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Cryogenic and non-cryogenic pool calcites indicating permafrost and non-permafrost periods: a case study from the Herbstlabyrinth-Advent Cave system (Germany)

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Abstract. Weichselian cryogenic calcites collected in what is referred to as the Rätselhalle of the Herbstlabyrinth-Advent Cave system are structurally classified as rhombohedral crystals and spherulitic aggregates. The carbon and oxygen isotopic composition of these precipitates (δ^{13}C = +0.6 to −7.3‰; δ^{18}O = −6.9 to −18.0‰) corresponds to those of known slowly precipitated cryogenic cave calcites under conditions of isotopic equilibrium between water and ice of Central European caves. The carbon and oxygen isotopic composition varies between different caves which is attributed to the effects of cave air ventilation before the freezing started.

By petrographic and geochemical comparisons of Weichselian cryogenic calcite with recent to sub-recent precipitates as well as Weichselian non-cryogenic calcites of the same locality, a model for the precipitation of these calcites is proposed. While the recent and sub-recent pool-calcites isotopically match the composition of interglacial speleothems (stalagmites, etc.), isotope ratios of Weichselian non-cryogenic pool-calcites reflect cooler conditions. Weichselian cryogenic calcites show a trend towards low δ^{18}O values with higher carbon isotope ratios reflecting slow freezing of the precipitating solution. In essence, the isotope geochemistry of the Weichselian calcites reflects the climate history changing from overall initial permafrost conditions to permafrost-free and subsequently to renewed permafrost conditions. Judging from the data compiled here, the last permafrost stage in the Rätselhalle is followed by a warm period (interstadial and/or Holocene). During this warmer period, the cave ice melted and cryogenic and non-cryogenic Weichselian calcite precipitates were deposited on the cave ground or on fallen blocks, respectively.

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1 Introduction

In contrast to most carbonate speleothems (e.g. stalagmites) which precipitate from supersaturated waters above 0 °C (e.g. Hill and Forti 1997) **c**ryogenic **c**ave **c**alcites (CCC sensu Žák et al., 2004) form during freezing of cave waters. This process takes place when seepage waters enter a cave characterized by mean temperatures below 0 °C. In present-day ice caves of the temperate zone with high ventilation, water freezes in a thin film on the surface of ice. Due to rapid kinetic escape of CO_2 from the solution, rapid freezing of cave waters leads to high δ^{13}C values of precipitated calcites (Lacelle, 2007; Spötl, 2008). In contrast, slowly freezing waters and related preferential ^{18}O incorporation into the ice in more or less isolated cavities within permafrost, leads to low δ^{18}O values of calcite precipitates from this fluid (Žák et al., 2004).

In recent years, Quaternary cryogenic cave calcites formed by slow growth conditions from Central European caves have been described in a series of publications (locations between Scandinavian and Alpine ice sheets; Žák et al., 2004, 2008, 2009; Richter and Niggemann, 2005; Richter and Riechelmann, 2008; Richter et al., 2008, 2009, 2010). The genesis of these calcite particles is essentially bound to water pools on top of ice bodies in caves during the transition periods between glacial/stadial to interglacial/interstadial. Conversely, the precipitation of similar calcites from pool waters on the cave floor is not yet documented. Nevertheless, during these transitional periods, mean annual temperatures outside of the cave gradually decreased and then fell below freezing point. Because of the low heat conductivity of rocks this decrease in temperature reached the subsurface with some delay (as described by Pielsticker, 2000) so that low-frequency temperature changes are not recorded in cryogenic cave calcite records, depending on the overburden of the cave. Following a subsequent temperature rise, cave ice formed during

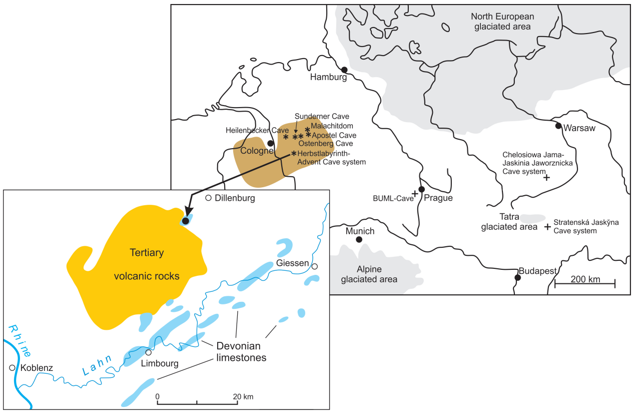

Fig. 1. Map showing the position of the Herbstlabyrinth-Advent Cave system as well as other caves of Central Europe from which cryocalcite has been described (light brown – Rhenish Slate Mountains, light grey – Weichselian glaciated areas). See lower left inset for more details.

