

Fe isotope fractionation induced by aqueous Fe-siderophore complexes

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The equilibrium Fe isotope fractionation induced by organic ligands was determined by experiments with pH 2 solutions that had coexisting inorganic Fe(III) species (Fe_{inorg}) and siderophore complexes, Fe-desferrioxamine B (Fe_{DFOB}).

In the experiments, the two differently complexed Fe pools were separated by addition of Na_2CO_3 , a method previously applied to separate aqueous Fe(II) and Fe(III) [e.g. 1]. Tests showed that the addition of Na_2CO_3 scavenged the inorganic Fe quickly and effectively, without causing significant dissociation of Fe_{DFOB} .

Preliminary experiments using enriched ^{57}Fe tracer indicate that isotope equilibration between the ^{57}Fe -labelled inorganic species and the isotopically "normal" Fe of the organic species was minor during the 1 s precipitation induced by Na_2CO_3 addition. Although Fe isotope fractionation during precipitation may cause some changes in the isotope composition of the Fe_{inorg} , the results suggest that only negligible isotope re-equilibration occurs within the time of the separation, meaning that precipitated Fe faithfully records the Fe isotope composition of Fe_{inorg} and the remaining Fe_{DFOB} .

In experiments with starting solutions having $\delta^{56}\text{Fe} = 0.76$ ‰, desferrioxamine-complexed Fe has $\delta^{56}\text{Fe} \sim 1$ ‰, whereas inorganic Fe has lighter $\delta^{56}\text{Fe} \sim 0.5$ ‰. This indicates that co-existing Fe-desferrioxamine B and inorganic Fe complexes have an equilibrium Fe isotope fractionation of 0.5‰ at a temperature of 25 °C. This value is comparable to the kinetic Fe isotope fractionation induced by desferrioxamine-promoted dissolution of hornblende [e.g. 2], suggesting that equilibrium Fe isotope fractionation induced by strongly coordinating organic ligands may fractionate Fe isotopes strongly in seawater, where above 99 % of aqueous Fe is bonded by such ligands.

References

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Ocean crust formed from E-MORB overlying an ultra-depleted mantle on Macquarie Island: Implications for mantle heterogeneity

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Macquarie Island (Southern Ocean) is a fragment of young (Miocene) ocean crust and upper mantle uplifted and exposed above sea-level in an entirely intra-oceanic setting, without being obducted onto a continental margin. As such, it is unique in the world and it is generally considered as an important type-locality of oceanic crust and mantle and as a key link between oceanic basement and ophiolites. Several workers have pointed out the similarity between the crustal section on the island and the 'classical' ophiolite sequence. Recent work has, however, shown that the formation history of the island is more complex than originally envisaged.

There is evidence from field relations that the volcanics, dykes and gabbros were formed during different magmatic episodes and it seems unlikely that the main crustal units are co-magmatic. We have dated the formation of the gabbros at 9.0-8.6 Ma (U-Pb zircon SHRIMP ages). Secondly, the volcanic rocks on the island are unusual: there are few N-MORB and the majority of the volcanics are strongly incompatible element enriched E-MORB ($\text{La}/\text{Sm} < 8$). Moreover, our new geochemical data show that the dykes, evolved gabbros and cumulate rocks on the island are derived from parental melts that range from slightly depleted to enriched MORB, but that they were significantly less enriched ($\text{La}/\text{Sm} < 5$) than the volcanic rocks on the island, ruling out a co-magmatic origin. Nd isotope data confirm that there is little compositional overlap between the parental melts of the gabbroic rocks ($\epsilon_{\text{Nd}}^{(9\text{Ma})} = +7.8-9.3$) and the volcanics ($\epsilon_{\text{Nd}}^{(9\text{Ma})} = +7.2-8.3$).

In addition, we will show that the mantle harzburgites on the island are much more depleted (residue of >20% near-fractional melting) than expected from the tectonic setting and slow spreading rate of the Macquarie paleo-ridge system. Their ultra-depleted character is also inconsistent with the thin magmatic crust (<~3 km), and with the highly enriched character of the volcanics. This means that these mantle rocks are not the source residue of the magmatic rocks and that their depleted character is the result of an earlier melting episode.

We will attempt to tie these disparate observations into one model for the formation of the oceanic basement section on Macquarie Island. The parental magmas that formed the crust were probably derived from enriched and isotopically distinct lithological heterogeneities within the mantle, with a limited contribution from depleted mantle. Over a short time interval (~1 My), the input of enriched melts increased dramatically due to changes in the magma plumbing system, in the spreading geometry, or in the nature of the mantle material entering the base of the melting domain underneath the ridge system.