Reconciling theoretical and experimental estimates of Ca isotopes fractionation between mineral and solution

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So far, the comparison of theoretically predicted and measured Ca isotopes fractionation in Nature show disappointing, without clues whether it originates from the limits of theoretical methods, or whether Ca isotopes do not fractionate at equilibrium in nature.

To assess mineral-water fractionation with electronic structure methods, the choice of the theoretical scheme (TS) is determining. Mineral and solution should be computed consistently, but some TS are better suited for solids, such as PZ, PBE, PBEsol, whereas others are recommended for solutions, such as BLYP, BLYP with Grimme-D2 correction for dispersion (BLYP+D2), or vdW-DF2. In this work, we realized a comprehensive study on 7 well-characterized materials (aragonite, calcite, dolomite, CaO lime, diopside, aragonite, anhydrite) modeled within 7 TS (PZ, PZ+QHA, PBE, PBEsol, BLYP, BLYP+D2, vdW-DF2). We show that TS has a significant effect, with a 2‰ variation for an overall 7‰ fractionation amplitude at 25°C. This seems due to large theoretical errors on vibrational frequencies for the modes contributing to Ca isotopic fractionation. After careful and exhaustive analysis, PBEsol appears the most reliable TS. At 25°C, the predicted fractionations w/r to calcite are grossular (+4‰) > CaO (+2‰) > diopside (0‰) > anhydrite (-1.8‰) > aragonite (-3‰).

On another hand, BLYP+GD2, although poor for many materials, seems to account correctly for calcite properties. This is further confirmed by calculations on dissolved Ca^{2+}, giving good agreement with experiment[1] for the calcite-Ca^{2+} fractionation (+0.2‰).

Comparison with existing experimental and natural estimates of mineral-Ca^{2+} fractionation leads to conclude that, apart from the calcite-Ca^{2+} fractionation, theoretical estimates for aragonite-Ca^{2+} (-2.8‰) and anhydrite-Ca^{2+} equilibria are significantly larger (around twice as large) than observations[1,2]. We interpret this disagreement as arising from speciation effects. Within uncertainties, an additional calculation of gypsum-Ca^{2+} fractionation agrees with experimental estimates[3]. The dolomite-Ca^{2+} fractionation accompanying biochemical precipitation[4] might follow equilibrium, whereas the one observed during dolomitization (0‰)[5] should not.

References:

[1] Harrison et al 2023 EPSL 603 117985
[2] Syverson et al 2018 GCA V236 pp160-178
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