

The Global U Isotopic Cycle

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The mobility of U under oxic conditions and its enrichment in the oceanic crust has long led to speculations about the importance of these low temperature processes in the global distribution of U [e.g. 1]. Notably, the return flux of U from surface to mantle, via subduction, is potentially sufficient to perturb the mantle U abundance. This mechanism has been used as a means to explain puzzling features of mid-ocean ridge basalt (MORB) U-Th-Pb systematics [e.g. 2]. Advances in multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) allow the hitherto presumed invariable ²³⁸U/²³⁵U ratio to provide new constraints on this cycle. Recent work has shown that the U in the near surface environment can be fractionated by about 1‰ [e.g. 3,4]. Therefore, recycling of significant amounts of isotopically fractionated U from the surface to the mantle has the potential to perturb not only its U abundance but also its isotope ratio.

In order to exploit this potential we have had to tune our torch. Using a ²³³U-²³⁶U double spiking approach and by measuring intense U beams (>1nA), we have obtained precisions of ~0.02‰ on ²³⁸U/²³⁵U ratios of mantle derived samples. This provides sufficient resolution to detect the influence of recycled U in the mantle.

We have determined that the net effects of alteration and subduction leave deep recycled slab with isotopically heavy U [5]. The preferential return of this U into the upper mantle, as invoked to explain the anomalously low Th/U ratio of MORB [e.g. 2], predicts that MORB should be ~0.1‰ heavier than pristine mantle. We show that this prediction is realised in our measurements of MORB glasses relative to ocean island basalts and chondritic meteorites. Thus we provide striking, independent confirmation of the importance of recycling in shaping the U budget of the mantle courtesy of the capabilities of modern MC-ICPMS.

[1] Albarède & Michard (1986) *Chem Geol* **57** p1-15 [2] Elliott, Zindler & Bourdon (1999) *EPSL* **169** p129-145 [3] Stirling, Andersen, Potter & Halliday (2007) *EPSL* **264** p208-225 [4] Weyer *et al.* (2008) *GCA* **72** p345-359 [5] Freymuth, Andersen & Elliott this volume

Tracing changes in the biogeochemical cycling of iron during the annual subtropical spring bloom east of New Zealand

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The turnover time of iron in the surface ocean can vary from days to weeks and months, while within cells the turnover time can be on the order of hours to days. Accordingly, the iron isotope ($\delta^{56}\text{Fe}$) composition of particulate organic matter should be sensitive to changes in the cycling of iron in the surface ocean and immediately below. Here we present data showing a dynamic change in the $\delta^{56}\text{Fe}$ composition of particulate organic matter during the development and subsequent export of phytoplankton bloom material. Our results, obtained from two FeCycle voyages in 2008 and 2012, suggest that before the onset and development of the phytoplankton bloom iron regeneration dominates the dissolved iron signal with lighter dissolved $\delta^{56}\text{Fe}$ values (-0.14‰ at 100 m to 0.07‰ at 500 m) relative to particulate iron (-0.02‰ at 60 m to 0.13‰ at 300m). In contrast, during the development and export phase of the bloom, iron scavenging and/or iron consumption by heterotrophic bacteria community appears to dominate the dissolved iron isotope signal with heavier dissolved $\delta^{56}\text{Fe}$ values (0.15‰ at 30 m to 0.16‰ at 500 m) relative to particulate $\delta^{56}\text{Fe}$ values (-0.11‰ at 30 m to -0.33‰ at 300 m). A strong relationship was also observed between particulate $\delta^{56}\text{Fe}$ and Fe/Al ratios with lighter values. The dissolved and particulate $\delta^{56}\text{Fe}$ results were modelled with Rayleigh-type functions and produced the following fractionation factors: 1.00015 prior to the onset and development of the bloom and 0.99945 during the subsequent export of the bloom material to depth. Taken together our results show that the iron isotope composition of dissolved and particulate material can be used to monitor changes in the biogeochemical cycling of iron in the marine realm.