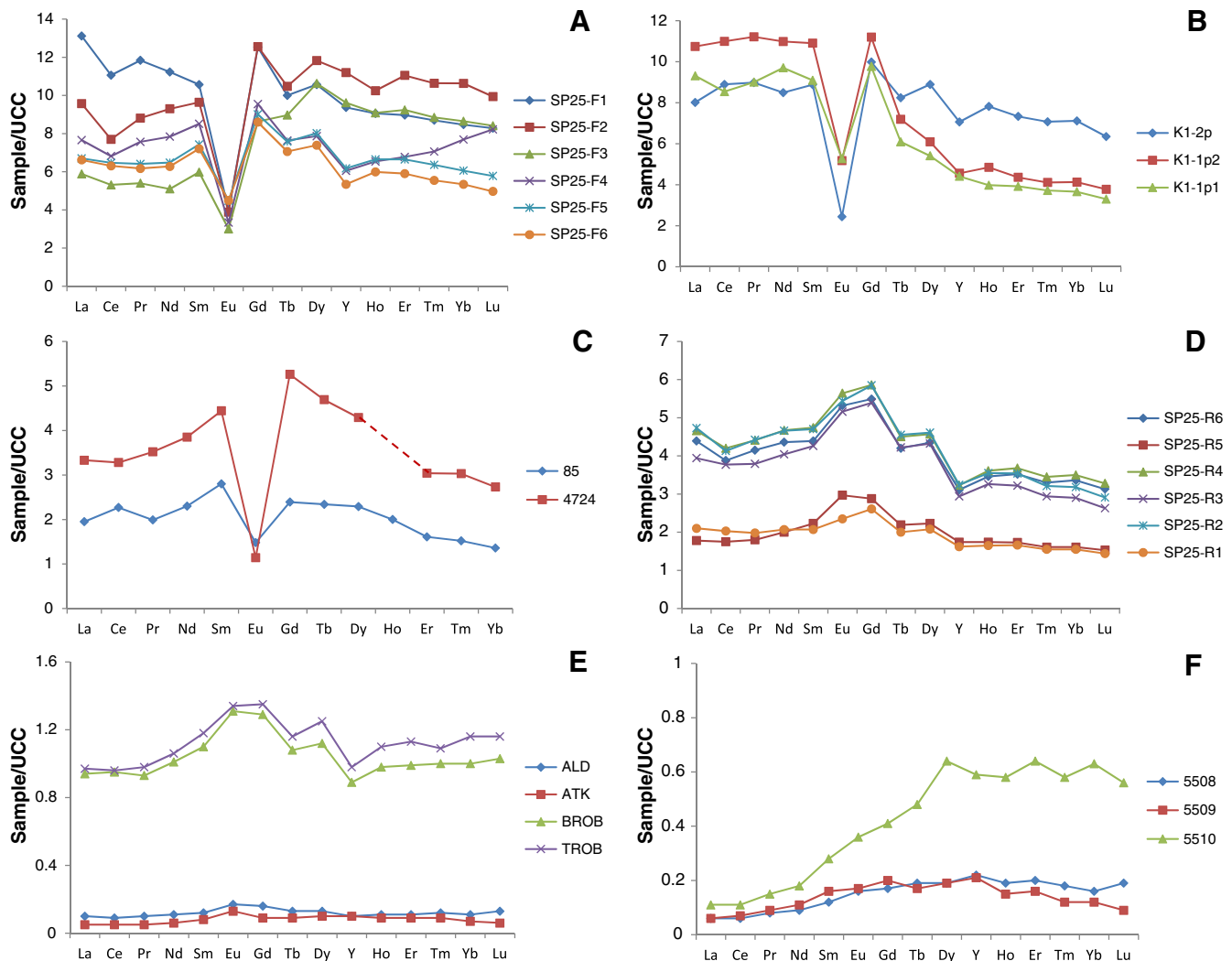


Fig. 5. REY distribution patterns of host rocks (floor strata, tonsteins, and roof strata) and coal. (A), Floor strata of the No. 25 Coal from the Guxu Coalfield, data from Dai et al. (2015e). (B), Three tonsteins of alkali rhyolites from the Huayingshan Coalfield (China), data from Dai et al. (2014a). (C), Two tonsteins from the Fire Clay coal bed (Eastern Kentucky; sample 4724) and the Upper Triassic Xujiahe Formation of southern Sichuan Province (China; sample 85), data from Hower et al. (1999) and Burger et al. (2000), respectively. (D), Roof strata of the No. 25 Coal from the Guxu Coalfield, data from Dai et al. (2015e). (E), Coal (nos. ALD and ATK) and overburden strata (nos. BROB and TROB) in Assam from North-east India, data from Saikia et al. (2015). (F), Gray Hawk coal in Eastern Kentucky, USA; data from Hower et al. (2015b). All REY data are normalized to UCC (Taylor and McLennan, 1985). The Lu value of sample 85 and the Ho value of sample 4724 in (C) are excluded. The Lu value for sample 4724 in Hower et al. (1999) was not reported.

by negative Eu anomalies (Fig. 3D), indicating a similar sediment source region to that supplying the upper portion of the floor strata below the coal seam.

