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Variations in the stable isotope composition of mercury in coal-bearing sequences: Indications for its provenance and geochemical processes

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ABSTRACT

Mercury (Hg) stable isotope variations provide a potential tool to better understand the provenance and geochemical processes that control Hg occurrences in coal deposits. In this study, we explore the variations in Hg isotope compositions in coal benches of a single coal seam (No. 3-1 coal seam, Daizhuang Coal Mine, Jining Coalfield, Shandong Province), and in successive coals seams of a coal-bearing sequence (No. 1 to No. 11-2 coal seams, Zhuji Coal Mine, Huainan Coalfield, Anhui Province) to assess Hg isotopes as a Hg biogeochemical tracer in coal deposits. Large variations in mass dependent Hg isotope fractionation (MDF) were observed in both Daizhuang and Zhuji coal deposits, with δ^{202}Hg values ranging from −2.34 to −0.25 ± 0.12‰ (2 SD, n = 8), and from −1.62 to 0.44 ± 0.12‰ (2 SD, n = 18), respectively. Daizhuang coals showed insignificant mass independent Hg isotope fractionation (MIF) in most samples (−0.04 to 0.12 ± 0.08‰ for Δ^{199}Hg, 2 SD, n = 8), whereas MIF in the younger Nos. 7-11 coal seams of Zhuji coals (0.06 to 0.22 ± 0.08‰ for Δ^{199}Hg, 2 SD, n = 7) were positive and significant. Increased trends in both Hg concentrations and δ^{202}Hg values going from older to younger Zhuji coal seams were observed, and were possibly related to variations in coal-forming environment of different coal seams. The significant negative correlations of δ^{202}Hg vs. 1/Hg in the Zhuji coals, and of δ^{202}Hg vs. Δ^{199}Hg in the Daizhuang coals suggest that Hg isotopes can potentially be used to trace organic and inorganic Hg end-members in coal deposits. Natural coke, a metamorphosed form of coal, is on average two-fold enriched in Hg compared to coal, indicating that hydrothermal fluids derived from magmatic intrusions bring Hg into coal deposits. In addition, coke has either distinctly higher (0.70 to 0.91 ± 0.12‰, 2 SD, n = 2) or lower δ^{202}Hg (−4.00 to −3.47 ± 0.12‰, 2 SD, n = 3) than corresponding coals, demonstrating that significant Hg MDF occurred when coals were thermally contacted by intruded magmas.

1. Introduction

Mercury (Hg) is a naturally occurring, potentially toxic element. As a geological sink for biogenic and geogenic Hg, coal is commonly enriched in Hg as compared to other sedimentary host rocks (Dai et al., 2012a; Ketris and Yudovich, 2009). In some geologically active areas such as southwest China and eastern Russia, Hg concentrations can be locally enriched by several orders of magnitude through coal matrix sequestration of Hg from hydrothermal fluids (Dai et al., 2012b; Yudovich and Ketris, 2005; Zhuang et al., 2006). The combustion of coal for heat and electricity generation has emitted large amounts of geologically sequestered Hg to the atmosphere. At present, coal combustion contributes to approximate half of anthropogenic Hg emissions into the atmosphere, with an annual emission flux of 700–900 tons (Pacyna et al., 2010; Pirrone et al., 2010; Streets et al., 2011).

Extensive studies have been conducted on Hg abundances, occurrence and geological provenances in coal seams and their associated rocks (i.e. coal roof, parting and floor) (Hower et al., 2005; Quick et al., 2003; Toole-O'Neil et al., 1999; Yudovich and Ketris, 2005; Zheng et al., 2007a). Mercury concentrations in coal vary significantly, up to several orders of magnitude, among different countries, coal basins, coal mines and even benches within individual coal seams. The modes of Hg occurrence in coal largely depend on its environment of deposition. Reduced-sulfur groups in plant-derived organic matter and inorganic sulfide minerals (primarily pyrite) are commonly identified as the main Hg carriers in coal (Diehl et al., 2004; Hower et al., 2008; Yudovich and Ketris, 2005). However, the controlling factors that influence Hg accumulation and migration in coal-forming swamps are still a matter of debate (Yudovich and Ketris, 2005), and quantitative tracing of primary Hg sources in coal seams is subject to large uncertainty. Therefore, an appropriate and robust tracer is needed to better understand the Hg geochemistry of coal deposits.

