



Mercury enrichment and Hg isotopes in Cretaceous–Paleogene boundary successions: Links to volcanism and palaeoenvironmental impacts



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ABSTRACT

We investigate the use of Hg as a proxy for volcanism by studying four distal and two proximal sections in relation to the Deccan volcanic center, straddling the Cretaceous–Paleogene (KPg) boundary at (a) Højerup (Denmark), Bottaccione and Padriciano (Italy), (b) Meghalaya and Jhilmili (India), and (c) Bajada del Jagüel (Argentina). Hg sequestration by organic matter results in constant Hg/TOC ratio and linear correlation between Hg content of the sediments and total organic carbon (TOC).

Elevated Hg concentrations that deviate from this linear relationship represent most likely true Hg anomalies and these notable Hg/TOC spikes (all TOC <1%) are found in the Meghalaya, Bottaccione and Højerup sections within the CF2 planktic foraminiferal biozone (spike I), at the KPg boundary (spike II), and within the P1a planktic foraminiferal subzone (spike III). Spike III occurs also in the Jhilmili section. No clear correlation between Hg/TOC and Al₂O₃ exists in any of the studied sections. The Hg anomalies probably result from strong volcanic episodes of the Deccan phase-2 (started 250 kyr before the KPg boundary and lasted for 750 kyr) that exhaled sulfuric aerosols, carbon dioxide and other toxic agents which reached a critical threshold, represented in true Hg enrichments in the paleoenvironments. The possibility that Hg enrichments resulted from anoxia scavenging on the seafloor and penetration downward into sediments is not supported in the stratigraphic record of Mo/Al ratios redox proxy.

Hg isotopes were analyzed in samples from all KPg boundary sections in this study and from Bidart, France, the latter for comparison. Hg isotopes yielded $\delta^{202}\text{Hg}$ values ranging from -1 to -2% and $\Delta^{201}\text{Hg}$ signatures from 0 to 0.05‰ (spike II in Højerup, Bottaccione and Meghalaya KPg boundary layers) consistent with volcanic emission of Hg (0 to -2%). The $\delta^{202}\text{Hg}$ in spike I in Meghalaya and Padriciano and spike III in Jhilmili is consistent with volcanic emission of Hg. Two samples from Bajada del Jagüel and four from Bidart, however, display isotope signals compatible with volcanic emission/chondritic Hg. The results of three other samples are characteristic for reworked sediment, soil and/or peat. Most of the data show small positive $\Delta^{201}\text{Hg}$, in favor of long-term atmospheric

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transport prior to deposition, supporting a volcanic origin for the Hg. The present study broadens, therefore, the potential use of Hg as stratigraphic marker and, moreover, confirms that in the critical KPg transition, Hg was enriched in paleoenvironments at three distinct stages during the Deccan phase-2.

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1. Introduction

Volcanic emissions have the potential of injecting large amounts of Hg into the atmosphere and, therefore, contribute with a significant natural input of Hg to the atmosphere (e.g. Schuster et al., 2002; Pyle and Mather, 2003). Many studies have reported Hg enrichments in sedimentary records that are synchronous with modern (e.g. Martínez-Cortizas et al., 1999; Roos-Barracough et al., 2002; Roos-Barracough and Shoty, 2003) and prehistoric volcanic events (e.g. Palinkas et al., 1996; Sial et al., 2010, 2013, 2014; Nascimento-Silva et al., 2011, 2013; Sanei et al., 2012; Grasby et al., 2013, 2015a, 2015b; Percival et al., 2015; Font et al., 2016). In contrast to most elements present in ash, Hg derived from volcanic activity is mainly in gaseous form (Hg^0), can be transported far in the atmosphere, reaching even global-scale distribution prior to deposition in terrestrial and marine environments and has a long atmospheric residence time (1–2 years). Through oxidation in the atmosphere, Hg^0 forms reactive Hg^{+2} , soluble in water and, therefore, enriched in the rain (e.g. Schroeder and Munthe, 1998; Witt et al., 2008 and references therein). Organic matter and clay minerals scavenge Hg in the marine environment and fix it in bottom sediments on the sea floor (Grasby et al., 2015a; Percival et al., 2015).

