Mass-dependent molybdenum isotope variations in ocean island basalts

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Systematic differences in the mass-dependent molybdenum (Mo) isotopic composition of chemical sediments have recently been used to infer the oxygenation state of past and present oceans [1-4]. Sediments deposited under oxic conditions (i.e. Fe-Mn-oxides) are marked by overall light isotopic compositions (δ^{98}Mo<0.5‰ [1,3]), whereas sediments deposited in euxinic environments (i.e. black shales) have heavier isotopic compositions (δ^{98}Mo >0.5‰ [1,5]) relative to the convecting mantle value (δ^{98}Mo ~ 0; [1-3]). In contrast, it is generally accepted that magmatic processes do not induce any mass-dependent Mo isotope fractionation [6].

Here we investigate the use of mass-dependent Mo isotope data as a tracer for recycled crustal components in the source of ocean island basalts. The Mo isotopic compositions of samples from the ocean islands of La Palma, Hawaii, Iceland, Tubuaii, and Mangaia were determined by MC-ICPMS using a double spike (^{97}Mo-^{100}Mo) approach. Repeated measurements of the USGS basaltic reference material BHVO-2 over a period of two years yielded a δ^{98}Mo reproducibility of ca. 0.06‰ (2σ; N=62).

Samples from Iceland, Tubuaii, and Mangaia have similar values with δ^{98}Mo = -0.02 to +0.07‰. In contrast, samples from La Palma show an offset to more negative values in δ^{98}Mo (0.00 to -0.25‰), whereas samples from Hawaii display a much larger spread in δ^{98}Mo extending from -0.25 to +0.18‰ with the majority of data ranging between δ^{98}Mo -0.04 to +0.18‰.

Thus ocean island basalts record significant mass-dependent Mo isotopic heterogeneity in the Earth's mantle. We interpret the Mo isotopic variability as reflecting different contributions of crustal-derived components that have recycled into the mantle, although further work is required in more precisely constraining the Mo isotope composition of different deep subducted protoliths. However, it appears that mass-dependent Mo isotopic compositions of oceanic basalts can be used as a sensitive tracer of recycled component in the convecting mantle.

References

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Fractionation of iron stable isotopes by magmatic processes: progress and potential

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The last five years have seen unprecedented advances in the measurement and application of non-traditional stable isotope systems, including the transition metals and elements such as Li, Mg, Si, Tl and U. Improvements in analytical precision have facilitated the application of these isotope systems to magmatic processes, where the magnitudes of stable isotope fractionation ($\propto 1/T^2$) are expected to be small. Previous studies have shown that Fe stable isotopes in igneous rocks are a potential tracer of changes in mantle oxidation state [1, 2]. Variations in the Fe isotope composition of the mantle may, therefore, provide an independent means of monitoring secular variations in mantle oxygen fugacity (fO_2) complimenting information from other tracers, such as V/Sc ratios [3], V partitioning data [4], and Fe^{3+}-bearing mineral equilibria. However, it has also been shown that Fe isotopes are fractionated by processes such as metasomatism [5] and magma differentiation [6, 7] and it is important to be able to distinguish these effects from fractionation induced by melting and variations in fO_2. In order to investigate this further, a series of highly characterised peridotite xenoliths from Salt Lake Crater, Oahu, Hawai'i [8], which display extreme variations in fO_2 [9], were analysed for their Fe isotope compositions. The Fe isotope compositions of both separated minerals and bulk samples display striking negative correlations with indicators of melt extraction such as Mg/Mg+Fe as well as Hf isotope compositions. No correlation exists between Fe isotopes and fO_2, Sr or Nd isotopes or highly incompatible elements such as the LREE, which are all considered to have been reset by metasomatic processes. Iron stable isotopes therefore have the potential to "see through" metasomatic events and record primary melt extraction processes.

The Fe isotope compositions of metabasalts and ultramafic rocks from Isua (3.6 Ga) and komatiites from Belingwe (2.7 Ga), Vetreny (2.4 Ga) and Gorgona (0.089 Ga) define clear arrays with Mg/Mg+Fe and redox-sensitive trace element ratios such as V/Sc [10, 11]. These data provide evidence for the fractionation of Fe isotopes during melting, with the partitioning of Fe^{3+} and isotopically heavy Fe into the melt phase and, critically, demonstrate that the nature of this fractionation appears has remained more or less constant over the last 3.6 Ga. This observation implies that the Earth's mantle has been oxidised since the Archean, in agreement with other studies.

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