



## Chemical and physical evolution of dolomite precipitation at 180°C and 220°C from calcite and aragonite seeds

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In this present study an experimental approach is taken to gain a better understanding of secondary dolomite formation under diagenetic hydrothermal conditions. A series of 60 experiments were set up in closed bomb reactors with Teflon inserts to simulate exposure of calcium carbonate materials of (i) aragonite and (ii) calcite to hydrothermal conditions. 30 reactors were prepared using calcite as a seed material and 30 using aragonite. In each experiment 330mg of the seed calcium carbonate was placed in 30mL of 0.2M MgCl<sub>2</sub> solution along with 252mg NaHCO<sub>3</sub> to balance charges. 15 of each the calcite and aragonite prepared reactors were placed in an oven at 180°C and 15 of each at 220°C. Samples were then progressively removed from the ovens beginning in short time intervals and increasing the time apart as the phase transformations became less rapid (ie. after 3, 6, 13, 21, 31, 56 days \*ongoing\*). Samples were separated into fluid and solid phases by filtration for separate analysis. Fluids were analysed by titration for alkalinity and ICP-OES for elemental concentrations of major cations to determine the migration of major cations between the calcium carbonate seed material and the reaction fluid. Solid samples were analysed with FTIR-spectroscopy and X-ray diffraction of powdered smears on glass loading slides to identify the present mineral phases. Rietveld analysis was conducted on the XRD patterns to quantify the mineral phases and to determine the stoichiometry and the superstructure of the formed magnesite and dolomite.

Although experiments are still running, several trends have been identified. Transformation of the aragonite seed material occurs at a much faster rate than transformation of the calcite seed material, with each precursor material first transforming into a Ca-rich magnesite. With increased reaction time the Ca-rich magnesite recrystallizes to purer phases of magnesite, the Ca concentration of the fluid increases as the Ca is liberated into the fluid and the Mg concentration decreases as it is taken up by the solid. With further reaction time dolomite formation begins as non-stoichiometric dolomite (57-54 mol% CaCO<sub>3</sub>) with poor cation ordering within the superstructure. The rate of initial dolomite formation tends to be relatively rapid (changing with seed material and temperature) and then becomes increasingly slower as more dolomite precipitates. Reactions at 220°C show a rapid change in the stoichiometry of the dolomite being formed with the calcite reactors reaching approximately ideal stoichiometry (CaMgCO<sub>3</sub>) within 21 days reaction time, dolomite precipitated at 220°C from the aragonite seed material reaches a stoichiometry of ~51.2 mol% CaCO<sub>3</sub> rapidly (within 6 days) however plateaus and does not change notably with further reaction time. In each reaction the cation ordering within the superstructure increases linearly with reaction time and reached the same degree of ordering at approximately equal reaction times (ie. 0.45-0.52 within 21 days, 0.60-0.65 within 31 days) suggesting a strong kinetic control on superstructure.

Future experiments through mixed-flow reactors will see an increase in CO<sub>2</sub> pressure and decrease in temperature. A multi-proxy isotopic study will be conducted measuring  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{26}/^{24}\text{Mg}$ ,  $\delta^{44}/^{40}\text{Ca}$ ,  $\delta^{88}/^{86}\text{Sr}$  and clumped isotope ( $\Delta 47$ ) fractionation throughout the process of dolomitization to gain a better understanding of the isotopic proxies within the Ca-Mg-CO<sub>2</sub>-H<sub>2</sub>O system.