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Mercury anomalies across the end Permian mass extinction in South China from shallow and deep water depositional environments

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ABSTRACT

Life on Earth suffered its greatest bio-crisis since multicellular organisms rose 600 million years ago during the end-Permian mass extinction. Coincidence of the mass extinction with flood basalt eruptions in Siberia is well established, but the exact causal connection between the eruptions and extinction processes in South China is uncertain due to their wide spatial separation and the absence of direct geochemical evidence linking the two. The concentration and stable isotope analysis of mercury provides a way to test these links as its concentration is thought to be tied to igneous activity. Mercury/total organic carbon ratios from three Permian–Triassic boundary sections with a well-resolved extinction record in South China show elevated values (up to 900 ppb/wt.% relative to a background of <100 ppb/wt.%) that exactly coincides with the end-Permian mass extinction horizon. This enrichment does not show any correlation with redox and sedimentation rate variations during that time. Hg isotope mass-independent fractionation (Δ^{199}Hg), with sustained positive values, indicate a predominant atmospheric-derived signature of volcanic Hg in deep-shelf settings of the Daxiakou and Shangsi sections. In contrast, the nearshore environment of the Meishan section displays a negative Δ^{199}Hg signature, interpreted to be related to terrestrial Hg sources. Such temporal differences in Δ^{199}Hg values shed new light on Hg geochemical behavior in marine settings, and also on the kill mechanisms associated with volcanism that were responsible for biotic mortality at the end of the Permian.

1. Introduction

The end-Permian mass extinction (EPME; 252 million years ago) was the most severe biotic crisis of the Phanerozoic. Most workers agree that intense volcanic activity of the Siberian Traps Large Igneous Province (STLIP) was a driver of environmental change (Wignall, 2001; Svensen et al., 2009; Sun et al., 2012; Black et al., 2014; Clarkson et al., 2015; Burgess et al., 2017). The STLIP has an estimated volume of up to 3–4 $\times$ 10^6 km^3, which is larger than any other continental basalt province, including the Emeishan traps ($\sim$ 1 $\times$ 10^6 km^3), Central Atlantic Magmatic Province ($\sim$2 $\times$ 10^6 km^3), Karoo and Ferrar traps ($\sim$2.5 $\times$ 10^6 km^3) and Deccan traps (2–4 $\times$ 10^6 km^3) (Courtillot and Renne, 2003, references therein). Its original volume is likely considerably larger as most is buried and inaccessible beneath the younger sediments of the West Siberian Basin (Reichow et al., 2009; Saunders, 2016). Recent high-precision U–Pb dating of STLIP basalts have shown that the onset of eruptions began shortly before the start of the mass extinction crisis (Burgess and Bowring, 2015). More recently, Burgess et al. (2017) further categorized the dated volcanic rocks from STLIP into lava- and sill-originated rocks, and found that major transfer from lava to sill eruptions coincided with the main episode of biotic extinction. Although there is a clear temporal correlation between the extinction event and volcanic activity, the precise mechanism that drove the environmental change is unresolved. In recent years, stable isotope systems have been shown to provide important insights into the response

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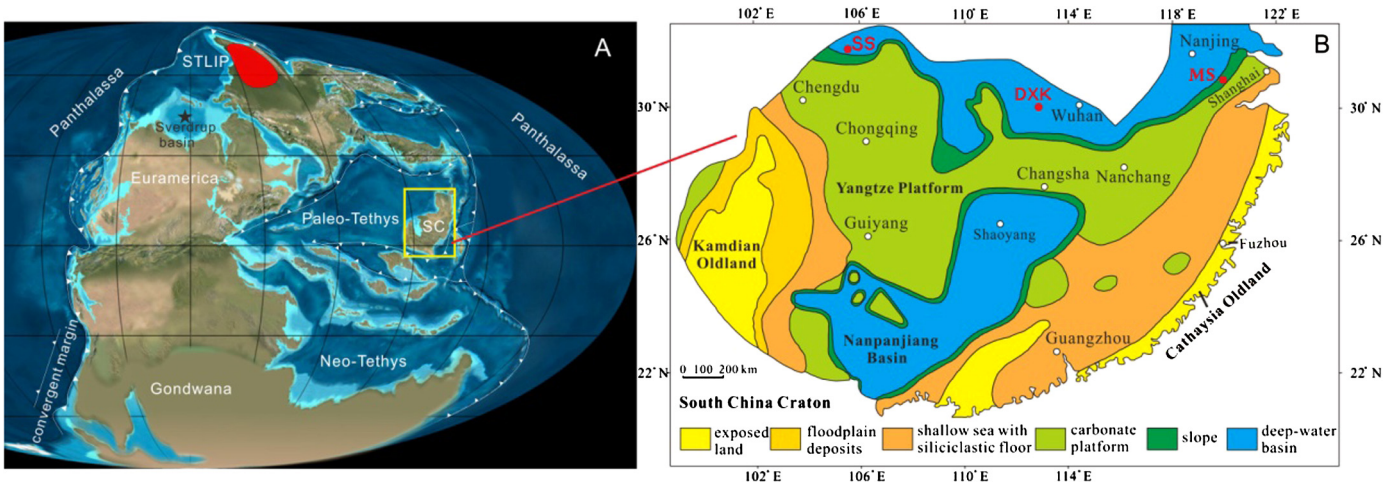

