Stable Zr isotope fractionation during magmatic differentiation: insights into the evolution of Earth's crust

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The high-field strength elements (HFSEs) serve as excellent tracers of historic mantle depletion events and the petrogenesis of Earth's crust through time. This is largely as a result of their incompatible behaviour during partial melting of the mantle and a resistance to late metamorphism and alteration. Traditionally, HFSE geochemists have relied upon elemental concentrations to trace HFSE systematics but more recently mass dependant variations of the HFSE stable isotopes have been drawn upon.

A new method for the determination of Zr stable isotopes by double-spike MC-ICPMS is presented. By this protocol the natural variation of Zr stable isotopes, expressed as $\delta^{94/90}Zr_{IPGP\text{-}Zr}$, have been measured for the first time in geological samples with a routine precision <50 ppm (2*sd*). Using this method a suite of MORB, OIB and komatiites have been analysed to constrain the Zr stable isotope composition of BSE and primitive mantle melts. In addition a magmatic differentiation suite from Hekla (Iceland) has been measured to examine the behaviour of Zr stable isotopes during the differentiation and evolution of silicate melts. Data for basalts falls within a tightly clustered array of $\delta^{94/90}Zr$ = 0.047 +/- 0.037 and show no systematic variation between MORB and OIB source regions, suggesting that there is no dominant source control for Zr isotopes within the mantle. The Hekla samples show a range of $\delta^{94/90}Zr$ values which are positively correlated with SiO_2, suggesting isotopic fractionation of Zr during igneous differentiation. As Zr is similar in its geochemical behaviour to Ti it is likely that this isotopic variation results from the accumulation of Fe-Ti oxides, and the preferential sequestration of light isotopes within such oxide phases. Because of this, Zr stable isotopes can be used as a sensitive tracer of SiO_2 during the formation of igneous rocks and minerals. Furthermore, owing to its highly refractory nature its is unlikely that this signature will be reset by later-stage modifications. We suggest that Zr stable isotopes can serve as a powerful tool to comment upon the evolution of crustal rocks over Earth's history.