

# The challenges of the theoretical evaluation of equilibrium Ca isotope fractionation between solid and solution.

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Equilibrium fractionation properties can be obtained from atomistic modeling, generally based on electronic structure calculations, both for solids and liquids.

In the common approach, standard for solid systems, isotopic fractionation is derived from the vibrational properties calculated in the harmonic approximation. This approach has been adapted for liquids [1-3]. For solids, the structure is known from X-ray diffraction. For liquids, it necessitates a proper description of the structure, which can be obtained by molecular dynamics trajectories. In the case of calcium, this faces two challenges:

1/ the precise structure of Ca in solution is not known, in particular its coordination number. This is critical for fractionation properties. We have evaluated this quantity by molecular dynamics [4]. Applying Markov chain analysis, we could constrain the accuracy of our estimates. Our study suggests that Ca coordination is around 6.2 at 300K and a density of 1g/mL, but increases with temperature at fixed density, reaching 6.8 at 600K. <sup>VI</sup>Ca<sup>2+</sup>, <sup>VII</sup>Ca<sup>2+</sup> and <sup>VIII</sup>Ca<sup>2+</sup> aqua complexes coexist in various proportions depending on temperature.

2/ Reliably estimating fractionation properties necessitates that both solid and liquid be computed with the same description of atomic interactions. However, the theoretical schemes accurate for solutions (e.g. BLYP+GD2, PBE+GD2, vdW-DF2, including dispersion corrections) are not those considered for solids (PZ, PZ+QHA, PBE, PBEsol). We realized a comprehensive study on 7 well-characterized solid materials (aragonite, calcite, dolomite, CaO lime, diopside, aragonite, anhydrite) modeled within 7 theoretical schemes (PZ, PZ+QHA, PBE, PBEsol, BLYP, BLYP+D2, vdW-DF2). “Solution-friendly” schemes appear to induce large errors for solids (up to 2 permil at 300K), whereas results based on “solid-friendly schemes” were giving consistent results, except for a few notable exceptions. PBEsol appears as the more reliable scheme, although it behaves particularly badly for liquids.

Different approaches to combine these studies and obtain solid-liquid fractionation will be discussed, together with geochemical applications.

References