



## Recrystallization-induced oxygen isotope changes in inclusion-hosted water of speleothems – Paleoclimatological implications



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### ABSTRACT

The issue of diagenetic alteration of carbonate deposits in caves (speleothems) has gained increasing importance in recent years, as this process has serious consequences for speleothem-based paleoclimate studies. In this study stable hydrogen and oxygen isotope data of water trapped in fluid inclusions were collected for recently forming stalagmites and flowstones in order to determine how dripwater compositions are reflected and preserved in the inclusion water compositions. Hydrogen isotope compositions were found to reflect dripwater values, whereas the oxygen isotope data were increasingly shifted from the local dripwater compositions with the time elapsed after deposition. The  $\delta^{18}\text{O}$  data are correlated with X-Ray diffraction full width at half maximum values (related to crystal domain size and lattice strain), suggesting that the oxygen isotope shift is related to recrystallization of calcite. Transmission electron microscope analyses detected the presence of nanocrystalline (<50 nm) calcite, whose crystallization to coarser-grained calcite crystals (>200 nm) may have induced re-equilibration between the carbonate and the trapped inclusion water. The Ostwald ripening process provides an explanation for unexpectedly low oxygen isotope compositions in the inclusion water. The detected diagenetic alteration and its isotopic effects should be taken into consideration during sampling strategies and data evaluation as speleothems containing nanocrystalline calcite during their deposition are prone to late-stage oxygen isotope water-carbonate re-equilibration, which may shift the oxygen isotope composition of the inclusion water to more depleted values while the hydrogen isotope composition remains intact.

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### 1. Introduction

Unlike sedimentary carbonate deposits, diagenetic alteration is relatively rarely detected in speleothems (cave-hosted carbonate deposits), as burial-related temperature elevation and influx of exotic fluids are not characteristic in cave environments. Most studies investigating the effects of diagenesis on speleothems have dealt with the transformation of primary aragonite to calcite

associated with changes in the stable C and O isotope compositions and trace element contents (Martín-García et al., 2014; Zhang et al., 2014), or with infiltration of drip water into porous stalagmites, altering U–Th distribution and resulting in erroneous age dates (Scholz et al., 2014). Recrystallization in stalagmites has been studied by optical microscopy investigations that defined the main textural types and determined their evolution (Frisia, 1996; Frisia et al., 2000, Frisia and Borsato, 2010). Ostwald ripening has been proposed (Frisia and Borsato, 2010) as a responsible mechanism for crystal-size coarsening, although purely on the basis of optical microscopy characteristics. Besides altering the carbonate's stable isotope and trace element compositions, diagenetic alteration and

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recrystallization may influence the isotopic compositions of inclusion-hosted water whose investigations became one of the most promisingly developing fields in speleothem research in the last decade (Vanhof et al., 2006; van Breukelen et al., 2008; Dublyansky and Spötl, 2009; Griffiths et al., 2010; Wainer et al., 2011; Rowe et al., 2012; Arienzo et al., 2013; Ayalon et al., 2013; Affolter et al., 2014). The stable H and O isotope ratios of inclusion-hosted water are thought to be preserved after the inclusion entrapment in speleothems (Harmon and Schwarcz, 1981; Yonge, 1982), as they rarely suffer late-stage alterations and isotope exchange at usual cave temperatures is negligible. In recent years the number of studies that presented inclusion-water compositions in agreement with expected values increased significantly, with limitations, however, in paleotemperature calculations (Wainer et al., 2011; Rowe et al., 2012). In this paper a set of speleothem deposits, including stalagmites and flowstones, with coupled  $\delta D$ – $\delta^{18}O$  (inclusion water) values were studied by optical microscopy, powder X-Ray diffraction (XRD) and transmission electron microscopy (TEM), in order to determine whether the observed oxygen isotopic shifts are related to textural, mineralogical or structural changes. This is the first study that reports speleothem crystallinity changes well beyond the resolution of optical microscopy analysis and demonstrates that these changes may be associated with alteration of stable oxygen-isotope composition of water trapped in fluid inclusions.

## 2. Samples and analytical methods

The studied speleothems formed in closed cave environments with constant ambient temperatures of around  $10 \pm 0.5$  °C. After collection the samples were stored at room temperature (around 20 °C). A ~2 cm high, rather irregular stalagmite “hump” formed on the ground created in 1995, was collected in 2013 in the Csodabogyós (“CSB”) Cave (W Hungary). The drip water’s isotopic compositions are  $\delta D = -71.9 \pm 1.1\text{‰}$  and  $\delta^{18}O = -10.35 \pm 0.22\text{‰}$ ,  $n = 27$ . Two stalagmites of about 5 and 7 cm were collected from the Nehézút room (“NU”) of the Baradla Cave (NE Hungary) where the drip water’s compositions are  $\delta D = -66.2 \pm 1.3\text{‰}$  and  $\delta^{18}O = -9.52 \pm 0.18\text{‰}$ ,  $n = 8$ . The third site is the travertine-like flowstone deposit formed within the Béke Cave (Nagy-tufa, BNT) where two cores were drilled. One of the cores yielded meaningful U–Th dates (Shen et al., 2012) and was selected for detailed studies. The local drip water’s isotopic compositions are  $\delta D = -66.3 \pm 0.9\text{‰}$  and  $\delta^{18}O = -9.47 \pm 0.17\text{‰}$ ,  $n = 19$ . Stream water at the deposit had practically identical isotope compositions ( $\delta D = -65.7 \pm 1.3\text{‰}$  and  $\delta^{18}O = -9.43 \pm 0.12\text{‰}$ ,  $n = 15$ ) during the dripwater sampling period in 2013 and 2014.