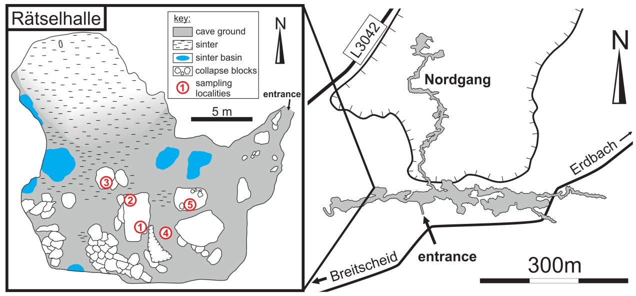

Fig. 2. Sketch map of Herbstlabyrinth-Advent Cave system showing the location of Rätselhalle as well as a speleological map of this chamber with sampling locations.

previous cold periods, melted and different types of cryogenic cave calcites accumulated on the cave ground or on collapsed blocks covering the cave floor.

Unconsolidated sediments of calcite particles with a broad range of structures are present on the cave floor and on blocks in the Rätselhalle of the Herbstlabyrinth-Advent Cave system (sensu Grubert (1996) and Hülsmann (1996)) in NW Hesse (see Fig. 1). These deposits were sampled in 2004 and 2009 for detailed structural and geochemical analyses and are the topic of the present publication.

The age of the main type of the calcite particles found, namely aggregates of euhedral calcite crystals, was dated to 29 170 ± 480 years based on the U/Th method (Kempe et al., 2005). These precipitates were interpreted as having formed as rafts on pool water situated on cave ice bodies (Kempe, 2008). The less commonly found types of calcite aggregates, here referred to as composite spherulites, were petrographically compared with cryogenic calcites described by Richter and Niggemann (2005) and Richter and Riechelmann (2008). The later ones were attributed to a precipitation setting in slowly freezing pools on ice bodies due to their low δ^{18}O signature (-14 to -18‰ VPDB).

The genetic relation between before-mentioned types of "crystal sand" present in the Rätselhalle was previously poorly constrained. Here, the petrographic and geochemical properties of the different types of these crystal sands are documented in detail and a comparison with recent/subrecent calcite formations in a pool in the Rätselhalle is presented. The aim of this publication is to improve the understanding of cryogenic cave calcites as novel archives of cold continental climate phases.

2 Geographical and geological setting

The Herbstlabyrinth-Advent Cave system formed in the Upper Devonian Iberg Limestone of Breitscheid on the NE margin of the Tertiary Westerwald volcanic complex (Fig. 1). The reefal deposits of the Iberg Limestone (Kayser, 1907; Krebs, 1966), located on a volcano basement in the Rhenohercynian trough of the Rhenish Slate Mountains (Krebs, 1971), is well known for its abundant epi- and endo karst phenomena of Late Cenozoic age (Stengel-Rutkowski, 1968). The Herbstlabyrinth-Advent Cave system was first discovered in the winter of 1993/1994 during quarry works (Grubert, 1996). Deposits with bones of small mammals as well as some remains of cave bears indicate at least episodic connections to the surface in the past. A second artificial entrance was built in order to develop a touristic cave. Following Dorsten et al. (2005), this cave system formed in a shallow phreatic system. Several of the cave levels reflect the palaeo-position of ancient long-lasting ground water tables. Kaiser et al. (1998, 1999) identified four karst levels, which today are situated in the vadose zone with a temporal active fluvial system in the lowest part of the cave, and three subsequent stages of speleothem formation have been identified but not yet dated. The Herbstlabyrinth-Advent Cave system is located between the villages of Erdbach and Breitscheid (Fig. 2). With an overall length of more than 5300 m, it is the largest cave system in Hesse and one of the most significant ones in Germany. The Rätselhalle (altitude 363 m above sea level) providing the sampling material for this study belongs to the western part of the EW trending main cave area and is 20 m long, 15 m wide and 5 m high on average. This part of the cave can be accessed via a narrow passage. Because of its remote location the average annual air temperature in this chamber is about 9 °C. The thickness of the hostrock above the Rätselhalle reaches about 40 m.

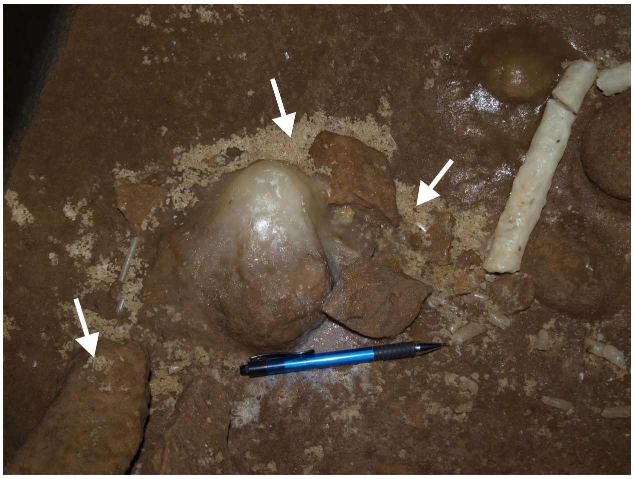

Fig. 3. "Crystal sand" on collapse block (arrows) in the Rätselhalle.

