

Three Types of Fractionation of REY: Applications in Geology, Astrobiology, and Oceanography

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The vast majority of igneous and clastic sedimentary rocks are characterized by smooth REE and Y (REY) patterns which show chondritic Y/Ho ratios. They may show Ce or Eu anomalies, but do not display any La and Gd anomalies or tetrad effects. In aqueous systems, however, decoupling of the geochemical twins Y and Ho is common, and not only are Ce and Eu anomalies observed, but also La and Gd anomalies and even tetrad effects.

Three types of REY fractionation can be distinguished: (i) smooth fractionation along the REY series, that results from ionic radii of the REY(III), which decrease smoothly with increasing atomic number; (ii) redox-induced fractionation of Ce and Eu from their REE neighbours under physico-chemical conditions that allow for the stabilization of significant amounts of Ce(IV) and Eu(II); (iii) radius-independent fractionation of Y from Ho, of La and Gd from their REE neighbours, and the generation of tetrad effects, that all result from subtle differences between the electron structures of the individual REY. It is these different types of fractionation that make the REY a valuable geochemical tool that can be applied to a vast range of different geochemical problems.

The REY distribution in marine chemical precipitates, for example, allows us to distinguish between two modes of REY removal from solutions, such as seawater. Incorporation of REY into limestones, dolomites and phosphorites occurs via substitution of REY³⁺ for Ca²⁺ and is strongly controlled by the ionic radii of the REY³⁺. Thus, fractionation during this process is minor and the REY patterns of these chemical sediments are similar to that of the ambient solution. REY scavenging by (oxyhydr)oxides, however, occurs via surface-complexation (and in case of Ce(IV) surface-precipitation) and is accompanied by strong fractionation. Hence, the REY patterns of Fe-Mn oxides differ significantly from that of the ambient solution. Since seawater is characterized by super-chondritic Y/Ho ratios whereas river and lake waters are close to the chondritic ratio, the REY distribution is a simple but effective way to distinguish between a freshwater and a marine-sedimentary carbonate or phosphorite. It also allows us to tell whether or not the REY in such a sample have been affected by secondary overprint, which is a screen to pick samples suitable of Nd isotope studies. Because radius-independent REY fractionation only occurs in aqueous systems, non-chondritic Y/Ho ratios, La and Gd anomalies, and tetrad effects in samples from Mars, other planets or moons are indicative of the presence of water.

High Temperature inter mineral Fe isotope fractionation

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High precision Fe isotope analyses of coexisting minerals from ultramafic, mafic and intermediate composition igneous and metamorphic rocks have been conducted to evaluate the degree of inter-mineral Fe isotope fractionation between ol-opx-cpx, gt-cpx, and magnetite and silicate phases. Mineral compositions, determined by electron microprobe analysis, have also been measured to evaluate if Fe isotope variations are associated with open or closed system behavior and the equilibration temperatures of these rocks.

There is no detectable inter-mineral fractionation between magnetite and silicate minerals as determined by analysis of coexisting minerals from 4 andesitic volcanic rocks from the Chaos Crags of Mt Lassen, CA. The average $\delta^{56}\text{Fe}$ values of these minerals is 0.00 ± 0.05 ‰ (1-SD; n = 12) which is identical to the Fe isotope composition measured in 46 igneous rocks. In contrast, the calculated $\Delta^{56}\text{Fe}_{\text{olivine-magnetite}}$ is -0.51 at 800 °C (Polyakov and Mineev, 2000).

There is a small but significant inter-mineral fractionation between garnet and cpx as determined by Fe isotope analysis of 7 eclogites and garnet peridotites. The average $\Delta^{56}\text{Fe}_{\text{cpx-gt}} = +0.32 \pm 0.07$ ‰ for six of the seven samples. One sample, that has low grossular content, has $\Delta^{56}\text{Fe}_{\text{cpx-gt}} = +0.08$ ‰. It is uncertain if this low $\Delta^{56}\text{Fe}_{\text{cpx-gt}}$ fractionation reflects a crystal chemical control on isotopic fractionation or some other process. Trends in $\delta^{56}\text{Fe}$ value of gt (+0.01 to -0.39 ‰) versus cpx (+0.30 to 0.00 ‰), a slight inverse correlation between $\Delta^{56}\text{Fe}_{\text{cpx-gt}}$ and Fe-Mg cpx-gt equilibration temperature, and consideration of the overall Fe isotope mass balance with bulk rock $\delta^{56}\text{Fe}$ values equal to 0 ‰, suggest that the inter-mineral isotopic fractionation between gt and cpx is a result of equilibrium Fe isotope exchange.

Fe isotope analysis of coexisting ol-opx-cpx from 8 spinel peridotite defines a large range in $\delta^{56}\text{Fe}$ values, where for example olivine $\delta^{56}\text{Fe}$ values range from -0.01 to -0.52 ‰. There is no discernable Fe isotope fractionation between ol and opx; the average $\Delta^{56}\text{Fe}_{\text{opx-ol}}$ is $+0.02 \pm 0.09$ ‰, which agrees well with the calculated $\Delta^{56}\text{Fe}_{\text{opx-ol}} = -0.03$ ‰ of Polyakov and Mineev (2002) at 1000°C. $\Delta^{56}\text{Fe}_{\text{cpx-ol}}$ fractionation varies from -0.01 to +0.21 ‰. $\Delta^{56}\text{Fe}_{\text{cpx-ol}}$ is negatively correlated with $\delta^{56}\text{Fe}$ value and forsterite content of olivine. The correlations of $\Delta^{56}\text{Fe}_{\text{cpx-ol}}$ with isotope composition and mineral chemistry indicate the isotopic fractionations in these spinel peridotite xenoliths are associated with open system behavior, perhaps caused by mantle metasomatic processes.