

Cerium and europium isotope signatures of igneous differentiation

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Rare-earth element analyses have long been used to gain key insights into the origin and evolution of silicate melts on the Earth and other planetary bodies. It is now possible to measure natural, non-radiogenic variations in the isotopic compositions of many of these elements. This development suggests new possibilities for studying partitioning and differentiation, if we can figure out what controls rare-earth element isotopic fractionation in igneous settings. Predicting equilibrium isotope fractionation in rare earth elements is a challenging problem because both mass dependent effects and field shift effects appear to be important. The field shift effect, caused by differences in nuclear sizes and shapes, has previously been observed in nature mainly in elements with higher atomic numbers such as uranium and thallium. Theoretical estimates of equilibrium cerium and europium isotope fractionations are the focus of this presentation. For both elements, oxidation state is a dominant control on fractionation, with mass-dependent and field shift components typically opposing each other. In the case of $^{153}\text{Eu}/^{151}\text{Eu}$, field shift effects dominate fractionation, so that Eu(II)-bearing species such as plagioclase will have higher $^{153}\text{Eu}/^{151}\text{Eu}$ than Eu(III)-bearing species, by $\sim 0.2\text{--}0.3\%$ at magmatic temperatures. For Ce(IV) vs. Ce(III), the relative importance of mass-dependent vs. field shift fractionation is expected to be strongly dependent on the isotope pair measured. For $^{142}\text{Ce}/^{140}\text{Ce}$ at typical Earth surface temperatures, the two components roughly cancel each other out. At higher temperatures field shift fractionation wins out, driving slightly lower $^{142}\text{Ce}/^{140}\text{Ce}$ in Ce(IV)-bearing phases, such as zircon, relative to Ce(III). In contrast, mass-dependent effects are expected to dominate $^{138}\text{Ce}/^{140}\text{Ce}$ and $^{136}\text{Ce}/^{140}\text{Ce}$ fractionation across a range of temperatures and materials. The importance on mass-independent equilibrium fractionation in lanthanides suggests that a closer look at field shift effects in period 6 transition elements (particularly Ta through Pt) may find other potentially useful signatures of high-temperature processes.