Calcite-cemented debris on the cave walls marks the former presence of ice attached to the cave wall (Pielsticker, 2000).

3 Methodology

Accumulations of "crystal sand" (loose individual crystals and aggregates – mostly sand-sized, sometimes more than 2 mm in diameter) consisting of speleothem particles covering the cave floor or lying on collapsed blocks (Figs. 2 and 3) were sampled at five locations. In addition, specimens of recent and sub-recent rafts of speleothem deposits in a pool located in the NW-part of the Rätselhalle (Fig. 2) were collected for comparative studies.

The sample material was cleaned in an ultrasonic bath prior to a manual separation of the various speleothem types under the reflected-light microscope. The particles were examined using a high-resolution field emission scanning electron microscope (HR-FEM) of type LEO/Zeiss 1530 Gemini. For this purpose, selected samples were sputtered with a thin gold coating. X-ray diffraction analysis (XRD) was performed using a Philips counting-tube diffractometer (PW 1050/25) with an AMR monochromator using CuK_α radiation (40 kV, 35 mA) in order to identify the carbonate mineralogy. For this, powdered samples with quartz powder as internal standard were measured at a diffraction angle range of 26–38 $°2\theta$, identifying each d(104) value of the rhombohedral carbonates in terms of their Ca/Mg distribution (Füchtbauer and Richter, 1988).

The carbon and oxygen isotopic composition of calcite was determined with a Delta S mass spectrometer (Finnigan MAT) and reported relative to the V-PDB standard. The 1σ-reproducibility of the measurements is 0.04‰ for $\delta^{13}C$ and 0.08‰ for $\delta^{18}O$.

4 Data presentation and interpretation

4.1 Speleothem particles

Samples of speleothem particles are composed of nearly stoichiometric calcite (d(104) 3.034–3.036 Å) as documented by diffractometer analysis. This outcome is not unexpected given that the host rock of the cave is mainly composed of low Mg-calcite (d(104) 3.030–3.034 Å). Only small amounts of secondary dolomite are present in the hostrock carbonate. Below, speleothem particles sampled from the (i) cave floor and collapsed blocks and (ii) from pools are described separately, because different modes of formation are proposed based on field observations.

4.1.1 Speleothem particles collected from the cave floor and on collapsed blocks

The most common form of speleothem particles are aggregates and individual crystals with rhombohedral faces which occur at all sampling points (Fig. 2). In essence, two types are identified, (a) translucent aggregates and individual crystals with acute rhombohedral faces on the edges and obtuse rhombohedral faces at their growth termination, and (b) white to buff-colored, aggregates and individual crystals with rhombohedral faces.

Translucent aggregates and individual crystals with rhombohedral faces (type a) with acute rhombohedral faces on the flanks and obtuse rhombohedral faces at their growth termination (Fig. 4a, b) are present in the Rätselhalle. Rhombohedra are commonly connected to platy aggregates approaching more than 1 cm in size. In most cases one side of these platy aggregates is commonly straight but also curved ones are found (Fig. 4c). The opposite side of platy aggregates is commonly convex and covered by euhedral crystals (Fig. 4a). Less common are platy aggregates with euhedral crystals on both sides (Fig. 5a, b) reflecting sunken rafts of a former pool. Asteroidal intergrowth of the rhombohedra is uncommon (up to >1 mm in diameter) whereas individual rhombohedra are rare (<1 mm in diameter).

White to buff-colored aggregates and individuals of crystals with rhombohedral faces (type b) were exclusively observed at location 1 (Fig. 2). They commonly occur as aggregates of up to 1 cm in diameter (Fig. 4e) but rare examples of individual crystals were found, too (Fig. 4d). The inclusion-rich rhombohedra display pronounced zoning and, where fully developed, curved crystal faces, which are less acute relative to the before-mentioned translucent type a rhombohedra. Type b particles frequently overgrow nuclei of type a (Figs. 4f and 5c, d).

Only at locality 1 (Fig. 2) were frequent *spherulitic aggregates* (crystals with a radiate fibrous structure) found. They have a more white to buff-coloured appearance as a result of inclusions (see type b above) and rarely exceed 1 mm in size. Most spherulites are dumbbell-shaped and display complex

