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Equilibrium europium isotope fractionation in igneous and metamorphic systems

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Nuclear volume and mass-dependent isotope fractionations of europium isotopes are estimated using data from Mössbauer spectroscopy, NRIXS spectroscopy, and electronic structure calculations. The results indicate that Eu^{2+}-bearing species will have approximately 1‰ higher $^{153}Eu/^{151}Eu$ than Eu^{3+}-bearing species in equilibrium at 25ºC (298 K), and about 0.3‰ higher $^{153}Eu/^{151}Eu$ at 700ºC (973 K). The nuclear volume effect goes in the opposite direction from mass-dependent fractionation, and is predicted to dominate over mass dependent fractionation for most materials, especially at metamorphic and igneous temperatures. $^{153}Eu/^{151}Eu$ fractionation appears to be primarily dependent on the oxidation state of europium. Estimated nuclear-volume dominated fractionations favoring high $^{153}Eu/^{151}Eu$ in minerals that preferentially incorporate Eu^{2+}, such as plagioclase, are broadly consistent with recent measurements on igneous rocks showing low $^{153}Eu/^{151}Eu$ in samples with strongly negative europium anomalies [1]. Plagioclase-melt fractionation is predicted to be most pronounced at intermediate oxygen fugacities, where Eu^{3+} is the main oxidation state in the melt or bulk rock but plagioclase mostly incorporates Eu^{2+}. The results are also consistent with the recent finding that equilibrium fractionation cannot explain cosmochemical REE fractionations observed in primitive meteoritical materials [2], because inclusion of the nuclear volume effect still yields net fractionations that are too small (~0.2‰ or less) at temperatures >1200 K where vapor-phase REE species are relevant. Similar techniques applied to estimate nuclear volume fractionation for $^{142}Ce/^{140}Ce$ in Ce^{4+} vs. Ce^{3+} equilibria indicate that this effect nearly cancels the mass-dependent fractionation, leading to a muted overall fractionation. However, the isotope pairs $^{140}Ce/^{138}Ce$ and $^{140}Ce/^{136}Ce$ are expected to show dominantly mass-dependent fractionation, favoring more massive isotopes in Ce^{4+}-bearing species.

[1] Lee S-G and Tanaka T (2021) Geochemical Journal 55:e9-e17.

[2] Hu JY, et al. (2021) Science Advances 7:eabc2962.