Tonstein deposits derived from air-borne material of pyroclastic origin deposited in the peat-forming environment have been found in some coal seams (e.g., Burger et al., 2002; Hower et al., 1999; Zhou et al., 2000; Lyons et al., 2006; Guerra-Sommer et al., 2008; Dai et al., 2011, 2014b). Europium in the REY distribution patterns of tonsteins is largely inherited from the original magma. For example, three tonstein layers identified in coal from the Huayingshan Coalfield, which are deduced to have been derived from alkali rhyolite (Dai et al., 2014a), are characterized by strong negative Eu anomalies (Fig. 5B). Two intra-seam tonstein layers identified in the C3 coal (Xinde Mine, Xuanwei, China; Dai et al., 2014b) were derived from dacitic magma. Although these would be expected to have higher REY contents and negative Eu anomalies, they do not show distinct negative Eu anomalies, probably because the two tonsteins were mixed with terrigenous basaltic materials. The low total REY concentrations in the two partings are due to hydrothermal or groundwater leaching (Dai et al., 2014b). Burger et al. (2002) identified five layers of felsic tonstein from the 4th Member of the Upper Triassic Xujiahe Formation in southern Sichuan Province, China, which are characterized by strong negative Eu anomalies (Fig. 5C). For example, sample 85 (K_2 tonstein) has a Eu/Eu^* value of 0.56. The flint clay (tonstein) in the Fire Clay coal bed, Eastern Kentucky (no. 4724; location: Tiford, Letcher) also exhibits a strong negative Eu anomaly, with a Eu/Eu^* value of 0.25 (Hower et al., 1999). Tonsteins in the Azeisk deposit of the Irkutsk Coal Basin (Siberia, Russia) are characterized by distinctly negative Eu anomalies, consistent with a rhyolitic composition for the initial magma (Arbuzov et al., 2016). In a few cases, volcanic ash rather than materials from the sediment source region may have terminated peat accumulation. For example, a large-scale input of high-Ti alkali mafic volcanic ash terminated the peat accumulation phase of the C2 coal in the Xinde Mine (Xuanwei, Dai et al., 2014b), and thus the roof strata of the coal seam are characterized by a strong Eu anomaly, with a $\text{Eu}_N/\text{Eu}_N^*$ value of 1.38.

Not all the syngenetic volcanic ashes in coal form persistent tonstein layers. If the quantity of the volcanic ashes was too low to form a layer in the coal seam, the volcanic ash would be more intimately admixed with the peat and become part of the inherent mineral matter in the coal (e.g., Crowley et al., 1993; Dai et al., 2008b; Ward, 2002). These volcanic ashes may nevertheless significantly influence the REY distribution patterns of the coal. For example, Goodarzi et al. (2006) attributed the negative Eu anomaly in coal from northern Iran to syngenetic volcanic ashes. As well as the supply of detrital material from the sediment source, mainly composed of felsic rocks, the strong negative Eu anomaly in the M9 coal from the Yanshan Coalfield (Yunnan, China) is thought to be partly due to the addition of syngenetic volcanic materials (Dai et al., 2008b).

Sediment source regions comprising mafic basalts are characterized by strong positive Eu anomalies (Fig. 3A; Xiao et al., 2004), and thus coals with input from these terrigenous materials have large positive Eu anomalies (Fig. 3B; Dai et al., 2014b). The roof strata of the No. 25 Coal in the Guxu Coalfield, China, which was also mainly derived from tholeiitic basalts of the Kangdian Upland (Dai et al., 2015e), shows positive Eu anomalies (Fig. 5D) with an average $\text{Eu}_N/\text{Eu}_N^*$ of 1.22. A geochemical study by Saikia et al. (2015) showed that the REY distribution patterns of coals (nos. ALD and ATK) and overburden strata (nos. BROB and TROB) from Assam (North-east India) are similar, with weak but positive Eu anomalies (Fig. 5E), suggesting the same sediment-source rocks with mafic-dominated composition, unless the coal or overburden strata samples were subjected to high-temperature fluids.

Because of the sediment-source region dominated by felsic rocks, coals that are preserved within carbonate successions (e.g. Yanshan coal, Dai et al., 2008b; Fusui, Dai et al., 2013; Heshan, Dai et al., 2015a) and have also been subjected to hydrothermal fluids, display negative

Eu anomalies, indicating that the temperatures of the hydrothermal fluids were $<200^\circ\text{C}$. The injection of hydrothermal fluids is supported by the highly-elevated concentrations of organic sulfur, U, Se, Mo, Re, and V (Dai et al., 2008b, 2013, 2015a). Otherwise, strong positive Eu anomalies would be expected due to the action of hydrothermal fluids at $>200^\circ\text{C}$ in ambient seawater (Bau, 1991; Danielson et al., 1992) during the peat accumulation process, because the transformation from Eu^{3+} to Eu^{2+} not only requires extremely reducing conditions but also high-temperature, as mentioned above. UCC- or shale-normalized $\text{Eu}_N/\text{Eu}_N^*$ ratios of modern seawater do not show anomalies, in contrast to high-temperature hydrothermal fluids that show strong positive anomalies (Bau, 1991; Bau and Dulski, 1999; Douville et al., 2002; Schmidt et al., 2011).