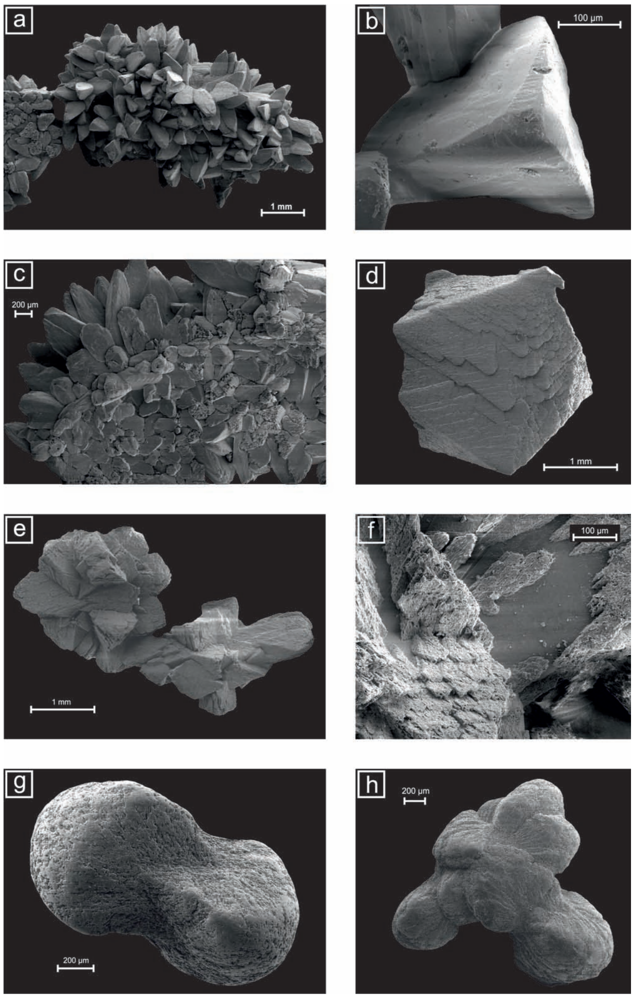

Fig. 4. SEM images of various types of "crystal sand". **(a)** Surface of a speleothem platelet (central particle) with translucent rhombohedral crystals (acute rhombohedral faces on the flanks, obtuse rhombohedral faces at growth end); particles to the left mark bottom of speleothem platelet. **(b)** Growth end of a translucent rhombohedral crystal with obtuse rhombohedral faces at the apex area of the crystal. **(c)** Moderately curved bottom of a speleothem, platelet with translucent rhombohedral crystals. **(d, e)** Aggregates and individuals of crystals with rhombohedral faces (whitish to buff-colored) without acute rhombohedral faces but with distinct domain development; d = single crystals, e = chain. **(f)** Partial overgrowth of translucent aggregates and individuals of crystals with rhombohedral faces (type a; smooth surfaces) by aggregates and individuals of crystals with rhombohedral faces (type b) with a distinct domain growth. **(g)** Dumbbell-shaped spherulithic crystal aggregates. **(h)** Braided-shaped spherulitic aggregates.

intergrowth features (Fig. 4g). Chain-like linked spherulites ("Zopfsinter" sensu Erlemeyer et al., 1991; Richter et al., 2008) are uncommon (Fig. 4h). Rhombohedra display a curved shape similar to aggregates and individuals of crystals with rhombohedral faces of type b.

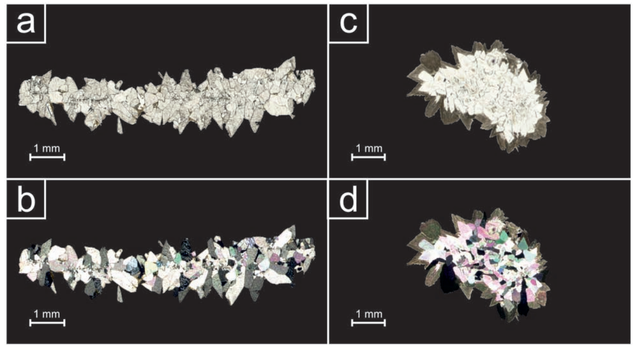

Fig. 5. Thin section photomicrographs of aggregates and individuals of crystals with rhombohedral faces at locality 1: **(a, b)** sunken rafts with rhombohedral crystals on both sides (b cross-polarized light). **(c, d)** Calcitic aggregates with translucent crystals in the interior and with darker (inclusion-rich) overgrowth (d cross-polarized light).

4.1.2 Speleothem particles from a modern carbonate-precipitating pool

At locality 6 (Fig. 2) crystal rafts, several centimeters in diameter, were observed in a pool. These crystal aggregates are characterized by a planar upper boundary at the air-water interface and a rhombohedral boundary downward (Fig. 7a, b) extending into the pool water. At the edge of this pool, above the present water level, former raft deposits are attached to flowstones (cp. Fig. 2). The morphology of these pool calcites, characterized by acute rhombohedral faces at the flanks and obtuse rhombohedral faces at their growth ends (Fig. 6a, b), are similar to calcite precipitates (Fig. 6c, d) on watch glasses placed beneath drip sites in Bunker Cave (Northern Sauerland/NRW; Riechelmann, 2010).

