

Relating the $\delta^{34}\text{S}$ of Carbonate Associated Sulfate to Solution Composition and Precipitation Rate

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Carbonate associated sulfate (CAS) is structurally bound sulfate found in carbonate minerals of biological and chemical origin. Modern biogenic carbonates taken from sites around the world host CAS, which displays sulfur isotope ratios similar to modern seawater sulfate ($\delta^{34}\text{S} = 21\text{‰}$ V-CDT), suggesting that CAS may faithfully record the $\delta^{34}\text{S}$ of the dissolved sulfate in seawater from which the carbonates precipitated. However, despite the growing use of CAS as a proxy for the isotopic composition of seawater sulfate, the abiotic CAS-SO₄²⁻ fractionation has not been tested experimentally.

We precipitated aragonite and calcite at variable sulfate concentrations, and calcite at variable precipitation rates. Both sulfate concentration and precipitation rates were varied over more than 2 orders of magnitude. All samples were measured for mineralogy, X-ray adsorption spectroscopy pattern, CAS concentration and $\delta^{34}\text{S}$.

We find a significant CAS-SO₄²⁻ fractionation of $\sim 1\text{‰}$ in synthetic aragonite and $\sim 1\text{-}3\text{‰}$ in calcite. While the CAS-SO₄²⁻ fractionation in aragonite is invariant with the ratio of sulfate to carbonate activity, $a\text{SO}_4^{2-}/a\text{CO}_3^{2-}$, the fractionation in calcite depends strongly on $a\text{SO}_4^{2-}/a\text{CO}_3^{2-}$ and weakly on precipitation rate.

We examined several possible explanations for the observed dependence of CAS-SO₄²⁻ fractionation in calcite on $a\text{SO}_4^{2-}/a\text{CO}_3^{2-}$. Thermodynamic modeling suggests that isotopic fractionation among the various aqueous species of sulfate is incapable of explaining the observations. Alternatively, the $a\text{SO}_4^{2-}/a\text{CO}_3^{2-}$ -dependent incorporation of CAS affects the lattice energetics enough to influence the equilibrium fractionation. We test this explanation by molecular modeling of a calcite supercell containing different CAS concentrations. Lastly, high $a\text{SO}_4^{2-}/a\text{CO}_3^{2-}$ may favor rapid isotopic exchange relative to sulfate entrapment in the lattice, and expression of near-equilibrium CAS-SO₄²⁻ fractionation. We test this explanation with a dynamic model of sulfate incorporation and crystal growth.