

On the effects of mineral surfaces on nucleation and transformation of ikaite (CaCO₃ x 6H₂O)

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Ikaite (CaCO₃ x 6H₂O) is a calcium carbonate mineral common to the cold regions of Earth. Apart of the various known occurrences, numerous pseudomorphoses of calcite after ikaite (Glendonites) indicate a past existence of metastable ikaite and point to its importance as a precursor of more stable calcium carbonate phases. The instability of ikaite is caused by its fragile crystal structure: CaCO₃⁰ ion pairs are encompassed by a hydration shell. The water molecules separate the ion pairs from each other and stabilize the structure by a hydrogen bonding network. According to DFT calculations of Chaka (2018), this structural unit corresponds to the hydrated ion pair complexes occurring in aqueous solutions. Despite these insights into the structural relations between ikaite and aqueous species, there is a lack of knowledge about the nucleation of ikaite and the conditions, which favor its formation over anhydrous carbonates. It only seems clear that cold temperatures, high pH values and high supersaturations with respect to ikaite facilitate its formation. Furthermore, dissolved Mg²⁺ and/or phosphate can promote the formation of ikaite by inhibiting a competing precipitation of calcite/vaterite (Purgstaller et al. 2017). It is remarkable that previous studies typically concern homogenous precipitation of ikaite, although mineral surfaces are ubiquitous in natural aqueous systems. Knowledge about the heterogeneous formation and transformation of ikaite could therefore enable a conclusion whether the viewpoint of classical nucleation theory applies to ikaite. For anhydrous calcium carbonates, it is known that mineral substrates can significantly affect nucleation by a decrease of interfacial energy according to classical nucleation theory (Li et al. 2014), whereas it remains unclear so far, if such an effect also applies to highly hydrated ikaite.

Using cryo mixed batch reactor (CMBR) experiments and in-situ flow-through cryo atomic force microscopy (CAFM), we investigated the effect of mineral substrates on the nucleation of ikaite and its subsequent disintegration into more stable calcium carbonates. The CMBR experiments were used to gain insights into the kinetics of nucleation and decomposition in presence and absence of quartz surfaces by an in-situ monitoring of the pH-value and the Ca²⁺-concentration of the aqueous growth solutions as well as by XRD phase analysis of the precipitates. The CMBR experiments were complemented by experiments employing a newly developed CAFM that showed the evolution of the reactions on mineral substrates in-situ with high spatial resolution and, therefore, enable information about mechanisms and rates of ikaite nucleation and transformation. Our results reveal that quartz substrates significantly increase the supersaturation range in which ikaite forms and, therefore, promote its formation.

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