

Precipitation of Mg-rich amorphous calcium carbonate and its transformation to Mg-calcite

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The presence of amorphous calcium carbonate with variable Mg contents (Mg-ACC) has been documented for a variety of biominerals [1] [2]. The transformation of such a Mg-rich precursor phase is suggested to play a significant role in the formation of biogenic Mg-calcite [3]. However, the mechanisms involved in the Mg-calcite formation via Mg-ACC as well as the physicochemical parameters controlling the Mg content of the resulting Mg-calcite are not well established.

In order to shed light on these aspects, we precipitated high Mg-calcite by computer controlled titration of a (Mg,Ca)Cl₂ solution at different Mg/Ca ratios into a NaHCO₃ solution under precisely defined physicochemical conditions (T = 25.00 ± 0.03°C; pH = 8.30 ± 0.05). The temporal evolution of 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 distinctive mechanisms of Mg-calcite formation. At initial aqueous Mg/Ca molar ratios ≤ 1/6 (Mg-)calcite was precipitated directly from solution. Conversely, higher Mg/Ca ratios induced the precipitation of Mg-ACC (up to 10 mol % of Mg), which was subsequently transformed to calcite with up to 20 mol % of Mg. The continuous enrichment of Mg in calcite throughout and subsequent to Mg-ACC transformation likely occurs due to the high carbonate alkalinity (0.1 M) and aqueous Mg/Ca ratio present in the reactive solution. The experimental results shed light on the insufficiently investigated inorganic component of biomineralisation pathways in many carbonate secreting organisms.

[1] Beniash *et al.* (1997) *Proc. R. Soc. Lond. B* **264**, 461-465.

[2] Politi *et al.* (2010) *Chem. Mater.* **22**, 161-166. [3] Raz *et al.* (2000) *Adv. Mater.* **12**, 38-42.