

## Spatio-temporal monitoring of ikaite ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) crystallization in a man-made river section

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During repository building measures a natural river was relocated and the river water was directed through a new artificial bed lined with a concrete basement and local colluvium. Shortly after, centimetre-thick, beige-colored coatings were observed in the river bed. To understand this rapid sedimentation process a monitoring program of aqueous solution and solids sampled along the stream was launched, including mineralogical, elemental and isotopic analyses. Stream water showed pH values up to 12.9,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  contents up to 196 and 647  $\text{mg L}^{-1}$ , respectively, and very high supersaturation with respect to calcite and other calcium carbonates ( $\text{SI}_{\text{calcite}}$  up to +2.5). Some distinct relationships are observed: Ca in solution covaries positively, Mg and  $\text{P}_{\text{CO}_2}$  negatively with pH. A first set of crystal aggregates collected in the field was found to disintegrate into a light-colored calcite powder within one day. Being suspicious, more crusts were recovered in original solution and a constantly-cooled refrigerator box. Immediate XRD and FT-IR analyses revealed ikaite – calcium carbonate hexahydrate – being the rarely documented mineral never reported from such an environmental setting before. Ikaite is precipitating in a narrow temperature range ( $<6^\circ\text{C}$ ) from strongly supersaturated and in particular high alkaline solutions, e.g. some specific lake-, sea- and spring-water mixing locations, Arctic- and Antarctic sea-ice. In our case, portlandite ( $\text{Ca}[\text{OH}]_2$ ) dissolution from the concrete basement by water inflowing during wintertime provided hydrochemical conditions for ikaite precipitation. In this “natural laboratory” distinct ikaite vs. calcite spatial distribution encountered along the stream and fluid-solid evolution over time was studied. Our findings do not support nucleation inhibitors (e.g. phosphate, organic constituents), strongly elevated ionic strength (salinar), or water-mixing as a crucial demand for ikaite formation. Elemental as well as C and O isotopic signatures are used to trace ikaite formation in respect to e.g. sources and fractionation of constituents in the precipitate, and their chemical evolution in the waters.