Unusual internal structure of cm-sized coldwater calcite: Weichselian spars in former pools of the Zinnbergschacht Cave (Franconian Alb/SE Germany)

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Abstract: The investigation of the internal structure of calcite crystals is a new focus in speleothem science, especially in the range of crystallization temperatures close to 0°C. Recently found calcite spars from Zinnbergschacht Cave of the Franconian Alb (SE Germany) are ideal for multi-method investigation. The elongated calcites (up to 6 cm in length) with three to six lateral faces and basal triangular faces at the ends are observed in collapse-zones in the cave. ²³⁰Th/U-ages of 38.9 ka suggest formation during the periglacial Weichselian, between the Scandinavian and Alpine Glaciations. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the calcite spars vary from -11.18 to -16.11‰ V-PDB and from -4.78 to -6.13‰ V-PDB, respectively. The exceptionally low $\delta^{18}\text{O}$ values of these calcites appear to be due to precipitation in pools on ice. The values deviate considerably from those of conventional interglacial speleothems ($\delta^{18}\text{O} = -7.21$ to -7.55 ‰, $\delta^{13}\text{C} = -9.77$ to -10.86 ‰) and also from true Weichselian cryogenic calcites (composite spherulites and rhombohedral chains with $\delta^{18}\text{O} = -15.06$ to -18.04 ‰ and with $\delta^{13}\text{C} = -3.52$ to -4.13 ‰). The $\delta^{18}\text{O}$ values of the latter calcites is typical of cryogenesis of calcites with extensive oxygen isotope fractionation (preferred incorporation of ¹⁸O into the co-occurring ice). Thus, the $\delta^{18}\text{O}$ values of the calcites suggest cold conditions up to the beginning of cryogenesis. Cathodoluminescence (CL) and backscattered electrons (BSE) indicate the distribution of impurities within the calcite spars as pigmented triangles surrounded by clear calcite, with a higher density of the triangles in the outer areas. Three hierarchies of triangles can be distinguished by BSE, documenting a filigreed primary structure of the spars. Electron backscatter diffraction (EBSD) reveals a divergent orientation of the triangular subcrystals from the center to the outer corners of the calcites. Thus, their internal structure reflects an example of fascicular optic fibrous calcites (FOFC), frequently discussed in carbonate petrology.

Keywords: Weichselian, cryogenic calcites, fascicular optic fibrous calcite, electron backscatter diffraction, Franconian Alb

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INTRODUCTION

Composition and morphology of cave minerals are highly diverse due to variation in host rock and physicochemical conditions within the system (Hill & Forti, 1997). The last 20 years of research have primarily focused on calcite and aragonite stalagmites due to their potential as climate archives (e.g., Fairchild & Baker, 2012).

Due to the frequent occurrence of calcite mineralogy in speleothems, their crystallography and chemical

composition is of particular importance. The calcite crystallographic composition (Goldschmidt, 1913) and diversity (Onac, 1997) are well known. In calcitic speleothems, the most common crystal type is the columnar - so called *normal*, *length-fast*, *palisade calcite* (Folk & Assereto, 1976, Kendall & Broughton, 1978). Recently, Riechelmann et al. (2014) investigated speleothem calcite crystals precipitated on watchglass surfaces from various caves with calcareous and dolomitic host rock and correlated crystal morphology and Mg/Ca composition of the drip water.

In this pilot study, we present unusual, elongated calcite spars with a size of up to 6 cm from a recently discovered cave in the Jurassic dolomites of SE Germany. In addition to the abnormal morphology, the discussion focuses on the unusual internal structure of the crystals and their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. This research is important due to the possibility to compare the stable isotope values of these calcites with conventional interglacial speleothems, such as stalagmites, as well as cryogenic calcites, such as spherulitic components (Richter et al., 2013), which occur in the same cave.

A special type of spherulitic calcite components are composite spherulitic calcites shaped like braided hair ("Zopfsinter" sensu Erlemeyer et al., 1992 and "braided sinter" sensu Richter & Riechelmann, 2008). Due to the negative $\delta^{18}\text{O}$ values (up to -20‰ V-PDB), this characteristic particle type in former ice caves is a main type of coarse cryogenic calcites (Richter et al., 2013).