4.2 Carbon and oxygen isotopic composition

Isotope analysis reveals a distinct difference between host limestone and speleothem samples. Host limestone samples exhibit δ^{13}C values between +1.8 and +2.7‰ and δ^{18}O values between −5.3 and −1.0‰. These values are characteristic of the isotopic composition of Middle/Upper Devonian limestones of the Rhenish Slate Mountains (Fig. 7).

Aggregates and individuals of crystals with rhombohedral faces as well as spherulitic aggregates collected at the cave floor and on collapsed blocks display δ^{13}C values between +0.6 and −7.3‰ and δ^{18}O values between −6.9 and −18.0‰ (Fig. 7). Carbon versus oxygen isotope plots reveal an overall trend towards elevated carbon and depleted oxygen isotope ratios. In essence, spherulitic aggregates represent the depleted δ^{18}O end-member whereas translucent aggregates and individuals of crystals with rhombohedral faces (type a) are characterized by higher δ^{18}O values close to those measured from stalagmites, stalactites and draperies collected in the Herbstlabyrinth-Advent Cave

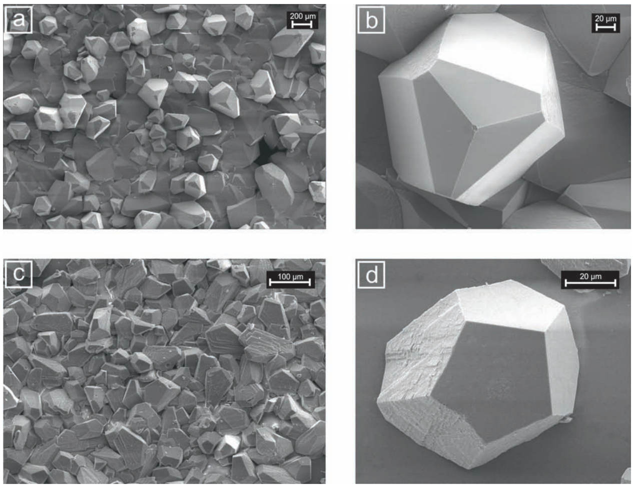

Fig. 6. **(a)** Crystals (precipitated in the pool, locality 6, Fig. 4b) with acute rhombohedral faces on the flanks and obtuse rhombohedral faces at growth end. **(b)** detailed view of a single crystal shown in a). **(c)** Calcite crystals grown on watch glass, placed on top of stalagmites in Bunker Cave (Riechelmann; 2010). **(d)** detailed view of a single crystal shown in c).

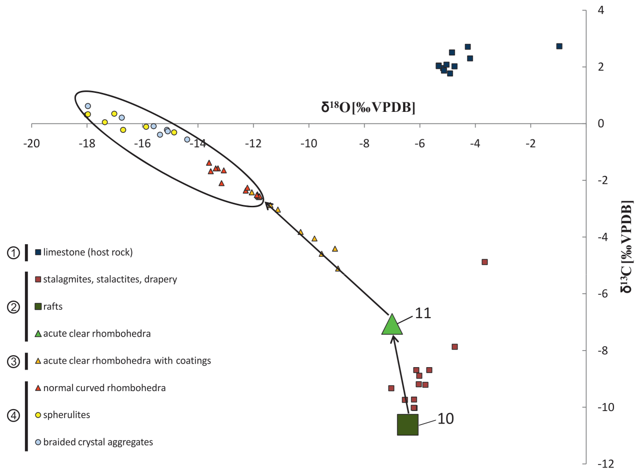

Fig. 7. Carbon and oxygen isotopic composition of various calcite particles from the Rätselhalle in comparison to those measured from calcitic host rock samples (1) and common calcites of stalagmites, stalactites and draperies (2). (3) acute clear rhombohedra overgrown by cryogenic cave calcites, (4) cryogenic cave calcites. Numbers represent amount of samples measured.

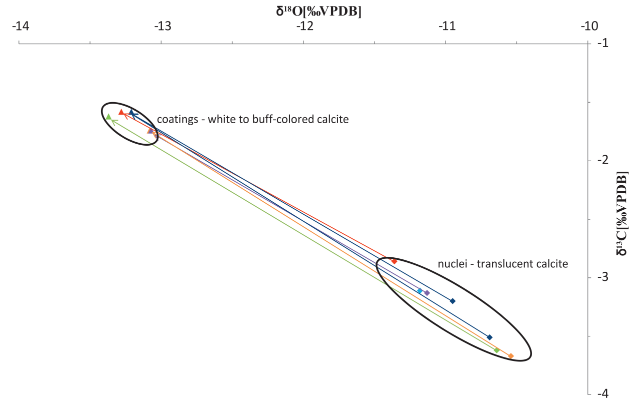

Fig. 8. Carbon and oxygen isotopic composition of selected zones of composite crystals with translucent nuclei and white to buff-colored coatings.

