



Invited review

Biogeochemical controls on mercury stable isotope compositions of world coal deposits: A review



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ABSTRACT

Coal deposits were important natural Hg sinks in the Late Paleozoic and Middle–Late Mesozoic. Coal combustion since the industrial revolution has emitted more than 35,000 t of Hg into the atmosphere. Environmental geochemistry research on Hg in coal is essential to understand the natural Hg cycle throughout Earth history and the present-day Hg cycle under human perturbation. In this review, we summarize the methods of Hg isotope measurement in coals, and compile recently published Hg isotope data of >200 world coal samples according to their locations, formation periods (Carboniferous, Permian, Jurassic, Cretaceous, Early–Middle Cenozoic) and ranks (anthracite, bituminous coal, subbituminous coal, lignite), and illustrate the controls of sources and biogeochemical processes on Hg isotope compositions in coal deposits. Up to 4.7‰ variation (−3.90 to 0.77‰) in mass dependent fractionation (MDF, represented by $\delta^{202}\text{Hg}$) and 1.0‰ variation (−0.63 to 0.34‰) in mass independent fractionation (MIF, represented by $\Delta^{199}\text{Hg}$) are observed in world coal deposit, with an average value of $-1.16 \pm 0.79\text{‰}$ (1SD) and $-0.11 \pm 0.18\text{‰}$ (1SD) for $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$, respectively. We find that coal $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ are broadly controlled by two source materials: terrestrial plants (biogenic Hg) and crustal rocks (geogenic Hg), accounting for 37–46% and 54–63% of Hg in coals. No clear trends are seen in neither $\delta^{202}\text{Hg}$ vs. coal-forming periods nor $\delta^{202}\text{Hg}$ vs. coal ranks, which we attribute to important overlapping of $\delta^{202}\text{Hg}$ in the source materials of different coal-forming periods and the multidirectional Hg MDF during coalification. Interestingly, a step-wise increase in total Hg and a disappearance of $\Delta^{199}\text{Hg}$ are observed along with increasing coal rank, suggesting the addition of hydrothermal Hg into high-rank coals. The hydrothermal fluids not only upgraded the coal ranks, but also increased the Hg concentrations and $\Delta^{199}\text{Hg}$ of coals. In addition, the addition of hydrothermal Hg into coal deposits was also partly responsible for the comparatively higher total Hg and $\Delta^{199}\text{Hg}$ in the Late Paleozoic coals relative to the Mesozoic and Cenozoic coals. The co-variation of atmospheric oxygen levels and $\Delta^{199}\text{Hg}$ of coals at different coal-forming time widows suggests that the removal of biogenic Hg in response to widespread swamp fires may have increased the $\Delta^{199}\text{Hg}$ in Late Paleozoic coals as well. Our study indicates that coal Hg isotopes provide new insights into the biogeochemical cycle of Hg in coal deposits, and that $\Delta^{199}\text{Hg}$ is a robust indicator to trace Hg addition/removal in coal deposits and biogeochemical processes (magmatic intrusion, hydrothermal fluids penetration, burning of coal swamp) occurring during coal deposition.

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1. Introduction

Mercury (Hg) is a toxic element, and is transported and deposited globally along with atmospheric circulation (Mason et al., 1994; Driscoll et al., 2013). Natural archives and model simulation suggest that modern-day atmospheric Hg deposition is augmented by a factor of 3–5 since the pre-industrial period (1750–1880), and by a factor of ~7 since 2000 BC (Martínez-Cortizas et al., 1999; Lamborg et al., 2002; Schuster et al., 2002; Fitzgerald et al., 2004; Faïn et al., 2009; Amos et al., 2013). At present, coal combustion accounts for approximately half of anthropogenic Hg emissions into the atmosphere, with an annual emission flux of 700–900 t (Pacyna et al., 2010; Pirrone et al., 2010; Streets et al., 2011). As a biological and geological Hg sink, Hg biogeochemistry in coal is essential in understanding the natural Hg cycle over Earth's history, and the perturbation of the natural Hg cycle by coal combustion. Numerous studies have been published to address the biogeochemical characteristics of Hg in coal deposits and their geological and environmental significances (Diehl et al., 2004; Hower et al., 2005; Mastalerz and Drobnik, 2005; Yudovich and Ketris, 2005a,b; Dai et al., 2006, 2014; Zheng et al., 2007a; Kolker et al., 2009). However, several key issues are still under debate, such as the tracing and quantification of syngenetic/epigenetic Hg and geogenic/biogenic Hg in coal deposits, the control of biogeochemical processes (e.g., evolution of coal-forming plants and source rocks; aqueous conditions of different coal depositional settings, penetration of hydrothermal fluids) on Hg accumulation in coal deposits, and the importance of coal deposits as a Hg sink in Earth's natural Hg cycle and its interaction with coeval climate and environmental factors (e.g., atmospheric oxygen level and terrestrial fires).

