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

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Hydrothermal precipitation experiments were performed to trace and quanitfy elemental (Ca, Mg and Sr) and stable isotopic $\delta^{18}O$ signatures during the (trans)formation of intermediate aragonite and low-Mg calcite to more stable dolomite and magnesite in the presence of Mg-/Na-chloride-rich brines by reacting 0.1M inorganic $CaCO_3$ seed material (aragonite or calcite) with an artificial brine originally containing 0.2M $MgCl_{2(aq)}$ and 0.1 or 0.05M of $NaHCO_3$ within Teflon-lined, 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 apparent solid-phase compositions and reactive fluid chemistry the following sequence of mineral growth was established: aragonite and/or low-Mg calcite reacted with aqueous Mg2+ 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% MgCO3) and magnesite (from 80 to 98 mol% MgCO3) 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.

Results from our study indicate that in the presence of Mg-rich brines metastable $CaCO_3$ polymorphs are transformed into more stable magnesite and dolomite via the formation of intermediate Mg-Ca carbonates. The experimental results are discussed in the scope of dolomitization of limestone platforms in natural surroundings.