Formation of cryogenic carbonates: experimental validation in a modern ice cave setting

Christoph Spötl\textsuperscript{1}, Gabriella Koltai\textsuperscript{1}, Yuri Dublyansky\textsuperscript{1}, and Peter Németh\textsuperscript{2}

\textsuperscript{1}Institute of Geology, University of Innsbruck, Austria (christoph.spoetl@uibk.ac.at)
\textsuperscript{2}Institute for Geological and Geochemical Research, Research Centre for Astronomy and Earth Sciences, Budapest, Eötvös Loránd Research Network, Hungary

So-called coarse-grained cryogenic cave carbonates (CCC) have gained increasing attention in recent years as indicators of past glaciation episodes in caves. Unlike the fine-grained variety, which forms seasonally by freezing water films, the coarse-grained type has never been observed in statu nascendi. This limits the significance of geochronological and geochemical data obtained from these speleothems.

The patchy distribution of coarse-grained CCC in currently ice-free caves and recent observations of CCC associated with ice in a few modern ice caves suggest that coarse-grained CCC form by very slow freezing of pools in ice created by drip water. It is assumed that an ice cap is formed on such pools by freezing and that CCC precipitation occurs subaqueously in a semi-closed system, limiting degassing of carbon dioxide, and producing a characteristic depletion in O and an enrichment in C isotopic values. This hypothesis has never been tested.

During winter 2021/22 we conducted freezing experiments in the inner and microclimatically fairly stable part of a large Alpine ice cave (Eisriesenwelt). We filled artificial holes in floor ice with water and monitored the freezing process. Freezing was completed within a few weeks and resulted in an updoming of the ice cap, formation of radial cracks, and episodic pulses of small amounts of residual water escaping through these cracks. The newly formed ice contained abundant pressurised gas inclusions which led this ice to break easily, sometimes associated with a distinct bursting noise.

The H and O isotope data of the newly formed ice define a slope lower than the meteoric water line, consistent with theoretical and experimental freezing studies. The H and O isotope values increase from top down and from the margin to the centre of the frozen pool, consistent with a progressive centripetal advance of the freezing front.

A few tenths of gram of CCC per litre of melted ice were obtained from the inner part of the former pools. The CCC range in size from a few hundredths to several tenths of a millimetre and would thus classify as the fine-grained type. Only calcite was identified by X-ray diffraction. A variety of morphologies were found including thin plates, branched aggregates, dumbbell- and rice-shaped forms. Despite their small particle size the CCC show depleted O and enriched C.
isotopic compositions, similar to coarse-grained CCC of Pleistocene age from this cave, and consistent with precipitation due to progressive freezing in a semi-closed system.

Our experiments provide a first field-based validation of the conceptual model of coarse-grained CCC formation in freezing water pools. The small crystal size suggests that the freezing rate at our experimental site was likely significantly faster than in settings where mm- to even cm-size aggregates formed during climatically cold periods.

Our data also show that grain size is not a reliable indicator of the mode of CCC formation, which calls for a revision of the currently used CCC terminology (coarse vs. fine grained).