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First-principle study of Ca, O and C isotope fractionation between $CaCO_3$ and aqueous solutions in the presence of magnesium and sulfate impurities

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The stable isotopes of Ca, O and C partition among aqueous reservoirs and $CaCO_3$ minerals during mineral precipitation. The isotopic compositions of these elements in sedimentary $CaCO_3$ minerals serve to constrain the minerals' formation conditions, allowing climate and environmental reconstructions. Other aqueous ions may co-precipitate with the major elements in $CaCO_3$ as impurities, with possible effects on the mineral-solution fractionation of isotopes. Indeed, the presence of magnesium and sulfate impurities in $CaCO_3$ has been shown in experiments to influence the isotopic fractionation of the major elements in an impurity concentration-dependent manner, particularly for the calcite-water O isotope fractionation.

The impact of impurities on climate and environmental reconstructions requires systematic study, but to our knowledge, few theoretical studies of the effects of magnesium impurities on the fractionation of Ca isotope between $CaCO_3$ minerals and aqueous solutions exist and no such studies exist on the effect of sulfate impurities. We use *ab initio* density functional theory (DFT) and density functional perturbation theory to study the equilibrium isotopic fractionation of Ca, O and C between $CaCO_3$ minerals and aqueous solutions in the presence of different concentrations of magnesium and sulfate impurities.

We find a difference of up to ~2‰ in δ^{44}Ca between pure calcite and aragonite supercells and supercells of those minerals with 1/24 and 1/32 mole fractions of sulfate, respectively. A δ^{44}Ca difference of up to ~1‰ is observed with similar mole fractions of magnesium. The δ^{18}O values of $CaCO_3$ are found to vary in an impurity concentration-dependent manner by up to ~0.5‰ (calcite) and 2.5‰ (aragonite) at a 1/16 mole fraction of magnesium and sulfate. The δ^{13}C values are found to vary by up to ~0.4‰ (calcite) and 2.2‰ (aragonite) over similar magnesium and sulfate impurity concentration ranges. Our study demonstrates the importance of understanding the effects of impurities on the isotopic composition of major elements in $CaCO_3$ minerals and the implications for interpretations of such isotopic records. *Ab initio* DFT methods of sufficient accuracy are a powerful tool for the development of such understanding.