Fig. 1. Global (A) and South China (SC) (B) paleogeographic configurations over the Permian–Triassic transition showing the locations of the Meishan (MS), Daxiakou (DXK) and Shangsi (SS) sections, and the Siberia Traps large igneous province (STLIP). Global paleographic map is available online http://jan.ucc.nau.edu/~rcb7/, and map B follows Feng et al. (1996). (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

of environmental systems to key climatic changes associated with extinction events (Payne et al., 2010; Clarkson et al., 2015; Song et al., 2017; Liu et al., 2017). For example, calcium and boron isotopes were successfully applied to demonstrate ocean acidification triggered by STLIP across the EPME (Payne et al., 2010; Clarkson et al., 2015). But for any isotopic system there are often multiple inputs and outputs that can control the isotopic fractionation process in the environment. In this paper we attempt to evaluate environmental controls on Hg associated with the EPME. Hg is a key gas associated with volcanic activity and has been linked to the end-Permian environmental crisis (Sanei et al., 2012; Grasby et al., 2013, 2017)—a link we aim to assess here using mercury concentrations and isotopes measured in Permian–Triassic boundary (PTB) sections in South China.

The ratio of mercury concentrations over total organic carbon (Hg/TOC) in sedimentary sections has been shown to provide a proxy for voluminous volcanism (Sanei et al., 2012; Grasby et al., 2013, 2017). Mercury is a highly toxic heavy metal and has a sufficiently long atmospheric residence time (>1.5 yr) for global distribution (Blum et al., 2014). Explosive volcanic events inject abundant Hg into the atmosphere ensuring its global reach (Pyle and Mather, 2003). Most volcanic mercury is released as gaseous Hg^0 and removed from the atmosphere mainly through oxidation to form Hg^{2+}, which then accumulates in oceans and on land through rainfall or adsorption onto organic matter ensuring a strong association between Hg and TOC in sediments (Gehrke et al., 2009; Ruiz and Tomiyasu, 2015). Hg isotopes can undergo both large mass-dependent fractionations (MDF) and mass-independent fractionations (MIF) in nature (Blum et al., 2014), and thus are capable of tracing Hg sources and cycling (Grasby et al., 2017). Hg-MDF (δ^{202}Hg) can result from many pathways, including physical, chemical and biological reactions, whereas Hg-MIF (Δ^{199}Hg) is controlled by more limited pathways (mostly photochemical) and is unlikely to be altered in the post-depositional processes (Blum et al., 2014; Thibodeau et al., 2016; Thibodeau and Bergquist, 2017). Hence, Hg-MIF (Δ^{199}Hg) is generally a more conservative tracer of volcanic signature (Thibodeau and Bergquist, 2017).

In recent years, Hg concentrations and isotopes have been used to explore the relationship between large igneous provinces and contemporary mass extinctions (Sanei et al., 2012; Grasby et al., 2013, 2017; Percival et al., 2015, 2017; Sial et al., 2016; Thibodeau et al., 2016; Gong et al., 2017). Anomalous Hg deposition was observed at the EPME crisis in the Sverdrup Basin, Canadian High Arctic that occupied a paleogeographic position near the STLIP (Fig. 1A) (Sanei et al., 2012; Grasby et al., 2013). More recently, Grasby et al. (2017) documented the difference in Hg isotopes near the EPME between Sverdrup Basin at a deep water setting and the shallower water Meishan section in South China. They attributed the negative Δ^{199}Hg values at the EPME in Meishan to terrestrial sources, and suggested that deeper water sections that are isolated from terrestrial input provide better records of the volcanic signature. Therefore, whether or not the signature of Hg enrichments associated with STLIP is recorded in the South China sections is unresolved. We further this work by examining a series of sections in South China covering a range of water depths. We provide new data for two deeper-water sections (200–500 m), at Daxiakou and Shangsi in South China, and integrate this with the data from the shallow water Meishan section (Grasby et al., 2017). We measured Hg concentrations and Hg isotopic compositions through the *Clarkina changxingensis* (*C. changxingensis*) to *Isarcicella isarcica* (*I. isarcica*) conodont zones, to clarify the timing and intensity of the eruption across the PTB and link its relationship with EPME in South China. The varied sedimentary environments in the three sections enable an assessment of the geochemical behaviors of Hg in different water depths and indicated that the effects of the STLIP extended to the Chinese sections.

2. Geological background

The Meishan, Daxiakou, and Shangsi sections are separated by over 1000 km and lie along the northern part of South China Craton. During late Permian time, the craton was situated at low latitudes in the eastern Paleo-Tethys (Fig. 1A). The craton was characterized by marine facies in its interior, and bounded by lands to the east and west (Fig. 1B). In the central part of the craton, the roughly east-west trending Yangtze carbonate platform is flanked to the north and south by deeper water basins (Feng et al., 1996; Fig. 1B). The three studied sections lie on the flanks of the northern basin and the EPME has been calibrated at the bottom of the *C. meishanensis* conodont zone, with the PTB was placed at the bottom of the *Hindeodus parvus* (*H. parvus*) conodont zone (Jiang et al., 2011; Zhao et al., 2013; Chen et al., 2015).

The Meishan section, which is located at Meishan Town, Changxing County, Zhejiang Province, lay on the northeastern margin of the Yangtze Platform at a shallow water depth of between 30–60 m based on sedimentary structures indicative of fair-weather wave base and storm wave base (Yin et al., 2001; Chen et al., 2015; Fig. 1B). This section is the Global Stratotype of Point and Section (GSSP) for the PTB (Yin et al., 2001). Biostratigraphy, lithofacies, geochronology, and geochemistry of the Meishan