system (Fig. 7). Particles with buff-colored rhombohedral aggregates form a cluster with slightly higher δ^{18}O values than spherulitic aggregates. Particles with composite crystals, built by nuclei of translucent aggregates and individuals of crystals with rhombohedral faces and white to buff-colored rhombohedral cortices are located in a transition zone between type a and type b aggregates and individuals of crystals with rhombohedral faces. In some cases it was possible to separate the translucent and the buff-colored zones of the composite crystals: the nuclei show lower δ^{13}C and higher δ^{18}O values compared to the coatings (Fig. 8). The C/O isotope composition of the separated nuclei is not identical to that of the particles with acute clear rhombohedra only, perhaps because of the polyphase composition of the nuclei (comparing Figs. 7 and 8)

The rafts of the pool at locality 6 show δ^{13}C values between -10.8 and -10.3‰ and δ^{18}O values between -6.5 and -6.4‰. These values match those obtained from stalagmites, stalactites or draperies sampled in the Herbstlabyrinth-Advent Cave system (Fig. 7).

4.3 U/Th age dating

TIMS U/Th age dating of "crystal sand" collected in the Rätselhalle yielded an age of 29 170 ± 480 yrs BP (Kempe et al., 2005). According to Kempe (2008), the dated material belongs to the most common type of crystals, i.e. type a of the aggregates and individuals of crystals with rhombohedral faces as described above. A similar date of 28 700 ± 1500 yrs BP was obtained by TIMS U/Th dating of aggregates of type b (white to buff-coloured, rhombohedral crystals) speleothems at the Research Centre for Radiometry, Heidelberg Academy of Sciences (using a Finnigan MAT 262 RPQ mass spectrometer; laboratory of A. Mangini). Analytical results: δU (corrected) = 431.5‰ (absolute error 8.2), ^{238}U = 0.9889 ng/g (absolute error 0.0035), ^{232}Th = 22.45 ng/g (absolute error 0.29), ^{230}Th = 5.48 pg/g (absolute error 0.24). As FE-SEM studies revealed overgrowths of type b on type a and as these two precipitates could not be separated prior to U/Th analysis, the resulting age data of 28 700 ± 1500 yrs likely underestimates the age of type b rhombohedral crystals.

5 Discussion

The accumulations of unconsolidated aggregates in the studied cave are exclusively characterized by calcite morphologies with rhombohedral faces of different steepness. According to Gonzales et al. (1992), this is a typical feature of calcite precipitation in caves. Similarly, calcite crystals with acute rhombohedral faces on the edges and obtuse rhombohedral faces at their free ends were described by Mergener et al. (1992) from pools of several caves of the Sauerland (NE Rhenish Slate Mountains).

Aggregates of this type dominate aggregates of "crystal sand" at locality 1 as well as recent to sub-recent pool precipitates (location 6) on pool walls and floors. Moreover, in the latter pool this type occurs below rafts up to a paleo-water level characterized by a shelfstone 10 cm above the present-day water level. In the case of the localities 1–5 there is no field evidence suggesting that fluctuating water levels in the cave represent a controlling factor for the formation of crystal accumulations and other modes of formation are consequently discussed. However, other authors (e.g., Andrieux, 1963; Diaconu, 1990; Onac, 1996) described various aspects of the morphology of speleothems as a result of a fluctuating paleo-water table in pools from other localities. Perhaps the strongest evidence is given by the different isotopic composition of these precipitates in comparison to other speleothem allowing for an interpretation of the formation conditions of calcites in pools under specific physicochemical conditions (Žák et al., 2004, 2008; Richter and Niggemann, 2005; Lacelle, 2007).

a. Recent and subrecent rafts (location 6) are isotopically depleted relative to normal speleothems (Fig. 7). This is perhaps best understood in the context of their precipitation in pools fed by drip water as opposed to the crystallization on stalagmite surfaces under a thin, semi-permanent water film. In addition, evaporation processes play an important role on stalagmite and stalactite surfaces including kinetic effects related to CO_2 degassing (Mickler et al., 2006). In contrast, these effects are far less significant in permanent cave pools.

b. The aggregates of translucent calcites with acute and obtuse rhombohedral crystal faces (locations 1–5) show only minor overlap with "normal" speleothems in terms of their isotope composition. Elevated carbon and depleted oxygen isotope values are probably indicative for less soil activity and a rather scarce vegetation cover related to an overall cooler climate in comparison to the present-day setting.

c. The calcite particles with obtuse and curved rhombohedra (loc. 1) reveal ^{13}C-enriched and ^{18}O-depleted values relative to precipitates mentioned under (a) and (b). This is interpreted as precipitation from gradually freezing residual water. During this process, ^{18}O is preferentially incorporated in the newly formed ice (O'Neil, 1968; Clark and Fritz, 1997). Possibly only at this locality a relict water pool on top of the ice which allowed the precipitation of cryogenic calcite below a frozen layer at the air-water contact due to progressive freezing. This shallow pool was apparently large enough to allow for a slow evolution of the water during slow freezing.

d. Acute, clear rhombohedra with coatings of buff-colored rhombohedra (location 1, cp. Figs. 4f and 5c, d) range, in terms of their isotopic composition, between the calcites described in (b) and (c). These precipitates suggest the transition from non-freezing to freezing pool waters. The isotopic values of the separated aggregates (Fig. 8) indicate the transition to freezing conditions with the change of the precipitation of particle type a to the overgrowth by type b.

e. Individual spherulites and spherulitically structured braid speleothems (location 1) reveal the highest carbon and the lowest oxygen isotope composition relative to other particles of the "crystal sand". This is considered evidence for the final freezing stages of the pool waters.

