In situ monitoring of $CaCO_3$ transformation processes between 6 and 25°C

B. PURGSTALLER[1]*, V. MAVROMATIS[1,2,] , F. KONRAD[1], A. BALDERMANN[1] AND M. DIETZEL[1]

[1]Institute of Applied Geosciences, Graz University of Technology, Rechbauerstraße 12, 8010 Graz, Austria (*correspondence: bettina.purgstaller@tugraz.at)
2Géosciences Environmental Toulouse, CNRS, UMR5563, avenue Edouard Belin 14, 31400 Toulouse, France

The formation of calcite and aragonite has been earlier suggested to be induced by the transformation of precursor phases, like amorphous $CaCO_3$. The mechanisms of this (trans)formation as well as the effect of the prevailing physicochemical conditions on the final product (e.g. pH, temperature and aqueous complexation) are not fully elucidated.

In the present study the (trans)formation of calcium carbonate has been studied in the temperature range from 6 to 25 °C under pH_{stat} conditions (8.3 ±0.1). $CaCO_3$ precipitation was induced by titration of a 0.6 M $(Ca,Mg)Cl_2$ solution with distinct Mg/Ca ratios (1/4 and 1/8) into a 1 M $NaHCO_3$ solution. The pathway of $CaCO_3$ formation was monitored by *in situ* Raman spectroscopy as well as by continuous sampling and analyzing of precipiates and reactive solutions.

The results reveal two pathways of calcium carbonate formation depending on the temperature and initial Mg/Ca ratio: (i) in experiments conducted with a Mg/Ca ratio of 1/4 at $T \leq 12°C$ as well as in experiments with a Mg/Ca ratio of 1/8 at $T \leq 18°C$, amorphous $CaCO_3$ (ACC) with ~2 mol% Mg was present for a few minutes (< 5 min) before it transforms to ikaite (CaCO3·6H2O). To our knowledge this is the first time, where ikaite was verified to be formed at ambient T of up to 18°C. Subsequently ikaite transforms to aragonite in a second reaction step. In contrast in experiments conducted with a Mg/Ca ratio of 1/4 at ≥ 18°C, ACC with ~10 mol% Mg is present for about 36 min before it transforms to Mg-rich calcite (~16 mol% Mg). The *in situ* Raman results revealed that the transformation of Mg-ACC to Mg-calcite was a rapid process (~ 8 min), whereas the transformation of ikaite to aragonite was comparently slow (~ 2h). In the latter case the formation of calcite is likely inhibited by the slow release of Ca^{2+} and CO_3^{2-} ions into the Mg-rich reactive solution during ikaite dissolution, which induced elevated apparent Mg/Ca ratios. Our data clearly show that aragonite vs calcite formation is not only simply controlled by Mg/Ca ratio of the solutions, but particularily at low temperatures by coupled reactions via the occurrence of transition phases.