The results of this pilot study must be put in context with recent articles discussing cold water and cryogenic calcites (e.g. Žák et al., 2012, 2018; Richter et al., 2013). First, it was important to identify the different calcites as cryogenic crystals (strongly negative $\delta^{18}\text{O}$ values). Furthermore, considering the $^{230}\text{Th}/\text{U}$ -ages and the typical depth of the cryogenic calcites in caves, it was possible to reconstruct a minimum thickness of permafrost in former periglacial areas (Žák et al., 2012). It is further important to decipher the crystallization path of single crystals as an evidence for the process of cryogenesis. Here, according to preliminary $\delta^{18}\text{O}$ values, an increasing cryogenesis in calcitic fibers of spherulites could be demonstrated (Richter & Riechelmann, 2008). Additionally, cathodoluminescence (CL) spectrography often reveals an incorporation of rare earth elements, such as dysprosium and samarium, in the central parts of the cryocalcites (e.g. Richter et al., 2008), a possible effect of concentration due to melting of frozen soil above the cave.

CAVE SETTING AND SAMPLING LOCATIONS

Zinnbergschacht Cave (No. HFA-A 205 in the register of assessment) is located 40 km ENE of Nuremberg (Fig. 1), near the show cave Maximiliansgrotte, and 20 km SE of the famous Zoolithen Cave. Upper Jurassic dolomites (Franconian Dolomite) comprise the host rock of the cave area (Meyer, 1972). The dimension of Zinnbergschacht Cave is currently investigated by the speleogroup "*Höhle und Karst e.V. Nürnberg*".

Within the 400 m long cave, calcitic crystals and aggregates were found 30-60 m SE to SSE of the entrance (Fig. 2), approximately 40 m below surface. The (now closed) entrance is formed by a 9 m shaft, followed by mainly flat galleries.

The host rock near the entrance is pure dolomite, whereas the partly calcitized dolomites in deeper galleries contain centimeter to decimeter-sized white silicious concretions, which are well developed in the Canyon site (Fig. 2). Over 2 m of centimeter to meter-

Fig. 1. Setting of Zinnbergschacht Cave. Locations of known caves with cryogenic calcite of Weichselian age between the Scandinavian and Alpine Glacial Areas in Germany are indicated by 1 to 14 (completed after Richter et al., 2013 and 2018): 1) Riesenberg Cave; 2) Malachitdom Cave; 3) Apostel Cave; 4) Ostenberg Cave; 5) Sundern Cave; 6) Hüttenbläterschacht Cave; 7) Dechen Cave; 8) Heilenbecke Cave; 9) Herbstlabyrinth-Advent Cave System; 10) Canyon Cave; 11) Lehmschacht Cave; 12) Zoolithen Cave; 13) Emmerthal Cave; 14) Sommerleitschacht Cave.

sized blocks of the host rock with a reddish brown loamy matrix filled the gallery. These collapse breccias are well developed around two depressions (I and II in Fig. 2), which may have formed from the dissolution of carbonates beneath the cave as in the case of dolines or from melting cave ice during late/postglacial time as in the case of solls (see discussion).

The investigated calcites occur in the areas around the two depressions in association with the collapse breccias (mostly between blocks) (Fig. 2). Crystals from the three studied locations are characterized as follows: Loc. A - translucent elongated crystals and aggregates with a size of up to 5 cm in the Alter Sulzbacher (Figs. 3b, 4) - in some places translucent crystals with whitish translucent overgrowths (Figs. 3c, 4a, and 5b); Loc. B - whitish composite spherulitic calcites with a size of up to 3 cm in diameter in the Canyon (Fig. 5c); Loc. C - whitish elongated crystals (Fig. 5a) and aggregates with a size of up to 2 cm as well as whitish rhombohedral chains and composite spherulitic calcites with a size of up to 1 cm in the Petersdom. The genesis of these calcite speleothems (crystals and aggregates) seems to be very young (Upper Pleistocene to Holocene) as indicated by the lacking lithification of most speleothem particles found in association with broken blocks or on loamy sediments. According to published articles on cryogenic calcite genesis (e.g. Žák et al., 2012, 2018),

Fig. 2. Sampling locations (A-C) in Zinnbergschacht Cave.

