The isotopic mass balance of zinc in the oceans

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Zinc isotopes represent a new tool that could track biological usage of trace metals in the ocean through time. Such an endeavour, however, must rest on a sound understanding of the biogeochemical cycling of zinc isotopes. Here we summarise this current understanding through analysis of the inputs and outputs of Zn to and from the modern ocean. The present Zn isotopic composition of the deep ocean is uniform, at ca. 0.5‰ for $\delta^{66/64}$Zn. This value is also an upper limit on the composition of the average whole ocean. Unlike some other transition metal isotopic systems studied so far, including Mo and Cu, this average value of δ^{66}Zn is similar to typical rock and detrital values (0.3‰) and to the principal sources of Zn to the oceans (including average global rivers = 0.33‰ [1], hydrothermal input = 0.24‰ [2], and dust ~0.2-0.4‰ [1,3]).

Both Mo and Cu isotopes are fractionated in seawater by preferential sorption of the light isotope onto Mn oxides in oxic settings. Ferromanganese crusts are isotopically light, and the imprint of their formation is stamped on the resulting heavy dissolved pool in seawater. Laboratory sorption experiments of Zn on δ-MnO_2 indicate that δ-MnO_2 also sorbs the light isotope of Zn, and an EXAFS study of three ferromanganese crusts indicates that Zn is associated with birnessite (δ-MnO_2) in these samples. This association with birnessite in nature, and the preferential uptake of the light isotope onto birnessite in experiments, are features that Zn shares with Cu and Mo. However, Zn isotope values from natural Fe-Mn crusts are uniformly heavier (at 0.7-1.2‰) than the deep ocean value. Either Zn is in a different crystal chemical environment on the oxide in experiment versus nature, or biology is, by an unknown mechanism, superimposed on Zn isotopes in crusts. In either case, the oxic sink for Zn, as sampled by Fe-Mn crusts, does not appear to significantly impact the average ocean isotopic composition. If anything, the isotope data for the inputs and for dissolved Zn in the deep ocean imply a total output that preferentially removes the light isotope. It is possible that the uptake of light isotopes into organic material [4] at least balances removal of the heavy isotope to Fe-Mn oxides.

The other key sink of redox sensitive elements is in anoxic settings, where, like Mo, Zn seems to undergo no isotopic fractionation on removal from seawater in to sediments. Data from the most Zn-enriched euxinic sediments of the Black Sea and Cariaco Basin give almost identical values to the deep ocean, of 0.5-0.6‰, whilst non-euxinic sediments from the margin of the Black Sea record the expected detrital value of 0.3‰. Hence the observed, small, difference between the input of Zn to the oceans and the average ocean isotopic composition is neatly replicated in these local anoxic-oxic settings.

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Orbitally-paced oscillations in benthic δ^{18}O in the early Paleogene: Implications for variations in deep sea temperature and ice-volume

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Introduction

The early Paleogene is generally accepted to have been a warm greenhouse world, with relatively high pCO_2 levels and little evidence for large-scale ice-sheets. However, ample geochemical and palaeontological evidence exists for both sustained and transient fluctuations in global climate during this time, which are often coupled to significant changes in the carbon-cycle [1, 2, 3, 4, 5, 6]. Controversially, some oxygen-isotope and sequence-stratigraphic evidence has been put forward to suggest that continental ice-volumes were large enough to drive significant changes in global eustatic sea-level during the early Paleogene [7, 8]. If ice-sheets capable of affecting global sea-level did exist, presumably on Antarctica, one would expect two things to be observed in early Paleogene marine geochemical records; 1. The presence of significant variance in eccentricity and obliquity periods in high-resolution benthic oxygen-isotope records, as is commonly observed in the icehouse world of the Oligocene–Neogene; and 2. A distinct residual seawater oxygen-isotope signal (i.e., $\Delta\delta^{18}O_{SW}$) once the temperature contribution to the benthic foraminifer δ^{18}O signal is extracted by applying the Mg/Ca or some other paleothermometer.

Results and conclusions

Here we present benthic foraminiferal δ^{18}O data from the South Atlantic (Site 1262, Walvis Ridge), which show orbitally-paced cyclic variations during the Late Paleocene and Early Eocene. Spectral analysis of these records reveals a strong eccentricity pacing throughout the entire ~6 Myr record, but no significant power in the obliquity band, suggesting global ice volumes were too low to influence $\delta^{18}O_{SW}$ beyond the background noise. Additionally, ongoing Mg/Ca analysis of benthic species at Site 1262 demonstrates that there were changes in deep-water temperature associated with eccentricity-paced carbon cycle fluctuations in the Late Paleocene, concurrent with changes in the oxygen-isotope record. Furthermore, these Mg/Ca records allow absolute temperatures to be estimated for the deep water of the South Atlantic during the Late Paleocene, which may help to establish a baseline for pre-PETM climate.

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