Do mercury isotopes record the signature of massive volcanism in marine sedimentary records?

Alyson M. Thibodeau[1] and Bridget A. Bergquist[2]
Department of Earth Sciences, Dickinson College, Carlisle, Pennsylvania 17013, USA
Department of Earth Sciences, University of Toronto, Toronto, ON M5S 3B1, Canada

Large Igneous Provinces (LIPs) are associated with a significant number of mass extinctions and ocean anoxic events (OAEs) during the Phanerozoic. However, the role of LIPs in triggering and sustaining biotic and environmental crises is controversial (e.g., Bond and Wignall, 2014). These controversies arise because direct indications of LIP volcanism are typically absent from marine sediments, where much of the evidence for biological and environmental change is archived. In the past five years, mercury (Hg) has emerged as a potential indicator of massive volcanism in marine sedimentary records, permitting new insights into the relationship between LIP emplacement and periods of environmental change, mass extinction, and biotic recovery.

Hg anomalies attributed to LIP activity have been identified in marine sedimentary sequences spanning at least four of the "big five" mass extinction events, in association with second-order extinctions, and in strata that record several Mesozoic OAEs (e.g., Sanei et al., 2012; Grasby et al., 2015; Percival et al., 2015; Font et al., 2016; Jones et al., 2016; Sial et al., 2016; Thibodeau et al., 2016). Hg anomalies are typically recognized as increases in the Hg content of sediments or as an increase in the ratio of Hg to total organic carbon (Hg/TOC) to account for the commonly observed association between Hg and organic carbon (e.g., Grasby et al., 2013, and references therein). Some of these anomalies appear to be global in their extents with Hg enrichments spanning geographically distant sedimentary sequences, a finding consistent with estimates of large Hg releases associated with LIPs (e.g., see Sanei et al., 2012). However, despite the increasing use of Hg as a volcanic proxy, linking sedimentary Hg enrichments to massive volcanism is not always straightforward. One problem is that massive volcanism is not the only possible mechanism for increasing Hg emissions during environmental crises. For example, it is possible that Hg could be derived from the combustion of coal deposits (by magma-coal interactions), from a meteoritic source, or from biomass burning due to wildfires and soil erosion (Grasby et al., 2017, p. 55 in this issue of *Geology*). There are also arguments that some Hg anomalies may form from post-depositional processes (Smit et al., 2016).

One approach to determining the origin of Hg anomalies is to investigate their isotopic compositions. Mercury has a complex biogeochemical cycle and undergoes transformations that may induce mass-dependent fractionation (MDF) and/or mass independent fractionation (MIF) of Hg isotopes (see Fitzgerald and Lamborg, 2014 and Blum et al., 2014). While MDF (denoted here by $\delta^{202}Hg$) is ubiquitous and occurs during many physical, chemical, or biological transformations of Hg, MIF (denoted here by $\Delta^{199}Hg$) arises through a more limited set of pathways (mostly photochemical) and is generally a more conservative tracer. For the most part, Hg emitted by volcanoes or derived from geogenic sources has no MIF ($\Delta^{199}Hg = 0$‰) and $\delta^{202}Hg$ values between approximately -2.0‰ and 0‰ (e.g., Zambardi et al., 2009). Once emitted to the environment, Hg cycles through the atmospheric, marine, and terrestrial reservoirs. The most abundant and long lived atmospheric species, $Hg^0_{(g)}$, is removed from the atmosphere either by oxidation to Hg^{2+} species (which are particle reactive) or by direct uptake of $Hg^0_{(g)}$ by vegetation and soils followed by oxidation. Aquatic environments can receive Hg by both direct Hg^{2+} deposition and runoff from terrestrial sources. Once in surface waters, Hg^{2+} may be scavenged or reduced (either abiotically including photochemical reduction or biologically) back to $Hg^0_{(g)}$, which can then evade back to the atmosphere. In this sense, the behavior of Hg differs from other metals because only some portion of Hg^{2+} deposited will be preserved in sediments.

Mercury isotopes are excellent tracers of the deposition pathways to marine sediments because the two different pathways, terrestrial runoff and atmospheric Hg^{2+} deposition, have very different isotopic signatures. Large odd-isotope MIF is generated during the aqueous photoreduction of Hg^{2+} (Bergquist and Blum, 2007), which occurs in cloud droplets and surface waters. This process produces odd-isotope excesses (i.e., positive $\Delta^{199}Hg$ values) in the residual aqueous Hg^{2+} pool. Thus, atmospheric Hg^{2+} and sediments dominated by atmospheric Hg^{2+} deposition tend to have positive $\Delta^{199}Hg$ values (e.g. Gehrke et al., 2009). In contrast, terrestrial reservoirs, such as biomass and soils, primarily accumulate $Hg^0_{(g)}$, which contains slightly negative $\Delta^{199}Hg$ values. During the uptake and sequestration of $Hg^0_{(g)}$ by plants and soils, additional MIF and MDF occurs during which these reservoirs acquire slightly more negative $\Delta^{199}Hg$ values and much more negative $\delta^{202}Hg$ values than atmospheric $Hg^0_{(g)}$ (e.g., Zheng et al. 2016). Due to these differences, marine sediments which receive Hg through terrestrial runoff tend to have more negative $\Delta^{199}Hg$ and $\delta^{202}Hg$ values compared with oceanic sediments dominated by atmospheric Hg^{2+} deposition, which have positive $\Delta^{199}Hg$ and less negative $\delta^{202}Hg$ values.