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Recent advances in multiple collector inductively coupled plasma mass spectrometry (MC–ICPMS) and associated techniques (e.g. sample preparation, purification and introduction) have allowed high-precision determination of Hg stable isotope ratios in natural samples with Hg concentrations down to ultratrace concentration range (Blum and Bergquist, 2007; Chen et al., 2010; Sun et al., 2013a). Both mass dependent Hg isotope fractionation (MDF, indicated by δ^{202}Hg) and mass independent Hg isotope fractionation (MIF, odd ^{199}Hg and ^{201}Hg isotopes mostly, indicated by Δ^{199}Hg and Δ^{201}Hg) vary by more than 10‰ in geological and environmental samples (Bergquist and Blum, 2009; Smith et al., 2014; Sonke, 2011; Yin et al., 2010). In addition, observations on atmospheric precipitations (snow and rain) also show up to 1‰ variation of MIF of even Hg isotopes (indicated by Δ^{200}Hg and Δ^{204}Hg) (Chen et al., 2012; Demers et al., 2013; Gratz et al., 2010; Sherman et al., 2012). Measurable Hg MDF is caused by most biogeochemical processes that affect Hg, such as reduction (biotic and abiotic), oxidation, adsorption, condensation, evaporation, volatilization, methylation and demethylation (Bergquist and Blum, 2007; Estrade et al., 2009; Kritee et al., 2013; Perrot et al., 2013; Zheng and Hintelmann, 2010a; Zheng et al., 2007b). Previous work has shown that significant Hg isotope variation, as large as 4.7‰ for δ^{202}Hg and 1‰ for Δ^{199}Hg, occurs in coal deposits worldwide. By using the combination of δ^{202}Hg (MDF) and Δ^{199}Hg (MIF) signatures, it has been demonstrated that coals from different countries, coal deposits and coal seams have distinct Hg isotope characteristics (Biswas et al., 2008; Lefticariu et al., 2011; Sun et al., 2014; Yin et al., 2014). In addition, the main Hg carriers, i.e. pyrite (diagenetic and hydrothermal) and organic matter, may possess characteristic and distinguishable Hg isotope signatures (Lefticariu et al., 2011). These observations highlight the potential of using Hg isotope signatures to trace Hg provenances and modes of occurrence in coal, and to understand the geochemical processes controlling Hg migration and accumulation in coal basins.

In this study, we present new data on coal samples, natural cokes, and coal associated rocks from Permian coal seams in two well-documented coal-bearing strata of Huainan Coalfield and Jining Coalfield, North China (Fig. 1). The case study focuses on: 1) Hg isotope characteristics of Permian coals deposited in different coalfields and different coal-forming environments; 2) identification of Hg provenances and geochemical processes occurring during and after coal deposition and; 3) the impact of high-temperature magmatic intrusion events on Hg isotope fractionation between contact-metamorphosed coke and coal.

