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Effect of temperature on the reaction pathway of calcium carbonate formation via precursor phases

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It has been earlier postulated that some biogenic and sedimentary calcium carbonate ($CaCO_3$) minerals (e.g. calcite and aragonite) are secondary in origin and have originally formed via a metastable calcium carbonate precursor phase (e.g. amorphous $CaCO_3$, [1-2]). Such formation pathways are likely affected by various physicochemical parameters including aqueous Mg and temperature.

In an effort to improve our understanding on the formation mechanism of $CaCO_3$ minerals, precipitation experiments were carried out by the addition of a 0.6 M $(Ca,Mg)Cl_2$ solution at distinct Mg/Ca ratios (1/4 and 1/8) into a 1 M $NaHCO_3$ solution under constant pH conditions(8.3 ±0.1). The formation of $CaCO_3$ was systematically examined as a function of temperature (6, 12, 18 and 25 ±0.3°C). During the experimental runs mineral precipitation was monitored by *in situ* Raman spectroscopy as well as by continuous sampling and analyzing of precipitates and reactive solutions.

The results revealed two pathways of $CaCO_3$ formation depending on the initial Mg/Ca ratio and temperature: (i) In experiments with a Mg/Ca ratio of 1/4 at $\leq$ 12°C as well as in experiments with a Mg/Ca ratio of 1/8 at $\leq$ 18°C, ikaite ($CaCO_3$ $6H_2O$) acts as a precursor phase for aragonite formation. (ii) In contrast higher temperatures induced the formation of Mg-rich amorphous $CaCO_3$ (Mg-ACC) which was subsequently transformed to Mg-rich calcite. *In situ* Raman spectra showed that the transformation of Mg-ACC to Mg-calcite occurs at a higher rate ($\sim$ 8 min) compared to that of ikaite to aragonite ($>$ 2 h). Thus, the formation of aragonite rather than of Mg-calcite occurs due to the slower release of $Ca^{2+}$and CO_3^{2-} ions into the Mg-rich reactive solution during retarded ikaite dissolution. This behavior is generally consistent with the observation that calcite precipitation is inhibited at elevated aqueous Mg/Ca ratios.

[1] Addadi L., Raz S. and Weiner S. (2003) *Advanced Materials* **15**, 959-970.

[2] Rodriguez-Blanco J. D., Shaw S., Bots P., Roncal-Herrero T. and Benning L. G (2014) *Geochimica et Cosmochimica Acta* **127**, 204-220