In this issue of *Geology*, Grasby and colleagues (2017) use Hg isotopes to explore the sources and pathways of anomalous Hg deposition during the Latest Permian Extinction (LPE) and possible connection to Siberian Traps volcanism. In particular, their work compares the Hg isotopic signatures of sediment deposited in a deep-water environment (where Hg enters marine waters by direct atmospheric Hg^{2+} deposition) with a shallower marine section (where both atmospheric and terrestrial runoff Hg inputs are possible). The two sequences are the Buchanan Lake section, a bathyl to near-abyssal mid-latitude sequence in the Sverdrup Basin, Canadian Arctic, and the Meishan section, China which represents an equatorial clastic-starved carbonate platform.

Their respective Hg isotope records reveal important differences in the sources and pathways of Hg entering the Latest Permian oceans. The shallower Meishan section contains sharp negative shifts in $\delta^{202}Hg$ and $\Delta^{199}Hg$ values at the LPE. These shifts are coincident with spikes in both Hg and Hg/TOC of sediments and have slightly negative $\Delta^{199}Hg$ values and very negative $\delta^{202}Hg$ values, consistent with influx of Hg from terrestrial sources. Grasby et al. propose that this flux is driven by massive wildfires occurring at the LPE, which would release Hg through biomass burning and subsequent soil erosion. The substantial temporal shifts in the isotopic signature of shallower Meishan sediments contrast with relatively unchanging $\delta^{202}Hg$ and $\Delta^{199}Hg$ values in the bathyl to near-abyssal sediments of Buchanan Lake section, despite large variations in Hg and Hg/TOC throughout that sequence. The Buchanan Lake sediments contain

Hg with small positive Δ^{199}Hg values, which Grasby et al. propose could result from the absorption of atmospheric Hg^{2+} by volcanic plume ash or the photoreduction of Hg^{2+} in the water column.

How does the evidence presented by Grasby et al. (2017) advance our understanding of Hg anomalies and their origin? First, this research clearly demonstrates that Hg anomalies, even those that appear to be part of the same global event, do not share the same isotopic fingerprint. Furthermore, despite the likelihood that both terrestrial and marine environments experienced enhanced Hg loads due to volcanism during the LPE, neither the Meishan nor the Buchanan Lake section contain Hg with the isotopic signature of what is thought to be volcanic Hg, in which no MIF would be expected (e.g., see Thibodeau et al., 2016). Instead, if the Hg anomalies in either the Buchanan Lake or Meishan sections are driven by volcanism, then environmental transformations between the points of emission and deposition have altered the original signature.

Second, these records imply that the isotopic signatures observed in modern marine sediments and associated with terrestrial runoff and atmospheric Hg^{2+} deposition can hold even in a world with potentially high levels of volcanic Hg in the environment. For instance, the slight positive Δ^{199}Hg values that are present throughout the Buchanan Lake section are similar to those measured in modern and pre-anthropogenic oceanic sediments that do not receive significant continental runoff (Gehrke et al., 2009; Brown et al., 2013; Mil-Homens et al., 2013; Yin et al., 2015). Similar Hg-MIF signatures have also been measured in Hg anomalies from deep-water sequences spanning the Cretaceous-Paleogene transition (e.g., the Neuquén Basin, Argentina; see Sial et al., 2016). Taken together, these data suggest that positive Δ^{199}Hg values may be an enduring characteristic of ocean sediments in regions that primarily receive Hg through direct atmospheric Hg^{2+} deposition and the Hg isotopic signatures of deep ocean sediments may not be very sensitive to Hg cycle perturbations. Conversely, large isotopic shifts in the Meishan section demonstrate that the Hg isotopic composition of near-shore sediments may be far more sensitive to changes in the Hg cycle because they receive variable proportions of their Hg from direct atmospheric and terrestrial inputs. Although different in magnitude and character, Thibodeau et al. (2016) also observe an isotopic shift in shallow shelf sediments that span the Triassic-Jurassic boundary from Muller Canyon, Nevada (USA) in concert with Hg enrichments, which were attributed to an overloading of the system with volcanic Hg from the Central Atlantic Magmatic Province that swamped out the Hg-MIF signatures.

Grasby et al. (2017) have produced important and novel records of Hg isotopes across the LPE and make a compelling case for large inputs of terrestrial Hg to near-shore marine environments during this event, a finding consistent with the occurrence of massive wildfires and/or soil erosion. Taken together with previous records, this study demonstrates the power of Hg isotopes to discern the causes of the large Hg anomalies associated with times of environmental change and massive volcanism. These records also highlight how Hg anomalies for both different time periods of volcanism and different locales for the same time period of volcanism reflect changes to Hg loading and cycling that might be dependent on many factors including how the Hg is released (time, amount), where the Hg is released, whether wildfires occurred, whether Hg was also released from organic-rich rocks during magmatic emplacement, and potentially many other factors. Thus, the addition of Hg isotopes to Hg chemostratigraphy can provide new insights into the pathways through which Hg anomalies form, and thus help better resolve the relationship between volcanism, environmental change, and extinction.

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