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Anomalies of rare metals in Lopingian super-high-organic-sulfur coals from the Yishan Coalfield, Guangxi, China

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ABSTRACT

The origin and modes of occurrence of rare metals in coal (e.g., rare earth elements, U, Se, Re, Ge, Ga, and Nb) have attracted much attention in recent years because such investigations can provide fundamental information for assessment of their economic significance. This paper investigates the abundance, modes of occurrence, and origin of rare metals in three Lopingian coals (LL5-K3, CG3-K6, and CG1-K7 Coals) from the Yishan Coalfield, Guangxi Province, southern China. The coals of this coalfield are preserved within carbonate successions and are characterized by super-high-organic sulfur (SHOS) contents (mostly 6–9%) and an elemental assemblage enriched in U-Se-Mo-V-Re. Two different hydrothermal solutions were responsible for the geochemical anomalies in the Yishan coals. One was responsible for the U-Se-Mo-V-Re enrichment in the three coal seams while the other was a high-temperature solution responsible for the positive Eu anomalies and the elevated rank ($R_{o,ran}$ = 2.05%) of the LL5-K3 coal. The U, Se, Mo, V, and Re in the CG3-K6 and CG1-K7 coals mainly have an organic association, but the same elements in the LL5-K3 coal have a mixed organic-inorganic affinity, attributed to high-temperature leaching in the early coalification stage. In addition to highly elevated concentrations of U-Se-Mo-V-Re, the average concentration of oxides of the rare earth elements and Y in the LL5-K3 coal (1387 ppm on average, ash basis) is higher than the cut-off grade for industrial deposits of these elements and thus the coals also have potential as raw materials for the recovery of rare earth elements.

1. Introduction

Rare metals in coal (including Sc, V, Ga, Ge, Se, Y, Zr, Nb, Mo, platinum group elements, Ag, Au, Re, U, and, particularly, rare earth elements) have attracted much attention for many decades (Goldschmidt and Peters, 1933; Gibson and Selvig, 1994; Finkelman, 1980, 1981; Swaine 1990; Yudovich and Ketris, 2006; Seredin and Dai, 2012; Hower et al., 2016a,b), because some coals or coal ashes, as well as host rocks adjacent to the coal seams (e.g., partings, roof and floor strata; Dai et al., 2016b; Saikia et al., 2015; Zhao et al., 2016a,b) and, in some cases, coal mine drainage waters (Stewart et al., 2017), may contain high concentrations of these elements, which are equal to or even higher than those found in conventional types of rare-metal ore deposits (Seredin and Finkelman, 2008; Seredin et al., 2013; Dai et al., 2016a,b). Coals with an organic sulfur content higher than 4% are usually considered as super-high-organic-sulfur (SHOS) coals (Chou, 2012); these are not common, but have been found, for example, in the Cenozoic coals of the Gippsland Basin, Victoria, Australia (Smith and Batts, 1974); a Permian coal seam in the Cranky Corner Basin, eastern Australia (Marshall and Draycott, 1954; Ward et al., 2007); and the Late Palaeocene Raša coal from Istria (Croatia) (White et al., 1990; Damste et al., 1999; Medunić et al., 2016). The Lopingian coals preserved within marine carbonate successions in southern China are also classified as SHOS coals, with the areas where these SHOS coals are present including the Guiding (Guizhou Province), Yanshan (Yunnan Province), Heshan and Fusui (Guangxi Province), and Chenxi (Hunan Province) Coalfields (Fig. 1).

SHOS coals preserved within marine carbonate successions in southern China are usually characterized by a U-Se-Mo-V-Re enrichment assemblage (Shao et al., 2003; Zeng et al., 2005; Dai et al., 2015a), and, in some cases, by elevated concentrations of rare

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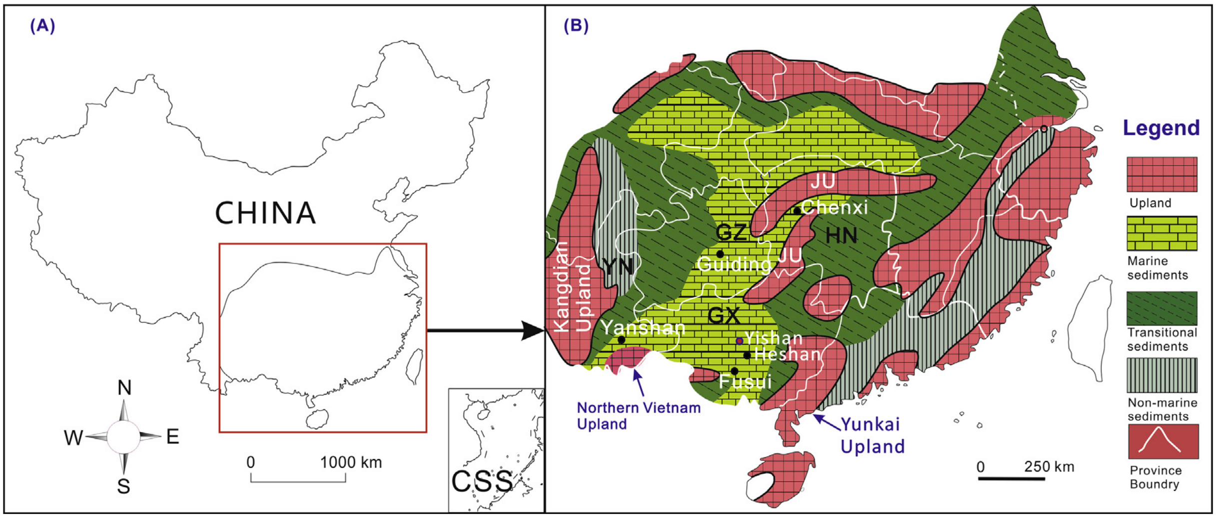