Fig. 3. Views of location A (Alter Sulzbacher): a) overview; b) large aggregates of Weichselian calcites (arrow); c) aggregates of translucent calcites with whitish ends.

the crystals and aggregates crystallized in pools on ice. Subsequent to the melting of the ice, they accumulated at the bottom of the cave.

METHODS

Samples were cleaned in an ultrasonic bath in order to remove fine-grained clastic spelean sediments. Images of crystals and aggregates were taken using a Canon EOS 50 D. The morphology was further documented in detail using a high-resolution field

emission scanning electron microscope (HR-FESEM type LEO/ZEISS 1530 Gemini).

X-ray diffraction of the different carbonate phases was performed using a Pananalytical MPD diffractometer. Ground samples were measured in a diffraction angle range of $26-38^\circ$ (2θ) using quartz powder as an internal standard. Each $d_{(104)}$ value of the rhombohedral carbonates was identified to determine the Ca/Mg distribution (Füchtbauer & Richter, 1988).

Cathodoluminescence (CL) investigations utilized a "hot-cathode" CL microscope HC1-LM (Neuser et al., 1995). CL spectra were recorded with a digitally controlled EG&G spectrograph attached to a peltier cooled PIXIS CCD camera by Princeton Instruments (for details, see Hoffmann et al., 2016).

Fluorescence microscopy was applied using a Leica DM4500P microscope equipped with a mercury short-arc reflector lamp, and coupled with a Leica EL6000 compact light source (Hoffmann et al., 2016).

For EBSD analyses, thin sections were chemo-mechanically etched with colloidal silica on an atomic scale (Massonne & Neuser, 2005) and coated by a thin carbon layer. All coated thin sections were analyzed using backscattered-electrons (BSE) in high contrast mode. Crystallographic orientation of the calcite spars was determined by EBSD (Nordlys, OXFORD, Instruments). The data acquisition and analysis was performed using the software packages AzTec and Channel5 by Oxford Instruments. EBSD analyses were performed at a beam energy of 20 kV, an aperture of 60 μm , a working distance of 25 mm, and a tilt angle of 70° .

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the carbonates was determined using a delta 5 mass spectrometer (Finnigan MAT) and calibrated with V-PDB (Standards: CO-1 and CO-8). The 1σ -reproducibility of the measurements is 0.04‰ V-PDB for $\delta^{13}\text{C}$, and 0.08‰ V-PDB for $\delta^{18}\text{O}$.

Samples for $^{230}\text{Th}/\text{U}$ -dating were prepared and analysed at the Max Planck Institute for Chemistry, Mainz. Chemical separation of U and Th isotopes was performed as described by Scholz & Hoffmann (2008) and Yang et al. (2015). Uranium and Th isotopes were analysed using a Nu Plasma MC-ICP-MS. Analytical details are described by Obert et al. (2016). Details about the calibration of the mixed U-Th spike are given by Gibert et al. (2016). To account for the potential effects of detrital contamination, all ages

Fig. 4. Translucent calcitic aggregates of location A: a) longitudinal view of a cm-sized calcite spar with milky ends (red arrows) and smaller crystals at the lower right (blue arrow); b) view of a cm-sized calcite spar with triangular end faces (green arrow) and filling of small aggregates within the hollow spars to the right (black arrow).

Fig. 5. Whitish calcitic speleothem components: a) elongated calcites of location C; b) whitish spherulitic overgrowths on translucent calcites of location A; c) whitish spherulitic calcite of location B.

were corrected assuming an average upper continental crust $^{232}\text{Th}/^{238}\text{U}$ weight ratio of 3.8 for the detritus and ^{230}Th , ^{234}U , and ^{238}U in secular equilibrium. All activity ratios were calculated using the half-lives from Cheng et al. (2000), and all age are reported at the 2σ -level.

