Mercury, volcanism, and mass extinctions

Bridget A. Bergquist

Understanding the causes and timings of mass extinctions are important for our understanding of the evolution of life on Earth and how major biogeochemical cycles have been and can be perturbed. Four of the five biggest mass extinctions (1) are associated with large igneous provinces (LIPS), which are the most voluminous volcanic events on Earth, but whether LIPS triggered the extinctions is disputed due to the difficulty in correlating evidence for the onset and duration of LIPS with mass extinction records (2). These challenges arise largely because direct evidence of LIPS is generally absent from the sedimentary records that contain the fossil extinction records; causal relationships must instead rely on comparing radiometric dating of LIPS with biostratigraphic ages in fossil records. A new tool in understanding the relationship between volcanism and mass extinctions is mercury chemostratigraphy (3). Because large amounts of Hg are emitted from volcanism, it is argued that increases in Hg preserved in sedimentary records can be used as a proxy for increased volcanic inputs. If true, Hg concentration changes measured in the same sedimentary records that preserve biotic and environmental crises allow for detailed insights into the timing of volcanism and changes in the fossil and sedimentary records (3–11). One of the most extensive examples of this new proxy is the study by Percival et al. (12) in PNAS, which finds Hg anomalies in five different records (both marine and terrestrial and from both hemispheres) that span the end-Triassic mass extinction, demonstrating both the global extent of the increased Hg and the pulsed nature of the LIP volcanism. The end-Triassic extinction is one of the top five mass extinctions and is associated with major perturbations to the carbon cycle that are thought to be driven by the Central Atlantic Magmatic Province (CAMP) (13, 14). Percival et al. (12) build upon a study (11) of Hg and Hg isotopes in a single record that observed elevated Hg throughout the extinction and depauperate intervals with biotic recovery only occurring after Hg levels returned to background levels.

Earlier studies demonstrated that Hg anomalies are associated with many of the mass extinctions (3–11) but were limited by questions about how representative single records were of increases in the global Hg pool, whether elevated Hg is linked to volcanism, or whether changes in Hg concentration were due to preservation or diagenetic effects. Increased concentrations of Hg in sediments can either be due to (i) an increase in the overall input of Hg to the atmospheric–ocean–terrestrial system or (ii) increased preservation of Hg within sediments either through increases in deposition via scavenging/absorption onto particles or post depositional migration of Hg within the sediments. The biogeochemical cycle of Hg is complicated (Fig. 1), with primary sources of Hg making up less than one-half of the Hg emissions to the atmosphere even in the modern world (15, 16). Most emissions are secondary sources, with Hg being reemitted after deposition from waters, soils, and biomass burning. Primary natural sources are dominated by volcanic sources, and the two largest primary anthropogenic sources are artisanal and small-scale gold mining and coal burning. Mercury is often emitted to the atmosphere in its reduced form, gaseous elemental Hg\(^0\). Gaseous Hg\(^0\) is relatively stable and has a long residence time (~0.5–1 y) with respect to atmospheric mixing, allowing it to be distributed globally. Removal of atmospheric gaseous Hg\(^0\) happens either by direct uptake and absorption or by oxidation to more particle reactive forms. Terrestrial systems remove Hg\(^0\) via uptake by plants and trees or by absorption onto organic matter in soils. Once in plants and soils, it is oxidized to Hg(II) species. Gaseous Hg(II) can also be oxidized to Hg(III) species in the atmosphere that have short residence times (hours to weeks), which are deposited to terrestrial and aquatic systems via wet or dry deposition. One of the major complexities of the Hg cycle is that, after deposition, significant portions of the Hg can be reduced back to gaseous Hg\(^0\) and be emitted back to the atmosphere.

