

An *ab initio* study of sulfate and magnesium impurities in CaCO₃ and their effects on mineral-solution equilibrium isotope fractionations

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Various impurities are readily incorporated into CaCO₃ minerals. For example, tetrahedral SO₄²⁻ ions substitute for planar CO₃²⁻ ions in the CaCO₃ lattice to form carbonate-associated sulfate (CAS). Experiments have demonstrated an effect of the CAS concentration on multiple mineral-solution isotopic fractionations (e.g., CaCO₃-water O isotopes, CaCO₃-Ca²⁺ Ca isotopes, CAS-SO₄²⁻ S isotopes, and carbonate-clumped isotopes), and similar effects have been documented for other impurities in CaCO₃ minerals (e.g., Mg²⁺). A mechanistic understanding of the effects of impurities in CaCO₃ minerals on multi-isotopic fractionation is necessary for the use of carbonate minerals as paleo-environmental archives.

Equilibrium isotopic fractionations among different reservoirs can be determined by *ab initio* quantum chemistry methods. Computational constraints limit such methods to relatively small supercells, and the use of periodic boundary conditions (PBC) results in impurity concentrations much higher than those in natural and synthetic carbonate minerals. Consequently, isotopic fractionations calculated this way may be in error if the fractionations depend on the impurity concentration, as observed in experiments.

To quantify such computational artifacts and determine the impurity concentration-dependent mineral-solution isotopic fractionations, we systematically studied these fractionations with variable lattice sizes and levels of theory. We performed density functional theory (DFT) calculations with PBC, using the Quantum ESPRESSO package to model SO₄²⁻ and Mg²⁺ impurities in calcite and aragonite lattices of up to 270 atoms. The Gaussian16 quantum chemistry program was used to calculate SO₄²⁻, HCO₃⁻, Mg²⁺ and Ca²⁺ hydration shells with up to 32 explicit water molecules and an implicit solvation model. The impurity concentrations in the largest supercells in our study are still higher than in most natural and synthetic samples. However, the computational artifacts decay with increasing supercell size and our results with the larger supercells are expected to be robust. We propose that a weighted average isotopic fractionation of a single large ‘doped’ supercell and an arbitrary number of ‘pure’ supercells should allow calculations of the isotopic fractionations at an arbitrary impurity concentration. We will present the impurity concentration-dependent mineral-solution fractionation of O, C, Ca, Mg, and S isotopes and the carbonate-clumped isotope composition of the CaCO₃, and compare these to observations, where available.