RESULTS

Here we focus on the elongated calcite spars, whereas observations of other speleothem components are only marginally presented. Such considerations are important for the subchapters concerning crystal morphology, x-ray diffraction and stable isotope values.

Crystal Morphology

The millimeter- to centimeter-sized calcites of location A and, less frequently, location C are mostly parts of aggregates, whereas single crystals are more rare (Figs. 4 and 5a). The crystallographic characteristics and the position of the transect for thin section analyses are shown in Fig. 6. The elongated crystals contain three or six triangular shaped side faces with basal triangular faces at the end (Figs. 4-7), often containing one large triangular channel. The side faces are stepped, whereas basal faces are rough to fragmentary (Fig. 4). Due to preferential crystallization at the edges between side and basal faces, the diameter of the elongated crystals is larger at the ends than in the middle portion and often results in funnel-like ends of the crystals (Fig. 4b).

Notably, elongated crystals with completely intact faces are rare. In general, crystals are of filigreed composition with indications of high porosity. Thus, degradation of these crystals is widespread, and small movements can result in re-deposition of skeletal crystals (Fig. 3c).

Fig. 6. Sketch of hollow cryogenic cm-sized calcite spar with position of transect of thin section for OM, CL, BSE and EBSD analyses.

The other components of the calcites are similar to other cryogenic calcites found in several German caves (e.g. Richter et al., 2013). Composite spherulitic components (dominantly at location B, Fig. 5c, rare at location C) are composed of spheroidal aggregates of fibrous calcites, with steep rhombohedral faces at the end. Rhombohedral chains are rare and were only found at location C.

Coloration seems to be important with regard to the formation of the speleothem components. The translucent spars are sometimes more whitish (richer in gas/fluid inclusions) at the crystal ends only, and some crystals have white coatings of spherulitic calcites. We conclude that the white calcites must be younger than the translucent crystals, and the white ends of the crystals, the white coatings of spherulitic calcites as well as the white spherulitic components must be younger than the translucent crystals.

X-ray diffraction (XRD)

The $d_{(104)}$ values of the investigated calcite spars vary between 3.031 and 3.028 Å ($n = 5$) indicating a MgCO_3 content of 1.3 to 2.4 mol-% in the lattice. This non-stoichiometric composition is not surprising because of the dolomitic host rock ($d_{(104)} = 2.888 - 2.905$ Å; $n = 10$). For comparison, other calcites ($n = 5$ for each type) were also analysed. Spherulitic calcites (location B) produced $d_{(104)}$ - values between 3.023 and 3.021 Å (4.0 to 4.7 mol-% MgCO_3), whereas dolomite host rock calcites were nearly stoichiometric (3.035 - 3.032 Å; <0.1 to 1.0 mol-% MgCO_3).

Cathodoluminescence

The calcite spars show an intrinsic CL as most calcitic speleothems (Richter et al. 2002). This blue CL colour is indicative of very low (or no) Mn^{2+} content in the calcite lattice (<10 ppm according to PIXE (Proton Induced X-ray Emission) measurements) (Habermann et al., 1998, 1999). However, it is possible to distinguish

between dark blue and pale blue sub-crystal areas within the CL pattern of the calcites (Fig. 8a). The dark blue CL corresponds to pure calcite, whereas the areas showing a lighter blue CL are rich in sub-microscopical pigmentation, which can defect the crystal lattice and result in the lighter coloration (Richter et al. 2002).

Furthermore, the CL-distribution of dark and pale blue areas is common throughout the sample type. Pale blue triangular areas of sub-crystals are generally rich in inclusions and are joined by triangular shaped, dark transparent blue calcite (Figs. 7 and 8). Mn^{2+} -activated calcite is visible only in the very thin zones of the cm-sized crystals due to the cleavage planes (Fig. 7b).