It appears that volcanogenic hydrothermal solutions could also cause Eu anomalies in coal. For example, the Ge-rich coals of the Wulantuga deposit in the Shengli Coalfield (Inner Mongolia) have high concentrations of Hg and As, up to 6.44 and 666 $\mu\text{g/g}$, respectively (Dai et al., 2012; Zhuang et al., 2006), indicating an injection of Hg-As-rich volcanogenic solutions to the peat swamp (Dai et al., 2012; Seredin, 2005). Relative to the low-Ge coals of the same area (Fig. 6A), the high-Ge coals have a distinctly higher Eu content. A similar case occurs in the Ge-rich and low-Ge coals from the Pavlovka deposit, Russian Far East (Seredin, 2005), where the high-Ge coals are enriched in Eu relative to the Ge-free coals. The Gray Hawk coal of Early Pennsylvanian age in Eastern Kentucky, USA, is characterized by medium- and heavy-REY enrichment types (Fig. 5F), indicating input of acid waters or hydrothermal solutions (Hower et al., 2015b). The Eu in the Gray Hawk coal would be expected to have negative anomalies because the sediment-source region is mainly of felsic to intermediate composition (Hower et al., 2015b). However, Eu does not show anomalies (Fig. 5F), probably due to the injection of high-temperature hydrothermal solutions, which overprinted the negative Eu anomalies caused by the terrigenous materials.

Most of the Early Jurassic U-rich coals from the Yili Coalfield (Xinjiang Province, China), which would be expected to have negative Eu anomalies (Fig. 7A) because their sediment source region mainly comprises Hercynian granite, Permo-Carboniferous intermediate felsic igneous rocks, and pyroclastic rocks interbedded with carbonate layers (Min et al., 2005), are characterized by positive Eu anomalies (Fig. 7). The coals with positive Eu anomalies are characterized by a high pyrite content (as well as traces of millerite, chalcopyrite, cattierite, siegenite, ferroselite, krutaite, and eskebornite), highly-elevated concentrations of a Hg-As assemblage, and heavy- and medium-REY enrichment types, all indicating an input of volcanogenic hydrothermal solutions (Dai et al., 2015d). The $\text{Eu}_N/\text{Eu}_N^*$ values do not seem to have a clear relationship to the K-feldspar content of the coal (Fig. 7B). These positive Eu anomalies are therefore most likely due to the injection of volcanogenic hydrothermal solutions.

A positive Eu anomaly could be attributed to the presence of Ca-rich minerals such as plagioclase feldspars, which show Eu enrichment due to isomorphous replacement of Ca^{2+} with Eu^{2+} (Birk and White, 1991). However, Birk and White (1991) also showed that the carbonate-rich roof rock (21% Ca) of the Sydney Basin, Canada, exhibited an identical Eu content to a low-Ca roof clay (Ca = 0.45%), and the apatite-rich top of the Harbour seam, with 3.8% Ca, had a much weaker Eu anomaly than a sample with only half the Ca (1.9%). A study by Dill (1994) showed that REY distribution patterns, including the Eu anomaly, can be used as a tool to determine the origin of apatite in clastic rocks. It seems that a positive Eu anomaly in coal can be caused by apatite but not calcite, dolomite, fluorite, or ankerite. For example, the sediment source region for the middle Jurassic inertinite-rich coals of the Muli Coalfield, on the Tibetan Plateau, has felsic or intermediate characteristics and thus the coal would be expected to have negative Eu anomalies. However, these coals are mostly characterized by positive Eu anomalies (mostly $\text{Eu}_N/\text{Eu}_N^* > 1$), which is probably due to the high apatite contents of the coal (Fig. 8A).

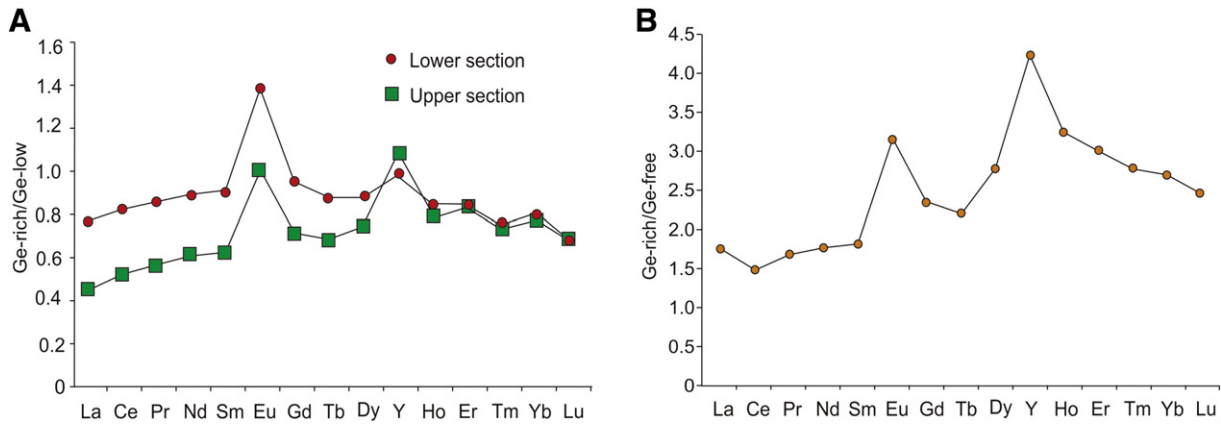


Fig. 6. REY distribution patterns for Ge-rich coals from the Wulantuga (A) and Pavlovka (B) deposits. Normalized to low-Ge coals (A) and Ge-free coals (B). Wulantuga deposit: Ge-high coals of upper section with 348 $\mu\text{g/g}$ Ge; Ge-high coals of lower section with 510 $\mu\text{g/g}$ Ge; Ge-low coals with 115 $\mu\text{g/g}$ Ge. Pavlovka deposit: Ge-rich coals of seam I (drill hole 4), Ge-762 $\mu\text{g/g}$; Ge-free coals of seam I (open mine), Ge-1 $\mu\text{g/g}$. Data from Seredin (2005).

