

Iron isotopes in the marine system

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Iron is an essential micronutrient and is proposed to play a role in climate change by influencing primary production in the ocean. Although the importance of Fe in the ocean has been recognized for the past decade, it is difficult to study because of its complex chemistry and behavior. Fractionation of Fe isotopes could be an effective tool to investigate and quantify the marine geochemistry of Fe. Initial studies of stable Fe isotopes show measurable fractionation in both natural samples and laboratory studies spanning 4‰ (in the 56/54 ratio, $\delta^{56}\text{Fe}$). However, most natural samples measured are in the solid phase (high Fe) with only a few studies of natural aqueous or biological samples (typically lower concentrations of Fe). This study addresses questions about the modern Fe cycle using direct measurements of stable Fe isotopes in a variety of natural samples including trace metal clean plankton tows, river samples, aerosol leachates, marine sediment trap samples, and marine porewaters. Fe isotopic composition was measured on a GV Instruments IsoProbe Multi-collector ICPMS. External precision for the $\delta^{56}\text{Fe}$ measurement is typically better than $\pm 0.2\text{‰}$ (2σ) for natural low-level Fe samples using sample-standard bracketing.

The $\delta^{56}\text{Fe}$ of the marine samples varied by over 4‰ with plankton tows showing a large range (-3.87‰ to +0.36‰). The range in the $\delta^{56}\text{Fe}$ of the plankton tow samples demonstrates that significant and potentially useful fractionation is associated with cycling of Fe in the upper ocean. The Fe in the plankton tow samples in this study was a mixture of intracellular and extracellular Fe. For plankton samples with Fe:C ratios greater than 70 $\mu\text{mol/mol}$, the $\delta^{56}\text{Fe}$ values were more variable and became isotopically heavier with increasing Fe:C ratios suggesting that extracellular Fe is isotopically heavier than the intracellular Fe. Plankton samples from the Atlantic scatter around a hypothetical mixing line between a planktonic intracellular $\delta^{56}\text{Fe}$ of approximately -1.5‰ and an extracellular component of Fe that is isotopically similar to igneous rocks (0‰). The North Pacific plankton tow samples were isotopically lighter in $\delta^{56}\text{Fe}$ than the Atlantic plankton samples.

Boron isotope variation and its environmental implication in Wuquan River Estuary, Hainan Island, China

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The boron-isotope composition of authigenic carbonate skeletons may provide a useful tool to record secular boron-isotope variations in seawater at various times in the geological record. The potential use of boron-isotope geochemistry in skeletons can be as a tracer for palaeoenvironments (Vengosh *et al.*, 1991). Gastropoda skeletons for this study were isolated from Core K4 collected in Samei Lagoon located in Wuanquan River Estuary, Hainan Island, China. Their isotopic compositions of boron were measured by TMIS with the method of negative thermal ionization producing BO_2^- ions. The results are shown in the table below.

Sample Depth (cm)	Group	$\delta^{11}\text{B}$ (‰)
14-15	Gastropoda	6.3
34-35	Gastropoda	10.0
125-126	Gastropoda	10.4

$\delta^{11}\text{B}$ values of Gastropoda skeletons range from 6.3-10.4‰. Below the depth of 34-35 cm in the core, the values are about 10‰, which are similar to those in modern marine biogenic carbonates (13.3-32.2‰) (Barth, 1993). In the depth of 14-15 cm (about 1900 AD, Ge *et al.*, 2003), the value is relatively lower (6.3‰), which may reflect a more "terrestrial" boron-isotope signature of the water (Vengosh *et al.*, 1991). $\delta^{11}\text{B}$ record implicates that Shamei Lagoon was formerly an embayment and since 1900, the water salinity has become much lower, which is consistent with those of organic carbon isotope values and C/S ratios (Ge *et al.*, 2003).

References

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