

Iron isotope fingerprinting of mantle mineralogy

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Mineralogical and lithological variations in the Earth's mantle have important implications for mantle dynamics, magma generation, and the fate of recycled surface material. Directly tracing such variations is challenging. While the elemental and radiogenic isotope compositions of mid oceanic ridge and ocean island basalts (MORB and OIB respectively) are thought to reflect variable amounts of enriched mineralogies within the mantle, in the form of pyroxenite or eclogite derived from oceanic crust or metasomatised lithosphere, directly linking geochemical and mineralogical variation is difficult. Iron (Fe) stable isotopes potentially offer a solution to this problem, as the Fe isotope compositions ($\delta^{57}\text{Fe}$) of mafic rocks primarily reflect mineral-specific partitioning [1, 2]. Here we present Fe isotope data for sub-oceanic lithosphere peridotite and pyroxenite xenoliths from Oahu, Hawaii and demonstrate that Fe isotopes can be used as a new tracer of mantle mineralogical heterogeneity. Pyroxenite $\delta^{57}\text{Fe}$ values are heavy (0.10 to 0.27‰) relative to MORB and OIB ($\delta^{57}\text{Fe} \sim 0.15‰$) [3-6] and reflect isotopic fractionation during magmatic differentiation and pyroxene cumulate formation at the lithosphere-asthenosphere boundary. In contrast, peridotites have light $\delta^{57}\text{Fe}$ values (-0.34 to 0.14‰) that correlate with elemental and radiogenic isotope tracers of melt extraction, providing evidence for Fe isotope fractionation during partial melt extraction and the generation of depleted, low- $\delta^{57}\text{Fe}$ peridotitic residues. The heavy $\delta^{57}\text{Fe}$ values of MORB and OIB relative to mantle peridotites can therefore be explained by partial melting, where isotopically heavy Fe is preferentially concentrated in the melt phase. However, the considerable range in MORB and OIB $\delta^{57}\text{Fe}$ requires a $\delta^{57}\text{Fe}$ -heterogeneous mantle, containing enriched (pyroxenite, heavy $\delta^{57}\text{Fe}$) and depleted peridotite (light $\delta^{57}\text{Fe}$) domains. Iron stable isotopes thus provide a powerful new means of fingerprinting mineralogical variations within the Earth's mantle and identifying depleted and enriched components within the source regions of volcanic rocks.

[1] Weyer & Ionov *EPSL* (2007); [2] Williams *et al.* *EPSL* (2005); [3] Dauphas *et al.* *EPSL* (2009); [4] Teng, *et al.* *Science* (2008) [5] Weyer *et al.* *EPSL* (2005); [6] Teng *et al.* *GCA* (2013).

Analysing conodont $\delta^{18}\text{O}$ by SIMS

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Oxygen isotope compositions of phosphatic conodont microfossils are a more robust indicator of early Paleozoic sea surface temperatures than the O compositions of calcitic brachiopods. SIMS microanalysis allows conodont O compositions to be determined on an $\sim 30 \mu\text{m}$ scale, so the isotopic homogeneity of individual conodont elements and of multiple elements from a single rock sample can be assessed. Analyses can be obtained on very small and/or rare specimens, and targeted on those parts of conodonts that are best preserved. Differences in composition between co-existing species from different biofacies can be measured. SIMS analyses, however, are less precise and more sensitive to differences in the chemical composition of the sample than conventional IRMS analyses. The latter is important because the conodont crown can consist of two tissue types: albid—large ($>100 \mu\text{m}$) crystals containing mostly PO_4 , and hyaline—microcrystals with PO_4 and some CO_3 , and a higher trace element content. Some conodonts also contain poorly mineralised basal tissue that can be isotopically contaminated. In addition, conodont crystal structure can be modified at temperatures above $\sim 100^\circ\text{C}$. No conodont sample is available that is both isotopically uniform and abundant enough to be distributed between SIMS and IRMS labs as an O isotope standard. SIMS measurements are currently referenced to a mineral apatite standard (Durango 3 at ANU), and potential systematic bias is assessed by comparing SIMS and IRMS analyses of large bioapatite samples (e.g. shark enameloid), and of conodonts from the same or closely equivalent rock samples. As part of our study of sea surface temperatures at critical periods of biotic crisis and environmental change in the Paleozoic and Early Mesozoic using conodont O isotopes, we have addressed issues of bias, inter- and intra-conodont heterogeneity, and thermal alteration (as indicated by Colour Alteration Index). In some samples we find O variation within and between elements, but more commonly there is inter- and intra conodont uniformity between genera and species in a single rock sample within the sub-permil precision of the measurements. The rare exceptions have both biological and geological explanations.