Radiaxial-fibrous and fascicular-optic Mg-calcitic cave cements: a characterization using electron backscattered diffraction (EBSD)

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Abstract: Electron backscattered diffraction (EBSD) applied to crystal fabric research in speleothems aids in our understanding of the origin of those fabrics. A significant advantage of this approach is the three dimensional data set of crystal c-axes. Here, we show a rare case of both convergent (radiaxial-fibrous) and divergent (fascicular-optic) orientations of the c-axes in pool calcites. The seemingly defective structure of the calcite lattice resulting in radiaxial-fibrous crystal orientations is probably caused by differential incorporation of Mg during crystal growth. The observation that radiaxial-fibrous and fascicular-optic fabrics co-exist in the same pool environment is remarkable and documents the complexity of the system.

Keywords: Mg-calcite; cave cements; radiaxial-fibrous; fascicular-optic; EBSD

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INTRODUCTION

Most calcitic speleothems are characterized by a crystal structure of isometric (equicrystalline) grains or oblong crystals (columnar to fibrous) with different length in the growth direction (Frisia et al., 2000; Railsback, 2000; Self & Hill, 2003; Frisia & Borsato, 2010). According to Folk & Assereto (1976) two subtypes of calcites with oblong crystals are distinguished: Such with (i) the c-axis oriented along the longitudinal extent of the calcite (length-fast) and such with (ii) the c-axis approximately perpendicular to the longitudinal extension of the calcite (length-slow; a rare subtype). For more detail, the reader is referred to Onac (1997) for a comprehensive review on the crystal types and morphologies of carbonate and sulfate minerals.

Given that some of the calcite crystals building speleothems display a radial fibrous texture (type 2.1.1 or 2.1.2 in Self & Hill, 2003) and show strong undulatory extinction, a quantitative understanding of the spatial c-axis orientation in the crystals can be of particular importance. For an accurate characterization of the oblong calcites with different undulatory extinction the reader is referred to Kendall (1985) who established a classification for marine cements (Fig. 1). Accordingly, three cement types require attention in this context: (i) such with divergent c-axes in growth direction (“fascicular-optic”), (ii) such with converging c-axes in growth direction (“radiaxial-fibrous”) and (iii) such with uniform c-axes (“radial-fibrous”). Following this classification, Neuser & Richter (2007) have presented oblong calcite crystals with converging and diverging c-axes in growth directions within stalagmites from caves located in dolostone host rock lithologies. Data obtained at these sites clearly documented that the Mg content of the drip waters is significant (Richter et al., 2011).

Orientation of c-axes in oblong calcites

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<tr>
<th>Orientation of c-axes in oblong calcites</th>
<th>undulose extinction</th>
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<tr>
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<td>convex cleavage</td>
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<td>RADIAXIAL-FIBROUS</td>
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Fig. 1. Types of oblong calcite crystals according to internal orientation of the c-axis (modified after Kendall, 1985). Arrows: c-axis orientation; solid lines: cleavage cracks; dashed lines: subcrystal boundaries.
In this study, two cave cements with different c-axis orientations in calcites from subaqueous environments (pools) of Zoolithen Cave (Germany) are presented and discussed in the context of their environment and crystallography.

CAVE SETTING AND SAMPLE LOCATIONS

The calcite samples were taken from rimstone pools of Zoolithen Cave, Germany, a cave being mainly known for its fossil vertebrate remnants (Heller, 1972). We only collected 6 samples due to the protection status of the cave. The cave is located in the Upper Jurassic Franconian dolostone (Frankendolomit) at Burggailenreuth (E Forchheim; Fig. 2A) above the Wiesent Valley, and exhibits a labyrinth shape with many lixiviations (most recent cave survey: Dreyer, 2000).

The entrance level of the Zoolithen Cave (Kataster-Nr. D 109) is located 455 m above sea level (the Wiesent Valley is 310 m above sea level). The mean temperature in the cave was previously documented in Tietz (1988) as 7.5°C for the 1977/78 period, and by the Bochum Geology Group as 8-9°C since 2010. The two sampled rimstone pools (Fig. 2B) are found in the central part of the cave.

