

## A history of inhibition: thresholds and echinoderm Mg/Ca

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Oscillations between an ocean which generates a primary abiotic precipitate of calcite or aragonite have been identified throughout the Phanerozoic and attributed to variability in the major ion chemistry of the ocean (magnesium, calcium and sulphate concentrations as lead candidates). Such variability represents fundamental changes to Earth surface processes, notably the balance among continental weathering, sedimentation, and volcanic activity. These cycles in seawater chemistry and primary mineralogy of marine carbonates have implications for reconstructing the drivers of changes in atmospheric CO<sub>2</sub>, for the feedbacks in the global carbon cycle, and for the evolution of biomineralising life. Yet the record of precisely how, when and what these major changes have been is scant at best. Further definition of the chemical thresholds and a quantitative reconstruction and mechanistic understanding of the drivers of these fundamental ocean chemistry changes remains elusive.

First we shall explore how the combined effects of chemical inhibitors can alter the potential thresholds for a change in primary marine carbonate precipitate (Bots *et al.*, 2011). We then employ an established method (Dickson, 2002) to provide insight into refining the Meso-Cenozoic history of the dominant kinetic inhibitor of calcite precipitation, namely magnesium. We demonstrate the utility of a uniquely pristine sample compilation of echinoderm fragments collected from clay hosted sediments to preserve a history of seawater Mg/Ca. Our reconstructed history of seawater Mg/Ca is largely concordant with existing results except for a part of the middle Jurassic which appears to be characterised by much lower Mg/Ca ratios than predicted by most models.

[1] Bots P., L. G. Benning, R. E. M. Rickaby, S. Shaw, 2011, The role of SO<sub>4</sub> in the switch from calcite to aragonite seas, *Geology* **39**, 331-334. [2] Dickson, J. A. D., 2002, Fossil echinoderms as monitor of the Mg/Ca ratio of phanerozoic oceans, *Science*, **298**, 1222-1224.

## Boundary addition of Hf and Nd in the Southern Ocean

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Hf and especially Nd isotopes are increasingly used to reconstruct past ocean circulation. Many of these applications rely on their quasi-conservative behaviour implying that the key process that governs their distribution is circulation. Here, we report new elemental (Hf, Zr, Nd) and isotope data ( $\epsilon$ Hf,  $\epsilon$ Nd) from the Pacific sector of the Southern Ocean, which document the relative significance of circulation vs boundary processes on the Hf and Nd distribution adjacent to Antarctica. Seawater depth profiles were sampled in the Ross Sea, along the West Antarctic continental rise and in the vicinity of the Marie Byrd Seamounts offshore the Amundson Sea Embayment (ASE). In addition, several samples were taken within 1.5 m to the seabed in the ASE. The samples were not filtered, which implies that some of the observations may be accentuated by contributions from the leaching of particulates during sample acidification.

The key observations for Nd include (a) the shift to radiogenic  $\epsilon$ Nd and elevated Nd concentrations in the ASE ( $\epsilon$ Nd up to -5.4), (b) a gradual increase in  $\epsilon$ Nd with depth from 1000 m to 3000 m water depth in the open ocean (-9 to -7.8) along the entire West Antarctic margin and (c) distinctly more radiogenic deep waters beneath 3000 m, especially at the Haxby seamount (up to -3.1). (a) is indicative of boundary release of Nd. (b) probably reflects the mixing of freshly forming boundary affected deep waters with circumpolar deep water (CDW) upon sinking. (c) indicates that, in addition to the shelf, the deep ocean floor and basaltic seamounts act as sources of radiogenic Nd.

Hf isotopes are relatively homogenous in the data set ( $\epsilon$ Hf mostly between +2 and +3.8). Boundary release is, however, evident from elevated Hf and Zr concentrations in the embayment. In addition, distinctly unradiogenic  $\epsilon$ Hf of -1 are observed in deep waters at the Haxby Seamount. The data thus suggests that relatively unradiogenic Hf is released from Antarctica in the sampling area, which probably also accounts for the slight but systematic difference between measured  $\epsilon$ Hf of CDW and deep waters of the eastern Pacific compared to the Atlantic sector of the Southern Ocean.