A study by Uysal and Golding (2003) of coals from the Bowen Basin of eastern Australia showed that highly illitic clays have a distinct Eu anomaly, due to the higher formation temperature of the illite-rich samples relative to the less illitic samples with no Eu anomalies (Uysal et al., 2000). However, for the Guxu coals from Sichuan province (China), the illite content does not correlate well with the Eu anomaly (Fig. 8B) (Dai et al., 2015e), probably because the formation temperature of the authigenic illite in the coal did not meet the requirement for reduction from Eu^{3+} to Eu^{2+} ($>250^\circ\text{C}$).

3.2.2. Analytical problems and positive Eu anomalies in quadrupole-based ICP-MS

Determination of rare earth elements by quadrupole-based inductively coupled plasma mass spectrometry (ICP-MS) shows several spectroscopic overlaps from M^+ , MO^+ and MOH^+ ions (Raut et al., 2005). For example, spectroscopic interferences are observed from the atomic and molecular species of light rare earth elements and Ba during the determination of Eu, Gd and Tb. Among these interferences, the most distinct interference for coal analysis is Ba on Eu because: 1) both of the two Eu isotopes can be interfered with by Ba, for example, interference by $^{135}\text{Ba}^{16}\text{O}$ and $^{134}\text{Ba}^{16}\text{OH}$ to ^{151}Eu , and $^{137}\text{Ba}^{16}\text{O}$ and $^{136}\text{Ba}^{16}\text{OH}$ to ^{153}Eu ; 2) Barium in coal usually has a much higher concentration than Eu. For example, the average concentrations of Ba and Eu for world coals are 150 and 0.47 $\mu\text{g/g}$ respectively, and the Ba/Eu ratio is ~ 319 (Ketris and Yudovich, 2009). Coals with Ba/Eu >1000 , moreover, are

not uncommon, for example, Ba and Eu data reported by Hower et al. (1999), Zhao et al. (2012, 2014), and Dai et al. (2015c). Therefore, identification of positive Eu anomalies should be carried out with great caution in Ba-rich coals.

Europium is generally measured on mass 153, and if a correction is not applied for mass interferences by $^{137}\text{Ba}^{16}\text{O}$, $^{136}\text{Ba}^{17}\text{O}$, $^{135}\text{Ba}^{18}\text{O}$, and $^{134}\text{Ba}^{18}\text{OH}$ the Eu values would be expected to be overestimated. A number of studies have also shown interference of Ba with Eu in REE evaluations of geological samples (e.g., Gray and Williams, 1987; Jarvis et al., 1989; Cao et al., 2001; Raut et al., 2003, 2005; He et al., 2005; Loges et al., 2012; Wang et al., 2013). Eu values from some ICP-MS laboratories are not interpreted if the Ba/Eu ratio is >1000 , to exclude interference from BaO and BaOH (Loges et al., 2012). In some coal samples with high Ba/Eu (e.g., >1000), the Eu anomaly may thus be incorrect. For example, Zhao et al. (2012) showed a distinct positive Eu anomaly (Fig. 9A) in a Ba-rich coal from the Huanglong Coalfield, China, which, however, was subject to interference from BaO and/or BaOH during the ICP-MS analysis. The Eu concentration is positively correlated to that of Ba ($r^2 = 0.99$; Fig. 9B), further indicating interference between Ba and Eu.

With the exception of Eu, other rare earth elements are not correlated with Ba (see Supplementary electronic file). If these rare earth elements are measured on a proper mass different to BaO and/or BaOH (e.g., La measured on mass 139, Ce on 140, Pr on 141, Nd on 144, Sm on 147, and Gd on 160), the BaO and BaOH would not be expected to

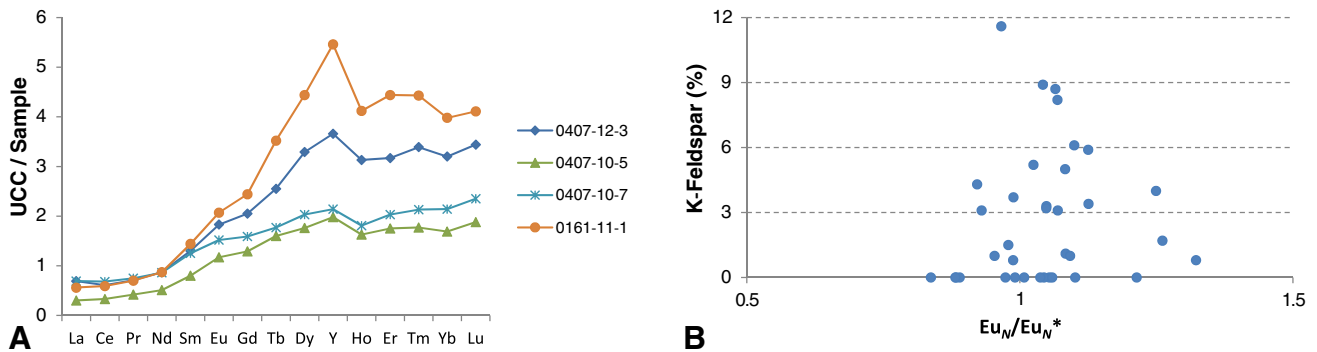


Fig. 7. REY distribution patterns (A) and relationship between $\text{Eu}_\text{N}/\text{Eu}_\text{N}^*$ and K-feldspar percentages (B) of U-rich coals from the Yili Coalfield, Xijiang Province, China. The pyrite content of samples 0407-12-3, 0407-10-5, 0407-10-7, and 0161-11-1 are respectively 4.4, 1.1, 9.7, and 4.5%. Data from Dai et al. (2015d).