Location 1 (Zaunikhalle):

In Zaunikhalle Room the largest rimstone pool extends NNE - SSW (5.3 m below the entrance level, length = 10.3 m, maximum width = 3.2 m, maximum depth = 0.88 m; Fig. 3A). The black color of the rimstone is likely due to soot from torch activities carried out during the paleontological excavations by Esper from 1770 to 1790 (see Heller, 1972). Furthermore, recent construction (wood-piles for visitor paths) has affected the natural conditions of the Zaunikhalle at least temporarily.

Location 2 (Windspalte):

In Windspalte Room, 19 m below the cave entrance next to the visitor’s path, between Zaunikhalle and Löwengrube, a second rimstone pool (now dry) was sampled (10 m below the entrance level, length = 1.7 m, width = 1.4 m, maximum depth of the now empty basin = 0.35 m; Fig. 3B). This locality 2 corresponds to the extraction point of stalagmite ZOO2 studied at high-resolution by Wurth (2002).

ANALYTICAL WORK

CONVENTIONAL METHODS

For documentation, the outer contours of the filigreed cements have been cleaned in an ultrasonic bath and afterwards been sputtered with gold to prevent charging in a high-resolution field emission scanning electron microscope (HR-FESEM) type LEO/ZEISS 1530 Gemini.

Polished thin sections were prepared to obtain first information concerning the internal structures of the cement crystals using a polarizing microscope.

The mineral compositions of the carbonate phases were obtained by X-ray diffraction (XRD) using a pananalytical MPD diffractometer equipped with a copper tube, 0.5° divergent and diffracted beam, 0.04 rad soller slits, and a secondary graphite monochromator as documented by Mioa et al. (2009). Methodically ground samples with quartz powder as internal standard have been measured by a diffraction angle range of 26-38° (2θ), identifying each d_{104} value of the rhombohedral carbonates in terms of their Ca/Mg distribution (Füchtbauer & Richter, 1988).

Carbon and oxygen isotopic compositions of the carbonates were determined with a delta S mass spectrometer (Finnigan MAT) and calibrated against V-PDB (standards: CO-1 and CO-8). The
The smallest calcite crystals could be measured at a resolution of at least 100 points.

The scanned crystals were color-coded to better visualize their orientations, where the colors indicate angular deviation within crystal bundles. In addition, the crystal axes were plotted in a Schmidt net (lower hemisphere).

**SAMPLE MATERIAL**

The sample material was taken from localities with similar cave waters. The Mg/Ca weight ratio of the recent water is nearly identical (0.88 versus 0.83), but the saturation index of the dripwater in the rimstone pool of Windspalte is significantly higher than that of Zaunikhalle (0.87 versus 0.54).

The studied rimstone pools are characterized by up to 5 cm (Loc. 2) and 50 cm (Loc. 1) thick calcitic cement crusts with a highly porous filigreed structure and small (<1 mm to 2 cm), leaf-like individual elements of calcite crystal bundles. Macroscopically, the thickest crusts of Zaunikhalle (Loc. 1) resemble subaquatic coralloids described and illustrated by Hill & Forti (1997).

The sampled pool cements of Zaunikhalle reflect a Holocene to subrecent age because in thin section only a thin layer of clear calcite crystals is observed on the black crusts. U/Th dating of the crust yielded a corrected age of 5.7 ± 4.0 ka. The imprecision was due to high proportion of $^{232}$Th (1.36 ng/g) and low amounts of $^{238}$U (0.03051 µg/g). The high Th concentrations are probably due to the presence of clay-sized insoluble components.

The calcitic cement crusts taken from the chamber wall of Windspalte correspond to a speleothem crust level of equal crystal formation in ZOO2 (Fig. 4), which according to U-Th datings (Fig. 4) were younger than...
13 ka and older than 10 ka and probably correspond to the period of Younger Dryas (12.6 - 11.6 ka BP). Under a similar calcite layer at the bottom of the dry rimstone pool a <3 cm thin debris deposit is present (crusts, calcitic crystal bundles of the same type as in the rimstone pool of Zaunikhalle, fragments of flowstone, bones, and siliciclastic detritus all of which had fallen to the floor and were not collected in situ).

