High-Temperature Calcium isotope Fractionation: Theory vs. Nature

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Reports of δ^{44}Ca in igneous and metamorphic mineral assemblages indicate that Ca isotope fractionation can be large, even at high temperatures [1-3]. However, the use of Ca isotopes for thermometry or as a crystal growth rate proxy [4] requires understanding of kinetic and equilibrium factors that control fractionation behaviour.

We present density-functional theory (DFT) calculations, ε^{40}Ca, and δ^{44}Ca measurements for high-temperature minerals in granulite facies metamorphic rocks including: garnet (alm, pyr, grs, sps), diopside, enstatite (with variable Ca/Mg), anorthite, labradorite, and forsterite. DFT calculations indicate that δ^{44}Ca should increase in the approx. order: plagioclase < clinopyroxene < garnet ≤ orthopyroxene < olivine. δ^{44}Ca is inversely proportional to Ca in most solid-solution minerals, with the exception being plagioclase (anorthite > labradorite).

Plagioclase-clinopyroxene pairs in granulites generally corroborate the DFT calculations, while orthopyroxene enrichments are generally higher than predicted, showing opx-plag Δ^{44}Ca up to 3.5‰. Six out of eight orthopyroxene samples follow a rough inverse correlation between Ca/Mg and $\Delta^{44}Ca_{opx\text{-}wr}$, consistent with our DFT simulations and previous work [1-3, 5]. However, garnet-plagioclase and garnet-clinopyroxene fractionations are highly variable (Δ^{44}Ca -1.5 to +1.0‰), as are garnet δ^{44}Ca values (-2.1 to +0.7‰, rel. BSE). Although garnet excludes K, some late Archean samples have large ε^{40}Ca enrichments up to +41. Variability between minerals can provide information on growth sequence and transport effects. Garnet ε^{40}Ca may provide novel constraints on large scale K depletion during granulite metamorphism.

[1] Kang et al. (2016) GCA 174, 335-344 [2] Antonelli et al. (2016) Goldschmidt Abstracts, 83 [3] Huang et al. (2010) EPSL 292, 337-344. [4] Watson & Muller (2009) Chem Geo 267, 111-124. [5] Feng et al. (2014) GCA 143, 132-142.