Massive volcanism is a simple way to increase Hg input to the atmosphere–ocean–terrestrial system and perturb the carbon cycle at the same time, but other mechanisms could also result in simultaneous changes in Hg and the carbon cycle. Because Hg is stored in
plants and soils and is also found in organic-rich rocks including coal deposits, biomass burning and thermogenic release from coal and organic-rich deposits release significant amounts of Hg at the same time as releasing carbon. Because both biomass and organic-rich rocks have isotopically light carbon, release of carbon from these sources should also lead to negative isotope excursions in carbon. Negative carbon isotope excursions are observed in the mass extinction records including the end-Triassic. However, the very detailed records from Percival et al. (12) identify several pulses of Hg that were not associated with negative excursions in carbon isotopes, arguing that the Hg was likely not from the organic-rich sources and instead was mostly from volcanic sources. This is a question where Hg isotopes may help to distinguish between different sources of Hg. Although there is not much data on volcanic Hg, it appears that volcanic Hg and Hg from biomass and organic-rich rocks have very different isotopic signatures (17). Thibodeau et al. (11) measured Hg isotopes across the end-Triassic mass extinction and argued that the Hg isotopic signatures associated with the elevated Hg intervals were consistent with volcanic sourced Hg. In contrast, Grasby et al. (7) observed that the elevated Hg during the end-Permian extinction had Hg isotopic compositions more consistent with biomass and organic-rich rocks, and argued that the Hg anomalies were likely from massive wildfires and increased soil erosion.

The second complication with interpreting sedimentary Hg is that the concentration is strongly influenced by lithology because not all of the Hg that enters a water body will eventually deposit and be removed to the sediments. In most aquatic systems, Hg is dominantly associated with organic matter and the Hg organic complexes are particle reactive (15). Some fraction of the Hg in the water column can be reduced back to gaseous Hg\(_0\), which is volatile and evades back to the atmosphere. The other fraction will be scavenged onto particles (absorbed) that are removed to the sediments. Thus, Hg concentrations and organic matter in sediments are highly correlated (15, 18). Although considered less important, Hg can also be associated with sulfides and clays (19). Because sediment Hg and organic matter are highly correlated, Hg records are usually reported as a ratio of Hg to total organic carbon (%TOC) to account for variations in the organic matter content of the sediments. Positive anomalies in Hg/%TOC are then interpreted as increased input of Hg to the water body (usually the ocean). However, criticisms have been raised that records may be sensitive to local or regional factors that affect Hg preservation, such as local high inputs of clays, and that increases may not necessarily reflect an increase in the global Hg pool (19). Furthermore, some critics argue that there may also be postdepositional changes to Hg contents (20). During mass extinctions associated with LIPS, large inputs of carbon dioxide, sulfur dioxide, and other volcanic gases can lead to major changes in climate and ocean chemistry including warming and marine anoxia (2). Because Hg is sensitive to anoxia, it may undergo transformations and possible migration. Mercury is also very sensitive to heating, so any rocks that have undergone slight metamorphism may be compromised. However, this would lead to losses of Hg and not enrichments. All of these criticisms are valid, but with five additional records in addition to the record from Thibodeau et al. (11), Percival et al. (12) make a strong case for the global increase in the Hg inventory for the end-Triassic mass extinction. In addition, one of the records is terrestrial and would not be sensitive to changes in the preservation of Hg in the ocean.

Percival et al. (12) establish that Hg anomalies associated with the end-Triassic extinction were global in extent and also had
distinct pulses, strengthening the use of Hg as a marker of global change and volcanism. Nonetheless, Hg concentrations alone cannot be used as evidence of massive volcanism as other mechanisms can lead to increases in the global pool of Hg that would be coincident with major changes in carbon cycling. As demonstrated by two Hg isotope studies, Hg anomalies can have very different isotopic signatures that are probably related to different sources of the Hg [i.e., biomass burning during the Late Permian extinction (7) and volcanism during the end-Triassic extinction (11)]. Despite some uncertainties, the ability to measure Hg and Hg isotopes in the same records that preserve the fossil and environmental changes will allow for a better understanding of the links between extinctions, volcanism, and environmental changes.