Mercury anomaly, Deccan volcanism, and the end-Cretaceous mass extinction

Eric Font¹*, Thierry Adatte², Alcides Nobrega Sial³, Luiz Drude de Lacerda⁴, Gerta Keller⁵, and Jahnavi Punekar⁶

¹IDL-FCUL (Instituto Dom Luis, Faculdade de Ciências da Universidade de Lisboa), Campo Grande, Edifício C1, Piso 1, 1749-016 Lisbon, Portugal
²ISTE (Institute of Earth Sciences), Geopolis, University of Lausanne, CH-1015 Lausanne, Switzerland
³NEG-LABISE (Nucleus of Geochemical Studies Stable Isotope Laboratory), Department of Geology, Federal University of Pernambuco, P.O. Box 7852, Recife, PE 50740-530, Brazil
⁴LABOMAR, Institute of Marine Sciences, Federal University of Ceará, Fortaleza, 60165-081, Brazil
⁵Department of Geosciences, Guyot Hall, Princeton University, Princeton, New Jersey 08544, USA

ABSTRACT
The contribution of the Deccan Traps (west-central India) volcanism in the Cretaceous-Paleogene (KPg) crisis is still a matter of debate. Recent U-Pb dating of zircons interbedded within the Deccan lava flows indicate that the main eruptive phase (>1.1 × 10⁶ km³ of basalts) initiated ~250 k.y. before and ended ~500 k.y. after the KPg boundary. However, the global geochemical effects of Deccan volcanism in the marine sedimentary record are still poorly resolved. Here we investigate the mercury (Hg) content of the Bidart (France) section, where an interval of low magnetic susceptibility (MS) located just below the KPg boundary was hypothesized to result from paleoenvironmental perturbations linked to the paroxysmal Deccan phase 2. Results show Hg concentrations >2 orders of magnitude higher from ~80 cm below to ~50 cm above the KPg boundary (maximum 46.6 ppb) and coincident with the low MS interval. Increase in Hg contents shows no correlation with clay or total organic carbon contents, suggesting that the Hg anomalies resulted from higher input of atmospheric Hg species into the marine realm, rather than organic matter scavenging and/or increased runoff. The Hg anomalies correlate with high shell fragmentation and dissolution effects in planktic foraminifera, suggesting correlative changes in marine biodiversity. This discovery represents an unprecedented piece of evidence of the nature and importance of the Deccan-related environmental changes at the onset of the KPg mass extinction.

INTRODUCTION
Large igneous province (LIP) volcanism is a possible cause in four of the five major mass extinctions in Earth history. However, this link remains controversial because for most LIPs there is no direct evidence of the mass extinction within the volcanic sequences. The Cretaceous-Paleogene (KPg) boundary is the most famous example where there is a direct correlation between the KPg mass extinction and both a meteorite impact and massive Deccan Traps (west-central India) volcanism within a very short geological time interval (Chenet et al., 2007; Renne et al., 2015; Schoene et al., 2015). The mass extinction in planktic foraminifera was documented between Deccan lava flows in the Krishna-Godavari Basin >1000 km from the Deccan Traps; these lava flows correspond to magnetochron C29r (Keller et al., 2011). On a global basis, quantification of the paleoclimatic and paleoenvironmental effects of volcanism and their impacts on and contributions to the KPg mass extinction remain a challenge. One potential method to investigate these global effects is to identify key exceptional sedimentary sequences that span the KPg mass extinction interval. With such sections changes in key proxy elements such as mercury (Hg), which have been identified as possible markers for LIPs (e.g., Grasby et al., 2015), can be assessed and discussed in the context of both the meteorite impact and volcanism.

Here we investigate the Hg composition of the Bidart (France) section (Fig. 1), considered one of the most complete KPg sections worldwide (Bonté et al., 1984; Font et al., 2014; Galbrun and Gardin, 2004), and where an interval of low magnetic susceptibility (MS) resulting from partial dissolution of detrital magnetite and disappearance of biogenic magnetite (magneto-fossil) was hypothesized to be driven by paleoenvironmental perturbations induced by Deccan volcanism (Abrajevitch et al., 2015; Font et al., 2014). This peculiar interval of low MS, also observed in Gubbio (Italy) (Ellwood et al.,

*E-mail: font_eric@hotmail.com
Mechanisms responsible for subsequent Hg sequestration in sediments are rather complex, but generally rely on the formation of organic Hg-rich complexes. Covariation between Hg contents and organic matter in modern and ancient sediments suggests that Hg deposition rates are controlled by variations in biologic productivity and organic matter burial (e.g., Grasby et al., 2013; Outridge et al., 2007; Sanei et al., 2012). Alternatively, Hg can be adsorbed onto clays (Krupp, 1988). Covariation between Hg and Al₂O₃ observed in some sections across the KPg also suggests that Hg was probably adsorbed onto continental clays with subsequent transport and deposition into the ocean realm (Sial et al., 2013).

