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First results on stable isotopes in fluid inclusions in cryogenic carbonates from Ural Mountains (Russia)

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Cryogenic cave carbonates (CCC) were found in a number of caves in the Ural. In contrast to the CCC previously reported from Central Europe, the Uralian CCC have larger sizes (up to 4-5 cm), which allows for more detailed petrographic and geochemical studies. CCCs from Uralian caves commonly show spherulitic shapes due to crystal splitting, supporting the model of calcite precipitating in a freezing water pond.

δ^{18}O values of studied CCCs are lower by 1 to 14 ‰ compared to noncryogenic speleothems of Pleistocene and Holocene age from the same caves. δ^{18}O and δ^{13}C values are inversely correlated and typically show a fractionation between the core and the rim of individual samples. These trends are similar to those reported for CCCs from European caves (Žák et al., 2004).

Petrographic observations performed on doubly polished, 100-150 micron-thick sections revealed abundant fluid inclusions, trapped between fibres of the spherulites. Petrographic relationships suggest that these inclusions are primary.

The isotopic composition of water trapped in fluid inclusions in CCCs from two caves was analyzed following mechanical crushing at 120 ºC, cryo-trapping of released water, pyrolysis on glassy carbon at 1400 ºC (TC/EA device; Thermo), and analysis of the evolved gases on an isotope ratio mass spectrometer (Delta V Advantage; Thermo Fisher). The lack of peaks on the m/z 2 trace during the heating of the loaded crushing cell attests for a good sealing of the fluid inclusions.

The measured δD values range between -136 ‰ and -145 ‰ VSMOW. The values measured in CCCs are more negative than the typical values of fluid inclusion water measured in the Holocene stalagmites from central Ural (-99 to -108 ‰). This shift toward more negative values is attributed to the isotopic fractionation between ice and water during the freezing.

Reference: Žák et al., 2004, Chemical Geology, 2006, 119-136.