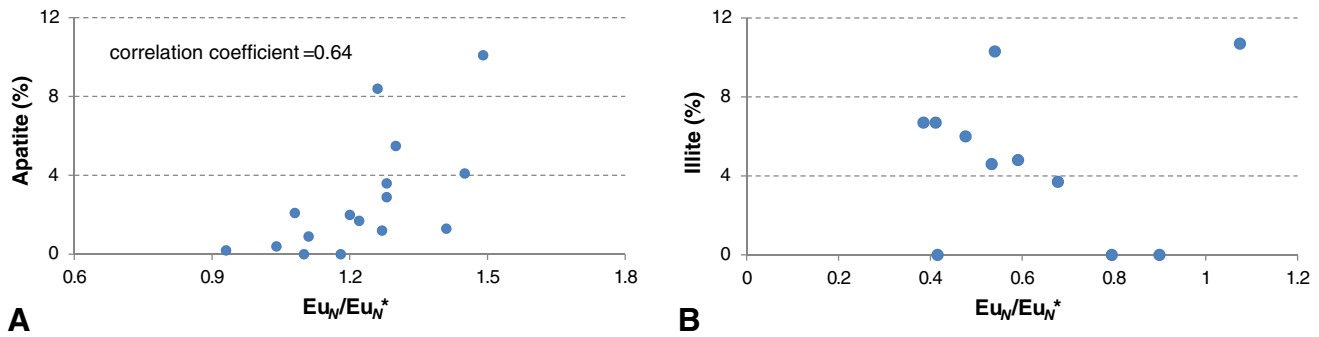


Fig. 8. Eu_N/Eu_N^* against apatite and illite percentage in low-temperature ash of coal. (A) Muli coals, data from Dai et al. (2015f). (B), Guxu coals, data from Dai et al. (2015e).

cause interference with the concentrations of these rare earth elements. Rare earth elements Tb, Dy, Ho, Er, Tm, Yb, and Lu, are not interfered with by BaO or BaOH, which do not produce ions with the same masses as these REEs. In addition to correction of spectral interference of Ba on Eu (e.g., Jarvis et al., 1989; Raut et al., 2005), an investigation by Wang et al. (2013) showed that using a high-resolution ICP-MS could avoid the Ba interference on Eu. Raut et al. (2005) suggested that ^{151}Eu is a better isotope than ^{153}Eu for determination of Eu concentration, but also pointed out that the two Eu isotopes may not produce significantly different Eu concentration results.

Quartz-carbonate metasomatites occur as the floor and a parting layer of the Ge-rich Z2 Coal, and carbonate metasomatites occur as the roof strata of the X1 Coal, in the Lincang Coalfield, China (Dai et al., 2015c). The REY in these metasomatites are characterized by heavy-type enrichment and distinct positive Eu anomalies (Fig. 9C), which were previously ascribed to two factors: Firstly, the ionic radii of Eu^{2+} and Ca^{2+} are similar, and thus Eu^{2+} could be easily incorporated into

calcite, leading to fractionation between Eu and other REY (Qi et al., 2002). However, positive Eu anomalies caused by calcite have never been observed in coal. This is possibly because the temperature of calcite formation is generally thought to be low (e.g., around 80 °C in cleat and fracture fillings; Ward, 2002), and calcite is easily decomposed under acidic conditions. As mentioned above, the reduction of Eu^{3+} to Eu^{2+} only occurs under extreme reducing conditions and at temperatures >250 °C. Secondly, Eu is generally concentrated in the K-feldspar of granite; therefore, intense leaching of this abundant mineral by hydrothermal solutions passing through alkaline basement granites could lead to Eu enrichment in those solutions (Seredin et al., 2006). However, the Ge-rich coals that have also been subjected to the same hydrothermal solutions do not show any positive Eu anomalies (Dai et al., 2015c). It should be noted that the concentration of Ba in these metasomatite samples are also high (Dai et al., 2015c), and thus the strong positive Eu anomalies could possibly be caused by interference from BaO and/or BaOH during ICP-MS analysis. The elevated

