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Ikaite in the Scărişoara Ice Cave (Romania): origin and significance

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Ikaite, $CaCO^3 \cdot 6H_2O$, is a rare, metastable carbonate mineral first identified in submarine reef-like columns growing from the bottom of Ikka Fjord (SW Greenland) at temperatures between -1.9 and 7ºC. Inactive tufa towers found along the shore of Mono and Pyramid lakes in western United States are believed to represent former ikaite structures that were converted to calcite. These sites, along with two others in Japan and Patagonia are so far the only terrestrial occurrences of this particular hydrated calcium carbonate mineral. Notes reporting its presence in ice accumulations and icicles around some saline springs from Shiowakka (Japan), prompted us to search for ikaite in the perennial ice deposit of the Scărișoara Ice Cave.

A reconnaissance mineralogical study undertaken between 1996 and 2000 pointed out the presence in the glacial and periglacial sectors of the cave of large surfaces covered with thousands of micro-pearls (< 400 μm), pearl conglomerates, fibrous efflorescent (soft and moist) calcite (var. lublinite) as well as monohydrocalcite. Except for monohydrocalcite, which precipitates in an aerosol-rich environment with temperatures changing seasonally (below 0º from October to April and slightly above 0ºC in the rest of the year) the deposition of all the other mineral phases are triggered by freezing of dripping and seeping water. In addition, phosphate minerals and abundant organic material (leaves, branches, logs) are common in many parts of the cave.

Two types of ikaite were positively identified by XRD and environmental scanning electron microscope studies: 1) various crystal shapes (< 670 μm across) forming white-light cream patchy accumulations within certain ice layers and at the surface of ice stalagmites/domes, and 2) glendonite (calcite pseudomorphs after ikaite), typically shaped as rosettes (up to 4.7 cm). Glendonite samples were found protruding out from the ice tongue in the Great Reservation. Considering the particular cave settings and microclimate (temperature is always below 2ºC) in which the two types of ikaite occur, it appears that they were cryogenically precipitated. This preliminary conclusion is largely based on similarities between the stable isotope signature in cryogenic calcites and two glendonite samples recovered from the Great Reservation in Scărișoara Ice Cave.

The high δ^{13}C (0 to 10‰ and δ^{18}O (-1 to -10‰ values, typical for cryogenic carbonates in Scărișoara Ice Cave, are due to rapid water freezing that is accompanied by swift kinetic CO_2 degassing. In comparison to the cryogenic calcite samples, the very low δ^{13}C values (-14‰ found for the ikaite precursor of glendonite, implicate biogenic CO_2, as the main carbon source for its precipitation. Therefore, glendonites may be considered useful indicators of warm/wet conditions outside the cave, time when biogenic-derived CO_2-rich waters seeped into the cave.

Future work on these carbonate precipitates may shed light on the relationship between the oxygen isotope values in the ice layers and ikaite's temperature-restricted field of formation. The aim of this study is 1) to infer the δ^{18}O from hydration water of ikaite and cross-calibrate it against the δ^{18}O obtained from ice layers that contain ikaite and 2) better understand the precipitation of ikaite and its transformation into anhydrous carbonate. The results can serve as basis to further explore other paleoclimatic and paleoenvironmental implications the presence of ikaite in perennial ice cave accumulations might have.