EXPERIMENTAL DETERMINATION OF SULFATE INCORPORATION IN CALCITE, Mg-CALCITE AND ARAGONITE

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The incorporation of trace elements in carbonate minerals provides key information to unravel past chemical-physical conditions of the Earth's surface environments. Sulfate is the second most concentrated anion in modern seawater and is readily incorporated as an impurity in marine carbonate minerals. This fraction of sulfate is commonly referred to as carbonate-associated sulfate (CAS) and it is presumed that the tetrahedral sulfate ion substitutes the trigonal-planar 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. Its sulfur isotopic composition (given as $\delta^{34}S_{CAS}$ value) equals that of the dissolved marine sulfate whose $\delta^{34}S_{SW}$ (SW = seawater) value reflects the redox conditions, input-output balance (e.g. evaporates, sulfur-containing ores, leaching/weathering of rocks), and biological activity of the ancient ocean (BURDETT et al., 1989; KAMPSCHULTE & STRAUSS, 2004). However, a mechanistic understanding of the mode and the extent of sulfate incorporation into carbonate minerals is largely lacking.

In this study, we investigate the sulfate incorporation into calcium carbonate minerals and their sulfate partitioning coefficients ($D_{SO4} = (SO_4/CO_3)_{solid} / (SO_4^{2-}/CO_3^{2-})_{fluid}$). To shed light on the mineral growth rate dependence of D_{SO4} we performed steady-state precipitation experiments at varying growth rates, but at constant temperature, pH and sulfate concentration of the reactive fluid (30 mM SO_4). The overgrowth experiments were carried out using synthetic calcite or aragonite seeds at 23 ± 1 °C and pH 6.3 ± 0.1 or 8.3 ± 0.1 and in the presence or absence of aqueous magnesium.

Preliminary results from experiments at pH 8.3 suggest that increasing growth rates promote sulfate incorporation in both calcite and aragonite. At low growth rates the extent of incorporated sulfate in calcite and aragonite is similar, whereas with increasing growth rate the sulfate uptake in calcite is much higher compared to aragonite. Calcite grown at pH 6.3 in the presence of sulfate and magnesium exhibits a 3.5 to 5 times higher sulfate content than calcite, which was grown at pH 8.3 at a similar growth rate. The obtained results improve our fundamental understanding on controls of mineral growth rate, pH and aqueous complex formation on sulfate incorporation in (Mg-)calcite and aragonite, and allow determining apparent partitioning coefficients of sulfate between precipitated mineral and reactive fluid for individual precipitation environments.

BURDETT, J.W., ARTHUR, M.A., RICHARDSON, M. (1989): Earth Planet. Sci. Lett., 94, 189-198.
KAMPSCHULTE, A., STRAUSS, H. (2004): Chem. Geol., 204, 255-286.