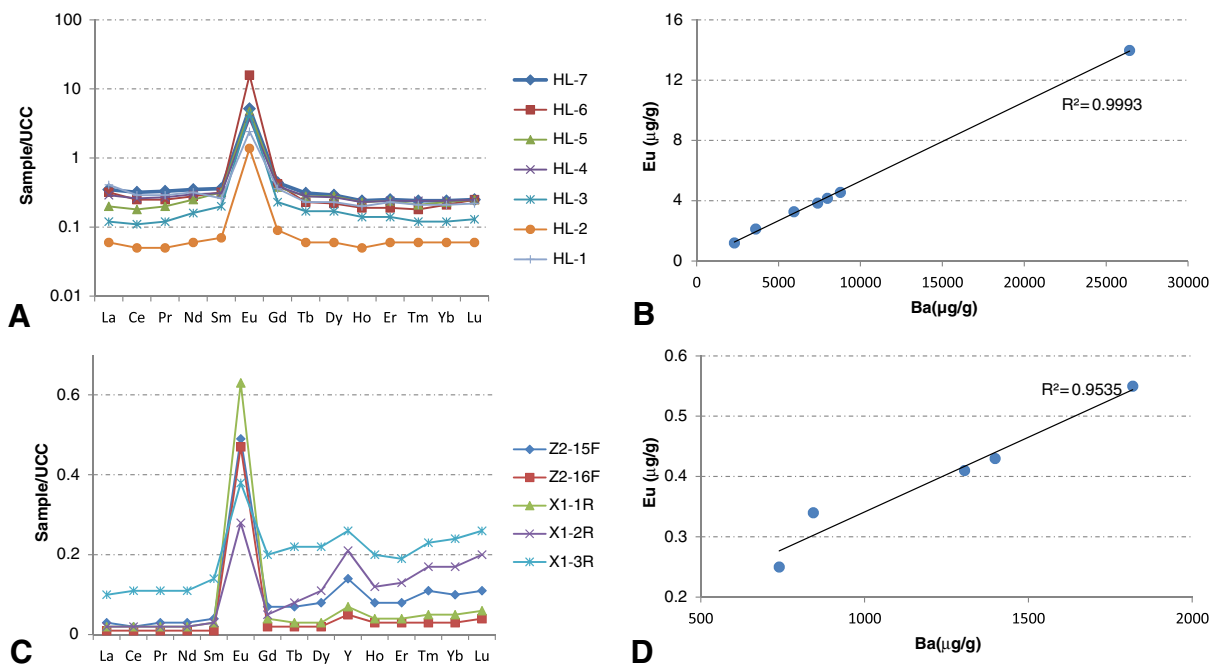


Fig. 9. REY in high-Ba coal samples; Eu values in high-Ba coals interfered by BaO and/or BaOH during ICP-MS analysis. (A), Distribution patterns of REY of coals from the Huanglong Coalfield, China. (B), Relation between Eu and Ba of the coals from the Huanglong Coalfield. (C), Distribution patterns of REY of coals from the Lincang coal-hosted Ge ore deposit, China. (D), Relation between Eu and Ba of the coals from the Lincang coal-hosted Ge ore deposit. Data for (A) and (B) are from Zhao et al. (2012) and (Zhao et al., 2014); Data for (C) and (D) are from Dai et al. (2015c).

concentrations of Eu in these metasomatite samples are positively correlated to Ba concentrations ($r^2 = 0.95$; Fig. 9D), further indicating the interference between Ba and Eu.

3.3. Yttrium anomalies in coal

The Y_N/Ho_N ratio represents decoupling of the geochemical twins Y and Ho, which produces Y anomalies in REY patterns (Bau et al., 2014). $Y_N/Ho_N < 1$ and > 1 represent negative and positive anomalies, respectively. Generally, the Y anomaly occurs in aqueous or highly evolved magmatic systems with high complexing capacity (Bau, 1996), tetrad effects in fluorine-rich magmatic-hydrothermal systems (Bau, 1996; Bau and Dulski, 1995; Monecke et al., 2011) and low-temperature aquatic environments (Tanaka et al., 2004).

Several factors may cause Y anomalies in coal, including previous geochemical processes within the sediment source rocks, the sedimentary environment (e.g., seawater injection, hydrogenetic environment), and hydrothermal fluids (e.g., epithermal solutions, submarine exhalations, acid waters, alkaline N_2 -bearing hydrothermal solutions, CO_2 -bearing chloride-sulfide solutions, meteoric waters, and volcanogenic solutions). Relative to the UCC, yttrium in coal may display positive, negative, or no anomalies. Yttrium in common Chinese and US coals shows very weak negative anomalies (Fig. 2), and, as indicated by Bau et al. (2014), almost all hydrogenetic deposits are characterized by negative Y anomalies.

Yttrium in mafic basalts displays weak positive anomalies (Fig. 3A). For example, both the high-Ti and low-Ti mafic basalts of the Kangdian Upland have an average Y_N/Ho_N value of 1.12. Yttrium in the felsic-intermediate rocks shows weak or no anomalies (Fig. 3C), with an average Y_N/Ho_N value of 0.95. Consequently, yttrium in coals with input of basaltic (Fig. 3B) and felsic-intermediate terrigenous materials generally shows weak or no anomalies, similar to those of Chinese or US coals (Fig. 2).

In a few cases, Y- (and REY-) bearing phosphates input from the sediment-source region can cause positive Y anomalies. Two bench samples (Nos. 6262 and 6368) of the Middle Pennsylvanian coals in Darby, Kentucky (USA), have strong Y anomalies compared to any of the other coal benches (Johnston et al., 2015). Relative to other Darby benches, P_2O_5 and TiO_2 are also high, suggesting that an influx of Y- (and REY) bearing phosphates could have accompanied the TiO_2 influx. Some studies have shown that TiO_2 -minerals, phosphates, and zircon are common in detrital (often the basal coal) lithotypes (Hower and Pollock, 1989; Andrews et al., 1994).

Seawater is characterized by positive Y anomalies (Zhang et al., 1994; Bau et al., 1995) and hence coals subjected to seawater influence would be expected to have positive Y anomalies. Coals preserved within marine carbonate successions (Fig. 4D) show positive Y anomalies. On the other hand, since those coals were also subjected to injection of hydrothermal fluids during peat accumulation, the positive anomalies

may have resulted from the joint influence of seawater and hydrothermal fluids. Thus it may be difficult to evaluate detrital siliciclastic (Y/Ho = ~25–30) and seawater (Y/Ho = ~60–70) inputs by using Y/Ho ratios, which are more applicable to marine sediments (Webb and Kamber, 2000; Chen et al., 2015a).

