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Towards accurate Ca isotope fractionation at equilibrium between minerals and solutions with electronic structure calculations: multi-framework comparison for validation and correction, and the control of structural cations.

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Theoretical calculation of equilibrium fractionation of Ca isotopes shows particularly challenging due to the limitations of DFT frameworks to properly reproduce the important vibrational properties. This is even more challenging for mineral-solution equilibria, as frameworks adapted to minerals do not properly reproduce solution structures. Based on carefull correction of calculated frequencies by experimental ones, a rescaling parameter can be proposed to obtain reference lnβ values from eight different theoretical frameworks, within an uncertainty (σ) ranging between 0.25‰ (PBEsol and PBE functionals) and 0.75‰ (LDA functional, PBE or BLYP functionals with Grimme-D2 correction) at 300K. Frameworks showing more consistent structural prediction (with consistent offsets on Ca-O distances) also show more consistent predicted fractionation properties. Eight well characterized minerals (anhydrite, fluorite, diopside, grossular, calcite, dolomite, aragonite, CaO lime) were used for the validation and correction procedure, and six more (wollastonite, anorthite, huntite, monticellite, akermanite, gypsum) were calculated to infer the controls of Ca isotope fractionation and compare to experimental or natural estimates. Taking CaO lime as reference, Ca isotopes fractionation shows connected to Ca-O distance, coordination and the type of structural cation:

$\ln\beta = \ln\beta(CaO) \times (1 + b \times \Delta d + c(coord) + d(cation))$,

where Δd is the relative Ca-O distance variation with respect to CaO lime; b=-7.499; c is the coordination effect, varying monotonically from 0 for c(6) to +0.311 for c(8)=c(9), d is the effect of the cations present in the structure (in addition to Ca^{2+}), determined for P^{5+} (based on calculations by[1]), Si^{4+}, S^{5+}, C^{4+}, and H^{+}. The obtained cation effects appear connected to electronegativities.

Assuming calcite-$Ca^{2+}_{(aq.)}$ fractionation as null, predicted aragonite-$Ca^{2+}_{(aq.)}$ and anhydrite-$Ca^{2+}_{(aq.)}$ fractionations are found twice larger as experimental mineral-solution fractionations, suggesting perturbing effects in solution (speciation, kinetic effects). On the contrary, predicted gypsum-$Ca^{2+}_{(aq.)}$ fractionations are in agreement with gypsum-solution fractionation. Predicted dolomite-$Ca^{2+}_{(aq.)}$ fractionation agrees with fractionation during biogenic dolomite precipitation, but dolomitization does not seem to follow equilibrium.

[1] Antonelli et al (2019), EPSL 517, 71-82