

## New insights to the formation of dolomite and magnesite through hydrothermal alteration of Ca-carbonates: An experimental approach

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Advanced knowledge about the physicochemical conditions and reaction paths underlying Ca-Mg carbonate formation, such as dolomite and magnesite, during the advanced stage of diagenesis is a pre-requirement for the accurate interpretation of proxy signals established from carbonate-hosting sedimentary archives. In this study, hydrothermal precipitation experiments were performed in order to trace and quantify the evolution of elemental (Ca, Mg and Sr) and stable isotopic  $\delta^{18}\text{O}$  signatures during the (trans)formation of intermediate aragonite and low-Mg calcite to more stable dolomite and magnesite in the presence of Mg- and Na-chloride-rich brines. Therefore, 330 mg of inorganic  $\text{CaCO}_3$  seed material (aragonite or calcite) was reacted with 30 mL of an artificial brine solution, originally containing 0.2 M of  $\text{MgCl}_{2(aq)}$  and 0.1 M or 0.05 M of  $\text{NaHCO}_3$ , in Teflon-lined stainless steel autoclaves at temperatures of 150, 180 and 220°C over the course of 365 days. The evolution of reaction products and of the experimental solutions was monitored by ICP-OES, CRDS, FTIR, XRD, EMPA and SEM analyses as well as pH and alkalinity measurements.

Based on the apparent solid-phase composition and reactive fluid chemistry the following sequence of mineral growth was established: aragonite and/or low-Mg calcite reacted with aqueous  $\text{Mg}^{2+}$  ions to form intermediate huntite, brucite and high-Mg calcite, subsequently altered to Ca-excess dolomite and Ca-rich magnesite and finally converted to nearly stoichiometric endmembers. A progressive evolution in the stoichiometry of dolomite (from 42 to 50 mol%  $\text{MgCO}_3$ ) and magnesite (from 80 to 98 mol%  $\text{MgCO}_3$ ) as well as the increase in the degree of cation order in dolomite (from 0.26 to 0.74) were observed during this reaction sequence, implying a kinetic drive towards the (thermodynamically stable) end members. The latter processes were also traced, by means of  $\delta^{18}\text{O}$  isotope exchange kinetics between fluid and precipitating solids in bulk ( $\Delta = \delta^{18}\text{O}_{\text{fluid-dolomite}\pm\text{magnesite}}$ ) which was possible by using a reactive fluid highly depleted in  $^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{VSMOW}} = -46.4$ ). Our first results show the progressive evolution towards near-equilibrium conditions is highly temperature-dependent but is also affected by the nature of the seed material initially introduced to the reactor, with aragonite reacting much faster than calcite. Plotting the  $1000 \ln(\alpha^{18}\text{O}_{\text{fluid-dolomite}\pm\text{magnesite}})$  values for almost pure dolomite and magnesite or mixtures between the two phases against  $1/T$  supports existing experimental and theoretical fractionation lines for dolomite and magnesite.

Our obtained results indicate that in the presence of Mg-rich brines metastable  $\text{CaCO}_3$  polymorphs are on the long term transformed into more stable magnesite and dolomite through the formation of intermediate Mg-Ca carbonates. The experimental results are discussed in the scope of dolomitization of limestone platforms in natural surroundings.