Volcanogenic hydrothermal solutions could also cause positive Y anomalies in coal. For example, the Ge-rich coals of the Wulantuga deposit in the Shengli Coalfield, as described above, have been subjected to Hg-As-rich volcanogenic solutions (Dai et al., 2012; Seredin, 2005). Relative to the low-Ge coals in the same coalfield (Fig. 6A), the high-Ge coals have a distinctly higher Y content. In comparison with Ge-free coals in the same coalfield, the high-Ge coals of the Pavlovka deposit (Russia Far East; Seredin, 2005) are also enriched in Y. Owing to the influence of volcanogenic hydrothermal solutions (as described above), the Early Jurassic U-rich coals from the Yili Coalfield are also characterized by strong Y anomalies (Fig. 7A).

The high-Ge coals of the Lincang coal-hosted Ge ore deposit, which was subjected to a mixture of alkaline N_2 -bearing and volcanogenic CO_2 -bearing fluids (Dai et al., 2015c), are characterized by strong positive Y anomalies (Fig. 10A). The Guxu coals, which were subjected to hydrothermal solutions during the early stages of peat accumulation (Dai et al., 2015e), as mentioned above, also have positive Y anomalies (Fig. 3D).

3.4. Gd anomalies in coal

The ratio of Gd_N to Gd_N^* can be used to quantify decoupling of Gd from the other REY, where Gd_N is the ratio of the Gd concentration in the investigated samples to the Gd value in the UCC. Gd_N/Gd_N^* can be calculated (Bau and Dulski, 1996) as:

$$Gd_N/Gd_N^* = Gd_N / [(Sm_N \times 0.33) + (Tb_N \times 0.67)] \quad (5)$$

Gadolinium anomalies in coal have rarely been discussed (Dai et al., 2014b, 2015b). Gadolinium displays positive, weak (mainly positive but in a few cases negative) or no anomalies. Gadolinium in common Chinese and US coals shows very weak negative anomalies (Fig. 2). In addition to the rocks in the sediment source region, Gd anomalies are mainly controlled by the influence of seawater, hydrothermal fluids and other waters, all of which could lead to positive Gd anomalies in coal. Seawater generally shows positive Gd anomalies (Elderfield and Greaves, 1982; Bau et al., 1996). For example, the coals preserved within carbonate successions show weak positive Gd anomalies, from 1.02 to 1.23, with an average of 1.08 (Fig. 4D; Dai et al., 2015a). Samples of the C3 coal (C3-2c and C3-6c) from the Xinde Mine, Yunnan (Fig. 3B; Dai et al., 2014b) and coals from the Shengli Coalfield, China (Fig. 10B; Dai et al., 2015b) are characterized by M-type REY spectra with a Gd maximum; such patterns are typical of acid waters, including high pCO_2 -waters in coal basins (Shand et al., 2005).

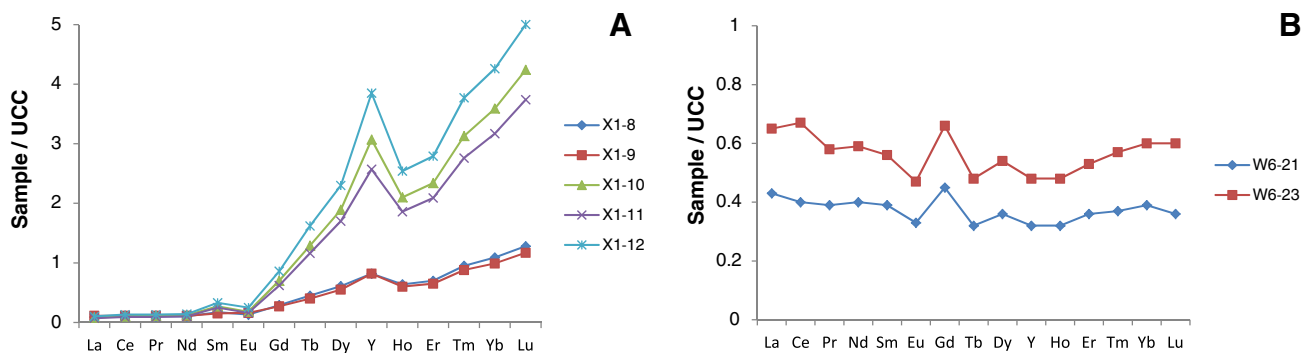


Fig. 10. Positive Y anomalies in the Ge-rich coals from Lincang, Yunnan province, China (A; data from Dai et al., 2015e) and positive Gd in the Early Cretaceous coals from the Shengli Coalfield (B; data from Dai et al., 2015b; Gd_N/Gd_N^* values for W6-21 and W6-23 are 1.31 and 1.30, respectively).

