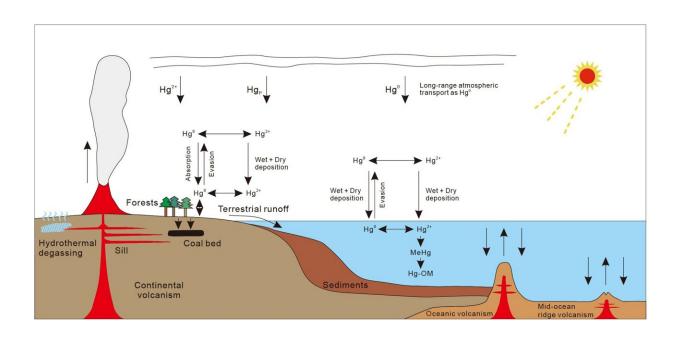


A review of the applications of mercury stable isotopes for tracing volcanism in geologic events

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The continental volcanism, oceanic volcanism and mid-ocean ridge volcanism emit Hg to the atmosphere and ocean. Mercury in atmosphere deposit to aquatic and terrestrial systems via wet or dry deposition, and Hg on land enter the ocean through the terrestrial runoff. Credit: Science China Press

Mercury is a toxic heavy metal that can exist stably as a gas, with high volatility and global distribution in the atmosphere. Volcanoes represent a primary natural source of Hg in the atmosphere, with significant



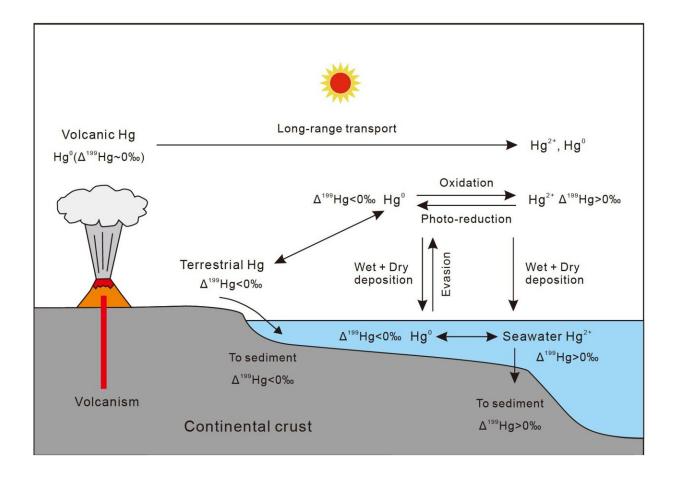
effects on Hg cycles on both global and regional scales. Mercury can undergo both mass-dependent fractionation (MDF) and massindependent fractionation (MIF) in Earth systems.

Hg-MDF is omnipresent and associated with numerous processes, while Hg-MIF can provide a unique signature to identify the specific pathways of Hg. Volcanic-sourced Hg exhibits near-zero Δ^{199} Hg values. The photoreduction of Hg(II) generates negative MIF (Δ^{199} Hg 199 Hg > 0) in the residual aqueous Hg(II) pool in water columns. As a result, the marine and terrestrial systems tend to have positive and negative Δ^{199} Hg values, respectively.

Utilizing Hg <u>stable isotopes</u> to reliably trace the origin of Hg in the <u>geologic record</u> has been reported in a number of studies. Mercury isotope records of Hg enrichments for volcanic origin exhibit Hg/TOC (total organic carbon) peaks with near-zero Δ^{199} Hg values that reflect direct deposition of volcanic Hg or slight positive Δ^{199} Hg values that reflect photoreduction of Hg(II) during atmospheric transport of volcanic Hg.

The "Big Five" mass extinctions, several secondary extinctions, ocean anoxic events (OAEs) in the Phanerozoic Eon, and some atmospheric redox changes in the Precambrian period have all been thought to display volcanic-sourced Hg isotopes, implying that volcanism has played an important role in these extinctions and environmental events.





Volcanic-sourced Hg show close to zero Δ^{199} Hg values. The photoreduction of Hg²⁺ result in negative MIF (Δ^{199} Hg⁰ and positive MIF (Δ^{199} Hg > 0) in Hg²⁺, thus the marine and terrestrial systems show positive and negative Δ^{199} Hg values, respectively. Credit: Science China Press

Mercury isotope records of Hg enrichments for non-volcanic origins have different characteristics. Hg enrichment can be driven by ocean redox changes, and Hg input can be derived from terrestrial runoff, combustion of organic-rich sediments, asteroid impact and atmospheric Hg(0), showing varying Δ^{199} Hg values.

There are some influencing factors on sedimentary Hg enrichments and Hg isotopic variations. The differences in global or local volcanism,



submarine or subaerial volcanism, the distance from volcanism, the volcanic eruptive intensity and the existence of hydrothermal activities may all have effects on Hg concentrations and Hg isotopes.

The ocean redox state, such as oxic or dysoxic conditions and anoxic or euxinic environments may both primarily influence the host phases of Hg. And during and/or after diagenesis and metamorphism, Hg enrichments and Hg isotopes can also be affected.

The applications of Hg enrichments and Hg isotopes for tracing major volcanism in geologic records may significantly improve understanding of the relationship between LIP eruptions, biotic crises and environmental changes in ancient scenarios, providing strong evidence for a true cause-and-effect linkage between LIPs and geological catastrophic events.

Nevertheless, there are still unresolved issues that require future work, including controversies about the LIP-trigger mechanism for certain extinctions and complicated variations in Hg isotopes. Thus, future work such as extending the scope of research, application of Hg isotope models and combining Hg with other proxies is needed to gain broader insights into the volcanic event and the related environmental and biotic impacts.

More information: Qing Gong et al, Applications of mercury stable isotopes for tracing volcanism in the geologic record, *Science China Earth Sciences* (2024). DOI: 10.1007/s11430-023-1236-8

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