Based on arguments given above and constrained by the U/Th date (29 170 ± 480 yrs BP – Kempe et al., 2005) crystal precipitates as well as crystal aggregates present as "crystal sand" in the Rätselhalle are explained by a climate model involving different stages of evolution (I to VI in Fig. 9):

I. Permafrost stage prior to (Weichselian) Greenland interstadial no. 4 (terminology in accordance with Johnsen et al., 1992 and Bond et al., 1997); no speleothem formation is recorded.

II. Beginning of cave ice formation when the 0 °C isotherm reached the roof of the cave with some delay, because of the low heat conductivity of the rock (Pielsticker, 2000), during the beginning of Weichselian interstadial no. 4. The precipitation of small calcite crystals from rapidly freezing dripping water is possible but no evidence was found yet.

III. Residual ice still exists on the cave floor during the Weichselian interstadial no. 4. Formation of calcite-cemented debris along the cave walls ("ice attachments") took place and precipitation of aggregates with isotopic values that overlapped with those of stalagmites and stalactites occurred in meltwater pools on ice.

IV. Slow freezing of water in pools on the ice bodies in the cave during cooling at the beginning of renewed permafrost conditions following Weichselian interstadial no. 4. Cryogenic calcites precipitated from slowly freezing pool water.

V. Permafrost after Weichselian interstadial no. 4 inhibited crystal precipitation as all water in the cave was frozen.

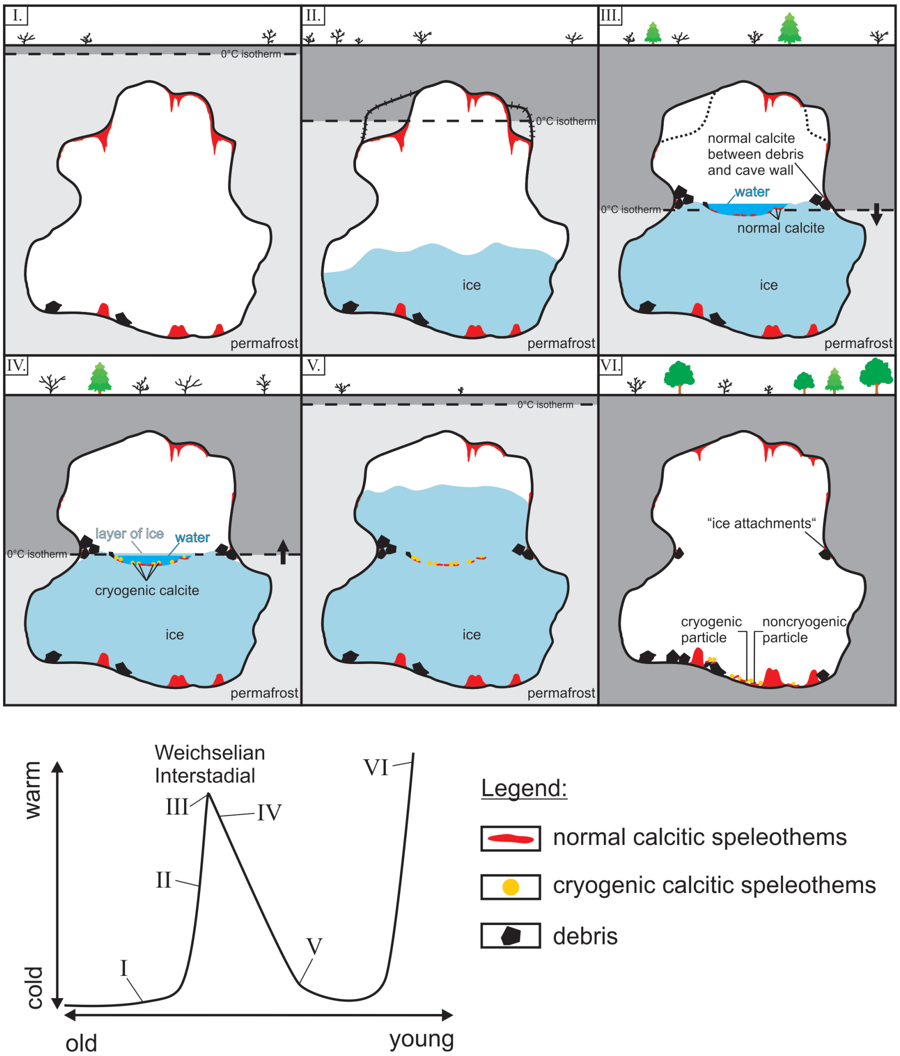

Fig. 9. Cartoon illustrating proposed succession of events that lead to the formation of cryogenic and non-cryogenic calcites during a Weichselian interstadial. Refer to schematic temperature evolution in lower left inset. See text for details.

