



Experimental crystallization of CaCO₃ polymorphs for trace element and isotope fractionation

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Trace element distribution and isotopic signatures in carbonate minerals are suitable to decipher the formation conditions such as temperature and aqueous chemistry in natural and anthropogenic environments. In order to understand more about the mechanisms of CaCO₃ crystallization and to find out the potential factors controlling the trace element and isotope fractionation during CaCO₃ growth, three different techniques were used in the present study to crystallize CaCO₃ polymorphs. These three techniques are CO₂ diffusion through membranes, double diffusion of reactants through hydrogel, and pH-stat titration of aqueous solutions.

Preliminary experimental results indicate that, at a temperature range from 10° to 40°C, single types of CaCO₃ polymorph may be produced by controlling the Mg²⁺/Ca²⁺ molar ratio and precipitation rates in the reaction solution.

For example, Mg²⁺/Ca²⁺ molar ratios less than 0.01 yield calcite as sole precipitate, whereas a Mg²⁺/Ca²⁺ molar ratio of about 2 exclusively induces aragonite formation for CO₂ diffusion technique. In general, most calcite crystals exhibit rhombohedral habit and several crystals show short prisms. Aragonite occurs as fibrous crystals, usually in radiating groups. The distribution of trace elements is very sensitive to CaCO₃ polymorphs due to the respective cation radii and crystal type. Under all experimental conditions, Sr²⁺/Ca²⁺ molar ratio in aragonite is higher than that in calcite at analogous experimental conditions. Accordingly, e.g. for calcite a continuous enrichment of dissolved Sr²⁺ vs. Ca²⁺ is observed due to Sr²⁺ discrimination in the crystal lattice, which can be followed by a Rayleigh fractionation process. Moreover, distribution of trace elements in calcite is also correlated to the precipitation rate. Higher precipita-

tion rates usually lead to lower discrimination effects during the precipitation. Results gained from the above three crystallization techniques at similar physicochemical conditions are discussed.