

The control of mineral growth rate on sulfate partitioning in calcite and aragonite – An experimental study

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Sulfate is the second most abundant anion in modern seawater and is readily incorporated as an impurity in marine carbonates. This fraction of sulfate is commonly referred to carbonate-associated sulfate (CAS) and it is presumed that the tetrahedral sulfate ion substitutes the trigonal carbonate ion in the respective crystal lattice. CAS is used as a proxy for reconstructing the primary sulfur isotopic composition of oceanic sulfate and the evolution of the marine sulfur cycle in the geological past. However, a mechanistic understanding of the mode and the extent of sulfate incorporation into carbonate minerals is largely lacking.

To shed light on the mineral growth rate dependence of sulfate incorporation in CaCO₃ and the sulfate partitioning coefficients ($D_{\text{SO}_4} = (\text{SO}_4/\text{CO}_3)_{\text{solid}} / (\text{SO}_4^{2-}/\text{CO}_3^{2-})_{\text{fluid}}$) of calcite and aragonite we performed steady-state precipitation experiments at varying growth rates and 25 °C. The overgrowth experiments were carried out using synthetic calcite or aragonite seeds at pH 8.3 ± 1 and at same conditions, except adding MgCl₂ to avoid calcite nucleation during aragonite growth.

Preliminary results suggest that increasing growth rates promote sulfate incorporation in both calcite and aragonite. Although sulfate is incorporated in calcite at a higher degree than in aragonite, we observe higher D_{SO_4} values during aragonite growth. This contrasting behaviour can be explained by the higher alkalinity concentration existing during aragonite precipitation and the effect of aquo-complex formation in the forming fluid. These results will improve the general understanding of the controls of mineral growth rate and aquo-complex formation on the sulfate partitioning in calcite and aragonite. For instance, the linear correlation of D_{SO_4} and mineral growth rate is essential in order to reconstruct (i) reliably the sulfate concentration of the forming fluid and/or (ii) mineral growth rate regimes of natural samples by estimating their sulfate partitioning coefficient, assuming that seawater sulfate concentration is known.