Backscattered electron (BSE) imaging

High resolution BSE-images acquired with the HR-FESEM display dark and bright calcite phases (Figs. 8b, c and 9).

Thin sections cut perpendicular to the c-axis of the elongated calcites reveal a complex, dark framework of triangular sub-crystals (2–20 μm in size). The space between the dark portions is filled by bright calcite. The darker areas show dark triangles and laths in transmitted light as well as light domains in BSE. The translucent areas mostly display light areas in transmitted light, and dark triangles and laths in BSE (compare Table 1). Brighter areas in BSE are more likely to be composed of near-stoichiometric $CaCO_3$ with higher average atomic masses (mainly Ca), whereas darker areas in BSE correspond to lower average atomic masses (Hoffmann et al., 2016). The reason for lower average atomic masses in calcites may be organic material or small solid and fluid inclusions.

There are three hierarchies of crystal habit concerning the cm-sized crystals: 1. Triangles with lateral faces up to 500 μm ; 2. triangles with lateral faces between 100 and 10 μm ; 3. triangles with lateral faces below 10 μm (Figs. 6, 8, and 9).

Fig. 7. Micrographs of a thin section perpendicular to an elongated calcite spar: a) optical microscopy (yellow rectangle indicates location of Fig. 8, orange rectangle indicates location of Fig. 9); b) cathodoluminescence showing dark blue calcite with bright orange microcracks filled with late calcite, c and d) EBSD map and Pole plot (Schmidt net - lower hemisphere) illustrating the crystallographic orientation of the c-axis {001} of the large crystal, divergence angle of c-axes from red to blue positions is 9°, pink areas in c not defined.

Fluorescence microscopy

The fluorescence images of thin sections cut perpendicular to the c-axis of the calcite spars show a complex framework of triangular figures resembling the patterns seen in CL and BSE. Pigmented areas are lighter green in fluorescence, while translucent areas are characterized by lower fluorescence. According to Wanamaker et al. (2009) and Hoffmann et al. (2016), the brighter portions reflect areas, which incorporate organic matter or crystal defects (such as inclusions) within the crystals.

Fig. 8. Detail of Fig. 7 for comparison of CL (a), OM (b) and BSE (c). Large triangular area corresponds to red delineated area in Fig. 9a (turned by 90°). Pale blue CL of the subcrystals corresponds to darker areas in transmitted light and to mainly pale areas in BSE.

Table 1. Comparison of physical characteristics of the studied calcite crystals. OM = optical microscopy, CL = Cathodoluminescence, BSE = backscattered electron images.

origin	OM	CL	BSE
primary	dark, inclusion-rich	pale blue, cloudy	dark triangles and laths, light domains
secondary	light, translucent	dark blue, intrinsic	mostly light domains, dark triangles and laths

Fig. 9. Detail BSE image of subcrystals in the calcite spar (Fig. 7); a) overview with areas marked for higher magnification; b) area marked yellow; c) area marked green; d) area marked blue (area of e marked black); e) area marked in d - filigree darker structures within the calcite are visible at high magnification; f) detail of e.

Electron backscatter diffraction (EBSD) mapping

The crystallographic orientation of the calcite spars was studied in a section perpendicular to the long axis of the crystal. The orientation of the c-axis in the center deviates from the orientation of the outermost edges by 9°. To visualize the directions and deviations of the c-axes, a rainbow color code was applied, which ranges from red to blue from the center towards the edges of the calcite (Figs. 7c and d). The resulting pattern is a central area with three regions towards the side planes of the crystal showing a similar 0° orientation of the c-axis (red). The deviation angle increases towards the corners of the triangle and gains a maximum value of 9° (blue). EBSD mapping reveals a divergent orientation of the c-axes within the calcite crystal. The central point of the grain is more or less a single crystal, with the strongest divergence observed in the most distal points from the center.