Recent advances in high precision stable Hg isotope measurement and the observation of multiple Hg isotope fractionation signatures in coals have provided a new means to study these questions (Biswas et al., 2008; Lefticariu et al., 2011; Sherman et al., 2012; Sun et al., 2013a,b, 2014a,b; Yin et al., 2014a). Mercury has seven stable isotopes: ^{196}Hg (0.16%), ^{198}Hg (10.0%), ^{199}Hg (16.9%), ^{200}Hg (23.1%), ^{201}Hg (13.2%), ^{202}Hg (29.7%) and ^{204}Hg (6.82%), with a relative mass span of ~4% (Blum and Bergquist, 2007; Meija et al., 2010). Nearly all biotic and abiotic reactions involving Hg (e.g., reduction, oxidation, methylation, demethylation, diffusion, volatilization, vaporization, condensation and adsorption) have been observed to separate Hg isotopes as a function of isotope mass, i.e. mass dependent isotope fractionation (MDF) indicated by $\delta^{202}\text{Hg}$ (Bergquist and Blum, 2007; Zheng et al., 2007b; Estrade et al., 2009; Wiederhold et al., 2010; Zheng and Hintelmann, 2010a,b; Jiskra et al., 2012; Ghosh et al., 2013; Jiménez-Moreno et al., 2013; Koster van Groos et al., 2013; Kritee et al., 2013; Perrot et al., 2013). Specific reactions (e.g., photochemical reduction, vaporization of liquid Hg, equilibrium complexation of aqueous Hg^{II} with –SH groups) (Bergquist and Blum, 2007; Estrade et al., 2009; Zheng and Hintelmann, 2009; Wiederhold et al., 2010; Ghosh et al., 2013) could additionally separate Hg isotopes (mainly odd isotopes ^{199}Hg and ^{201}Hg) as a function of nuclear magnetic moment or nuclear volume (Schauble, 2007; Buchachenko, 2013), i.e. mass independent isotope fractionation (MIF) indicated by $\Delta^{199}\text{Hg}$ or $\Delta^{201}\text{Hg}$. The observation of significant even Hg isotopes (^{200}Hg and ^{204}Hg) MIF in atmospheric samples (snow, rain) further expands the application of Hg

isotopes as geochemical tracers, although the underlying fractionation mechanisms are not yet understood (Gratz et al., 2010; Chen et al., 2012; Demers et al., 2013). These multiple Hg isotope signatures have been widely used in studying the sources, transformation, transfer and sinks of Hg in the Earth environment (Sonke and Blum, 2013; Blum et al., 2014; Yin et al., 2014b).

The first high precision Hg isotope measurements of coals were reported by Biswas et al. (2008) who found that selected coal deposits from China ($n = 11$), Russia-Kazakhstan ($n = 9$) and USA ($n = 11$) are characterized by distinguishable $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$. Subsequently, Lefticariu et al. (2011) and Sun et al. (2014b) investigated in detail the Hg isotope variations within coal seams in Late Paleozoic coals from USA and China. They found that selected coal seams (or groups) can be distinguished by their $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$, and Hg isotope signatures can be used to trace Hg from different sources. These studies highlighted the potential of Hg isotopes to trace coal combustion Hg emissions and the geochemical processes occurring in coal deposits. Further investigation of the traceability of coal combustion Hg emissions was made by Sherman et al. (2012) and Sun et al. (2013b). Sherman et al. (2012) showed how Hg in precipitation downwind from a large USA coal-fired utility boiler (CFUB) has different $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ than precipitation Hg in remote areas, but also different than feed coal $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$. Sun et al. (2013b) examined Hg MDF in six Chinese CFUBs and observed negative $\delta^{202}\text{Hg}$ in fly ash and gypsum by-products, suggesting that CFUBs modify feed coal $\delta^{202}\text{Hg}$, but not $\Delta^{199}\text{Hg}$. Both studies reiterated opportunities, but also pitfalls for coal Hg emission tracing by revealing complex isotope relationships between feed coal, CFUB emissions and Hg deposition. Recently, Yin et al. (2014b) measured Hg isotope compositions of coal samples from major coal producing fields in China ($n = 61$), and attributed their spatial Hg isotope variations to their varying proportions of biogenic and geogenic Hg sources. Meanwhile, Sun et al. (2014a) established a world coal Hg isotope database by measuring an additional >100 coal samples from China and USA, former USSR, South Africa, Europe, India, Indonesia and Mongolia, in an effort to reconstruct historical coal Hg isotope emission curves. While the study of Sun et al. (2014a) mainly focused on the environmental significance of the global coal Hg isotope database, the biogeochemical factors controlling $\delta^{202}\text{Hg}$, $\Delta^{199}\text{Hg}$ across regional coal deposits were not investigated.

In this review, we first review the analytic protocols of Hg isotope measurement in coal, and compile the Hg isotope compositions of reported coal reference materials for future inter-laboratory comparison. Then, the global coal Hg isotope library of Sun et al. (2014a) is updated by integrating recent data of Yin et al. (2014b) to revisit Hg isotope variations among and within regions for future global, regional and local coal Hg emission tracing. Subsequently, the sources (plants, crustal rocks, hydrothermal fluids) and biogeochemical processes (magmatic intrusion, hydrothermal fluid circulation, coal swamp fires) occurring during and after coal deposition are discussed in detail to identify the controlling factors of Hg isotope compositions of world coal deposits. The dependence of total Hg concentration, $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ on coal ranks, coal-forming periods and other coal chemical parameters are discussed, and provide important clues to understand the evolution of $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ in coal deposits.

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