

Large Ca Isotope Fractionation in Granulite Facies Minerals

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Measurements of Ca isotope fractionation in volcanic phenocrysts have demonstrated that reasonable mineral-specific crystal growth rate estimates may be obtained through kinetically-driven (diffusive) deviations from isotopic equilibrium [1], which can occur if the crystal growth rates (R) are large relative to the diffusion rates (D) for Ca in the magma [2, 3]. However, variables affecting the requisite equilibrium fractionation factors are complex, and still require further exploration to properly represent the large range of possible temperatures, pressures, and mineral compositions.

Equilibrium Ca isotope fractionation depends on temperature, the number of oxygens coordinating Ca, and on the length of these Ca-O bonds [4]. However, compositionally-driven changes in the mineral structures (such as Ca content of opx, which is inversely proportional to $\Delta^{44}\text{Ca}_{\text{opx-cpx}}$) also have large effects on the bonding environment for Ca and on equilibrium $\Delta^{44}\text{Ca}$ [5,6]. Several groups have reported significant ($\sim 1\%$) $\delta^{44}\text{Ca}$ differences between clinopyroxene, orthopyroxene, and olivine from mantle xenoliths [5,6] and from slow-cooling layered mafic intrusions [1], which are inferred to represent equilibrium conditions. However, the individual histories for such xenolithic and plutonic samples are complex and their compositional and thermobarometric ranges are limited.

We report $\delta^{44}\text{Ca}$ values for mineral separates (plagioclase, clinopyroxene, orthopyroxene, & garnet) from six texturally-equilibrated granulite rocks, and estimates of their thermobarometric equilibration conditions based on Fe-Mg exchange techniques. Preliminary analyses indicate that there are large $\Delta^{44}\text{Ca}$ differences, with $\delta^{44}\text{Ca}$ for garnet, opx, cpx, and plagioclase ranging from -3.23 to +0.9‰. Equilibrium $\delta^{44}\text{Ca}$ is likely garnet \leq plag $<$ cpx $<$ opx (based on rough bond length estimates), which agrees with our preliminary analyses and will serve to further constrain the equilibrium values needed for calculating crystal growth rates in other settings.

[1] Antonelli & DePaolo (2015) Goldschmidt Abstracts, **93**. [2] Watson & Muller (2009) Chem. Geo. **267**, 111-124. [3] Watkins *et al.*, **GCA** 75, 3103-3118. (2011). [4] Feng *et al.* (2014) **GCA** 143, 132-142. [5] Huang *et al.* (2010) **EPSL** 292, 337-344. [6] Kang *et al.* (2015) **GCA** 174, 335-344.