δ¹³C and δ¹⁸O values

Mass spectrometric analyses of the translucent cm-sized calcite spars show δ¹³C values between -4.78 and -6.13‰, and δ¹⁸O values ranging from -11.18 and -16.11‰ (Fig. 10). The δ¹⁸O values of the calcites correspond to the largest values of cryogenic calcites from Zoolithen Cave (10 km NW of Zinnbergschacht Cave), but are lower than the values of conventional stalagmites (Fig. 10). Mixed calcitic components with translucent cores (cm-sized calcites and parts of them) and whitish overgrowths (Fig. 5b) show δ¹³C (-4.42 to -4.79‰) and δ¹⁸O values (-15.51 to -16.26‰) plotting at one end member of the calcite spars, with negative δ¹⁸O and more positive δ¹³C values. The whitish rhomboedral chains of locality C exhibit more negative δ¹⁸O values (-17.69 to -18.04‰) and more positive δ¹³C values (-3.52 to -3.58‰) compared to the composition of the investigated calcites. The

composite spherulites of locality B are characterized by $\delta^{18}\text{O}$ values from -15.06 to -15.94‰ and $\delta^{13}\text{C}$ -values from -3.59 to -4.13‰ (Fig. 10).

$^{230}\text{Th}/\text{U}$ -dating

Ages between 33.4 and 38.9 ka were determined by $^{230}\text{Th}/\text{U}$ -dating, thus confirming a growth period of approximately 5.5 ka during the Late Weichselian (Table 2). Since this time span is characterized by a succession of several stadial and interstadial periods (Fig. 11), it is likely that several cryogenic calcite generations developed and are present within the system today. This is particularly important for the oldest translucent crystals (38.9 ka), which may contain many growth phases.

DISCUSSION

The character of the elongated calcite spars of Zinnbergschacht Cave is similar to the “type E” carbonate (sample I), which precipitated from dolomite host rocks in the monitored Zoolithen Cave in close proximity (20 km north, Riechelmann et al., 2014). The development of these deposits is typical for drip waters with high Mg/Ca ratios.

The stepped and rough faces of the calcite spars coincide with the composition of the contained sub-crystals. The internal structure of the cm-sized spars is dominated by crystals with prismatic or near-prismatic side faces. This distribution is illustrated by pigmented fibers with relatively fast crystallization

Fig. 10. Comparison of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of coarse grained cryogenic calcites of Zinnbergschacht Cave with the composition of the host rock (Franconian Dolomite) and normal interglacial speleothems (e.g. stalagmites, stalactites, flowstones) of non-dated Quaternary age from the same cave; += cm-sized calcite spars with whitish overgrowths from Loc. A, pale brown area indicates the position of Holocene stalagmites of Zoolithen Cave according to Wurth (2002), brown area = Franconian Dolomite around Zoolithen Cave (Richter et al., 2014).

Table 2. $^{230}\text{Th}/\text{U}$ -data of calcite crystals from the three studied locations

No.	Notation	^{238}U [μg/g]	^{232}Th [ng/g]	$(^{234}\text{U}/^{238}\text{U})$	$(^{230}\text{Th}/^{238}\text{Th})$	$(^{230}\text{Th}/^{232}\text{Th})$	Age uncorrected [ka]	Age corrected [ka]
1	cm-sized calcite loc. A Alter Sulzbacher	0.1965±0.0012	5.327±0.051	2.6758±0.0079	0.8337±0.0046	94.01±0.85	39.16±0.28	38.89±0.31
2	spherulitic calcite loc. B Canyon	0.5669±0.0032	9.159±0.090	2.5973±0.0054	0.7078±0.0036	133.9±1.3	33.61±0.21	33.44±0.22
3	rhombohedra chain loc. C Petersdom	0.1846±0.0012	23.54±0.23	3.817±0.011	1.206±0.013	28.90±0.38	39.52±0.51	38.63±0.79

and clear cement in between. The pattern type of the sub-crystal is very systematic, as documented in BSE images. The center of the crystals is more transparent than the outer portions, with differential rates of crystallization resulting in the funnel-type ends of the elongated crystals. The different rates of

crystallization seem to be causal for a more prismatic or near prismatic shape of the fibers, with only three triangular side faces in the central parts of the calcites, and very steep rhombohedra with six elongated side faces towards the exterior. The microscopic features of the sub-crystals are summarized in Table 1.