Age–depth relations were established for all the samples on the base of collection dates, information on the beginning of deposition, lamina counting, position of  $^{14}C$  “bomb peak” and U–Th dates. Detailed information on the locations, speleothems and dating methods are given in the Supplementary Material and in Demény et al. (2013).

Microscopic pictures were taken in crossed-polarised transmission light using a Nikon Eclipse E600 POL optical microscope. Thin sections polished on both sides were prepared with 0.3 mm thickness for fluid inclusion petrographic analyses using the optical microscope as above. For trace element concentration measurement about 10 mg of powdered sample was weighed into high purity 15 mL polypropylene centrifuge vials using an ultra-micro balance. The samples were dissolved in 12 mL 0.5 mol dm<sup>-3</sup> nitric acid (Suprapure grade, E. Merck, Darmstadt, Germany). The analysis was carried out using an Element 2 inductively coupled plasma sector field mass spectrometer (Thermo-Finnigan, Bremen, Germany). External calibration and internal standard solutions

were prepared from multi and single element ICP standard stock solutions (E. Merck, Darmstadt, Germany).

Samples for X-Ray diffraction (XRD) analyses were broken from the stalagmites and hand-powdered using an agate mortar and pestle in order to avoid structure distortion due to excessive grinding. XRD analysis was performed on a Philips PW-1730 diffractometer (PW-1820/00 goniometer) equipped with a graphite monochromator using Cu-K $\alpha$  radiation at 45 kV and 35 mA with 1° divergence slit and 1° receiving slit. Scanning rate was 0.05° 2 $\theta$  per minute from 3° to 70°. Calcite (–104) reflection was also measured at 0.01° 2 $\theta$ /s scanning speed (0.02° 2 $\theta$  step size, 2 s scan time) in the 27.5–31.0° 2 $\theta$  range. Domain size was calculated using the well-known Scherrer equation (Scherrer, 1918) with Philips X’pert software from the parameters of the –104 peak with 0.01 width of standard profile. Based on replicate analyses, an average uncertainty of 25 Å can be attributed to the domain size data.

For transmission electron microscopy (TEM) study a few milligrams of the samples were crushed in ethanol and deposited onto a 3 mm lacey-carbon coated copper grid. Morphological and structural investigations of calcite samples were performed with a MORGAGNI 268D transmission electron microscope (100 kV accelerating voltage; W filament, top-entry; point-resolution = 0.5 nm).

Stable H and O isotope compositions of inclusion-hosted waters were determined by laser spectroscopic analyses. The method is based on the procedure described for fluorite-hosted water measurements (Czuppon et al., 2014) and modified for carbonate deposits (see Supplementary Material).

## 3. Results

### 3.1. Petrographic analyses

The textures of stalagmite samples are dominated by elongated columnar calcite with grain sizes of ~0.1–1 mm width and ~1–10 mm length (Supplementary Figs. S1 and S2). Mosaic texture was observed at the very base of the NU-1 stalagmite that was not sampled for isotope analyses. No systematic crystal-size change was observed within the individual stalagmites, starting from the surface at the top toward the inner parts. The textural characteristics of travertine-like flowstone are more variable, covering several texture types (elongated columnar calcite, isometric clear calcite with cm-scale grain-crystal size, small dendritic crystals, pisolite-like structures; Supplementary Fig. S4) with straight or wavy layering of the growth laminae.

The appearance of fluid inclusions in the stalagmites (NU-1, NU-2 and CSB) and in the tufa deposit (BNT-2) are very similar to those described by earlier studies, although with texture-related differences in the different deposits. Both liquid and air-filled inclusions (see Scheidegger et al., 2010) are present. In the followings only the water-filled inclusions will be described as these were analysed for their H<sub>2</sub>O contents. In the studied stalagmites columnar calcites contain predominantly large (up to 0.5 mm in length), strongly elongated, frequently spindle-shaped inclusions (Fig. 1A, B, E, G, H). The inclusions frequently show thorn- (Fig. 1F) or capillary-shaped (Fig. 1G, H) ends in the growth direction, similarly to the inclusion pictures presented by Meckler et al. (2015). Two-phase inclusions containing liquid bubble (Fig. 1A, B, C, E) can also be detected. The stalagmite of the Csodabogyós Cave (sample CSB) is very inclusion-rich with numerous large inclusions oriented parallel with the growth direction (Fig. 1G). The inclusion-rich layers are alternating with inclusion-free or -poor ones (Fig. 1H), with very small inclusions in the latter. Opposite to the columnar calcite, the mosaic textured calcite detected at the oldest part of NU-1 stalagmite contain very few inclusions (Fig. 1D). Considering the generally

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