VI. A renewed stage of warming followed the permafrost interval. Ice bodies in caves melted and cryogenic and other speleogenic particles accumulated in an unsorted manner on the cave floor or on collapse blocks.

The isotopic composition of genetically different, small cryogenic speleothems (aggregates and individuals of crystals with rhombohedral faces, spherulitic aggregates) found in the Rätselhalle ranges from the typical $\delta^{18}O$ and $\delta^{13}C$ signature of "normal" speleothems to high $\delta^{13}C$ and low $\delta^{18}O$ values of cryogenic cave calcites (see arrow B–C in Fig. 7). A compilation of published data on slowly precipitating cryocalcites from various Central European caves suggests a site-specific isotope signature (Fig. 10). This implies cave-specific climate conditions. Žák et al. (2004) and Richter et al. (2009a) proposed enhanced ventilation of the cave or of portions of a given cave resulting in a trend towards elevated $\delta^{13}C$ values, because degassed CO_2 is increasingly removed under increasing ventilation. This is important for the stage at which the slowly freezing of the water pool starts when the isotopic exchange is inhibited, at least to some extent, by a layer of ice at the water/cave air interface.

6 Conclusions

Based on the data shown here, these following main points are concluded:

– Weichselian cryogenic cave calcites from the Herbstlabyrinth-Advent Cave system are present as rhombohedral and spherulitic aggregates.

– Geochemical data ($\delta^{18}O$ and $\delta^{13}C$) of these precipitates match those of known slow cryogenic cave precipitates reported from other Central European caves.

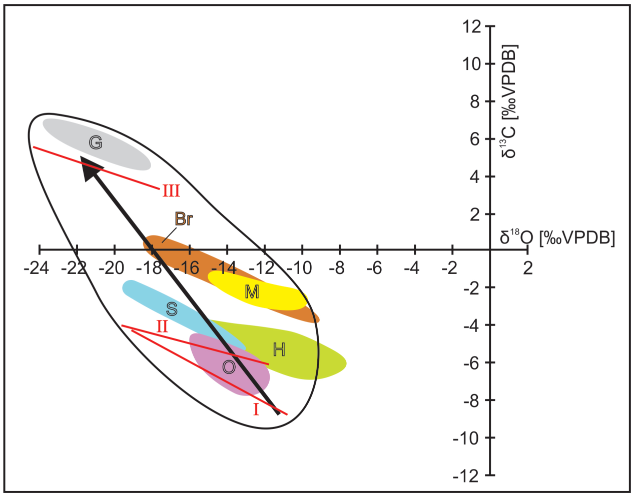

Fig. 10. Carbon and oxygen isotopic composition of cryogenic cave calcites from various cave localities in Central Europe: I–III: regression lines according to Žák et al. (2004): I Jaskinia Jaworznicka Cave system, II BUML Cave, III Stratenská Jaskya Cave. The different data fields are based on the interpretation by the Bochum group. O = Ostenberg Cave - Richter and Niggemann (2005); S = Sunderner Cave - Richter et al. (2009a); H = Heilenbecke Cave - Richter et al. (2008); M = Malachitdom – Richter and Riechelmann (2008); Br = Herbstlabyrinth-Advent Cave system – this work, G = Glaseis Cave – Richter et al. (2009b).

– The oxygen and carbon isotopic composition of composite crystals indicates the transition from non-freezing to freezing conditions.

– Variable geochemical signatures probably reflect cave air ventilation changes.

– The overall isotope trend is in agreement with a model of permafrost conditions followed by an interstadial causing ice melt, and finally renewed cold, stadial conditions.

– After melting of the ice body polymict "crystal sand" accumulated on the floor and on collapsed blocks.

– The combined petrographical and geochemical data are clear evidence for the significance of cryogenic cave calcites as important but complex cave archives of cold (glacial) climate periods.

7 Outlook

The need for more research of the often complex cryogenic calcites in caves of the Rhenish Slate Mountains and in other localities is great. Specifically, attention should be paid to overgrowth on nuclei of older crystals. Furthermore, different generations of cryogenic calcites must be separated in terms of their mineralogy, crystallography and geochemical composition. If successful, the combination of paleoenvironmental information from stalagmites recording primarily interglacials and locally also interstadials with evidence from cold-climate periods during which cryogenic cave calcite formed, will allow an improved reconstruction of the Pleistocene climate evolution of Central Europe.

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