According to XRD-analyses the crystal crusts are composed of ellipsoidal shaped crystal aggregates of Loc. 2 show a botryoidal shape (Fig. 7C), and the fibers have less steep rhombohedral faces at their tips (Fig. 7D).

The fibers from both locations exhibit undulatory extinction, a feature that is particularly pronounced in the larger fibers of rimstone pool 2. In order to quantify the systematic change in lattice orientation of the calcite fibers, electron backscatter diffraction (EBSD) was applied.

**DATA PRESENTATION OF ELECTRON BACKSCATTERED DIFFRACTION**

The section perpendicular to the ellipsoidal (Loc. 1) or botryoidal (Loc. 2) shape of the bundles reveals a concentric color coding, were the red color indicates the strongest deviation from the central phase (blue) of the bundle (Fig. 8A/B and D/E). The result is a circular bundle-shaped orientation of the fibers. In sections parallel to the length of the bundle (Fig. 8C/F), the EBSD analysis reveals a divergent c-axis orientation in single fibers of Zaunikhalle calcites (Loc. 1), while the individual fibers of Windspalte calcites (Loc. 2) are characterized by a converging c-axis orientation.

The measured maximum angle of convergence of a fiber is 15° while the angle of divergence of a fiber achieves a maximum of 7°. As documented in Fig. 8B and D, the internal bundle-like c-axis orientation is three-dimensional as exemplified for individual fibers.

**INTERPRETATION AND DISCUSSION**

The filigreed structured calcite crusts of both rimstone pools are made up of a multitude of fiber bundles, which in turn are made of sub-individual calcite fibers. In the classification scheme of Maltsev (1996, cited in Onac, 1997), this structure corresponds to the “second-order individuals.” This is accomplished by splitting the end of the calcites at the end of growth (especially in the bundles of the speleothems of Loc. 1).

Considering extensive literature the descriptions and classifications by Onac (1997) primarily refer to the calcite shape and the formation of the crystal surfaces. But as the crystals of the rimstone pools of Zoolithen Cave revealed an undulatory extinction, the EBSD method was applied for accurate quantification of the crystal lattice orientation. Obviously, the different patterns - divergent c-axis in the calcite fibers of Zaunikhalle pool, versus converging c-axis in the calcite fibers of Windspalte pool - requires attention.

Following Füchtbauer & Richter (1975), an undulatory extinction in carbonate crystals is primarily due to their spatially heterogeneous chemical composition (Mg in calcite, excess Fe and Ca in dolomite) and due to the frequency distribution and type of solid and fluid inclusions (especially non-carbonatic doping) or secondarily to epitactic displacement of recent mineral phases with undulatory extinction. Given that the calcites from the rimstone pools of Zoolithen Cave are virtually free of inclusions and evidence of epitactic
recrystallization of a precursor mineral is missing, the third option, i.e. the spatially heterogeneous chemical composition offers itself as the most likely reason for the formation of undulatory extinction in calcite. This notion is consistent with the variable 4-6 mol% MgCO\(_3\) in the calcite of the rimstone pools. The divergent c-axis orientation in the calcite fibers of Zaunikhalle, however, is in contrast to the converging c-axis orientation in the calcite fibers of Windspalte. This contrasting pattern cannot be explained by Mg incorporation as both calcite fabrics have identical Mg contents. According to previous EBSD work by Richter & Riechelmann (2008), stoichiometrically composed calcite fibers of cryogenical precipitates of the Malachitdom near Brilon equally reveal divergent c-axis orientation. Given these contrasting observations, other potential mechanisms require attention.

An alternative mechanism leading to diverging and converging crystal c-axes in the same precipitation environment might include the molarity of the pool.
waters. Evidence for this is based on ongoing cave monitoring. First data sets suggest, that the saturation index of the drip water in the rimstone pool of Windspalte is significantly higher than that of Zaunikhalle (0.87 versus 0.54 - SI calcite), a fact, that is likely to affect the growth rate. This may also explain the moderately higher carbon and oxygen isotope values of Windspalte calcites compared to Zaunikhalle calcites (see Fig. 5). Given & Wilkinson (1985) suggest a stronger saturation and/or increased fluid flow to explain oblong calcite crystals, yet this is still no explanation of divergent versus convergent c-axis orientation as observed here.

