

Iron isotope composition of mid-ocean ridge basalts and mantle peridotites

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The importance of igneous processes in the fractionation of Fe isotopes remains a subject of controversy. In this study, we investigate Fe isotope variations in mid-ocean ridge basalt (MORB) glasses and minerals separated from mantle peridotites from different tectonic settings. Samples include MORB glasses from the Mid Atlantic Ridge and the East Pacific Rise, peridotites from the base of the mantle wedge section of the Kohistan Arc (Pakistan), and mantle xenoliths from the Cameroon Line. Iron isotope measurements were carried out by MC-ICP-MS following sample dissolution and Fe extraction by anionic exchange chromatography. Iron isotope compositions are reported relative to IRMM-14; external reproducibility, based on repeat analyses of our internal standard, is better than 1.0 ‰ for $^{57}\text{Fe}/^{54}\text{Fe}$, 4.0 ‰ for $^{58}\text{Fe}/^{56}\text{Fe}$ and 2.0 ‰ for $^{57}\text{Fe}/^{56}\text{Fe}$ (2 s.d.). The reproducibility of individual samples is comparable to or better than this.

MORBs show relatively invariant Fe isotope signatures; the average Fe isotope composition calculated from all the samples analysed so far is: $\epsilon^{57}\text{Fe}/^{54}\text{Fe}$ 1.0 ± 1.5 , $\epsilon^{58}\text{Fe}/^{56}\text{Fe}$ 0.8 ± 3.0 , and $\epsilon^{57}\text{Fe}/^{56}\text{Fe}$ 0.5 ± 1.0 (uncertainties are 2 s.d.). Given this remarkable homogeneity, we propose that the above values can be adopted as the average Fe isotope composition of the depleted mantle reservoir. This composition is indistinguishable from that previously ascribed to the inner solar system.

Whereas the whole-rock compositions of unmetasomatized LREE-depleted Cameroon Line xenoliths plot within the MORB field, silicate minerals (olivine, ortho-/clinopyroxene, garnet, amphibole) from these xenoliths have Fe isotope signatures that are significantly more variable than the MORB range. In general, these minerals have isotopic compositions that are indistinguishable, although clinopyroxene displays the heaviest Fe isotope signature relative to its whole-rock ($\epsilon^{57}\text{Fe}/^{54}\text{Fe}_{\text{cpx}} - \epsilon^{57}\text{Fe}/^{54}\text{Fe}_{\text{w-r}}$ is typically 2-3 ‰). However, the Fe isotope signatures of the Kohistan samples are more complex. In one peridotite, garnet displays a much lighter value than the other silicate minerals and the whole-rock ($\epsilon^{57}\text{Fe}/^{54}\text{Fe}_{\text{gt}}$ of -2.4; $\epsilon^{57}\text{Fe}/^{54}\text{Fe}_{\text{gt}} - \epsilon^{57}\text{Fe}/^{54}\text{Fe}_{\text{w-r}}$ of -4.0). Furthermore, a dunite from the same section gives extremely light Fe isotope compositions: $\epsilon^{57}\text{Fe}/^{54}\text{Fe}$ values are -5.0, -5.2 and -5.4 for chrome-spinel, olivine and the whole-rock, respectively, making this sample anomalous given the range of magmatic rocks analysed so far. Such light compositions may reflect the influence of hydrous metasomatic agents the mantle wedge. Further work is required to confirm this hypothesis.

Natural attenuation of chiral mecoprop in a fractured limestone aquifer

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Disposal of up to 40 tonnes of a racemic mixture of the herbicide mecoprop into landfills in the UK Lincolnshire Limestone, has polluted a public supply borehole 2.5 km away. Differences in the biological behaviour of the mecoprop enantiomers in different redox zones have been used to evaluate in situ biodegradation. Changes in enantiomeric ratio along a flow path from the landfill show that in the methanogenic/sulphate reducing zone, mecoprop is still racemic, (i.e. it contains equal concentrations of the two enantiomers) suggesting that mecoprop does not degrade in these conditions. Further from the landfill, but still within the landfill plume, (*S*)-mecoprop dominates and could be explained by inversion of (*R*)- to (*S*)-mecoprop or faster degradation of (*R*)-mecoprop. With a change to aerobic conditions, an increase in the proportion (*R*)-mecoprop is explained by the faster degradation of the (*S*)-mecoprop in accordance with the literature. Associated changes in $\delta^{13}\text{C}$ were slight and inconclusive.

Laboratory microcosms using groundwater and crushed limestone left to acclimatise in the aquifer, showed that under aerobic conditions both enantiomers degraded with zero order kinetics with (*S*)-mecoprop degrading faster than (*R*)-mecoprop. Under anaerobic conditions in an identical microcosm (*S*)-mecoprop failed to degrade but (*R*)-mecoprop was transformed to 4-chloro-2-methyl phenol with Monod kinetics. The latter compound only degraded once the (*S*)-mecoprop has disappeared. Addition of nitrate stimulated degradation in dormant sulphate reducing microcosms. In none of the microcosms was there any evidence of enantiomeric inversion.

This study provides new evidence for mecoprop degradation under nitrate reducing conditions, and demonstrates that changes in enantiomeric ratios can provide subtle evidence for natural attenuation.