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High-precision cadmium isotope fractionation determined by double spike thermal ionisation mass spectrometry

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Wombacher et al. (2003) have shown recently that natural Cd isotope fractionations in terrestrial materials are extremely limited ($<$1.1 εCd/amu, deviation in 1:10^4 per mass unit). Thus, excellent external precision is absolutely paramount if Cd isotope fractionations are to be adequately quantified. Here we present a new double spike technique for Cd isotopes in which the Cd is measured by thermal ionisation mass spectrometry (ThermoElectron Triton), drawing on previous work (Rosman et al., 1980). The double spike and its composition were chosen to minimize the final error on εCd (Galer, 1999). Using these protocols we achieve an external reproducibility of ± 0.05 εCd/amu (2SD, N=23) on 100 ng loads of JMC Cd shelf standard. Compared to recently developed MC-ICPMS techniques for Cd isotopes (Wombacher et al., 2003; Cloquet et al., 2005; Lacan et al., 2005; Shiel et al., 2005; Wichtlhuber et al., 2005), reproducibilities are 4 to 20 times better, and the method offers benefits in terms of superior sensitivity. Cd abundances by isotope dilution are obtained as a biproduct. Measurements of the isotopically heavy Cd standard VTA-3 yielded +10.73 ± 0.08 εCd/amu (N=5) relative to our JMC standard, which is marginally higher than the 9.7 ± 0.6 reported by Wombacher et al. (2003).

One obvious application of Cd isotopes is the marine environment: Cd is a biologically-mediated trace constituent of seawater which substitutes readily into calcite and is distributed analogously to nutrients such as phosphorus. Because of the low Cd concentration in seawater, the Cd/Ca “nutrient-like” ratio has been instead used as a proxy for changes in thermohaline circulation and biological productivity (e.g. Boyle et al., 1976; Bruland, 1980; Boyle, 1981). We have investigated the distribution of Cd isotopes in the oceans by measuring Fe-Mn nodules whose radiogenic isotope signatures have been interpreted as reflecting those of ambient seawater. So far, analyses of five samples from the Atlantic, Pacific, Indian and Circum-Antarctic oceans show a total range of εCd/amu from -0.10 to +0.14. Variations in εCd are thus barely resolvable, indicating that there is no gross inter-ocean Cd isotope fractionation. This result is in accordance with the long residence time of Cd in seawater ($\sim$50 kyr) relative to the ocean mixing time. Overall, our first results are encouraging, and complementary data will be crucial for assessing the extent of Cd isotope fractionation in the oceans as well as understanding the controlling mechanisms. At this stage, the high precision of the Cd double spike method provides a potentially promising tool for paleoceanographic studies.

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