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Upper Pleistocene cryogenic spherolites with unusual calcite structure and C/O-isotopic composition: Cupulas of the Malachitdom cave (Sauerland/ NRW Germany).

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Calcitic particles of cryogenic origin are widespread especially on the floor of former ice caves in central to eastern Europe (Žák et al. 2004, Richter & Niggemann 2005). In the Malachitdom cave such cryogenic calcites were formed as spherolites mainly. Such spherolites show sizes between 1 and 11 mm and a rhombohedral rich periphery often with a beak-shaped structure. Many of the spherolites contain a dish-shaped depression with a quite smooth surface (first described by Schmidt 1992 as cupula-spherolites).

According to Scanning Electron Microscope (SEM)-observations the rhombohedral faces of the surfaces are bent-shaped, which coincides with the results of Electron Backscatter Diffraction (EBSD)-analyses. These pigmented single fibres are distinguished by a diverging c-axis orientation within the crystals. This characteristic configuration is caused by systematic crystal-defects, which are not influenced by foreign cations like Mg. Beak-shaped spherolites, which do not have the characteristic indentation but show the same alignment of fibres, are counted to the cupulas in the broader sense as they are found next to the real cupulas.

The results of the C/O-isotope analyses of the cupulas show δ^{13}C-values ranging from –1 to –5 ‰ VPDB and δ^{x8}O-values between –7 and –14 ‰ VPDB. Within the

spherolites a trend becomes apparent for a lighter O-isotopy and a heavier C-isotopy from the inner to the outer parts. According to Žák et al. (2004) these values differ significantly from the composition found in other speleothems and can be explained by the formation of calcites due to slowly freezing water. During this process, the O-isotopy is mainly affected by the formation of ice whereas the C-isotopy is merely influenced by the degassing of CO_2.

The $^{87}Sr/^{86}Sr$-isotopic ratio of cupula-spherolites shows different values (0.70950 and 0.70942) than the isotopic ratio of the limestone (0.70827). The limestone shows a value which is equal to the typical Middle/Upper Devonian seawater composition (Veizer et al. 1999). This abnormal Sr-isotopic ratio of the cupula-spherolites has its origin in hydrothermal calcite dykes located above the place where the cupula-spherolites were found ($^{87}Sr/^{86}Sr$-isotopic ration between 0.70882 and 0.70981).

The age of the cupula-spherolites ranges from 14.48 ± 0.12 kyr to 15.61 ± 0.20 kyr (U/Th-analyses by Denis Scholz, Heidelberg). This substantiates a genesis during the Weichselian-glacial shortly before the Bölling-interstadial.

Probably due to a slow climatic warming lasting for centuries water infiltrated temporarly into the cave (lying within the permafrost) and formed an ice-body. On top of the ice, liquid water form small pools in which cryogenic calcites developed very slowly (sensu Žák et al. 2004). These were enclosed when the water froze. Minor climate fluctuations caused a formation of several generations. Later they sedimented on the cave floor during the melting of the ice. A Weichselian formation of an icebody is proved for the Malachitdom cave because of ice-accretion (“Eishaftung”).

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