

On the Study of Natural and Synthetic Ikaite Crystals

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In addition to the anhydrous calcium carbonate (CaCO_3) minerals like calcite, aragonite and the metastable vaterite, there are metastable hydrous CaCO_3 phases, ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) and monohydrocalcite ($\text{CaCO}_3 \cdot \text{H}_2\text{O}$), of considerable interest for their role as precursors to stable carbonate minerals (Clarkson et al., 1992). In spite of the importance of these hydrous phases, very little attention has been paid to their study.

Although the synthetic $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ was known from earlier laboratory studies (Pelouze, 1865), ikaite in nature was first observed quite late (Pauly, 1963) at the bottom of Ikka Fjord in Greenland. There it precipitates due to mixing of cold (3°C) carbonate rich submarine springs with seawater. Discoveries of ikaite and its pseudomorphs in different natural environments followed (Suess et al., 1982; Jansen et al., 1987; Bischoff et al., 1993a, b; Larsen, 1994; Ito, 1996, 1998).

Ikaite is metastable in comparison to calcite and aragonite at all temperatures in the presence of liquid water at atmospheric pressure. The solubility trend of ikaite is opposite to calcite, aragonite, and vaterite, and it is more soluble than these minerals above 0°C at atmospheric pressure. Nevertheless, ikaite forms in environments where temperatures are close to 0°C and transforms rapidly to calcite and vaterite at ambient temperature (Shaikh & Shearman, 1986).

The study of the synthetic ikaite structure, of micro-environments during calcium carbonate precipitation and of kinetics (Bischoff et al., 1993a; Ito, 1998) has provided a fundamental framework for defining the limits for its occurrence in nature. All known occurrences are limited by its stability

field close to near-freezing temperatures, alkaline conditions and elevated phosphate concentrations. It has been proved in laboratory experiments that dissolved phosphorus in extremely small amounts has the ability to inhibit the precipitation of calcite (House, 1987).

It is also known that natural ikaite samples disintegrate, within minutes to hours, into a mush of water and small whitish crystals of vaterite and/or calcite when exposed to atmospheric conditions. This explains why the natural occurrence of this mineral has remained unknown until so recently. However, sometimes the rapid conversion of ikaite to calcite and water results in the generation of pseudomorphic calcite aggregates whose external form is controlled by the ikaite crystal morphology (Glendonites). Thus, the occurrence of these calcite

pseudomorphs, typically found in cold-water deposits from Late Precambrian to the Pleistocene, can be used as a valuable paleoclimatological indicator. Since these calcite pseudomorphs directly replace ikaite above 4°C , there is potential for using their stable isotope characteristics as a recorder of water isotope chemistry in the depositional to early burial setting.

Recently, ikaite has been found also in freshwater lakes in the Patagonian steppe (locations in Fig. 1). The aim of an ongoing study is 1) to describe the ikaite from these new localities 2) to explain the transformation behavior and possible isotopic fractionation of natural and synthetic ikaite crystals during transformation to calcite and 3) to understand the environmental conditions that lead to ikaite precipitation in these freshwater to subsaline lakes.

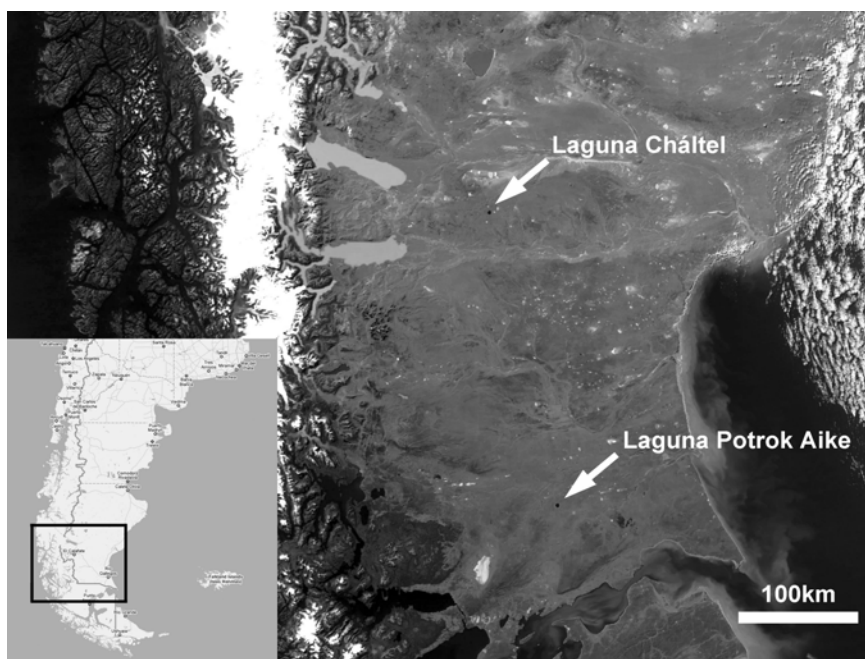


fig 1. Satellite image showing the position of the Laguna Potrok Aike and the Laguna Cháltel, Patagonia, Argentina. (Stand 25.7.2008), google maps.

palabras clave: Ikaite, Calcita, Fosfato, Morfología cristalina, Crecimiento cristalino, Análisis isotópicos.

key words: Ikaite, Calcite Precipitation, Phosphate, Crystal morphology, Crystal growth, Isotopic analysis.

resumen SEM 2009

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Samples of water, natural ikaite and its pseudomorphs were collected from two different lakes in Southern Patagonia, Argentina: Laguna Potrok Aike and Laguna Chálitel (Fig. 1). The ikaite crystals collected in winter in Laguna Potrok Aike (Fig. 2a) were found growing on plants. Disaggregating pseudomorphs were found also at the lakeshore. At Laguna Chálitel, calcite-pseudomorphs after ikaite were found in sediment cores and at the lakeshore (Fig. 3). Both lakes are characterized by high TP (total phosphate) concentrations in the lake water, polymixis (the water stratify intermittently during calm sunny periods, and then mix to the bottom during storm events) and relatively low water temperatures.

