A simple vertical model of marine Zn and Cd stable isotope cycling

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The measurement of trace-metal stable isotope ratios in seawater can provide new tools for studying trace-metal cycling in the oceans. Recent developments in ICP-MS technology and new methods for extracting Zn and Cd isotopes from large volumes (1-5 L) of seawater have led to the publication of vertical profiles of dissolved $\delta^{66}Zn$ [1] and $\varepsilon^{114}Cd$ [2, 3]. By comparing these observations with a new model of vertical Zn and Cd isotope transport in the oceans, we hope better understand the marine biogeochemical cycling of these elements.

We have constructed a steady-state 1-dimensional model of Zn and Cd isotope cycling in the oceans. Our model incorporates three processes to account for the vertical movement of Zn and Cd: 1) mixing of seawater parcels with different dissolved isotope ratios, 2) active biological uptake of Zn and Cd by growing phytoplankton in the surface oceans, with preferential incorporation of lighter isotopes into particles, 3) scavenging of dissolved Zn and Cd onto sinking particles, with preferential adsorption of heavier isotopes.

Our model for isotope cycling in the oceans leads to some surprising hypotheses when applied to the available isotope data. Minimum values of both $\delta^{66}Zn$ [1] and $\varepsilon^{114}Cd$ [2] are observed at ~100m in the North Pacific, a feature which can only be reproduced in our model by scavenging of Zn and Cd onto sinking particles. Preliminary calculations based on fitting our model to the observations of Bermin *et al.* indicate that a large proportion of downward Zn flux occurs by scavenging. This hypothesized importance of scavenging contradicts some prior assumptions about Zn cycling in the oceans. For example, it suggests that the deep regeneration maximum of Zn compared to N, P, and Cd may not result from the refractory nature of organic Zn but from Zn adsorption onto falling particles. Also, the remarkable correlation between dissolved Si and Zn throughout the world ocean may mask important differences in the processes by which these elements are cycled between dissolved and particulate phases, reflecting only a similarity in *net* remineralization rates.

[1] Bermin *et al.* (2006) *Chem. Geol.* **226**, 280-297. [2] Ripperger *et al.* (2007) *EPSL* **261**, 670-684. [3] Lacan *et al.* (2006) *GCA* **70**, 5104-5118.

The chlorine isotope signature of mantle endmembers

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Sharp *et al.* [1] reported $\delta^{37}Cl$ values for MORB (EPR, PARC, Iceland, Macquarie), and other primitive materials, that might suggest an isotopically uniform mantle source of chlorine ($\delta^{37}Cl=0\pm1$). Nevertheless, the isotopic distribution of chlorine in the diverse tectonic regimes that produce basaltic magmas has not yet been fully explored.

New determinations on a broad selection of oceanic basalts, representative of isotopic mantle end members (HIMU, EMI, EMII) suggest that there may be a systematic and discernible variation in the ranges of Cl isotopes in these sources. Improvements to the SIMS method for $\delta^{37}Cl$ determination originated by Layne *et al.* [2] and Godon *et al.* [3] have enabled individual determinations in basalt glass fragments to better than 0.3 per mil (1s) precision and 0.7 per mil overall reproducibility for Cl contents >150 ppm.

Replicate determinations in a subset of the samples characterized by Stroncik & Haase [4] yielded mean $\delta^{37}Cl$ values of -3.5 (range -5.2 to -1.6; n=4) for EMI/II and -0.8 (-2.6 to 0.8; n=6) for HIMU. The observation that EM-type basalts have the most negative $\delta^{37}Cl$ supports the model that the mantle source of these lavas contains recycled sedimentary material. The moderately negative $\delta^{37}Cl$ values of some HIMU-type lavas overlap with those of altered basalts, which are generally assumed present in the HIMU source.

Basalts from the northern Kermadec island arc (Monowai) display slightly heavier, positive $\delta^{37}Cl$ (0.3 to 0.5) - compared to dacites from the southern Kermadec arc (Brothers; -0.3). The former could be explained by a strong flux of Cl from subducting serpentinite whereas the latter agree with the observed increasing influence of subducting sediments in the southern Kermadec arc.

[1] Sharp *et al.* (2007) *Nature* **446**, 1062-1065. [2] Layne *et al.* (2004) *Chemical Geology* **207**(3-4)**,** 277-289. [3] Godon *et al.* (2004) *Chemical Geology* **207**(3-4), 291-303. [4] Stroncik & Haase (2002) *Geology* **32**(11), 945-948.