Synthesis of dolomite analogues at ambient conditions

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The so-called *Dolomite Problem* is one the most interesting and longstanding mineralogical questions. The problem deals with the uncommon formation of dolomite ($CaMg(CO_3)_2$) in present natural environments despite its abundance in the geological record. Moreover, while dolomite-analogues, such as norsethite ($BaMg(CO_3)_2$) and $PbMg(CO_3)_2$ can be easily synthesized at room temperature and atmospheric pressure, this does not occurs in the case of dolomite. In fact, experimental conditions for the synthesis of dolomite at ambient conditions are not well defined yet.

This opens the door to an indirect investigation of the mechanisms of dolomite formation in nature.

By using an experimental protocol based on the precipitation method proposed by Hood et al. [1], we were able to determine and monitor the reaction pathways towards the formation of the dolomite-analogues norsethite and $PbMg(CO_3)_2$ at room temperature. In brief, the experiments consisted in mixing equal volumes of two aqueous solutions: solution A with concentrations of 0.06 M of $BaCl_2$ (or 0.02 M of $Pb(NO_3)_2$) and 0.1 M of $MgCl_2$ (or $Mg(NO_3)_2$) and solution B with a concentration of 0.5 M Na_2CO_3. As a result, instantaneous precipitation of amorphous gels was observed in all cases. Subsequent ageing of initial gels led to the formation of various crystalline phases, which eventually transformed into norsethite or $PbMg(CO_3)_2$. X-Ray Powder Diffraction and Scanning Electron Microscopy imaging of the precipitates removed after given ageing times allowed us to identify the sequences of dissolution-crystallization reactions, which produce the dolomite-analogues. Furthermore, we monitored the evolution of the characteristic cationic ordering of norsethite and $PbMg(CO_3)_2$ by determining ratios between the intensity of certain superstructure peaks and no-superstrucure peaks (e.g. $I_{01.5}$ / $I_{00.6}$ and $I_{10.1}$ /$I_{01.2}$ [2]).

The results obtained from our experiments provide new insights into the mechanisms of formation dolomite-like structures under ambient conditions.

[1] Hood, W.C. et al (1974) *Am. Mineralogist*, **59**, 471 - 474.
[2] Pimentel, C. and Pina, C. M. (2014) *Geochimica et Cosmochimica Acta*, **142**, 217 - 223.