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Cadmium Isotope Variations in the Peruvian Oxygen Minimum Zone – New Constraints on Micronutrient Cycling

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Recent studies have recognized that micronutrient elements, such as cadmium (Cd), play an important role in marine biological productivity. The distribution of dissolved seawater Cd is correlated with that of phosphate [1], with low concentrations in surface waters due to biological utilization and higher abundances at depth from remineralization of organic material.

Previous studies have furthermore shown that biological uptake of Cd in the surface seawater can generate significant Cd isotope variability, whilst the deep ocean appears to be characterized by a relatively constant Cd isotope composition of $\varepsilon^{114/110}$Cd $\approx$ +3 [2,3], which is roughly similar to results obtained for the silicate Earth [4] ($\varepsilon^{114/110}$Cd is the deviation of the ^{114}Cd/^{110}Cd ratio of a sample from the NIST 3108 Cd isotope standard in parts per 10,000). The most fractionated Cd isotope compositions have been determined for highly nutrient depleted open ocean surface waters from the Atlantic and Pacific Ocean, which exhibit $\varepsilon^{114/110}$Cd values of between +20 and +40. In contrast, the comparatively nutrient rich surface waters of the Southern Ocean HNLC region display relatively high Cd contents of up to 0.2 nM and only limited Cd isotope fractionation with $\varepsilon^{114/110}$Cd values of between + 5 and +8.

These results are of interest because they provide new constraints on the cycling of the micronutrient Cd in the present oceans [2,3]. In addition, they also imply that Cd isotopes may be a useful proxy for the study of past changes in marine nutrient utilization. This conclusion is supported by further results that were recently obtained for seawater samples from the oxygen minimum zone (OMZ) of the coastal upwelling area in the South Pacific Ocean off Peru. Cadmium concentration and isotope data were obtained for 9 depth profiles in this region at between 3˚S and 12˚S.

The surface water samples from these locations display $\varepsilon^{114/110}$Cd-[Cd] signatures that are distinct from those found in the Southern Ocean HNLC region and nutrient depleted open ocean areas. In the Peruvian OMZ, the seawater from $<$25 m depth displays highly variable Cd contents (of between 0.01 and 0.2 nM) combined with surprisingly constant and unfractionated Cd isotope compositions of $\varepsilon^{114/110}$Cd $\approx$ +5 to +8. This signature most likely reflects a quasi steady-state situation, whereby the removal of Cd by biological utilization (and associated isotope fractionation) is balanced by Cd inputs from upwelling of Cd-rich and isotopically unfractionated deep water masses. This conclusion is supported by data that were obtained for deep water samples from the OMZ. These exhibit a mean $\varepsilon^{114/110}$Cd value (of +3 $\pm$ 1) that is essentially identical to the previously inferred global deep water mean [3]. Also unusual are the slightly fractionated Cd isotope compositions that were observed at intermediate depths of 500 to 1200 m and which may reflect either incomplete remineralization of (isotopically light) biological material within the OMZ and/or a distinct isotopic signature of the Peru-Chile Undercurrent.

Reference:

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