Ca isotope fractionation and crystal growth rates of volcanic phenocrysts

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Recent studies have demonstrated that measurable equilibrium and non-equilibrium (kinetic) Ca isotope fractionation can occur at high temperatures in magmatic systems. Ca isotope differences between orthopyroxene and clinopyroxene in mantle xenoliths (Δ^{44}Ca of +0.3 to +0.7‰) [1] are attributed to equilibrium fractionation and modeled with DFT [2]. Higher δ^{44}Ca is predicted for mineral sites with lower coordination and shorter Ca-O bond lengths.

Kinetic isotope effects may also occur at the mineral surface or during diffusion in magma [3, 4, 5]. As up to 2% diffusive fractionation of ^{44}Ca/^{40}Ca can occur in silicate liquids [3], substantial Ca isotope effects are possible for high-Ca minerals if crystal growth rate (R) is fast relative to diffusion (R/D > 1 cm^{-1}) [5].

We report δ^{44}Ca for phenocrysts with variable Ca partition coefficients (K) (plagioclase, clinopyroxene, hornblende and olivine), and groundmass in six basaltic to rhyodacitic samples. Minerals with K >> 1 are expected to have negative kinetic isotope effects due to diffusion; those with K << 1 could show small positive effects. All phenocrysts measured thus far have δ^{44}Ca within +0.3 and -0.1‰ of groundmass. Plagioclase (K = 2 to 5) has Δ^{44}Ca ≈ 0 to -0.1‰ relative to groundmass in both basalt and rhyodacite, suggesting growth rates of about 0.05 - 0.5 cm/yr. Cpx phenocrysts (K ≈ 2 to 4) are isotopically heavy (Δ^{44}Ca = +0.3‰) which indicates equilibrium Δ^{44}Ca probably ≥ +0.4‰. Olivine (K ≈ 0.03) shows small positive Δ^{44}Ca values of ~0.1‰, consistent with near-zero equilibrum Δ^{44}Ca. Hornblende in rhyodacite (K ≈ 3) has Δ^{44}Ca of +0.2‰, also suggesting positive equilibrium Δ^{44}Ca. Our results suggest that Ca isotopes, especially if combined with trace element analyses, will allow for delineation of equilibrium and kinetic effects and the estimation of crystal growth rates in a variety of settings.

[1] Huang *et al*. (2010) *EPSL* **292**, 337-344. [2] Feng *et al*. (2014) *GCA* **143**, 132-142. [3] Watkins *et al*., *GCA* **75**, *3103-3118*. (2011) [4] Richter *et al*. (2009) *GCA* **73**, 4250-4263. [5] Watson & Muller (2009) *Chem.Geo*. **267**, 111-124.