Maximum Hg deposition rates in recorded history, following the Indonesian Tambora (A.D. 1815) and Krakatau (A.D. 1883) eruptions and preserved in the glacial ice core of Upper Fremont Glacier (Wyoming, USA), reached 15 × 10³ and 25 × 10³ ppb, respectively, equivalent to 18× background deposition rates (Schuster et al., 2002). Major Hg fluctuations (maximum 116 ppb) linked to Siberian Traps volcanism have been observed across the Permian–Triassic biotic crises (Grasby et al., 2013; Sanei et al., 2012). Grasby et al. (2015) estimated that the Siberian Traps may have released up to 9.98 Gg yr⁻¹ Hg (for a sporadic eruption rate over 40 k.y.), equivalent to 400% above modern natural emissions. Hg-rich levels also feature in the records of the latest Pliensbachian–Toarcian oceanic anoxic event and have been linked to the Karoo–Ferrar LIP (primarily South Africa and Antarctica), although considerable variability between sections is observed on a global basis (Percival et al., 2015). Anomalous Hg concentrations have also been reported from end-Cretaceous–Paleogene sediments in Brazil, Argentina, Denmark, and Italy, and attributed to the Deccan Traps (Sial et al., 2013, 2014; Silva et al., 2013). However, Hg anomalies show strong variability among sections and lack of normalization against total organic carbon (TOC); this limits their correlation on a global scale. Therefore, Hg concentrations analyzed here are normalized to TOC and phyllosilicate content to determine whether the observed increase reflects increased organic matter sequestration and/or runoff processes or increased Hg deposition from atmospheric Deccan volcanic emissions.

MATERIALS AND METHODS

The Bidart section crops out in the Errètega beach (43.46°N, 1.58°W, at sea level), in the Basque-Cantabric Basin (southwest France), and consists of hemipelagic to pelagic sediments deposited in a deep basin. The Maastrichtian section (latest Cretaceous) is dominated by marls and calcareous marls, whereas Danian (earliest Paleogene) sediments are composed of pink and white biogenic limestone beds.
Hg analyses were conducted in the same samples previously analyzed in Font et al. (2011). Hg content was determined at the University of Lausanne (Switzerland) using the Zee-man R-915F (Lumex, St. Petersburg, Russia), a high-frequency atomic absorption spectrometer specifically designed for Hg determination with a detection limit of 0.3–3 ppb (described in Percival et al., 2015). Measurements are based on the direct thermal evaporation of Hg from solid samples and do not require chemical pretreatment of samples, thus avoiding potential contamination during sample preparation. Analyses were conducted on two aliquots. The accuracy was confirmed by the analysis of certified reference materials (Chines alluvium GSD-11 [Zintwana et al., 2012]; Hg content of 72.0 ppb). Excellent correspondence to the certified values was obtained with a correlation coefficient of 0.99 and a standard residual deviation of 0.44.

Total organic carbon analyses were carried out with a Rockeval 6 and quantified by flame ionization and infrared detection (±0.14% error). Mineralogical analyses were carried out with a Thermo Scientific ARL X’TRA diffractometer (±10% error). TOC and mineralogical analyses were performed at the University of Lausanne, Switzerland.

RESULTS AND DISCUSSION

Our results at Bidart show Hg concentrations two orders of magnitude higher in the stratigraphic interval beginning 20 cm below the onset of the low MS interval and 80 cm below the KPg boundary (Fig. 2; data are available in Table DR1 and Fig. DR1 in the GSA Data Repository1). The onset of Hg concentrations is abrupt (46.6 ppb), then gradually decreases to background values (<0.1 ppb) in the early Danian zone P1a(2) (~50 cm above the KPg boundary (Fig. 2).

At Bidart, latest Maastrichtian and early Danian sediments show low TOC contents (<0.16%; see Table DR1), although subtle increases are noted just below the KPg boundary and at 100 cm above (Fig. 2). After normalizing Hg concentrations by TOC values, there is no significant correlation in the Maastrichtian samples and at the KPg boundary, suggesting that Hg peaks are not linked to organic matter scavenging.

Clay minerals are the alternative host for scavenging Hg in marine sediments via adsorption and subsequent deposition on the ocean seafloor. At Bidart, clay mineral concentrations are quantified based on phyllosilicic contents, which average 30% of the bulk mineralogy during the latest Maastrichtian (zone CF1), increase to 41% at the KPg boundary, and decrease gradually to <10% in the earliest Danian (Fig. 2; see Table DR1). Correlation between phyllosilicate content and Hg concentrations is poor, indicating that Hg fluctuations are not controlled primarily by clay content, even if some Hg is probably adsorbed onto clay. The strong non-correlate trends of Hg, TOC, and phyllosilicate through time suggest that the Hg anomalies are not linked to increased organic matter burial and/or runoff. Such negative or noncorrelative trends between Hg and TOC have also been observed at the Permian-Triassic boundary and linked to Siberian Traps activity (Grasby et al., 2013; Sanei et al., 2012).

