



In situ monitoring of calcium carbonate formation processes via an amorphous precursor in the presence of aqueous magnesium and sulfate

Katja Goetschl, Bettina Purgstaller, Vasileios Mavromatis, and Martin Dietzel

Graz University of Technology, Institute of Applied Geosciences, Graz, Austria (katja.goetschl@tugraz.at)

Calcium carbonate minerals (CaCO_3) are widely distributed in natural environments and have been extensively studied for their chemical, structural and isotopic composition. The replacement of Ca by Mg is very common in sedimentary trigonal carbonate minerals and a large body of studies has been devoted in the last decades to characterize the impact of different physical and chemical parameters on the incorporation of Mg in marine but also terrestrial calcite. The occurrence and formation of calcite is in most cases related to precipitation from aqueous solution where mineral growth proceeds along different pathways. The formation of Mg-bearing calcite via an amorphous precursor is despite intensive research still a poorly understood process that is of relevance for biogenic and abiogenic carbonate precipitation. The role of different dissolved ligands on the transformation of ACC has been also widely discussed. A few studies have addressed the role of sulfate in controlling CaCO_3 formation and polymorphism, although sulfate is the second most concentrated anion in seawater. In this study, we examine the effect of dissolved sulfate on Mg-calcite formation via an amorphous precursor phase and the extent of magnesium and sulfate incorporation during the crystallization process. The transformation from an ACC standard material to the crystalline phase was monitored by in situ Raman spectroscopy at high temporal resolution. The preliminary results of this approach lead to a better understanding of the abiotic crystallization process from ACC to Mg-calcite and elemental partitioning. This study also highlights the applicability of in situ Raman spectroscopy to study rapid transformation and crystallization reactions.