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High-resolution Hg chemostratigraphy: A contribution to the distinction of chemical fingerprints of the Deccan volcanism and Cretaceous–Paleogene Boundary impact event

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ABSTRACT

There is a renewed interest in volcanism as the major trigger for dramatic climatic changes at the Cretaceous–Paleogene transition (KTB), which were accompanied by a decrease in biodiversity and mass extinction. We have used Hg contents as proxy for volcanic activity at the classical localities of Gubbio (Italy) and Stevns Klint (Denmark) where the KTB layer is easily recognizable, and at a near-complete succession exposed at the Bajada del Jagüel locality in the Neuquén Basin, Argentina. These three localities display similar $\delta^{13}C_{carb}$ trends with markedly negative excursion at the KTB layer. Bulk-rock oxygen isotopes yielded similar pathways across the KTB layers in these localities and, if considered near-primary, the negative $\delta^{18}O$ excursion at the KTB in Gubbio and Bajada del Jagüel suggest warming temperatures during this transition, whereas the negative excursion immediately followed by positive one at Stevns Klint points to a cycle of warm followed by colder climate. At Stevns Klint, Hg contents reach 250 ng g^{-1} within the KTB layer (Fiskeler Member) and 45 ng.g^{-1} at 1.5 m above that, while within the Scaglia Rossa Formation at Gubbio, three Hg peaks across the KTB are observed, one of them within the KTB layer (5.3 ng g^{-1}). Hg shows several peaks across the KTB in the Neuquén Basin, with up to 400 ng g^{-1} in the Jagüel Formation. The phenomena that caused dramatic changes at the KTB probably expelled huge amounts of Hg into the atmosphere as recorded by these high Hg levels. A co-variation between Hg and Al_2O_3 in the studied sections suggest that Hg is adsorbed onto clays. Hg concentrations and also Hg isotopes are perhaps a powerful tool in the assessment of the role of volcanic activity during extreme climatic and biotic events, and in assessing the role of meteorite impact versus volcanism as the predominant cause of past global catastrophes and mass extinction.

1. Introduction

It is well known that major geologic time boundaries in the Phanerozoic are marked by dramatic changes in the geological record, including biological extinction, fluctuations of sea-level and atmospheric composition. These changes are reflected in sharp change in biotic activity and included major mass extinction at the Permian–Triassic and Cretaceous–Paleogene transitions, and also by the chemical composition of sediments.

It is well known that major catastrophic events concurrent to massive mass extinction occurred in the Phanerozoic. Magaritz (1989) observed that $\delta^{13}C$ values drop from a high level, reaching a minimum after the Ediacaran–Cambrian, Permian–Triassic and Cretaceous–Paleogene transitions, and then increase to a new level. He proposed that these changes reflect variations in the exogenic carbon cycle that may correlate with variations in the total biomass. Recently, it was proposed that the variation in Hg abundances may correlate with some major geologic time boundaries such as the Permian–Triassic (PTB) (Sanei et al.,

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2012) and the Cretaceous–Paleogene (KTB) transitions (Sial et al., 2013).

Since the early 1980s, after the work by Alvarez et al. (1980), the KTB mass extinction has been often ascribed to an impact of a huge meteorite that generated the large Chicxulub multi-ring crater in the Yucatán Peninsula, Mexico. Some studies, however, have raised the possibility that such a colossal impact may have predated the Cretaceous–Paleogene transition (e.g. Keller et al., 2004, 2009). However, Renne et al. (2013) proposed on the basis of ^{40}Ar–^{39}Ar dating of tektites and bentonite beds that the KTB mass extinction and the Chicxulub impact were synchronous to within 32,000 years. Alternatively, the Deccan volcanism whose second phase, the world's longest lava flows (Self et al., 2008), has been correlated with the KTB at 65.5 Ma, spanning the magnetochrons 29r and 29n of the geomagnetic polarity time scale (Chenet et al., 2007; Hooper et al., 2010), has been regarded as responsible for this mass extinction (Keller et al., 2008). Rapid climate changes, sea-level fluctuations and volcanism during 100,000 years preceding the Cretaceous–Paleogene transition have also questioned the bolide impact theory as being solely responsible for the mass extinction (e.g. Keller, 2010, 2011; Gertsch et al., 2011 and references therein). The renewed interest in volcanism as the major trigger of the KTB crisis has stimulated Nascimento-Silva et al. (2011, 2013) and Sial et al. (2013) to initiate a preliminary investigation using Hg as a proxy of volcanism in the sedimentary record across this chronological time boundary. Major tools for this is the geochemical behavior of some elements and their isotopic ratios such as C, O and Sr isotopes, well-established tools in reconstructing past climate and sea water compositions.

Ocean acidification has been claimed as an additional factor contributing to the decline in biodiversity just before and during the KTB. Deccan eruptions likely caused acid rains in an extensive are of the globe, resulting in weathering and dissolution effect on the continental surface. Dissolution of foraminifera (Gertsch et al., 2011) and iron oxide minerals (bio- and detrital magnetite) dissolution are, perhaps, important evidence of the acidification of the oceans during this critical period (Font et al., 2014).