Fig. 11. Relation of measured cryogenic calcite $^{230}\text{Th}/\text{U}$ -ages (Table 1) to $\delta^{18}\text{O}$ -values of the NGRIP ice core (North Greenland Ice Core Project members 2004). 1-25 = interstadials of Weichselian ice age (e.g. Wolff et al., 2010). Identically labelled stadials follow interstadials. Permafrost of periods (thick lines = continuous, thin lines = discontinuous, dash lines = assumed) in Middle Europe after Liedtke (1993) and Vandenberghe and Pissart (1993) - see also the newer review by Vandenberghe et al. (2014). Main distribution of coarse grained cryogenic calcites according to Žák et al. (2012) and Richter et al. (2018). Remarks: Some cryogenic cave carbonate ages reported by Žák et al. (2012) fit to the older part of the Holocene (e.g. Na Javorce Cave, Bohemian Karst, Czech Republic). It is also probable that permafrost survived at depth until the Late Holocene in some parts of Europe. Such relic permafrost survives deep seated in NE Poland till this day (Szewczyk & Nawrocki, 2011).

The distribution of the sub-crystals in the calcite spars becomes evident by EBSD mapping. From the middle of the elongated crystals towards the edges, an increasingly three-radial divergence of the sub-crystals is observed. For this reason, thin sections parallel to the c-axis show an undulose extinction of fascicular-optic fibrous calcite (FOFC, Kendall, 1985) with crossed polars. The cause of this pattern is currently unknown. The Mg-content as an exclusive cause seems unlikely because of stoichiometric calcites found in the Malachitdom Cave of NW Germany, which show similar FOFC patterns (Richter & Riechermann, 2008). However, two pools in Zoolithen Cave (20 km north) have produced comparable Mg-containing calcites, but with a different orientation of sub-crystals (FOFC versus radiaxial fibrous calcite (RFC) - Richter et al., 2015). In the latter case, the only difference between the two rimstone pools is the saturation index of the drip water. In the pool containing RFC, the saturation index (SI) is 0.87, while the pool containing FOFC has a SI of 0.54. The change in the textural character of calcites during growth is another aspect, with the rate of crystallization probably being an important factor. The crystallization of calcites begins with very steep rhombohedral faces and a fast growth rate, while the final growth phases exhibit less steep rhombohedra and a slower growth rate. Further work is needed to explain this phenomenon. In summary, there are no hints for an original crystallization of hydrated carbonate phases and later recrystallization to calcite. Due to the typical habit of calcite in dolomite caves, we consider the observed features as primary.

The $\delta^{18}\text{O}$ values of the calcites are more negative than those of Holocene stalagmites due to cold

water conditions up to the start of freezing of the pool water with the corresponding oxygen isotope fractionation. During freezing, the co-precipitated calcites expose more negative $\delta^{18}\text{O}$ values (Souchez & Jouzel, 1984; Žák et al., 2012). There is no exact boundary between coldwater calcite and cryogenic calcite within the cm-sized calcites. Thus, we assume a very slow transition during crystallization. The mixed speleothem components with translucent cores and whitish spherulitic overgrowths show more negative $\delta^{18}\text{O}$ values than the cm-sized calcites with a translucent composition. This is due to the final stage of crystallization of fibrous calcites in freezing water pools. In summary, the speleothem components of locality A (Alter Sulzbacher) formed within in a pool containing ice during interstadial 8 during the Weichselian (Fig. 11). Žák et al. (2012) assume several intervals of growth and melting of permafrost (up 100 m thick) during the periglacial time span between the Scandinavian and Alpine glacial areas (10-70 ka before present). In this context, it is possible to form pools on ice in caves that subsequently froze and crystallize coarse grained cryogenic calcites. Different pools are assumed for the cryogenic calcites of localities A to C within Zinnbergschacht Cave due to the various types and ages of the calcite grains (A/C versus B - see Table 2).

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