

Effect of sulfate on Mg partitioning during its incorporation in calcite

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Chemical and isotopic signatures of traces and impurities in carbonate minerals are used as tools in order to reconstruct environmental conditions at the time of mineral formation. Previous experimental work has shown that temperature and growth rate are two parameters that significantly influence Mg partitioning in calcite. More recently the role of aqueous complexes has been acknowledged as an additional parameter affecting both elemental partitioning and isotope fractionation. In this study we examine the role of sulfate on Mg partitioning during calcite formation. Our work aims to shed light on the effect of sulfate-bearing aquo complexes with Ca^{2+} and Mg^{2+} during calcite growth. Moreover we investigate its role on the formation of the predominant abiotic CaCO_3 polymorph which was oscillating between calcite and aragonite throughout the Phanerozoic. In this study the effect of sulfate on the Mg partitioning in calcite is examined as a function of growth rate. Therefore steady-state co-precipitation experiments with calcite seed material at 25 °C were performed. Throughout the experimental runs, the aqueous Mg concentration was kept constant, whereas different growth rates and different concentrations of dissolved SO_4^{2-} have been used. Our data show a strong dependence of complexed Mg on the concentration of SO_4^{2-} in the fluid. At elevated growth rates the Mg partitioning is significantly decreasing with an increasing amount of sulfate due to the formation of MgSO_4^0 complexes. Furthermore the presence of sulfate induces the formation of aragonite on calcite seeds at elevated growth rates, whereas we see no formation of aragonite at low growth rates and in the absence of sulfate. Our findings suggest that - beside Mg ions - both the amount of dissolved SO_4^{2-} and the growth rate are controlling the formation of aragonite. On a future step the effect of sulfate on Mg isotope fractionation in calcite will be examined. These results will improve the general understanding of the controls of solution chemistry on the formation of CaCO_3 minerals and specifically the effect of sulfate on the incorporation of Mg into the calcite crystal lattice.