Cadmium isotopic composition of Cenozoic seawater from ferromanganese crusts

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Cadmium shows a nutrient-like concentration profile in the oceans that is similar to those of nitrate and phosphate. Analysis of the isotopic composition of Cd can reveal key information about the biogeochemical cycles that control its distribution. Typically, nutrient-depleted surface waters with very low Cd concentrations exhibit heavy isotope compositions ($\varepsilon^{114/110}$Cd values up to +40 reported relative to NIST 3108 Cd), whilst deep waters with higher Cd concentrations exhibit fairly uniform $\varepsilon^{114/110}$Cd values of about +3. These observations are attributed to phytoplankton at the surface preferentially taking up isotopically light Cd, leaving surface water enriched in heavier isotopes. Subsequent sinking and remineralisation of organic matter releases lighter Cd at depth.

The use of Cd isotopes as a proxy for nutrient utilisation is of particular interest in paleoceanography, and here we use ferromanganese (Fe-Mn) crusts as archives of past deep water isotope composition. Surface scrapings of these crusts were previously shown to have Cd isotope compositions that are identical, within uncertainty, to that of the deep water from which they formed.

Sixty samples from Fe-Mn crusts Alvin 539 2-1A (North Atlantic, 2665 m), VA16 13KD-1 (Indian Ocean, 2100 m) and CD29 (Pacific Ocean, ~2200 m) were analysed by MC-ICP-MS for their Cd isotope composition using the double spike technique to correct for instrumental mass bias. Excluding a few outliers, the data show that the Cd isotope composition of the deep ocean has remained relatively constant during the Cenozoic, with an $\varepsilon^{114/110}$Cd that is similar to the current deep water value of about +3. If we can exclude diffusion as a process to homogenise the Cd signal in Fe-Mn crusts, our data provide evidence that Cd cycling has not undergone major long-term changes during the last 60 Ma.