

What controls ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) formation in Ikka Fjord, Greenland?

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In the shallow inner parts of the marine Ikka Fjord in SW Greenland, ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) forms up to 18 m tall columns growing over sodium carbonate- and phosphate-bearing springs issuing from the bottom of the fjord. Thermodynamic calculations of the mixed spring- and seawater solutions predict supersaturation with respect to several Ca- and Mg-carbonate minerals, but in Ikka Fjord only ikaite forms as the primary carbonate mineral. Aqueous PO_4^{3-} has been assumed to inhibit calcite precipitation favouring growth of the metastable mineral ikaite.

In a series of laboratory experiments simulating the conditions of Ikka Fjord, the role of PO_4^{3-} for the precipitation of ikaite was investigated. Four naturally occurring and one artificial seawater composition were mixed with sodium carbonate solutions of pH 9.9-10.6 with 0-50 ppm $\sigma\text{-PO}_4^{3-}$ (aq) at 5, 10, 15, and 20°C. In a subset of experiments, a 0.031 M CaCl_2 solution was substituted for seawater. The results showed that ikaite formed at 5, 10 and 15°C in natural or artificial seawater solutions, but with increasing amounts of a co-precipitating amorphous phase at higher temperatures. This phase was most likely amorphous calcium carbonate (ACC). Ikaite formation was independent of phosphate concentration, including PO_4^{3-} -free seawater and sodium carbonate solutions. In contrast, a concentration of at least 25 ppm PO_4^{3-} (aq) was needed to precipitate ikaite from the 0.031 M CaCl_2 solution, otherwise calcite formed as the main precipitate. The addition of MgCl_2 to the CaCl_2 solution (but no phosphate) led to mixed precipitation of nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), ikaite, and calcite.

Our experiments demonstrated that ikaite precipitation is independent of phosphate concentration. As long as the precipitation takes place in seawater, ikaite forms at the expense of other thermodynamically stable Ca,Mg carbonate minerals at $\leq 15^\circ\text{C}$, which suggests that the ionic composition of seawater is more likely the controlling factor for ikaite formation in Ikka Fjord.