The Hg anomalies are found within sedimentary layers overlapping the ~50-cm-thick low MS interval and spanning the KPg boundary (Fig. 2). Whether the Chicxulub (Yucatan, Mexico) impact contributed to the Hg anomalies observed here and worldwide is still an open question, but the absence of impact markers and iridium anomalies in the interval of interest at Bidart (Bonté et al., 1984), just below and above the KPg boundary, argues for a major contribution from the Deccan Traps (Fig. 2). The low MS interval has been identified in two distinct marine realms, at Bidart (Atlantic) and Gubbio (Tethys), suggesting a widespread signature (Font et al., 2011), although this still has to be confirmed by at other localities. This signal resulted from partial dissolution of detrital magnetite and total absence of biogenic magnetite, features consistent with changes in redox conditions, including ocean acidification and acid rains (Abrajевич et al., 2015; Font et al., 2014). The presence of akaganeite (β-FeOOH-Cl) in the low MS of both sections, hypothesized to be of a volcanic origin, is further evidence of these peculiar paleoenvironmental conditions (Font et al., 2014).

On a global basis, the Hg anomaly documented here is correlative with similar anomalies reported worldwide (Sial et al., 2013), albeit with considerable variability among sections in term of Hg concentrations and stratigraphic position (Fig. 1). However, low sample resolution at these KPg intervals made any correlation with the low MS interval of Bidart uncertain. In summary, the close association of high Hg contents, iron oxide dissolution, and presence of akaganeite at Bidart strongly argue for widespread paleoenvironmental and paleoclimate perturbation induced by Deccan phase 2 volcanism across the KPg boundary.

Deccan magmas are estimated to release as much as 6 ± 1.7 Mt of SO2 km–3 (Self et al., 2014). Assuming a volume of 1.1 × 106 km3 of basalt erupted within the 750 k.y. of magnotochron C29r that encompasses Deccan phase 2 (Schoene et al., 2015), the total SO2 release would approximate 4.73–8.47 × 1010 Mt, which corresponds to a total Hg input of 99.3–177.8 Mt (considering the Hg/SO2 ratio of 0.21 × 10–4; Nriagu, 1989). For comparison, estimates of Hg released by the Chicxulub impact do not exceed 0.4 ± 0.2 Mt (Sial et al., 2013). These huge amounts of volcanic Hg emitted into the atmosphere readily explain the Hg anomalies recorded here and in other KPg sections. Although the role of Hg in the KPg mass extinction is still unknown, it may have poisoned both marine and continental waters. Clues to possible Hg effects are observed at Bidart, where Hg-enhanced intervals correlate with high planktic foraminiferal dissolution evident in shell fragmentation (10%–20%) and imperfect tests with holes (50%–70%) (Punekar et al., 2016; Fig. 2). In contrast, benthic assemblages show significantly lower test fragmentation (<10%) and imperfect tests (20%–30%). On a global basis, high-stress conditions in zones CF1 and CF2 below the KPg are correlative with Deccan volcanism phase 2 and have been documented in planktic foraminifera by including species dwarfing, diversity decrease, and dominance of disaster opportunist species (Keller et al., 2016).

Another stress marker possibly associated with Hg is biogenic magnetite produced by magnetotactic bacteria, which are controlled by the position of the anoxic-oxic boundary interface in the water or sediment columns (Moskowitz et al., 2008). These bacteria are particularly sensitive to changes in redox conditions, as reflected by their absence in the low MS intervals of the Bidart and Gubbio sections (Abrajевич et al., 2015). However, they are present at the KPg boundary in both sections, suggesting that the Chicxulub impact had no environmental effects on their life and preservation. Therefore, these biodiversity proxies, together with the newly found Hg anomalies, provide new and promising clues to unravel the contribution of Deccan phase 2 volcanism in the end-Cretaceous mass extinction.

CONCLUSIONS

We report anomalous concentrations of Hg in the KPg section at Bidart within stratigraphic layers correlative with the major Deccan eruption episode, phase 2. The absence of correlation between Hg anomalies and organic matter and/or clay content (phyllosilicate) indicates a volcanic origin, probably via deposition of atmospheric Hg species into the oceanic realm, rather than via scavenging organic matter and/or increase in runoff processes. The Hg-enhanced level spans from 80 cm below the KPg to 50 cm above into the early Danian and encompasses an ~50-cm-thick interval of low MS below the KPg boundary. The Hg anomalies and low MS interval correlate with a high fragmentation index in planktic foraminifera, suggesting that the associated paleoenvironmental and paleoclimate perturbations had significant effects on biodiversity in marine calcifiers. Thus, our study supports the use of Hg as a valuable volcanic

1GSA Data Repository item 2016053, Figure DR1, field photographs, and Table DR1, mercury, TOC, and mineralogical data, is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
LIP indicator and highlights its importance in the Deccan-related environmental changes at the onset of the KPg mass extinction.

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