

C and S isotope records in Doushantuo Formation: Implication for Redox Fluctuation of the Ediacaran Ocean

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Carbon and sulfur isotope evidence from Oman and iron speciation data from Newfoundland suggested a stepwise oxidation of the Ediacaran ocean from ca. 635 Ma to ca. 542 Ma (Fike *et al.*, 2006; Canfield *et al.*, 2007). New isotope data obtained from the Ediacaran Doushantuo Formation, however, reveal alternative oxidation events from ca. 635 Ma to ca. 551 Ma that suggest stepwise oxidation of the Ediacaran ocean, with significant ocean anoxia following each oxidation event. No $\Delta\delta^{34}\text{S}$ values exceed 46‰ in the Doushantuo Formation, indicating the absence of sulfur disproportionation before 551 Ma and a complete oxidation of deep oceans did not occur until the latest Ediacaran or early Cambrian. Our data of $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$, $\delta^{34}\text{S}_{\text{CAS}}$, and $\delta^{34}\text{S}_{\text{py}}$ provide an alternative environmental interpretation for the evolution of early animal life and subsequent Cambrian explosion.

Increases of $\delta^{13}\text{C}_{\text{carb}}$ and $\Delta\delta^{34}\text{S}$, with occurrence and diversification of Doushantuo-Pertatataka acritarchs (DPA), in the lower and middle Doushantuo Formation after the Nantuo (or Marinoan) glaciation indicate the first oxidation event to cause oxic water column in the shelf. Constant $\delta^{13}\text{C}_{\text{org}}$ values (about -29‰) with variable $\delta^{13}\text{C}_{\text{carb}}$ (-6.93‰ ~ +6.17‰) are consistent with the existence of DOM (dissolved organic matter) rich deep-ocean. Following negative shifts in $\delta^{13}\text{C}_{\text{carb}}$ (down to -9.62‰) and $\delta^{34}\text{S}_{\text{CAS}}$ (down to +9.5‰), a temporary anoxia occurred between the middle and upper Doushantuo Formation that is concordant with DPA's extinction. Another oxidation in the upper Doushantuo Formation, where multicellular, macroscopic algae (the Miaohe biota) were found. The prominent negative $\delta^{13}\text{C}_{\text{carb}}$ (down to -8.98‰) excursions and associated decline of $\delta^{34}\text{S}_{\text{CAS}}$ (from +43.5‰ to +10.2‰) imply both oxidations of DOM and sulfide from anoxic water column of deep-ocean. Unusually low $\delta^{13}\text{C}_{\text{org}}$ values (down to -38‰) and increasing $\delta^{13}\text{C}_{\text{carb}}$ (from -8.16‰ to -2.00‰) in the uppermost Doushantuo Formation (ca. 551 Ma) suggest involvement of anaerobic methane oxidation, possibly associated with the upwelling of anoxic deep-ocean seawater. Eventually, another anoxia possibly occurred at the near Dengying-Doushantuo boundary.

References

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Geochemical structure of the Hawaiian plume: Inferences from Mahukona volcano

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Young, <2Ma, Hawaiian volcanoes define two parallel spatial trends, Loa and Kea. Most Loa- and Kea-trend shield lavas are geochemically distinct in major and trace element compositions and radiogenic isotopic ratios. Lassiter *et al.* (1996), among others, proposed a radially concentrically zoned plume with Loa shields forming closer to the plume center than Kea shields. Abouchami *et al.* (2005) proposed that Pb isotopic ratios are the best Loa-Kea discriminant, e.g., $^{208}\text{Pb}^*/^{206}\text{Pb}^* > 0.95$ for Loa lavas; they proposed a bilaterally asymmetrically zoned plume with geochemical differences between the northeast and southwest halves of the plume. These models are oversimplified because they do not consider local (Ren *et al.*, 2005) or vertical heterogeneities (Blichert-Toft *et al.*, 2003) in the plume; nevertheless the alternative large-scale zonation models can be evaluated with geochemical data for shields formed at varying distances from the plume center; e.g., Bryce *et al.* (2005) suggested that when active the submarine Mahukona volcano was southwest of the current location of Mauna Loa, a Loa-trend volcano; hence Mahukona lavas should be Kea-like in the concentrically zoned model and Loa-like in the bilaterally zoned model.

We report major and trace element compositions, Pb and Hf isotopic ratios for 18 Mahukona lavas; these include three transitional to slightly alkalic basalts from the large 125–350 m cones that may represent preshield lavas based on their $^3\text{He}/^4\text{He}$ ratios of ~20 R/Ra (Garcia *et al.*, 1990). Consistent with this inference, the cone samples overlap with the distinctive Pb isotopic field defined by preshield lavas from Loihi seamount. All other Mahukona lavas are tholeiitic basalt that define three groups based on CaO content at a given MgO content. The high CaO group, >12%, has unusually low $^{206}\text{Pb}/^{204}\text{Pb}$ (<18.0) and may be derived from a peridotite source (Herzberg, 2006). All other tholeiitic lavas straddle the Loa-Kea boundary in Pb isotopic space with $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ between 0.940 and 0.951 compared to the range of 0.947 to 0.956 for Mauna Loa lavas. In a $^{176}\text{Hf}/^{177}\text{Hf}$ vs $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ plot (Huang *et al.*, 2005), the inverse trend of Mahukona lavas also straddles the Loa-Kea boundary. Their Zr/Nb ratios (12.1–14.8), another Loa-Kea discriminant, are also at the Loa-Kea boundary. Clearly, Mahukona tholeiitic basalt has a weaker Loa geochemical signature than Mauna Loa lavas. This result may require modification of the simple large-scale zonation models.