Fig. 1. Location of the Yishan Coalfield and distribution of Lopingian sedimentary environments in southern China. CSS, China South Sea. JU, Jiangnan Upland; GZ, Guizhou Province; GX, Guangxi Province; YN, Yunnan Province; HN, Hunan Province.

earth elements and Y (REY, or REE if Y is not included) (Dai et al., 2015a; Kang and Li, 2016). These rare metals could potentially be utilized from the relevant coal combustion products (Dai et al., 2013a,b; Seredin and Finkelman, 2008). The enrichment assemblage of U-Se-Mo-V-Re occurs not only in SHOS coals preserved within marine carbonate successions, but also within some coals deposited directly on mafic tuff layers (e.g., Lopingian coals in the Moxinpo Coalfield, Chongqing, China; Dai et al., 2017a) and in coals closely related to sandstone-hosted roll-type uranium deposits (Yang et al., 2011a,b; Dai et al., 2015b). The latter two enrichment types strongly support the hypothesis that enrichment in U-Se-Mo-V-Re is related to hydrothermal solutions (Dai et al., 2015a), rather than to seawater influence as proposed by Shao et al. (2003), Li and Tang (2013), and Li et al. (2013), or the formation of soil horizons prior to peat accumulation as suggested by Zeng et al. (2005). In this paper, we present evidence for the first hypothesis, namely that hydrothermal solutions were responsible for the enrichment in U-Se-Mo-V-Re, and that another different high-temperature hydrothermal fluid led to REE anomalies in the super-high organic sulfur coals of the Yishan Coalfield, Guanxi Province, southern China.

2. Geological setting

The Yishan Coalfield is located in the northern part of Guangxi Province, southern China (Fig. 1). The coalfield covers an area some 60-km long (elongated in a W-E direction) and 3-14-km wide. There are a number of small mines that are currently being worked, including the La-Lang #1 – #6 mines and the Chong-Gu #1 – #6 mines. The sedimentary sequences in the coalfield include the Guadalupian Maokou Formation, the Lopingian Heshan and Dalong Formations, the Lower Triassic Luolou Formation, the Middle Triassic Pingerguan Group, and Quaternary deposits.

The coal-bearing stratum is the Heshan Formation (Fig. 2A), which overlies limestones of the Maokou Formation with an unconformable contact and conformably underlies the Dalong Formation. The Heshan Formation, with a thickness of 300–519 m (mostly ~394 m), is mainly composed of thick limestones interlayered with coal seams and chert-bearing limestone beds. It is subdivided into three portions; an upper portion containing six coal seams (Nos. K4, K5, K6, K7, K8, and K9), a lower portion containing two coal seams (Nos. K2 and K3), and a middle portion devoid of any coal seams. The K3, K6, and K7 coals are the main mineable coal seams (Fig. 2B); they are overlain and underlain by limestones, and, in some cases, a thin silicified mudstone roof is interlayered between the coal seam and the thick limestone above. The lithological characteristics of the roof and floor suggest that the coal-bearing strata, like those of the Guiding (Guizhou Province; Dai et al., 2015a), Yanshan (Yunnan Province; Dai et al., 2008), and Heshan Coalfields (Guangxi Province, Dai et al., 2013a), formed in tidal flat environments on a restricted carbonate platform (Shao et al., 2003; Wang et al., 1995, 1997).

The sediment source region for the Yishan Coalfield, as with that for the Heshan and Fusui Coalfields discussed by Dai et al. (2013a,b), was the Yunkai Upland (Feng et al., 1994; Fig. 1), rather than the Kangdian Upland that supplied terrigenous materials to most of the Lopingian coal-bearing areas in southwestern China (Dai et al., 2015a; He et al., 2010; Huang et al., 2014; Xu et al., 2010). The Kangdian Upland was derived from the Emeishan mantle plume; it consists mainly of massive flood basalts, and to a lesser extent, contemporaneous mafic and felsic intrusions (Chung and Jahn, 1995; Shellnutt et al., 2011; Xiao et al., 2004).

The Maokou Formation is mainly composed of medium-thick limestone layers interbedded in some cases with cherts. The Dalong Formation, with an average thickness of 30 m, consists of siliceous sandstone and mudstone. The Lower Triassic Luolou Formation has an average thickness of 220 m and is mainly made-up of shales interbedded with marl and thinly-layered limestone. The lower portion of the Luolou Formation consists of thick limestone layers.

The Middle Triassic Pingerguan Group conformably overlies the Luolou Formation and dominantly consists of thick sandstones, interbedded with yellow and gray shales. The Cretaceous sediments include mainly sandstone and mudstone in the upper portion and conglomerate in the lower part. The thickness of the Quaternary sequence is 5–10 m; although it mostly unconformably overlies the Cretaceous sediments, in some cases it unconformably overlies the Heshan, Dalong, and Luolou Formations.

3. Samples and analytical procedures

3.1. Sample collection

A total of 48 samples (including 22 coal benches and 26 non-coal partings, roof, and floor strata) were collected from under-