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Tracing structural relicts of the ikaite-to-calcite transformation in cryogenic cave glendonite

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Abstract

Ikaite is a calcium carbonate hexahydrate that forms at temperatures close to the freezing point of water; thus, its occurrence is associated with cryogenic conditions. This mineral is metastable and quickly transforms to calcite at temperatures above 5 °C. Pseudomorphs of calcite after ikaite are known as glendonite. The nanostructure of 25 000–43 000 year old glendonite from Victoria cave (Southern Ural, Russia) was investigated in search of structural features indicative of the ikaite-to-calcite transformation. Scanning electron microscope images display several micrometer- to submicrometer-size pores and indicate high intergranular porosity among the loosely aggregated grains. Transmission electron microscopy (TEM) data show evidence of 10–20 nm nanotwins [twin law $(10\bar{1}4)$] and 10–40 nm overlapping nanograins. Scanning TEM images reveal that the individual grains contain 5–10 nm long and 2–4 nm wide mesopores (sizes between 2 and 50 nm), which are aligned parallel to $[10\bar{1}0]$ of calcite and might be associated with a crystallographically oriented dehydration of the precursor ikaite. Fourier transform infrared spectroscopy reveals no evidence of structural water but absorption bands related to molecular water trapped in fluid inclusions are present. Nitrogen absorption/desorption measurements show that the specific surface area of 5.78 m^2/g and the pore volume of ~0.07 cm^3/g for calcite, the constituent of glendonite, are comparable to those of a common natural calcite. We suggest that the aligned mesopores, frequently occurring twins, small grain size, presence of aqueous inclusions and the high micrometer- to submicrometer-size intergranular porosity arise from the ikaite-to-calcite transformation and thus may be used as criteria for the former presence of ikaite and hence for cold paleotemperatures. However, since similar features might also be common in biogenic carbonates, the diagnostic macroscopic pseudomorphs after ikaite are equally important for identifying glendonites and inferring cryogenic conditions.

Keywords: Ikaite, glendonite, cryogenic, calcite, TEM