A first possible line of circumstantial evidence for the mechanisms causing undulatory extinction of carbonate crystal textures comes from plain-light microscopy. After determination of the general c-axis orientation in a calcite fiber using a compensator tube slot, or taking into account the orientation of the curved cleavage cracks, the observed extinction under crossed polarizers shifts to the opposite direction at converging c-axes (see Richter et al., 2011) during rotation of the fiber in the clockwise direction. The limitation of this approach is that data obtained represents two-dimensional observations only. This is where the here applied EBSD method provides three-dimensional information.

In sections perpendicularly to the long fiber orientation, the color coding indicates a circular pattern in three-dimensional convergence and divergence and a more linear pattern in two-dimensional convergence and divergence. Regarding the precipitates in the rimstone pool of Zoolithen Cave, EBSD analyses of the sample from Zaunikhalle displayed a three-dimensional divergence, while the Windspalte sample exhibited a three-dimensional convergence. A filigreed structure of the calcitic cements of the rimstone pools, such as those presented here, is rather common in caves (e.g., Meyer & Dorsten, 2009; Railsback, 2000). According to Frisia & Borsato (2010) this is indicative of dry and instable conditions during dripstone growth. The structure of speleothems from pools of Zoolithen Cave is quite dendritic, but the crystals do not show skeletal shape in a crystallographic sense. The above mentioned authors did not respond to a potential undulosity of the crystals in the dendritic fabric.

At present, speleogroups from Bochum and Mainz (Germany) are working together on stalagmites and pool calcites of Zoolithen Cave in combination with laboratory experiments to find more clues to convergent/divergent crystal growth. Preliminary results concerning mineralization in water films suggest a predominance of stalagmite layers with convergent crystal structure within several stalagmites of caves with dolomitic host rocks (Niggemann &
Richter, 2006, Wassenburg et al., 2012). Currently performed laboratory experiments using solutions of different Mg/Ca ratio suggest a relationship of crystal nucleation to the respective crystal faces of calcite (Schreuer, oral comm.). This corresponds to crystal formation in cave pools.

Summing up, the here presented data document the full petrographic complexity of cave carbonate fabrics. The validity of state-of-art technological approaches in the characterization of the complex three-dimensional texture of these precipitates is shown. A further understanding on the controlling reasons requires a combination of field and laboratory experiments including the strict control (laboratory) and monitoring (cave) of physico-chemical and environmental parameters.

SUMMARY

Non-ideal calcite crystals from rimstone pools in dolostone caves have been studied for their three-dimensional c-axis orientation using the electron backscatter diffraction method (ESBD). The two studied locations (cave pools, Zaunikkhalle, Windspalte) from the central part of Zoolithen Cave in Germany yield filigreed speleothem structures (crusts) with different internal calcite lattice structure.

From a three-dimensional viewpoint, both of these calcitic cement crusts are composed of a texturally complex array of bundles of calcite fibers. Remarkably, the fibers of the Zaunikkhalle location show a 3D diverging c-axis orientation whilst those of the Windspalte sampling location display a 3D converging c-axis orientation.

The underlying mechanism of this abnormal c-axis behavior of the fibrous calcites of pure calcite composition (similar to Iceland spar) is considered. The free Mg aquo ions are derived from the Franconian dolomite and transported in the cave setting by aquifer waters into the sinter basin where they are incorporated into calcite at 4-6 mol% MgCO₃.

The mechanistic reasons for different orientation of the c-axes in the calcite samples investigated (diverging or converging c-axes in growth direction) are at present not understood. Possible reasons might include variable degrees of Mg saturation of mother fluids promoting convergence of the calcite lattice structure. Experimental work and field monitoring campaigns are instrumental have a significant potential for the improved understanding of these enigmatic fabrics.

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