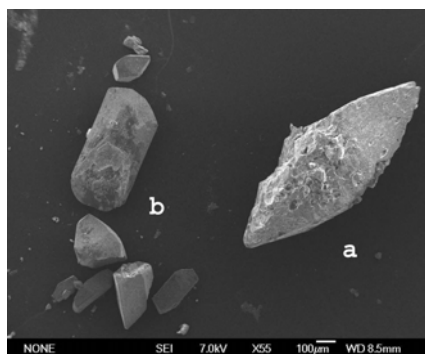


fig 2. SEM images. (a) Natural calcite pseudomorphs showing the typical ikaite habit. (b) Crystals grown from the lake water via evaporation.

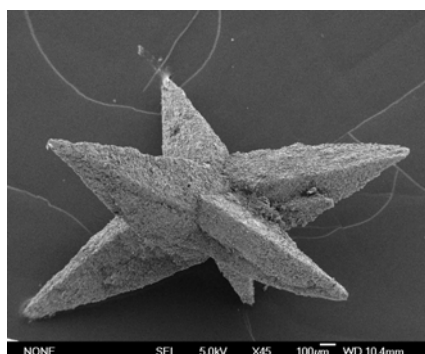


fig 3. Calcite pseudomorph after ikaite from a sediment core (62 cm) of Laguna Chálitel.

The crystallization of ikaite is presently aimed to be carried out by using different methods: (i) via evaporation from the lake water (Fig. 2b), (ii) gel experiments in test-tubes using the lake water to prepare the gel and diffusing CaCl_2 , Na_2CO_3 or ethanol to reach the supersaturation with respect to ikaite, and (iii) silica gel experiments in a double diffusion system where the experimental arrangement consist in a U-tube where a column of silica hydrogel occupies the horizontal branch, while the vertical branches correspond to the reservoirs filled with CaCl_2 and Na_2CO_3 . Moreover, different concentration of phosphate (5, 50, 500 and 1000 ppm) were added to the silica gel during the preparation. In this case, where the gel was doped with phosphate, calcite and vaterite (Fig. 4) crystals were also obtained, although all the experiments were carried out in a fridge at 2-3 °C.

Both, natural and synthetic crystals were examined by using light- and scanning electron microscopy (SEM). The elemental composition of the crystals was studied by EDAX analysis.

Moreover, the mineral composition of the natural and synthetic minerals was identified by using X-Ray powder diffraction (XRD) and single crystal diffraction.

Isotopic analysis, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, of the calcite pseudomorphs after ikaite crystals from the sediment core from Laguna Chálitel showed decreasing $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in the initial phase of precipitation and more or less constant isotope values thereafter.

ACKNOWLEDGEMENTS.

Collection of ikaite was made possible due to DFG-grants in the framework of the ICDP drilling project PASADO.

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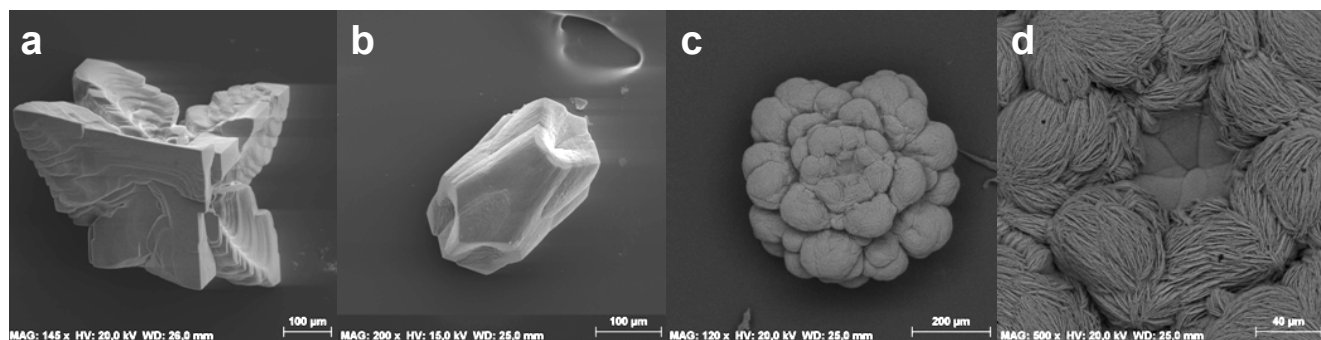


fig 4. Crystals grown in a gel medium (U-tubes) doped with different phosphate concentrations. (a) Calcite crystal grown with 5 ppm phosphate (b) Calcite crystal grown with 500 ppm phosphate (c) Vaterite crystal grown with 500 ppm phosphate. (d) Zoom of the vaterite crystal shown in (c).