

Ferromanganese crusts as archives of deep-water Cd isotope compositions

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The geochemistry of Cd in seawater has attracted significant attention, mainly due to the nutrient-type distribution of this element, which resembles the distribution of phosphate [1]. The origin of this similarity is still disputed, but a number of studies have suggested that Cd in the oceans is a micronutrient with an important biological function [2]. This conclusion is supported by recent Cd isotope data for seawater and cultured phytoplankton [3, 4]. Ripperger *et al.* [4] found that Cd-depleted surface waters typically exhibit fractionated Cd isotope compositions, with $\epsilon^{114/110}\text{Cd}$ values of up to $+38 \pm 6$, which were interpreted to reflect preferential uptake of isotopically light Cd by phytoplankton. In contrast, seawater samples from ≥ 900 m depth were found to display uniform isotope compositions of $\epsilon^{114/110}\text{Cd} = +3.3 \pm 0.5$.

In this study, we investigated whether ferromanganese (Fe-Mn) crusts are suitable archives of deep-water Cd isotope compositions. To this end, we acquired Cd isotope data for the recent growth surfaces of 15 Fe-Mn crusts from the Atlantic, Southern, Indian and Pacific Oceans using MC-ICPMS in conjunction with a double-spike technique.

All but two of the Fe-Mn crusts have Cd isotope compositions, which are identical within uncertainty ($\pm 1 \epsilon^{114/110}\text{Cd}$) to the mean deep-water Cd isotope value reported by Ripperger *et al.* [4]. These samples yield a mean $\epsilon^{114/110}\text{Cd}$ of $+3.3 \pm 0.7$ (1sd). This indicates that Fe-Mn crusts record seawater Cd isotope compositions without significant isotope fractionation, in agreement with the results of an earlier study [5]. In contrast, two samples from the S. Atlantic and Southern Ocean have lighter Cd isotope compositions of $\epsilon^{114/110}\text{Cd} \approx +1$. The origin of this signature is unclear but it may reflect variations in deep-water isotope compositions related to differences in surface water Cd utilization. This suggests that time-series analyses of Fe-Mn crusts may be utilized to study changes in marine nutrient utilization.

[1] Boyle *et al.* (1976) *Nature* **263**, 42. [2] Price & Morel (1990) *Nature* **344**, 658. [3] Lacan *et al.* (2006) *GCA* **70**, 5104. [4] Ripperger *et al.* (2007) *EPSL* **261**, 670. [5] Schmitt *et al.* (2007) *GCA* **71**, Supplement, A898.

Improving the utility of detrital zircon studies through chemical abrasion

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U-Pb isotopic dating of detrital zircon has the potential to yield important insight into a variety of geologic processes, including, but not limited to: understanding sedimentary provenance and deciphering the exhumation history of mountain belts.

Most studies of detrital zircon use either SIMS or ICP-MS methods to obtain U-Pb isotopic ages on large numbers of single crystals. However, an almost ubiquitous problem with this approach is the presence of large numbers (up to 50% for random detrital zircons) of crystals that yield discordant ages. Discordance generally results from radiogenic lead loss, either through radiation-damage and/or diffusion along imperfections within the crystal lattice.

The presence of a significant number of discordant analyses from an individual sample complicates data interpretation and severely limits the geologic utility of this approach. Following the 'chemical abrasion' method developed by Mattinson [1], we investigate the potential for this preparation technique to significantly improve the overall concordance of a detrital zircon data set where Pb-loss is the cause of discordance. Previous applications of this approach to magmatic samples suggest >90% of analyses from any given sample could be moved to within 5% of concordance. Initial data indicate that annealed and non-annealed aliquots of the same sample have comparable age distributions, suggesting that this method does not introduce any additional bias into the age-population spectra.

As a consequence of this approach, high-U and/or radiation-damaged zircon are often reduced to small irregular fragments or skeletal morphologies. In order to compensate for this, such that these types of grains are not under-represented in any analysis, we have developed novel sampling strategies in order to obtain isotopic information without degradation of data quality.

Through chemical abrasion, the proportion of detrital zircon analyses that can be included in an age spectrum could be increased dramatically without significant sampling bias. Although further work is required, the potential to improve the number of useful data points and confidence in interpreting difficult detrital zircon spectra, is significant.

[1] Mattinson (2005) *Chem. Geol* **220**, 47-66.