2. Study area

The Huainan Coalfield and Jining Coalfield, located in northern Anhui and western Shandong, respectively, (Fig. 1), are some of the most active coal-producing districts in China. Abundant Permo-Carboniferous bituminous coal with middle–high volatile matters (~35–40 wt.%, dry ash-free basis) and calorific values (~20–30 kJ/kg, dry basis) occur underground in both coalfields (Liu et al., 2005; Sun et al., 2010a,b). The Zhuji Coal Mine (ZJ, covering an area of 45 km^2 with a coal reserve of 947 Mt) and Daizhuang Coal Mine (DZ, covering an area of 66 km^2 with a coal reserve of 370 Mt) in these two coalfields were selected in the present study. The studied coals are reported to have <1 wt.% total sulfur contents (average value is ~0.5% for No. 1 to No. 11-2 coal seams of ZJ, and is ~0.7% for No. 3-1 coal seam of DZ, Fig. 2), classifying them as low-sulfur coals, and lower values of maximum vitrinite reflection (0.6–0.9%) (AICE, 2007; SICE, 2010). Coal macerals are dominated by vitrinite (>50%) followed by inertinite (<30%) and liptinite (<10%) (AICE, 2007; SICE, 2010). In ZJ, abundant intrusive rocks in the forms of dikes and sills were observed at Shanxi Formation coals and decrease upwards along coal-bearing sequences (AICE, 2007). The Rb/Sr isotope age for these intrusion bodies is ~110 Ma at Late Cretaceous Period The hydrothermal effect resulted in the transformation of the surrounding coal to coke. These cokes have a fragmented and porous texture. Intrusive dikes of granite porphyry and gabbro can be found in contact with cokes or as interlayers between coal associated rocks (Yang et al., 2012).

2.1. Coal-forming environment

The studied Zhuji and Daizhuang coal deposits are situated on the North China Platform. In the Middle Carboniferous, the North China Platform subsided and formed the large down-warped North China Coal Basin (NCCB) (Dai et al., 2012a; Han and Yang, 1980; Han et al., 1996). The NCCB has an area of ~1,200,000 km^2, representing ~60% of Chinese coal reserves. The continuous uplift of northern Yinshan

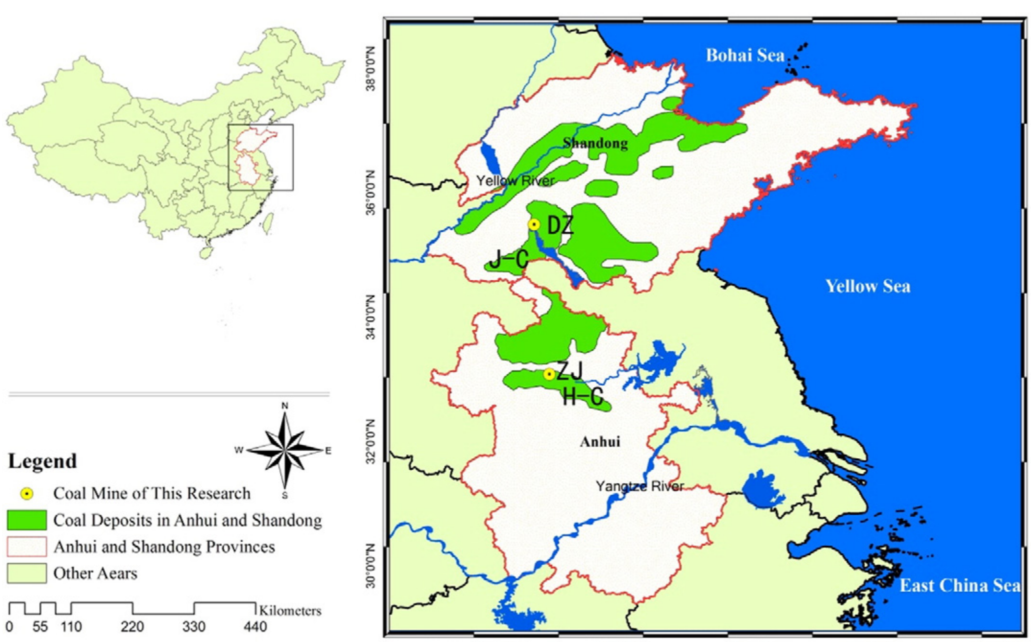

Fig. 1. Geographical map showing the locations of studied coal mines. DZ: Daizhuang Coal Mine; ZJ: Zhuji Coal Mine; J-C: Jining Coalfield; H-C: Huainan Coalfield.