This report aims at extending and better understanding the use of Hg as a volcanogenic trace-element in identifying whether or not volcanism has played significant role in climatic reorganization during the KTB and on the most famous and persistent paleontological murder riddle. Hg concentrations and C-isotope chemostratigraphy, in parallel, are traced along the two classical KTB localities of Gubbio and Stevns Klint where the KTB clay layer is well preserved, and substantial evidence for a meteorite impact has been put forward by Alvarez et al. (1980). In addition, this study also focuses on the sedimentary transition within the Neuquén Basin, Argentina, a locality with a near-complete KTB stratigraphic record in South America, thus expanding the results of previous Hg investigations on the Yacoraite Formation (Salta Basin, Argentina) and Paraíba Basin, Brazil (Nascimento-Silva et al., 2011; Sial et al., 2013). Previous studies have not found the influence of meteoritic impact ejecta on the sedimentary sequences bracketing the KTB in South America (e.g. Barrio, 1990; Marquillas et al., 2003, 2007, 2011; Aberhan et al., 2007; Keller et al., 2007; Nascimento-Silva et al., 2013; Sial et al., 2013 and references therein). However, Scasso et al. (2005) have referred to the presence of tsunami deposits at the KTB in the Neuquén Basin.

We add new Hg analyses to the preliminary data for the KTB layer (Fiskeler Member) at Stevns Klint, previously reported (Sial et al., 2013). We also report preliminary Hg-isotope data for this KTB site, as a further approach to assessing the role of meteorite impact versus volcanism as the major cause of the catastrophe and concurrent mass extinction during the KTB.

2. The Cretaceous–Paleogene transition

Substantial evidence for a giant bolide impact on the Earth's surface coincident with the best-studied global biotic event, the Cretaceous–Paleogene mass extinction event (~65.5 Ma), has been built up for over the last three decades (Schultze et al., 2010 and references therein). The importance of this impact (or impacts) as the sole extinction mechanism, however, is still a matter of debate.

Anomalously high iridium and platinum-group element concentrations in almost one hundred KTB sites worldwide (e.g. Alvarez et al., 1980; Claeys et al., 2002), presence of glass microspherules (Smit and Klaver, 1981; Smit, 1999) and shocked quartz (Bohor et al. 1984; Bohor, 1990; Morgan et al., 2006, Kamo et al., 2011) have been used to argue in favor of the bolide impact hypothesis as the mechanism responsible for the KTB mass extinction. Presence of high temperature/high pressure (HTP) phase of fullerenes (complexes C molecules) in deposits supposedly associated with events involving an impact of a large bolide (e.g., Chicxulub and Bedout craters; Becker et al., 2000a) provides further evidence for a crucial role of bolide impacts in the mass extinction. Parthasarathy et al. (2008) reported the presence of the natural toluene-soluble fullerene and the toluene-insoluble high-pressure/temperature phase of fullerene C_{60} in carbonaceous matter extracted from iridium-rich intertrappean sediments of the Anjar KTB site, India. The conditions of high-pressure/temperature regimes required for the formation of HTP fullerene phases can be created by an energetic impact event (Parthasarathy et al., 2008). This has led these authors to suggest that the occurrences of such phases in the KTB layer at Anjar could be linked to a contemporaneous bolide impact. The cage structure of fullerene has the unique ability to encapsulate and retain noble gases and this has allowed one to determine that Allende and Murchison meteorites and KTB fullerenes contain trapped noble gases (He, Ar, Xe), the isotopic composition of which can only be described as typical of extraterrestrial origin (e.g. Stevns Klint; Becker et al., 2000a, 2000b; Anjar, Parthasarathy et al., 2008). Denne et al. (2013) have reported a KTB massive deposit in deep waters of the Gulf of Mexico that substantiates widespread slope failure induced by the Chicxulub impact and that provides further evidence of a single impact coincident with the KTB mass extinction.

However, some Maastrichtian–Danian deposits in several basins around the globe show prominent geochemical and isotopic anomalies preceding the KTB. Analyses of stratigraphic variations of whole-rock elemental concentrations and stable isotopic compositions in some of these basins have led to detection of Ba anomalies far below the KTB in the Cauvery Basin (India), in Israel, in northeastern Mexico and in Guatemala (Ramkumar et al., 2004, 2005), and Hg anomalies across the KTB in the Yacoraite Basin, Argentina, and in the Paraíba Basin, Brazil (Sial et al., 2013). Stüben et al. (2005) reported the presence of bentonite layers and Pt and Pd-dominated PGE anomalies below and above the KTB in Mexico as an indication of volcanic activity. A complete shallow-marine succession with preserved KTB clay layer reported by Racki et al. (2011) at Lechówka near Chełm, southeastern Poland, shows anomalous amounts of iridium (9.8 ng g^{-1}), gold, nickel, and elevated Ir/Au ratios. These signals are consistent with a chondrite meteoritic origin, but a major positive iridium spike in Maastrichtian marls has been found 10 cm below the thin KTB clay layer at this location. Keller et al. (2004) also reported iridium enrichment in Maastrichtian sediments at about 20 cm below the KTB in the Yaxcopoil-1 core drilled within the Chicxulub crater, leading these authors to assume that the Chicxulub bolide impact predated the KTB mass extinction.

Multiple iridium-enriched layers have been observed at some KTB sections (e.g. McLean, 1985; Donovan et al., 1988; Graup and Spettel, 1989) in contrast to most reported KTB sites. Such a distribution of iridium anomalies implies episodic, iridium-delivering events over an extended period of time. In KTB sites where there is no evidence for a bolide impact (e.g. Lattengebirge, Bavarian Alps), the multiple iridium-enriched layers probably had a common volcano source, according to Graup and Spettel (1989). The iridium enrichment observed in airborne particles from the Kilauea volcano (Zoller et al., 1983) consubstantiates the hypothesis that volcanism could be the iridium source.