



Preparation of the metastable phases amorphous calcium carbonate (ACC) and calcium carbonate hexahydrate (ikaite) and their transformation into stable calcium carbonate phases

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Calcium carbonate occurs in five crystalline modifications. Three of them, i.e. calcite, aragonite and vaterite (with the thermodynamic stability decreasing in this order), are anhydrous with the same chemical composition. Besides these, the less stable water containing phases monohydrocalcite $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ [1] and ikaite $\text{CaCO}_3 \cdot 6 \text{H}_2\text{O}$ exists. In addition to the crystalline modifications, amorphous calcium carbonate (ACC) is known, which is highly unstable. ACC is an interesting substance, because it is a widespread (often transient) material in biomineralisation where advantage is taken of its higher solubility.

Amorphous calcium carbonate was prepared without any additives. CO_2 was bubbled into a saturated $\text{Ca}(\text{OH})_2$ -solution at 1-2 °C under continuous control of the conductivity of the solution. The precipitate was then vacuum-dried overnight. The ACC is even stable for several weeks at room temperature as long as it is prevented from moisture. The final transformation product is the more stable phase calcite [2]. As it is known that magnesium ions inhibit the formation of calcite, we studied the transformation of the ACC in magnesium solution. The products were monohydrocalcite or aragonite depending on time for which ACC was kept in the magnesium solution and the magnesium concentration.

Ikaite was prepared in a very similar way. The main difference was that the precip-

itate was not dried after filtration, but instead stored in a freezer after washing with cold acetone. At this temperature ikaite forms from the amorphous calcium carbonate which acts as a transient precursor. After six weeks the main phase was still ikaite, but weak peaks of calcite were detected by XRD-measurements. At room temperature and exposed to air ikaite was stable only for some hours before it transforms into calcite under loss of crystal water.

[1] M. Neumann, M. Epple, "Monohydrocalcite and its relationship to hydrated amorphous calcium carbonate in biominerals", *Eur. J. Inorg. Chem*, 2007, 1953.

[2] C. Günther, A. Becker, G. Wolf, M. Epple, "*In vitro* synthesis and structural characterisation of amorphous calcium carbonate", *Z. Anorg. Allg. Chem*, 2005, 631, 2830.