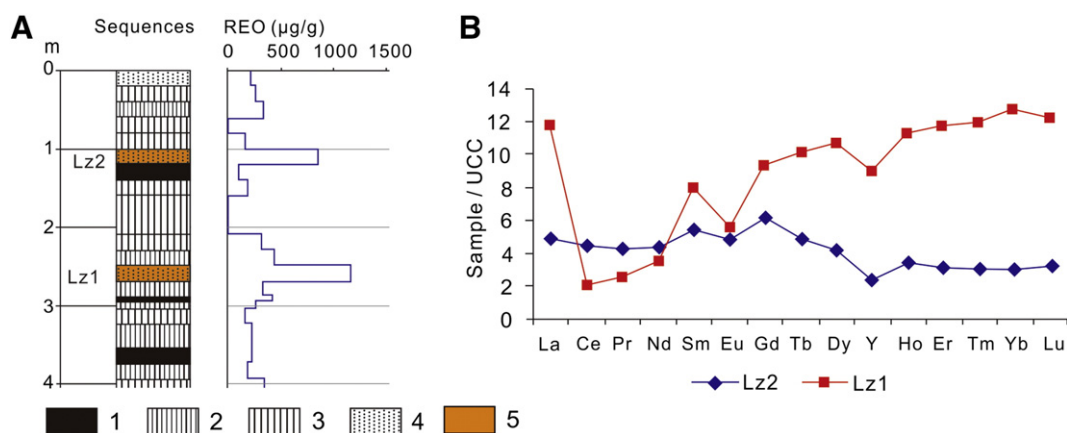


Fig. 11. REY distribution patterns in REY-rich siltstone from the Luzanovka open-cut coal mine. Data from Seredin and Mokhov (2007). 1 - coal; 2 - coaly clay; 3 - clay; 4 - aleurolite and sandstone; 5 - REY-rich layers.

The Gd anomalies in coal may sometimes be caused by the analytical procedure. For example, using INAA technology, Birk and White (1991) found the Gd positive anomalies in the bituminous coals and underclays of the Sydney Basin, Nova Scotia (Canada) was due to Th interference, and therefore was attributed to analytical error.

3.5. Lanthanum anomalies in coal

The ratio of La_N to La_N^* (La_N/La_N^*) can be used to quantify decoupling of La from the other REY, where La_N is the ratio of the La concentration in the investigated samples to the La value in the UCC. (La_N/La_N^*) can be calculated (Bau and Dulski, 1996) as:

$$La_N/La_N^* = La_N / (3Pr_N - 2Nd_N). \quad (6)$$

As with Gd anomalies, lanthanum anomalies have rarely been investigated in coal (Seredin and Dai, 2012). Relative to the UCC, common Chinese and US coals show positive anomalies of La, both having an overall La_N/La_N^* value of 1.43.

The La_N/La_N^* values of the high- and low-Ti mafic basalts of the Kangdian Upland are 1.11 and 1.52, respectively. La_N/La_N^* for the felsic-intermediate rocks at the top of the Kangdian Upland is 0.75–0.89, with an average of 0.85. The C2 and C3 coals from the Xinde Mine (Fig. 3B) have positive La anomalies, 1.16 and 1.20 respectively; these are very close to those of the high-Ti mafics but much lower than the low Ti mafics, further indicating that the sediment source region mainly comprised high-Ti basalts.

Both samples W6-21 and W6-23 from the Shengli Coalfield, which have been subjected to acid waters, have positive La_N/La_N^* anomalies ($La_N/La_N^* = 1.16$; Fig. 10B). As the typical REY_N features of modern seawater are characterized by positive La_N (Elderfield and Greaves, 1982), coals preserved within carbonate successions show positive anomalies (Fig. 4D).

The main REY-bearing minerals in the REY-rich siltstone from the Luzanovka open-cut coal mine are Sr-Mn-carbonates with selective La enrichment (Seredin and Mokhov, 2007). The abundance of these minerals in the ore (Lz1) is reflected in the unusual shape of the REE plot, which is characterized by a prominent La-maximum (Fig. 11).

In addition to the above REY anomalies in coal (e.g., Ce, Eu; La, Gd, and Y), other REY-bearing minerals have been identified, although rarely, in coal deposits. For example, Nd- and Dy -bearing minerals without other REY, as well as REY compounds with other metals (Sm-Fe-Co, Sn-Ca-Co, Dy-Fe, Y-Ni), have been observed in the coal and fossilized xylem of the Pavlovka deposit (Seredin, 1996; Seredin and Mokhov, 2007), where they were considered to represent significant fractionation of the trivalent lanthanides under unique conditions.

4. Conclusions

Anomalies of redox-sensitive Ce and Eu, and, in some cases, of non-redox-sensitive La, Gd, and Y, may occur in the coal and associated non-coal rocks of a coal seam. A number of factors may control REY anomalies in coal deposits, including the terrigenous materials from the source region, ingress of hydrothermal fluids, seawater, natural waters, volcanic ashes, and the sedimentary environments of peat formation. In some cases, the REY anomalies in coal deposits appear to have resulted from two or more geochemical processes, making them more complex. With the exception of Ce and Eu, as well as, in some cases, La, Gd, and Y, other REY are generally not expected to be anomalous; otherwise, the quality of the analytical REY data may be questionable. Analysis of REY anomalies can be used to provide indicators for inferring the terrigenous source region, reconstructing the sedimentary environment, or understanding the post-sedimentary history of coal deposits.

Although some studies show that certain diagenetic processes can lead to anomalies of REY in some geological materials (e.g., Himmler et al., 2013; Chen et al., 2015a; Pattan et al., 2005), this paper has not discussed the influence of diagenetic processes associated with coal-rank advance (e.g., temperature, pressure, and time) on anomalous rare earth elements and yttrium in coal. Some interaction mechanisms, e.g., overprint of seawater, hydrothermal fluids, and natural waters on peat swamp, are also unknown. These important issues require further investigation to evaluate more fully the anomalous origin of REY in coal.

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Appendix A. Supplementary data

Relation between rare earth elements and Ba. Data of rare earth elements and Ba are from Zhao et al. (2012) and (Zhao et al., 2014), respectively. The unit for x- and y-axes is μg/g.

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