

# Testing *ab initio* calculations of garnet-clinopyroxene Ca-isotope fractionation using natural samples

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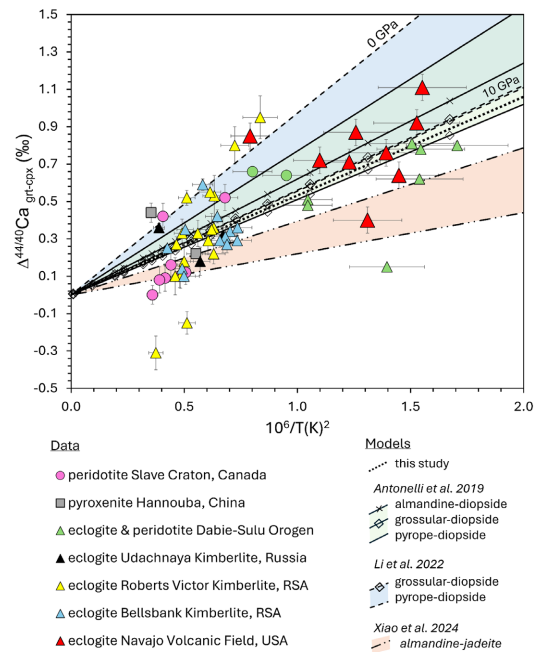
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Calcium stable isotope variations are used to examine numerous processes, from melt generation to recycling of crustal material in the mantle. However, full application of this system requires an understanding of the variables that affect inter-mineral and mineral-melt isotopic fractionation. Previous studies have shown that garnet preferentially incorporates  $^{44}\text{Ca}$  compared to silicate melts or other Ca-bearing silicate phases. Several studies<sup>1-3</sup> have used density-functional theory (DFT) models to constrain inter-mineral Ca-isotope fractionation between garnet and clinopyroxene as a function of temperature, pressure, and mineral composition. However, DFT models have limitations in systems with complex solid solutions. To date, little experimental data exist to test DFT model predictions for equilibrium  $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$ .

We measured  $\delta^{644/40}\text{Ca}$  values in coexisting clinopyroxene and garnet in a suite of eclogite xenoliths from the Navajo Volcanic Field (NVF), Colorado Plateau, USA. These eclogites have lower equilibration temperatures (530 to 995°C, average 655±133°C, n=16) than most other eclogite or peridotite suites for which garnet and clinopyroxene  $\delta^{44/40}\text{Ca}$  measurements are reported. We then examined correlations between measured  $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$  in natural samples with estimated temperature, pressure, and mineral composition, to test the predictions of previously published DFT models. Pressure and temperature were estimated from mineral compositions using clinopyroxene-garnet thermobarometers<sup>4</sup>.

Consistent with DFT predictions,  $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$  is most strongly correlated with  $1/T^2$  (Figure 1) in the compiled suite of natural samples ( $R^2 = 0.55$ ;  $p < 0.001$ ; MSWD = 6.8), although scatter exceeds that predicted from uncertainties in  $\delta^{644/40}\text{Ca}$  measurements and temperature estimates. However, whereas DFT models predict that  $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$  should decrease with increasing pressure, we observe no correlation between  $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$  and pressure once temperature is accounted for. Similarly, no correlation is observed between temperature-corrected  $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$  and garnet composition. The source of scatter in the  $1/T^2$ - $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$  correlation remains unclear. Major or trace element indications of clinopyroxene-garnet disequilibrium (e.g., from REE Kd trends) are lacking in most samples. Whether this scatter reflects limitations of current DFT models or non-equilibrium (e.g., diffusion) processes requires further investigation.

[1] Antonelli et al., EPSL (2019). [2] Xiao et al., GCA (2022). [3] Li et al., Chem. Geol. (2022). [4] Ravna & Paquin, EMU Notes in Mineral. (2003).



**Figure 1:** Garnet-clinopyroxene calcium isotope fractionation ( $\Delta^{44/40}\text{Ca}_{\text{grt-cpx}}$ ) plotted against  $1/T^2$  for the samples in this study and previous work. Natural data for eclogites (triangles), peridotites (circles) and pyroxenites (squares) are compared to DFT models by Antonelli et al., (2019) (green highlight, solid lines), Li et al., (2022) (blue highlight, dashed line) and Xiao et al., (2022) (tan highlight, alternating line). Finely dotted line is linear regression through sample data. Error bars represent 1 standard error, some are smaller than symbols