

# Mechanisms of equilibrium and kinetic oxygen isotope effects in synthetic aragonite at 25°C

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Aragonite was precipitated in the laboratory at 25°C in isotopic equilibrium with Na-Ca-Mg-Cl-CO<sub>3</sub> solutions over two different pH ranges (i.e., pH = ~8.2 and ~10.8) by a constant addition method. On the basis of its isotopic composition and a newly determined mineral-specific acid fractionation factor (i.e., 1.01063), a new value is proposed for the oxygen isotope fractionation factor between aragonite and water at 25°C:

$$1000\ln\alpha_{(\text{aragonite-water})} = 28.84 \pm 0.09$$

In order to elucidate the mechanism(s) of aragonite precipitation, the equilibrium oxygen isotope fractionations between HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> and H<sub>2</sub>O at 25°C were also determined. The oxygen isotope compositions of BaCO<sub>3</sub> precipitated quantitatively and quasi-instantaneously at three distinct pH and the mole fractions of the carbonic acid species in these solutions were combined to yield the following equilibrium oxygen isotope fractionation factors between HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> and H<sub>2</sub>O at 25°C:

$$1000\ln\alpha_{(\text{bicarbonate ion-water})} = 30.53 \pm 0.08$$

$$1000\ln\alpha_{(\text{carbonate ion-water})} = 23.71 \pm 0.08$$

The oxygen isotope composition of witherite obtained from fractional precipitation experiments, along with the estimated δ<sup>18</sup>O values of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions in the parent solution, revealed that CO<sub>3</sub><sup>2-</sup> ions are preferentially incorporated into the growing crystal. In addition, preferential deprotonation of isotopically light HCO<sub>3</sub><sup>-</sup> ions and the incorporation of the light CO<sub>3</sub><sup>2-</sup> isotopologues are proposed to account for the kinetic isotope effects observed in the course of aragonite and witherite precipitations.