

## Trace metal proxies for ancient oceanic anoxia: Perspectives from modern biogeochemical cycles

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Anoxia is rare in the modern oceans. Thus, the rigorous testing of proxies used to infer anoxic conditions in the ancient ocean is difficult. Trace metals, and their emerging isotope systems, are both increasingly used as such proxies. This presentation will highlight recent advances in our understanding of the cycles of trace metals in the environment, particularly Mo, and assess the implications of these advances for the interpretation of the geological record.

Closed oceanic mass balances are an essential component of the use of any proxy for past oceanic conditions. In this regard, the recent realisation that the Mo isotopic composition of the riverine flux to the oceans is significantly heavier than the bulk continental crust [1] has important implications for data for the past oceans. Ongoing work [2, 3] suggests that Mo isotopic fractionation in soils may control rivers, and that such fractionation is an inevitable consequence of chemical weathering under an oxic atmosphere. Such findings imply that the modern riverine isotopic signal may be relevant to all of Earth history since the early Proterozoic. The anoxic events that have been studied record isotopic values very like the input flux to the modern oceans. Thus the new riverine data imply much greater euxinia during both Jurassic OAEs [4] and in a postulated Proterozoic sulphidic ocean [5].

At the other end of the cycle, new field and laboratory studies are pushing forward our understanding of the fractionations of Mo isotopes into sediments. For example, Mo isotope fractionation on adsorption to Fe (oxyhydr) oxides is substantial [6], and has the potential to elucidate the sub-oxic conditions that must precede full development of anoxic conditions during OAEs. Finally, studies of pore water and sediments beneath modern anoxic but non sulphidic ocean basins, such as Golfo Dulce [7] inform Mo isotope studies in Archean sediments.

[1] Archer, C. & Vance, D. (2008) *Nature Geoscience* **1**, 597-600. [2] Keech, A. *et al.*, this volume. [3] Siebert, C. *et al.*, this volume. [4] Pearce, C.R. *et al.* (2007) *Geology* **36**, 231-234. [5] Arnold, G.L. *et al.* (2004) *Science* **304**, 87-89. [6] Goldberg *et al.*, *Geochim. Cosmochim. Acta*, submitted. [7] Archer, C. *et al.*, this volume.

## Atlantic Ocean water mass distribution over the past 32,000 yrs from Nd isotopes in deep-sea corals

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Deep-sea corals from unique, high-resolution archives of ocean chemistry that can be dated directly using the decay of uranium to thorium. They are abundant in the global ocean and can provide unprecedented insights into ocean circulation on sub-millennial time-scales.

The neodymium (Nd) isotopic composition of marine precipitates is increasingly recognized as a powerful tool in paleoceanography. Unlike nutrient proxies, such as  $\delta^{13}\text{C}$  or Cd/Ca ratios, Nd isotopes are not thought to be altered by biological processes, and may serve as a quasi-conservative tracer for water-mass mixing in oceanographic settings that are not affected by 'boundary exchange'.

In previous studies we have shown that deep-sea corals are reliable recorders of seawater Nd isotopes. The aragonitic skeletons of five different species of modern scleractinian deep-sea corals record ambient seawater Nd isotopes. Furthermore, the aragonitic skeleton of carefully cleaned fossil *D. dianthus* corals maintains the past seawater signal.

Building on this ground-truthing work, we will present results on the Nd isotopic composition of *D. dianthus* and *Caryophyllia* from the Atlantic Ocean and the Southern Ocean. Deglacial-aged deep-sea corals from the NW Atlantic (New England seamounts) indicate an unchanged Nd isotopic signature in the northern-sourced component waters during the Younger Dryas, and thus far there is not evidence for Nd isotopic change during the rest of the last glacial cycle. This understanding has been used to interpret the results of a Heinrich event 1 aged coral from the Southern Ocean to infer significantly reduced export of northern-sourced neodymium to the Southern Ocean around 17,000 years ago. We will furthermore present preliminary data from corals from the New England seamounts that indicate that the Nd isotopic composition of northern component seawater did change during marine isotope stage 3 (~30,000 years ago), which may reflect increased presence of Southern Ocean waters in the intermediate depth North Atlantic Ocean.