If Hg reaches an environment with low organic scavenging capacity on the surface, then Hg^{+2} remains in solution and is, eventually, adsorbed onto clays and transported from land to sea. Therefore, high levels of Hg associated with argillaceous sediments can be explained by increased flux of volcanogenic Hg from continents into the oceans. Higher Hg accumulation rates are typical and more pronounced in sediments deposited after glacial maxima, when runoff is increased, compared to sediment layers deposited before such events. This peculiarity is perhaps a phenomenon that can be observed globally as similar results have been observed in the Amazon region (Santos et al., 2001), Antarctica (Vandal et al., 1993) and Europe (Martínez-Cortizas et al., 1999). Biotic or abiotic reduction of Hg^{2+} to Hg^0 (g) limits the scavenging and biological fixation of Hg from the atmosphere and, in consequence, allows Hg re-emission and higher concentration in the atmosphere (Percival et al., 2015). Under reduced bioproductivity, Hg availability stops being captured by organic matter which is one of the major Hg sinks (Sanei et al., 2012).

A strong linear correlation between Hg and total organic matter (TOC) contents in sediments and an apparent affinity of Hg for terrestrial organic matter has been recognized (Outridge et al., 2007; Stern et al., 2009; Sanei et al., 2014) but the importance of terrestrial versus aquatic retention of Hg is still an open question (Percival et al., 2015). Increased Hg concentrations in sediments that deviate from a linear relationship between Hg and TOC represent true Hg anomalies. On the other hand, Hg can be adsorbed onto clays (Krupp, 1988). In this case one would expect a covariation between Hg and Al_2O_3 , as for example observed in some sections across the KPg boundary (e.g. Sial et al., 2013).

It has also been suggested that Hg emission rates can be significantly enhanced in periods of large igneous province (LIP) volcanic activity when the marine buffering control on Hg can be

overwhelmed and thus generating Hg spikes in sediments (Sanei et al., 2012; Grasby et al., 2013, 2015a; Font et al., 2016). Therefore, Hg anomalies could serve as proxy for periods of extensive volcanic activities when LIPs, for example, could have released toxic quantities of Hg into environment. The Hg flux to the sedimentary realm accompanying large amounts of magmatic sulfur and other toxic metals released by LIPs (e.g. Deccan Traps, Callegaro et al., 2014) can provide missing links between the terrestrial and marine records of biota extinctions as suggested by Grasby et al. (2015a).

Sanei et al. (2012) related enhanced atmospheric Hg depositions at the Permian–Triassic transition to catastrophic volcanic eruptions of the Siberian Trap LIP event, followed by the discontinuity of the organic Hg fixation that lead to an increased dissolved Hg flux. The Permian–Triassic biotic crisis, as well as the extinction events in the late Capitanian and at the Smithian/Spathian boundary in NW Pangea, has been linked to enhanced Hg deposition (Grasby et al., 2013, 2015a, 2015b). In addition, the end-Pliensbachian extinction and Toarcian oceanic anoxic event (OAE) are probably related to LIP activities (Karoo–Ferrar), according to Percival et al. (2015). Acidic rain has been deemed responsible for the mass extinction associated to the KPg boundary (Hsü and McKenzie, 1985) and Hg enrichments in KPg boundary sedimentary rocks have been regarded as an evidence for this type of rain (Hildebrand and Boynton, 1989). Anomalous Hg concentrations in deposits spanning the KPg boundary in Dolenja Vas, Slovenia, likely resulted from sub-aerial volcanic activity (Palinkas et al., 1996).

Subsequent work suggested a possible connection between enhanced Hg concentrations in sedimentary rocks across the KPg boundary and Deccan Traps events (Nascimento-Silva et al., 2011, 2013; Sial et al., 2013, 2014) and enabled a distinction of chemical fingerprints related to the Deccan volcanism from an impact event at the KPg boundary (Sial et al., 2014). However, these studies have not taken the mutual relationship between TOC content and Hg concentrations into account, and this precludes an evaluation on how lithological variation (organic matter-poor versus organic matter-rich sediments) was related to the reported Hg anomalies.

Post-emission or post-discharge Hg transformations may not drastically modify the isotopic composition of particulate Hg according to several authors (e.g. Foucher et al., 2009; Sonke et al., 2010; Estrade et al., 2011; Gehrke et al., 2011; Chen et al., 2012; Sun et al., 2013). When Hg transformations lead to change of Hg isotope signatures, this change tends to be constant under certain conditions (Laffont et al., 2009, 2011; Gehrke et al., 2011). Multiple Hg transformations may modify the Hg isotope signatures in unpredictable way, making difficult to trace the Hg source (Sonke and Blum, 2013).

The Hg isotopic composition may help in the distinction between volcanogenic and meteoritic Hg. It is not simple to precise the isotope composition of mantle-derived Hg because usually it is not entirely mantle-derived and/or because it has undergone fractionation during chemical/phase transformation at near surface regions (Bergquist and Blum, 2009). Mantle-derived Hg probably has $\delta^{202}\text{Hg}$ values close to 0‰ according to Sherman et al. (2010), but Zambardi et al. (2009) have reported values from –1.74‰

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