Deep ocean interactions between hydrothermally-sourced iron and organic carbon

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Hydrothermal venting at mid-ocean ridges is globally widespread, and responsible for a gross dissolved iron (Fe) flux to the ocean that is approximately equal to continental riverine runoff. Previously, it had been assumed that most of this Fe was precipitated in inorganic forms that were deposited close to their sources of venting and, consequently, represented a negligible flux to the global deep ocean. However, recent perspectives from our isotopic[1], voltammetric[2], and spectroscopic [3] studies appear to contradict this. Taken together, our research builds the case that hydrothermal Fe may indeed enter into deep- and open-ocean cycles. Isotopically, it appears that a significant proportion of the Fe incorporated into authigenic minerals in deep open-ocean environments may be hydrothermal in origin. In support of this, our most recent work has revealed a potentially important role for both dissolved and particulate organic matter in the complexation of Fe that may be exported off-axis in hydrothermal plumes. These discoveries are opening new avenues of inquiry regarding the properties of organic materials in hydrothermal plume systems and indicate that highly-localized vent-systems along mid-ocean ridges could play an influential role in the global-scale biogeochemical cycle of Fe, a bio-limiting micro-nutrient, throughout the deep ocean.

[1] Chu, N. C. *et al*. (2006) Earth Planet. Sci. Lett. **245**, 202-217. [2] Bennett, S. A. *et al*. (2008) Earth Planet. Sci. Lett. **270**, 157-167. [3] Toner, B. M. *et al*. (2009) Nature Geosci. **2**, 197-201.

D/H of bone collagen as environmental and trophic indicator

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Organic deuterium/hydrogen stable isotope ratios (i.e. D/H, expressed as δD value in ‰) in the tissue of an organism are related to the D/H of precursor hydrogen in its diet and ingested water. Bone collagen preserves the biochemical D/H isotopic signal in the δD_n value of collagen's non-exchangeable hydrogen. Therefore, δD_n preserved in fossil bone collagen can potentially be used to constrain paleoenvironmental and trophic conditions. Our data calibrate δD_n values of modern collagen in terms of environmental forcing factors in preparation for future work on archeological and fossil specimens. Collagen δD_n is mainly affected by D/H of environmental water and the trophic level of an individual [e.g., 1, 2]. Minor isotopic variation occurs among individuals of a population, possibly even among different body parts of an individual, due to dietary and time differences associated with collagen biosynthesis and bone mineralization. δD_n values of collagens from arid Joshua Tree National Park indicate evapotranspirative D-enrichment of physiological fluids relative to local spring (oasis) drinking water. Collagen δD_n values from terrestrial species collected in south central Indiana with local meteoric average δD_{water} ~ -47‰ ranged from -100‰ to +100‰ and thus reflect strong trophic differences; herbivores tend to have low δD_n values, omnivores rank intermediately, and carnivores express the highest δD_n values. Body size and metabolic rate may be additional factors since smaller animals with typically faster metabolic rates and relatively high evapotranspiration tend to be D-enriched (e.g. white-footed mouse). California sea lions from San Nicolas Island, California, express a δD_n variance of 20‰ indicating intraspecific diversity that can arise from individual dietary differences (e.g. pre-weaned infants vs. adults). Although ocean water is relatively D-enriched, our preliminary data suggest that marine carnivores have lower δD_n values than many terrestrial carnivores, possibly because the latter are more affected by evapotranspiration.

[1] Cormie *et al*. (1994) *GCA* **58**, 377-391. [2] Reynard & Hedges (2008) *J. Archaeol. Sci.* **35**, 1934-1942.